

A Brief Review of the Modern Progresses in Biofouling Prevention by Modified PDMS Silicon Elastomer Coating

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Abstract: The goal of obtaining maximum efficiency, conservation of energy and reducing emissions in the marine transportation sector is greatly hindered by biofouling. While mechanical scrubbing, water jet treatment and other measures are in place, scientists in the modern day are inclining more toward the preventive solution. At the same time, this is environment-friendly yet has the recovering ability despite prolonged exposure to the elements. One such research, as well as some contemporary research, have been briefly summarized here.

Keywords: Antifouling, Biofouling, Elastomer, Silicone.

1. Introduction

Significant attention has been given to increasing the efficiency of transportation and power generation in the last few decades. While fossil fuels remain the bulk energy provider in the transportation sector, their dependence is being reduced steadily. For passenger and freight transportation through land, air and water, efforts were made to increase efficiency. This would reduce the dependency on fossil fuels and thus reduce emissions. This is obtained by improved powerplants' design, increasing heat transfer efficiency [1]-[3], and generating energy from renewable sources such as solar [4]-[7], wind and geothermal energy. Detailed attention is given to the vehicles' construction materials, whether airplane, ship or truck. The older trend of all metal construction is being replaced by lightweight carbon fiber and glass fiber composite, which is particularly apparent in the aviation industries, where attempts are ongoing not only to replace the metals with high-strength polymer composites of thermoplastic and thermosetting plastics reinforced with [8], [9] glass, Kevlar and carbon fiber but also to optimize and tailoring their orientation to engineer the maximum strength, safety and minimizing the material losses in repair [4], [10], [11]. So, in all transport mediums, the common goal that the scientists are working on is obtaining more power at the expense of lesser energy. However, transportation in the waterbody faces a unique and somewhat sinister natural barrier that substantially penalizes efficiency, which is biofouling.

The unwanted accumulation of biological substances on the surfaces of the submerged structures, such as the ship hulls, radar, propeller, pier pylons, etc., is termed marine biofouling [12]. Biofouling significantly increases the drags in the ships. It

reduces the overall hydrodynamic performance of vessels, resulting in increased emission as the boats, ships, and submarines have to produce more propulsion power by the increased fuel consumption to compensate for the efficiency loss [13]-[16]. Over time, the accumulation of bio-foulants on hulls increases the hydrodynamic volume of a vessel and the frictional effects that could increase the drag up to 60% which could decrease speeds up to 10%, increasing the fuel consumption as high as 40% to make up for these losses¹⁷. Even damage in hull structure and propulsion systems isn't rare¹⁸. The US Navy alone spends an estimated \$1 billion annually on increased fuel consumption, maintenance, and controlling biofouling.



Fig. 1. Extensive Biofouling in the hull of a ship [14]

One promising solution to this problem without affecting the marine ecosystem is poly(dimethylsiloxane) (PDMS), a well-known silicone polymer. A combination of this PDMS along with polyurea (PDMS-PUa) and (4,5-dichloro-2-n-octyl-4-isothiazolinone-3-one) (DCOIT) shows a promising result in this aspect.

2. Biofouling Prevention using PDMS Polymer

Polydimethylsiloxane (PDMS), a silicone elastomer, is a

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capable candidate to use as the coating on ship surfaces to prevent biofouling. Due to their low surface energy and elastic modulus, it provides minimal adhesion to the fouling organisms. As a result, the marine organisms' adherence to the coating is minimal. Hydrodynamic shear forces could easily remove the loosely attached organisms during mechanical cleaning or the navigation of the vessel [13], [19]-[21].



Fig. 2. Working process of fouling release coating
Left to right: Organisms settling, Hydrodynamic shear force and Removal of the organism [21]

3. Characteristics of PDMS

Besides the lower surface energy and inertness, PDMS also has a low modulus of elasticity, ranging between 0.57 to 3.7 MPa [22], making the surface easy to deform. In other words, the coating contour isn't as rigid as the surface itself, making it difficult for the microorganisms to settle and cling onto the surface, even detaching hard foulants like barnacles [23]-[26]. The coating also comes with a smooth surface finish that reduces drag and results in better fuel consumption as a result [27]. The advantages and shortcomings of this elastomer are mentioned below.

A. Advantages

Low Surface Free Energy, low elastic modulus, low surface roughness in the range of 1 μ m, drag reduction, chemical stability.

B. Shortcomings

Although flexible to some extent, PDMS is still a thermosetting plastic [28], and its cross-linked network of structure makes it difficult to repair once damaged. Weak adhesion between coating and substrate, poor mechanical properties, susceptibility to cutting, tearing, puncturing and mechanical damages reduce the service life. Poor antifouling performance in static conditions only makes it better for vessels with speeds greater than 15 knots and performs poorly in static conditions [29]. Fouling by diatoms couldn't be released even at speeds greater than 30knots [29], [30]. Finally, PDMS silicone alone cannot successfully deter or efficiently restrict marine fouling without using antifouling chemicals.

4. Improving Anti-fouling Ability through PDMS Functionalization

Many studies are addressing the disadvantages of PDMS by modifying PDMS both physically and chemically. However, this review focuses on one specific methodology, described by Ma *et al.* (2017) [27].

A. PDMS based Polyurea

The development of PDMS-based polyurea (PDMS-PUa) imparts self-repairing properties by intense secondary hydrogen bonding between carbonyl oxygen atoms and amide hydrogen

atoms just like the nylons. This PDMS-PUa (PDMS-based Polyurea) could also be a carrier for the organic antifoulant DCOIT (4,5-dichloro-2-n-octyl-4-isothiazolin-3-one).

The components used for making the polymer coating are Aminopropyl-terminated poly(dimethylsiloxane) (APT-PDMS), Isophorone diisocyanate (IPDI), Tetrahydrofuran (THF), and Isopropyl Alcohol (IPA). After synthesizing the PDMS-PUa, it is combined with different weight percentages of the organic antifoulant 4,5-dichloro-2-n-octyl-4-isothiazolinone-3-one (DCOIT). The steps are further described below.

1) APT-PDMS (Silicone elastomer)

The commonly used method of preparing the PDMS elastomer is Hydrosilylation and Condensation.

• Hydrosilylation

In this step, two types of polysiloxane groups react with each other in the presence of a Platinum catalyst (Pt). One of them contains the vinyl end group (H₂C=CH-), while the other includes the hydrosilane group (=SiH-). The reaction is as follows [31]-[39].

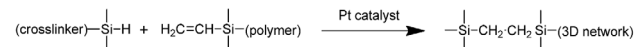


Fig. 3. Hydrosilylation of APT-PDMS [34]

• Condensation

A silicone crosslinker with an Alkoxysilane group and Silanol containing polysiloxane undergoes the condensation reaction resulting in PDMS [13].

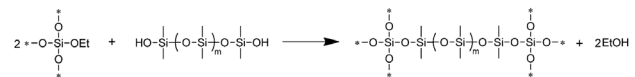


Fig. 4. Condensation to form PDMS [13]

The PDMS comes with a terminal silanol group ($\equiv\text{Si}-\text{OH}$), and the structural formula is as follows:

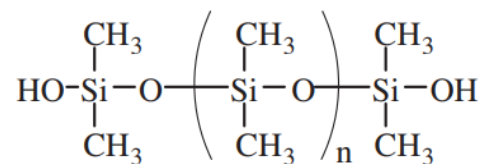
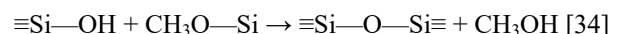


Fig. 5. PDMS with terminal silanol group [33]

A multifunctional silane ($\equiv\text{Si}-\text{O}-\text{X}$) caps the end $-\text{OH}$ groups. One example could be the Alkoxy-Silane group, $\equiv\text{Si}-\text{O}-\text{CH}_3$. When the reaction takes place between ($\equiv\text{Si}-\text{OH}$) and ($\equiv\text{Si}-\text{O}-\text{CH}_3$), H atom from the first one is replaced by the CH_3-O as shown:



Thus, the reaction between PDMS and (3-aminopropyl) dimethylethoxysilane results in Aminopropyl terminated poly(dimethylsiloxane) (APT-PDMS).

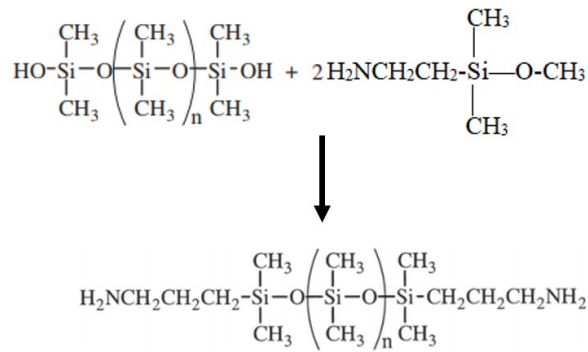


Fig. 6. Synthesis of Aminopropyl terminated poly(dimethylsiloxane) (APT-PDMS) [34]

2) Isophorone diisocyanate (IPDI)

It is produced by the phosgenation of isophorone diamine [40].

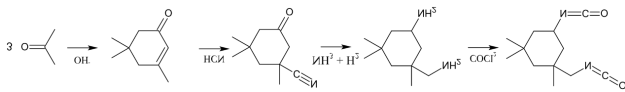


Fig. 7. Synthesis of Isophorone diisocyanate (IPDI) [40]

3) PDMS-PUa

The PDMS based polyurea, otherwise known as PDMS-PUa is prepared by the following steps. The quantities are extensively described by Ma et al. (2017) [27]. Here, the quantities are avoided for easier understanding:

IPDI (isophorone diisocyanate) and THF (Tetrahydrofuran) are dissolved and stirred in a nitrogen atmosphere at room temperature. APT-PDMS is then dissolved into the previous THF, now containing IPDI with the isocyanate group. The isocyanate from IPDI then reacts with the terminal amine group in APT-PDMS, producing the copolymer of PDMS based Polyurea ($-\text{H}_2\text{N}-(\text{C}=\text{O})-\text{NH}_2-$). Finally, the mixture is precipitated into excessive water and dried under a vacuum.

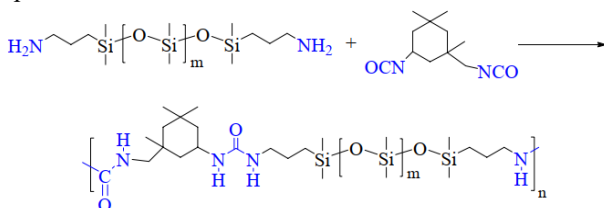


Fig. 8. PDMS-PUa Synthesis, adopted from Ma et al. (2017) [27]

4) PDMS-PUa with DCOIT

The organic antifoulant 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT), although not polymer, yet plays an important role in the effectiveness of the coating to incorporate the long-prepared lasting antifouling properties.

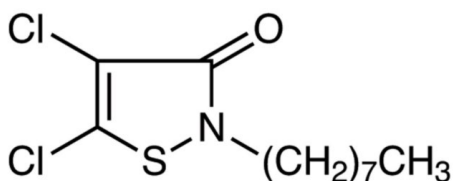


Fig. 9. Chemical structure of DCOIT [41]

PDMS-PUa with DCOIT is prepared by mixing PDMS-PUa and DCOIT into the THF solvent and stirring to obtain a homogeneous solution. The solution is then cast on the desired surface to form the coating film.

5. Advantages of PDMS-PUa/DCOIT

PDMS-PUa with DCOIT has some desirable properties to be used as a coating to prevent marine biofouling. Due to the extensive hydrogen bonding, this PDMS-PUa is very soft, has self-healing properties, enables the steady release of DCOIT in the marine environment, and also possesses good adhesion to the substrate due to lower surface energy. Some of the works here are taken from the comprehensive research done by Zhang et al.²⁷. As their work presented seen in Figure 9, the self-repairing feature of the PDMS-PUa with varying DCOIT content is eminent. They showed that DCOIT is not effective with Acrylic resin at any combination, but when used in tandem with PDMS-PUa, shows excellent antifouling property, where with DCOIT of 2.5 wt% and above is not affected by barnacles at all, even after 6 months.

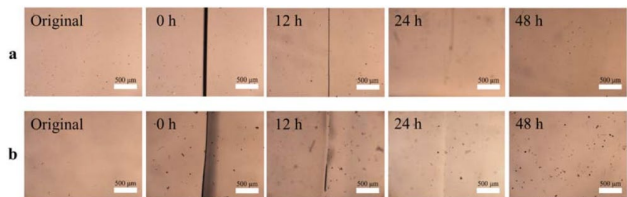


Fig. 10. Self-healing properties PDMS-PUa without (top row) and with DCOIT 5wt% (bottom row), in sea-water, as observed by Ma et al. (2017) [27]

A. Marine Field Tests

Zhang et al., [27] also conducted extensive marine testing to observe the presence of actual desired properties from PDMS-PUa/DCOIT as a coating. The natural seawater where the samples were tested has heavy fouling pressure caused by barnacles, mussels, and sponges. In a time span of 6 months, GFRP panels with different coatings of samples were tested, ranging from bare samples, Acrylic Resin with DCOIT, PDMS-PUa with and without DCOIT (1% to 10% wt). PDMS-PUa with 2.5% wt DCOIT all exhibited excellent antifouling properties

6. Conclusion

Despite its amazing properties like lower surface energy, better adhesion, self-healing, and malleability, the mechanical properties still leave a concern. It hasn't been clearly mentioned whether this PDMS-PUa with DCOIT is strong enough to adhere to the substrate in the long term. Regardless of the minor shortcomings, if addressed properly, this might well be a savior of the marine industries from biofouling.

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