Preparation and characterization of amphiphilic polymer coating for marine biofouling control

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Abstract. Biofouling is a major issue prevalent in marine industry resulting in losses in billions of dollars for repairing and maintenance. Coatings developed to tackle marine biofouling are either toxic towards environment or have shorter lifespan. Amphiphilic block copolymer coatings have gained wide attention recently to mitigate biofouling. In this work, performance of synthesized coating towards biofouling was studied. Hydroxyl terminated polydimethylsiloxane as hydrophobic and chitosan as hydrophilic moiety was used to synthesize the amphiphilic coating. Characterization of the prepared coating using Scanning Electron Microscopy (SEM) showed heterogeneous microstructure. Antifouling performance using egg white as the protein testing probe was done as it simulates the adhesives used by biofouling organism. Resistance to protein adhesion was seen on the surface of the coating. So, the developed environmental-friendly coating can be used effectively for the mitigation of marine biofouling.

1. Introduction

Marine biofouling is the growth of undesired marine microorganisms like bacteria, algae, sponges, etc. along with macro-organisms like barnacles, mussels, balanus etc. over the surfaces immersed in seawater[1,2]. This results in increased weight and skin-friction which increases the frictional resistance and deteriorates the surface[3]. This leads to a reduction in the speed and manoeuvrability of the ships and vessels and increases the fuel consumption for the same distance travelled without fouling[4]. The more fuel burnt releases more harmful emissions from ships which are also a monetary loss in billions for the marine industry. The deterioration of ship hull and its coating generate other problems as well like corrosion, deposition of the released coating in the sea bed leading to chemical waste[2]. Therefore, over the years, scientists have researched to find a novel technique to protect the marine industry from fouling by developing various protective antifouling coatings.

Amphiphilic copolymer composite coating is the dominating fouling control strategy. They have low interfacial energy and low surface energy because of hydrophobic moiety which makes the adhesion bond weak and easy to detach. Also, they possess low modulus of elasticity which deforms the organisms attached to the surface by peeling off[5]. They have hydrophilic moiety which forms a strong hydration layer. Because the interfacial energy of strong hydration layer with the surface is high enough, the fouling organisms are not able to make a bond with the surface which makes the surface protein resistant and biofouling settlement[6,7]. Polydimethylsiloxane (PDMS) is the most generally used hydrophobic polymer used for marine applications. Hydroxyl terminated PDMS has more functional groups make the crosslinking easier by blending. Many hydrophilic polymer coatings like polyethylene glycol (PEG), zwitterionic, grafted and blended coatings have been used to control
marine fouling[8–10]. They have hydrophobic as well as hydrophilic elements at the surface rendering both detachment of biofoulers and prevention of attachment mechanism into a single polymer by presenting an ambiguous surface to the protein adhesive to have a better antifouling coating than the standalone[11–13]. Currently used amphiphilic polymers have some issues with the synthesis and applicability. Instability of hydrophilic polymers is an issue like oxidation of PEG occurs which deters the surface[14]. Chemistries involved in the fabrication are quite complex in harsh environment which make it difficult to commercialize[11,15]. The blending technique can provide an easy step to synthesize an amphiphilic copolymer[16].

Recently, chitosan has gained wide application due to biocompatibility, anti-microbial activity, non-toxicity, hydrophilicity[17]. It is derived from chitin which is a by-product of sea-food industry[18]. It has polycationic nature which imparts more functionalities to the surface[19].

In this work, we developed a novel and stable amphiphilic coating for marine biofouling control. A direct crosslinked network of hydroxyl terminated PDMS and chitosan was formed at room temperature. The prepared coating showed excellent protein resistance which can infer good antifouling performance indicating its potential to use as a non-toxic marine biofouling control coating.

2. Experimental

2.1. Materials

Epoxy resin consisting of Bisphenol A diglycidyl ether (BADGE) and silicone elastomer hydroxyl terminated polydimethylsiloxane (HTPDMS) was purchased from Sigma Aldrich, Inc.(3-Aminopropyl)triethoxysilane (APTES) was purchased from Sisco Research Laboratories Pvt. Ltd. and was used as an elastomer coupling agent. Epoxy hardener triethylenetetramine (TETA), chitosan flakes and acetic acid were purchased from Loba Chemie Ltd. All the reagents were used as received without purification.

2.2. Preparation of substrate and chitosan solution

Mild steel plates of size 7cm×5cm×0.5cm were used as primary substrate. The top side of plates are roughened to make the surface rough enough so that the coating is well adhered onto it. The surface is cleaned with acetone and distilled water to remove remaining grease and impurities. Chitosan is insoluble in water but dissolves in weak acids like acetic acid. So, 2g of 75% deacetylated chitosan flakes were dissolved in 200ml of 0.1M acetic acid at 80°C under constant stirring at 200rpm with magnetic stirrer. All the undissolved large molecules and impurities present in the solution was filtered using syringe filter and a homogeneous chitosan solution is obtained.

2.3. Preparation of epoxy primer coating

10g of BADGE and a stoichiometric amount 1.43g of TETA curing agent is mixed thoroughly. The desired stoichiometric amount of curing agent required is calculated using the following equation:

\[
\text{Amount of curing agent} = \frac{\text{Equivalent weight of amine}}{\text{Equivalent weight of epoxy resin}} \times \text{Amount of epoxy} 
\]

In present work, molecular weight of TETA is 146g/mol, number of active hydrogen atoms of TETA is 6, molecular weight of BADGE is 340g/mol and the number of epoxy groups of epoxy resin is 2. In accordance to the above equation, the stoichiometric amount of TETA required to cure 10g of epoxy resin is 1.43g. After homogeneous mixing, the solution is applied on the substrate using hand bar coater and allowed to cure. Curing of epoxy mixture was done at room temperature for 12 hours.

2.4. Synthesis of HTPDMS-chitosan coating
10ml of HTPDMS silicone elastomer and 1ml of APTES coupling agent are added into a beaker. 1ml of prepared chitosan solution is added to it. The solution is mixed thoroughly in magnetic stirrer at 800 rpm for 3 hour at room temperature. The prepared solution is coated over the epoxy coat using a hand bar coater. Curing of this solution mixture was carried out for 7 days and at room temperature.

2.5. Characterization of the prepared sample
The surface morphology of the synthesized coating was revealed using a scanning electron microscopy (ZIESS EVO 18 Special Edition) at an accelerating voltage of 15kV. The sample was coated with gold to make it conductive before taking the images. The dispersion studies were carried out. Scratch resistant test was done to check the durability of the applied coating using a knife and applying moderate hand pressure to it. Water contact angle analysis and critical surface tension was also calculated using Zisman plot with pure liquids of known surface tension like water, glycerol and methanol.

2.6. Antifouling performance testing
The initial step of biofouling is conditioning film formation which is mainly protein. The antifouling performance assessment were tested using a pseudo-model of protein mixture contained in egg white simulating the adhesives secreted by the biofouling organisms to adhere. 1ml of egg white was applied on the coating surface and left to dry for 24 hours. Analyzing the dried egg white visually gives a better understanding of the adhesion strength. The dried egg white fell off the coating surface by simply shaking.

3. Results and discussion
Chitosan has very weak solubility in water and when it is allowed to react with acetic acid, amine group present in chitosan gets protonated which forms polycation chitosan[18]. This results in dissolution of the solid chitosan. The epoxy primer applied to the pristine metal plate adheres strongly to it. The heterogeneous amphiphilic microstructure can be confirmed from the SEM images shown in figure 1. The chitosan size ranges from hundreds of micrometre to nanometres. This gives the topographic surface an irregular heterogeneity. This is beneficial for the antifouling performance because fouling organisms ranges from few nanometres to millimetres and they prefer to attach to surfaces non-familiar to their behaviour[20]. The formation of blend can also be seen evidently from the image. Scratch resistant test was done using a knife and applying moderate hand pressure. The surface resisted scratches from moderate pressure but applying high pressure scratched the surface.

![Figure 1. SEM image of the prepared sample showing amphiphilic heterogeneous structure](attachment:image)

Average water contact angle was found to be 72.44° implying that surface became hydrophilic. This confirms the formation of amphiphilic copolymer network. Because, the water contact angle of polydimethylsiloxane is around 116.7° rendering hydrophobicity[21]. Decreasing of contact angle shows incorporation of hydrophilic chitosan in the polymer matrix. The critical surface tension
calculated using Zisman plot was found to be 19.34 mN/m. So to completely wet the surface, a liquid with critical surface tension of 19.34 mN/m is required.

![Figure 2. Water contact angle measurement of the coating surface](image)

![Figure 3. Zisman plot for calculating critical surface tension](image)

![Figure 4. Egg white protein adhesion test simulating protein adhesives secreted by biofouling organisms showing image (a) applied egg white (b) egg white after 24 hours (c) egg white shaken off](image)

The antifouling test performed using egg white confirms the applicability of the prepared sample[22]. 1ml of egg white when allowed to adhere on the coating didn’t attach at all and was easily
dried after 24 hours and shaken off without any effort leaving the surface clean as before. The pseudo model assumed here showed excellent antifouling performance towards protein adherence.

4. Conclusion
In this study, a novel amphiphilic marine antifouling coating was developed which shows excellent antifouling property and fair mechanical strength. The surface was heterogeneous with variable blend size domains. This will make the surface effective against most of the biofouling organisms when real time field tests will be performed.

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