



## Synthesis and characterization of amphiphilic copolymer composite for marine antifouling/foul-release coating

Lokeshwar Mahto\* and Dharm Pal

Department of Chemical Engineering, National Institute of Technology Raipur, Raipur-492010, Chhattisgarh, India

\*E-mail: lmahto.mtech2018.che@nitrr.ac.in

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Amphiphilic coating has gained a wide interest recently because of its comprehensive approach to tackle the problems arising from marine biofouling. In this study, the amphiphilic copolymer nanocomposite is synthesized using hydroxyl-terminated polydimethylsiloxane (HTPDMS) as the matrix and the chitosan nanoparticles. Chitosan nanoparticles are synthesized using ionotropic gelation method where nanoparticles of the size 200 nm to 10  $\mu$ m are obtained which is confirmed by the SEM images. The presence of different phases in the amphiphilic nanocomposite is also confirmed by the comparison of XRD patterns of chitosan nanoparticles, pristine HTPDMS, and amphiphilic nanocomposite. The wettability study reveals that the contact angle of pristine HTPDMS decreases from 96.97° to 74.77° with the dispersion of chitosan nanoparticles in the HTPDMS matrix making the surface amphiphilic. The critical surface tension as calculated by Zisman plot categorizes the amphiphilic coating in the foul-release zone. Fair resistance to wear was seen in the scratch-resistant test. The antifouling/foul-release behaviour of the samples is studied and the best results were seen in the case of the amphiphilic surface.

Keywords: Amphiphilic, marine biofouling, nanocomposite, coating, elastomer

### Introduction

Marine biofouling taking place over submerged artificial surfaces like ships, submarines, boat, etc. has adversely affected the marine industry over the years.<sup>1</sup> The cost of operation and maintenance of the submerged surfaces has taken a heavy toll on the finances of the marine industry estimated to be in billions of dollars per year.<sup>2</sup> The environmental threat is also a major concern as the wear and tear of existing coating material releases chemicals associated with it like copper oxide and zinc oxide into the seabed.<sup>3,4,5</sup>

To counter this problem, a novel non-toxic strategy is desired which is mechanically

robust and performs the given task of preventing marine biofouling efficiently. Polymer-based amphiphilic coatings are seen as a green alternative approach which imparts surface functionality such that it can possess both the activity of hydrophobic and hydrophilic moiety.<sup>6</sup> The hydrophobic component imparts very low surface energy which makes the removal of attached fouling species very easy. Hydrophilic component repels the attachment of fouling species as it forms a very strong hydration layer. With the combination of both the moieties, the coating surface will have combined antifouling/foul-release (AF/FR) property inherently.<sup>7,8</sup>

Numerous approaches have been employed to enhance the antifouling property

of the coating like incorporating antimicrobials, oils, and nanofiller into the Polydimethylsiloxane (PDMS) matrix but their efficiency towards microfouling is not adequate to sustain commercial viability for a long duration. Also, the optimum ratio of the moieties need to be studied thoroughly.<sup>7</sup>

PDMS is the most commonly used hydrophobic elastomer.<sup>9</sup> In this method, hydroxyl-terminated polydimethylsiloxane (HTPDMS) is used as the hydroxyl group of HTPDMS adds more functionality to it and enhances cross-linking behaviour.<sup>10</sup> To make the surface amphiphilic, chitosan nanoparticles which are hydrophilic in nature is added into HTPDMS.<sup>11</sup> Chitosan nanoparticles are synthesized according to ionotropic gelation method using sodium tripolyphosphate as the polyanion.<sup>12</sup> Coating samples are prepared using the direct mixing technique with the help of magnetic stirrer and applied over the surface using the hand bar coating technique.<sup>13</sup> The coated samples are characterized using analytical techniques and then it is tested for its AF/FR performance.<sup>14</sup>

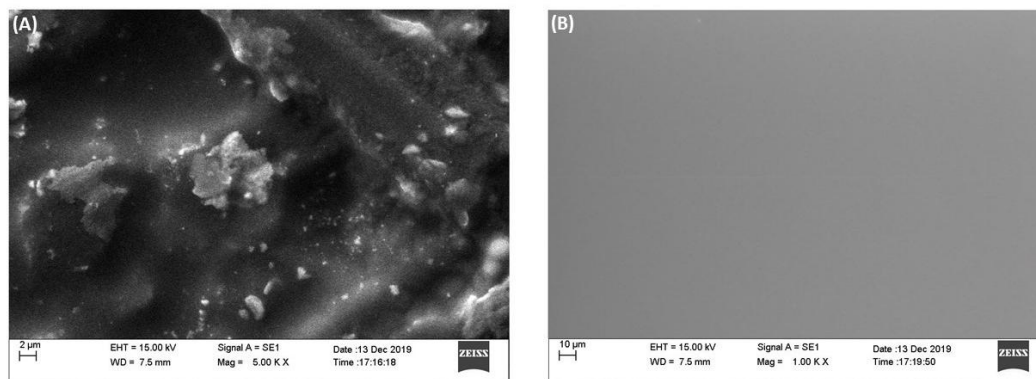
## **Material and methods**

*Materials:* Hydroxyl-terminated polydimethylsiloxane having a kinematic viscosity of 750 cSt and epoxy resin Bisphenol A diglycidyl ether (BADGE) were purchased from Sigma-Aldrich. (3-aminopropyl) triethoxysilane (3-APTES) having 98% purity acting as a crosslinker for HTPDMS and polyanion sodium tripolyphosphate (TPP) having 94% purity were purchased from SRL Chemicals. Chitosan flakes having 75% degree of deacetylation, epoxy hardener triethylenetetramine and 99.50% glacial acetic acid were purchased from Loba Chemie.

*Chitosan preparation:* Chitosan nanoparticles are produced by following the ionotropic gelation method with the help of polyanion sodium tripolyphosphate (TPP) where polycation chitosan and TPP spontaneously form chitosan nanoparticles under high stirring.<sup>15</sup> One g of 75% deacetylated chitosan flakes are dissolved in 100 ml of 1% v/v acetic acid at a temperature of 80 °C and stirring at 200 rpm for 2 hr. The undissolved higher molecular weight chitosan and other impurities are filtered using glass wool filter. Distilled water is further added into it to make a chitosan solution of 0.10% w/v concentration and pH 5. A 0.10% w/v TPP solution is obtained by dissolving 1 g of TPP in 1000 ml of distilled water under constant stirring for 30 min. A 4:1 ratio of chitosan and TPP solution respectively is taken for the synthesis.<sup>16</sup> A 4 ml of TPP solution is added dropwise into the 16 ml of chitosan solution kept in a beaker over the magnetic stirrer at 800 rpm for 30 min. It is further stirred for 30 min so that no agglomerates form. Spontaneous formation of chitosan nanoparticles occurs as TPP reacts with chitosan. The suspension is centrifuged at a high speed of 11000 rpm for 40 min. The obtained nanoparticles are washed with distilled water and then dried for further use.

### *Sample preparation:*

Three samples S0, S1 and S2 are prepared and further tested in this study. S0 is the control sample of galvanized mild steel plate having a size 7×5×0.5 cm<sup>3</sup>. Its surface is cleaned with sandpaper having grit size 150 and 400 and then it is washed with acetone



**Fig. 1.** SEM images showing the morphology of (A) amphiphilic nanocomposite at 5000X magnification and (B) pristine HTPDMS at 1000X magnification.

and later with water to further remove any impurities.<sup>13</sup> The surface is cleaned and ready to be coated. S1 is the pristine HTPDMS coating sample where 5 g of HTPDMS and 0.50 g of 3-APTES is set to react under the influence of magnetic stirring for 2 hr at room temperature where crosslinking takes place. The obtained viscous solution is applied over the control substrate following the hand bar coating technique and allowed to cure at room temperature for 72 hr. S2 is the polymer nanocomposite coating having HTPDMS as the polymer matrix and chitosan nanoparticles. In this, an epoxy tie layer is first applied over the control surface above which the nanocomposite coating is applied so that it adheres properly to the surface. To make the epoxy tie layer, 5 g of BADGE and 0.72 g of TETA, the stoichiometrically calculated curing

The presence of heterogeneous microstructure-nanostructure is visible in the nanocomposite whereas a clear smooth surface can be seen in the case of pristine HTPDMS in Fig.1.

The formation of chitosan nanoparticles is confirmed by the images with sizes ranging from 200 nm to 10  $\mu\text{m}$ . The variation in nanoparticle size is due to the

agent is mixed together at room temperature for 1 hr and applied over the control surface using hand bar coating technique which is cured at room temperature for 24 hr. A nanocomposite having 3.63% chitosan nanoparticles is prepared by taking 5 g of HTPDMS, 0.50 g of 3-APTES and 0.20 g of chitosan nanoparticles. The mixture is stirred at 800 rpm and 60  $^{\circ}\text{C}$  for 1 hr. After which, it is applied onto the tie layer using hand bar coating technique. The sample is allowed to cure at room temperature for 7 days.<sup>17</sup>

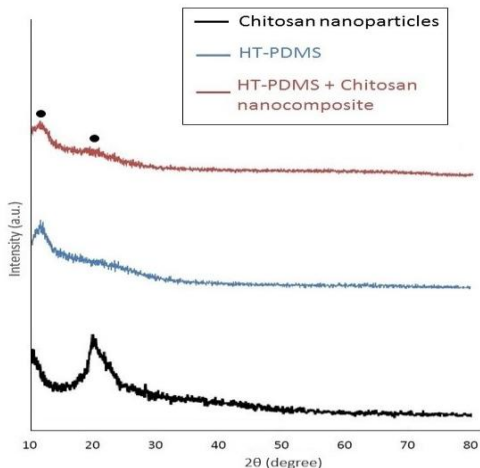
## Results and discussion

### Scanning electron microscopy analysis

The surface of pristine HTPDMS and amphiphilic nanocomposite as observed by scanning electron microscopy (SEM) reveals the distinct surface morphology. formation of agglomerates.<sup>18</sup> The presence of heterogeneous microstructure-nanostructure makes the surface ambiguous for fouling organisms and fouling species to adhere to it.

*X-ray diffraction analysis:* X-ray diffraction (XRD) analysis is done on chitosan nanoparticles, pristine HTPDMS and amphiphilic nanocomposite to compare and identify the presence of phases present in the

nanocomposite as shown in Fig. 2.



**Fig. 2.** Comparison of XRD patterns of amphiphilic nanocomposite, pristine HTPDMS, and chitosan nanoparticles.

For amphiphilic nanocomposite, both the distinguishable characteristic peaks of chitosan and pristine HTPDMS are visible at their values of  $2\theta = 20.09^\circ$  and  $2\theta = 12.16^\circ$  respectively where  $2\theta$  is the angle between the incident and diffracted X-ray. The peak of chitosan in the nanocomposite is slightly short because of less quantity of chitosan present. The broad peaks of chitosan and HTPDMS suggests that they are slightly amorphous in nature and there is interference of other

components present in the compound which might have come during the synthesis process.

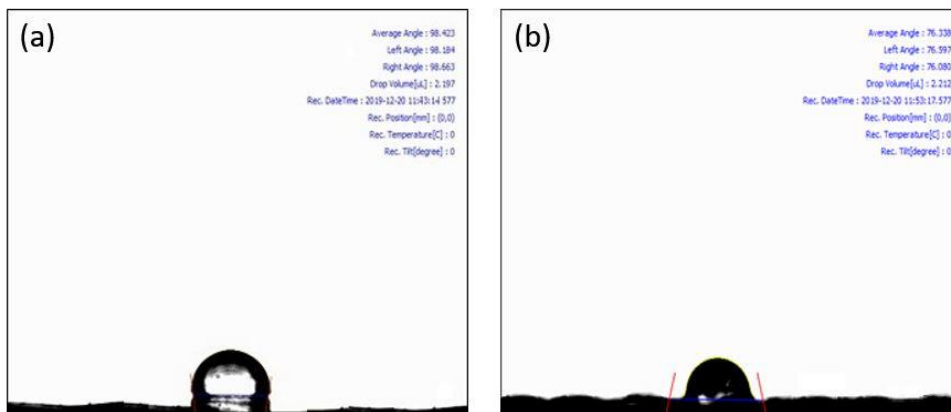
*Contact angle analysis:* The average contact angle of pristine HTPDMS and amphiphilic nanocomposite is calculated using contact angle analyser as shown in Fig.3.

The contact angle of pristine HTPDMS is  $96.97^\circ$  rendering hydrophobic nature which becomes hydrophilic with the incorporation of chitosan nanoparticles in it having a contact angle of  $74.77^\circ$ . This decrease in contact angle validates the formation of an amphiphilic surface having hydrophobic as well as hydrophilic moieties.<sup>19</sup>

Amphiphilicity of the nanocomposite is confirmed by the reduction in the contact angle of pristine HTPDMS from  $96.97^\circ$  to  $74.77^\circ$  of HTPDMS/chitosan nanocomposite.

*Critical surface tension*

The critical surface tension of a surface is calculated by using the Zisman plot where the surface tension of known liquids is taken at X-axis and the cosine of their contact angle is taken on Y-axis. The critical surface tension of the amphiphilic nanocomposite as calculated from the Zisman method is 19.34 mN/m which



**Fig. 3.** Image showing contact angle of (a) pristine HTPDMS (b) amphiphilic nanocomposite.

classifies it into the foul-release zone according to Baier's curve.<sup>20</sup> The coating is leaned towards the foul-release zone because the content of HTPDMS is greater in the sample and chitosan content is very less. But still, the influence of chitosan nanoparticles can be seen as the critical surface tension of the nanocomposite is less than the pristine HTPDMS.

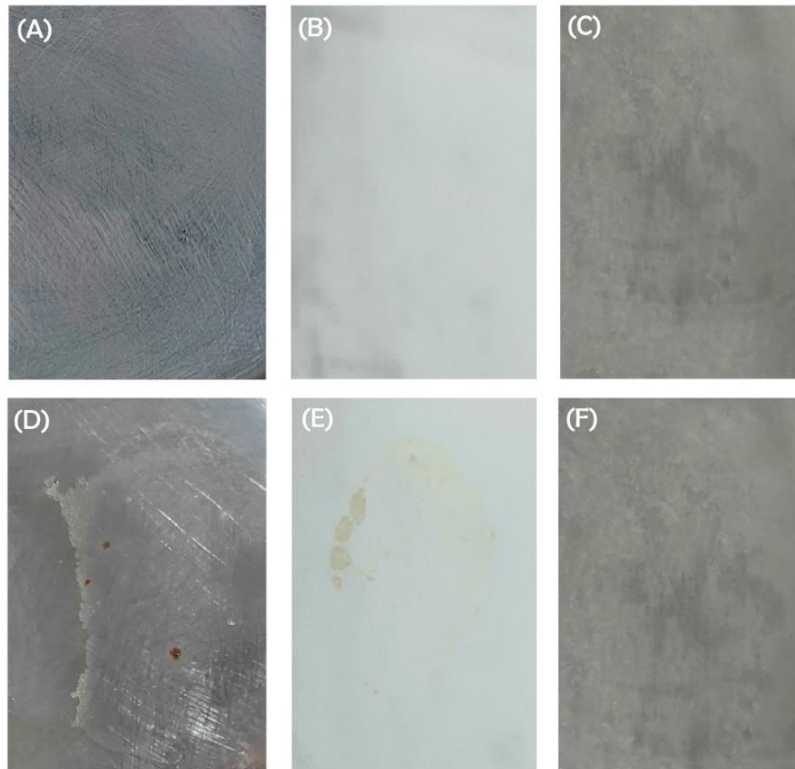
*Antifouling(AR)/foul-release(FR) performance test*

The AF/FR performance test is done using egg-white as a model test probe because egg-white contains 54% natural proteins which simulate the proteinaceous amphiphilic

structure of fouling species.<sup>21</sup> One ml of egg-white is spread over the control, pristine HTPDMS and amphiphilic nanocomposite and left to dry for 24 hr. The evaluation is done by grading them 1 to 4 where 1 is the best performing and 4 is the least performance as discussed in Table 1.

**Table 1.** Grading of the surface to find the AF/FR behaviour

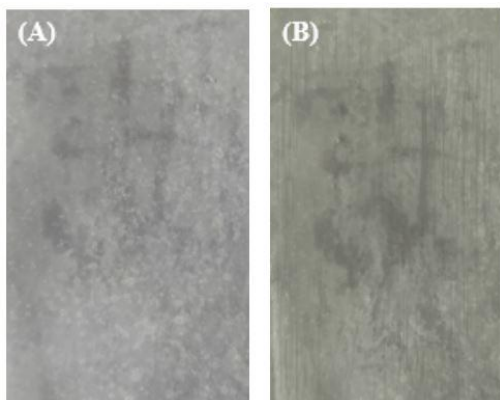
Grade	Activity
1	Clean after shaking
2	Clean after brushing
3	Less than 25% remains
4	Greater than 25% remains



**Fig. 4.** Images showing AF/FR performance test, where (A) control, (B) pristine HTPDMS, and (C) amphiphilic nanocomposite shows the surfaces before the test and (D) control, (E) pristine HTPDMS and (F) amphiphilic nanocomposite show the surfaces after the test is performed.

From Fig. 4, we can see that the control surface is heavily fouled showing grade 4 while amphiphilic nanocomposite showed the best performance having grade 1. While pristine HTPDMS showed grade 3 performance which validates that the prepared amphiphilic nanocomposite coating successfully resists the attachment of egg-white model test probe.<sup>14</sup> This is a test model made to target amphiphilic fouling species. But, the diversity of fouling species demands to test this sample with more species preferably marine field test to check the actual performance.

**Scratch-resistant test:** The scratch-resistant test was conducted on amphiphilic nanocomposite coating as shown in Fig. 5.



**Fig. 5.** Scratch-resistant test of sample S3 under (a) 500g load (b) 1000g load.

Firstly, adding 500 g weight above a sandpaper of grit size 150 and then pulling the sandpaper horizontally. After which the surface is taped and peeled off.<sup>19</sup> The surface examined shows a negligible scratch. Later, the weight is increased to 1000 g and the above procedure is repeated. In the case of 1000 g, the surface showed fair scratches which indicate that the coating resists only moderate scratches and its mechanical strength needs to improve.

## Conclusions

We reported the probable use of HTPDMS elastomer and chitosan nanoparticles together to form an amphiphilic surface which resists biofouling. The chitosan nanoparticles synthesized using the ionotropic gelation method gave nanoparticles in the size range 200 nm to 10  $\mu$ m. The successful incorporation of chitosan into the HTPDMS matrix is confirmed by the SEM and XRD analysis. The critical surface tension classifies the nanocomposite in the foul-release zone. The AF/FR test validates that the amphiphilic nanocomposite can resist the adhesion of fouling organisms effectively. Also, the mechanical robustness needs to improve which can be done by incorporating epoxy resin in the matrix. Real-time field test is required to find the actual performance.

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