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Anti-fouling Behaviors of Polyethersulfone – Coated Glass Fibre Reinforced Polymer Composite

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Abstract

In the realm of anti-fouling applications, coatings are essential in preventing the accumulation of fouling organisms, acting as a barrier against unwanted particles, contaminants, and microorganisms. However, traditional coating materials face limitations in resisting fouling growth, often accompanied by various drawbacks. This study delves into the effectiveness of different coating materials on glass fiber in marine environments. Specifically, it compares polyethersulfone (PES) coatings with Kossan paint coatings in terms of their anti-fouling properties. The primary aim is to assess the performance of these coatings over time (0, 14, 28, 60, 90, and 120 days) in marine settings. The degree of bio-fouling attachment on the samples was evaluated through visual observation and image J analysis. Results showed that glass fibers coated with Kossan paint exhibited a lower percentage of bio-fouling attachment compared to those with PES coatings. However, despite its efficacy in reducing bio-fouling, Kossan paint tends to detach from the glass fiber surface, necessitating repainting every four months, leading to higher maintenance costs. In contrast, PES coatings demonstrated superior adherence to the glass fiber surface, suggesting their potential as effective anti-fouling coatings. Nonetheless, modifications in properties such as surface roughness, hydrophobicity, and wettability are needed for PES coatings to efficiently prevent bio-fouling growth. This study highlights the need for balancing fouling resistance and durability in coating materials for sustainable marine applications.

1. Introduction

Biofouling in the marine environment involves the colonization of any solid surface, whether living or non-living, natural or artificial, by micro- and macroorganisms [1]. Submerged surfaces, including ship hulls, offshore platforms, and underwater pipes, are prone to biofouling. [2], resulting in reduced efficiency, corrosion, and higher resistance. [3]. The four most common groups of macro-fouler that impact marine devices or structures deployed at sea include mussels, bryozoans, calcareous tubeworms, and acorn barnacles. The formation of bio-fouling on submerged structures is influenced by factors such as the physicochemical properties of the surface [4,5], chemical composition [6-9], surface roughness [10,11], porosity [11-13], hydrophobicity [7], and pH [11-17]. However, the understanding of these factors in the marine environment is less developed [18-20].

Biofouling growth includes the colonization of macro-fouling species like macroinvertebrates and macroalgae, as well as micro-fouling creatures such viruses, bacteria, cyanobacteria, fungi, protozoa, and microalgae (21). Non-calcareous algae, sponges, anemones, tunicates, and hydroids, as well as calcareous hard-fouling animals such as acorn barnacles, mussels, and tubeworms, contribute to macrofouling. The amount of biofouling on a surface is determined by a variety of factors, including the type of surface, the features of the surrounding environment, and the fouling organism's properties [22]. To reduce the negative impacts of biofouling, solutions such as anti-fouling coatings, antibacterial coatings, bio-fouling resistant materials, and mechanical cleaning are used [23]. Antifouling coatings, which are commonly employed in the marine sector, limit the growth of marine biofouling, with some releasing biocidal substances onto seawater-exposed surfaces [24].

Natural and synthetic fibers are the main components of fiber materials [25, 26]. This study selected synthetic fiber (glass fiber) for its superior ductility and durability [27]. In various applications, such as in this study, glass fiber is coated with a selected coating materials to prevent or reduce bio-fouling attachment. PES and Kossan paint are among a range of coatings, including polytetrafluoroethylene (PTFE), polydimethylsiloxane (PDMS), and polyvinylidene fluoride (PVDF), that have been employed to combat marine biofouling [3]. These coatings function by creating surfaces unfavorable for bio-fouling attachment, combining properties like low surface tension, resistance to environmental stresses, and specific physical characteristics that deter organism settlement. PTFE creates a slick surface, difficult for organisms to attach to due to its low friction and stick properties. PDMS forms a soft, elastic covering that discourages settlement. PES acts as a barrier against fouling owing to its surface roughness [28]. PVDF, with its low surface energy and hydrophobic nature, repels living organisms [29]. Thus, the goal of this research is to evaluate and compare different types of coatings that can effectively prevent bio-fouling growth while minimizing impact on the marine environment.

This study aims to provide a comprehensive analysis of PES and Kossan paint, assessing factors such as their longevity, resistance to various types of marine biofoulers, and the cost-effectiveness of their application. The findings will contribute valuable information to the field of marine engineering and environmental science, offering guidance for selecting appropriate anti-fouling strategies in marine applications. Ultimately, this research seeks to advance our understanding of effective bio-fouling prevention methods, thereby aiding in the protection and preservation of marine infrastructure.

2. Methodology

2.1 Materials and Methods

PES powder was the primary material used to fabricate the PES coating. The PES powder was selected based on its high-performance characteristics, including excellent thermal stability, chemical resistance, and mechanical strength. The PES powder was sourced from a reputable supplier, Innovative Pultrusion Sdn. Bhd. Ensuring its quality and consistency. The PES membrane served as the coating material for the glass fibre reinforced polymer composites, imparting enhanced properties and protection to the composite structure.

Dimethylformamide (DMF) used as the solvent for the PES coating formulation. It is a clear, colourless liquid with a slightly sweet odour and is miscible with water and most common organic solvents. DMF is widely used in various industrial applications due to its excellent solvent properties and unique characteristics. DMF is a highly effective and versatile solvent known for its ability to dissolve various organic and inorganic compounds, including PES. The high solvency power of DMF facilitated the uniform dispersion of PES powder and the formation of a homogeneous PES coating solution. Using DMF as the solvent ensured the successful application of the PES coating onto the fibre reinforced polymer composites.

For the glass fibre composite laminate samples, the glass fibre called the CWR 200 C-type glass fibre was used. This synthetic chemical-based fibre has an incredibly high level of chemical resistance. The supplier of the CWR 200 glass fibre supply is Vistec Technology Sdn. Bhd. In plain weave patterns, direct roving is interwoven to create the CWR 200 woven roving fabric. The polymer resin used was Konudur 250 OM-PL, an organic-mineral polyurethane resin manufactured by MC-Bauchemie. The ratio between Part A and Part B is 1 to 2.

Kossan® paint is a commercial anti-fouling paint typically applied to a marine craft's hull and propellers to slow the growth of marine creatures, including algae, slime, mossy weeds, and barnacles. The coating is made to produce biocides, a type of poison. This paint was obtained from the local hardware as it is commercially used in broad applications.

2.2 Samples Preparation

a) Glass fibre reinforced polymer (GFRP) composite laminates

GFRP laminates were fabricated using hand lay-up and vacuum bagging techniques. The process started by cleaning and preparing the aluminium plate (5 mm) for the hand lay-up vacuum bagging process. The required amount of 2 parts (A and B) Konudur 250 OM-PL organic-mineral resin manufactured by MC-Bauchemie were then weighted and mixed thoroughly. The ratio between Part A and Part B is 1 to 2. The resin was chosen because its viscosity is low and has good adhesion properties with concrete, bricks and ceramics. The mixed resin (parts A and B) was applied alternately with a layer of fibre ply and finished with a resin layer. This process was repeated until the required thickness was achieved according to the test standard requirements.

b) PES coating
The casting solution was initially prepared by mixing a preset PES powder solution with a solvent containing 15% polyether sulfone (PES) and 85% Dimethylformamide (DMF). At 60°C, the casting solution swirled for 24 hours. The result was subjected to sonication before casting to eliminate air bubbles trapped inside the casting solution. The solution was poured onto a clean, dry glass plate and cast using a glass rod with a set separation of roughly ~100 µm between the plate and rod. To complete the phase inversion, the glass plate was immediately submerged horizontally in deionized (DI) water at a temperature of 25°C. The created coated membrane was immersed in DI water for 24 hours to allow for full-phase inversion. The coated membrane was dried at room temperature for characterization after being soaked in DI water.

c) Glass (TW)/ Kossan paint
The GFRP composite laminate samples were painted with Kossan Paint using the painting brush for 2 layers and left to dry at room temperature for 24 hours.

d) Glass (TW)/ PES
The PU resin was measured according to the required ratio of Part A to Part B. A square mould was prepared to pour the resin mixture onto the GF composite. The casted PES membrane was put in the bottom layer of the mould. Then, the resin was poured and uniformly distributed in the mould, covering the PES membrane. After that, the final layer, which is the GFRP laminate, was carefully placed into the mould. This has to be done cautiously as the PES might tear during this process. Then, the samples were left to cure at room temperature for 24 hours before removing them from the mould.

2.3 Surface Roughness

The surface roughness was analysed using Alicona InfiniteFocus optical 3D surface metrology, as shown in Fig. 1.

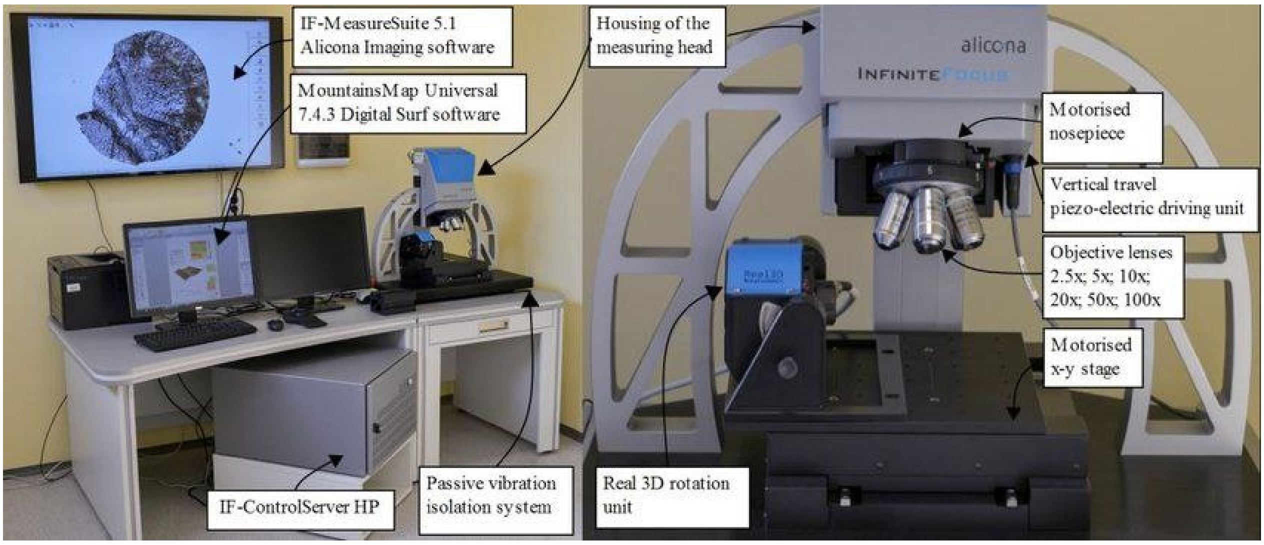


Fig. 1 *Alicona Infinite Focus G4*

The samples were prepared in the size of 2cm x 2cm. They were then placed on the passive vibration isolation system. The lens size used for the testing was 5x magnification. After the lens was adjusted, it was slowly lowered until the image became apparent on the monitor. The best height, placement, and brightness were determined to get a clear image. Once a clear image was achieved, the lens was lowered further until the image blurred, and this point was set as the z lower limit. Subsequently, the image was clarified again, and the lens was raised until the image became blurred once more, setting this as the z upper limit. Finally, the vertical resolution was set, and the measurement commenced.

2.4 Actual Condition (Seawater Exposure)

The bio-fouling mechanism is a complex process involving several stages. The early stage of bio-fouling begins with the initial attachment of microorganisms to the surface. The surface's physical and chemical properties can influence this initial stage. Once the microorganisms have attached to the surface, they produce an extracellular polymeric substance that forms a sticky matrix. This matrix helps other organisms attach easily to the surface and protects them from environmental stress. Over time, the attached microorganisms may form micro colonies on the surface. Subsequently, larger organisms such as barnacles and mussels can attach to the biofilm-covered surface, further growing and increasing the complexity of the fouling community.

The field testing for this study carried out at the Marine Materials and Structures Research Site of UiTM, based on Pulau Tuba, Langkawi, Malaysia (6.2487° N, 99.8245° E), as illustrated in Fig. 2. The samples were examined at intervals of 0, 14, 28, 60, 90, and 120 days. The coated glass fiber samples were positioned on a rack and immersed to a depth of 30 cm in saltwater. Prior to submersion, photographs of each sample were captured using a Nikon D5300 camera and documented as the 0-day data. After 14 days, the rack was removed from the seawater, and the samples were collected for visual observation and data gathering. For data collection, photos were taken of each sample, followed by a two-step analysis technique. Initially, visual inspection was accomplished by attentively observing the photographs. Later, the photos were examined using Fiji's ImageJ software. This stringent procedure was regularly applied at each observation interval throughout the research project.

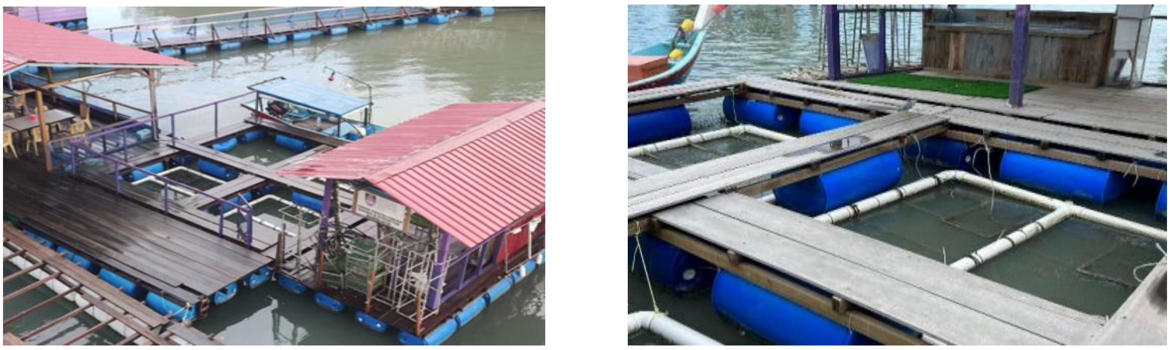


Fig. 2 *View of Tapak Penyelidikan Bahan & Struktur Marin UiTM at Chalet Terapung Bestuba, Pulau Tuba, Langkawi, Malaysia*

3. Results and Discussion

Upon submersion in seawater, the surfaces of the test samples were rapidly colonized by marine bacteria, forming highly complex, dynamic, and three-dimensional biofilm structures [30,31]. This initial colonization by marine bacteria on submerged objects is followed by the adhesion and growth of other microorganisms like algae and larvae, leading to the second major step in biofouling, often referred to as macrofouling [27,32].

As the study progressed, noticeable differences in biofouling formation between the GF/PES (glass fiber/polyethersulfone) and GF/Kossan paint samples were observed, as detailed in Table 2. By day 28, macrofoulers began to adhere to the GF/PES coating, while the GF/Kossan paint samples showed no signs of biofouling. This could be attributed to the anti-fouling properties of the commercial Kossan paint, which served as a reference sample in this study. The disparity in bio-fouling formation on the GF/PES samples became more pronounced after 60 days in seawater. However, at this same 60-day mark, the paint began to leach from the GF/Kossan paint samples.

After 120 days, the GF/PES samples exhibited a fouling-release effect. This observation was made as the percentage growth of bio-fouling was higher at 90 days compared to 120 days. The PES coating demonstrated its ability to reduce the adhesion and growth of fouling organisms, likely due to its low hydrophobicity [34]. Although GF/PES is hydrophobic, the results indicate that it was significantly effective only until the end of the first month of immersion in seawater. Conversely, for the GF/Kossan paint samples, the leaching of paint exposed the glass fiber to the marine environment, thereby favoring bio-fouling growth starting after 90 days and intensifying after 120 days.

Table 1 *Progressive formation of bio-fouling on the tested samples from 0 to 120 days using visual observation*

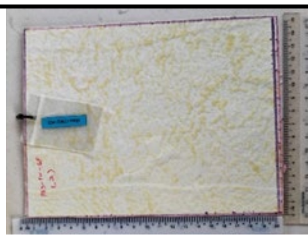
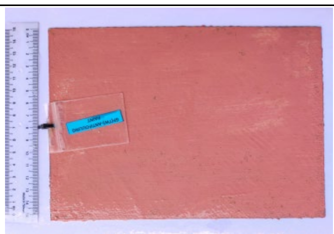
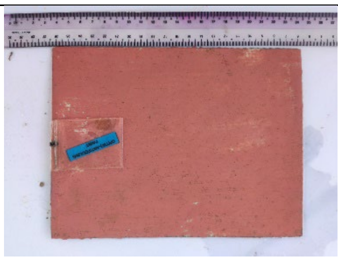
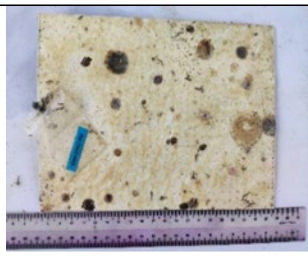
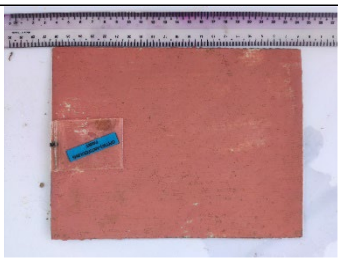
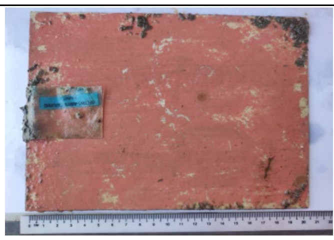
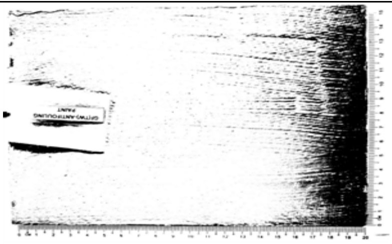
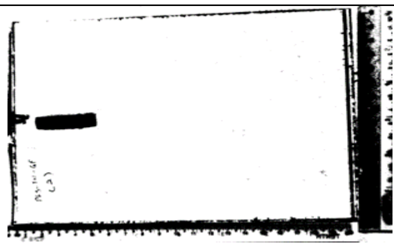
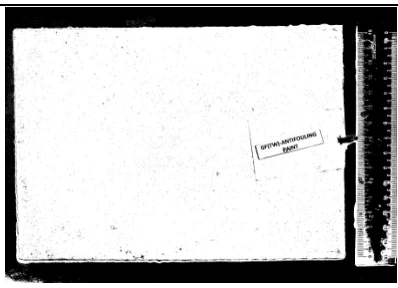
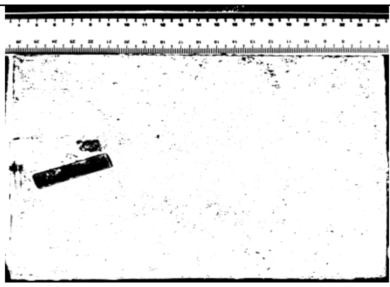
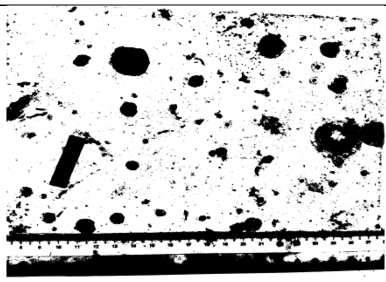
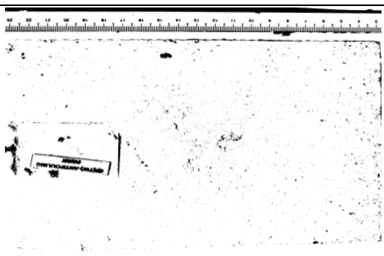
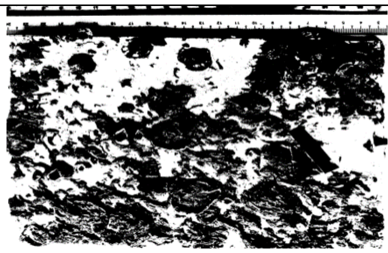
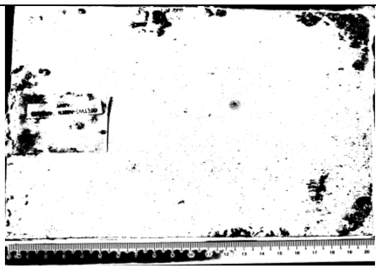
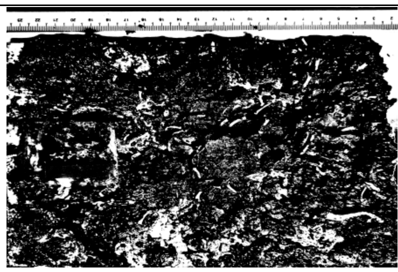
Day of observations	Glass (TW)/ KOSSAN PAINT	Glass (TW)/ PES
0		
14		
28		
60		
90		
120		

Table 2 *Progressive formation of bio-fouling on the tested samples from 0 to 120 days using Image J software*

Day of observations	Glass (TW)/ KOSSAN PAINT	Glass (TW)/ PES
0		
14		
28		
60		
90		

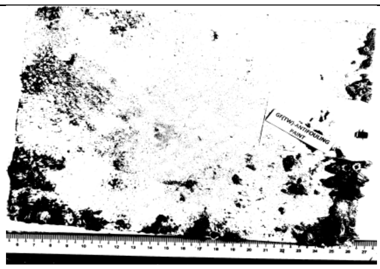
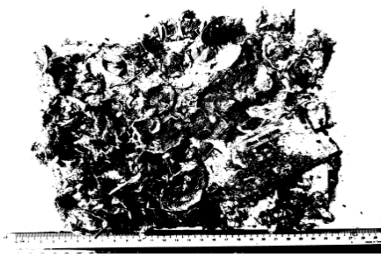
120		

Table 3 *Percentage of bio-fouling attachment by Fiji Image J analysis*

Day	**Bio-fouling growth (%)**	
DAY	**GF/PES**	**GF/KOSSAN PAINT**
0 DAY	0	0
14 DAYS	2.16	1.23
28 DAYS	24.31	1.42
60 DAYS	58.54	1.66
90 DAYS	80	5
120 DAYS	63.30	17.64

Table 3 presents the percentage of bio-fouling growth on both GF/PES (glass fiber/polyethersulfone) and GF/Kossan paint samples over 120 days of exposure in seawater. After 14 days, no significant difference in bio-fouling growth was observed between the two types of samples. However, a significant difference began to emerge after 90 days, where GF/Kossan paint recorded only 5% bio-fouling attachment compared to 80% for GF/PES. Although this significant difference in terms of bio-fouling growth was noted after 90 days, the Kossan paint on the GF had already started to leach, leading to increased bio-fouling as microorganisms could easily attach to the exposed GF.

After 120 days, due to the leaching process, an increase in bio-fouling growth was observed on the GF/Kossan, which rose by about 12% from the initial 5%. Despite this, Kossan paint is still considered an effective coating for deterring bio-fouling growth since the percentage remained below 50%. In contrast, bio-fouling growth on GF/PES increased with the duration of exposure. However, at 120 days, the percentage of bio-fouling growth was 16.70% less than at 90 days. This reduction could be attributed to the surface characteristics of GF/PES, which is smooth, making it difficult for bio-fouling to attach firmly. When bio-fouling becomes too heavy, the attachment site cannot support the weight, leading to the detachment of bio-fouling when subjected to forces such as tidal waves or sea currents. Fig. 3 illustrates the results of the surface roughness analysis for GF/PES.

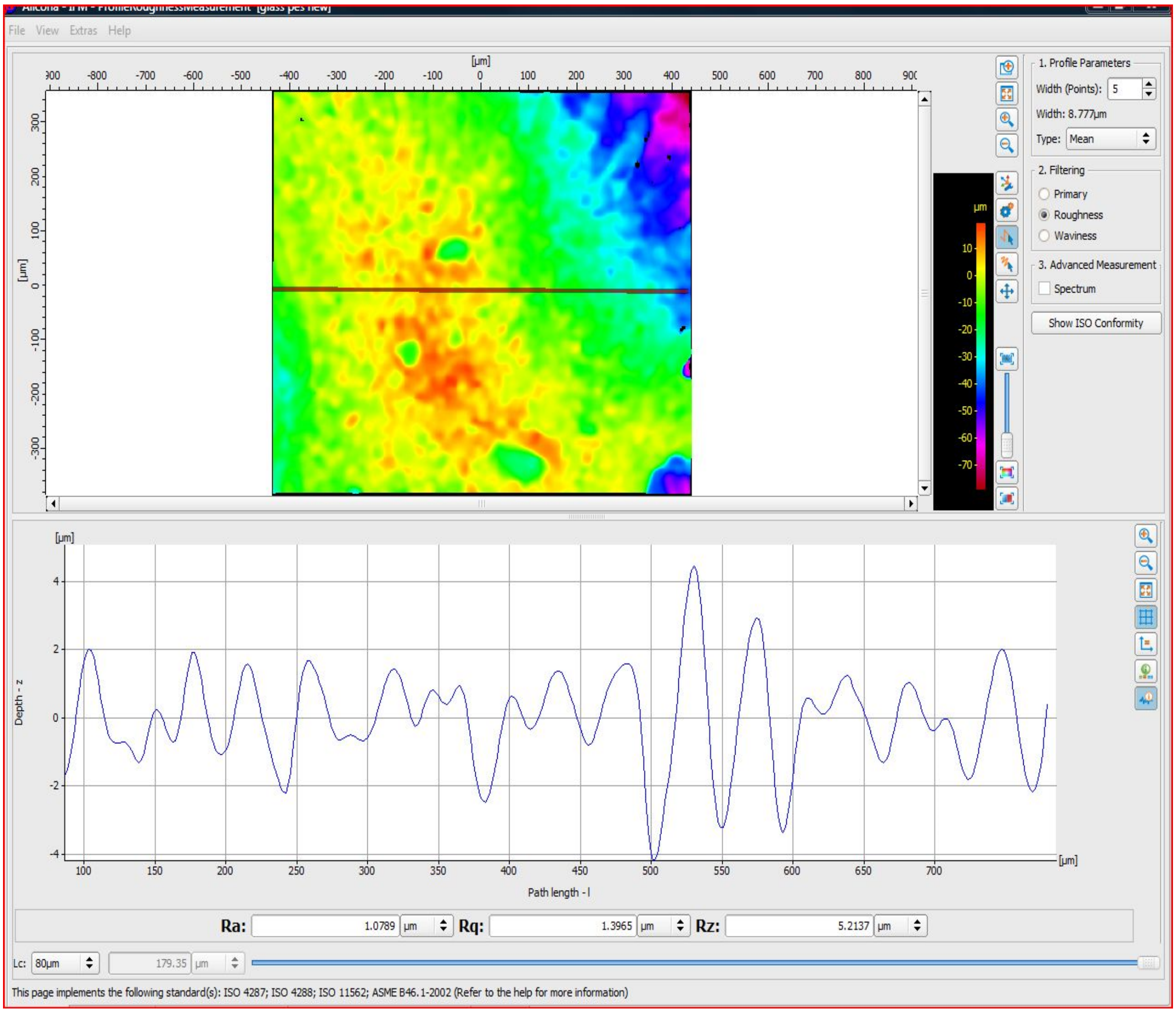


Fig. 3 *Surface roughness result for GF/PES using Alicona*

The results obtained from the surface roughness analysis of GF/PES (glass fiber/polyethersulfone) indicate a roughness average (Ra) value of 1.0789 micrometers. This measurement of surface roughness is critical in understanding the interaction between the coating and marine bio-fouling organisms. Referring to Fig. 4, which is a Surface Finish Cross Reference Chart, the Ra value of 1.0789 micrometers places the GF/PES surface finish between that of a satin sheet and a satinary finish. Such a finish is characterized by a relatively smooth texture.

The significance of this smoothness lies in its impact on bio-fouling attachment. In marine environments, the surface characteristics of submerged materials play a pivotal role in the initial stages of bio-fouling. A smoother surface, as evidenced by the GF/PES's Ra value, typically offers fewer crevices and less surface area for microorganisms to adhere to. This reduced availability of anchoring points on the surface makes it challenging for bio-fouling organisms to establish a stable and strong attachment.

Therefore, the smooth surface of GF/PES, as indicated by its placement between satin and satinary finishes on the reference chart, contributes to the weak attachment of bio-fouling. This attribute can be particularly beneficial in marine applications, as it suggests that GF/PES coatings might require less frequent cleaning and maintenance due to their inherent ability to resist heavy bio-fouling. This quality of GF/PES, therefore, becomes an essential factor to consider when evaluating its effectiveness and practicality as an anti-fouling solution in marine environments.

Surface Finish Cross Reference Chart

Feed in Inches Per Revolution Tool Nose Radius		Ra Micro Inch	Feed in MM Per Revolution Tool Nose Radius		Ra Micron	RMS Micro Inch	Grit Number	Common Name	ISO Number	USA Number
0.0156"	0.0313"		.3969	.7938						
.0274	.0387	2000	.6956	.9837	50				N12	
.0194	.0274	1000	.4919	.6956	25				N11	
.0137	.0194	500	.3478	.4919	12.5				N10	
.0099	.0137	250	.2469	.3492	6.3		60	Mill Plate	N9	#1
.0069	.0097	125	.1760	.2489	3.2				N8	
		40 to 70				80	80	Satin Sheet		#2
.0049	.0069	63	.1244	.1760	1.6				N7	
.0044	.0062	52				58	100 to 120			#3
		40 to 60					120	Commercial #4		#4
		30 to 40				42-47	150	Sanitary Finish		#
.0035	.0049	32	.0880	.1244	0.80			ANSI #4	N6	
		20 to 32				34	180	3ASanitaryFinish		#4
		20 to 25					200 to 220	Biotech Finish		#4
		15 to 20				17	240			#6
.0025	.0035	16	.0622	.0880	0.40	17			N5	
		8-12				14	320			#7
.0021	.003	12	.0539	.0762	0.30	13 to 14				
.0017	.0025	8	.0440	.0622	0.20	9			N4	
		4 to 8					400	Mirror Finish		#8
		3 to 8					500	Supermirror Finish		#8
.0012	.0017	4	.0311	.0440	0.10	4 to 10	500	Supermirror Finish	N3	#8
.0009	.0012	2	.0220	.0311	0.050				N2	
.0006	.0009	1	.0156	.0220	0.025				N1	

Fig. 4 *Surface finish cross reference chart*

4. Conclusion

In conclusion, this study demonstrates that after being submerged in seawater for up to four months, the smooth surface of the GF/PES (glass fiber/polyethersulfone) samples facilitates the detachment of bio-fouling. This detachment occurs because, after four months, the bio-fouling becomes too heavy for the attachment site to support its weight, leading to its separation from the sample. In contrast, GF/Kossan samples exhibit efficiency in preventing bio-fouling growth. This is evidenced by the relatively low bio-fouling growth on GF/Kossan paint, which was only 17.64% after four months in seawater.

To summarize, although GF/PES can facilitate the detachment of bio-fouling that grows on its surface, bio-fouling can still attach more easily to GF/PES compared to GF/Kossan paint, owing to the biocidal properties of Kossan paint. This suggests that GF/Kossan paint is a more effective option for preventing bio-fouling growth than GF/PES, despite the need for repainting after four months. However, while Kossan paint significantly prevents bio-fouling growth, its higher maintenance cost due to a lack of durability is a drawback. PES could be a viable anti-fouling coating but requires modifications in properties such as surface roughness, hydrophobicity, and wettability to enhance its efficiency in preventing bio-fouling growth. Further research is needed to identify the optimal coating that can effectively prevent bio-fouling and offer enhanced durability in seawater conditions.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design:*** *Muhammad Hazim Abdul Kadir, Mohd Akmal Hashim, Aidah Jumahat;* ***data collection:*** *Muhammad Hazim Abdul Kadir, Mohd Akmal Hashim, Ummu Raihanah Hashim;* ***analysis and interpretation of results:*** *Muhammad Hazim Abdul Kadir, Mohd Akmal Hashim, Aidah Jumahat, Ummu Raihanah Hashim;* ***draft manuscript preparation*** *Muhammad Hazim Abdul Kadir, Mohd Akmal Hashim, Aidah Jumahat, Ummu Raihanah Hashim. All authors evaluated the results and endorsed the final version of the manuscript.*

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