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RESEARCH ARTICLE

ENHANCING CORROSION RESISTANCE OF WELDED METALS WITH SELF-HEALING COATINGS: EVALUATION OF EPOXY FORMULATIONS AGAINST MICROBIOLOGICALLY INFLUENCED CORROSION

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Abstract. Corrosion of welded metals poses a significant challenge in industrial contexts, especially when joints are exposed to harsh environmental conditions. Although traditional corrosion protection methods, such as coatings, offer a cost-effective solution, their effectiveness can be undermined by aggressive corrosive agents or microorganisms. Recent advancements in self-healing coatings present a promising alternative, as these coatings can autonomously repair and prevent corrosion, thereby extending the service life of the metal. Microbiologically influenced corrosion (MIC), driven by microorganisms such as Pseudomonas aeruginosa, accelerates metal degradation in nutrient-rich simulated sea water medium (NRSS). This study aims to evaluate the efficacy of self-healing coatings in mitigating MIC on dissimilar welded metal substrates. Specifically, it assesses the performance of epoxy coatings incorporating 7 wt.% microcapsules and 10 wt.% chitosan particles compared to pure epoxy coatings. The coatings were applied to welded substrates and subsequently inoculated with Pseudomonas aeruginosa for 3, 7,14,28 and 42 days immersion test. Field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS) were used to analyze biofilm formation, bacterial cell morphology, and corrosion precipitates. The results indicate that the self-healing coatings containing microcapsules and chitosan particles significantly improved corrosion protection, as evidenced by FESEM images showing reduced bacterial adhesion and biofilm formation. Chitosan particles, with their positively charged nitro-groups and high surface area, proved particularly effective in inhibiting biofilm development and exhibiting biocidal properties.

Keywords: Corrosion resistance, epoxy formulations, microbiologically influenced corrosion (MIC), self-healing coating.

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1. INTRODUCTION

Microbiologically Influenced Corrosion (MIC), commonly referred to as Bio-Corrosion, is an electrochemical process [1] that involves the formation of biofilms and bacterial attachment. These processes alter the electrochemical disorder at the metal substrate/solution interface, accelerating the MIC corrosion process [2,3]. MIC can be introduced and facilitated by microorganisms including bacteria, viruses, archaea, and even fungus. Microorganisms can greatly accelerate localized and pitting corrosion and attack most metal substrate materials, such as copper, stainless steel, and low carbon steel [2-4]. In many different habitats, such as freshwater, saltwater, soil, cooling water, oil field produced water, etc., MIC is a present and significant issue.

The environment is full of bacteria, which are tiny microorganisms that are especially common in seawater. For instance, low carbon steel and stainless steel are commonly welded together in maritime environments, where they are exposed to highly caustic bacteria like Pseudomonas aeruginosa [5]. As an aerobic bacterium, Pseudomonas aeruginosa can survive and grow in an oxygen-rich environment.

Although 316L stainless steel and low carbon steel have different welding processes, they are nonetheless utilized in a variety of applications, including offshore structures and pipelines [6,7]. Dissimilar welded joints are used in oil and gas because of their strong corrosion resistance, lightweight design, and inexpensive cost of materials [8,9]. The process underlying MIC concerns in marine environments is not well understood. Research on the MIC of dissimilar welded connections made of 316L stainless steel and low carbon steel in a marine environment is still lacking [10].

Commercial paint and polymer coatings are frequently used to alter substrates' appearance for aesthetic or corrosion-resistant reasons [4]. The paint layer changes mechanically during application and maintenance, leading to microcracks, scratches, blasting, and other flaws that spread and expose the metal substrate to oxygen, seawater, chloride, and atmospheric moisture. Flake production from the substrate's coating interface and increased coating disbanding or peeling are the results of this operation [5]. One way to conceptualize polymer coating is as a unique class of binders, composite materials, colors, and specific additives. In order to give coatings greater durability, the idea of self-healing cracks-which has been documented for composites-can thereafter be utilized. An attempt to heal scratches on oil and gas coatings using secret polymer properties has been reported [6].

The intriguing capability of self-healing coatings to restore their structural integrity on their own following the emergence of microcracks-which can be caused by mechanical damage or the release of internal stress in a coating-is probably what has generated such a surprising amount of interest in them. It is anticipated that this kind of functionality will lead to lower maintenance costs, which is particularly desirable for offshore projects like pipelines and platforms. Because tung oil can form films by air oxidation, it was selected as a healing agent in this investigation along with driers. Microcapsules with urea–formaldehyde as the shell and drying oil as the core were made using in situ polymerization [8].

To simulate marine environmental conditions, this study investigated the corrosion behavior of a dissimilar welded joint between low carbon steel and 316L stainless steel in nutrient-rich simulated seawater (NRSS), both in the presence and absence of Pseudomonas aeruginosa. The objective of this study was to evaluate the influence of microbiologically influenced corrosion (MIC) on the integrity of dissimilar metal welds in a simulated marine environment. Immersion tests were conducted to evaluate the impact of microbial activity on corrosion. Surface morphology, pit formation, biofilm development, and bacterial attachment including extracellular polymeric substances (EPS) were analyzed using field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS) for samples exposed to both sterile and bacteria-inoculated media.

2. MATERIALS AND METHODS

2.1 Preparation of Welded Joint as Substrate Material

Low carbon steel and 316L stainless steel plate were used in the current study. Both materials arrived as plates that were 12 mm thick. Table 1 displays the base's and the filler's chemical makeup. Both 100 mm × 50 mm × 12 mm plates served as the basis material for the gas tungsten arc welding (GTAW) process in this investigation, while ER316L electrode was used as the filler. The joint utilized in this project is a butt joint, which has a single V shape and a 60° angle.

Table 1: Chemical composition (wt. %) of the base metal and filler used

Alloy element	C	Si	Mn	P	S	Cr	Ni	Cu	Fe
Filler (ER316L)	0.055	0.702	1.48	0.036	-	16.12	9.82	0.120	Balance
316L Stainless Steel	0.031	0.301	1.51	0.052	-	17.90	9.52	0.555	Balance
Low Carbon Steel	0.157	0.166	0.613	0.030	0.021	0.106	0.078	0.230	Balance

The welded components performed a Dye Penetrant test and X-ray radiography after the welding process. Pieces that were defective or severely welded were not included. Defect-free welded components were ready for investigation using microbial-induced corrosion testing. A Sodick AQ537L CNC wire cut machine was used to cut all test samples into smaller pieces, each measuring around 50 mm by 10 mm by 12 mm. Before the test, every specimen was cleaned. The cleaning process involved utilizing a grinding machine to crush SiC paper up to 1200 grit, followed by an alcohol solution for cleaning.

In-situ polymerization in an oil-in-water emulsion was used to make microcapsules [8–10]. Ten milliliters of a 5 weight percent aqueous solution of polyvinyl alcohol (PVA) and 160 milliliters of deionized water were combined at room temperature in a 1000 milliliter beaker. Five grams of urea, half a gram of ammonium chloride, and half a gram of resorcinol were dissolved in a solution while being shaken. A 5 weight percent solution of hydrochloric acid in deionized water was used to bring the pH down to roughly 3.5. As an antifoaming agent, one or two drops of octanol were used. To create an emulsion, 60 ml of tung oil was gradually added, and the mixture was stirred for 15 minutes to stabilize. 12.67 g of a 37 weight percent aqueous formaldehyde solution was gradually added after stabilization. After being covered, the emulsion was gradually heated to between 55 and 60 degrees Celsius while being stirred at 700 rpm for five hours. At room temperature, the contents were chilled. Microcapsules were extracted from the suspension by vacuum-assisted filtration. These were washed with xylene and rinsed with water to get rid of the oil that was suspended [11,12]. A vacuum oven was used to dry the capsules.

2.2 Preparation of NRSS Medium

The NRSS medium was made according to E. Hamzah et al.'s and A. Abdolahi et al.'s formulation [13,14], and 5M NaOH was added to bring the pH down to about 7.2. 3.917 g/L Na_2SO_4, 0.192 g/L $NaHCO_3$, 0.664 g/L KCl, 0.096 g/L KBr, 10.61 g/L $MgCl_2.6H_2O$, 1.469 g/L $CaCl_2.2H_2O$, 0.026 g/L H_3BO_3, 0.04 g/L $SrCl_2.6H_2O$, 3 g/L bacteriological peptone, 1.5 g/L yeast extract, and 23.476 g/L NaCl make up the medium. All of the chemicals were bought from QreC Company, with the

exception of the yeast extract, which was bought from Scharlay Company. To guarantee sterility, both media were autoclaved for 20 minutes at 121 °C at 15 psi pressure.

2.2.1 Pseudomonas Aeruginosa Bacterial Culture

The bacteria employed in this investigation, Pseudomonas aeruginosa, with code number DSM 50071, was acquired from the German Collection of Microorganisms and Cell Cultures (DSMZ) at the Leibniz Institute. To prepare and cultivate Pseudomonas aeruginosa on agar plates, the following procedure was followed, as shown in Figure 1.

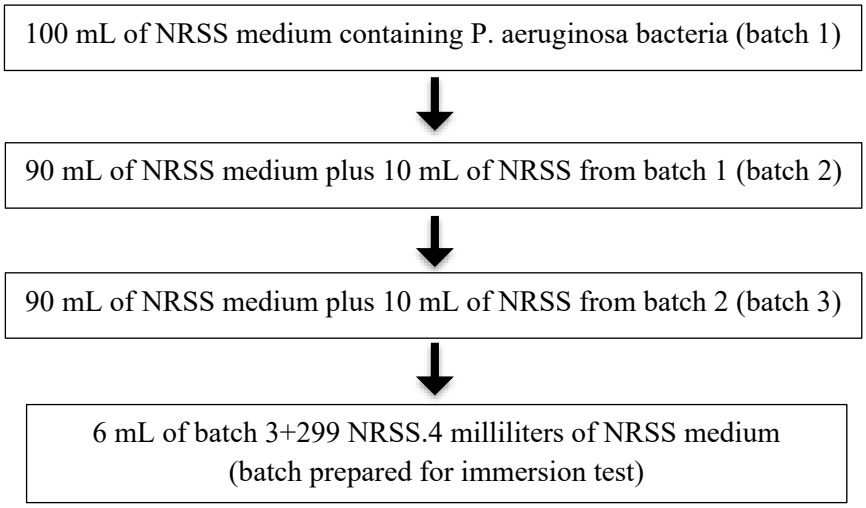


Figure 1: Procedure to prepare and cultivate Pseudomonas aeruginosa

Each batch was prepared by shaking the mixture in a shaker for 24 hours at 30 degrees Celsius at a speed of 150 revolutions per minute. The concentration of bacterial cells was determined using the optical density (OD) data. An OD of 1.0 is equivalent to approximately 10^9 cells mL-1, based on the standard calibration. The aseptically prepared specimens were hung on nylon strings and added to the inoculation medium when the OD value was near 1.0 [15-17].

2.3 Immersion Test

For the immersion testing, the dissimilar welded joint samples were submerged in two different kinds of NRSS medium: (i) biotic (bacteria infused medium) and (ii) abiotic (control) (sterile medium). Every sample was stored in a stagnant condition at room temperature. Seventy-five percent (225 mL) of the pseudomonas aeruginosa-inoculated NRSS medium drained away every seven days, and the same volume of new NRSS medium was added. Throughout the experiment, this was done to maintain the bacterial density around the steady-state growth phase.

The data acquired were for qualitative observation, which offers some insight into the corrosion performance of the coating materials. After being removed from the immersion test, the coated dissimilar welded metal samples were sent for FESEM examination.

2.4 FESEM/ EDS

The biofilm layer that developed on the different welded joint substrate was examined using an Energy Dispersive X-ray Spectrometer (EDS) attached to a Field Emission Scanning Electron Microscope (FESEM, VP35 Zeiss Supra, Germany).

3. RESULTS AND DISCUSSION

To prevent the MIC of coated dissimilar metal welded joints subjected to sterile and bacterially infected media, a self-healing coating containing 7 weight percent microcapsule was employed. In order to examine their MIC inhibition capabilities, the linseed oil microcapsule was first created and applied to the welded substrate as a coating using epoxy. The MIC inhibition behavior of self-healing coating performance using immersion and electrochemical testing will be covered in the next section.

3.1 Visual Inspection

Figure 2 illustrates the optical appearance of a self-healing coating applied to dissimilar welded metal that contains 7 % of a microcapsule-exposed bacterial inoculation medium following varying immersion time. From the surface look, it was evident that the coatings were in good condition and that the bacterial colonization attachment had not caused any failures or damage, such as blistering, peeling, or delamination. This demonstrated the self-healing coating's strong adherence to the dissimilar metal welded joint substrate. According to the initial outcome, the substrate welded metal is shielded from bacterial attack and corrosive solution by the healing agent's ability to recover the scribed area. However, there was no biofilm growth or bacterial adherence around the new layer (scribe region) or coating surface. The visual appearance results were qualitative, and the FESEM imaging results provided additional quantitative confirmation.

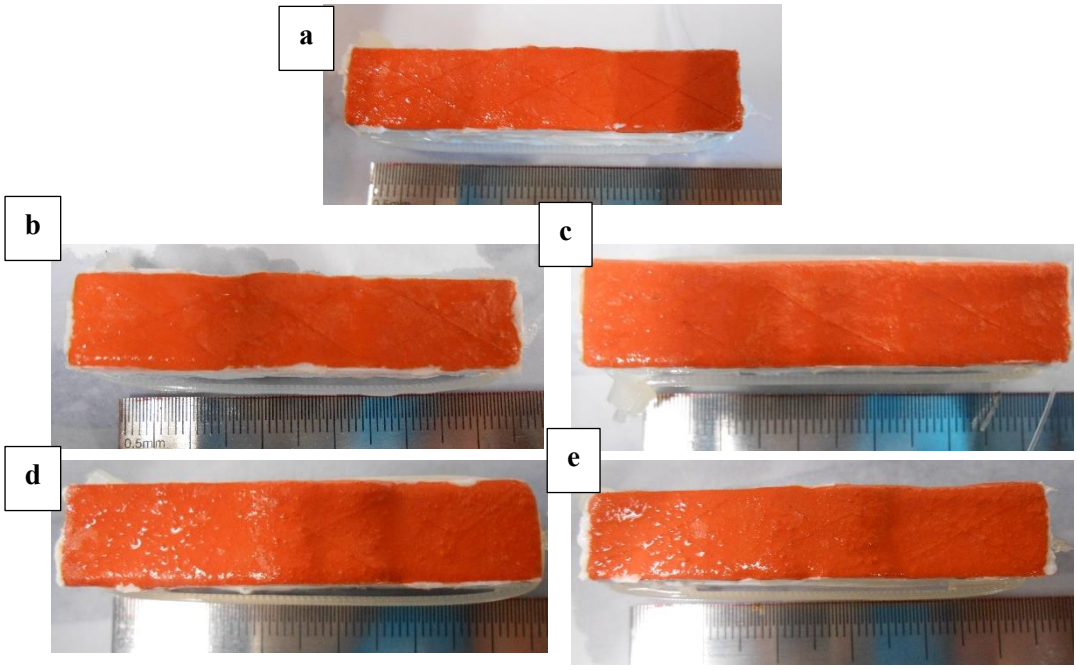


Figure 2: Visual inspection of self-healing coating-coated substrates for dissimilar metal welded joints exposed to inoculation medium at varying immersion times (a) 3 days, (b) 7 days, (c) 14 days, (d) 28 days and (e) 42 days

3.2 Characterization by FESEM/ EDX

Figure 3 shows the FESEM picture of dissimilar welded metal substrates coated with a self-healing coating and subjected to the bacterially infected media after varying immersion times. During the first three days of immersion, no bacterial cells adhered or biofilm formed on the self-healing coating that contained 7 weight percent of microcapsule-coated dissimilar welded metal substrate, as seen in Figure 3(a). Long chain bacterial cells were adherent to the coated surface following seven days of

immersion (Figure 3 (b)). The number of bacterial cells reduced when the immersion time was extended by weeks (Figure 3 (c-e)). Additionally, biofilm formation was suppressed. It is demonstrated that only a small number of individual bacterial cells were dispersed independently on the coating surface and that, following varying immersion times, there was no biofilm on the self-healing coated dissimilar welded metal substrate. The chitosan particle's positively charged nitro-groups were partly to blame for preventing the formation of biofilm [11]. Furthermore, chitosan particles with a high surface area may potentially exhibit biocidal qualities [12].

The chitosan particle and linseed oil microcapsule interacted with Pseudomonas aeruginosa's outer membrane to produce structural alterations that would impact the bacteria's ability to operate and ultimately lead to its demise. The self-healing coating's biocidal qualities were brought about by the chitosan particle's positive charge. Furthermore, the chitosan particle's high surface area and polycationic structure allow it to interact with the macromolecular structures and anionic chemicals found in bacterial cells [12, 14]. As in the original study, linseed oil application provided excellent corrosion protection in the scribed area. Furthermore, the bacteria may be killed by the dry linseed oil's biocidal qualities. The hydrophilic surface profile was largely determined by the physical overview of the coating, which included high surface tension, high surface roughness, and a composite of both added qualities for the self-healing coating, as seen in Figure 4. Enhancement of the surface profile causes bacterial cell rupture and biofilm development.

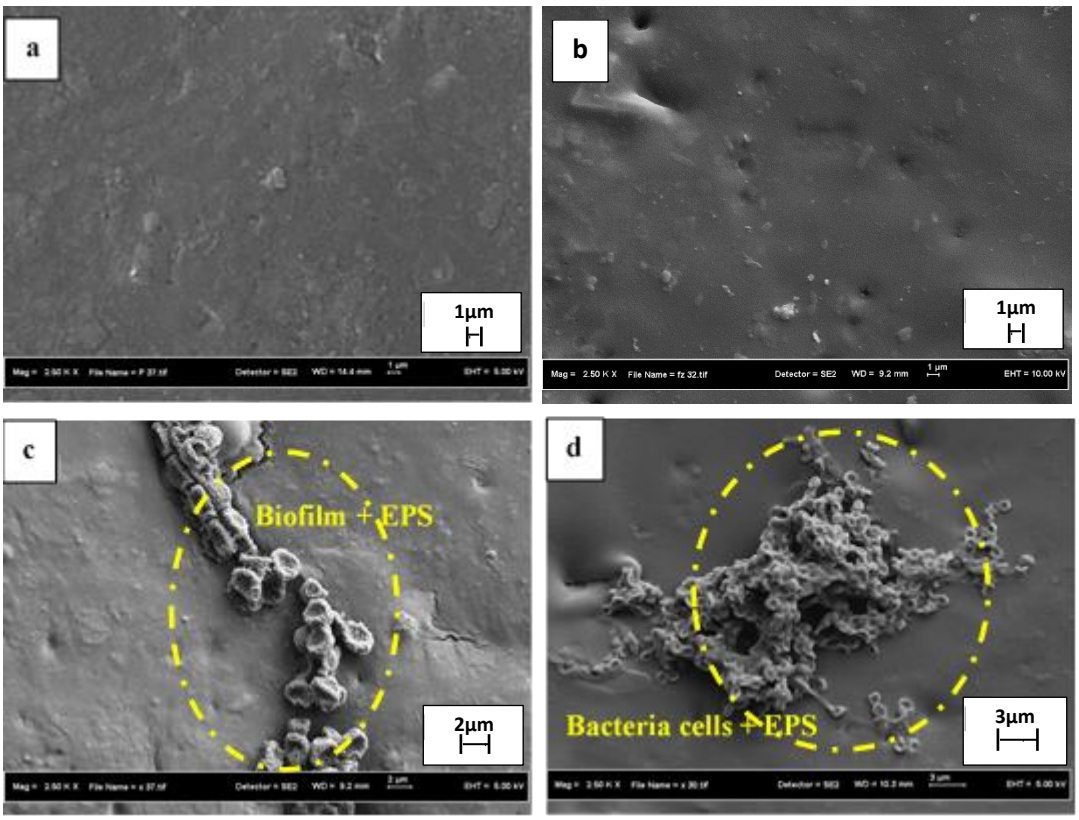
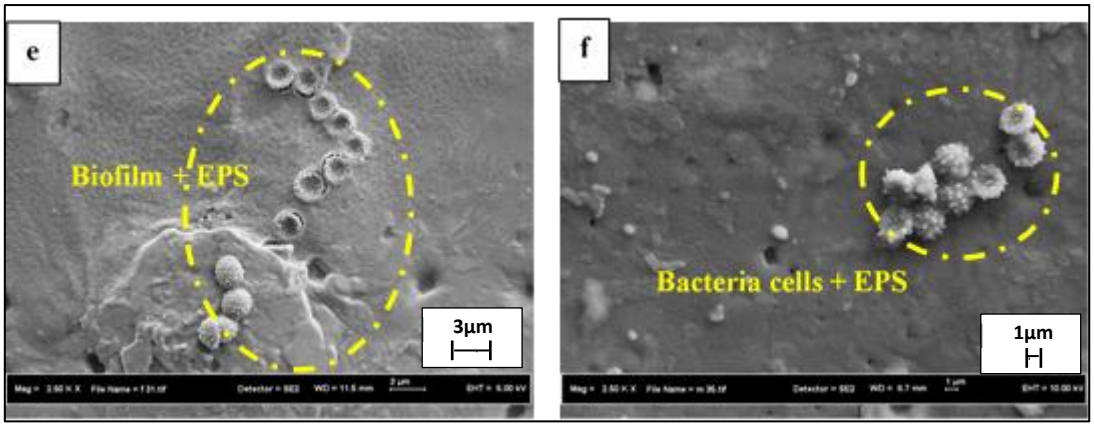


Figure 3: FESEM micrograph of self-healing coated dissimilar welded joint substrate embedded with 7 wt.% linseed oil encapsulated (a) before immersion (b) 3 days, (c) 7 days, (d) 14 days, (e) 28 days and (f) 42 days after exposed to pseudomonas aeruginosa inoculated NRSS medium



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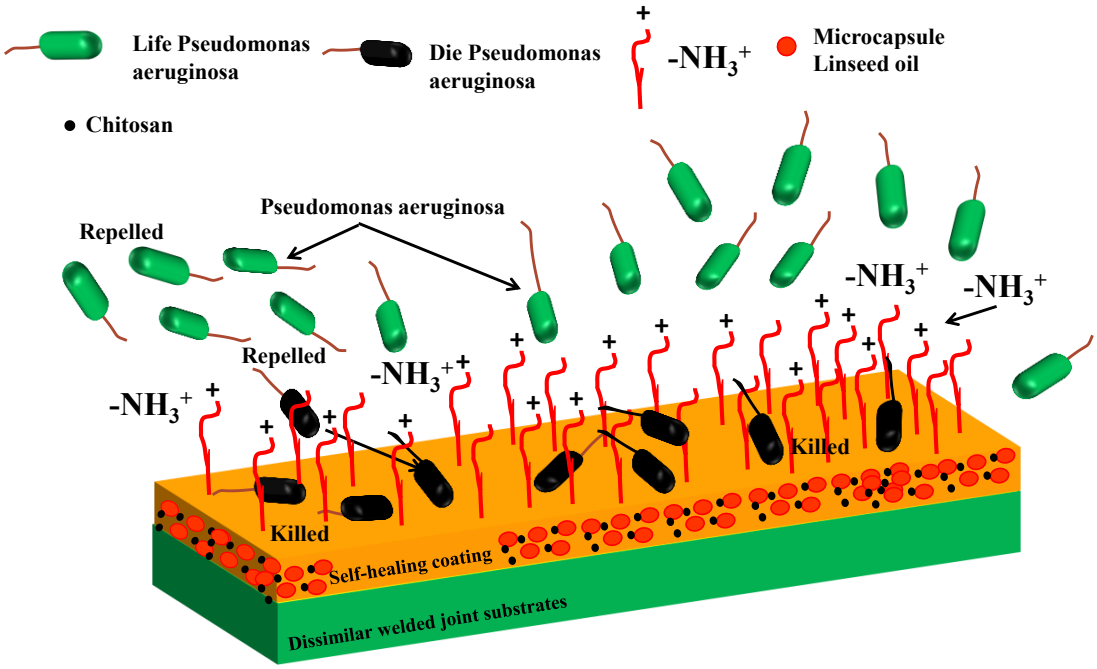

Figure 4: Graphical illustration of chitosan compounds' antibacterial properties

As long as the scribe or scratch is covered by a linseed oil healing agent, even though the agent might not completely fill the entire scratch depth, the corrosion protection of the self-healing coating will be restored when a linseed oil microcapsule of self-healing coating is damaged, such as by a microcrack (scribed area). In the actual application, the dry oil fills the scratch depth as much as possible to create a fresh layer of protection inside the scribed area, eventually reaching the dissimilar welded joint substrate for long-term corrosion protection [18-19].

Linseed oil drying oil not only inhibits corrosion and prevents the passage of hostile ions like Cl^- and O^{2-}, but it also kills bacteria and prevents biofilm development [19]. The self-healing coating coated with 7 wt.% of linseed oil microcapsule causes the bacteria to go dormant and die, as seen in Figure 5. Omega 3 essential fatty acids are most abundant in flaxseed or linseed oil. Palmitic, arachidic, stearic, oleic, linolenic, and other acids make up the majority of the fatty acid content in linseed oil. The composition of oleic and linoleic acids was shown to have strong antibacterial qualities. Linseed oil's antibacterial qualities include the ability to directly enter and damage bacterial cell walls [20].

Therefore, the initial bacterial adherence and biofilm formation can be inhibited by the content of fatty acids [21].

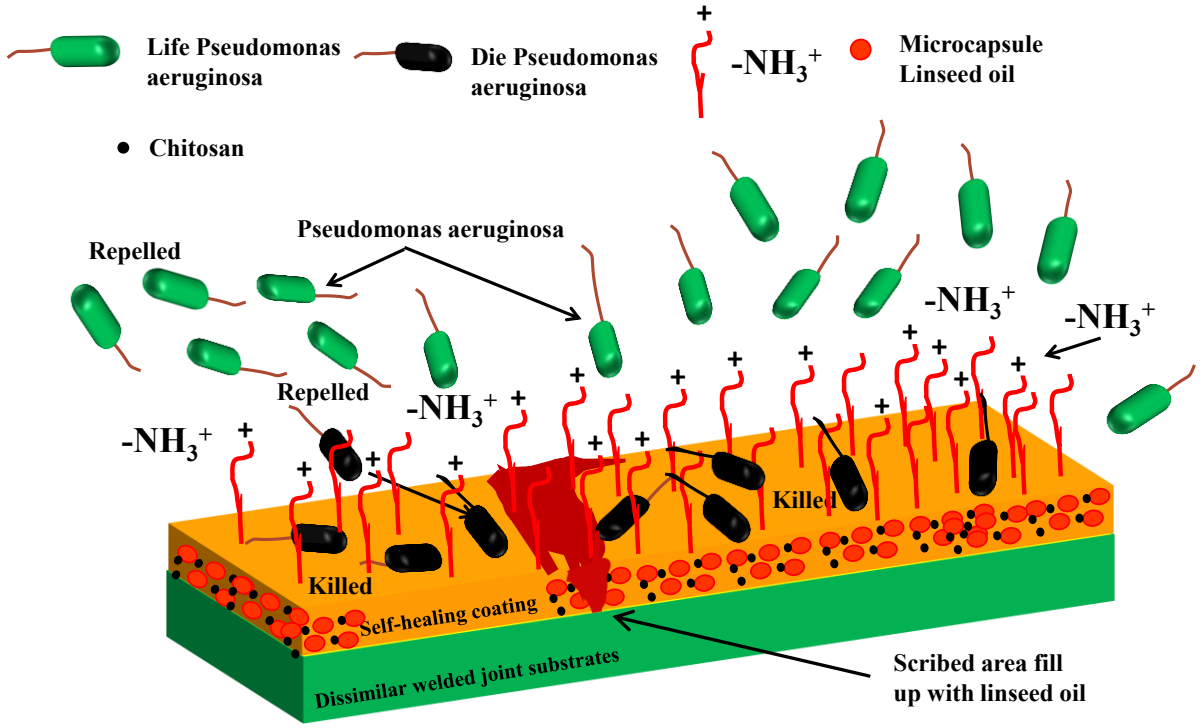

Figure 5: Graphical illustration of the scratched area filled with linseed oil and the way chitosan additions work to prevent corrosion and provide antibacterial qualities

4. CONCLUSIONS

In a nutrient-rich simulated seawater-based media, the corrosion behavior of coated dissimilar welded joints with self-healing coating was examined both in the presence and absence of a marine aerobic strain Pseudomonas. The whole covered dissimilar welded surface augmented exposure duration, and the heterogeneity and coverage of biofilms generated intact, were shown by FESEM pictures of the surface and interface. Additionally, the corrosion beneath the biofilms was extensive, uniform, and localized.

The synergistic action of violent chloride ions and bacterial cell colonization and EPS led to localized corrosion, which was validated by EDX spectra. This breakdown of the passive oxide film raised the risk of MIC. In comparison, the welded surface showed no outward indications of uniform or localized corrosion during exposure in the sterile nutrient-rich media, with the exception of mineral deposition and the development of thin conditioning layers.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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