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The Calcium Gluconate Filled Epoxy Waterborne Primer Coating for Marine Application

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ABSTRACT

The synthesis of corrosion protection in the waterborne epoxy primer coating, which included calcium gluconate (CG), was synthesized. Various compositions of CG, ranging from 0 to 8 grams were applied to the carbon steel substrate using this water-based epoxy coating. The investigations included FTIR characterization, Tafel plot polarization, immersion, adhesion, and hardness tests. The presence of CG at 2868.88 cm^{-1}, corresponding to calcium ion (Ca^{2+}), was confirmed by the FTIR result, while the epoxy functional group was detected at 1506 cm^{-1}. Furthermore, it was observed that the immersion test, hardness test, and adhesion test revealed that the highest formulation for corrosion inhibition was 8 g of CG, which also exhibited a lower corrosion rate of 0.262

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mmpy, improved mechanical properties (4H), and 0 % area removed. The presence of CG, which facilitated interaction with the epoxy resin through coordination between gluconate ions and Ca^{2+} *ions, was believed to be responsible for increasing the concentration of dissolved* Ca^{2+} *ions in the solution. This, in turn, enhanced the formation of* $Ca(OH)_2$ *on the surface of the aluminium alloy, leading to corrosion inhibition. Ultimately, the utilization of CG as an anti-corrosive pigment resulted in a reduction of corrosive properties and an enhancement of mechanical properties in waterborne primer coatings.*

Keywords: Epoxy Waterborne Coating; Calcium Gluconate; Tafel Polarization; Brushing Technique

INTRODUCTION

The application of metals in various industries, particularly in building construction, has been widespread. Carbon steel, for instance, is a highly versatile material extensively utilized in a range of applications, including ships, platforms, buildings, bridges, and more, owing to its exceptional mechanical and physical properties. Nevertheless, corrosion remains a significant concern when these metals are exposed to both inland and marine environments. This susceptibility to corrosion has led to the collapse and deterioration of numerous metal structures, attributed to aggressive environmental factors. Consequently, substantial financial losses, totalling millions of dollars, have been incurred due to corrosion-related issues. While corrosion is a natural phenomenon beyond immediate control, many scientists have developed various solutions aimed at enhancing corrosion resistance. These solutions encompass environmental modifications, cathodic protection, corrosion inhibitors, and the application of protective coatings to safeguard the metal surfaces [1–3].

Coating is a material that is applied on the surface or substrate of the product to provide barrier protection. The purpose of using a coating in metal applications is to prevent corrosion, which can lead to substrate failure, as well as to prepare the substrate for better adhesion within the layers. In protective coating, there are different types of coating layers which consist of five layers [1]. The first layer is known as primer, the second layer is a sealer, the third layer is an undercoat, the fourth layer is an intermediate coat and the fifth layer is a finishing coat. The primer layer is the first layer that is applied to the surface of the product or substrate. The primer gives protection to the surface after treatment which extends the time between the preparation of the adherent surface and bonding. It also provides enhance adhesion by providing a compatible surface for the adhesive and dissolving low levels of organic contamination. Thus, with a proper surface application of primer, the preservation of the metal surface could be done. Epoxy resin and unsaturated polyester are the most commonly used materials in primer coating.

Epoxy resin provides excellent flexibility, improves resistance to cracks, and gives better adhesion than the other material [4]. However, epoxy resin cannot be exposed to sunlight or being exposed to pollutants because it is viscous to nature. The epoxy waterborne system is used because it offers more advantages such as less toxicity, lower volatile component, less cost used, and less reaction to the substrate. Waterborne systems only use water as a solvent which will make them eco-friendly and easy to apply. It is also available for many applications such as coating. Waterborne coating is applied on the metal in this study because it can help in lowering the volatile component during the corrosion process. Hence, the epoxy resin proposed to be used together with the anti-corrosive pigment. The addition of fillers has a great impact to compensate for the mentioned disadvantages of epoxy primer coating. The adherence of polymeric coatings to metal substrates, permeability, thickness, and chemical and mechanical resistance in harsh environments are all factors that influence their corrosion performance [5].

The addition of filler to epoxy can improve the protective properties of epoxy coatings. Zinc-rich pigments, zinc phosphate, zinc chromate, mica oxide, calcium gluconate (CG), aluminum, aluminum oxide, and nanofillers such as microcrystalline cellulose is examples of anticorrosive pigments (MCC) [6]. According to some studies, CG is an effective pigment because it can prevent steel corrosion [3,7,8]. It also has the efficiency to inhibit the corrosion of mild steel in a neutral aqueous solution containing chloride ions. CG is an organic calcium salt that is used in the food, medicine, and chemical industries as a buffer, curing agent, and chelating agent. CG was investigated as a carbon steel corrosion inhibitor [9].

In this research, epoxy waterborne resin filled various loading of CG on the primer layer of protective coating on the metal substrate. The brushing technique of application was used in this study which offers a simple, low-cost, and practical application method. The characterization and study of corrosions and mechanical properties were carried out using Fourier Transform Infrared Spectroscopy (FTIR), Tafel polarization plot, immersion, hardness, and adhesion tests.

EXPERIMENTAL

Material and Chemicals

Epoxy resin with a molecular weight of 340.41 g/mol, Ancamine K54, and Anquamine 401 curing agent were purchased from Sigma Aldrich. Calcium Gluconate and Zinc dust powder with a molecular weight of 448.39 g/mol and 65.38 g/mol respectively were obtained from Merck and used as received.

Pre-coating of mild steel plate

Five samples of mild steel plates, each measuring approximately 15 cm × 10 cm × 0.2 cm, underwent a degreasing process using sandpaper as part of the pre-coating procedure. Subsequently, the steel plates were washed with acetone and then rinsed with distilled water to eliminate contaminants. Finally, they were left to air dry for 24 h. To prevent defects from occurring during the testing phase, it is crucial to ensure that the mild steel plates are free from any dirt and rust.

Preparation of Calcium Gluconate-epoxy waterborne Coating

Firstly, various loading of CG (0, 2, 4, 6, and 8 g) were dissolved in 5 parts of cold water which depends on the amount of calcium gluconate used in each formulation. The zinc dust powder and titanium dioxide then were mixed with the help of distilled water and epoxy resin to disperse it well. Then, curative agents of ancamine 401 and anquamine K54 were added after the mixture was homogeneous. This process was done by using a high-speed mechanical stirrer with 400 rpm for about 10 min.

Preparation of Wet Paint on mild steel plate

By using a hand brush, the coating ingredients were applied in 3 layers on the mild steel surface. After applying it, the paint was allowed to dry for a while to measure the thickness. The thickness of the paint was measured by using a digital caliper. The mild steel that has been coated was left to cure for a week at room temperature.

CHARACTERIZATION

Fourier Transform Infrared (FTIR) Spectroscopy was used to identify the functional group present in the CG-epoxy sample. FTIR is a method of absorbing radiation and converting it into energy, which is then reflected by sample molecules based on their structure and interaction. The samples were scanned over a wavelength ranging from 4000 cm^{-1} to 650 cm^{-1}, which was used to identify the sample's molecular fingerprint.

Corrosion Testing

Immersion test

The immersion test was performed in accordance with ASTM G3712. First, each epoxy primer-coated plate was scratched with an 'X' mark before being immersed in a corrosion environment containing 3.5 % NaCl solution. The plate was left out in the open for 9 days at room temperature. At three-day intervals, the coating condition for the corrosion rate of the plate was observed.

Tafel polarization method

Tafel polarization was performed in accordance with ASTM G5997. The Autolab PGSTAT204 was employed to investigate the corrosion process and the protective performance of pretreatment and organic coating on mild steel. In this study, a deposited epoxy coating material on the mild steel was examined. The experiments were conducted at room temperature, with the mild steel immersed in a 3.5% NaCl solution.

The experimental setup consisted of an anode and a cathode that played a crucial role in polarization. The cathode served as the working terminal and contained the epoxy-coated mild steel. At the anode terminal, a saturated calomel electrode was placed, serving as the reference terminal and carbon counter electrode. Corrosion occurred when the electrode reached the base of the pores. This analysis was carried out under open-circuit conditions with a current of 1mA. To ensure accurate comparisons between each set of five sample plates in subsequent tests, the electrodes had to be cleaned to prevent mixing with previously deposited material.

Physicomechanical Test

Hardness Test

The hardness test was performed to investigate the hardness of the mild steel coating on the surface. This test was performed to determine whether the protective coating ingredients could be easily scratched or penetrated on the surface layer after they were applied. A pencil with different types of leads ranging from 2B, B, HB, H, 2H, 3H, and 4H was used and adhered to the ASTM D3363 standard method.

Adhesion Test

The adhesion test was performed at room temperature using Nichiban tape following the ASTM D3359 standard method. This test was done at room temperature and the surface of the steel must be cleaned. The specimens need to be washed and cleaned by deionised water if it was immersed before the adhesion test was done.

RESULTS AND DISCUSSION

Fourier Transform-Infrared Spectroscopy (FTIR) Analysis

Figure 1 shows two strong peaks of the functional group from epoxy on the FTIR spectrum, which represent OH and CO stretching at 3400 cm^{-1} and 1235 cm^{-1}, respectively. The presence of OH bending was detected at 1506 cm^{-1} with a strong band, which is consistent with Armelin et al. [10]. CG is a material that was created by combining calcium with gluconic acid. When CG is used as an anti-corrosion pigment, the absorption of C=O is observed at 1605 cm^{-1}, and the absorption of calcium ion is observed at 2868.88 cm^{-1} with a weak band. The calcium ion results are consistent with previously reported by Petrei E.M. (2007) who discovered the calcium ion at

2750 cm^{-1} to 2900 cm^{-1} . Although the band formed was weak, the corrosive activities improved when a high concentration of calcium gluconate was used. The proposed reaction mechanism of calcium gluconate and epoxy as exhibited in Figure 2.

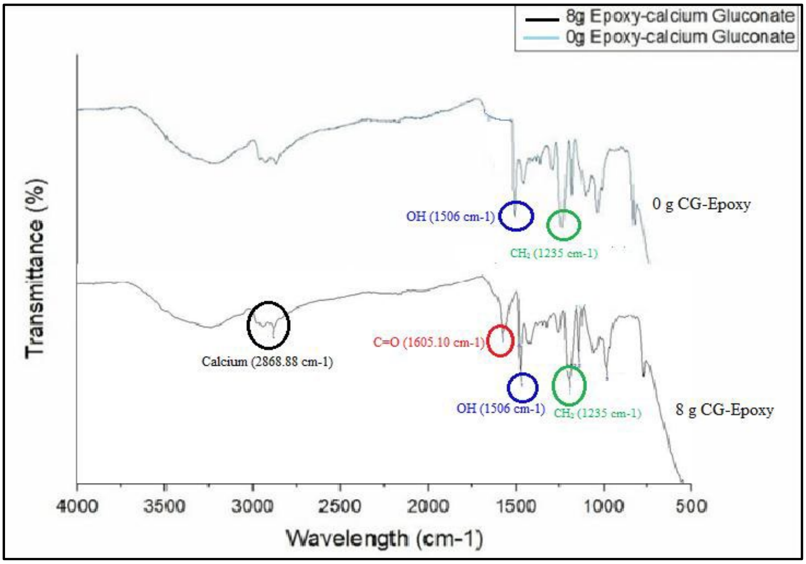


Figure 1: FTIR spectra of epoxy without calcium gluconate and epoxy filled calcium gluconate

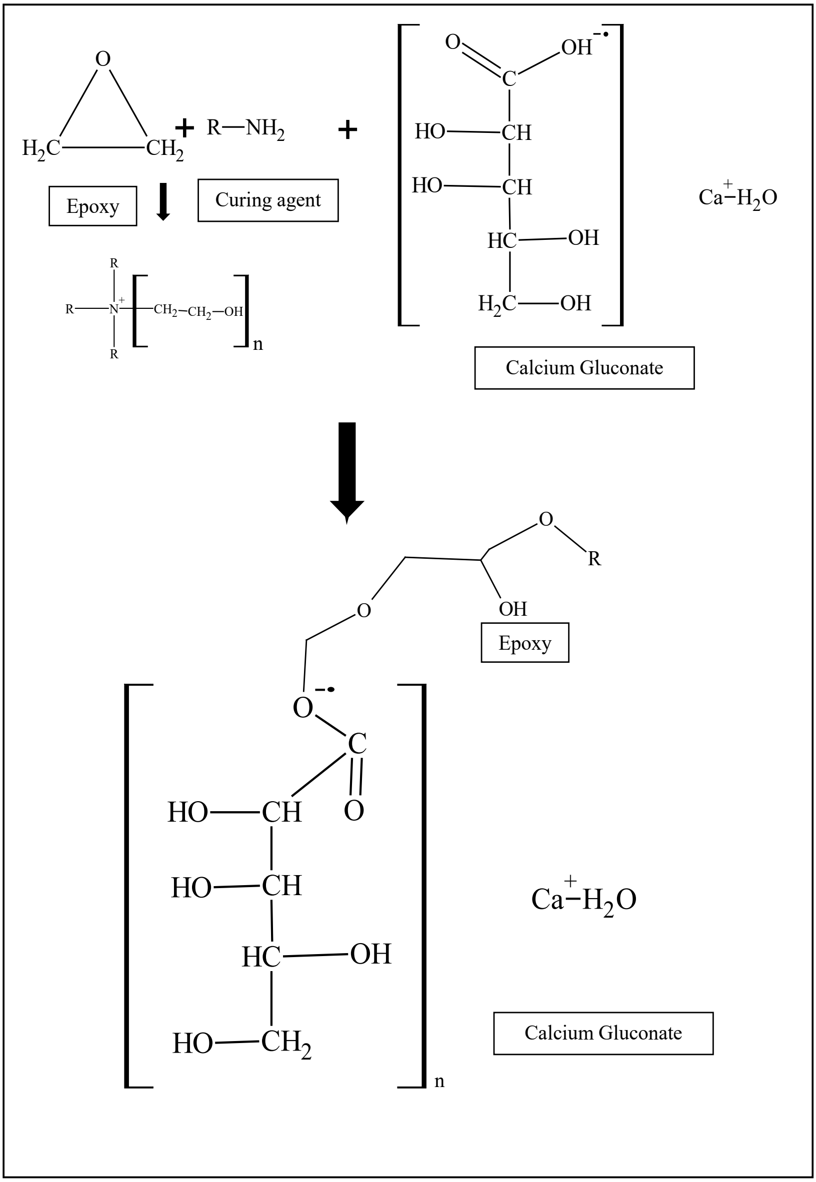


Figure 2: Proposed reaction scheme for polymer composite of epoxy filled calcium gluconate.

Immersion Test

Seawater

The immersion test for the protective coating was performed in accordance with ASTM D6943. The test was carried out for 9 days at room temperature using two different solutions: seawater and 3.5 % NaCl. Before immersing the coated steel plate in the solution, the "X" mark was scratched on it. The observation for days 3, 6 and 9 were recorded. The image of the coated steel plate was captured, and the results were compared. Table 1 shows the surface of the coated steel plate in the seawater.

The corrosion activities were retarded with an increase in CG based on the results of immersion for all formulations, regardless of loadings. The corrosion in the control sample began on day 3 due to the lack of CG in the coating. Meanwhile, even after 3 days of exposure, the other formulation of 2 g of CG-epoxy to 8 g of CG-epoxy shows no corrosion on the steel plate. This is due to the presence of multiple hydroxyl groups (OH-) and one carboxyl group (COOH-) in the gluconate molecule. Calcium gluconate has a high ability to inhibit corrosion in anti-corrosive pigments. This type of hydroxycarboxylic acid chelating agent has an excellent metal ion binding ability. On the one hand, the carboxyl and hydroxyl groups have the ability to bind to Al^{3+}. Coordination of gluconate ions and Ca^{2+} ions, on the other hand, can increase the concentration of dissolved Ca^{2+} ions in the solution, enhancing the formation of $Ca(OH)_2$ on the aluminium alloy surface and inhibiting corrosion [12].

There was visible corrosion on the "X" mark after 9 days with 2 g CG-epoxy addition as compared to 8 g CG-epoxy addition, with only a small area affected by corrosion. Because of the CG's ability to inhibit corrosion, the addition of 2 g - 8 g CG decreased the corrosion rate of epoxy primer coating. As the CG used increases, the rate of corrosion on the steel plate decreases. The steel only showed a small amount of rust on the "X" mark at 8 g CG-epoxy. The findings are consistent with the findings of Akanji et al. [13] who discovered that increasing CG concentration to 0.5 percent decreased rust formation [13].

After 3 days and 9 days of immersion in seawater, the paint begins to peel and flake. However, for 6 g CG-epoxy, the paint peels off in a large area and corrosion occurs on the surfaces where there is no coating paint. Peeling is caused by insufficient curing time. According to Park and co-worker (2015), the environmental condition factor, the ratio of mixing material, and the defective batch of coating are the factors that cause the coating to not cure properly [14].

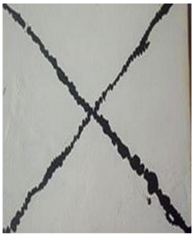
3.5 % NaCl solution

When the use of CG loading is increased from 2 to 8 g, the corrosion rates of the steel plate in 3.5 % NaCl are reduced. On day 3 of immersion, corrosion occurred in the controlled sample (0 g CG- epoxy), and the coating began to peel off slowly. However, when compared to the immersion test in seawater, the coating still adheres properly to the metal surface. When CG is used, the peel of properties appears to improve in the solution. According to Akanji et al. (2016), the CG has compatibility to work as an anti-corrosive pigment in a variety of environmental conditions and has the ability to improve the corrosion rate [13].

Thus, in this test, the CG demonstrated good anti-corrosion performance in a variety of environmental conditions [15,16]. This is due to CG's ability to inhibit corrosion in an acidic environment at pH 4 and above. Meanwhile, the study by Karim et al. (2010) mentioned that the CG inhibition process is effective when immersed in 3.5 % NaCl on day 9, resulting in less rust on the coated surface [17]. The surface of the coated steel plate in 3.5 % NaCl solution for 3, 6 and 9 days are shown in Table 2.

Table 1: The surface of the coated steel plate in seawater after 3, 6 and 9 days

Sample	Day 3	Day 6	Day 9
Control Sample	 “X” mark started to corroded	 The corrosion occured on the “X” mark and the coating start to peel off	 The corrosion observed and the coating peel off from the side of “X” mark
2 g CG-Epoxy	 No corrosion occurred with a small amount of flakes presence	 Corrosion occurred on the edges of X mark and the coating peel off at the centre of “X” mark	 Thecorrosion increased the “X” mark
4 g CG-Epoxy	 The corrosion does not occur.	 Corrosion occured on the coating and the paint peel off	 The corrosion occured on the steel and the paint increasing peel off

6 g CG-Epoxy	 No rust and only small amount of coating that peel off.	 The rust occurred on the coating paint and “X” mark also the paint started to peel off.	 The corrosion occurred on the paint and the steel only rust on small area of “X” mark.
8 g CG-Epoxy	 No area affected	 There is no corrosion occured and the coating does not peel off	 Only small area was affected by rust on the steel

After 3 days and 9 days of immersion in seawater, the paint begins to peel and flake. However, for 6 g CG-epoxy, the paint peels off in a large area and corrosion occurs on the surfaces where there is no coating paint. Peeling is caused by insufficient curing time. According to Park and co-worker (2015), the environmental condition factor, the ratio of mixing material, and the defective batch of coating are the factors that cause the coating to not cure properly [14].

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Table 2: The surface of the coated steel plate in 3.5% NaCl solution after 3, 6 and 9 days

Sample	Day 3	Day 6	Day 9
Control Sample	 The corrosion occured on the "X" mark and the coating start to peel off.	 Corrosion increased.	 100 % area was affected by corrosion and the coating peel off

2 g CG-Epoxy	 No corrosion occurred and the flakes slowly to occur	 Corrosion occurs on the edges of “X” mark and the coating peel off at the centre of “X: mark	 The corrosion occurred almost all area and the coating were seen to peel off slowly
4 g CG-Epoxy	 No rust and only small flakes of paint occur.	 The rust occured and the coating peel off.	 Almost all area affected by rust.
6 g CG-Epoxy	 Small corrosion occurred on the other part of steel.	 The corrosion occured on “X” mark and the coating are less peel.	

8 g CG-Epoxy	 No corrosion occurred.	 Small rust occurred on the “X” mark.	 The other part of steel plate corroded

Tafel Polarization

The effect of the surface coating was assessed using an electrochemical process on the test samples with the Autolab PGSTAT204. Tafel polarization data and corrosion rate of the protective coatings are presented in Table 3 and Figure 3, respectively. It is observed in the data that a high corrosion potential was achieved by all formulations of protective coatings, indicating their significant capacity to resist corrosion. This corrosion potential was enhanced from 0 g CG to 8 g CG-epoxy, resulting in a gradual reduction in the corrosion rate. Specifically, when 0 g CG-epoxy (control sample) was employed, a corrosion rate of 4.335 mmpy was recorded, while 8 g CG-epoxy demonstrated a considerably lower corrosion rate of 0.262 mmpy.

Additionally, an increase in polarisation resistance was observed as the corrosion rate decreased. In cases of high corrosion rates, such as with 0 g CG, a polarisation resistance of 62.57 was measured, whereas in situations with low corrosion rates, as seen with 8 g CG, the polarisation resistance significantly increased to 356.24. This elevated resistance to potential changes during electrochemical processes is attributed to the remarkable corrosion-inhibiting properties of CG. Thus, it is evident that a strong connection exists between lower corrosion rates and higher polarisation resistance, highlighting the positive influence of the coatings on corrosion resistance. These findings are consistent with the conclusions drawn by

Yue and co-worker which investigated the effectiveness of epoxy coatings incorporated with aluminium alloy for anti-corrosion purposes [18].

Meanwhile, it was determined by Ismail et al. (2016) that when the corrosion potential value is found on the negative side, the steel's ability to corrode is diminished due to the involvement of the process of oxygen, water, and air diffusion from either the polymer matrix itself or the surrounding environment [19]. It is evident that superior anti-corrosion properties are conferred by 8 g CG-epoxy when compared to the other formulation with a corrosion potential of 304.015 mVr [17]. Consequently, the potential for inhibiting corrosion on metal substrates is significantly increased by the addition of CG to an epoxy waterborne coating system. When compared to alternative formulations, the lowest corrosion rate of 0.262 mmpy was exhibited by 8 g CG-epoxy. This value signifies that the steel plate is effectively safeguarded from rusting by the paint, highlighting its excellence as an anti-corrosive coating.

Table 3: The Tafel polarization data of the protective coating

	Control sample	2 g CG-Epoxy	4 g CG-Epoxy	6 g CG-Epoxy	8 g CG-Epoxy
Corrosion potential, Ecorr (mV)	-390.55	-355.68	-348.06	-327.05	-304.05
Polarization resistance (Ω)	62.57	238.37	302.20	325.19	356.24

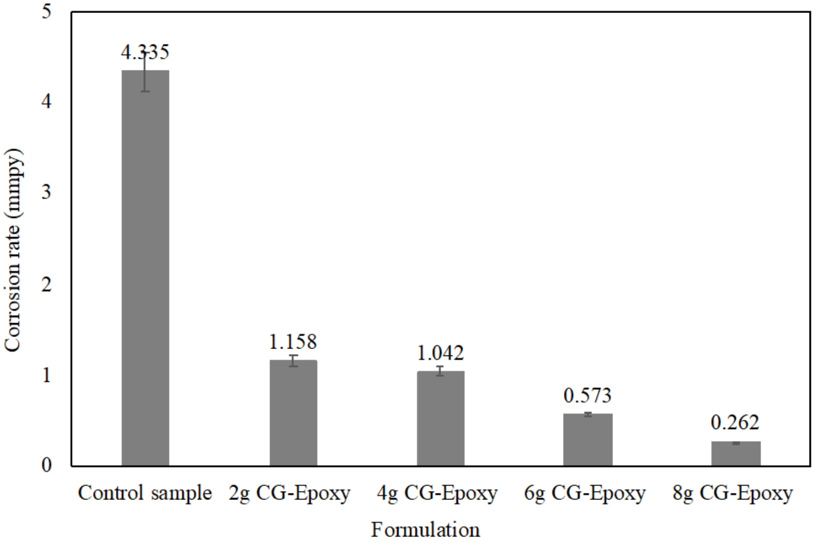


Figure 3: The corrosion rate of the protective coating

Hardness test

The hardness of the coating was tested using different lead pencils, including 2B, B, HB, H, 2H, 3H, and 4H following ASTM D3363. The coating was scratched by holding the 45-degree position of the pencils and using the different leads of pencils on each formulation steel plate which start from the soft lead to the hard lead. The range of hard lead to soft lead was 4H, 3H, 2H, H, HB, B, and 2B. Table 4 below shows the hardness measurement of the coating formulation. According to Table 4, the coating for the control sample (0 g CG-epoxy) has the lowest resistance to scratching with B scale. The addition of 2-8g of GC improved the hardness of the coating system from 2H to 4H. This indicates that epoxy as a skeleton structure has better interaction and formed a bond with calcium gluconate. The rigidity of epoxy and calcium gluconate also helps in improving the hardness of the coating [10].

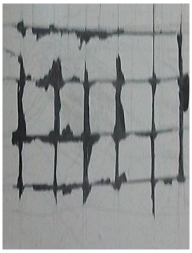
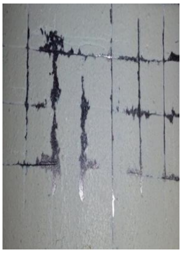
Table 4: The hardness test results of the coating on the steel plate.

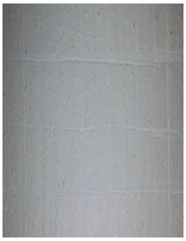
Sample	Hardness
Control sample	B
2g CG-Epoxy	2H
4g CG-Epoxy	3H
6g CG-Epoxy	3H
8g CG-Epoxy	4H

Adhesion test

Table 5 shows the adhesion test result of CG-Epoxy protective coating. The control sample has the highest percentage of area removed, indicating that the coating flakes are detached at the edges and crosshatch intersections. Meanwhile, the percentages of affected areas removed for 2 g CG-epoxy are lower when compared to the control sample, which has 10 % affected areas removed. While the area removed for 4 g CG-epoxy and 6 g CG-epoxy is the smallest due to improved interaction between the constituent materials, which increased adhesion strength. The lowest area removed is found at 8 g CG-epoxy, where the most calcium gluconate was used on this formulation, and the flakes were properly adhered on the steel plate, with no flakes removed after tapping it with Nichiban tape. It has been demonstrated that the addition of CG as an anti-corrosive pigment increases the adhesion of the protective coating [20]. The higher the amount of CG used, the stronger the protective coating's adhesion. The findings are consistent with Akanji et al.[13], in which the amount of CG used at a minimum concentration of 8 % improved the adhesion properties.

Table 5: The adhesion test result for each protective coating sample

Sample	Before	After	Percentage Removed (%)
Control sample			10-15%
2g CG-Epoxy			5-10%
4g CG-Epoxy			5%
6g CG-Epoxy			< 5%

8g CG-Epoxy			0%

CONCLUSION

In summary, the utilization of calcium gluconate results in an enhancement of the anti-corrosion characteristics within the CG-epoxy waterborne protective coating applied to steel plates. The evaluation and determination of CG's mechanical and corrosive properties underscore its potential as a highly effective corrosion inhibitor. The outcomes of both immersion and Tafel polarization tests consistently reveal that augmenting CG loadings leads to improved anti-corrosive performance. The onset of rust formation was observed on day 6 following immersion in the original seawater when CG loadings ranged from 2-8 g. This observation leads to the conclusion that increasing the formulation from 0 g CG-epoxy to 2 g CG-epoxy showcases the coating's ability to maintain adhesion over an extended duration across various CG loadings, in comparison to the control sample. Furthermore, the coating's hardness on the steel plate exhibits a progressive increase from 0 g CG-epoxy to 8 g CG-epoxy, with the results indicating that the hardest pencil lead used is rated at 4H. Ultimately, it was determined that the optimal loading to combat corrosion on metal substrates is achieved at 8 g CG-epoxy.

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