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Effect of Sintering Temperature on the Interfacial Adhesion Strength and Corrosion Behavior of Hydroxyapatite Coatings on Mild Steel

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Abstract. This study investigates the upcycling of fish scale waste into hydroxyapatite (HAp)-based coatings for sustainable corrosion protection of mild steel. Using locally available parrot fish scale as renewable raw material together with polyvinyl alcohol and tapioca starch as eco-friendly binders, the research promotes a circular economy strategy for developing sustainable alternative to conventional corrosion protection used in the construction industry. HAp powder was extracted through calcination and the steel specimens were dip coated and sintered at 100°C, 150°C and 200°C. The HAp coated mild steels were placed in a salt spray test environment for 45 days to determine the corrosion rate by the weight loss method according to ASTM B117 and ISO 13779 standards. Statistical analysis revealed that the best corrosion resistance was achieved at a sintering temperature of 100°C, with a corrosion rate of approximately 0.1 mm per year over 45 days of exposure. In terms of coating adhesion, a sintering temperature of 200°C yielded the highest performance, with a mean tensile adhesion strength of 3.85 MPa. These findings suggest that the adhesion properties of HAp coating are comparable to that of existing protective coatings, including the widely used red oxide primer (4.9 MPa). By transforming waste into a value-added protective material, this study provides a blueprint for industrial adaptation of biomaterial coatings in corrosion-prone environment. Nanoscale HAp particles can be explored in the sol-gel matrix to further enhance adhesion and flow properties for a uniform coating while minimizing the presence of air pockets between the substrates. The low-energy sintering requirement and the use of non-toxic renewable bio-materials make this coating highly scalable for large -scale steel production industries while reducing environmental risk associated with fish waste disposal and creating valuable product through effective waste management to recover useful resources.

Keywords: Fish scale; sustainable coating; corrosion resistance; recycled biomaterials, circular economy

INTRODUCTION

Corrosion, a universally occurring degradation process, involves the irreversible transformation of metals into more stable chemical compounds when exposed to reactive environment [1]. Rapid infrastructure development has increased the reliance on materials like iron and steel which are inherently susceptible to corrosion. Their exposure to atmospheric conditions makes them prone to degradation, resulting in significant maintenance and replacement costs in building and structural applications [2]. According to the National Association of Corrosion Engineers, the global cost of corrosion is about USD 2.5 trillion [3].

In small island developing states with tropical climates like Mauritius where high humidity and temperature are common, corrosion presents significant challenges to the longevity and performance of metal structures and components. According to ISO 9223, the atmospheric corrosivity level in Mauritius is classified as C3, indicating a medium level of corrosion exposure [4]. Although conventional protective coatings such as epoxy, acrylic paints and zinc are commonly applied to mitigate corrosion, these materials are not always environmentally sustainable. Their production often involves non-renewable resources and contributes to environmental degradation through waste generation. In response to these concerns, this study aims to evaluate the corrosion resistance of mild steel using hydroxyapatite as an alternative, eco-friendly protective coating. The study focuses on assessing the corrosion resistance and adhesion strength of the hydroxyapatite-coated mild steel, with a strong emphasis on utilizing locally sourced waste materials and bio-based binders to support sustainable engineering practices.

Fisheries and aquaculture serve as essential sources of livelihood for millions and play a crucial role in global food security. In 2021, global production reached nearly 182 million tonnes to meet the demands of a rapidly increasing population [5]. However, large-scale fishery produces 20% to 80% waste during the processing of fish, leading to environmental pollution and contaminating the ecosystems mainly because it is improperly discarded [6]. These wastes can be converted into valuable products and have the opportunity to bring high economical value. Fish scales, a by-product of the fishing industry, make up approximately 2% of the total body weight of a fish contain hydroxyapatite (HAp) and collagen [7]. Past studies have shown that it is economically viable to extract HAp from fish scale and is known to be a biocompatible material. HAp is commonly extracted from fish scales using alkaline hydrolysis, thermal treatment (calcination) or a combination of these methods [8].

HAp has been successfully extracted from fish scales using the calcination method at varying temperatures. Jaffri et al. extracted HAp from black tilapia via calcination at 900 °C with XRD results showing a Ca:P ratio of 1.74 and no changes in the chemical composition and molecular structure [9]. Similarly, Sockalingam et al. obtained HAp from tilapia scales at 800℃ and 1000℃ to achieve a Ca:P ratio of 1.598 and 1.939 respectively [10]. Analysis of HAp under scanning electron microscopy in transmission mode revealed that ultrafine nanoparticles with diameters ranging from 20 to 30 mm when sintered at 1200℃ produced a highly crystalline structure with a Ca/P ratio of 1.83 [11]. On the other hand, Muralithran & Ramesh used a commercially available HAp powder and observed that sintering HAp at an optimum temperature of 1250℃ achieves a pure hydroxyapatite phase with densities over 99% of the theoretical value and a hardness of 6.08 GPa [12]. Decomposition to tricalcium phosphate phases occurs above 1400℃ due to the loss of OH functional group through dehydration. This hampers the densification and degrades the mechanical properties. These studies highlight that both calcination temperature and sintering conditions critically influence the purity, crystallinity and mechanical performance of HAp.

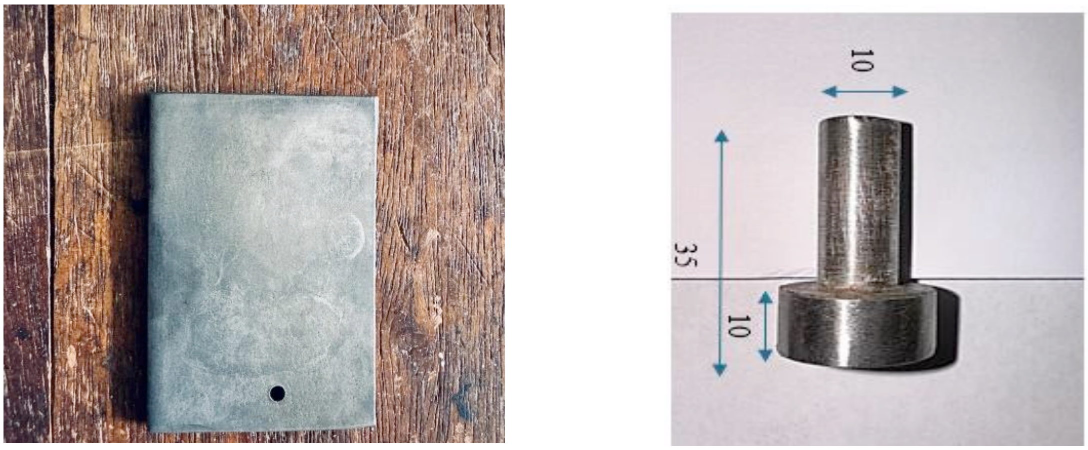
HAp coatings have demonstrated substantial benefits in improving the corrosion resistance of metallic substrates. Büyüksağiş & Çiftçi employed the sol-gel process to apply HAp coatings to Ti, Ti6Al4V and AISI 316L stainless steel substrates and reported that the coatings delivered pronounced improvements in corrosion resistance in Ringer's solution and 0.9% NaCl solutions [13]. Similarly, Swadi reported that HAp coatings on 316L stainless steel act as effective barriers, reducing metal ion release and prevent corrosion. Cyclic polarization curves for both uncoated and HAp-coated substrates were recorded at applied potentials between 30 and 90 V for 3 minutes, with all coated. All coated sample exhibited a nobler potential shift compared uncoated substrates, indicating greater resistance to corrosion [14]. Hiromoto & Yamamoto demonstrated that highly crystallised HAp coatings on pure magnesium and AZ alloys virtually eliminated visible pitting under dry and wet NaCl exposure and reduced anodic current density by 3-44 orders of magnitude in polarization test [15]. While these studies highlight the strong anti-corrosion performance of HAp on titanium, stainless steel and magnesium substrates, research on its effects for mild steel remains scarce, representing a notable gap in literature.

MATERIALS AND METHODS

Materials and Sample Preparation

Two types of mild steel cross sections were used for this study. Rectangular mild steel specimens measuring 40 mm x 60 mm were prepared for the corrosion assessment while circular rods with a diameter of 20 mm were used for adhesion strength test as shown in figure 1 (a) and (b) respectively. The circular rods were partially machined on a lathe to reduce their diameter to 10 mm so as to allow a secure attachment to the Universal Testing Machine (UTM).

All samples were prepared as per the ASTM G1 – Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens. The samples were cleaned using hydrochloric acid and distilled water, dried with a hot air dryer and stored in a desiccator. The surfaces were then subjected to longitudinal and transverse pattern using 80-grit SiC paper on a belt sanding machine for 2 minutes, followed by a 120 and 320 grit SiC paper on a Metaserv 250 grinder-polisher machine for 3 minutes at 250 rpm to achieve a surface roughness of 0.33 µm.



(a) (b)

FIGURE 1. Two types of specimens used for coating

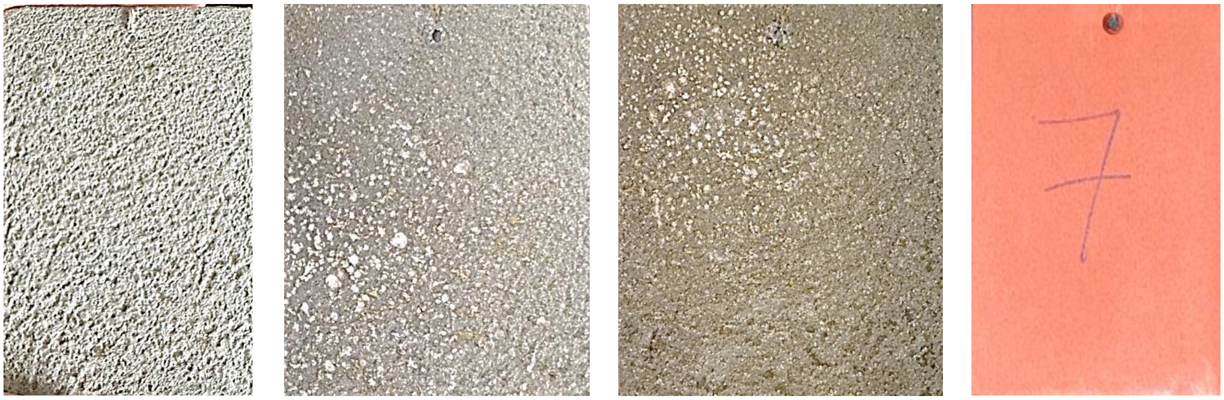
Preparation of the Hydroxyapatite coating solution

Fish scales waste from parrotfish species were sourced from local fishmongers in Mauritius to extract hydroxyapatite (HAp) powder as per the methodology outlined by Hamzah et al. [16]. The scales were thoroughly washed with tap water to remove any surface contaminants. Initially, the fish scales were deproteinized by immersion in hydrochloric acid solution for 6 hours at room temperature. The acid-treated scales were then repeatedly washed with tap water until a neutral pH was achieved. The remaining protein were treated with sodium hydroxide solution for an additional of 6 hours at room temperature and heated at 60°C for 48 hours to eliminate all protein on the scale. The treated fish scales were calcinated at 1000 °C for 2 hours in a muffle furnace to obtain pure HAp.

To prepare the HAp suspension solution, food-grade tapioca starch was used as a binder. 25g of tapioca starch was dissolved in 400 ml of distilled water and heated on a hot plate magnetic stirrer at 350 rpm for 10 minutes to obtain a homogeneous solution. Then, 200 g of pure HAp powder was gradually added to the solution and the pH was adjusted to 4 using diluted nitric acid. Subsequently, the mixture was further homogenized at 650 rpm and 130 °C for 16 hours for hydrolysis and condensation to occur.

Coating of Mild Steel Specimens

Thirty rectangular specimens were immersed into the HAp solution for 30 seconds and withdrawn at a controlled rate of 4 mm/s. The samples were then dried in a convection oven at 60 °C for 1 hour. Ten coated specimens were then sintered in a furnace at 100 °C, 150 °C and 200 °C to investigate the effect of corrosion with different sintering temperatures. A second set of ten rectangular specimens were similarly immersed in a Red Oxide primer and then allowed to air dry at room temperature. These samples served as a reference for subsequent comparison with the performance of the HAp coating. Figure 2 illustrates the surface finish of the coating on the specimens



(a) HAp coating sintered at 100 ℃ (b) HAp coating sintered at 150 ℃ (c) HAp coating sintered at 200 ℃ (d) Red oxide primer coating

FIGURE 2. Surface finish of coating on rectangular specimens

A split mould as shown in figure 3 (a) was manufactured using 3D printing to cast the HAp solution onto the surface of the circular rod to achieve a coating thickness of 100 µm. After the coating was applied via casting method, the samples were left to air dry at room temperature for 20 minutes and followed by drying in an oven at 60℃ for 1 hour. The samples were then sintered in a muffle furnace at 100 ℃, 150 ℃ and 200 ℃ for 1 hour to study the impact of sintering temperature on adhesion strength.

(a) Split mould mounted on specimen (b) HAp coating on specimen sintered at 100 ℃

FIGURE 3. HAp Coating applied on cylindrical specimens for assessment of adhesion strength

Adhesion Strength Testing

The adhesion strength of the HAp coating was evaluated in accordance with the ISO 13779 standard. A uniaxial tensile load was applied to a cylindrical test assembly consisting of a HAp-coated specimen bonded to an uncoated counterpart with epoxy adhesive. The assembly was then mounted in the grips of a tensile testing machine as shown in figure 4 and a tensile load is applied at a consistent crosshead speed of 2.5± 0.5mm/min until the components are completely separated.

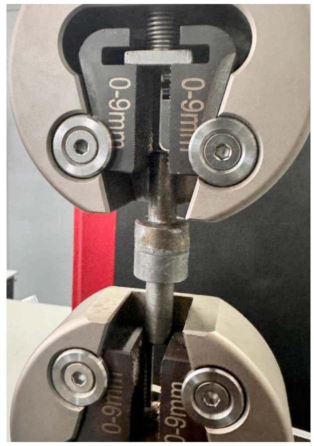


FIGURE 4. Setup of specimen on the tensile testing machine for adhesion strength test

Corrosion Testing

The corrosion test of the HAp coating on the rectangular specimens was conducted in a salt fog test apparatus for accelerated corrosion in accordance with ASTM B117. The samples were exposed in a controlled condensing salt fog environment for durations of 360, 720 and 1080 hours. The test was performed in a chamber at a temperature of 35 °C and a relative humidity of 95 %. A condensing fog was generated using a salt solution composed deionized water and sodium chloride with a pH range of 6.5 to 7.2. After the exposure period the weight loss method was used to assess the rate of corrosion. After the exposure periods, the samples were cleaned using running water and a soft brush to remove the corrosion layer. The final mass of the samples was recorded to the nearest 0.001g and the difference between the initial and final mass represented the material lost due to corrosion. This mass loss was then used to calculate the corrosion rate in mm/year using the standard formula provided by Upadhyay & Chandrakala [17]. The HAp coating derived from the fish scales were benchmarked against red oxide primer coating and uncoated samples.

RESULTS AND DISCUSSION

Effect of Sintering Temperature on Adhesion Strength

The HAp coatings on the specimens were sintered at 100 °C, 150 °C, and 200 °C, as shown in **Figure 5**. Increasing the sintering temperature to 200 °C markedly improved the average tensile adhesion strength of the HAp-coated mild steel to 3.85 MPa. In contrast, specimens sintered at 100 °C and 150 °C exhibited significantly lower adhesion strengths of 0.97 MPa and 1.01 MPa, respectively. One-way ANOVA confirmed that the differences in adhesion strength across sintering temperatures, based on ISO 13779, were statistically significant ($p < 0.05$). Tukey's post-hoc test further revealed significant differences between the 200 °C and 100 °C interval as well as the 200 °C and 150 °C intervals. Thus, sintering temperature is a key determinant and higher sintering temperatures enhance coating adherence to the substrate.

The reduced adherence at lower temperatures was primarily attributed to the water-based coating reacting with air in the oven during drying and curing, leading to oxidation and premature rusting. Additionally, as shown in **Figure 6**, thermal degradation induced cracks from thermal stresses, further diminishing adhesion properties. Microstructural observations indicate that increasing the sintering temperature reduced voids and trapped gases formed by evaporation within the coating. This promoted enhanced atomic diffusion at higher temperatures, improving grain bonding and growth. Larger grains formed stronger bonds while reducing porosity by eliminating gas particles. Furthermore, at elevated temperatures, thermal degradation facilitated interaction between starch and PVA, resulting in a cross-linking effect between tapioca starch and PVA, which contributed to improved adhesion strength.

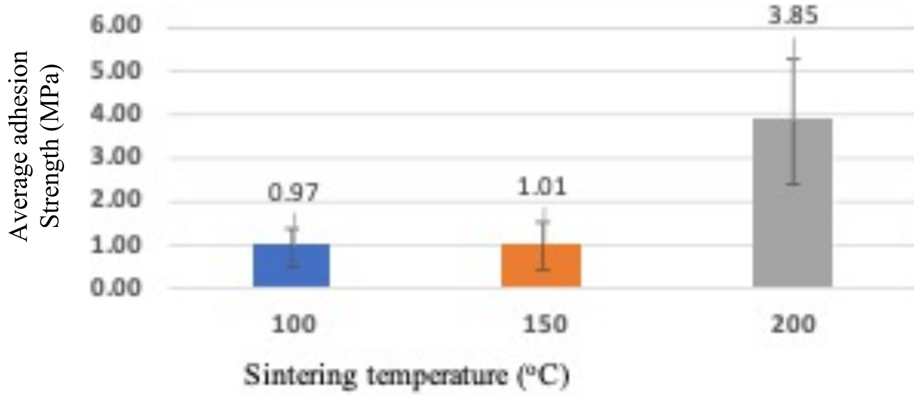


FIGURE 5. Adhesion Strength of HAp-Coated Mild Steel at Different Sintering Temperatures

(a) Thermal degradation of binder (b) Cohesive failure (c) voids and trapped air in the coating

FIGURE 6. Microstructure of HAp coatings after adhesion strength test

Effect of Sintering Temperature on Corrosion Rate

The HAp- coated mild steel sintered at 100ºC demonstrated the most effective corrosion resistance, with a stable corrosion rate of approximately 0.15 mm per year. While the red oxide primer outperformed the HAp coatings sintered at 150ºC and 200ºC, it was less effective than the 100ºC sintered specimen. The 200ºC sintered coating showed the highest corrosion rate, initially at 0.56mm per year, indicating a poor performance, though it stabilized over time due to passive oxide layer formation on the surface of the specimen. Despite lacking a protective coating, the uncoated samples outperformed the 200ºC sintered specimens and achieved identical corrosion rates by the end of the 45-day exposure as shown in **Figure 7**. The corrosion behaviour of HAp-coated mild steel was significantly affected by the differences in the thermal expansion properties of the coating and the underlying steel substrate. The use of PVA and tapioca starch as binders introduced thermal stresses at 200ºC causing microstructural defects such as cracks, pores and voids. The defects allowed the corrosive agents to penetrate into the steels and accelerate corrosion.

Despite the presence of microstructural imperfections, an increase in sintering temperature led to improved adhesion strength. This improvement is attributed to intensified cross-linking reactions between the polyvinyl alcohol (PVA) and tapioca starch binders which strengthened the bonding between the hydroxyapatite (HAp) coating and the mild steel substrate. Higher sintering temperatures promoted atomic diffusion and grain growth, contributing to a denser microstructure with reduced porosity. However, the evaporation of the water-based coating components during sintering introduced air pockets within the coating matrix. These trapped voids resulted in incomplete densification and created localized structural weaknesses. Such defects acted as pathways for the ingress of corrosive elements, including oxygen, moisture, and chloride ions from ASTM B117 salt fog testing.

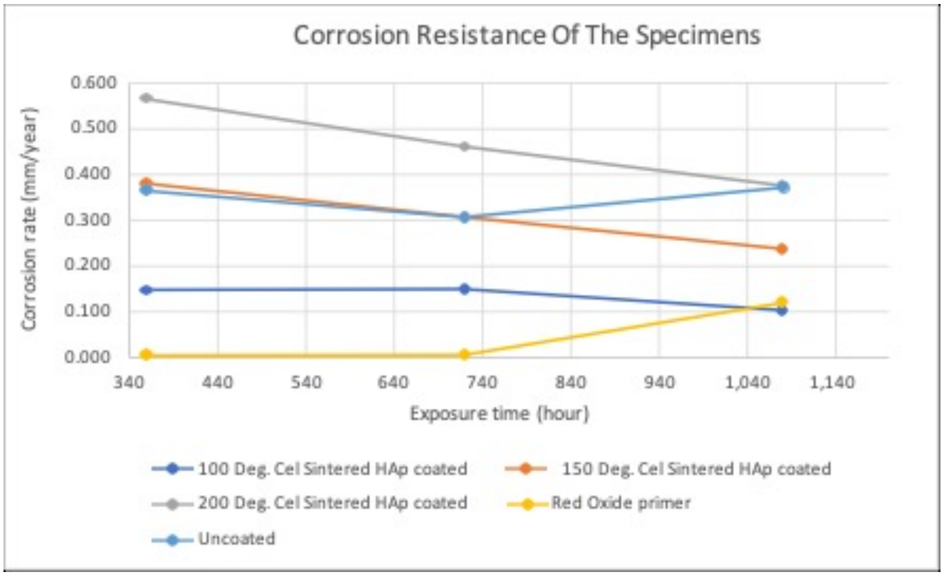


FIGURE 7. Corrosion rate of coated and uncoated specimens over time

CONCLUSION

This study demonstrated the potential of hydroxyapatite derived from fish scale as a sustainable, biodegradable coating for corrosion protection of mild steel. By incorporating natural binders such as tapioca starch and polyvinyl alcohol, the coating aligns with environmentally friendly practices while reducing reliance on synthetic primers. The corrosion resistance and adhesion strength of the coatings were found to be highly dependent on sintering temperature, with the 100 °C sintered specimens offering better corrosion resistance and the 200 °C samples exhibiting superior adhesion. Nonetheless, certain challenges remain, particularly the delamination of the water-based coating during the salt fog testing at lower sintering temperatures.

To enhance the durability and performance of the coating in corrosive environments, future work should focus on improving adhesion through the incorporation of hydrophobic binders or the addition of a sealing topcoat. Investigations into factors such as coating thickness, binder ratio, and particle size refinement are also recommended to reduce structural defects like pores and voids. Extending the exposure duration to 90 days would also provide a more comprehensive understanding of long-term corrosion behavior. Additionally, exploring the integration of alkyd or oil-based solution in the HAp mixture could further improve its protective capabilities. Despite current limitations, hydroxyapatite derived from natural resources presents a promising, non-toxic alternative for metal protection, with considerable potential for further development in sustainable corrosion mitigation strategies.

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