Jurnal Polimesin
Department of Mechanical Engineering
State Polytechnic of Lhokseumawe
http://e-jurnal.pnl.ac.id/polimesin

e-ISSN	: 2549-1999	No.	: 6	Month	: December
p-ISSN	: 1693-5462	Volume	: 23	Year	: 2025

Processing dates: received on 2025-8-24, reviewed on 2025-10-28, accepted on 2025-11-16 and online availability on 2025-12-31

Investigation for adhesion enhancement of hydroxyapatite coatings on Ti-12Cr alloy using the dip-coating method for orthopedic implant

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Abstract

Titanium and its alloys are extensively applied in biomedical due to their light weight, corrosion resistance, and biocompatibility. However, conventional alloys such as Ti-6Al-4V possess a high elastic modulus (~110 GPa), much greater than that of natural bone (10-30 GPa), leading to stress shielding and delayed bone healing. To overcome this limitation, β-type titanium alloys with lower modulus have been developed, including Ti-12Cr, which is intended for spinal fixation implants. Previous studies have reported frequent surface cracking in HA layers, potentially reducing implant durability. In this study, bio-HA derived from scales of *ikan kakap putih* (*Lates calcarifer*), an abundant fishery by-product, was applied as a coating suspension. The natural collagen present in the scales was expected to enhance coating adhesion. HA layers were deposited on Ti-12Cr substrates using dip coating with dipping times of 20, 24, 34, and 40 seconds. The results show that HA derived from scales of *ikan kakap putih* exhibits good coating adhesion strength. This improvement in adhesion helps minimize cracking in the HA layer. The highest adhesion was achieved at a dipping time of 20 s, with only 2% of the coated area peeling off. In addition, the dip-coating process produced thin and uniform HA layers, with surface coverage reaching 98.14% at a dipping time of 40 s. The improved adhesion of the HA coating is expected to enhance osseointegration and reduce implant inflammation effects in biomedical applications.

Keywords:
Adhesion strength, dip coating, hydroxyapatite, orthopedic implants, Ti-12Cr.

1 Introduction

Titanium and its alloys are extensively applied in biomedical due to their low density, excellent corrosion resistance, and superior biocompatibility. However, conventional alloys such as Ti-6Al-4V still exhibit a relatively high elastic modulus (~110 GPa), which is significantly greater than that of natural bone (10–30 GPa) [1]. This mechanical mismatch often leads to stress shielding, thereby impairing the bone healing process [2].

To overcome this issue, β-type titanium alloys with a lower elastic modulus (<70 GPa) have been developed. Among these, Ti-12Cr has attracted considerable attention. In addition to its favorable mechanical performance, Ti-12Cr demonstrates excellent passivation behavior through the formation of a stable oxide film, which improves corrosion resistance and prevents chromium ion release into the human body [3]. This alloy has been specifically designed for spinal fixation implants, offering both adaptive mechanical properties and high biocompatibility [3]. Further details can be found in Table 1.

Table 1. Chemical composition and mechanical properties of Ti-12Cr [3]

Chemical composition		
No	Element	Content (wt.%)
1	Chromium (Cr)	± 12
2	Iron (Fe	≤ 0.25
3	Oxygen (O)	≤ 0.15
4	Nitrogen (N)	≤ 0.05
5	Carbon (C)	≤ 0.05
6	Hydrogen (H)	≤ 0.015
7	Titanium (Ti)	Balance
Mechanical properties		
1	Density	4.6 $g \cdot cm^{-3}$
2	Elastic modulus (GPa)	80-95
3	Tensile strength (MPa)	750-950
4	Yield strength (MPa)	600-850
5	Elongation (%)	10-20
6	Hardness (HV)	250-320
7	Corrosion resistance	Excellent
8	Fatigue strength (MPa)	450-600

Despite these advantages, Ti-12Cr possesses limited bioactivity [2]. Consequently, hydroxyapatite (HA) coatings are required to ensure effective osseointegration at the bone–implant interface [3]. However, previous studies have reported frequent cracking within HA coatings [3-8], which could compromise implant longevity.

Commercial HA powders are commonly used as coating suspensions, yet their application often results in poor adhesion between HA and metallic substrates. This weak interfacial bonding originates from the intrinsic brittleness of ceramic HA during sintering. Upon heating, the titanium substrate undergoes significant thermal expansion, whereas HA exhibits limited strain tolerance, generating thermal stresses that promote crack formation [3].

Therefore, in this study, bio-derived HA from sisik ikan kakap putih (Lates calcarifer) was applied as a coating suspension. The natural collagen (organic protein) present in the scales is expected to improve interfacial adhesion, while the high calcium phosphate mineral content provides enhanced fracture resistance during consolidation [9]. Compared with commercial HA, fish-scale-derived HA is eco-friendly, cost-effective, and exhibits superior strain tolerance, thus reducing the likelihood of cracking during sintering.

Previous studies have shown that coating failure typically originates from the mismatch in thermal expansion coefficients between titanium alloys (~10.3 µm/mK) and commercial HA (~14 µm/mK). Such disparities cause differential expansion and contraction during thermal cycling, resulting in stresses that drive crack initiation and propagation [3-8]. Further details can be found in Table 2.

Table 2. Summary of related literature [3-8]

No	Coating Method	Material/ Suspension	Coating Results
1	Dip Coating	Ti-6Al-4V Commercial HA	/Non-uniform; cracks detected at 900 °C sintering [3]
2	EPD	Ti-6Al-4V ELI/ Commercial HA	Brittle coating; cracks observed [4]
3	EPD	Ti-6Al-4V ELI/ Commercial HA	Uniform coating; cracks detected at 900 °C sintering [5]
4	EPD	Ti-6Al-4V/ Commercial HA	Uniform coating; cracks detected at 850 °C sintering [6]
5	Dip Coating	Ti-6Al-4V/ Commercial HA	Uniform coating; minor cracks detected at 900 °C sintering [7]
6	Dip Coating	Ti-6Al-4V/ Commercial HA	Uniform coating; no cracks at 800 °C sintering, but cracks observed at 900 °C sintering [8]

Previous studies explained that the HA suspension coating used commercial hydroxyapatite (HA) with the Electrophoretic

Deposition (EPD) and Dip Coating methods. These were applied to Ti-6Al-4V and Ti-6Al-4V ELI implant materials. The results showed that cracks were still found on the test samples. These cracks occurred due to the weak adhesion strength of the commercial HA coating on the implant surface. The weak adhesion was caused by the brittle nature of HA ceramics when heated during the sintering process for layer densification. During heating, metals experience greater strain, while HA exhibits smaller strain. This mismatch creates thermal stress that promotes cracking [3,4].

In addition, the studies also reported that the coating layers were often non-uniform. Generally, cracks were detected in samples subjected to the sintering process at 900 °C [5,6]. Cracking during sintering commonly results from differences in the thermal expansion coefficients between the base material and HA. Titanium alloys have a lower thermal expansion coefficient (~10.3 µm/mK) compared to commercial HA (~14 µm/mK). This difference causes thermal mismatch between the HA coating and the substrate during heating and cooling in the sintering process, leading to thermal stress. Such thermal stress is what drives the formation of cracks.

Furthermore, in previous studies that used commercial HA with the Dip Coating method, many samples exhibited uniform coatings; however, cracks were detected during the sintering process at 900 °C [7,8]. A summary of the literature review is presented in Table 2.
This study aims to develop a hydroxyapatite (HA) coating on Ti-12Cr substrates with strong adhesion and high crack resistance to enhance its performance in orthopedic implant applications. The outcomes are expected to enhance osseointegration performance, contribute to sustainable biomaterial development through the utilization of fishery waste, and provide new opportunities for the commercialization of natural bio-HA as a prospective domestic biomaterial.

2 Research methodology

2.1 Materials

Four Ti-12Cr specimens in the form of square plates (10 mm × 10 mm × 4 mm) were prepared for this study, as shown in Fig. 1. Following sectioning, the specimens were ground with silicon carbide abrasive papers of 800-1500 mesh size, and subsequently polished using alumina powder [10].

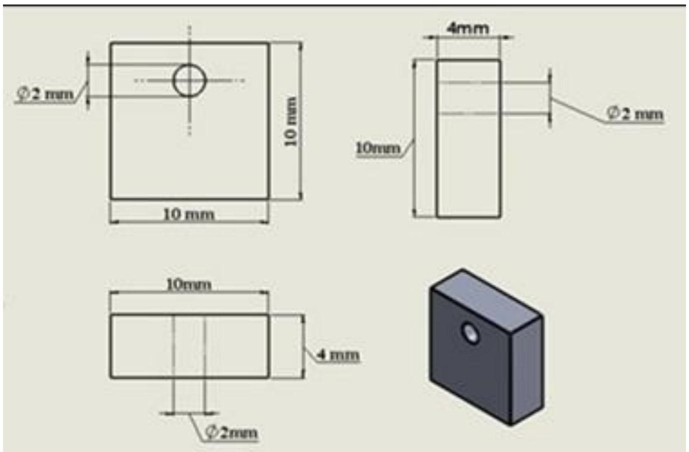


Fig.1. Ti-12 Cr test specimen

The polished specimens were sequentially cleaned in acetone, 70% ethanol, and 25% nitric acid (pH 7.3), then rinsed in distilled water for 30 minutes. They were further immersed in 1 mol NaOH solution for 1 hour. Final cleaning was performed using a multi-frequency ultrasonic bath, and the specimens were dried on a stirring hot plate at 50 °C for 5 minutes [11]. For the coating suspension, nano-hydroxyapatite (HA) powder (~10 nm) derived from sisik ikan kakap putih (Lates calcarifer) with 99% purity was applied, as shown in Figure 2 and Table 3.

Fig.2. Bio-HA powder as a suspension material for coatings

Table 3. Specifications of Bio-HA [9]

No	Specifications	Type
1	Material Name	Natural Bio HA
2	Particle Size	10 nm (Nano Powder)
3	Purity	Non-synthetic (99%)
4	Raw Source	Sisik Ikan Kakap Putih
5	Synthesis Method	Mild Processing (Furnace-free)
6	Morphology	Spherical

The powder was dispersed in 100 ml ethanol (pH 4.0), using nitric acid (HNO_3) as a dispersant [12]. The suspension was homogenized with a magnetic stirrer for 1 hour and then sonicated in an ultrasonic bath for 2 hours. The homogenization of the solution using a magnetic stirrer was carried out for 1 hour, as this duration is the optimal time to form a uniform suspension, ensuring that the hydroxyapatite particles are evenly distributed throughout the solvent. Then, the sonication process in the ultrasonic bath was conducted for 2 hours, since this duration is the optimal time to achieve suspension stability before the coating process. This is important to ensure that, during coating, the resulting layer has consistent thickness and composition [12].

After deposition, the HA layer on the specimen surface was air-dried for 24 hours at room temperature, as shown in Fig. 3. The surface of the test specimen was dried for 24 hours at room temperature, as this period is the optimal time to enhance the quality and adhesion strength of the coating. Hydroxyapatite (HA) particles tend to agglomerate due to strong intermolecular attraction forces [12].

Fig.3. HA suspension for Ti-12Cr coating.

2.2 Methodology

The HA coating process was carried out using the dip coating technique, chosen due to its simplicity and cost-effectiveness [3]. Dipping was conducted at a withdrawal speed of 4 mm/s, as this condition had previously yielded uniform coatings. Four dipping times were applied: 20, 24, 34, and 40 seconds [3-8], as shown in Fig. 4.

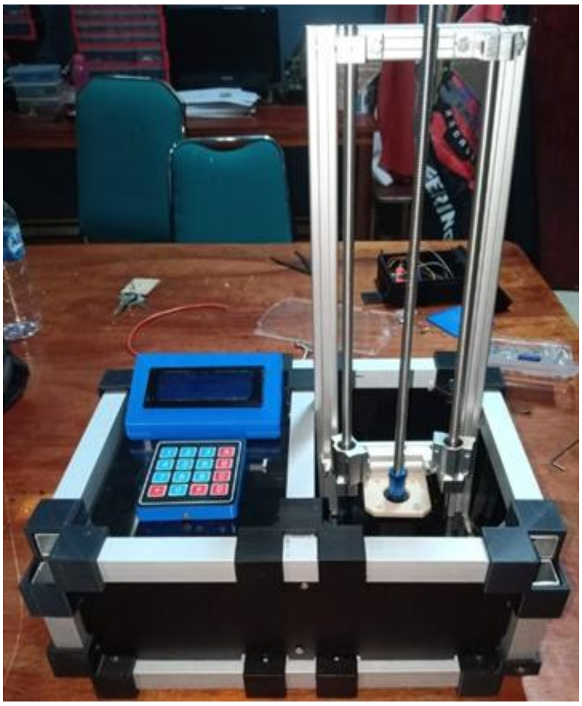


Fig.4. Dip coating experimental setup.

Subsequently, the coated specimens were sintered in a Vacuum Tube Furnace (GSL-1100) at 900 °C with a heating rate of 50 °C/min. After reaching the target temperature, the specimens were held for 2 hours to ensure uniform heat distribution, followed by annealing for 24 hours [3-5], as shown in Fig. 5.

Fig.5. Sintering carried out in a vacuum tube furnace GSL-1100.

The coating thickness was measured using a Sanfix Thickness Gauge (μm), model GM 280. Surface coverage was analyzed using ImageJ software [13]. Coating morphology and surface cracking were examined using an Olympus LG-PS2 stereo optical microscope. Due to the small size of the specimens, direct adhesion testing via tensile pull-off methods was not feasible. Instead, adhesion strength was assessed using the cross-cut tape test with an ETOPOO cross cutter and Scotch transparent adhesive tape [14]. According to the standard, the number of cut lines and spacing depends on the film thickness: six cuts with 1 mm spacing were applied for coatings of 50-125 μm thickness [15], as shown in Fig. 6.

Fig.6. Cross-cut adhesion test of the HA coating.

In this test, grid lines were scored into the coating, tape was applied to the scored area, and then peeled off at a 180° angle. Adhesion was rated on a scale of 0-5, where 0 indicates >65% removed area and 5 indicates 0% removed area [16]. The percentage of removed area was correlated with coating adhesion, where lower values represented stronger adhesion.

3 Result and discussion

3.1 Coating thickness and surface coverage

Overall, all specimens exhibited thin HA layers with uniform surface coverage. Such uniform and thin coatings promote effective densification during sintering, thereby minimizing the likelihood of cracking. Quantitative analysis using ImageJ software revealed the surface coverage values of HA coatings on Ti-12Cr substrates, as presented in Table 4 and Fig. 7. The highest surface coverage (98.14%) was obtained at a dipping time of 40 seconds.

Table 4. Thickness and surface coverage of HA layers on Ti-12Cr

No.	Dipping time (s)	Thickness (μm)	Surface Coverage (%)
1	20	85.60	90.27
2	24	87.40	93.95
3	34	89.78	85.05
4	40	92.50	98.14

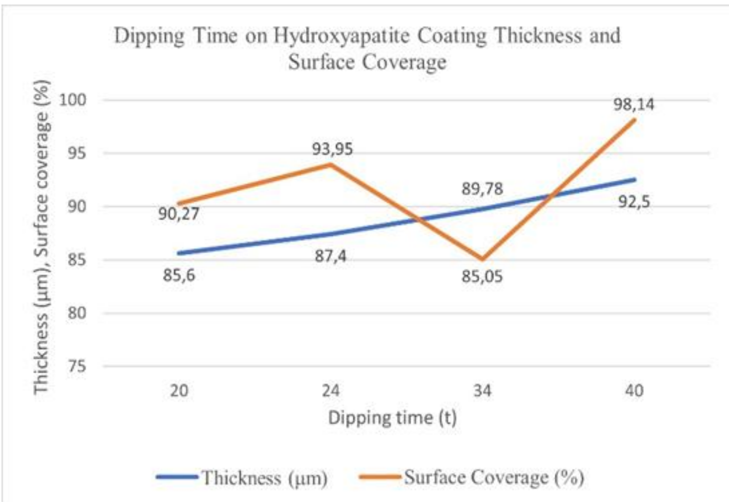
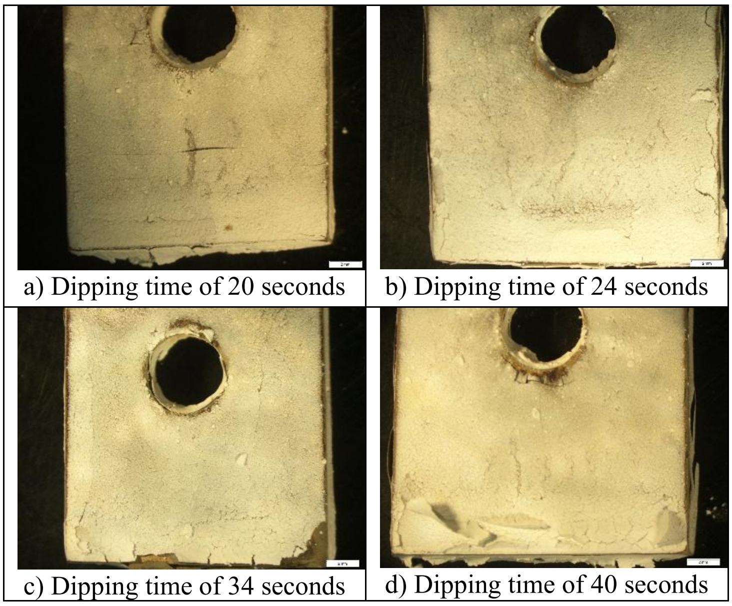


Fig.7. Variation of coating thickness and surface coverage with dipping time.

As shown in Fig. 7, both coating thickness and surface coverage increased with longer dipping times. Prolonged immersion allowed more HA particles to adhere to the Ti-12Cr surface, resulting in enhanced coverage. This suggests that bio-derived HA suspension possessed good adhesive properties, enabling strong bonding between HA and the Ti-12Cr substrate. The uniform distribution of the coating after sintering is further illustrated in Fig. 8.



a) Dipping time of 20 seconds
b) Dipping time of 24 seconds
c) Dipping time of 34 seconds
d) Dipping time of 40 seconds

Fig.8. Morphological characteristics of HA coatings after sintering

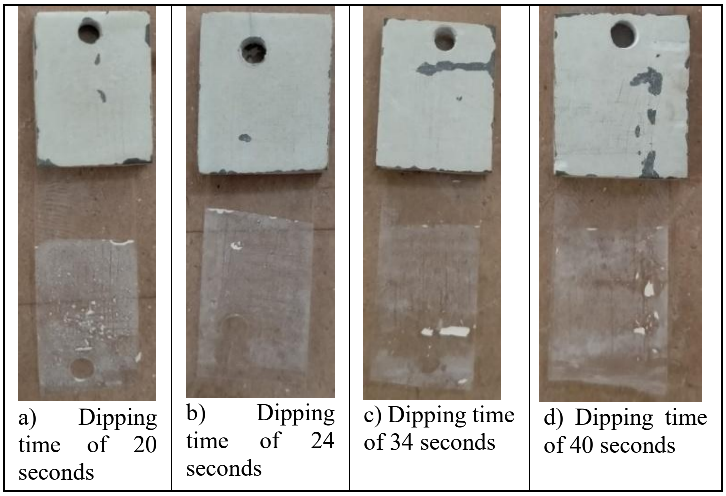
3.2 Adhesion strength of HA coatings

The adhesion strength of the HA coatings obtained in this study was satisfactory, as indicated by the relatively small removed area (2.00-5.25%). Table 5 presents the percentage of removed area for different dipping times.

Table 5. Removed area percentages of HA coatings on Ti-12Cr.

No.	Dipping time (s)	Removed Area (%)
1	20	2,00
2	24	3.75
3	34	4.75
4	40	5.25

From Table 5, it can be observed that the removed area tended to increase with longer dipping times. Thinner coatings (shorter dipping times) generally exhibited stronger adhesion with fewer cracks. This is consistent with the results shown in Fig. 9.



a) Dipping time of 20 seconds
b) Dipping time of 24 seconds
c) Dipping time of 34 seconds
d) Dipping time of 40 seconds

Fig.9. Removed area of HA coatings at different dipping times.

As shown in Fig. 9, increasing the dipping time resulted in thicker coatings, which were more susceptible to cracking and delamination. The strongest adhesion was achieved at a dipping time of 20 s, with only 2% of the removed area. The superior adhesion performance of bio-HA derived from sisik ikan kakap putih can be attributed to its high fracture toughness and flexural strength. These mechanical properties enable the material to dissipate energy during the tetragonal-to-monoclinic phase transformation occurring in the sintering process [9]. Moreover, fish-scale-derived HA exhibits a relatively high thermal expansion coefficient (~14 μK/mK) [9], which improves its thermal compatibility with Ti-12Cr. This compatibility reduces interfacial mismatch stresses and suppresses crack initiation. In addition, the bio-HA coating functions as a diffusion barrier, preventing substrate decomposition and preserving coating integrity during high-temperature processing.

4 Conclusion

The dip coating method produced thin and uniform HA layers on Ti-12Cr alloy substrate, which making it suitable for orthopedic implant applications, as they can support effective osseointegration. The strongest adhesion was achieved at a dipping time of 20 s, with only 2% of the area removed. Hydroxyapatite derived from scales of *ikan kakap putih* (*Lates calcarifer*) exhibited good adhesion properties. The improved adhesion minimized crack formation within the HA layer, thereby enhancing the reliability of Ti-12Cr as a candidate material for orthopedic implants.

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