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Research article

Adhesion Improvement of Hydroxyapatite Layer on Ti-6Al-4V ELI with the Contribution of PVA and Zirconium Oxide for Biomedical Applications

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A B S T R A C T

Ti-6Al-4V Extra Low Interstitial (ELI) is one of the most widely used titanium alloys for orthopedic implants. However, its drawback is that titanium has less bioactive properties. Therefore, Ti-6Al-4V ELI needs to be coated with hydroxyapatite (HA) to achieve good osseointegration in the human body. Nevertheless, several studies have shown that there are still cracks found on the HA surface layer. This research aims to focus on biomedical applications, specifically to obtain strong adhesion of the implant material layer, which is expected to improve osseointegration and reduce inflammation effects from implantation. The research method is experimental (testing), using both qualitative and quantitative methods. The coating method used is the Dip Coating method. Research variables include variations in the weight percentage (wt%) of PVA+ZrO_2, and HA suspension, as well as variations in sintering temperatures, 800, 900 dan 950^{0}C. The study results showed that the addition of Polyvinyl Alcohol (PVA) and Zirconium Oxide (ZrO_2) in the suspension can reduce cracks on the test specimen layer. Optimal results were obtained with the addition of 20% PVA and ZrO_2 weight at a sintering temperature of 900°C. The implant material surface was uniformly coated, and no cracks were found.

1. INTRODUCTION

Cracks in the HA coating are caused by the weak adhesion strength of the HA layer to the implant material surface [1]. As is known, HA is a bioceramic that becomes brittle when sintered for layer densification. During heating, the metal experiences large strain, while HA undergoes small strain. This condition results in thermal stress, which drives the formation of cracks [2,3].

Several previous studies have mentioned that cracks initially occur due to the thick and uneven coating of the HA layer on the surface [4-13]. This condition causes surface cracking during the sintering process. The more HA agglomeration occurs, the more cracks are found in the layer [4]. This forms the research problem to be studied, which is to see how the addition of PVA and ZrO_2 to the HA suspension affects the creation of a thin and even layer across the surface of the implant material. Furthermore, it also aims to observe how the addition of PVA and ZrO_2 influences the enhancement of the adhesion strength during the sintering process.

The urgency of this research benefits biomedical applications, specifically to achieve a strong adhesion bond of the implant material layer, which is expected to improve osseointegration and reduce inflammatory effects from implantation [4,14].

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The problem-solving approach is carried out through a literature study of research from the past five years [4-13], focusing on similar studies that utilized the Electro Phoretic Deposition (EPD) and Dip Coating methods. The materials used include Ti-6Al-4V, Ti-6Al-4V ELI, TNTZ titanium, and CpTi. The suspensions used are commercial HA and bovine bone-derived HA [4, 11,12]. From this literature review, research gaps can be identified, and a problem-solving strategy can be formulated, specifically on how to find a good suspension formulation to improve HA layer adhesion on implant materials that tend to crack when heated at high temperatures above 800°C.

The state of the art is derived from several recent studies as references and comparisons for conducting this research. Seven journals are included, consisting of two nationally accredited journals and five reputable international journals, as listed in Table 1 below.

Table 1. State of the art of research

No	Material/ Method/Suspension	Coating Result
1.	Ti-6Al-4V ELI/ EPD / Bovine bone HA	Not evenly distributed, cracks during sintering 900 °C [5, 8]
2.	Ti-6Al-4V/EPD/ Bovine bone HA	Coating is easily brittle, there are cracks [5, 9]
3.	Ti-6Al-4V ELI /EPD/ Commercial-HA	Evenly distributed, but cracks during sintering 900 °C [4,6,13]
4.	Ti-6Al-4V/*Dip Coating/* Gelatin-HA	Even coating, but cracks during sintering 850 °C [11, 12]
5.	CpTi/*Dip Coating/* Commercial-HA	Even coating, slight cracks during sintering 900 °C [7, 9, 10]
6.	Ti-6Al-4V/*Dip Coating/* Commercial-HA	Even coating, no cracks found during sintering 800 ^{0}C. However, cracks were found when sintering 900 ^{0}C [5, 6, 7].
7.	TNTZ/EPD/ Commercial-HA	The coating did not adhere strongly, cracks found during sintering at 900 ^{0}C [8].

Based on the state of the art above, it can be concluded that HA coatings on implant materials tend to crack when heated at high temperatures, above 800°C [14]. This is due to the weak adhesion of the HA layer at high sintering temperatures. This becomes an entry point to create novelty in this research, namely the addition of PVA and ZrO_2 to improve adhesion and reduce coating cracks, especially at high sintering temperatures above 800°C [13-15].

There are two hypotheses as to why PVA and ZrO_2 need to be added in this research. Firstly, PVA has good crack resistance and flexural strength because it can absorb energy during the transformation from tetragonal to monoclinic structure when heating temperatures exceed 800°C [14,15]. Secondly, ZrO_2 can efficiently conduct heat to Ti-6Al-4V ELI because the thermal expansion coefficient of PVA is close to the thermal expansion coefficient of Ti-6Al-4V ELI [16]. The ZrO_2 phase bond in the HA coating becomes a diffusion barrier, protecting the coating from cracks.

PVA is a synthetic polymer that has biocompatible and good adhesive properties [17-20]. Additionally, ZrO_2 acts as a diffusion barrier to protect the coating from cracks. In short, PVA and ZrO_2 contribute as barriers to prevent the adhesive bond between the material and HA suspension from being disrupted during the heating process. With a coating surface that is not prone to cracking, it is expected to improve osseointegration and reduce the inflammatory effects of the implant.

2. MATERIALS AND METHOD

2.1. Material

This study used 9 test specimens of Ti-6Al-4V ELI (square plate shape) with dimensions of 10 mm x 10 mm x 4 mm. After cutting the specimens, they are sanded using silicon carbide sandpaper sheets with mesh sizes of 800-1500, then polished using alumina powder [21]. Next, the specimens are cleaned with acetone solution, 70% ethanol, 25% nitric acid at a pH of 7.3, and rinsed with pure water (Aquades) for 30 minutes [21]. The specimens are then soaked for 1 hour in a 1 mol NaOH solution [12]. The final cleaning uses a multi-frequency ultrasonic bath, and they are dried using a stirring hot plate for 5 minutes at a temperature of 50 °C [21]. The indicator of success at this stage is to

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ensure the test specimen surface is flat, clean, and rough, making it easier to coat with HA.

For the suspension layer, commercial HA (Sigma Aldrich, USA) nano size (200 nm), PVA and ZrO_2 (XFNANO brand) were used, model number XFI01-3, 95% purity. The suspension consisted of 4 grams of HA powder plus 0.8 grams of PVA+ZrO_2 (17 wt%) and 4 grams of HA powder plus 1.0 grams of PVA+ZrO_2 (20 wt%) which were mixed in 100 ml of ethanol solution at pH 4.0 using the addition of HNO_3 solution [14]. After that, homogenization of the solution was carried out with a magnetic stirrer for 1 hour, followed by sonication in an ultrasonic bath for 2 hours. The HA which had been attached to the surface of the test specimen was dried for 24 hours at room temperature.

2.2. Methodology

HA coating using the dip coating method. This method was chosen because it is easy to do and the cost is not expensive [15]. Immersion was carried out with a withdrawal speed of 4 mm/s, referring to the results of an even layer of HA in previous studies [15-19]. Furthermore, the resulting layer will be compacted by a sintering process using the Vacuum Tube Furnace GSL-1100. The sintering process is carried out with temperature variations of 800 ^{0}C, 900 ^{0}C and 950 ^{0}C, heating rate of 50 ^{0}C/minute. After being heated, it is held for 2 hours so that the temperature is even in the test specimen, followed by annealing for 24 hours [3-5].

Then, the thickness of the coating was measured using the Sanfix Thickness Gauge (μm), GM 280 series, followed by measuring the surface coverage of the layer using ImageJ software [17]. The Olympus LG-PS2 Stereo optical microscope was used to observe the morphological and cracking characteristics of the coating. To get the percentage of layer cracks, ImageJ software is also used. Then the percentage of crack reduction in the test specimen layer without the addition of PVA+ZrO_2 with the addition of PVA+ZrO_2 will be compared at each sintering temperature of 800 ^{0}C, 900 ^{0}C, and 950 ^{0}C.

Furthermore, the last stage: to assess the adhesion strength of the coating, a cross-cut tape test method is used. This test uses the Cross Cutter Adhesion tester from ETOPOO, and Scotch transparent tape. The cross-cut test lines are made according to ASTM D3359 standards [17], which specify cut lines and spacing based on film thickness: 6 lines; 1 mm spacing for 50-125 μm thickness. The test is conducted by scoring the sample's coating layer. Afterward, tape is applied across the entire scratched surface, and the tape is pulled at a 180-degree angle. The adhesion strength is measured on a scale of 0 to 5, where 0 indicates more than 65% of the HA coating has peeled off (removed area), and 5 indicates a removed area of 0%.

The success indicator for this stage is to obtain data on coating adhesion strength, indicated by the percentage of removed area on the coating. Ideally, the pull test would be used to assess coating adhesion strength, but due to the small dimensions of the test specimens, the cross-cut tape test method was employed [11,12].

3. RESULTS AND DISCUSSION

3.1. Coating Thickness and Surface Coverage

From the research results, it can be generally seen that the test specimen is uniformly coated with hydroxyapatite across almost the entire surface. This is observed from the calculation using the ImageJ software, where the surface coverage of the implant material coated with hydroxyapatite is measured at 90.40% to 95.68% (Table 2).

Table 2. HA Coating Thickness and Surface Coverage on Ti-6Al-4V ELI

PVA+ZrO_2 (wt %)	Thickness (μm)	*Surface Coverage* (%)
0	91.90	90.40
17	89.67	93.87
20	87.90	95.68

Furthermore, the obtained coating is a thin layer with a thickness ranging from 87.90 to 91.90 μm. This is consistent with the results of several previous studies, which state that the standard thickness of the hydroxyapatite layer for implant materials is between 50-100 μm. The optimal parameters obtained in this research are the addition of 20% PVA and ZrO_2, a surface coverage percentage of 95.68%, and a layer thickness of 87.90 μm (Table 1). Overall, the uniform surface

coating is beneficial for the densification process, especially in minimizing cracks during the sintering process. The results of the thickness and surface coverage measurements of the test specimen can also be seen in Figure 1.

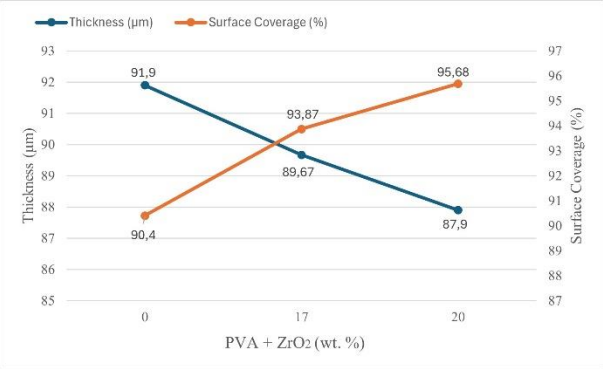


Figure 1. The thickness and surface coverage of the HA layer on variations in the addition of PVA+ZrO_2

From Figure 1, it can be seen that the surface coverage of the HA layer increases with the addition of PVA+ZrO_2. This indicates that PVA+ZrO_2 has good adhesion properties. so that the bond of the HA suspension with the Ti-6AL-4V ELI material becomes strong. The more addition of PVA+ZrO_2, the better the adhesion bond between the suspension and the substrate.

3.2. Checking of Coating Crack

After measuring the thickness and surface coverage of the layer, then inspection of the layer cracks is carried out by observing the morphological characteristics of the test specimens as shown in Figure 2. It can be seen that at a sintering temperature of 800°C, no cracks in the coating layer were found in the test specimens coated with HA with the addition of PVA+ ZrO_2 (17% and 20% wt). This absence of cracks is due not only to the thin and uniform layer but also to the fact that the sintering temperature of 800°C is an optimal temperature that stabilizes the chemical properties of the HA coating (HA does not undergo structural changes) as it adheres well to the surface of the material. At this sintering temperature of 800°C, there is no degradation of Ti-6Al-4V ELI, and no HA decomposition induced by the metal either.

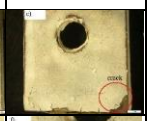
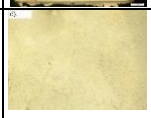
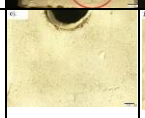
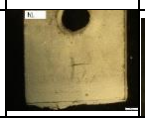
T sintering (^{0}C)	800	900	950
0 % PVA+ZrO_2			
17 % PVA+ZrO_2			
20 % PVA+ZrO_2			

Figure 2. Observation of the layer morphology on each test specimen

Conversely, at a sintering temperature of 900°C, cracks were found in the test specimens coated with HA without the addition of PVA+ ZrO_2. Cracks were initiated by some peeling of the layer, which caused voids and debonding at the interface, subsequently leading to micro-cracks in the layer [10].

As is known, sintering is necessary for layer densification. However, the drawback of high sintering temperatures is that they can cause cracks in the HA surface due to HA's brittle nature and the difference in thermal expansion coefficients between HA and the material during the sintering process, which results in thermal stress, promoting crack formation.

In addition, cracks are also caused by the difference in thermal expansion coefficients [11, 12]. During sintering, the thermal expansion coefficient of HA (15.2 × 10^-6/°C) is lower than that of Ti-6Al-4V ELI (8.6 × 10^-6/°C). Since HA has a lower thermal expansion coefficient than the metal, it cannot effectively transfer heat to Ti-6Al-4V ELI. The expansion and contraction mismatch between the HA and Ti-6Al-4V ELI layers also generates thermal stress and residual tensile stress, which promotes crack formation [12].

Furthermore, cracks are also caused by imperfect densification, namely, a rapid temperature change during heating (thermal shock). The ethanol used as a solvent for HA gets trapped in the pores formed during the coating process. This leads to surface

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cracks in the coating layer as the trapped ethanol evaporates rapidly [12, 15].

However, at the sintering temperature of 900°C, no cracks were found in the test specimens coated with HA with the addition of PVA+ ZrO_2 (17% and 20% wt). This indicates that the addition of PVA and ZrO_2 improves the adhesion of the coating layer. Subsequently, at a sintering temperature of 950°C, cracks and peeling were found in all test specimens, except for the test specimen coated with HA with the addition of 17% wt PVA+ ZrO_2.

It will cause cracks on the surface of the layer, because the trapped ethanol evaporates quickly [11, 21]. However, at T sintering 900 ^{0}C, cracks are not found in the test specimens coated with HA with the addition of ZrO_2 (17% and 20% wt). This indicates the effect of the addition of ZrO_2 to increase the adhesion of the coating. In Figure 2, it can also be seen, there is no layer crack (0%).

3.3 Removed Area of Coating

The cross-cut tape test method was used to determine the adhesion strength of the coating. This test utilized a Cross Cutter Adhesion test tool from the brand ETOPOO. The adhesion strength of the coating is indicated by the percentage of the removed area on the test specimen's coating. The lower the percentage of the removed area, the better the adhesion strength of the coating, also the other way around. In general, the adhesion strength of the coating obtained in this study is quite good. This is evident from the small removed area values, ranging from 3.25% to 9.25%. As shown in Table 3 and Figure 3, the test specimens with the addition of PVA+ZrO_2 exhibited better removed area values compared to the test samples without PVA+ZrO_2 at sintering temperatures of 800°C, 900°C, and 950°C.

Table 3. Removed area of coating with variation of T sintering and the addition of PVA+ZrO_2.

No.	PVA+ZrO_2 (wt %)	T Sintering (°C)	Removed Area (%)
1.	0	800	9.25
2.	17	800	3.75
3.	20	800	4.25
4.	0	900	7.50
5.	17	900	3.25
6.	20	900	4.50
7.	0	950	8.25
8.	17	950	5.50
9.	20	950	6.50

Furthermore, the removed area for the coating with the addition of 17 wt% PVA+ZrO_2 was better than that with 20 wt% PVA+ZrO_2. The optimal result for coating adhesion strength was obtained from the test specimen with 17 wt% PVA+ZrO_2, sintered at 900°C, with a removed area value of 3.25%. Meanwhile, in terms of sintering temperature, the optimal adhesion strength was achieved at 900°C, followed by 800°C and 950°C.

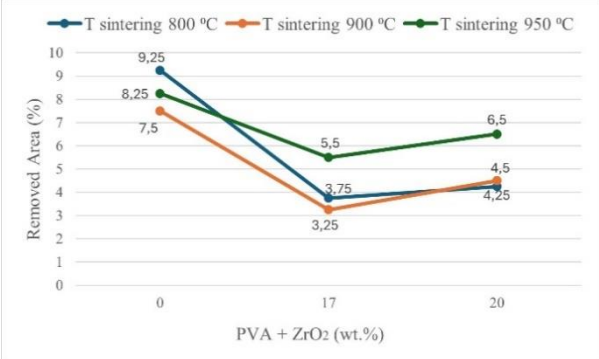

Figure 3. Value of removed area to variations the addition of PVA+ZrO_2 and sintering temperature.

The removed area values obtained in this study are slightly better than those from Ficky et al. [22], who used the EPD method. In their study, the removed area value was 2.25% at a voltage of 5V with a deposition time of 5 minutes. The optimal removed area value of 3.25% obtained in this study indicates a fairly high adhesion strength between the coating and the material [4]. It is caused by PVA+ZrO_2 has good fracture toughness, as it absorbs energy during the transformation from a tetragonal to a monoclinic atomic arrangement [9]. Additionally, PVA+ZrO_2 conducts heat well to Ti-6Al-4V ELI because its thermal expansion coefficient (9.6×10^{-6}/°C) is close to that of Ti-6Al-4V ELI (8.6×10^{-6}/°C) [10]. This low thermal expansion coefficient slows down chemical reactions, making the coating crack-resistant. PVA+ZrO_2 also has corrosion resistance properties due to its neutral electron configuration. PVA+ZrO_2 is also resistant to strong acids like sulfuric and nitric acids. This chemical inertness of PVA+ZrO_2 further enhances its corrosion resistance [20].

The adhesion strength of the hydroxyapatite coating to the material surface is also influenced by the sintering temperature. The results show that the adhesion strength at a sintering temperature of 900°C is better than at 800°C, as evidenced by the smaller removed area value at 900°C. Increasing the sintering temperature can improve adhesion strength due to increased particle diffusion at the interface, promoting bonding between the coating and the material [4]. Additionally, the adhesion strength of the coating is also influenced by the thin and uniform morphological characteristics of the layer. Hydroxyapatite agglomeration on the surface was also rarely observed.

4. CONCLUSION

The addition of PVA+ZrO_2 to the hydroxyapatite coating suspension can improve the adhesive strength of the surface layer on Ti-6Al-4V ELI. This is demonstrated by the smaller removed area compared to the test specimens without PVA+ ZrO_2 coating. The strong adhesion of this layer is achieved due to its thin, homogeneous, and even distribution across the entire surface of the material. The hydroxyapatite layer with strong adhesive strength can lead to a good osseointegration process and biocompatibility within the human body for biomedical implant applications.

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REFERENCES

[1] Gunawarman et al., "Adhesion Strength of Hydroxyapatite Coating on Titanium Alloy (Ti-6Al-4V ELI) for Biomedical Application," in IOP Conference Series: Materials Science and Engineering, 2021, vol. 1062, no. 1, doi: 10.1088/1757-899X/1062/1/012031.

[2] D. Juliadmi, Harlendri, D. Hon Tjong, M. Manjas, and Gunawarman, "The Effect of Sintering Temperature on Bilayers Hydroxyapatite Coating of Titanium (Ti-6Al-4V) ELI by Electrophoretic Deposition for Improving Osseointegration," in IOP Conference Series: Materials Science and Engineering, 2019, vol. 547, no. 1, doi: 10.1088/1757-899X/547/1/012005.

[3] O. Albayrak, O. El-Atwani, and S. Altintas, "Hydroxyapatite coating on titanium substrate by electrophoretic deposition method: Effects of titanium dioxide inner layer on adhesion strength and hydroxyapatite decomposition," Surf. Coatings Technol., vol. 202, no. 11, pp. 2482–2487, 2008, doi: 10.1016/j.surfcoat.2007.09.031.

[4] E. Mohseni, E. Zalnezhad, and A. R. Bushroa, "Comparative investigation on the adhesion of hydroxyapatite coating on Ti-6Al-4V implant: A review paper," Int. J. Adhes. Adhes., vol. 48, pp. 238–257, 2014, doi: 10.1016/j.ijadhadh.2013.09.030.

[5] B. Beig, U. Liaqat, M. F. K. Niazi, I. Douna, M. Zahoor, and M. B. K. Niazi, "Current challenges and innovative developments in hydroxyapatite-based coatings on metallic materials for bone implantation: A review," Coatings, vol. 10, no. 12, pp. 1–29, 2020, doi: 10.3390/coatings10121249.

[6] R. Drevet, N. Ben Jaber, J. Fauré, A. Tara, A. Ben Cheikh Larbi, and H. Benhayoune, "Electrophoretic deposition (EPD) of nano-hydroxyapatite coatings with improved mechanical properties on prosthetic Ti6Al4V substrates," Surf. Coatings Technol., vol. 301, pp. 94–99, 2016, doi: 10.1016/j.surfcoat.2015.12.058.

[7] G. E. Guraksin, E. C. Bicer, and A. Evcin, Characterization of Hydroxyapatite Coating on Ti6Al4V by Sol-gel Method, vol. 4, no. 3. 2018.

[8] W. Xia, L. Fu, and H. Engqvist, "Critical cracking thickness of calcium phosphates biomimetic coating: Verification via a Singh-Tirumkudulu model," Ceram. Int., vol. 43, no. 17, pp. 15729–15734, 2017, doi: 10.1016/j.ceramint.2017.08.134.

[9] M. Peron, J. Torgersen, and F. Berto, “Effect of Zirconia ALD coating on stress corrosion cracking of AZ31 alloy in simulated body fluid,” in Procedia Structural Integrity, 2019, vol. 18, pp. 538–548, doi: 10.1016/j.prostr.2019.08.198.

[10] A. Jemat, M. J. Ghazali, M. Razali, Y. Otsuka, and A. Rajabi, “Effects of TiO2 on microstructural, mechanical properties and in-vitro bioactivity of plasma sprayed yttria stabilised zirconia coatings for dental application,” Ceram. Int., vol. 44, no. 4, pp. 4271–4281, 2018, doi: 10.1016/j.ceramint.2017.12.008.

[11] C. Domínguez-Trujillo et al., “Bioactive coatings on porous titanium for biomedical applications,” Surf. Coatings Technol., vol. 349, no. May, pp. 584–592, 2018, doi: 10.1016/j.surfcoat.2018.06.037.

[12] Y. Bai et al., “One-step approach for hydroxyapatite-incorporated TiO 2 coating on titanium via a combined technique of micro-arc oxidation and electrophoretic deposition,” Appl. Surf. Sci., vol. 257, no. 15, pp. 7010–7018, 2011, doi: 10.1016/j.apsusc.2011.03.058.

[13] S. Eraković et al., “The effect of lignin on the structure and characteristics of composite coatings electrodeposited on titanium,” Prog. Org. Coatings, vol. 75, no. 4, pp. 275–283, 2012, doi: 10.1016/j.porgcoat.2012.07.005.

[14] D. Juliadmi, D. Oktaviana, D. Hon, and M. Manjas, “Hydroxyapatite Bilayers Coating on Screw Implant Ti6Al4V ELI with Electrophoretic Deposition Method for Improving Osseointegration,” vol. 51, no. 51, pp. 14–18, 2018.

[15] A. Thangprasert, C. Tansakul, N. Thuaksubun, and J. Meesane, “Mimicked hybrid hydrogel based on gelatin/PVA for tissue engineering in subchondral bone interface for osteoarthritis surgery,” Mater. Des., vol. 183, p. 108113, 2019, doi: 10.1016/j.matdes.2019.108113.

[16] P. Husni Hidayah, “Pelapisan hidroksiapatit pada Stainless Steel 316 L menggunakan metode dip coating dengan variasi rasio binder pati sagu dan waktu pengadukan,” vol. 50, no. February, pp. 3–10, 2016, [Online]. Available: file:///F:/ali/payanname/Article/ىطخ دنچ هريغتم و نويسرگر ياهشور جياتنهسياقم ؛ لنوترفحنيشامذوفذخرن ىنيبشيپ ىبصعيزافىقيبطتجاتنتسامتسيسيريصبنيسحيزير 2 ،دمحم.pdf.

[17] R. I. M. Asri, W. S. W. Harun, M. A. Hassan, S. A. C. Ghani, and Z. Buyong, “A review of hydroxyapatite-based coating techniques: Sol-gel and electrochemical depositions on biocompatible metals,” J. Mech. Behav. Biomed. Mater., vol. 57, pp. 95–108, 2016, doi: 10.1016/j.jmbbm.2015.11.031.

[18] S. Monica, “Ti-6Al-4V Terlapis Hidroksiapatit-Gelatin Menggunakan Metode Dip-Coating Termodifikasi Sebagai Implan Tulang,” Ph.D. dissertation,. Dept. Teknik Mesin, Institut Pertanian Bogor. 2017.

[19] R. Tan et al., “High-Performance Biocomposite Polyvinyl Alcohol (PVA) Films Modified with Cellulose Nanocrystals (CNCs), Tannic Acid (TA), and Chitosan (CS) for Food Packaging,” J. Nanomater., vol. 2021, 2021, doi: 10.1155/2021/4821717.

[20] F. H. Schünemann et al., “Zirconia surface modifications for implant dentistry,” Mater. Sci. Eng. C, vol. 98, no. January, pp. 1294–1305, 2019, doi: 10.1016/j.msec.2019.01.062.

[21] S. Gnanavel, S. Ponnusamy, and L. Mohan, “Biocompatible response of hydroxyapatite coated on near-β titanium alloys by E-beam evaporation method,” Biocatal. Agric. Biotechnol., vol. 15, no. June, pp. 364–369, 2018, doi: 10.1016/j.bcab.2018.07.014.

[22] N. F. Nuswantoro, I. Maulana, H. T. Djong, and M. Manjas, “Hydroxyapatite Coating on New Type Titanium, TNTZ, Using Electrophoretic Deposition,” J. Ocean. Mech. Aerospace-Science Eng., vol. 56, no. 1, pp. 1–4, 2018, [Online]. Available: www.isomase.org.