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INTERNATIONAL ADVANCED RESEARCHES and ENGINEERING JOURNAL

Journal homepage: www.dergipark.org.tr/en/pub/iarej

e-ISSN: 2618-575X

International Open Access

Volume 06
Issue 02

August, 2022

Research Article

Hydroxyapatite coating processes with EPD method and investigation of mechanical properties of coatings

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ARTICLE INFO

Article history:
Received 12 April 2022
Accepted 10 August 2022
Published 15 August 2022

Keywords:
Electrophoretic deposition
Hydroxyapatite
Ti6Al4V
SS 316L

ABSTRACT

This paper reports on electrophoretic deposition of hydroxyapatite coatings on 316L stainless steel and Ti6Al4V alloy. Coatings were carried out at 60 sec. deposition time and voltage values of 40, 80, 120, 160 Voltage. Suspension: It was prepared by using Ethanol, Hydroxyapatite, Polyvinyl Alcohol, Sodium dodecyl sulfate, N-N-Dimethylformamide chemicals. The findings and results acquired at the end of the study have been presented and discussed. When the Ca/P values calculated in the study are examined, it was seen that there are values close to the ideal Ca/P ratio (1.67) in all parameters. When the roughness values are examined, it was seen that coatings close to the ideal surface roughness value (1-1.5 µm) are obtained. When the nano indentation test results were evaluated, it was observed that coatings suitable for shell bone implants were obtained.

1. Introduction

Ti and its alloys and 316 L stainless steels (SS) have been used in orthopedic and dental applications because of their biocompatibility and high mechanical properties [1].

The human body has a corrosive environment because of the natural ions in its structure [2]. SS 316L and Ti6Al4V alloy are implant materials with high corrosion resistance [3]. Although their corrosion resistance is high, it is normal for implant materials to be affected by this environment. Because they will be exposed to this corrosive environment for a long time. The use of metal implants in this corrosive environment can causes of the harmful ions in their structure to in the body. Some ions in metal implants have carcinogenic and allergenic effects [4,5]. Therefore, direct use of these implants is not preferred.

HA has high biocompatibility and bioactivity. It is also a calcium phosphate-based bio ceramic material that forms the main inorganic compound of human bones and teeth [4-8]. The reason why HA is preferred in biomedical applications is its osteoconductive and biocompatibility properties [7-10]. The biggest disadvantage of HA is low mechanical properties. This prevents its application as a direct implant [11-14]

Since direct application of metallic biomaterials in implantation processes is not supported, it is a preferred application to be coated with HA, which has high biocompatibility and bioactivity [15-16].

With this application, the high bioactivity and biocompatibility of HA is combined with the high mechanical properties of the metal implant, resulting in a superior biomaterial. In addition, HA acts as a barrier between the implant and the body, cutting off the contact of metal ions with the body and preventing the release of ions into the body [4,17].

Different methods are used for HA coating processes on metal implants. These; electrophoretic deposition (EPD), electrochemical deposition, thermal spray coating, Biomimetics, sol-gel, spray coating and plasma spray coating [18-25]. The EPD method has attracted attention in recent years [25-26]. EPD starts with the movement of charged particles in a stable suspension with the effect of an applied electric field and is completed by the accumulation of moving particles on the implant material surface [25-28].

The reasons why EPD is preferred that the coatings are obtained in a short time, the coatings are homogeneous, the cost is low, and the possibility of coating complex

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DOI:10.35860/iarej.1102381

materials [20-30].

In this study, coating surfaces were performed by SEM, EDS and XRD analysis. In addition, microhardness, Modulus of Elasticity (E), surface roughness and thickness were determined. All the results were discussed and contrasted with the studies in the literature. Thus, a contribution to the literature has been made.

2. Materials and Methods

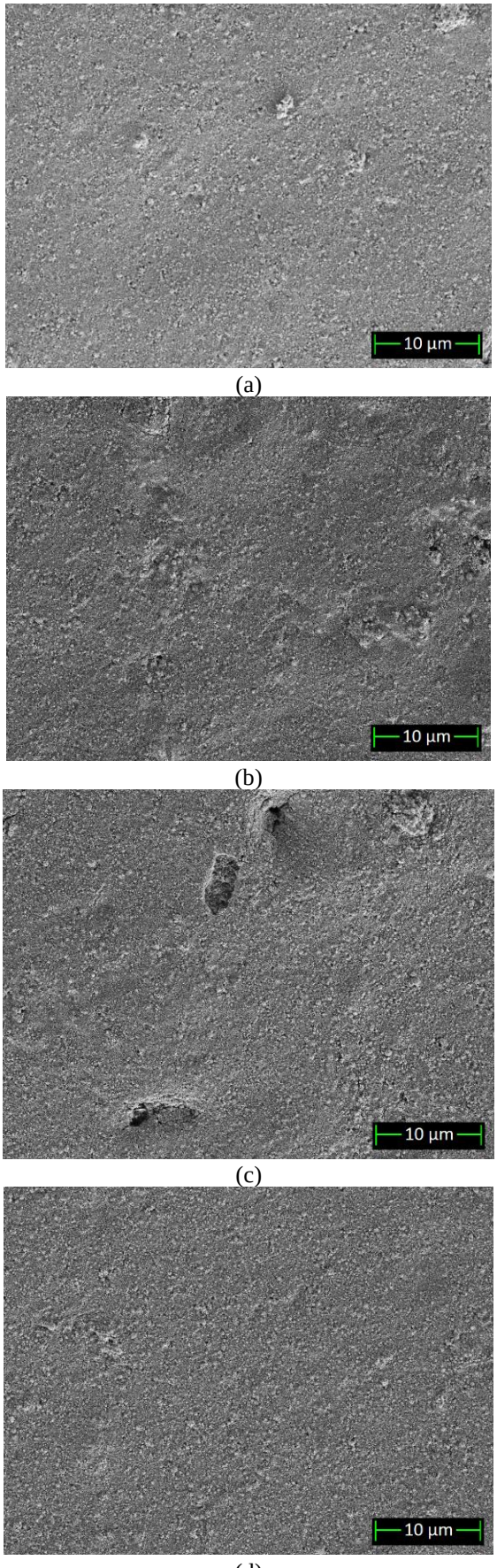
In this study, Ti6Al4V alloy and SS 316L were preferred to be used as substrate. The substrate materials to be used in the coating process was cut as D= 20mm, h=10 mm. In order for the substrates to be clean, they were cleaned in an ultrasonic bath in 70% ethyl alcohol solution for 30 minutes, washed with distilled water and dried again. In order to clean the oxide layers formed on the substrates, the surfaces were wearied with acid solution. This wearing was carried out in 95% distilled water, 2% HF, 3% HNO_3 solution. The substrates were kept in this solution and then washed with distilled water in an ultrasonic bath. 320x sanding process was applied to the substrate material surfaces. After the sanding process, it was washed with distilled water and ethyl alcohol. Then was made ready for the coating process.

Ethanol of 99.8 percent purity was used as solvent to prepare the coating suspension in the EPD process. 1 g HA and 0.001 g SDS were added to 100 mL of ethanol. Then were mixed in a magnetic stirrer to disperse the HA particles homogeneous. To increase the adhesion strength of HA particles, 1 g PVA and 10 ml N, N-Dimethylformamide chemicals were added to the suspension [31]. In order to ensure the stability of the prepared suspension, the suspension pH was adjusted to 4. The substrates to be used in the coating process were arranged as cathode and anode. The distance between the substrate were fixed to 10 mm. Prepared substrate were immersed in a stable suspension and connected to the DC power source. The coating process was carried out in 60 seconds of deposition time and 40, 80, 120, 160 V values.

3. Results and Discussion

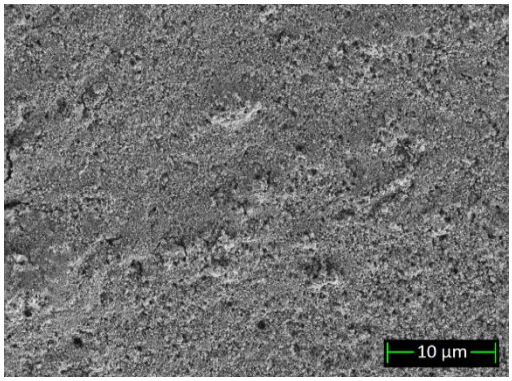
The microstructure analysis of the coated substrate was performed by using a ZEISS Gemini 500 model scanning electron microscope (SEM). 2500X images of the results in the SEM are given in Figure 1 and 2. When Figure 1 and 2 were examined, it was clear that HA coating the surface of the substrate in a homogeneous and intense manner.

The elemental components of the coated substrate were determined by using an EDX detector on SEM. One example of EDS analysis result is given in Figure 3. When Figure 3 was examined, it was seen that calcium phosphate structure was formed in the coating.

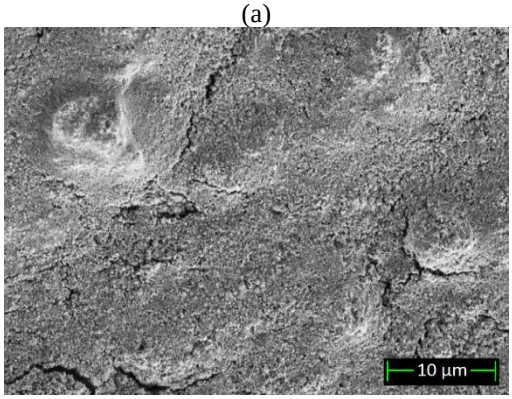


(a) (b) (c) (d)

Figure 1. SEM images of HA-coated Ti6Al4V alloys a) 40V /60s, b) 80V/60s, c) 120V/60s, d) 160V/60s



(a)



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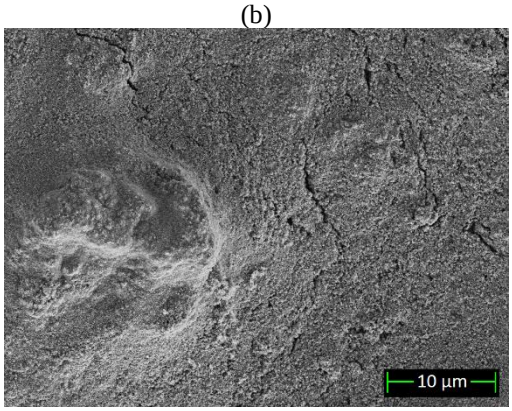

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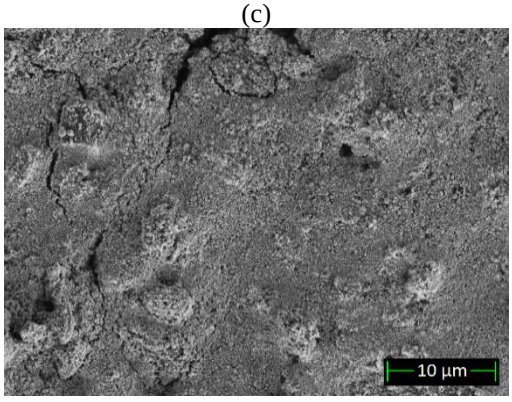
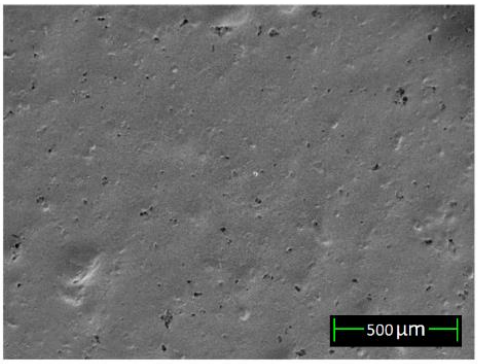


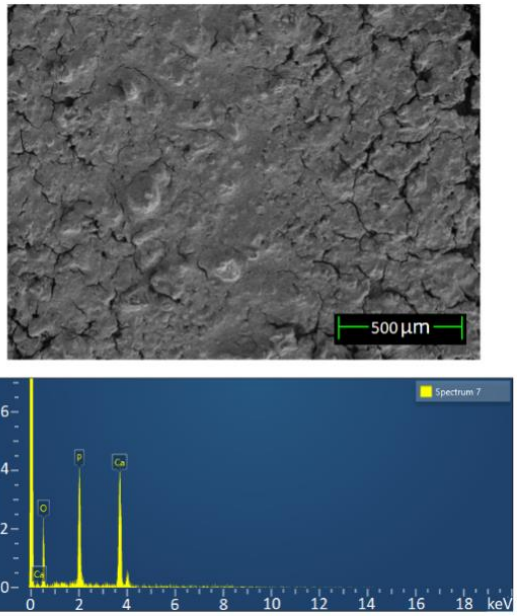
(d)

Figure 2. SEM images of HA-coated SS 316L a) 40V/60s, b) 80V/60s, c) 120V/60s, d) 160V/60s

For each parameter, the Ca/P ratio is given in Figure 4. In the literature, some of the Ca/P ratios obtained are as follows: 1.66 [27], 1.61, 1.65, 1.72, 1.73 [32], 1.59, 1.63, 1.66, 1.72 [33]. Ideal Ca/P proportion was determined in the literature for HA covers at 1.67 [34]. There are values in all parameters close to the ideal Ca/P ratio.



(a)



(b)

Figure 3. EDS analysis result of HA-coating (120V/60s) a) Ti6Al4V alloys, b) SS 316L

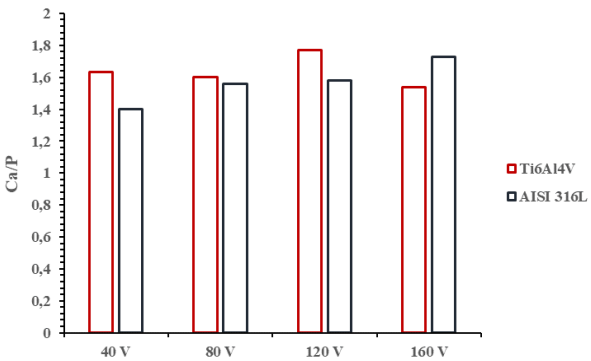


Figure 4. Ca/P ratios for different voltage values

Phase analysis of coated substrate was carried out XRD device at the Manisa Celal Bayar University-Applied Science Research Centre was used. The XRD analysis result of HA coatings applied to Ti6Al4V and SS 316L substrates was showned in Figure 5 and 6. When Figure 5 and 6 were examined, it was showed that HA powders preserved their structure during electrophoretic deposition, as in the literature [6, 35].

In the literature, some peak points of HA crystals obtained are as follows: 2 Theta= 26.0078°, 28.1945°, 32.2494°, 34.1778°, 39.9130°, 48.1571° and 50.5511° [32]. 2 Theta= 26.06°, 31.62° [35]. 2 Theta= 25.91°, 28.94°, 31.78°, 32.19°, 32.93°, 34.10°, 39.80°, 46.71° and 49.49° [7]. 2 Theta= 25.7182°, 28.7945°, 31.6402°, 32.0520°, 32.6648°, 32.7802°, 33.8369°, 33.926°, 39.6934°, 46.2985°, 49.3822°, and 70.7743° [33].

The thickness of the HA coatings was measured with a ElektroPhysik MiniTest 730/Sensor FN 1.5 HD trademark device. Measurements were made 5 times for each coating parameter and the averages were taken. The values of the coating thicknesses were given in Figure 7. When Figure 7 were examined, it was observed that the coating thicknesses increase as the voltage value increases.

The thicknesses of HA coatings obtained by EPD method in the literature were follows: 4.38, 5.43, 7.60, 9.42 µm [32]. 5.86, 7.73, 9.72 and 12.11 µm [33]. 10 µm [35]. 29.35 µm [36].2.6, 2.8, 4.2 µm [21].

The measurement of surface roughness (Ra) values was carried out with the Roughness Tester PCE-RT 1200 model device. Results were obtained in micrometres. Five measurements were made on each coating surface and the results were averaged. Evaluation results were given in Figure 8.

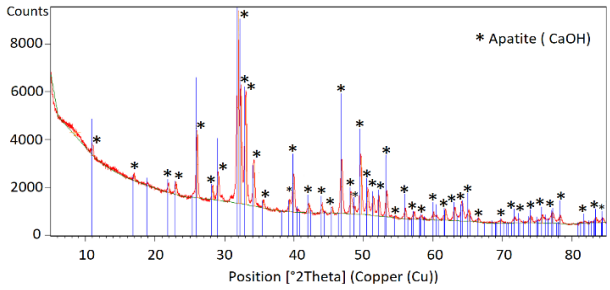


Figure 5. XRD Analysis Results of HA-Coated Ti6Al4V Alloys

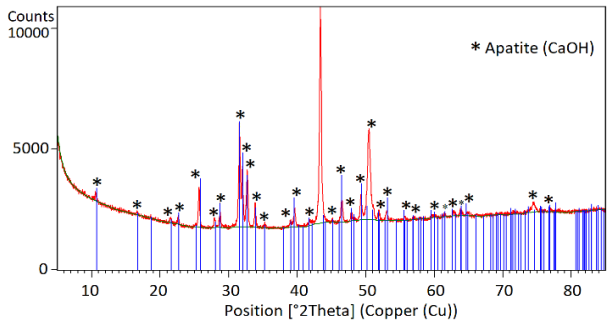


Figure 6. XRD Analysis Results of HA-Coated SS 316L

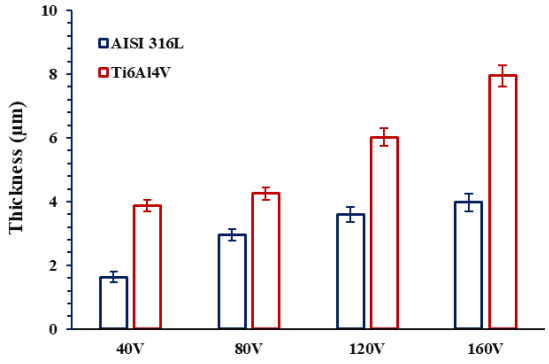


Figure 7. The Average Thicknesses of HA Coatings

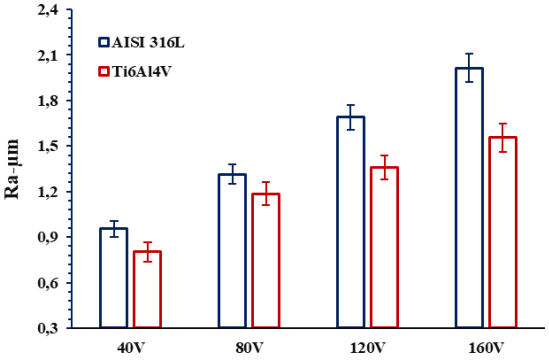


Figure 8. The Average Roughnesses of HA Coatings

When Figure 8. were examined, it was seen that successful results have been obtained. In addition, It was observed that the surface roughness of the coatings increases as the voltage value increases. The ideal surface roughness was measured of between 1-1,5 µm in the literature [4]. Surface roughness of HA coatings obtained by EPD method in the literature were as follows: 0.818, 1.055, 1.552 and 1.673 µm [32]. 1.18, 1.95, 2.26 and 2.83 µm [33]. 1.26 µm [36]. 1.8 µm [4].

Hardness and elastic modulus (E) of the coatings were investigated by using the indentation test device in the Middle East Technical University Central Laboratory. Tests conducted by this tester were performed under the load-unload test mode by applying a test force of 5 mN. Berkovich tip was used in the indentation process. At least 3 measurements were made for each substrate and Microhardness and E values were calculated by taking the average of these measurement results. The test results were showed Figure 9 and 10.

There are differences in the mechanical properties of the bones in different parts of the human body. For example, the E values is 0.001-0.01 GPa in joint cartilage, 0.05-0.5 GPa in cancellous bone, 1 GPa in tendon-bone, and 7-30 GPa in shell bone [2]. When Figure 9 and 10 were examined, it was seen that the HA coatings obtained in some parameters were applicable for shell bone implants.

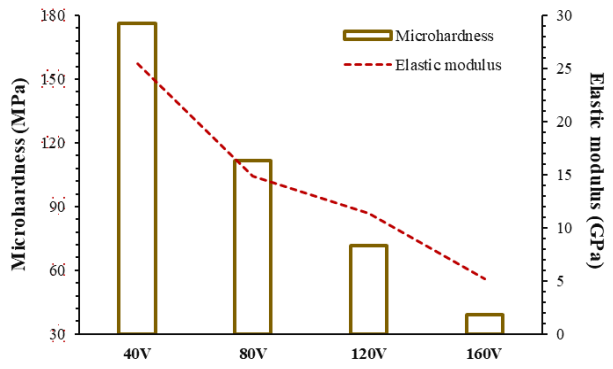


Figure 9. Vickers Hardness and Elasticity Modulus Values of HA-Coated SS 316L

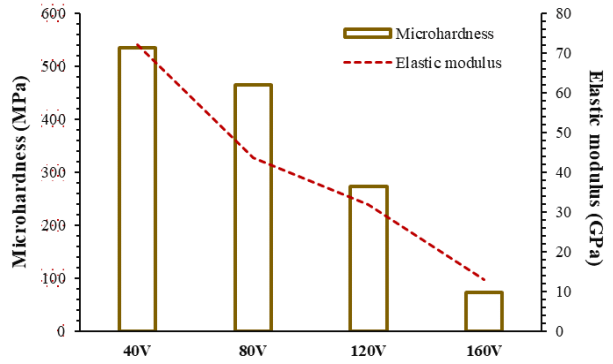


Figure 10. Vickers Hardness and Elasticity Modulus Values of HA-coated Ti6Al4V Alloys

Drevet et al. observed that the hardness value was 5.4-153.5 MPa and the E value was between 5.2-19 GPa in HA coatings which they applied to Ti6Al4V implants with EPD method with different parameters [27]. Bartmanski et al.observed that the hardness value was 0.0112-0.1349 GPa and the E value was between 1.25-30.31 GPa in HA coatings which they applied to Ti13Zr13Nb implants with EPD method with different parameters [36].

4. Conclusions

In this study, HA coating processes were performed on Ti6Al4V alloy and SS 316L implants using the EPD method. Obtained results are given below.

- When the SEM images of the HA coatings created as a result of the study, it was seen that there are homogeneous coatings on the substrate material surfaces in all parameters.
- When the EDS analysis results were examined, it was observed that calcium phosphate structure was formed in all parameters. In the literature, the ideal Ca/P ratio of HA coatings has been determined as 1.67 [34]. When the Ca/P values calculated in the study, it is seen that there are values close to the ideal Ca/P ratio in all parameters.
- When the surface roughness results were examined, it was observed that the surface roughness of the coatings increases as the voltage value increases. Surface roughness values of HA coatings applied to Ti6Al4V alloy implants were 0.803-1.554 µm, Surface roughness values of HA coatings applied to SS 316Limplants were obtained between 0.955 and 2.013 µm. In the literature, the ideal surface roughness value was determined between 1-1.5 µm [37]. When the roughness values were examined, it was observed that coatings close to the ideal surface roughness value was obtained.
- When the coating thickness results were examined, it was observed that the coating thicknesses increase as the voltage value increases. The thickness values of HA coatings applied to Ti6Al4V alloy implants were 3.87-7.95 µm, and the thickness values of HA coatings applied to SS 316L implants were between 1.63-3.97 µm.
- When the indentation test results were examined, it was observed that the hardness and E values of the coatings decrease as the voltage value increases. The hardness values of the HA coatings applied to the Ti6Al4V alloy implants were 72.432-534.74 MPa, E values were between 13.035-72.074 GPa, the hardness values of the HA coatings applied to the SS 316L implants were 39.038-176.067 MPa, and the E values were between 5.185-25.469 GPa. The E values is 0.001-0.01 GPa in joint cartilage, 0.05-0.5 GPa in cancellous bone, 1 GPa in tendon-bone, and 7-30 GPa in shell bone [2]. When the results were evaluated, it was observed that coatings applicable to shell bone implants were obtained.

Declaration

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article. The author(s) also declared that this article is original, was prepared in accordance with international publication and research ethics, and ethical committee permission or any special permission is not required.

Author Contributions

İ. Aydın developed the methodology. A.İ. Bahçepınar performed the analysis. M. Ayvaz supervised and improved the study. İ. Aydın and A.İ. Bahçepınar wrote the manuscript together. M. Ayvaz proofread the manuscript.

Acknowledgment

This work supported by the Manisa Celal Bayar University Scientific Research Projects Coordination Unit (project no: 2018-224), Turkey

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