Characterization of vickers hardness and corrosion rate of stainless steel-316L coated with hydroxyapatite-polyvinyl alcohol

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Abstract. This study aims to determine the effect of variations in the composition of the hydroxyapatite-Poly Vinyl Alcohol (HA-PVA) coating to the Vickers hardness and the corrosion rate of SS316L. Cylindrical stainless steel-316L (SS316L), which has a diameter of 8mm and a thickness of 5mm, was sterilized by immersion in ethanol then rinsed using distilled water. The coating material is made from a mixture of HA-PVA with variations in the composition of A (27: 3), B (25: 5), C (20:10) and D (15:15) (in wt%) dissolved in 70% distilled water (in wt%). HA-PVA solution was coated on SS316L using airbrush spraying method at a pressure of 3.5x10⁵ Pa, a nozzle diameter of 0.4 mm and a nozzle-sample distance of 10 cm. The test results show that the variations of the HA-PVA composition affect the hardness and the corrosion rate of SS316L. The more HA coating on the SS316L, the more it protects the SS316L substrate from corrosion. The conclusion show that the sample A with the HA-PVA composition of 27: 3 (in wt%) is found to be the best composition with a Vickers hardness of 2.43 VHN and a corrosion rate of 0.004 mm/year.

1. Introduction

Stainless steel 316L (SS316L) is a commonly used material for bone and dental implants due to its high resistance to corrosion. One of the main concerns of metal implants is the interaction with the surrounding host tissue [1]. Bone and dental implant failures occur frequently due to biological failure caused by a lack of adequate osseointegration because of poor contact between the bone and the implant material. The surface of the implant material interacts with body fluids, so the physicochemical characteristic is considered vital and it influences the survival and the long-term performance of the implant [2]. So far, SS316L surface modification has been carried out by providing heat treatment through the plasma nitriding method [3]. However, this method can only increase the wear resistance and corrosion resistance of SS316L, but cannot integrate with bone.

To increase implant integration, SS316L surface has to be modified. The modification can be done by coating it with bioactive materials that will support the growth of bone tissue on the surface of the biomaterial implant. Nano hydroxyapatite (nHA) is one of bioactive materials that is commonly used to coat metal implant surfaces. It is because nHA is osteoconductive which can stimulate the growth of osteoblasts [4]. The success of osseointegration depends on the quality, the distribution, and the
amount of bone tissue present at the implant site [5]. However, hydroxyapatite itself is brittle. It has low mechanical properties and structural instability when mixed with body fluids or blood. To overcome these weaknesses, the addition of a binder to HA is needed. One of the binders is PVA. Polyvinyl alcohol, also known as PVA, is used as a sufficient binder [6]. It has a good chemical stability, a high hydrophilicity property and the ability to form films. In addition, PVA is water soluble, biocompatible, biodegradable, and non-toxic. Moreover, it can form pores as well as forming an interface with body tissues.

Various methods of HA coating on Ti alloy substrates have been carried out including the pulsed laser deposition (PLD) method [7,8,9,10,11] and RF magnetron sputtered [12]. Both methods are expensive and high-tech coating method. In the present study, the spray coating method was used because of the simplicity of the process. Furthermore, it is cheap, flexible and efficient, thus providing a great opportunity for mass production. One of the spray coating processes in the form of airbrush spray includes atomization, evaporation, drop impact, drying processes and testing the results to determine the suitability as implant material [13]. The airbrush spraying method used in this study is a development from many researcher [6, 14, 15, 16]. It is the spraying coating process with HA-PVA coating material which will be applied to bone implants to improve microstructural and mechanical properties. The coating process is carried out by varying the composition of the HA-PVA layer. PVA serves as a binder so that HA is able to adhere to SS 316L substrates well [6].

The airbrush spraying is a multipurpose method which allows coating on substrates that have complex shapes with adequate coating thickness control [6]. This research was conducted by varying the composition of the slurry mixture on the SS316L substrate. HA-PVA coated SS316L is expected to be the material for artificial bone implants, especially in the femoral stem. This paper will examine the effect of variations in the composition of the HA-PVA coatings on the SS316L substrate in terms of its hardness and corrosion rate. Authors will also determine which one is the best composition of HA-PVA as the SS316L coating that has the potential to be used as a permanent bone implant.

2. Method

The materials used are 118-200 nm nanohydroxyapatite (nano-HA), SS316L with a diameter of 8 mm and a thickness of 5 mm, 96% alcohol, distilled water and PVA. The coating material was made from a mixture of nano-HA and PVA as a binder dissolved in distilled water and stirred for 24 hours so that it becomes homogeneous. The variations of distilled water: HA: PVA: (wt%) used are (A) 70: 27: 3; (B) 70: 25: 5; (C) 70: 20: 10; and (D) 70: 15: 15. Slurry HA: PVA, with various concentrations as mentioned above, was then coated on SS316L substrate using airbrush spraying method, as shown in Figure 1. The coating parameters include 10 cm nozzle-sample distance, 3.5 x 10^5 Pa airbrush pressure, 0.40 mm airbrush nozzle diameter with optimal total spraying time of 2s, which was selected based on a preliminary experiment (one spray) to avoid inhibition by slurry at the nozzle. Spraying was carried out 10 times in for one sample then the sample was dried at room temperature.

![Airbrush spraying method coating set-up and (b) HA-PVA coated SS316L.](image-url)
The SS316L sample, which had been coated with HA-PVA, was then tested for its hardness scale using the Microhardness Vickers Tester type G20ST (E, 230V). After that, the corrosion rate in the simulated body fluid (SBF) solution was tested using the Autolab Potentiostat (PGSTAT30). The Vickers hardness scale was obtained using equation (1)

\[ VHN = \frac{0.18544 F}{d^2} \]  

(1)

Where VHN is Vickers hardness number, F is load (kgf, 1kgf=9.8N); d is diagonal (mm, 1mm=10^{-3} m), and 1 VHN = 1.817x 10^{6} N/m^{2}. The vickers hardness test method was carried out by pressing the test object or specimen with a pyramid-shaped diamond indenter with a 4-sided base and the angle of the facing surface of 136°. The pressure by the indenter with force (F) produced a trace or indentation on the surface of the specimen, which is a diagonal line (d). Measurements were done at 3 different points in each sample. The corrosion rate was calculated from the current density of corrosion \( I_{corr} \) using Equation 2.

\[ CR = 3.27x10^{-3} \frac{I_{corr} \cdot EW}{\rho} \]  

(2)

Where CR is corrosion rate (mm/year), \( I_{corr} \) is corrosion current density (μAcm^{-2}), EW is equivalent weight of SS 316L metal and \( \rho \) is density (g/cm^{3}).

3. Results and Discussion

3.1. Vickers Hardness Test Results

The hardness test was done by using the Vickers Hardness method on HA-PVA coated SS316L samples with variations in composition. The hardness value of each sample was obtained from the average VHN value which is presented in Table 1.

| Sample | Composition Variations (wt%) (Aquadest: HA:PVA) | Vickers Hardness Number (VHN) |
|--------|---------------------------------------------|-------------------------------|
| A      | 70:27:3                                     | 2.43 ± 0.30                   |
| B      | 70:25:5                                     | 11.30 ± 0.24                  |
| C      | 70:20:10                                    | 12.30 ± 0.61                  |
| D      | 70:15:15                                    | 6.40 ± 0.19                   |

As shown in Table 1 and Figure 2, it can be seen that variation in the sample compositions has effects on the hardness characteristics of the HA-PVA coating on the SS316L substrate. In Figure 2, it can be seen that the hardness of the HA-PVA coatings have different scales. It is presumably due to the lack of homogeneity of the elements forming the sample itself and the unevenness of the HA-PVA coating. When the surface of a sample is compressed on 3 different points, the hardness scale shows a significant difference. So, this hardness result is not accurate because the 3 points of compression do not represent the entire surface of the sample. The addition of the binder ratio, namely PVA, may result in both an increase and a decrease of the coating hardness to a certain point. Hence, it will affect the results of the HA-PVA coating hardness test [17]. The hardness test result obtained in sample A shows a very small hardness scale compared to the other samples, which is 2.43 ± 0.30 HVN. This occurs because the hardness is strongly influenced by the level of homogeneity of the coating formed. The more homogeneous the coating formed, the stronger the hardness will be.

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Based on the statistical test with the Kolmogorov Smirnov normality test, all Vickers hardness data of HA-PVA compositions obtained are normal with sig values. = 0.897> α = 0.05. The homogeneity test of variance shows that all data are homogeneous with the sig = 0.054> α = 0.05.
After making sure that all groups of HA-PVA composition variations are normally distributed and homogeneous, a one-way Anova test was conducted between groups of variations in the HA-PVA composition. The probability obtained is $\text{sig} = 0.208 < \alpha = 0.05$, which indicates that there is no significant difference between groups of variations in the composition tested.

### 3.2. Corrosion Test Results

The corrosion test was carried out to determine the level of corrosion rate of HA-PVA coated SS 316L samples in SBF media. Corrosion current density ($I_{\text{corr}}$) was obtained from the results of the potential curve against logarithmic current intensity by determining the cut point of the reduction reaction Tafel line ($\eta_c$) and the oxidation reaction Tafel line ($\eta_\alpha$) on the corrosion potential line ($E_{\text{corr}}$). The corrosion test results are presented in Figure 2.

The corrosion test results, presented in Figure 2, show that the corrosion rate of the SS 316L substrate coated with HA-PVA in the SBF solution has a tendency to be smaller which can be seen in Samples A, B, and D. It means that the HA-PVA coating that covers SS316L surface is able to reduce its corrosion rate scale. SS316L without HA and PVA coated has a corrosion rate of 0.0533 mm/year. Thus, the use of SS316L as an implant material will not harm the body because it has a corrosion rate that is below the European standard, namely 0.0116 mmppy [18]. Hence, it can be said that the presence of a HA coating reduces the corrosion rate of SS316L. Based on Figure 3, it shows that the corrosion rate tends to be smaller with a greater HA composition than PVA. From Figure 2, the corrosion rate is obtained as shown in Figure 3.
Figure 3. The corrosion rates vs the variations in the HA-PVA composition. The variations of distilled water: HA : PVA : (wt%) used are (A) 70 : 27 : 3; (B) 70 : 25 : 5; (C) 70 : 20 : 10; and (D) 70 : 15 : 15

3.3 Discussion
This study aims to determine the effects of composition variations of the HA-PVA coatings on SS316L by examining the hardness scale and the corrosion rate and to determine which best composition is the best potential to be used as a permanent bone implant. The different scales of coating hardness obtained, as seen in Table 1, were due to variations in the composition of the HA-PVA. It is presumably due to the lack of homogeneity of the forming elements of the sample and the unevenness of the HA-PVA coating. Sample A has small hardness scale because the HA composition is higher than the composition of PVA. When a sample surface is compressed by taking up 3 different points, the hardness scale will show a significant difference. So, the results of the sample hardness are not accurate because the 3 points of compression on this sample do not represent the entire surface of the sample. The addition of the binder ratio, namely PVA, may result in both an increase and a decrease of the coating hardness to a certain point. Hence, it will affect the results of the HA-PVA coating hardness test [17].

HA-PVA coating has the ability to reduce the corrosion that may occur to SS316L. It means that the HA-PVA coating that covers the SS316L surface is able to reduce its corrosion rate. It is found that SS316L without HA and PVA coated has a corrosion rate of 0.05 mm / year [19]. In the present study, there are only two samples whose corrosion rates have met the requirements as implant material (Figure 4). It is because they have corrosion rate of < 0.0116 mmpy. In sample A, with the HA-PVA composition of 27: 3 (in wt%), the corrosion rate obtained was very low, namely 0.004 mmpy. Therefore, sample A is selected as the best sample with coating characteristics that are close to the standard for implants, namely a coating hardness scale of 2.43 ± 0.30 VHN and a corrosion rate of 0.004 mmpy.

The presence of the HA-PVA coating the SS316L substrate is capable of being an interface medium that can bond the implant with SS316L. HA is osteoconductive so it can trigger the growth of osteoblast cells. Moreover, PVA functions as a binder or adhesive for HA on the substrate. In addition, PVA is also biocompatible and biodegradable. Based on this research, it can be stated that the airbrush spraying method is a simple yet versatile method that is able to produce HA coating with standard quality for implant. Likewise, the use of PVA as a binder is able to attach HA to SS316L substrates better. For future researches, it is essential to develop the airbrush spraying method, especially for the design of the spray gun in order to maintain a solid frame design. By doing so, when the spraying
process is used there will be no movement of the spray gun that may consequently affect the coating results.

4. Conclusion
It can be concluded that variations in the composition of HA-PVA affect the hardness scale and the corrosion rate of SS316L. For the coatings, the bigger HA compositions, the more it will protect the substrate against corrosion. Meanwhile, the bigger PVA compositions, the stronger the hardness of the coatings. Sample A with the HA-PVA composition of 27:3 (in wt%) is found to be the best composition based on its hardness scale, 2.43±0.30 VHN, and the corrosion rate of 0.004 mm/year.

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