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Effect of electrolyte type on the morphology and crystallinity of TiO₂ nanotubes from Ti-6Al-4V anodization

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Abstract. A good biocompatibility material such as Ti-6Al-4V is needed for a dental application. However, Ti-6Al-4V has no antibacterial properties. Therefore Ti-6Al-4V is modified using anodizing methods to improve its anti-bacterial properties. One of the most influential factors in the anodizing process is the type of electrolyte solution. The influence of electrolyte solution based on glycerol and ethylene glycol to morphology and crystallinity of TiO₂ nanotubes is studied. Smoothing and chemical polishing was performed against the Ti-4Al-6V plate. Then, the anodizing process for each plate in glycerol and ethylene glycol solution was done for 2 hours and 50 volts. Calcination was carried out for 3 hours at a temperature 500°C. FESEM-EDX and XRD were employed to analyze the surface morphology and crystallinity of TiO₂ nanotubes. Viscosity of the electrolyte solution influenced surface morphology. Calcination process influenced crystallinity of TiO₂ nanotubes. The average tube diameter and thickness from glycerol electrolyte solution was 135.45 nm and 26.27 nm, while ethylene glycol was 68.52 nm and 35.62 nm respectively. The size of anatase crystal was 34.95 nm for glycerol and 44.77 nm for ethylene glycol.

1. Introduction

Many problems about teeth have been widely prevalent in society. To overcome this problem, the dental implantation technology is developed with the aim to replace broken or missing teeth [1]. In fact, the technology is quite high, but sometimes, it can cause some problems that occur after the installation process. One of which is *Peri-implantitis* which cause bone erosion around the implant, so that it can cause implant failure [2]. *Peri-implantitis* is caused by the formation of bacterial biofilms on the surface of implants without antibacterial activity. The Ti-6Al-4V alloy is a titanium-based dental implant material that is widely used in orthopedics and dentistry because of its high biocompatibility, low density, high mechanical resistance, high chemical inertness and toxicity and high corrosion resistance [3-7].

Surface modification methods are so important to improve the biocompatibility and corrosion resistance to get ideal surface properties for implant application [8]. Modifications of Ti-6Al-4V can be performed to enhance antibacterial properties to prevent *Peri-implantitis* formation. The modification is done by anodizing method aimed at growing TiO₂ nanotubes array so that photocatalytic activity to disinfect bacteria can occur effectively. One of the important factors

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affecting the anodized form of nanotubes is the electrolyte solution used during the nanotubes synthesis.

In this study, nanotubes synthesis was performed using electrolyte solution of ethylene glycol and glycerol to compare its surface morphology and crystallinity. The previous study investigated that the length and diameter of the tube formed were influenced by the concentration of fluoride in the electrolyte solution [9]. Ethylene glycol is an organic solution with high viscosity has a great possibility to get TiO₂ nanotubes with smooth and homogeneous walls [10, 11]. The use of ethylene glycol electrolyte solution yielded a more uniform diameter of nanotubes, finer nanotubes wall, and better photocatalytic degradation in Methyl Orange (MO) compared to glycerol [12]. However, this study has not yet led to the application of dental implants for anti-bacterial properties. The use of this type of organic electrolyte solution can produce different forms of nanotubes, so further research is necessary to determine the effect of surface morphology produced against anti-bacterial properties by using Ti-6Al-4V. The obtained result is expected to be different from the previous research and can be used for dental implant application.

2. Experimental

2.1. Preparation of TiO₂ nanotubes

The Ti-6Al-4V plate was cut to the size of 4 cm x 1 cm. Then, smoothed using 1000cc abrasive paper. The plate was washed thoroughly with soap and then the chemical polishing method was performed using the ratio of HNO₃: HF: H₂O = 3: 1: 6. The anodizing process was carried out with a variation of an electrolyte solution of ethylene glycol with a composition of 0.5% NH₄F and 3% water content and glycerol with a composition of 0.5% NH₄F and 25% water content. The electrolyte solution was mixed using a magnetic stirrer. The electrodes used during the anodizing process were Pt electrodes as cathodes and Ti-6Al-4V materials as anodes. The anodizing process was carried out on a beaker glass with an electrolyte amount of 60 ml. The constant process voltage was kept at 50 V for 2 hours at room temperature. This process was also done while stirred using a magnetic stirrer. After these processes had been completed, the material was rinsed with aquadest and then dried with a hair dryer. Then the calcination process was performed at 500^o C for 3 hours. All procedures were the same for both variations of the electrolyte solution.

2.2. Characterization of TiO₂ nanotubes

The surface morphological structure and elemental of the synthesized TiO₂ nanotubes can be seen with the characterization using Field Emission Scanning Electron Microscopy/Energy Dispersive X-ray (FESEM-EDX JEOL Type JIB 4610F) at 15 kV with magnification up to 100000 times. The length of the tube formed can also be seen through the measurement of its cross section., X-Ray Diffraction (XRD) was used to determine the crystal structure and composition of the material. The XRD patterns were obtained using PANalytical-Empyrean with Cu anode tube ($\lambda = 0.15406$ nm) runs at voltage 40 kV and current 30 mA, with the range of 2θ angle values 10^o to 80^o. The crystallite size of the specimen was estimated from FWHM (full-width at half-maximum) of XRD by Scherrer equation.

3. Result and discussion

It is necessary to know the morphology and crystal structure of TiO₂ nanotubes because it will certainly affect the photocatalytic performance and the stability of the materials when it used or medical application, such as dental implants. The result of FESEM analysis for TiO₂ anodized by electrolyte solution glycerol and ethylene glycol with the same calcination process conditions are shown in figure 1.

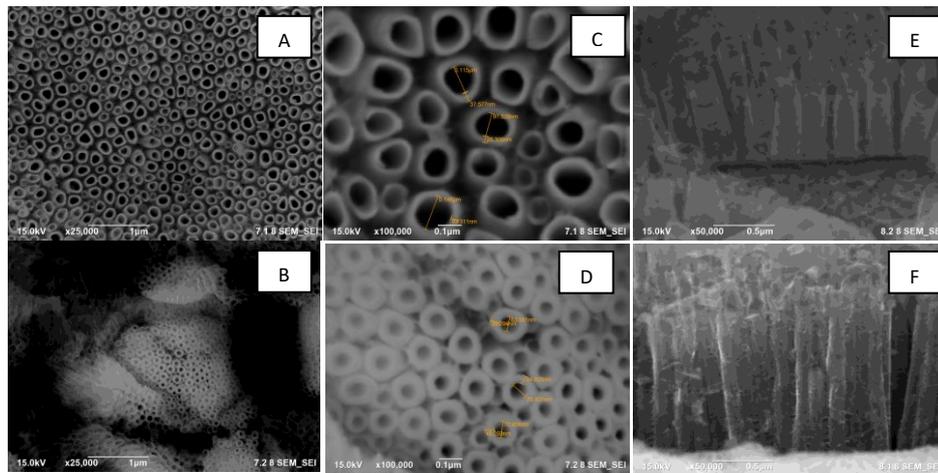


Figure 1. FESEM images of TiO_2 nanotubes from electrolyte solution glycerol (left) and ethylene glycol (right) with different magnification rates: (A and B) 25000x, (C and D) 100000x, (E and F) cross-sectional.

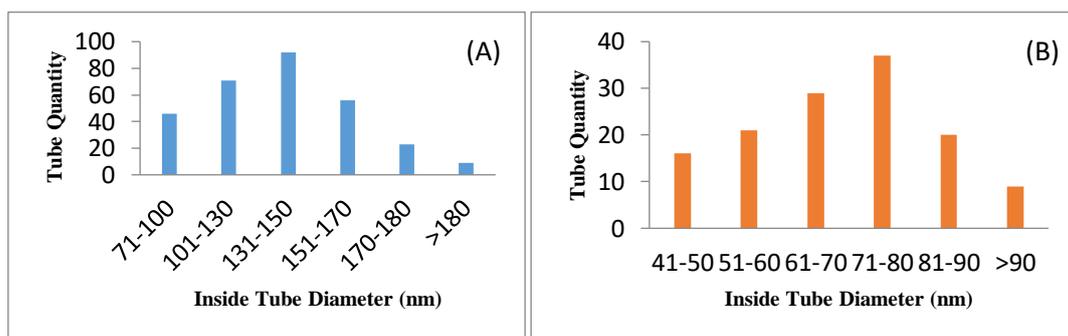


Figure 2. Graphic of diameter size from (A) Glycerol and (B) Ethylene Glycol.

Table 1. Diameter and thickness size of TiO_2 nanotubes.

Electrolyte solution	Inside diameter tube average	Thickness wall average
Glycerol	135.45 nm	26.27 nm
Ethylene Glycol	68.52 nm	35.62 nm

FESEM with 25000x magnification was used for estimating the tube diameter and the thickness of TiO_2 . It shows various nanotubes dimensions. Thus, the estimated tube average diameter and thickness is more representative. In glycerol, the structure of TiO_2 nanotubes formed has a large diameter in tube size. While on ethylene glycol, the TiO_2 structure has a tube diameter size smaller than glycerol. In table 1, the average diameter of Ti-6Al-4V nanotubes using glycerol electrolyte was 135.45 nm. While using ethylene glycol, the average diameter of Ti-6Al-4V nanotubes was 68.52 nm. But when viewed from the thickness of the formed tube, the synthesized TiO_2 nanotubes using ethylene glycol electrolyte solution have greater thickness compared to using glycerol. Its value from electrolyte glycerol and ethylene glycol were 26.27 nm and 35.62 respectively. The thickness is affected by the water composition in the electrolyte solution where a small amount of water will increase TiO_2 nanotubes thickness [13]. The photocatalytic performance will be better if the size of the photocatalyst is smaller because it will increase the active surface area to react.

The formed tube shape from TiO₂nanotubes can be seen from the cross-sectional FESEM analysis. In TiO₂nanotubes using ethylene glycol, tube forms look longer compared to those using glycerol. The structure also looks ruder than the more refined tube shape created using glycerol. The difference in length between the two caused by the viscosity of the two solutions. In the viscosity measurement results, the ethylene glycol electrolyte solution has a lower viscosity value than glycerol, 15.1 and 35.2 CSt, respectively. The lower viscosity electrolyte solution permits the dissolution rate of F⁻ ions during the anodizing process. It can grind down to the lower part of TiO₂ so that the tube length produced on TiO₂ using ethylene glycol is longer.

Table 2. Elemental composition of modified Ti-6Al-4V.

Elements	Elemental Composition (% wt)	
	Glycerol	Ethylene Glycol
Ti	60.9	51.9
O	31.9	41.6
Al	3.8	4.3
V	3.4	2.2

Characterization using Energy Dispersive X-Ray produces data as in table 2. It shows that Ti on Ti-6Al-4V successfully oxidized so that it can be said that TiO₂nanotubes successfully formed. But in each electrolyte solution, there is a difference of %wt from each element. It is influenced by the height, diameter and thickness of the tubes produced using glycerol and ethylene glycol electrolyte solutions. The result of previous FESEM analysis seen from the cross-section shows that tube height formed from glycerol electrolyte solution is shorter than ethylene glycol. It causes the EDX current into the inside of the tube to the alloy portion of Ti-6Al-4V. Thus, the % wt of the alloy of glycerol electrolyte solution is greater than using ethylene glycol.

The EDX analysis also shows that Al and V are also oxidized to form thin surfaces of Al₂O₃ and V₂O₅. The presence of these two oxide compounds improves the stability of the Ti-6Al-4V material. When viewed from the results of EDX analysis, TiO₂ nanotubes formed either by using electrolyte solution of ethylene glycol or glycerol can be utilized for dental implant applications [14].

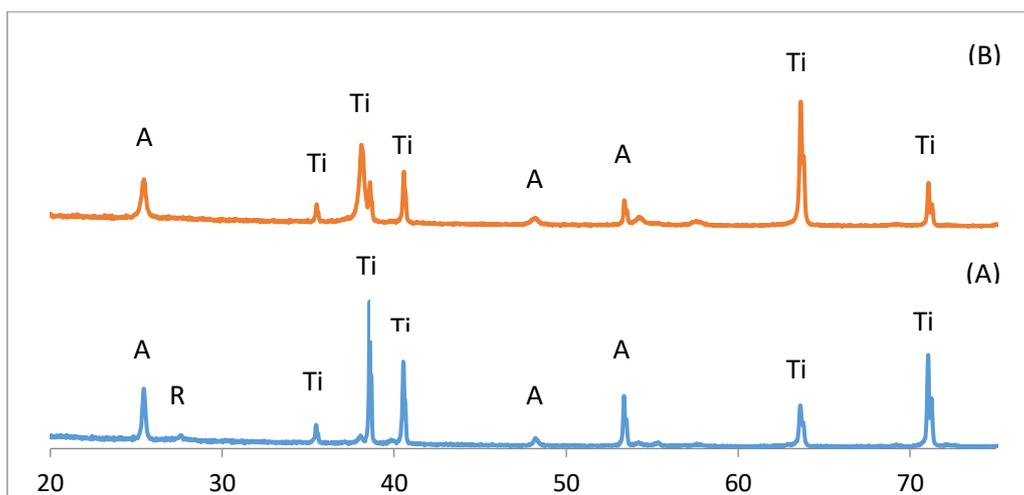


Figure 3. The XRD patterns of TiO₂nanotubes prepared from electrolyte solution (A) ethylene glycol, (B) glycerol.

Figure 3 shows that the TiO₂ crystal structure formed through reaction with glycerol electrolyte solution is entirely anatase. The anatase peaks are seen at an angle of $2\theta = 25.3^\circ, 48.0^\circ$ and 55.1° [15].

No crystal rutile structures are formed. The new rutile crystalline structure is formed at a calcination temperature of 600°C with a calcination time of 3 hours when using a glycerol electrolyte solution at the anodizing process [16], using an ethylene glycol electrolyte solution wherein the same calcination time as glycerol is 500° C for 3 hours, the rutile crystals begin to form even slightly. The rutile peak is at an angle of $2\theta = 27.45^\circ$ [17].

Tabel 3. Crystallite sizes of modified Ti-6Al-4V.

Crystal	Crystallite Size (nm)	
	Glycerol	Ethylene glycol
Anatase	34.95	44.77
Rutile	-	152.19

The crystallite size can be calculated by Scherrer equation[18]:

$$t = \frac{0,9\lambda}{B \cos \theta} \quad (1)$$

Where t is the average crystal size (nm), λ is the X-ray's wavelength, B is the width of the half-maximum peak (FWHM in radian unit), and θ is diffraction angle in degree (°). XRD data calculation can be seen in table 3. Anatase crystals formed on TiO₂ nanotubes use glycerol electrolyte measuring 34.95 nm while with ethylene glycol of 44.77 nm and rutile of 152.19 nm. Although by using ethylene glycol the formed anatase crystalline structure is larger, The difference between both is not too significant.

The difference in the formation of this rutile crystalline structure using glycerol and ethylene glycol are present in the crystallization process of TiO₂ nanotubes at the time of calcination. The anatase crystals of TiO₂ is formed from amorphous crystals while the rutile crystals are formed from anatase. Rutile crystals begin to form at high calcination temperatures where the amorphous crystals are no longer present. In the XRD patterns, it can be seen that by using glycerol electrolyte solution, the anatase crystals intensity is less than using ethylene glycol. It occurs because the amorphous crystals on TiO₂ nanotubes using glycerol still exist in them. As with the use of ethylene glycol electrolyte solution, it is seen that the intensity of more and more crystalline anatase crystals and rutile crystals has been formed even with little intensity. It is because the amorphous crystals of TiO₂ nanotubes are depleted to form a rutile crystal structure.

With the same calcination process, the rutile crystalline structure is formed more rapidly in TiO₂ using an electrolyte solution ethylene glycol than glycerol. It is one of them influenced by the boiling point of both types of the electrolyte solution. Glycerol has a higher boiling point than ethylene glycol, 290° C and 197.3° C, respectively[19]. When the anodizing process is completed, the electrolyte solution of glycerol and ethylene glycol on each plate is indicated to be still attached to its TiO₂ surface. At the time of the calcination process, the heating first evaporates the electrolyte solution still attached to TiO₂. Because of the higher boiling point of glycerol, the heating will first vaporize the electrolyte that is still attached to TiO₂ so that the crystallization process becomes longer. It is why the rutile crystal structure of the ethylene glycol electrolyte is formed first with the same temperature and the length of the calcination process.

Previous research has been reported that the rutile crystal structure begins to form at 580° C for 2 hours [20]. But in other studies, it was found that the rutile crystal structure began to form at a temperature of calcination of 600° C for 2 hours [21]. Of the two studies mentioned, Rutile crystals began to form at a temperature of calcination above 500° C for 2 hours. At the calcination temperature of 450° C for 3 hours, the rutile crystal structure was not formed [22]. In this study using a 500° C calcination temperature for 3 hours where the calcination time is longer than the previous study has been obtained rutile crystal structure of TiO₂ nanotubes.

4. Conclusion

TiO₂ nanotubes were synthesized by anodization method from two type electrolyte solutions which produced significant differences in its morphological structure. The morphological differences are caused by the difference in the viscosity value of the two solutions. The rate of F⁻ ion dissolution during the anodizing process affects tube size, thickness, and length of TiO₂ nanotubes. The average tube diameter and thickness that are resulting from electrolyte solution glycerol was 135.45 nm and 26.27 nm, while ethylene glycol was 68.52 nm and 35.62 nm respectively. During the calcination process, the combination of temperature, time, and the type electrolyte solution will affect the form of the produced TiO₂ crystals. Rutile is not formed when using glycerol electrolyte. The size of the anatase crystals formed by using glycerol and ethylene glycol electrolytes was 34.95 nm and 44.77 nm. While the size of the rutile crystals formed using electrolyte ethylene glycol amounted to 152.19 nm

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