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# Influences of the calcination temperature and polymethyl methacrylate templates to characteristic pore membrane of bioceramic titanium dioxide

Jan Ady<sup>1\*</sup>, Eka Viandari<sup>2</sup>, and Dewi W Hasanah<sup>2</sup>

<sup>1</sup>Department of Physics, Faculty of Science and Technology, Airlangga University, Surabaya, Indonesia

<sup>2</sup> Department of Biomedical Engineering, Faculty of Science and Technology, Airlangga University, Surabaya, Indonesia

\*Corresponding email address: jan-a@fst.unair.ac.id

Abstract. The synthesis of the bioceramics titanium dioxide on its template by polymethyl methacrylate to be a sample with forming TiO<sub>2</sub>/PMMA was made with sol-gel process, and its pore membrane characteristics has also been studied. Different calcination temperatures  $500^{9}$ C,  $550^{\circ}$ C, and  $600^{\circ}$ C were given to sample for 17 hours. This purpose themselves was to fill TiO<sub>2</sub> fissures with PMMA on different concentrations of 0.0, 2.0 wt%, 3.0 wt%, 4.0 wt%. Template leaching technique was used to remove PMMA from samples, and it was then sequentially found of the pore size of the membrane in approximate ranges (1900 nm - 2000 nm), (860.5 nm - 1669 nm), (312.8 nm-382.5 nm), and (136.1 nm - 269.7 nm). SEM test using and fourth it has average thickness in about 6.7 nm with Ellipsometer measurement. The percentage values of titanium and oxygen atoms are found by SEM-EDX from 3.03 at.% up to 66.81 at.% and there is amount 99,99% of the sample in anatase phase forming at 550 0C with angle of diffraction is 25.410 and it was prepared by XRD measurement.

#### 1. Introduction

The bioceramics titanium oxide (titania) as a matrix-forming compound to be a bioceramicbiocompositetitania hydroxyapatite (TiO<sub>2</sub>/HA) or its bioglass has been synthesized by means of solgel process to many needs in clinical applications especially for humans. Its characteristics were also studied, for instance, its role in the human body in playing the most important role in regenerating osteoblast bone [1]. This is similar to its titanium dioxide as a matrix-fiber of bioceramicbiocomposite which is qualified properties such as biomaterials bioinert, bioresorbable, and bioactive [2]. Titanium dioxide is also non-toxic, and it has photo catalytic effect reactions with UV light which makes it safe to use for in membrane bio composite [3].

Synthesis titanium dioxide can be prepared by means of the precursor matrix solution into the tangible gelatine known as sol-gel process [4]. In the synthesis, it does not require high temperature conditions, or in other words, it could be performed at room temperature. The crystalline grains produced by sol-gel always produce units to nanometer.

The membrane is portrayed as both selective and semipermeable thin layer types lying between of the concentrate or permeate phase [5]. Substance of the concentrate would be retained by its membrane because the grains size is too large than the size of the membrane pore. On the contrary, substance of the permeate phase is too small which makes it able to go through the membrane.

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Characteristics of the membrane poresize mostly depend on the sample arrangement on its substrate such as titanium dioxide on the polymethyl methacrylate (PMMA) substrate which becomes  $TiO_2/PMMA$ . It aims to discover the characteristics of pore membrane such as macroporous (pore size > 50 nm), mesoporous (2 nm - 50 nm), and microporous (pore size < 2 nm) [6].

Influences of the calcination temperature given to the sample have been studied in order to find the characteristics of crystalline phases of titanium dioxide for 500  $^{\circ}$ C, 550  $^{\circ}$ C, and 600  $^{\circ}$ C including its phases such titania-rutile, titania-anatase, and titania-brookite [7]. From the third phase, only titania-rutile and titania-anatase were stable with their tetragonal structure, and their lattice constant value is different from one another. Contrary tobrookite phase, it is an unstable structure, and the characteristics are usual. The differences of both of titania-rutile and titania-anatase are in their octahedron and octahedral atomics arrangement for each oxygen or titanium cations in its bonding form Ti – O – Ti and with triangle form in about 900, 1200, and 1800 [8].

The purpose of this study is to demonstrate the synthesis of titania bioceramic by means of sol-gel process and characterize the pore membrane under the influences of the calcination temperature from its crystalline structure phases in titania-rutile (500  $^{\circ}$ C), titania-anatase (550  $^{\circ}$ C), titania-brookite (600  $^{\circ}$ C). Then it was tobe added to different PMMA in order to make a template membrane such as in the form of TiO<sub>2</sub> / PMMA.

#### 2. Research method

#### 2.1. Equipment and materials

The apparatus used in measurement in this study included scanning electron microscope (SEM) and SEM-EDX such as Ellipsometer and X-ray diffraction (XRD). The tools used included Furnance, Beaker glass, pipette, and magnetic stirrer. The materials used included titanium tetraisopropoxide with98% (Sigma-Aldrich;St.Louis,MO,USA), Poly Methyl methacrylate (PMMA), glacial acetic acid, acetone, ethanol 96%, glass substrate preparations, and chloride acid (HCL) 37%.

#### 2.2. Preparation Sol – Gel $TiO_2$ (Titania) and PMMA Template

The prior glass should be cleaned using ethanol, and it was cut into small pieces with 1cm x 1cm in dimension. Next, it was dipped into PMMA solution and left to dry for PMMA coating on a glass to be a template for the sample.

The synthesis of titania with sol-gel process has been described in [4]. Prior to that is synthesis of sol-titania by mixing ethanol 225 ml and 15 ml of acetic acid for four minutes using a stirrer, then it was added with 6.0 ml of  $Ti(OH)_4$  or tetraisopropoxyde (TTIP). Next, 0.4 ml of HCL was added, and it was stirred for two hours. After that, the mixture was shaken for 24 hours and held up to 60 hours. From those processes was found precipitation of crystalline in the form of  $TiO_2$ . Steps of the chemical reactions are portrayed as below:

$$Ti(OH)_{4} \rightarrow -Ti-O-Ti- + H_{2}O$$
 (1)

$$-Ti - O - Ti - \rightarrow TiO_2 + 2H_2O$$
 (2)

Thermal treatment was given to remove titania from the gelatin, and it was followed by equation (2).

## 2.3. Preparation of the synthesis of $TiO_2$ (Titania) membrane

PMMA template was previously prepared with immersion process for one hour in order to create soltitania. Next, it was dried at room temperature  $25^{\circ}$ C for three hours. After that, titania was interstitial to the PMMA template and calcinated at different temperatures of 500 °C, 550 °C, and 600 °C for four hours to remove PMMA template from previous sample in the form of TiO<sub>2</sub>/PMMA. Subsequently, TiO<sub>2</sub>membrane was found with desired pore size.

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#### 3. Results and discussion

The pore membrane of titania was molded using template leaching technique with PMMA as a polymer, a primary component to form pore membrane. Titania is created with sol-gel process with titanium-tetraisopropoxyde (TTiP) precursor, a solution which begsn to be colloidal suspension particles through its hydrolysis and its condensation reactions [9], when cast by alcohol. The influences of calcination temperatures could be seen via XRD test for each temperature of 500  $^{\circ}$ C, 550  $^{\circ}$ C, 600 $^{\circ}$ C as shown in figure 1. 88.9% of anatase-titania was resulted at 500  $^{\circ}$ C, and 99.9% of it was resulted at 550  $^{\circ}$ C as shown in Figure 1(a) and (b). Meanwhile, rutile-titania was resulted at 600  $^{\circ}$ C with 44.15% of its anatase phase and then 55.85% in its rutile phase as shown in Figure 1.(c) [10]. The phases of the crystalline forming mostly depended on the photochatalysis which were also part of calcination process.



Figure 1. XRD test results of the samples for each temperature calcination are shown (a). Amount of anatase TiO<sub>2</sub>-88.9% at 500<sup>o</sup>C, (b). amount of anatase TiO<sub>2</sub>-99.9% at 550<sup>o</sup>C, and (c). amount of anatase TiO<sub>2</sub>-44.15% and amount of Rutile TiO<sub>2</sub>-55.85% at 600<sup>o</sup>C.

The presence of Titanium (Ti) and Oxygen (O) in its membrane is evidenced by Energy Dispersive X-Ray Spectroscopy (EDX), and it was molded on a glass in order to create a thin layer. Results of this test are shown in Table 1 and the Figure 2.

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Table 1. The elements (At. 76) and weight (Wt. 76) of the			
sample indicated by Energy Dispersive X-ray (EDX) test			
Wt. (%)	At. (%)		
53.12	66.81		
21 39	18 72		
21.37	10.72		
06.98	05.78		
11.29	05.67		
07.21	03.03		
	53.12   21.39   06.98   11.29   07.21		

Table 1. The elements (At	.%) and weigh	t (Wt.%) of the		
sample indicated by Energy Dispersive X-ray (EDX) test				
Types of Component	$W_{t}$ (%)	$\Delta t (0/2)$		

The forming process of membrane pores using PMMA template is based on the effect of temperature on the PMMA structure. When subjected to heat with some temperatures like in this study, PMMA shrank which eventually made  $TiO_2$  particles agglomerate each other. In Figure 3(a), (b), (c), and (d) is shown SEM image showing a lot of pores whose emergence was influenced by PMMA.



Figure 2. The weight (Wt.%) and Atomic (Wt.%) of elements or compounds in its membrane form are evidenced by Energy Dispersive X-Ray Spectroscopy (EDX) test

Membrane such as in Sample1 (S1) as shown in Figure 3(a) is without PMMA, and it cracked and fractured with broad spaces. The cracks occurred because the sample's solution contained high solvent [11]. Moreover, it did not interact with other elements or compounds which evaporated, hence huge cracks[12]. For sample 2(S2), sample 3(S3), and sample 4 (S4) as shown in Figure 3(b), (c), and (d) are membranes of titania into which PPMA was added using sol-gel process. However, they differed each other.



**Figure 3.** SEM image of TiO<sub>2</sub> Membrane Morphology with various PMMA for enlargement 10.000x (a). S1 Without PMMA, (b). S2 PMMA 2.0wt%, (c). S3 PMMA 3.0wt%, (d). S4 PMMA 4.0wt%

The pores formed were smaller, especially in Figure 3 (c) and (d) because the PMMA shrank after calcination with different temperatures. It was in membrane pore size, about (1900nm - 2000 nm), (860.5nm - 1669nm), (312.8nm-382.5nm), (136.1nm - 269.7nm). Additionally, the average thickness was 6.7nm with cracks or pinholes as measured using SEM test and ELLIPSOMETER. That is shown in Figure 4.



Figure 4. Pore size of TiO<sub>2</sub> Membrane for samples: (S1) without PMMA, (S2) PMMA 2.0wt%, (S3) PMMA 3.0wt%, and (S4) PMMA 4.0wt%. Its thickness was 6.7 nm as measured using ELLIPSOMETER

### 4. Conclusion

Bioceramic titania in  $TiO_2/PMMA$  formwith the sol-gel process was studied through its pore membrane characteristics, where the influence of calcination temperature enabled titania to form became perfectly intonanometer size. The pore size of titania membrane decreased along with the increase of PMMA concentrations in the samples. Furthermore, its optimum form with 4.0 Wt% of PMMA with anatase-titania phase at 550<sup>o</sup>C.

## References

- [1] Larry L 1991 Bioeramics: From concept to clinic J. Am. Ceram. Sos. 74 (7) 487-510
- [2] RamiresPA, Romito A, Cosentino F, Milella E 2001The influence of titania/hydroxyapatite composite coatings on in vitro osteoblasts behaviour *Biomaterials* **22** 146-1474
- [3] Gjevori A 2010 Phase Formation of Photoactive TiO<sub>2</sub> Thin Films by Metal plasma Immersion Ion Implantation and Deposition (Faculty of Natural Sciences University of Tyrana)
- [4] Septina W 2007 Sintesa Nanokristal Mesopori TiO<sub>2</sub> dengan Metoda Sol-gel (Unpublished Thesis Bachelor of Physics ITB)
- [5] Pinem J A and Angela R 2011 Sintesis Dan Karakterisasi Membran Hibrid PMMA / TEOT : Pengaruh Konsentrasi Polimer: Proc. Seminar Nasional Teknik Kimia Kejuangan ISSN 1693 – 4393.
- [6] Gupta KK, JassalM, Agrawal AK 2008 Sol-gel Derived Titanium Finishing of Cotton Fabric For Self Cleaning *Indian J. of Fibre & Textile Research* **33**pp 4430450
- [7] Afrozi AS 2010 Sintesis dan Karakterisasi Katalis Nanokomposit Berbasis Titania Untuk Produksi Hidrogen Dari Gliserol Dan Air(Unpublished Thesis Bachelor of Chemistry Engineering University of Indonesia)
- [8] Setiawati T, Amalia I S, Wisnu A A 2006 Sintesis Lapisan Tipis TiO<sub>2</sub> Dan Analisis Sifat Fotokatalisnya J. Sains Materi Indonesia pp 141 – 146 ISSN : 1411-1098
- [9] Septina W 2007 Sintesa Nanokristal Mesopori TiO<sub>2</sub> dengan Metoda Sol-gel(Unpublished ThesisBachelor of Physics Engineering ITB)
- [10] Byranvand M M, Kharat N A, Fatholahi L, Beiranvand L M 2013 Review on Synthesis of Nano-TiO<sub>2</sub> Via Different Methods J. of Nanostructure JNS 3 1-9
- [11] Hyodo T, Sasahara K, Shimizu, Y, Egashira, M 2005 Preparation of Macroporous SnO<sub>2</sub> films using PMMA Microspheres and Their Sensing Properties to NOx and H<sub>2</sub> J. of Sensor and Actuators B 106 pp 580-590
- [12] Zhang H, DongF, Fang S, Ye C. Wang M, Cheng H, Han Z, Zhai S 2012 Fabrication of Macroporous Titanium Dioxide Film Using PMMA Microspheres as Template J. of Colloid and Interface Science 386