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EFFECT OF BIODEGRADABLE PLA ON HYDROXYAPATITE COATING TO IMPROVE ADHESION PROPERTIES ON Cr-Co-Mo ALLOY

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ABSTRACT

Biomedical implants of Cobalt-Chromium-Molybdenum (Co-Cr-Mo) alloys have been reported difficult to bond directly on bone when inserted in human body. In order to improve this situation several attempts have been made including coating the implants with a bioactive layer such as hydroxyapatite (HA). However, major concerns arise when massive micro crack surface, delamination and low adhesion strength of HA coatings occurred which later caused the harmful releases of metal ions. The objectives of this research is to improve the adhesion strength of HA and produce crack free surface coating by adding biodegradable polylactic acid (PLA) into HA slurry as well as to enhance biocompatibility of Co-Cr-Mo alloy for long term used. In this research, the optimum HA slurry was determined by mixing different weight of PLA (1, 2 and 3 gram) before deposited on Co-Cr-Mo substrates using dip coating machine. Constant parameters for dip coating process were applied to all samples condition. Micro hardness test was done to measure the adhesion strength of the PLA/HA coating as well as to evaluate the effects of adding PLA at different weight. The corrosion resistance performance of the coated and uncoated Co-Cr-Mo substrates were investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The results also proved that the mixture of 2g PLA with 1g HA into 20ml chloroform able to eliminate micro cracks with acceptable coating thickness (~10µm). It is concluded that by adding a suitable amount of PLA into HA slurry able to gain positive effect in terms of increment of the adhesion strength of HA coating as well as bioactivity performance.

Keywords: Biocompatibility, Co-Cr-Mo alloy, PLA/HA coating, adhesion strength

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ABSTRAK

Bioperubatan implan Kobalt-Kromium-Molibdenum (Co-Cr-Mo) aloi telah dilaporkan sukar mewujudkan ikatan secara langsung dengan tulang apabila dimasukkan ke dalam badan manusia. Oleh itu, untuk meningkatkan situasi ini beberapa usaha telah dijalankan termasuk menyalut implan dengan lapisan bioaktif seperti hidroksiapatit (HA). Walaubagaimanapun, masalah utama timbul apabila berlakunya rekahan mikro yang besar di permukaan, pengelupasan dan kelemahan lekatan salutan HA yang menyebabkan terjadinya pembebasan logam ion berbahaya. Objektif kajian ini adalah untuk meningkatkan kekuatan lekatan HA serta menghasilkan permukaan salutan yang bebas rekahan dengan menambah biomudahlarut asid poli laktik (PLA) ke dalam larutan HA sekaligus mempertingkatkan biokompatibiliti Co-Cr-Mo aloi. Dalam kajian ini juga, larutan HA yang optimum dikenalpasti menggunakan percampuran pelbagai berat PLA (1, 2 dan 3 gram) sebelum salutan ke atas substrat Co-Cr-Mo dilakukan menggunakan mesin salutan celup. Parameter yang sama untuk proses salutan celup digunakan untuk semua sampel. Ujian kekerasan mikro juga dijalankan bagi mengukur kekuatan lekatan salutan PLA/HA di samping menganalisis kesan penambahan PLA. Prestasi rintangan kakisan ke atas sampel salutan dan sampel tanpa salutan substrat Co-Cr-Mo dinilai menggunakan polarisasi potentiodinamik dan spektroskopi impedans elektrokimia (EIS). Keputusan membuktikan campuran 2g PLA dan 1g HA ke dalam 20ml chloroform mampu menghilangkan rekahan mikro dengan ketebalan salutan yang boleh diterima (~10µm). Kesimpulannya, dengan penambahan PLA yang sesuai ke dalam larutan HA dapat menghasilkan kesan positif dari segi peningkatan kekuatan lekatan salutan HA dan juga prestasi biokompatibiliti.

Katakunci: Biokompatibiliti, Co-Cr-Mo aloi, PLA/HA salutan, kekuatan lekatan

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

It is known that Co-Cr-Mo alloy have been widely used in orthopaedic implants due to their high mechanical resistance combined with good corrosion properties in body fluids [1]. However, once implanted and exposed to the aggressive body environment, Co-Cr-Mo alloy tends to corrode over time and starts releasing harmful metal ions (Co, Cr, Mo) into the body fluids (serum, urine and blood). As time goes, the level of metal ions may become clinically significant resulting in implant failure, osteolysis, and allergic reactions [2]. The toxicity of metal ions release and abrasion of wear particles from the orthopaedic implants are well documented [2-5]. The accumulation of wear particles and dissolved metal ions in the body can cause adverse clinical responses which affect the stability of the implant [6, 7]. This phenomenon can result in bioactivity performance of Co-Cr-Mo alloy becomes low. In order to overcome these problems, hydroxyapatite (HA) coatings can be introduced onto the metal substrate surface to modify their features and surface properties for improving the implant reactions in the host body [4, 5, 8]. However, it has been reported that HA coating on metal implants using sol-gel dip coating method often results in severe cracks and delamination which eventually lead to coating failure [6]. This phenomenon occurs due to poor adhesion strength between HA and the underlying metal substrate [9, 10] and the low cohesive strength of the coated material itself [11]. It is also noted that the poor mechanical properties of HA such as brittleness and toughness have restrict it's used in load bearing applications [12]. Many efforts have been investigated to lessen the above issues including adding biodegradable polymers to enhance the adhesive metal-ceramic (HA) bonding and coating integrity [9]. Although the results showed promising in improving adhesion strength on other metallic

biomaterials, research on Co-Cr-Mo material is somehow still limited especially involving the addition of biodegradable polymers such as polylactic acid (PLA) into HA slurry. There is also lack of research studies in understanding the behaviour of the PLA/HA coating on Co-Cr-Mo in the body fluid and their responses to the cell growth.

1.2 PROBLEM STATEMENT

Despite the many advantages of HA coating, poor adhesion strength between HA and the underlying substrate [10, 11, 13] and the low cohesive strength of the coated material [9] are still major issues which remains unresolved. These issues often results in severe cracks and delamination of HA from the substrates, which would eventually lead to implant failure [14, 15]. Furthermore, high sintering temperatures used during heat treatment also lead to some crucial issues which reduce the biocompatibility performances of both coating material and the metallic implant [13, 16]. In addition, the difference between the thermal expansion coefficients of the coating material and metallic substrate also result in the formation of micro cracks during heating and cooling. Therefore, in order to overcome these issues, many types of polymeric binders have been used to act as reinforcement element into coating materials to provide good adhesion on the substrate. Although many successful report have been claimed by other researchers, the selection of polymer types as a binding agent still need to be reviewed to ensure the short- and long term performance of the coated surface especially on Co-Cr-Mo alloy. In this research, poly-lactic acid (PLA) is chosen as a binder and its details will be discussed in the next chapter. Based on extensive literature studies, this is the first study ever described using sol-gel technique for coating PLA/HA on Co-Cr-Mo alloy.

1.3 OBJECTIVES

i. To optimize the slurry preparation using different amount of PLA and HA before dip coating process.
ii. To evaluate the surface characterization and performances of PLA/HA coating in terms of adhesion strength and micro Vickers hardness.

iii. To study the anti-corrosion properties of the PLA/HA coated on Co-Cr-Mo alloy substrate.

1.4 SCOPE OF STUDY

The research was conducted in the following limits:

i. Cobalt-Chromium-Molybdenum (Co-Cr-Mo) alloy was used as the substrate material.
ii. PLA/HA coating was deposited on the samples using HTWL-01 Desktop Dip Coater (MTI Cooperation, USA) at room temperature.
iii. The quality and surface morphology of PLA/HA coating were examined using 3D measuring laser microscope and scanning electron microscopy (SEM, JEOL JSM-6390 LV).
iv. Potentiodynamic polarization test was carried out in SBF solution at 37 °C using a potentionstat/galvanostat (VersaSTAT 3, Priceton Applied Research) to determine the corrosion resistance of the PLA/HA coating.
v. Micro hardness of PLA/HA coating on Co-Cr-Mo alloy was measured using Vickers Microhardness tester machine with constant load of 5N load and being intended for 10 seconds.

1.5 PROJECT FLOWCHART

The overall project flow was described in Figure 1.1 below.

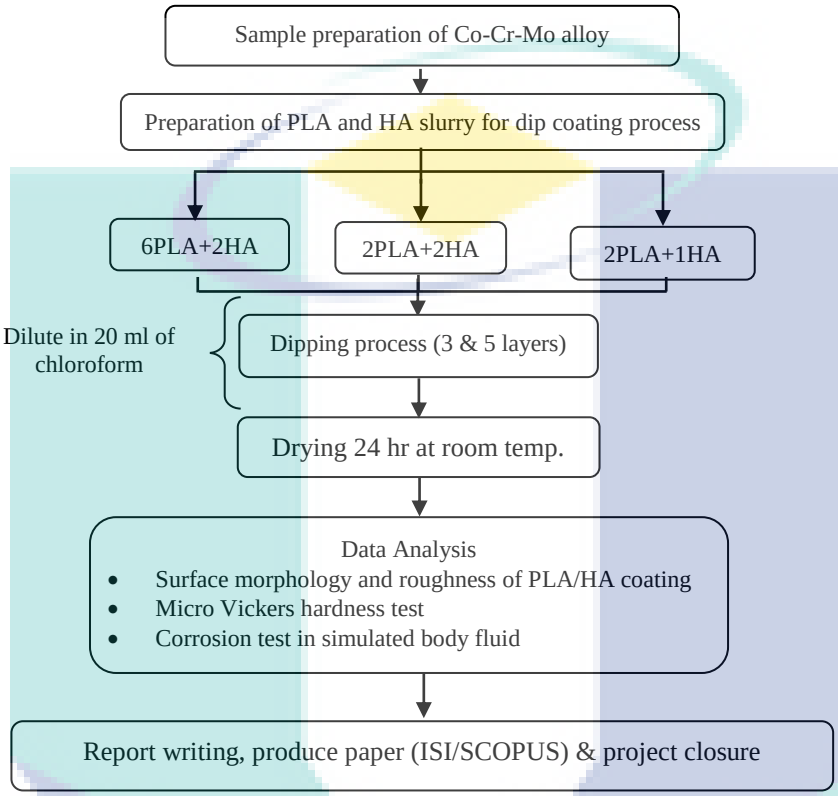

FIGURE 1.1: The overall project flow chart.

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Improving biocompatibility of cobalt based alloy using chemical etching and mechanical treatment

Verbesserung der Biokompatibilität von Kobaltlegierungen mittels chemischen Ätzens und mechanischer Behandlung

H. Mas Ayu[1], R. Daud[1], T. Kurniawan[1], J. Alias[1], S. Izman[2], A. Shah[3], M. Anwar[4]

Biomedical grade of cobalt based alloy have found a plethora of applications as medical devices especially in dental and articulation joints like in total ankle, knee and hip arthroplasty. However, the long-term performance of this material is highly dependent on their ability to withstand in harsh aqueous environment effects such as corrosion and wear once they are used inside a human body. Loss of surface integrity and subsequent leaching of toxic metal ions as well as particles to the surrounding tissues may undermine biocompatibility of metallic implants, also potentially causing untimely loss of mechanical function and device failure. In this study, a biomedical grade of Co–Cr–Mo alloy surface was treated with various surface modification techniques such as chemical etching and mechanical roughening in order to improve its biocompatibility. Investigation was done to study which surface modification techniques possesses the positive effect in cell growth and exhibit excellent cell response on Co–Cr–Mo alloy. In-vitro study showed that human osteoblast cells grown with good adherence and spread out with an intimate contact on the chemical treated surface after 14 days of incubation. It is believed that porous structure with grooves owned by chemical treated surface helps in anchoring the cells to the substrate surface and facilitates cells growth since more protein molecules expected to have more sites on this surface. Whilst on mechanical roughened surface, the cells appeared to show slightly less extended cell membranes and the cells remained retarded.

Keywords: Co–Cr–Mo alloy / biocompatibility / surface modification / cell growth / biomaterials

Schlüsselwörter: Co–Cr–Mo Legierung / Biokompatibilität / Oberflächenmodifikation / Zellwachstum / Biomaterialien

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1 Introduction

Cobalt based alloy are widely used in biomedical devices and components, especially as dental and articulation joints like in total ankle, knee and hip arthroplasty [1, 2]. However, this alloy is known to

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have low biocompatibility properties during implantation such as releasing toxicity ions and slow speed in promoting cell growth on the tissues-substrate interface [3]. Since the formation of a living bone with direct contact to the implant surface is a critical issue, many attempts have been made to modify the implant surface in order to improve bone bonding ability as well as accelerate the bone healing [4, 5].

Therefore, numerous research on surface modification techniques pertaining cobalt based alloy including thermal oxidation, surface coating, thermal spray, electrochemical deposition and ion implantation have been investigated many years to overcome these issues [4, 6–12]. At early implantation, protein film will respond with cells to multiply and form into various types of complex tissues [13]. It is believed that biomaterial surface with greater texture and porous structure able to entrap more protein molecules and later formed into thin layer of protein within few seconds. Hence, adsorption of proteins to the surface of biomaterial have become another major issue in promoting cell growth after implantation.

Although it is well established that surface morphologies such as surface roughness and its topography can strongly influence the protein adsorption, cell attachment and tissues formation, there are still lacks of information regarding the optimum surface roughness that can provide significance effects to cell growth and accelerates the cell regeneration. Therefore, in this study simple and yet effective surface modification techniques such as mechanical roughening and chemical etching were applied on cobalt-chromium-molybdenum (Co–Cr–Mo) alloy to investigate which techniques gives better performance in terms of cell attachment and growth. By achieving this purpose, hopefully will help the country to reduce power consumption and lessen the expensive costs in producing medical implants.

2 Materials and experimental methods

Samples of a biomedical grade Co–Cr–Mo alloy (ASTM F1537) with chemical composition in wt.%: Carbon (C): 0.24; chromium (Cr): 29.6; molybdenum (Mo): 6.5; silicon (Si): 0.7; nickel (Ni): 0.1; ferum (Fe): 0.12; manganese (Mn): 0.7 and cobalt (Co): balance was cut into disc size of 14 mm diameter and 2 mm thick. All samples were annealed in a muffle furnace at 1121 °C for 1 hour under atmospheric condition and cooled inside the furnace for 3 hours. This is to relieve residual stresses built-up in the samples during cutting. All samples were then ultrasonically cleaned in acetone for 30 minutes, followed by a steam cleaning and finally dried using a stream of compressed air [6]. Surface finish of samples were prepared using two different surface modification techniques, i.e. chemical etching and mechanical roughening in order to obtain two set of surface texture and roughness. Chemical treatment samples were pickled using acid etched solution of 50 ml nitric acid, HNO_3 (65 %) + 150 ml hydrochloric acid, HCl (37 %) for 3 minutes. While, mechanical roughening samples were wet ground using #500 grit silica carbide, SiC paper for 3 minutes for both surfaces. Method used to measure the surface roughness of the chemical treated and mechanical roughened samples was carried out using surface profilometer (Mitutoyo SJ-301) and atomic force microscope (AFM). All acid etched and ground samples were then ultrasonically cleaned in acetone for 30 minutes and left to dry overnight in the oven at 50 °C before tested and analysed in terms of cell attachment under a certain period of time. Surface treated samples for both conditions were characterized and evaluated its element phase using field emission scanning electron microscope (FESEM) and energy-dispersive x-ray (EDX) respectively.

The bioactivity performances of chemical treated and mechanical roughened surface samples were analysed based on cell morphologies observation using field emission scanning electron microscope. The experimental work on bioactivity of multipotent stromal cells (MSCs) were prepared according to the standard practice applied in Department of Orthopaedic Surgery, NOCERAL, Universiti Malaya [14]. The multipotent stromal cells also known as human osteoblast cells line were seeded directly on the chemical treated and mechanical roughened surface samples for 14 days before they can be analysed for cell behaviour. The analysis was based on three different samples taken under the same group of samples condition in order to minimize variance of cell morphologies. The evaluation was done after the sample removal from incubation bottles at the end of day 14 in cell study.

3 Results and discussion

Image of a chemical etched surface Co–Cr–Mo alloy after immersed for 3 minutes in acid solution of 50 ml nitric acid, HNO_3 + 150 ml hydrochloric acid, HCl was captured using field emission scanning electron microscope, *Figure 1*a. It was observed that a modification in surface morphology after acid etched was greater textures compared to the ground sample surface. The porous and rougher structure in chemical treated samples are believed to be formed due to the acid etching process. Formation of pitting-like corrosion on the Co–Cr–Mo alloy sample clearly shows that this metals reacts actively with nitric and hydrochloric acid solution. Most of the surface were peel-off with deep crater and pores. The measured surface roughness R_a of chemical treated sample was 1.63 ± 0.15 µm which is about 16 times higher than mechanical roughened surface roughness ($R_a = 0.10 \pm 0.02$ µm). Typical ground track morphologies on mechanical roughened sample after undergone wet ground using #500 grit SiC paper, revealing smoother surface than chemical treated surface sample, Figure 1b.

The variation in surface morphology for both treatments also studied using atomic force microscope. The results were found in line with the obtained images previously taken using field emission scanning electron microscope, which clearly revealing deep grooves and pores in chemical treated sample, *Figure 2*a. Whilst, on mechanical roughened surface sample demonstrated a mild modification with fine texture was observed, Figure 2b. It is believed that greater textures of chemical treated sample cues expose more surface area for cell interaction later. Further discussion of cell attachment

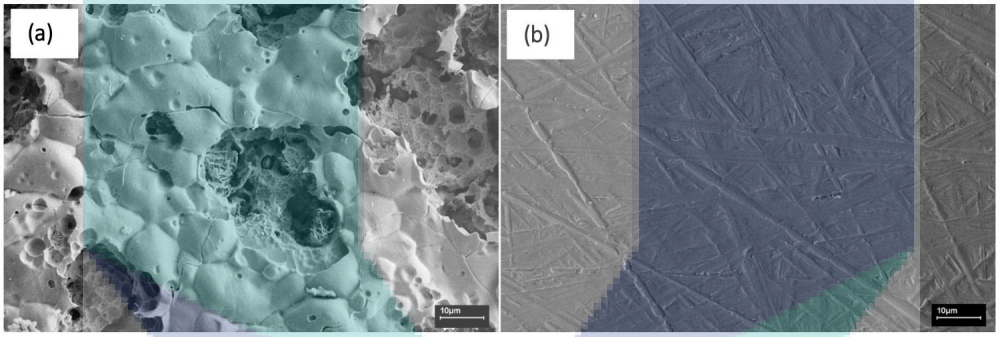

Figure 1. Images of Co–Cr–Mo alloy surface after treated with: (a) Chemical treatment (acid etching) and (b) mechanical roughening (grinding).

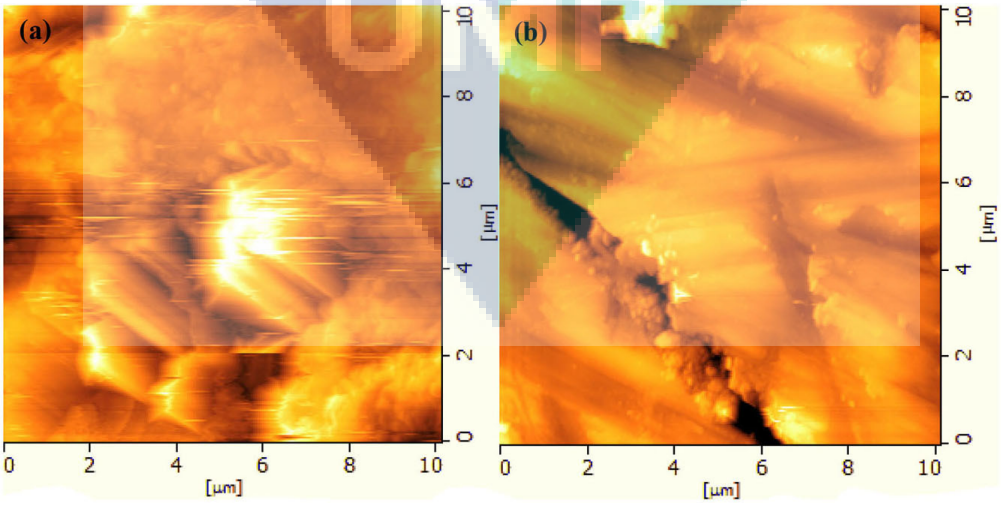

Figure 2. Atomic force micrographs taken on treated surface of Co–Cr–Mo alloy substrate. (a) Chemical treated sample, $R_a = 1.6 \pm 0.15$ µm and (b) mechanical roughened sample, $R_a = 0.1 \pm 0.02$ µm.

on chemical treated and mechanical roughened surface samples will be explained in the following results.

In addition, energy-dispersive x-ray was spotted on the chemical treated and mechanical roughened samples to examine which element dominates and appeared on the substrate surface. The selected area was spotted at the deep grooves on chemical treated sample area and the element detected was recorded, *Figure 3*. The weight percentage provided by energy-dispersive x-ray indicates that manganese is the highest percentage (38.45 %) followed by chromium (29.51 %). This phenomenon occurred due to manganese and chromium is known to have high reactivity with acid solutions that easily peel-off the substrate surface during etching process. There is also other element found such as oxygen, cobalt and carbon. Detection of oxygen on the chemical treated surface due to chemical reaction on the Co–Cr–Mo alloy that entrapped in pores after the acid etching process. However, difference in energy-dispersive x-ray results were obtained for mechanical roughened sample where cobalt and chromium element dominates on the substrate surface, *Figure 4*. Since there is no spallation on the substrate surface, higher weight percentage of cobalt (67.05 %) and chromium (24.64 %) is understandable due to high cobalt and chromium content in as-received materials. Other elements were also detected on mechanical roughened surface sample like molybdenum, carbon and silicon. The small amount of silicon (0.56 %) was detected on mechanical roughened sample due to previously samples were wet ground using SiC paper in order to modify the surface texture.

Further analysis was done to evaluate the cell behaviour on chemical treated and mechanical roughened surface samples. The visual inspection from both samples after multipotent stromal cells were seeded for 14 days, showed that chemical treated sample was completely covered with cells on its surface, *Figure 5*. Field emission scanning electron microscope images have demonstrated that the morphology of multipotent stromal cells were attached and spreading on chemical treated surface. The inset

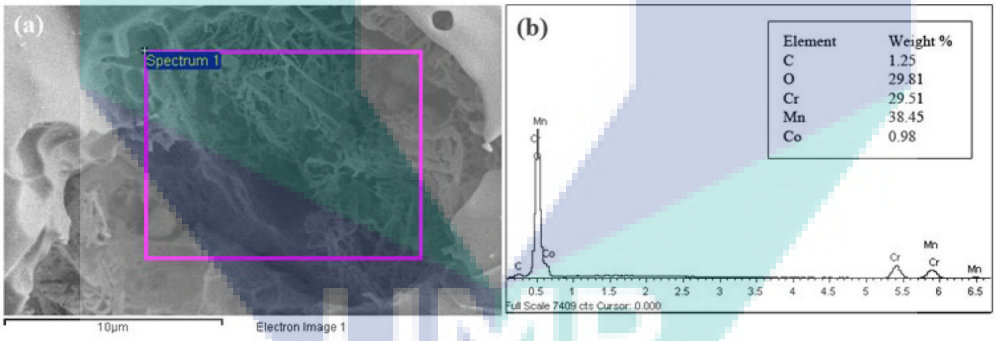

Figure 3. (a) Surface of chemical treated and (b) energy dispersive x-ray spectra obtained from chemical treated surface before biocompatibility test is done.

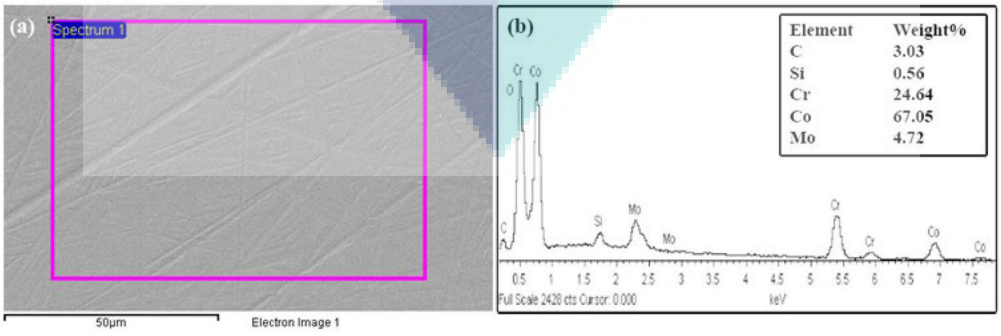

Figure 4. (a) Surface of mechanical roughened and (b) energy dispersive x-ray spectra obtained from mechanical roughened surface before biocompatibility test is done.

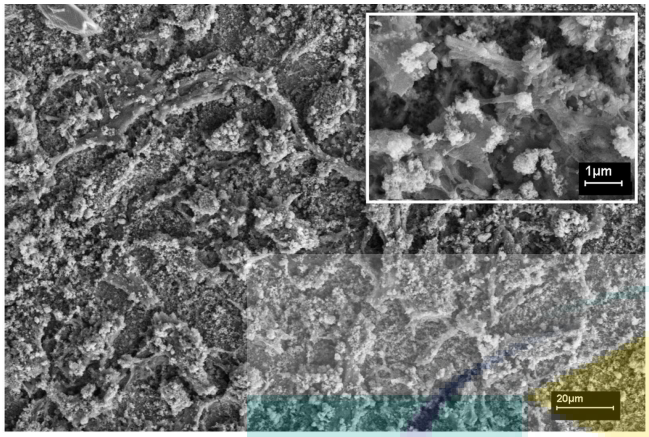

Figure 5. Cell attachment on chemical treated sample at day 14. The inset shows strong filopodium attachment on the substrate surface.

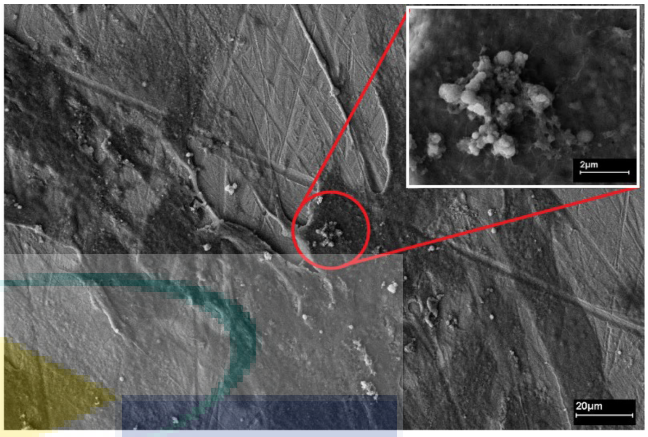

Figure 6. Cell attachment on mechanical roughened sample at day 14. The inset shows closed-up multipotent stromal cells image with small protrusion indicating slow growth of cells.

image clearly revealed more flattened of multipotent stromal cells, indicating strong attachment and well spreading of filopodium anchoring at the substrate interface. This phenomenon happened due to greater surface exposure is favourable for protein adsorption which leads for more cell to respond and grow on chemical treated sample. This finding indicates that chemical treated sample exhibited good biocompatibility and less release of toxicity ions. The results were found in agreement with other researchers where they also claimed that by introducing porous surface increased bone ingrowth at the metal implant interface and helps in faster fixation [13,15]. In addition, high weight percentage of manganese element detected in chemical treated sample probably helped in promoting cell growth and enhanced the elongation of filopodium. Similar results were also observed by other researcher when they studied the effect of manganese element on cell functions such as cell spreading, proliferation and maturation on biomaterial surface [16].

Whereas on mechanical roughened surface sample, the multipotent stromal cells appeared with less attachment after 14 days of cell cultured and also not fully covered the entire surface, *Figure 6*. The closed-up image indicated the formation of multipotent stromal cells exhibited less extended of filopodium in spotted area. Although multipotent stromal cells were appeared to attach on both treated surface samples, but they were more spreading and flattening on chemical treated sample as compared to mechanical roughened sample. These results revealed that mechanical roughened sample seem to be not favourable in promoting cell growth due to smooth surface roughness ($R_a = 0.1 \pm 0.02$ µm). Hence, less adsorption of proteins to the substrate surface which later cause less cells response as well as retard the cell growth [13]. Besides that, higher detection of toxicity element such as cobalt on the mechanical roughened surface may also cause slower speed of multipotent stromal cells to grow on the substrate surface. This finding is parallel with the results obtained from previous researchers [1, 3, 16].

4 Conclusions

It can be concluded that surface modification with chemical techniques on Co–Cr–Mo alloy may have high potential in contributing to successful cell growth as well as alleviate the cell regeneration at the tissues-substrate interface. The multipotent stromal cells on chemical treated sample were almost covering the entire surface with numerous filopodium extensions. On the other hand, mechanical roughened sample was found less cell growth compared to chemical treated sample after 14 days' cell cultured. This is probably due to only small amount of proteins were able attached on the smooth mechanical roughened surface ($R_a = 0.1 \pm 0.02$ µm vs. $R_a = 1.63 \pm 0.15$ µm) hence, affect their interaction with cells and stunned the cell growth. Another reason is because of high release of toxic metal ions such as cobalt that is not suitable for multipotent

stromal cells to grow and migrate. Based on these promising results in bioactivity performances achieved for chemical treated surface sample, further research work could be extended such as investigation on metal ions release test and cell proliferation in order to provide better understanding and reliable information. Hopefully this research work may help engineers and scientists to come up with more efficient implants for future usage.

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Effect of Polylactic acid/Hydroxyapatite Coating on Dental Implant using Finite Element Method

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Keywords: Dental implant, PLA/HA coating, Stress analysis, Bonding strength, Finite element analysis.

Abstract. Finite element analysis (FEA) has been proven to be a precise and applicable method for evaluating dental implant systems. This is because FEA allows for measurement of the stress distribution inside of the bone and various dental implant designs via simulation analysis during mastication where such measurements are impossible to perform in-vitro or in-vivo experiment. That is why the relationship between implant design and load distribution at the implant bone interface is a crucial issue to understand. This research study focuses on a static simulation and bonding strength for PLA/HA coating on V thread design of dental implant using three-dimensional finite element. The average masticatory muscle that involves in human biting such as X, Y and Z direction will be used to simulate force with load condition of 17.1N, 114.6N and 23.4N respectively. Based on result obtained, the coated dental implant model is more compatible than uncoated model due to lower maximum stress which is reduce about 16%. The coated model also shows lower deformation and higher bonding strength. Outcomes from this research provide a better understanding of stress distribution characteristics that would be useful in order to improve design of dental implant thread and evaluation of the PLA/HA bonding strength applied.

Introduction

Dental implants are a replacement for the root of a tooth which are secured in the jawbone and became not visible once surgically placed. They are used to secure the crown, which is the part of artificial teeth seen in the mouth. The success of dental implant critically depends on the initial stability and long-term of osseointegration of dental implant with the surrounding mandible bone where the implant being planted. Previous researcher proof that a study on surface modification on biomaterial such as coating techniques helps improve bone strength and its initial osseointegration rate [1]. The stability of dental implant can be achieved by having an excellent optimal stress distribution of dental implant to the surrounding mandible bone [2].

Many factors affect load transfer at the bone implant interface such as the type of loading, material properties of the implant and prosthesis, implant geometry, surface structure, implant design quality (diameter and length) and quantity of surrounding bone, and nature of bone implant interface [3, 4]. Thus, a better understanding on how the stress from dental implant being distributed to the surrounding bone is crucial for future dental prosthesis application. The use of FEA software helps in

analysing stress distribution of future dental implant design that could be useful for varies clinical situations [5, 6]. However, a key factor for the success of a dental implant is the particular way of stresses that are transferred from implant to the surrounding bone. The use of Finite Element Method (FEM) in the mechanical analysis of dental implants has been described by many authors such as Merdji et al. [7] studied the effect of the bone density on the mechanical damping behaviour of dental implants, Geng et al. [8] studied the mechanisms of fitting with conical tightening in dental implants and many more. This method, presents suitable degree of reliability and accuracy without the risk and expense of implantation [2, 3].

Although vast research has been done on modelling and simulation on dental implant, there is still lack of study on stress distribution of poly-lactic acid (PLA) with hydroxyapatite (HA) coating on dental implant. Therefore, the purpose of this research study is to investigate stress distribution and bonding strength of PLA/HA coated on V thread design of dental implant by using three-dimensional finite element.

Methodology

The three-dimensional geometrical model of a dental implant inserted to the jawbone (Fig. 1), was analyzed using Autodesk Simulation Mechanical version 2015. The geometric model generation in this study was based on previous works with the development of a model of implants fixed [9]. The bone was modelled a full structure with a portion enough for one dental implant placement into the bone with dimension of 29 mm height and 23 mm width. It was divided into two parts of bone which were cortical bone and cancellous bone. The cortical bone had 2 mm of thickness. Conical shaped abutment was used and adjusted to the implant head. The V thread design of dental implant in a form of screw with length of 14 mm and diameter of 4.2 mm shown in Fig. 2 (a). A layer of PLA/HA coating is created on the dental implant which act as a physical barrier between the implant surface in order to enhance osseointegration and reduce stress after implantation. Fig. 2 (b) shows the model of coated dental implant with thickness of coating layer is set at 10μm.

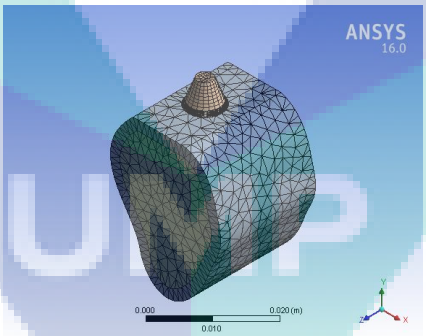

Fig. 1. Three-dimensional model of the dental implant inserted to the jawbone.

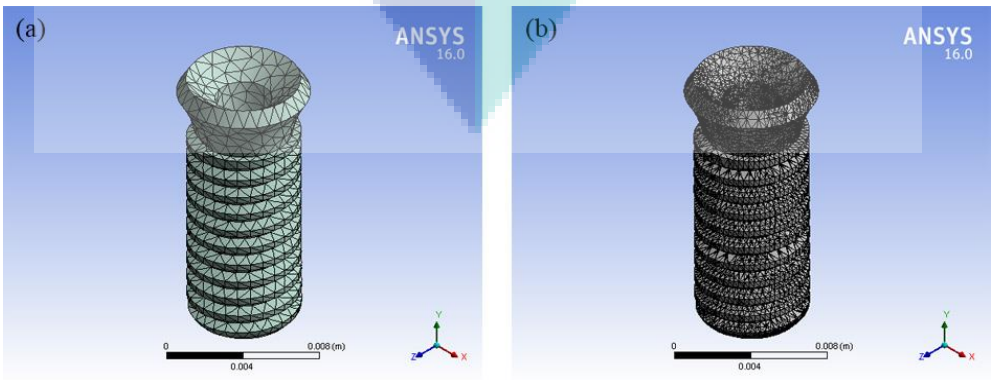

Fig. 2 (a) Three-dimensional mesh model of V thread design and (b) PLA/HA coated on dental implant.

For the loading condition, average masticatory muscle is used to simulate force in human biting. There are 3 direction of forces involves in masticatory muscle such as X-direction, Y-direction and Z-direction. The force loads used for X-direction, Y-direction and Z-direction are 17.1N, 114.6N and 23.4N respectively [10]. Fixed boundary conditions are setup around the jawbone and force are loaded at the top of abutment to imitate real biting as shown in Fig. 3 (a) and (b). The interface between the crown and the implant, as well as between the cortical and cancellous bone are treated as perfectly bonded interface. The material properties of the implant system and the mandibular bone used to setup ANSYS for analysis are shown in Table 1.

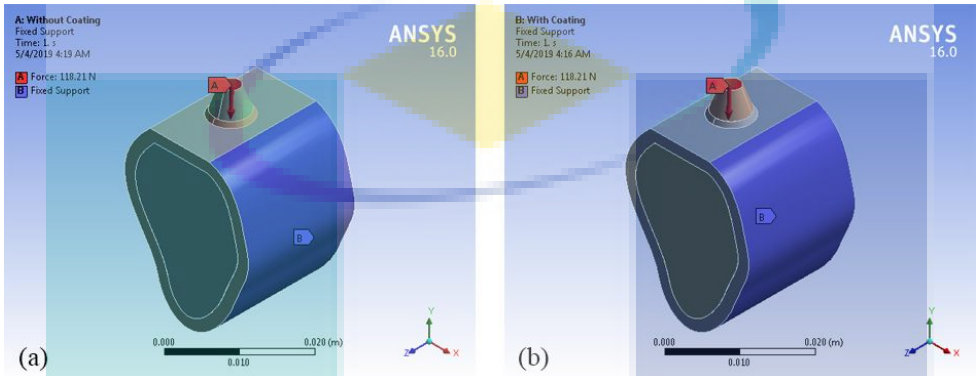

Fig. 3. Three-dimensional model of boundary conditions for (a) uncoated dental implant and (b) PLA/HA coated dental implant.

Table 1 ANSYS setup for uncoated and coated model [2].

Materials	Density	Young Modulus, E (GPa)	Poisson Ratio, v
Co-Cr-Mo alloy	8.4	220	0.3
PLA/HA coating	1.24	440	0.06
Cortical bone	1.9	14.7	0.3
Cancellous bone	1.8	1.47	0.3

Results and Discussion

The two models that have been analyzed which are uncoated model (Co-Cr-Mo alloy) and coated dental implant model (Co-Cr-Mo alloy with PLA/HA coating). Table 2 shows the static stress analysis for von-misses stress for uncoated and coated model design. High stress of 16.14 MPa was recorded for uncoated model. After applying the PLA/HA coating to the exterior of the dental implant in the simulation, the stress value for dental implant was reduce to 13.57 MPa. However, stress value for the PLA/HA coating layer model was obtained 37.36 MPa. Fig. 4(a), (b) and (c) shows stress value for von-misses stress on uncoated dental implant, coated dental implant and PLA/HA coating layer.

Table 2 Stress (Von-Misses) analysis on dental implant

Models	Von-Mises Stress (MPa)
Uncoated dental implant	16.14
Coated dental implant	13.57
PLA/HA coating layer	37.36

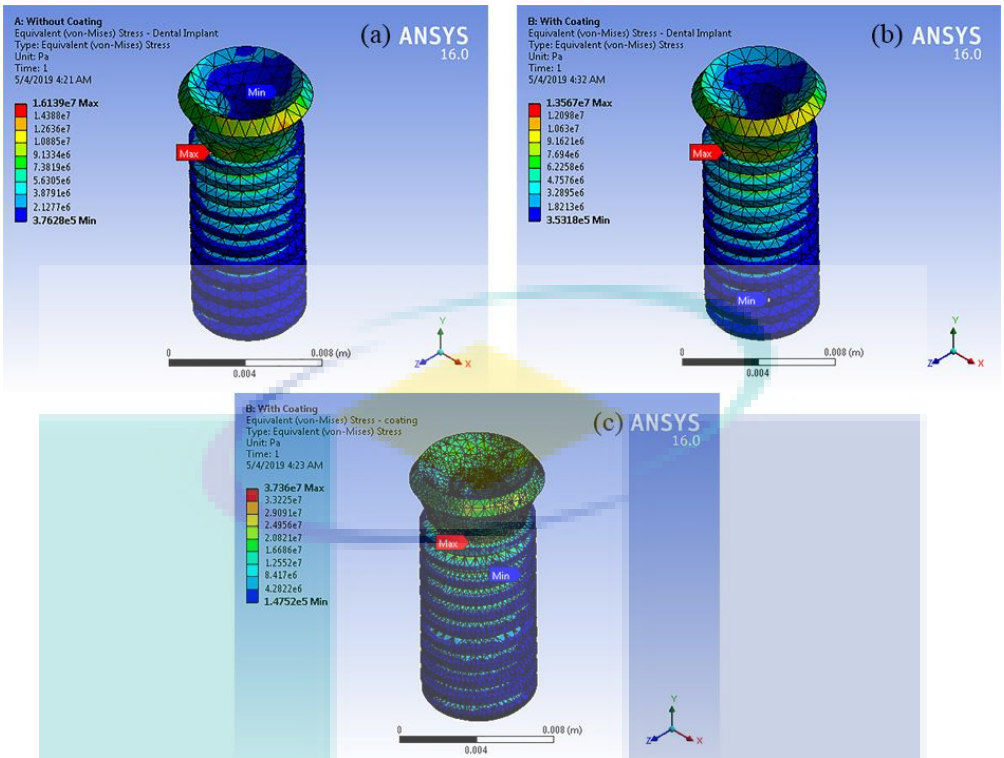

Fig. 4. Stress (Von-Misses) value for (a) uncoated dental implant, (b) coated dental implant and (c) PLA/HA coating.

Further analysis showed that high deformation for uncoated model was recorded 1.678 MPa. After applying the coating to the exterior of the dental implant, the deformation value of dental implant model was reducing to 1.651 MPa. Meanwhile, the deformation value for the PLA/HA coating layer after simulation is obtained at 1.652 MPa. Table 3 shows the static stress analysis for von-misses stress for coated and uncoated model. Fig. 5 (a), (b) and (c) shows deformation value obtained based on analysis run from FEA software.

By inverting the loading condition for Y axis, the bonding for coated and uncoated dental implant is evaluated. Shear stress is observed in order to measure the bonding strength of the PLA/HA coating on dental implant [11]. The higher the shear stress, the lower the bonding strength. Table 4 shows the static stress analysis for shear stress for coated and uncoated model. Maximum shear stress of 9.337 MPa and 6.946 MPa was recorded for uncoated and coated model respectively. After applying the PLA/HA coating on the dental implant, the shear stress value was decrease up to 26%. Fig. 6 (a) and (b) shows stress value for shear stress on uncoated and coated dental implant.

Table 3 Deformation analysis on dental implant and PLA/HA coating layer

Models	Deformation (MPa)
Uncoated dental implant	1.678
Coated dental implant	1.654
PLA/HA coating layer	1.652

Table 4 Shear analysis on dental implant

	Shear Stress (MPa)		
Model	XY plane	XZ plane	YZ plane
Uncoated dental implant	9.337 (max)	4.175	4.457
Coated dental implant	6.946 (max)	2.921	5.599

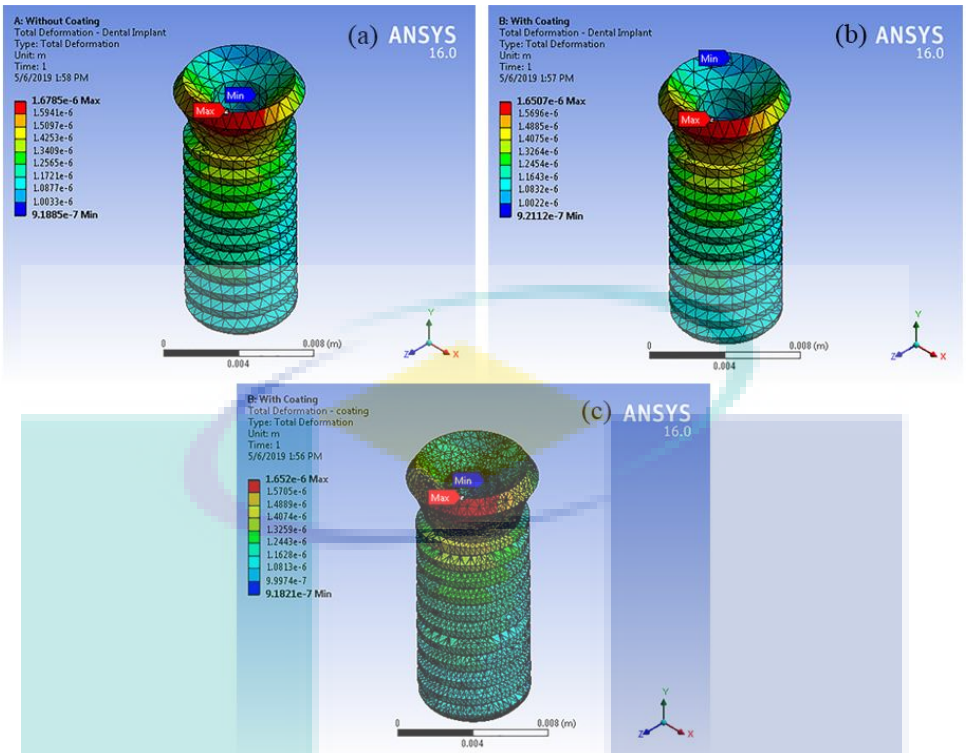

Fig. 5. Deformation value for (a) uncoated dental implant, (b) coated dental implant and (c) PLA/HA coating.

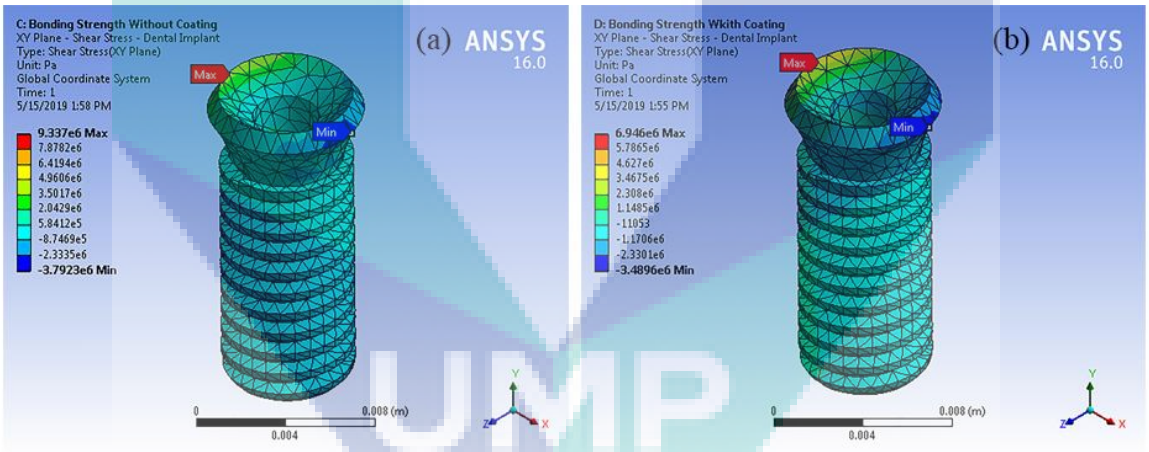

Fig. 6 XY plane shear stress for (a) uncoated dental implant and (b) coated dental implant.

Conclusion

This study was carried out in order to analyze the static analysis on dental implant with and without PLA/HA coating. A 3D FEM Study using ANSYS software was done to evaluate the structural stress and deformation value produced at the uncoated model, coated model and PLA/HA coating layer. Based on all the results, model for coated dental implant shows a better and lower stress and deformation value. The coated model was able to reduce ≈16% of the stress value and also reduced the deformation value to ≈2%. The loading condition tested for maximum stress value in this study does not exceed the yield strength of prosthetic screw of the dental implant which is 720 MPa [12]. Data obtained also revealed that the maximum stress for the PLA/HA coating is below the compressive strength of the coating (174MPa). These results proved analysis run for this study is successful. The coated dental implant model also showed an improvement of bonding strength between dental implant and bone compared to the uncoated dental implant.

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Thermal Oxidation Promotes Growth of Nanocrystalline Diamond on Co-Cr-Mo Alloy

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Abstract*: *Diamond coatings are employed to yield significant benefits in applications such as for cutting tools, optical lenses, biomedical components, microelectronics, engineering and thermal management systems. Although there are many research reporting the successful of diamond coating on titanium, tungsten carbide and steel alloys but there are still lacking of research on the cobalt based alloy as the substrate. In order to coat thin film diamond on these metals substrate, chemical vapor deposition (CVD) technique is commonly used. This paper reports on investigations of nano-crystalline diamond (NCD) coating on different carbon content (0.24% and 0.03%) of cobalt based alloys. Emphasis is given to achieve good adhesion of NCD coating on low and high carbon content of biomedical grade cobalt-chromium-molybdenum (Co-Cr-Mo) alloys using two different processes of surface pretreatment such as mechanical roughening and thermal oxidation. The results revealed that most of the diamond coating was peel-off on the roughened samples. However, there were small portion of diamond coating that still intact on sample that treated using thermal oxidation. The thickness diamond coating obtained was approximately 5µm on oxidized samples. Since the adhesion strength of the diamond coatings were very poor and easily delaminated on all samples condition, scratch test could not be performed. Surface morphology and characterization of diamond coatings were investigated by Field Emission Scanning Electron Microscopy (FESEM) and X-ray diffraction respectively.

Index Terms*: *Co-Cr-Mo alloy, thin film, NCD coating, surface morphology, biomaterial

I. INTRODUCTION

Cobalt-chromium-molybdenum (Co-Cr-Mo) alloys have long being used for orthopaedic and dental implants due to their good mechanical and biocompatibility properties [1, 2]. Although this material has been used to produce metal-on-metal artificial joint surfaces, which is said to be extremely good to resist surface wear, it has been shown that the use of these implants over the time result in the release of toxicity metal ions in many patients [3, 4]. To overcome these issues, surface modifications often required [5]. One of the solution that recently been gaining in popularity is by coating the metals with nanocrystalline diamond (NCD) using chemical vapour deposition (CVD). Many researchers agreed that CVD is a perfect technique which allows thin film of diamond coating deposited onto a range of different materials in a cost-effective manner [6, 7]. It is also believed that diamond coatings exhibit good biocompatibility, low friction, low wear rate and good corrosion resistance.

Although there are many research proof that nanocrystalline diamonds (NCD) films grown successfully on other metals such as tungsten carbide [7], titanium [8] and steel alloy [9] with effectively improve the performance of their mechanical properties but there is still few research have been done to study NCD coating on Co-Cr-Mo alloy.

In the present work, a two different processes of surface pretreatment such as mechanical roughened and thermal oxidation were carried out before diamond coatings were deposited on biomedical grade Co-Cr-Mo alloy using hot filament chemical vapour deposition (HFCVD) method. It is expected that NCD coatings able to anchoring substrate surfaces to reduce corrosion as well as enhance the bone growth. It is also hope that the findings from this research will help scientists and manufactures to produce a more sustainable biomedical implants.

II. EXPERIMETAL DETAILS

The Co-Cr-Mo alloy with two different carbon contents i.e. 0.24%C and 0.03%C were used as the samples. The chemical composition of samples material used in the present study is given in Table 1. These samples are referred as high carbon (HC) and low carbon (LC) respectively. The specification of substrate materials follows the international standards (ASTMF1537) and it is suitable for use as biomedical implant. The rod substrate was cut using a precision cutter into small disk samples with a diameter and thickness of 14 mm and 2 mm respectively. All samples preparation was ultrasonically cleaned with acetone for 30 minutes, followed by steam cleaning and finally were dried using a stream of compressed air before ready for next process [10]. Co-Cr-Mo alloys samples were then prepared using two different processes of surface treatment, i.e. mechanical roughened and thermal oxidation process in order to obtain different sets of surface roughness before underwent diamond coating deposition using HFCVD.

The first batch of HC and LC samples were prepared using mechanically roughened with wet ground using #500 grit SiC paper and the final average roughness obtained

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from the roughened samples was 0.10 ± 0.02µm. While, the second batch of HC and LC samples were undergone thermal oxidation at temperature 1050°C for 3 hours directly after the drying process. Their final surface roughness, Ra after oxidation for HC and LC samples were 1.0 ± 0.03µm and 1.52 ± 0.02µm respectively. Surface roughness of all samples condition was measured using Mitutoyo SJ-301surface profilometer.

The purpose of thermal oxidation process was done is to create oxide interlayer (chromium oxide, Cr_2O_3) on the substrate surface, which acts as an intermediate layer between the substrate and diamond coating. Types of oxide/carbide layer formed on the substrate were characterized using XRD and scanning electron microscope. All the prepared samples are then sent to CemeCon AG, Germany for smooth diamond coating in a CC800®/9 Hot Filament Chemical Vapour Deposition unit. The gasses involved were hydrogen, methane and oxygen involving oxygen pulsing every half an hour for 22 hours and 1-hour cooling. Surface morphology and thickness of the diamond coated samples were performed using the Zeiss Supra 35VP field-emission scanning electron microscopy (FESEM) with energy dispersive X-ray (EDX) attachment.

Table 1. Chemical composition of high carbon (HC) and low carbon (LC) of Co-Cr-Mo alloy as supplied by Carpenter Technology Asia Pacific PTE Ltd in Singapore.

Alloy Designation	**Element wt%**				
	C	**Co**	**Cr**	**Mo**	**Mn Si Ni Fe Cu**
HC	0.24	61.9	29.6	6.5	Residual elements
LC	0.03	65.3	27.5	5.5	Residual elements

III. RESULTS AND DISCUSSION

HFCVD diamond coated on high carbon (0.24%) and low carbon (0.03%) of Co-Cr-Mo alloy are shows in Fig. 1 to 4. It is observed that the diamond film nucleates and grows only on oxidized samples of HC and LC Co-Cr-Mo alloy but not presence in any samples that treated with mechanical roughened. This is probably due to the high solubility and diffusivity of carbon in cobalt, which acts as a carbon sink (with a formation of solid solution), that promotes the formation of non-diamond carbon (graphite [11] or soot [12]) and thus delays the onset of diamond nucleation on the samples.

Even though it is notable that there is the presence of thin film of diamond coating on oxidized LC sample, but the adhesion strength of the diamond film is very poor and easily delaminated from the substrate. Therefore, adhesion test is not able to performed on the samples.

Based on the FESEM images, diamond formed on oxidized LC as shown in Fig. 1d. No diamond formation was observed on roughened sample of HC and LC as shown in Fig. 1a and Fig. 1b respectively.

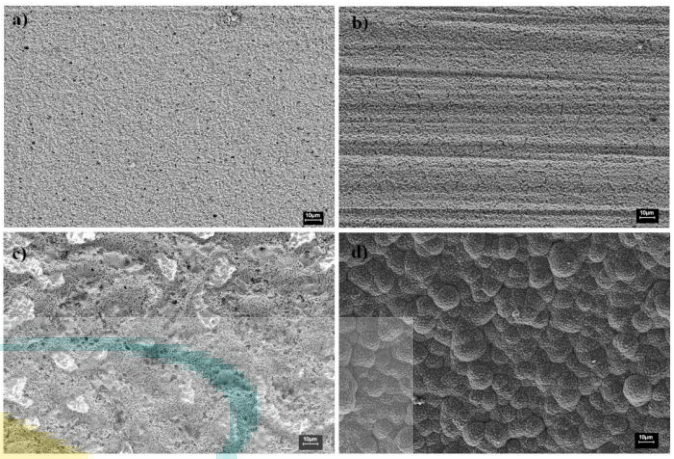

Fig. 1 FESEM surface morphology after diamond deposition at 500x magnification (a) Roughen HC, Ra ≈ 0.3µm. (b) Roughen LC, Ra ≈ 0.3µm. (c) Oxidized 1050°C, 3h HC. (d) Oxidized 1050°C, 3h LC.

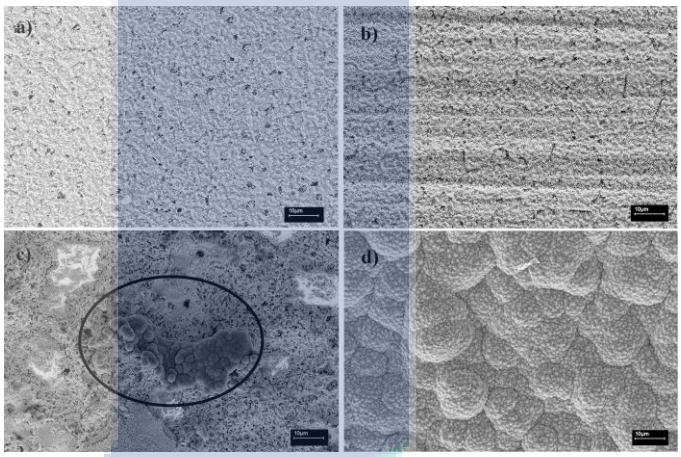

Fig. 2 FESEM surface morphology after diamond deposition at 1000x magnification (a) Roughen HC, Ra ≈ 0.3µm. (b) Roughen LC, Ra ≈ 0.3µm. (c) Oxidized 1050°C, 3h HC. (d) Oxidized 1050°C, 3h LC.

Fig. 2 shows a higher magnification of the diamond coating morphology on HC and LC of Co-Cr-Mo alloy. It is worth to note that in Fig. 2c there is diamond that nucleate and grow on oxidized HC sample as highlight in black circle. According to Fig. 2d the evidence of crystal structure with no facet and ball-like structure known as cauliflower structure was observed [13, 14]. Based on FESEM micrographs, the nanocrystalline diamonds (NCD) are grown in ballas or cauliflower morphology that deposited on oxidized LC substrate of Co-Cr-Mo alloy. The similar results also claimed by other researcher who studied about NCD coating on tungsten carbide samples [15].

However, only oxidized LC samples were able to measure the thickness of diamond coating in this research study. As mentioned earlier, a small site of diamond was nucleated on oxidized HC samples which is impossible to be measured. The average thickness of thin diamond film obtained on oxidized LC substrate is 4.92µm (Fig. 3). While in Fig. 4, the cross-section of diamond coating on oxidized samples HC and LC are shown.

Based on the FESEM observations, it is clearly shows

that diamond formation growth below the oxide layer in oxidized HC sample. While, the opposite manner was observed in oxidized LC sample as diamond formation growth on top of oxide layer with thickness about 4µm (Fig. 4d). Since the preparation samples of HC and LC prior to diamond deposition is similar, therefore this phenomenon can be explained by the different carbon content in Co-Cr-Mo alloy. Due to high carbon content in HC Co-Cr-Mo alloy (0.24%C) somehow have suppress diamond from growth outward as shown in Fig. 4c. Additionally, it is also known that nucleation of diamond ballas tends to prefer certain sites enhancing accumulation of ballas. Thus, oxidized LC sample possess higher surface roughness (1.52 ± 0.02µm vs. 1.0 ± 0.03µm), it is expected to obtain diamond film on this sample.

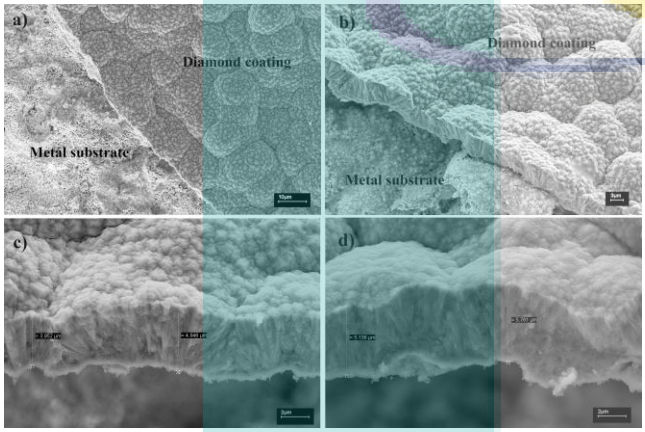

Fig. 3 (a) and (b) FESEM image showed that NCD coating peel-off from the oxidized LC substrate due to poor adhesion. (c) and (d) Thickness measurements of NCD coating on oxidized LC Co-Cr-Mo alloy at 5000x magnification.

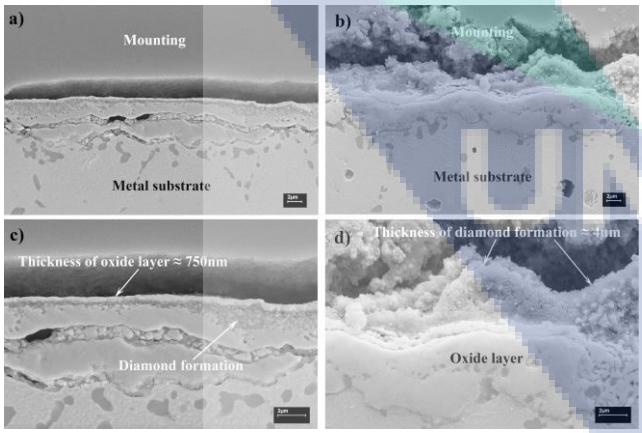

Fig. 4 The cross-section images of diamond coating on oxidized sample (a) Oxidized HC sample. (b) Oxidized LC sample. (c) The diamond growth below the oxide layer in oxidized HC sample. (d) The thickness of diamond coating on oxidized LC Co-Cr-Mo alloy about 4µm. Observation showed formation of oxide layer beneath the diamond coating.

IV. CONCLUSION

The following conclusions can be drawn from the above discussion;

1. Diamond coating were obtained on oxidized high carbon (HC) and low carbon (LC) Co-Cr-Mo alloys. However, the adhesion is very poor due to delamination occurred and left small portion of diamond coating on the both samples. Therefore, cobalt removal is necessary in order to obtain a good diamond nucleation and better quality diamond coating on Co-Cr-Mo alloys.

2. Although the mismatch of coefficient thermal expansion could be the cause of poor adhesion in diamond coating, but in not the major issues this study. Diamond coating of Co-Cr-Mo alloy seems to be un-achievable due to high content of cobalt in this alloy (~60%).

3. Creating oxide as interlayer on the substrate showed possibility of diamond nucleation to form and crystal growth but resulted in poor adhesion strength of diamond coating. Optimization of parameter used during diamond coating using HFCVD should be focused more in order to obtain good adhesion of diamond coating.

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CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

The research works done has demonstrated successful results as dip-coating technique can be used to obtain homogeneous crack-free coating, densely packed and optimum thickness coating of PLA/HA composite on Co-Cr-Mo alloy. Dip coating process parameters and polymer concentration were productively manipulated and modified to control the deposition amount and coating thickness. The addition of 2 gram PLA into 1 gram HA considerably improved the adhesion of HA coating onto Co-Cr-Mo substrate and thus, eliminated the need of post heat treatment of the coated sample and provided 35 times better corrosion protection when compared with bare substrate making this combination a potential candidate for biomedical application. Based on the findings, by adding PLA more than 4 gram will influence severely in coating thickness and coating surface roughness. In addition, too thick of PLA/HA coating may lead to rougher surface roughness which later will effect on cell growth as reported by previous researcher [17, 18]. Through this research, it is possible to obtain homogeneous crack-free coating, densely packed and uniform coating thickness of PLA/HA via sol-gel dip coating technique by modifying the PLA/HA mixture slurry.

5.2 Recommendations

Some recommendations regarding this research can be carried out for future works which are:

(i) Manipulation of various parameters in dip coating process and mixture of PLA/HA slurry can be done to study more details on the effect of coating performances on Co-Cr-Mo alloy. Further testing on the adhesion strength of the coating also should be done to analyse the coating behaviour.

(ii) For further investigation could be done is by using other type of binders to HA slurry for example poly ε-caprolactone (PCL) as this material approved by the FDA a biodegradable polymer and good biocompatibility properties. The hypothesis results from this future experimental could eliminate the sintering process and at the same time provide better adherence of HA coating on metal implants.

(iii) Further bioactivity performances should be done via in-vitro test and in-vivo test for a better understanding of cell responses and generation to new bone growth. Hopefully this approach may help engineers and scientists to come up with better and efficient implants for future usage.

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APPENDIX A

Gantt Charts and Milestone of Research Activities

	Research Activities	*Start on Oct 2017*			*Year 2018*												*End on Oct 2019*										*Extend until 4 Jan 2020*	
		10	*11*	*12*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*
1	Literature review																											
2	Acquisition of raw materials																											
3	Sample Preparation																											
4	PLA/HA Slurry Preparation & Coating Deposition																											
5	Material characterization of coated samples																											
6	Corrosion test in simulated body fluid																											
7	Publication and report writing																											

	Milestones	*Start on Oct 2017*			*Year 2018*												*End on Oct 2019*										*Extend until 4 Jan 2020*	
		10	*11*	*12*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*
1	Completion the sample preparation																											
2	Completion PLA/HA slurry preparation & coating deposition																											
3	Completion characterisation of PLA/HA coated samples																											
4	Completion corrosion test																											
5	Completion preparing technical publications & report closure																											

APPENDIX B

Related Publications

1. **H. Mas Ayu**, Rosdi Daud, A. Shah, H. M. Hazwan, S.H. Tomadi and M.S. Salwani, "Effect of Thermal Oxidation and Carbon Concentrations on Co-Cr-Mo Alloy in Enhanced Corrosion Protection", Materials Science Forum, 2018, 916, pp. 170-176. (Published)
2. A. Shah, S. Izman, S. N. F. Ismail, **H. Mas-Ayu**, R. Daud, "Study on adhesion strength of TiN coated biomedical Ti-13Zr-13Nb alloy", Jurnal Teknologi, 2018, 80(2), pp. 27-35. (Published)
3. A. Shah, S. Izman, S. N. F Ismail, **H. Mas Ayu**, R. Daud, M. R. Abdul-Kadir, "Physical Vapour Deposition on corrosion resistance: A review", ARPN Journal of Engineering and Applied Sciences, 2018, 13(10), pp. 3515-3523. (Published)