Development of Superhydrophobic Material SS 17-4 PH for Bracket Orthodontic Application by Metal Injection Molding

S Supriadi¹, B Suharno², T Widjaya and S T Ayuningtyas² and E R Baek³

¹ Mechanical Engineering Department, University of Indonesia, Depok, Indonesia
² Metallurgy and Materials Engineering Department, University of Indonesia, Depok, Indonesia
³ School of Materials Science and Engineering, Yeungnam University, South Korea

E-mail : sugeng@eng.ui.ac.id

Abstract. Dental’s plaque is a common problem that encountered during orthodontic treatment using bracket. It is caused by demineralization of enamel due to the activity of bacteria. The bacteria increase with remaining excess food which trapped in teeth and bracket. A hydrophobic surface could reduce food attachment on the bracket because of extremely low wettability properties that make it easy to clean with water. There are several methods to obtain hydrophobic surfaces, which are sol-gel, template replica and also etching. The propose of this work is to compare etching treatment and surface modification on sintered SS 17-4 PH as bracket material using CuCl₂ and HCl as an etchant while stearic acid was used for surface modification. Hydrophobic surfaces were produced under various etching time i.e 15, 30, 45 and 60 seconds for CuCl₂ and 40, 50, 60 and 70 minutes for HCl and also HCl concentration i.e 1,2 and 3 mol/L at room temperature. The hydrophobicity is observed using contact angle measurement while the microstructures observed by Scanning Electron Microscope. The result shows the contact angle could be achieved up to 60% higher than the as-sintered material. Hydrophobic structure has successfully fabricated using etching technique that might be applied to the orthodontic bracket.

1. Introduction
Dental’s plaque is one of the common problem that we could encountered during orthodontic treatment using the bracket. This problem is caused by demineralization of enamel due to accumulated bacteria in a high number on bracket [1]. Demineralization is a process of loss mineral on enamel in ion state [2]. Plaque’s microorganism could form organic acid which lowering pH value on dental’s plaque and caused ion calcium and phosphate diffusion from enamel through pellicle. When the pH value is already low enough, it would increase acid condition between plaque and bracket until the acid could not come out and finally attack the enamel [3]. The bacteria could increase because of remaining excess food which trapped between teeth and bracket. A hydrophobic surface is proposed to reduce food attachment on the bracket because of its potential use in self-cleaning properties which inspired from lotus leaves [3,4]. Lotus leaves have ability to always remain clean even though it is in a dirty pond. This self-cleaning performance is known as ‘Lotus Effect’[5]. These properties could occur on hydrophobic surfaces because of hierachial structure that has an extremely low wettability which depend on surface roughness and also free energy surface [6]. Self-cleaning properties is identified with high static contact angle (>150°), it is also called superhydrophobic surface [7]. There are several methods to fabricate superhydrophobic surfaces, such as plasma spray [8], sol-gel [9],
electrostatic spray deposition [10], template replica [11]. However most of these methods has a very slow process, poor bond strength and also difficult to apply for complex shape. Previous work by Supriadi et al. shows that fabrication of orthodontic bracket can be done by investment casting process using SS 316L with acceptable geometry, but it still has porosity in its surface which could affected the surface roughness [12]. The propose in this work is using a simple and low-cost method to achieve superhydrophobic surfaces for orthodontic bracket 17-4 PH stainless steel (AISI 630) produced by metal injection molding which has less porosity than investment casting process. The methods are chemical etching and surface modification [13,14]. This method was never used for 17-4 PH stainless steel before. The samples were chemically etched using a mixture of CuCl₂ and various concentration of HCl and also HCl without CuCl₂ to obtain microscale roughness and followed by surface modification to obtain low-free-energy surfaces so the contact angle would increase. This study’s aims to see the results of chemical etching and surface modification on orthodontic bracket surfaces and determine the optimum condition for superhydrophobic surfaces using wet chemical etching and we also compare the microstructure of samples that was already etched with and without CuCl₂.

2. Experimental

2.1. Materials

In this work, 17-4 PH stainless steel was used as substrate because it has excellent corrosion resistant. 17-4 PH stainless steel feedstock was manufactured by Ryer, Inc., HCl (37%), Ethanol (99.9%), CuCl₂ and stearic acid were bought from chemical industry in Indonesia. 17-4 PH SS chemical composition can be seen from Table 1.

| Table 1. Chemical composition of 17-4 PH stainless steel |
|-------------|-----|-------|-----|-----|-----|-----|-----|
| Fe (%)      | C (%) | Cu (%) | Co (%) | Cr (%) | Mn (%) | Mo (%) |
| 74.26       | 0.04 | 3.94   | 0.03  | 16.44 | 0.16   | 0.02  |
| Nb (%)      | Ni (%) | O (%) | P (%) | S (%) | Si (%) |
| 0.29        | 4.04  | 0.35   | 0.02  | -     | 0.39   |

2.2. Experimental Methods

In our research team, first the 17-4 PH stainless steel feedstock was injected into dies to form cubic shape (5 mm x 5 mm x 5 mm). The injection processed is done under certain conditions, which are injection pressure is about ±2700 psi, barrel’s temperature for about ±100°C, nozzle’s temperature for about ±200°C and mold’s temperature is about ±50°C. The product was called green part since it still has binder and metal powder in it. After that, we begin the debinding process for green part. Debinding process was performed in two stages, which are solvent debinding and also thermal debinding. In solvent debinding process, the samples were immersed in hexane at temperature of 50°C for 90 minutes with agitation method. The samples were then drying using vacuum atmosphere at temperatures of 50°C for 1 hour. Thermal debinding process was carried out after solvent debinding process, the samples were put into MTI tube furnace with temperature of 510°C, heat rate of 1°C/min for 60 minutes and then cooled by furnace cooling [15]. After thermal debinding process done, argon gas was flowed into MTI tube furnace to remove oxygen gas inside the tube furnace and then sintering process began. It was performed in vacuum condition with temperature of 1360°C, heat rate 5°C/min for 90 minutes [16].

Before chemical etching begin, the samples were cleaned with distilled water and grind with abrasive paper #400 to roughened the surface. The samples were immersed into the solution of HCl (1, 2, 3 mol/L) with and without addition of CuCl₂ (1 mol/L). After etching, the samples were washed in distilled water and alcohol to remove grease and residual solution and then, it was dried with hair dryer for about 5 min. Then, the dried samples were immersed into the solution of stearic acid (1 M) and ethanol for about 30 min. The samples were dried with hair dryer for 30 min.
2.3. Characterization
The contact angle (CA) were captured by digital camera and it was measured by averaging the angles that was formed on the left and right borders of the samples using ImageJ. The average contact angle (CA) were measured at three times with the same sample. The droplet volume of water was 5 µL. Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) were carried out to observed surface morphology and also elemental composition that was formed on the surface.

3. Results and Discussion

3.1. Wettability Properties of the stainless steel 17-4PH

3.1.1. Effect of HCl concentration on contact angle (with and without surface modification)
Based on Figure 1a, etching at 1 mol/L, 2 mol/L and 3 mol/L HCl with 40, 50, 60 and 70 minutes will cause decreasing contact angle at first, but it will increase with the increasing of etching time and decrease again after it reached the optimum time. Optimum time for 1 mol/L HCl is about 60 minutes, but for 2 mol/L and 3 mol/L HCl is about 50 minutes. From this experiment, 1 mol/L has better hydrophobic surface at 40 minutes than 2 mol/L solution concentration, but when the etching time is increase, samples will become more hydrophobic at 2 mol/L solution concentration in 50 minutes than 1 mol/L solution concentration. However, after 50 minutes the contact angle will decreased, it is because with the increasing of etching time, surface roughness will be destroyed. For 3 mol/L solution concentration, it has the lowest contact angle at beginning stage. it is in accordance with literature, when the HCl concentration is increased, it will affect the surface roughness which is it would be destroyed and reduce the contact angle [17]. Therefore, 2 mol/L was the optimal solution concentration to obtain hydrophobic surfaces with etching time is about 50 minutes with contact angle (θ) is about 96.4°.

Figure 1b shows the relationship between etching time and contact angles on the samples surface. It shows that the contact angle will increase after the samples were immersed in a 1 mol/L of stearic acid and ethanol. The experiment was carried out with different HCl concentration i.e 1 mol/L, 2 mol/L and 3 mol/L and etching time i.e 40, 50, 60 and 70 minutes. The result showed, contact angle (θ) will increase with the increasing of etching time up to the optimum time. From this experiment, 2 mol/L solution concentration at 70 minutes has super-hydrophobic surfaces with optimum contact angle is 142° while for 1 mol/L and 3 mol/L solution concentration is about 123° and 136° in 60 minutes. After the contact angle reached optimum time, it will be decreased. This is because the etching time will affect micro- and nano structures on the stainless-steel surface. So, when it is too long the structures will be destroyed and reduced the contact angle, because the sample will be corroded [17]. The comparison between Figure 1a and Figure 1b shows that after surface modification, the contact angle will always higher than 100°, it is because stearic acid has low free energy surface so it could increase the contact angle. Figure 2 shows a pits photograph from optical microscope on 17-4 PH stainless steel surface. We could see from the figure that with the increasing etching time the pits’ diameter would become larger. It is because of the etching solution would attack the grain and created pits. So, the longer etching time will make the samples has a larger pit’s diameter and make the sample corroded enough that it could lead to decreasing contact angle. Figure 3 shows an optical photograph of water droplet on samples surface after etching and without surface modification.
Figure 1. Water contact angles on 17-4 PH SS surface etched with different HCl concentration and time (a) without surface modification (b) with surface modification

Figure 2. Pits photograph from optical microscope of 2 mol/L HCl on 17-4 PH stainless steel surface (a) 40 minutes, (b) 50 minutes, (c) 60 minutes and 70 minutes
Figure 3. Optical photograph of water droplet on 17-4 PH stainless steel after etching with HCl (a) 1 mol/L for 60 minutes, (b) 2 mol/L for 50 minutes and (c) 3 mol/L for 50 minutes without surface modification and (d) 1 mol/L for 60 minutes, (e) 2 mol/L for 70 minutes and (f) 3 mol/L for 60 minutes after surface modification.

3.1.2. Effect of CuCl$_2$ and HCl in contact angle (without and with surface modification)

Figure 4a shows relationship between processing time and contact angle on samples surface. The contact angle was increased after it was immersed in mixture of CuCl$_2$ and various HCl concentration without surface modification. The contact angle was increased up to the optimum time and after that it would decrease. It is because the etching solution and time will affect micro and nanoscale surface roughness. By immersing the samples in to those solution, Cu particles will be deposited on to sample surface. Time and solution concentration play an important role in crystal Cu growth. The optimum contact angle that could be obtained is about 125° in 1 mol/L CuCl$_2$ and 1 mol/L HCl at 15 seconds. From this experiment by variating HCl solution concentration, the contact angle would decrease with increasing concentration.

Figure 4b shows an increasing contact angle with an increasing time after surface modification. This is due to the surface roughness that was created after etching and stearic acid which has low free energy surface, so that the contact angle value will higher than the one without surface modification. The contact angle reached 123° in 1 mol/L HCl after 15 seconds, with a longer time up to 45 seconds, the contact angle reached 142°. However, after 45 seconds the contact angle will decreased again and it is because the Cu crystal is destroyed with a longer time it could lead to decreasing of surface roughness [18]. Solution concentration is also an important factor that could affect contact angle. From this experiment, 3 mol/L and 2 mol/L HCl concentration has higher contact angle than 1 mol/L HCl at beginning stage but, decreased with a longer time. It shows that with higher concentration, the contact angle would be increased, but soon after that it would decreased.
3.2. Surface Morphology

Figure 4. Water contact angles on 17-4 PH SS surface etched with 1 M CuCl\(_2\) and different HCl concentration (a) without surface modification (b) with surface modification

Figure 5. a. SEM of 1 mol/L CuCl\(_2\) and 1 mol/L HCl in 15 seconds sample, (scale bar: 10 µm, b. 2µm), c. SEM of 2 mol/L HCl in 70 minutes sample

Figure 6. (a) EDS of 1 mol/L CuCl\(_2\) and 1 mol/L HCl in 15 seconds sample, (b) EDS of 2 mol/L HCl in 70 minutes sample

SEM characterization was conducted by comparing the samples with and without CuCl\(_2\). Figure 5 Test result showed high content of Cu up to 90 wt% in sample surface which was immersed in 1 mol/L CuCl\(_2\) and 1 mol/L HCl for 15 seconds, Figure 6a. This indicated that Cu was deposited on sample surface and formed crystal Cu layer. In small quantities, Cu\(^{2+}\) ions can be helpful for metabolic processes in human body, but Cu\(^{2+}\) ions in higher concentration can be harmful to cells in human
body, which will damage cells and eventually the cell will die [19][20]. While, Figure 6b showed high content of Fe, Cr, O and C in the sample. This indicated that during etching process with 2 mol/L HCl there is oxidation reaction with possibility formed chromium oxide layer (Cr₂O₃) and the rest of O and C signal was from stearic acid modification [14][18].

4. Conclusion
Wet chemical etching followed by surface modification process for superhydrophobic bracket orthodontic was successfully conducted in this study. By only using etching, the superhydrophobic properties could not obtained, but after it was modified using stearic acid material the contact angle could increase up to >140°. The most higher contact angle that could be obtained in this study is about 142° by using 1 mol/L CuCl₂ and 1 mol/L HCl for 15 seconds and also 2 mol/L HCl for 70 minutes. This study still has not obtained an appropriate standard for self-cleaning properties, which has contact angle >150°. It is because the surface roughness was not optimal enough to achieve contact angle >150°. As etching solution concentration and processing time increase, the contact angle will also increase up to its optimum contact angle but after that it would decrease, because of destroyed structures. Etching using CuCl₂ solution is not acceptable for orthodontic application because it would have formed Cu layer on stainless steel surface, however by using HCl solution it was not formed Cu layer and might be applied in bracket orthodontic application.

5. Reference
[1] Türkkahraman H, Sayin MÖ, Bozkurt FY, Yetkin Z, Kaya S and Önal S 2005 Archwire ligation techniques, microbial colonization, and periodontal status in orthodontically treated patients Angle Orthod. 75
[2] Sabel N, Robertson A, Nietzsche S and Nor JG 2012 Demineralization of Enamel in Primary Second Molars Related to Properties of the Enamel Sci World J.
[3] Shin S, Seo J, Han H, Kang S, Kim H and Lee T 2016 Bio-Inspired Extreme Wetting Surfaces for Biomedical Application Materials. 9
[4] Gurav AB, Xu Q, Latthe SS, Vhatkar RS, Liu S, Yoon H, et al 2014 Superhydrophobic Coatings Prepared from Methyl-modified Silica Particles Using Simple Dip-coating Method Ceram Int.
[5] Shirtcliffe NJ, McHale G and Newton MI 2009 Learning from Superhydrophobic Plants: The Use of Hydrophilic Areas on Superhydrophobic Surfaces for Droplet Control Langmuir 25
[6] Yeo I, Kim H, Lim KS, and Han J 2012 Implant surface factors and bacterial adhesion: a review of the literature Int. J. Artif. Organs. 35
[7] Zhang M, Feng S, Wang L and Zheng Y 2016 Lotus effect in wetting and self-cleaning Biotribology 5
[8] Sharifi N, Pugh M, Moreau C and Dolatabadi A 2016 Developing hydrophobic and superhydrophobic TiO₂ coatings by plasma spraying Surf. Coat. Technol.
[9] Mahadik SA, Sarika FP, Brahmanand SM, and Thorat SS 2016 Biocompatible superhydrophobic coating material for biomedical applications J. Sol-Gel Sci. Technol.
[10] Hu C, Liu S, Li B, Yang H, Fan C and Cui W 2013 Micro- / Nanometer Rough Structure of a Superhydrophobic Biodegradable Coating by Electrospaying for Initial. Adv. Healthc. Mater.
[11] Liu Y, Song Y, Niu S, Zhang Y, Han Z and Ren L 2016 Integrated super-hydrophobic and antireflective PDMS bio-templated from nano-conical structures of cicada wings RSC Adv.
[12] Supriadi S, Sitanggang TW, Irawan B, Suharno B, Kiswanto G and Prasetyadi T 2015 Orthodontic Bracket Fabrication using the Investment Casting Process. Int. J. Technol.
[13] Barshilia HC and Gupta N 2014 Superhydrophobic polytetrafluoroethylene surfaces with leaf-like micro-protrusions through Ar + O₂ plasma etching process Vacuum 99
[14] Alonso Frank M, Boccaccini AR and Virtanen S 2014 A facile and scalable method to produce superhydrophobic stainless steel surface. Appl. Surf. Sci. 311
[15] Supriadi S, Suharno B, Hidayatullah R, Maulana G and Baek E. 2017 Thermal Debinding Process of SS 17-4 PH in Metal Injection Molding Process with Variation of Heating Rate,
Temperature, and Holding Time. *Solid State Phenom.* **266**

[16] Suharno B, Ferdian D, Saputro HR, Suharno LP, Baek E and Supriadi S 2017 Vacuum Sintering Process in Metal Injection Molding for 17-4 PH Stainless Steel as Material for Orthodontic Bracket *Solid State Phenom.* **266**

[17] Zhang HF, Liu XW, Zhao M, Wang DB, and Shi CZ 2013 Fabrication of Super-Hydrophobic Surface on Stainless Steel Using Chemical Etching Method. *Key Eng Mater*

[18] Liu Y, Zhang K, Yao W, Liu J, Han Z and Re L 2016 Bioinspired structured superhydrophobic and superoleophilic stainless steel mesh for efficient oil-water separation. *Colloids Surfaces A Physicochem Eng Asp.* **500**

[19] Hadidi M, Bigham A, Saebnoori E, Hassanzadeh-tabrizi SA and Rahmati S 2017 Electrophoretic-deposited hydroxyapatite-copper nanocomposite as an antibacterial coating for biomedical applications *Surf. Coat. Technol.* **321**

[20] Gonzalez-mateos A, Bulcke F, Santofimia-casta P and Dringen R 2015 Modulation of copper accumulation and copper-induced toxicity by antioxidants and copper chelators in cultured primary brain astrocytes *J Trace Elem. Med. Biol.* **32**

**Acknowledgments**

Authors would like to thanks to Universitas Indonesia for financial support through HIBAH PITTA (747/UN2.R3.1/HKP.50.00/2017) and Directorate Research and Community Services Universitas Indonesia (DRPM UI)