Corrosion Resistance of Stainless-Steel Temporary Anchorage Device (TAD) Immersed in Fluoride, Povidone Iodine, and Chitosan Mouthwashes: in Vitro Study

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Abstract

This study aims to evaluate the corrosion resistance of stainless-steel (SS) TAD after immersion in three mouthwash solutions marked by topography surface and atomic composition.

Twenty-eight-unit stainless steel TADs were divided into 4 group of mouthwashes (0,2% sodium fluoride, 1% povidone iodine, 1,5% chitosan, and distilled water as control group) each consisting of 7 TADs. After 3 months of immersion, the corrosion resistance of SS TAD will be evaluated using Scanning Electron Microscope (SEM) to analyse the surface topography and Energy-Dispersive x-ray Spectroscopy (EDS) to investigate the atomic composition.

SEM images showed no significant difference between the surface topography of SS TAD after immersion in sodium fluoride, povidone iodine, and distilled water as they exhibit surface roughness and the presence of pitting/intergranular corrosion. However, SS TAD immersed in chitosan solution only displayed surface roughness without any sign of pitting/intergranular corrosion. EDS examination showed no significant difference between the atomic composition of SS TAD immersed in all mouthwash solutions.

Immersion of SS TAD 316L in three different mouthwashes induced corrosion process which is shown by the surface roughness after 3 months of immersion. Sodium fluoride and povidone iodine mouthwash have shown to be more corrosive, while chitosan mouthwash was the least corrosive. SS TAD 316L displayed good biocompatibility which is shown by minimal release of nickel and chromium ions on all TAD samples after immersion.

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Introduction

Temporary Anchorage Device (TAD), particularly mini screw type, is an additional skeletal anchorage used in orthodontic field that gains popularity in recent years due to its ease of placement and versatility.[1,2] TAD will be used in the oral cavity for lengthy period, therefore TAD need to have good corrosion resistance to prevent the release of metal ions into the oral cavity which in turn can interfere with the biocompatibility of the TAD material.[3]

Oral cavity environment tends to stimulate corrosion (biodegradation) of metallic orthodontic materials due to several factors such as dietary intake, temperature, quantity and quality of saliva, pH of oral cavity, and the mouthwash solution used.[3,4] Metal ions released from orthodontic appliance may enter the bloodstream causing various health problems, and inducing allergic reaction. The corrosion of the metal itself will also cause gradual destruction of material and weaken the metal which eventually lead to mechanical failure of TAD.[4,5,6] Nickel and chromium ion are known as allergen for human body, therefore their release is often considered as the cause of allergic reaction and contributing factor to mechanical failure.[5,7] However, some studies have shown that nickel and chromium also act as stabilizer to maintain the austenitic phase and they also play important role in corrosion resistance of SS.[8]

One of the TAD materials used in the orthodontic field is made of stainless steel (SS).[9]

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SS TAD has advantages in good physical and mechanical properties, thereby reducing the risk of fracture during installation and removal of TAD.[7,9,10] Stainless steel has a defense mechanism against corrosion by forming a protective oxide layer, namely Cr_2O_3, on the metal surface.[3] This protective oxide layer is very susceptible to mechanical and chemical disruption, i.e. it can dissolve when exposed to an acidic oral environment and fluoride-containing products such as toothpaste and mouthwash.[3]

During orthodontic treatment, plaque build-up often occurs on the tooth surface around orthodontic devices so that patients tend to be more susceptible to caries.[11] The most frequently recommended mouthwash in orthodontic treatment is fluoride solution because it has good antibacterial effect and stimulates enamel remineralization process so as to prevent caries.[12] Ever since covid-19 pandemic emerged, gargling with povidone iodine solution has become a standard procedure that must be carried out every time patient come for orthodontic visit to reduce the transmission of the covid-19 virus.[13,14,15] Recently, a biocompatible and non-toxic mouthwash is being developed, namely chitosan solution, which derived from crustacean (shrimp and crab) shells. [16,17] Chitosan has great potential to be used as an alternative mouthwash because apart from having antibacterial properties that are not inferior to fluoride, the basic ingredients of chitosan are abundantly available in Indonesia.[16,17]

Many studies have shown that fluoride ion can damage the protective system of the passive film Cr_2O_3 on SS metal resulting in corrosion and release of metal ions.[6] However, experimental studies of PVP-I and Chitosan effect on SS metal are still very limited. This study is aimed to see the effect of using these three mouthwashes (fluoride, povidone iodine, and chitosan) on the corrosion resistance of stainless steel TAD and the release of nickel and chromium ions so the safety of using these mouthwashes and the biocompatibility of SS TAD in the oral cavity can be confirmed.

Materials and methods

Twenty-eight TADs made of stainless steel (Mico One, Ze Fang Group, Taiwan) with head diameter and length of 10x2 mm were used as samples in this study. The mouthwashes used in this study were 0,2% sodium fluoride (Pepsodent Expert Protection Pro Complete, PT Unilever, Indonesia), 1% Povidone Iodine (BETADINE®, PT Mahakam Beta Farma, Indonesia), 1,5% Chitosan (KITOBE™, CV EcoShrimp, Indonesia), and distilled water (Aqua Pro Injection Sterile, PT Ikapharmaindo Putramas, Indonesia) used as control group.
These 28 samples of SS TADs were then be divided randomly into 3 subgroups of mouthwashes (0,2% Sodium Fluoride, 1% Povidone Iodine, and 1,5% Chitosan Mouthwash) each consisting of 7 SS TADs and 1 control group (distilled water) using 7 SS TAD. These TAD samples of each group were immersed in their respective solutions for 3 months (Fig.1).


a. b. c.

Figure 1. (a) Stainless Steel TAD, (b) Four groups of mouthwashes, (c) SS TAD samples immersed in four mouthwash groups.

By the end of 3rd month, TAD's surface topography and atomic composition are then evaluated to observe any sign of corrosion. SEM (Scanning Electron Microscope) will be used to investigate any surface roughness or porosity on TAD's surfaces with FEI type Inspect F50 (50x to 5000x magnification), and the reduction of atomic composition in tested TAD will be analysed using EDS (Energy Dispersive Spectrometer) with EDAX type Apollo X at Center for Materials Processing and Failure Analysis, University of Indonesia.

The data was processed and analysed statistically using SPSS version 20 software (IBM Corp., Armonk, USA). Test of Normality was calculated with Saphiro-Wilk to see the normal distribution of the data. Mann Whitney and Kruskal Wallis tests were performed to compare the mean atomic percentage of Fe, Cr, Ni, Mo, and C in the four groups. Fisher's exact test was used to identify significant differences between surface topography of TAD samples in each group, using smooth, rough, and pitting/intergranular corrosion. P-*value* < 0.05

was defined to be statistically significant for all the tests.

Results

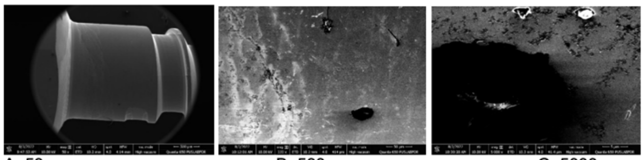
Scanning Electron Microscopy (SEM)

The results of the SEM test on seven SS TAD samples exposed to 0,2% sodium fluoride (NaF) solution and 1% povidone iodine (PVP-I) solution showed that all samples had rough surfaces accompanied by the presence of corrosion products deposited on the metal surface (Fig. 2 and Fig. 3). In addition, there were four samples (57,1% of the total sample) with corrosion pits which spread through the intergranular corrosion connecting different pits. The results of SEM test on seven TADs exposed to 1,5% chitosan solution showed that all samples formed deposits of corrosion products with a rough surface, but no pitting/intergranular corrosion was seen (Fig. 4). While the TADs on the control group (distilled water) showed small pitting corrosion scattered on the metal surface, as well as visible deposits of brightly coloured corrosion products in several areas (Fig. 5). The comparison of TAD's surface topography in four test groups can be seen in Table 1.

Mouthwash	Smooth surface	Rough surface	Pitting/intergranular corrosion	*P-value*
Sodium Fluoride (n=7)	0	3 (42.9%)	4 (57.1%)	1.000
Distilled water (n=7)	0	3 (42.9%)	4 (57.1%)	
Povidone Iodine (n=7)	0	3 (42.9%)	4 (57.1%)	1.000
Distilled water (n=7)	0	3 (42.9%)	4 (57.1%)	
Chitosan (n=7)	0	7 (100%)	0	0.023*
Distilled water (n=7)	0	3 (42.9%)	4 (57.1%)	
Sodium Fluoride (n=7)	0	3 (42.9%)	4 (57.1%)	1.000
Povidone Iodine (n=7)	0	3 (42.9%)	4 (57.1%)	
Sodium Fluoride (n=7)	0	3 (42.9%)	4 (57.1%)	0.023*
Chitosan (n=7)	0	7 (100%)	0	
Povidone Iodine (n=7)	0	3 (42.9%)	4 (57.1%)	0.023*
Chitosan (n=7)	0	7 (100%)	0	

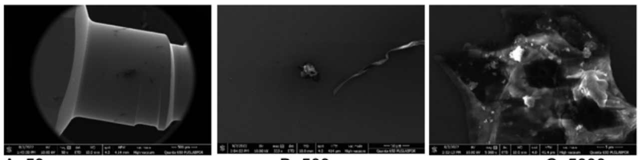
Table 1. Comparison of surface topography of SS TAD after 3 months immersion in 0,2% NaF, 1% PVP-I, 1,5% Chitosan, and Distilled water, observed by SEM. * $P<0.05$, significant difference between chitosan group with the control group, and the other test groups.

Statistical results from SEM test showed that there was no statistically significant difference in the surface topography of the SS TAD between the 0,2% sodium fluoride solution group and the control group ($p>0.05$), or between the 1% povidone iodine solution group and the control group ($p>0.05$). However, there was a statistically significant difference in the surface topography of the SS TAD between the 1,5% chitosan solution group and the control group ($P<0.05$). Therefore, immersion of SS TAD in all test groups appeared to induce corrosion after three months, but the TAD samples in chitosan solution showed the least corrosion among these four tested solutions.



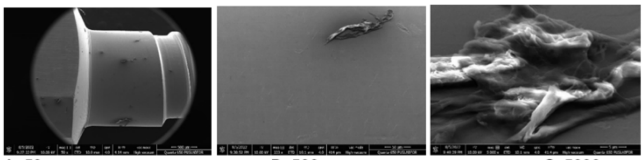
A. 50x B. 500x C. 5000x

Figure 2. Surface topography representation of head and neck of SS TAD 316L in sodium fluoride 0,2% assessed by SEM with magnification (A) 50x; (B) 500x, dan (C) 5000x.



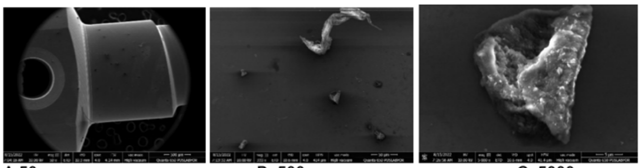
A. 50x B. 500x C. 5000x

Figure 3. Surface topography representation of head and neck of SS TAD 316L in povidone iodine 1% assessed by SEM with magnification (A) 50x; (B) 500x, dan (C) 5000x.



A. 50x B. 500x C. 5000x

Figure 4. Surface topography representation of head and neck of SS TAD 316L in Chitosan 1,5% assessed by SEM with magnification (A) 50x; (B) 500x, dan (C) 5000x.



A.50x B. 500x C. 5000x

Figure 5. Surface topography representation of head and neck of SS TAD 316L in distilled water assessed by SEM with magnification (A) 50x; (B) 500x, dan (C) 5000x.

Energy-Dispersive Atomic X-Ray Spectroscope (EDS)

The EDS test for each sample was

carried out 2 times, i.e. in areas with smooth surface and areas which were corroded or had deposits of corrosion products. Statistical test results from the EDS test showed that there was no difference in the atomic composition of the metal surface of SS TAD between after exposure to 0.2% sodium fluoride solution, 1% povidone iodine, 1,5% chitosan, and distilled water.

EDS test for non-corroded areas (smooth surface) shows that Fe (56-60%), Cr (16-17%), Ni (14-16%), and Mo are the major elements, while C, Mn, S, Si, and Al were minor elements. In the corroded area there is a significant decrease in the atomic composition of Fe (5-19%), Cr (2-8%), Ni (0.6-4%), and Mo (0.5-1.5%), while the carbon (C) and oxygen (O) increased dramatically.

Discussion

The duration of 3 months immersion time is based on Mandsaurwala's research (2015) which assumes that every time patient rinses his mouth with a mouthwash, the solution will stay in the patient's mouth for 6 hours.[18] If the patient rinses his mouth once a day (30x per month), and TAD is used for one year (12 months), it is estimated that the mouthwash is in the patient's mouth for 6 x 30 x 12 = 2160 hours, so the required time for this in vitro research is 2160 hours: 24 hours/day = 90 days (rounded up to 3 months).

The corrosion resistance of SS TAD was examined using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) to see changes in the surface topography of SS TAD and changes in its atomic composition after immersion in the test solution. This is based on the assumption that corrosion starts from the surface of the metal.

The results of the SEM examination showed that immersion of SS TAD 316L in three mouthwash solutions caused a change in the surface topography of the stainless steel. SS TAD samples of sodium fluoride and povidone iodine test group at 50x magnification showed surface roughening on all SS TAD samples, and at 500x and 5000s magnification, deposits of corrosion products were also visible in three samples, while the presence of intergranular corrosion and pitting corrosion were seen in the other four samples. A rough surface indicates that the protective oxide layer has been lost, causing a chemical reaction with the saliva.[19] Along with the release of ions from the metal surface, corrosion of orthodontic materials causes the metal surface to become rough which in turn can weaken the strength of the metal.[3]

Pitting corrosion in orthodontic metal materials often occurs due to aggressive attack from halogen ions on saliva or from dietary/fluid intake.[20] During the manufacturing process of orthodontic material, sometimes there are also factory defects which can act as the sites for the corrodent to form pits due to breakage of the protective oxide layer in that area.[6,21] Whereas in samples immersed in 1,5% chitosan solution, no pitting or intergranular corrosion was seen, only corrosion deposits with rough surface. Statistical tests confirmed that there was no significant difference in the surface topography of the TAD between the NaF and PVP-I test solutions, but there were significant differences between NaF and PVP-I test solutions with chitosan. As for the deposition of corrosion products on the surface of SS metal, it is actually a defence mechanism to decrease the rate of further corrosion.[21] This finding is in accordance with the research conducted by Erna et al (2017) that chitosan functions as a metal coating so that it inhibits corrosion on metal surfaces.[22] Thus, the SEM test results showed that immersion of SS TAD 316 L in the three mouthrinse solutions triggered a corrosion process that can be seen from changes in the topography of the stainless steel metal surface. NaF and PVP-I solutions are more aggressive, while chitosan solutions are the least corrosive.

The EDS test for each sample was carried out two times, namely in areas with smooth surfaces and areas that were corroded or had deposits of corrosion products. On the smooth surface of TAD SS, it can be seen that the main metal composition is still dominated by Fe (56-60%), Cr (16-17%), and Ni (14-16%) which indicates that the release of ions occurs very minimally on the fine surface. On the metal surface in the area of corrosion deposits, corrosion holes, or factory defects, there was a significant decrease in the atomic composition of Fe (5%-19%), Cr (2%-8%), Ni (0,6%-4%), and Mo (0,5% – 1,5%), while the content of C (55%-75%) and O (14%-24%) increased considerably. The increase in the content of C and O atoms indicates that the corrosion deposit is an oxide formed on the metal surface.[21] The protective oxide layer, namely Cr2O3, plays a very important role in the corrosion resistance of SS metals. [8,20]

Based on the results of the EDS statistical test, there was no significant difference in the atomic composition of TAD immersed in sodium fluoride, povidone iodine, chitosan, and distilled water for 3 months. In other words, this study found that SS AISI 316 L underwent corrosion process and released Fe, Cr, Ni, and Mo ions in all mouthwashes (sodium fluoride, povidone iodine, chitosan, and distilled water) with almost the same changes in atomic composition in all four test groups. The explanation for this phenomenon is that although this protective oxide layer is formed on the surface of the metal, metal ions can still be released because this protective oxide layer is susceptible to mechanical and chemical interference.[3] Some studies have reported that acidic environmental conditions and the presence of fluoride ions can dissolve the surface oxide which in turn causes pitting corrosion.[4,6,23] This finding is in line with a study conducted by Monica Pereira which showed that SS metal became more susceptible to corrosion in the presence of fluoride.[5] Iodine, like fluoride, is a halide ion which is often used as an antiseptic for wound healing.[24] Research conducted by Tsukaue et al also showed similar results, indicating SS 316 and 304 underwent corrosion in iodine solution and when exposed to iodine vapor.[25,26]

Halide ions (F, Cl, Br, I) are corrosive by attacking the oxide film layer on the metal through the chemical reaction $FeCl_2+2H_2O \rightarrow Fe(OH)_2+2HCl$ where the Cl atom represents other halide ions.[27,28] Migration of halide ions through hydrolysis reactions will cause a decrease in the pH (acidification) of the surrounding environment so that the metal will become porous. The level of aggressiveness of the halide ions in causing pitting corrosion can be sorted as follows : $Cl^- > Br^- > F^- > I^-$.[27] Chitosan is mentioned in many literatures to have an anti-corrosion effect and is utilized as an anti-corrosion coating on various metals.[22,29,30] However, the research results still showed the release of Fe, Cr, Ni, Mo ions even though the amount was small. There has been no previous research that examined the corrosion resistance of SS metal to immersion in chitosan solution for a long period of time so that it could be used as a comparison for this study. Another important information obtained from this study is that there was no significant decrease in Cr and Ni levels on smooth metal surfaces. This is in line with a literature study conducted by Rahilly, G et al who found that the crystal lattice of SS metal tightly binds nickel ions so that they are not easily separated from the metal surface even though the SS metal has a high nickel content.[3,31] It was concluded that the Ni and Cr atoms in SS TAD 316L were bound in the alloy quite stably so the risk of nickel or chromium allergy due to the release of these two ions was minimal.

Distilled water was chosen as the control group in this study by assuming that the patient rinses his mouth with plain water every day. In addition, distilled water is also a type of purified water so it is free of corrosive substances and ions.[32] However, this study showed that samples immersed in distilled water as a control also experienced pitting corrosion and ion release. This is similar to the findings of Mostafa (2016) who found that SS soaked in distilled water is free of ions so that it tends to attract ions from the metals around it to achieve equilibrium.[32]

The clinical relevance of in-vitro corrosion resistance study is still debated. In this study, a mouthwash was used under static conditions, but in the real clinical situation of the oral cavity there are dynamic factors that were not included in this in-vitro study such as the rate of saliva in the mouth, changes in pH due to various food and drink intakes, bacterial colonization and its by-product, the interaction of TAD with other metals such as ligature wire or closed coil springs, as well as mechanical friction such as brushing teeth. All these factors may influence corrosion resistance of SS TAD in different ways.

Conclusions

There was no difference between the surface topography of TAD made of stainless steel metal after exposure to Fluoride, Povidone Iodine, and control solutions (distilled water). However, different results were obtained in the chitosan solution immersion samples. The surface topography of SS TAD exposed to sodium fluoride solution became rough with pitting/intergranular corrosion formed, while SS TAD exposed to chitosan solution only experienced surface changes, i.e. increase in surface roughness without pitting/intergranular corrosion. There is no difference between the atomic composition of TAD made of stainless steel after exposure to fluoride, povidone iodine, chitosan, and distilled water (control) solutions. The atomic composition of Fe, Cr, Ni, Mo elements decreased, while the C and O elements increased after immersion in sodium fluoride, povidone iodine, chitosan, and distilled water (control).

Declaration of Interest

The authors report no conflict of interest.

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