COMPARISON OF SURFACE PROCESSES APPLIED TO PRESERVE THE HYDROPHILIC PROPERTY OF IMPLANTS

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Today, studies are carried out on many surface modification techniques to improve the surface properties of dental implants. The common goal of all these studies is to increase cell retention on the implant surface and to perform implantation with high biomechanical properties and biocompatibility. Anodized implants are hydrophilic due to their surface properties. The hydrophilic nature of the implant surface has been found to be beneficial for osseointegration in many studies. After the implant surface anodization process, the hydrophilicity on the surface is at the highest level and the hydrophilic feature on the surface decreases as it comes into contact with air. Many commercially hydrophilic implants lose their hydrophilic properties early in their shelf life. Researchers are in search of longer preservation of hydrophilic properties in implants. In our study, we aimed to preserve the hydrophilic feature on the titanium surface for a longer time by forming a thin layer of NaCl on the surface by cleaning the Ti Gr4 1cm³ plate pieces immediately after the micro-arc oxidation process and dipping them into isotonic NaCl solution. The study was done in 5 groups. In the first group, titanium was cleaned after the micro-arc oxidation (MAO) process and the water contact angle (WCA) on the surface was measured. The remaining 4 groups were divided as MAO applied and 15 days passed, MAO + NaCl applied and 15 days passed, MAO applied and 30 days passed, MAO + NaCl applied and 30 days passed. Water contact angle measurements were made for all groups and their hydrophilic properties were compared. In our experiment, the highest WCA was found in the parts measured immediately after anodization in the first group. Titanium surfaces coated with NaCl showed 14% lower WCA after anodization compared to untreated titanium after 15 days. In the 30-day groups, 20% lower WCA was found in the titanium treated with NaCl compared to the untreated ones. NaCl treatment on the hydrophilic surface of titanium helped to preserve its hydrophilic property over time. In this study, it was observed that the hydrophilic properties on the surface of the implants that were treated with NaCl for the first time on hydrophilic titanium were preserved for a longer period of time. We propose to increase the osseointegration quality by performing such applications on hydrophilic implants.

Keywords: dental implants, surface treatments, hydrophilic

BACKGROUND & AIM

Due to its strong corrosion resistance and excellent biocompatibility, titanium (Ti) is a material that is frequently used in orthopedic and dental implants (Adell *et al.*, 1990). Due to titanium oxide's (TiO₂) capability to create bone-like apatite in a body environment, TiO₂ has been demonstrated to exhibit strong physicochemical bonding between a Ti implant and live bone (Hazan *et al.*, 1993). When exposed to air and atmospheric water vapor, an oxide surface layer with a thickness of 1.5-10 nm naturally develops on titanium (Sul *et al.*, 2001). TiO₂ can have crystalline or amorphous forms, depending on the manufacturing conditions. Crystalline oxides, such as rutile and anatase, exhibit a number of unique characteristics, including photocatalytic behavior, super hydrophilicity, and biocompatible characteristic (Diamanti *et al.*, 2015). As a result of the mechanical qualities, corrosion resistance, non-biotoxicity, and biocompatibility, anodic oxidation is used to alter the surfaces and properties of titanium (Abdullah and Sorrell, 2007). The controlled formation of an oxide layer surface substantially thicker than that formed naturally is made possible by anodic oxidation of titanium. Depending on the

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circumstances, including the electrolyte type, solution concentration, and applied voltage, these coatings may be thick or porous, amorphous or crystalline (Jaeggi *et al.*, 2005). Sulphuric and phosphoric acids are the electrolytes that are most frequently used to anodize titanium.

Anodized implants are hydrophilic due to their surface properties. The hydrophilic nature of the implant surface has been found to be beneficial for osseointegration in many studies. After the implant surface anodization process, the hydrophilicity (Vangolu *et al.*, 2011) on the surface is at the highest level and the hydrophilic feature on the surface decreases as it comes into contact with air. Many commercially dry-state hydrophilic implants lose their hydrophilic properties early in their shelf life. Researchers are in search of longer preservation of hydrophilic properties in implants (Lüers *et al.*, 2016). In our study, we aimed to preserve the hydrophilic feature on the titanium surface for a longer time by forming a thin layer of NaCl.

MATERIALS AND METHODS

Preparation: The 200 samples was prepared by wet hand-polishing Cp-Ti foils (unknown source, China) with dimensions of 10 mm x 10 mm x 0.5 mm, immersion in an ultrasonic bath with acetone for 10 minutes, washing with distilled water, and compressed air drying. In an electrochemical cell with 4 L %10 concentration of aqueous solution of H_3PO_4 (Birpa, 85 wt%).



Figure 1. Ti Gr4 1cm³ plate pieces

Anodization: Titanium sheets dipped into microarc solution. Power source generated 110v DC, 10A through anode. For cathode we used stainless steel plate. Titanium plates stayed for 1 hour in the anodization process. After anodization all samples cleaned in a 180W ultrasonic bath for 20 minutes in distilled water. Then dried with air pressure. Except for MI group, other groups dipped in the isotonic 0,9 NaCl solution.

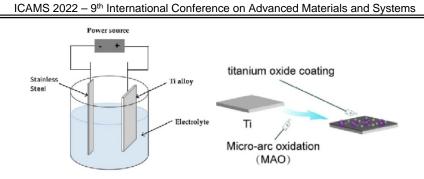


Figure 2. Ti anodizing process

The study was done in 5 groups. Every group have 40 samples. In the first group, titanium was cleaned after the micro-arc oxidation (MAO) process, and the water contact angle (WCA) on the surface was immediately measured after cleaning (MI). The remaining four groups were divided as MAO applied and 15 days passed (M15), MAO + NaCl applied and 15 days passed (MN15), MAO applied and 30 days passed(M30), MAO + NaCl applied and 30 days passed. All groups were held in the dry state in the open air. Water contact angle measurements were made for all groups and their hydrophilic properties were compared.

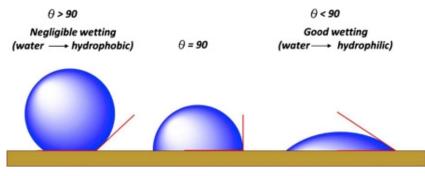


Figure 3. Water contact types

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Figure 4. Contact angle samples of groups. A:MI, B:M15, C:MN15, D:M30, E:MN30

Table 1. Contact angle table of groups

Group	Lowest WCA	Highest WCA	Average	SD
MI	15,61	17,22	16,28	
M15	34,31	42,66	37,52	15,01
MN15	28,13	36,41	32,26	11,29
M30	64,58	71,11	67,25	36,04
MN30	48,18	61,74	53,80	26,53

A few standard methods for analyzing surface wettability have been modified for titanium implant surfaces. The sessile drop technique, which involves placing a drop of the desired wetting liquid on the surface of the specimen and measuring the angle between the tangent of the drop at the solid/liquid/gas three-phase boundary and the horizontal baseline of the solid surface, is the most popular method for understanding the wetting behavior of a given solid material. The so-called contact angle (CA) measures how well the surface has been moistened by the particular liquid being utilized.

In our experiment, as we expect the highest WCA was found in the parts measured immediately after anodization in the first group (MI). The (MI) group shows average of 16,28 degrees WCA. When 15 days passed the M15 group lost some hydrophilicity. WCA decreases from an average 16,28 to 37,52 degrees. Titanium surfaces coated with NaCl showed 14% lower WCA after anodization compared to untreated titanium after 15 days. In the 30-day groups, the M30 group loses more hydrophilicity. WCA degreeses

from 15-day average of 37,52 to 67,25 degrees. 20% lower WCA was found in the titanium treated with NaCl compared to the untreated ones. NaCl remains on the titanium surface as a thin layer. This thin salt layer helps to keep hydrophilicity over time in dry state. It should be also the hydrophilic property of salt. TiO₂ layer itself has less durable hydrophilic property over time.

CONCLUSION

Salts are generally dissolves in water. When making a salt layer on some surface, the water first dissolves that salt that bound to surface. So it expected to give some hydrophilic properties (Ali *et al.*, 2022). Immediately anodized titanium, the hydrophilic state high at the TiO₂ surface. NaCl solution absorbed to the surface through deep in nanoholes with high hydrophilic energy and when dried, all nanotubes filled with hydrophilic salt molecules. NaCl treatment on the hydrophilic surface of titanium helped to preserve its hydrophilic property over time in dry state. In this study, it was observed that the hydrophilic titanium were preserved for a longer period of time. Lüers *et al.* (2016) also get similar results in their experiment with MgCl₂, CaCl₂, PBS, and KPB types salts. We know that hydrophilic feature is good for osseointegration in previous studies. We suggest salt layers to increase the osseointegration quality by performing such applications on hydrophilic implants.

REFERENCES

- Abdullah, H.Z. and Sorrell, C.C. (2007), "Preparation and Characterisation of TiO₂ Thick Films Fabricated by Anodic Oxidation", *Materials Science Forum*, 561–565, 2159–2162, https://doi.org/10.4028/www.scientific.net/MSF.561-565.2159.
- Adell, R., Eriksson, B., Lekholm, U., Brånemark, P.I. and Jemt, T. (1990), "Long-Term Follow-Up Study of Osseointegrated Implants in the Treatment of Totally Edentulous Jaws", *International Journal of Oral & Maxillofacial Implants*, 5, 347–59.
- Ali, M.A., Volmert, B., Evans, C.M. and Braun, P.V. (2022), "Static and Dynamic Gradient Based Directional Transportation of Neutral Molecules in Swollen Polymer Films", *Angewandte Chemie International*, 61(41), e202206061, https://doi.org/10.1002/anie.202206061.
- Diamanti, M.V., Ormellese, M. and Pedeferri, M. (2015), "Application-Wise Nanostructuring of Anodic Films on Titanium: A Review", *Journal of Experimental Nanoscience*, 10(17), 1285–1308, https://doi.org/10.1080/17458080.2014.999261.
- Hazan, R., Brener, R. and Oron, U. (1993), "Bone Growth to Metal Implants is Regulated by Their Surface Chemical Properties", *Biomaterials*, 14, 570–574, https://doi.org/10.1016/0142-9612(93)90172-X.
- Jaeggi, C., Kern, P., Michler, J., Zehnder, T. and Siegenthaler, H. (2005), "Anodic Thin Films on Titanium Used as Masks for Surface Micropatterning of Biomedical Devices", *Surface and Coatings Technology*, 200, 1913–1919, https://doi.org/10.1016/j.surfcoat.2005.08.021.
- Lüers, S., Laub, M. and Jennissen, H.P. (2016), "Protecting Ultra- and Hyperhydrophilic Implant Surfaces in Dry State from Loss of Wettability", *Current Directions in Biomedical Engineering*, 2(1), 557–560, https://doi.org/10.1515/cdbme-2016-0123.
- Sul, Y.T., Johansson, C.B., Jeong, Y. and Albrektsson, T. (2001), "The Electrochemical Oxide Growth Behaviour on Titanium in Acid and Alkaline Electrolytes", *Medical Engineering & Physics*, 23(5), 329– 346, https://doi.org/10.1016/S1350-4533(01)00050-9.
- Vangolu, Y., Alsaran, A. and Yildirim, O.S. (2011), "Wear properties of Micro Arc Oxidized and Hydrothermally Treated Ti₆Al₄V Alloy in Simulated Body Fluid", *Wear*, 271, 2322–2327, https://doi.org/10.1016/j.wear.2010.12.039.

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