EVALUATION AND COMPARISON OF MECHANICAL AND CHEMICAL SURFACE MODIFICATIONS OF COMMERCIAL TITANIUM FOR ORTHODONTIC IMPLANTS"

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ABSTRACT:. **Objective**: The study evaluated two different methods of modification of titanium surface by blasting with various materials and by acid etching with different acids and to compare the surface roughness levels, surface wettability and surface configuration of variously treated surfaces of titanium. **Materials and methods:** Commercially pure titanium (Grade I) sheets of 0.2mm thick and 4.5mm diameter are used for this study. Blasting of the titanium substrates with various blasting materials is done using Alumina, Hydroxyapatite, and Tricalcium phosphate, Acid etching with Hydrofluoric acid, Hydrochloric acid and sulfuric acid .Surface roughness levels were measured with the help of surface profilometer and surface analyzer. Surface wettability is measured with help of contact angle measurement using light microscope and surface configuration was determined with the help of scanning electron microscopy. **Results:** Titanium sheets Blasted with alumina (100μ), and dual etched with HCL+H2SO4 Showed highest surface roughness values, samples, blasted with biphasic material (combination of Hydroxyapatite and tricalcium phosphate) showed uniform rougher surface in scanning electron pictomicrograph. And Samples blasted with biphasic material and those treated with Hydrofluoric acid 2% showed lowest contact angle Measurements. **Conclusion:** The modification of the titanium surface by both chemical and mechanical methods, have shown the uniform surface roughness and increase in the surface area of the samples.

KEYWORDS: Biphasic material, surface analyzer ,surface modification, surface profilometry.

INTRODUCTION

Titanium has been used in dentistry for over 30 years although use in surgery has been reported even earlier. Per-Ingvar Branemark began his initial research in to the development of a dental implant system nearly a century ago in 1960 and strongly suggested the possibility of osseointegration[1]. Titanium encourages the formation of bone and it's bonding directly to the implant. A strong tissue – implant bond may be chemical or micro-mechanical in nature and there may be interplay between surface morphology and chemical composition. The bonding between the living bone and the surface of the load bearing implant is believed to be important factor in implant success. Many factors contribute to this process and they include composition, surface texture, chemistry, and surface energy[2]. Bone fixation strategies of titanium and titanium alloy implants are being actively investigated. The success or failure of implant can be related not only to chemical properties of implant surface, but also to its micro morphologic nature. And the treatment outcomes in dental implantology, is dependent on surface designs[3]. The response of cells and tissues at implant interfaces can be affected by surface topography on a macroscopic basis as well as by wettability. Thus the aim of this study is to evaluate different methods of surface modification of the Titanium surface ,to compare the surface roughness level of variously treated surfaces of the Titanium, to measure the surface wettability of the variously treated surfaces of the Titanium and to determine the surface configuration of variously treated surfaces of Titanium .

Materials and Methods

Titanium plates of 4.5mm length X 4mm wide and 0.02mm thick are used for this study. Titanium plates are cut from the commercially pure (grade I) Titanium sheet that is provided by Mishra Datu Nigam Ltd Hyderabad. All the thirty five plates were standardized to 4.5mm length X 4mm wide and 0.02mm thick and are ultrasonically cleaned before being subjected to following surface modifications **(Fig.1.)**

I. **Mechanical treatment group**:

1. **Blasting the surface of the titanium with alumina[5]**

Alumina of 100 microns size particles is filled in the conventional sandblasting machine. Titanium sheet of 0.2mm-thickness and 4×4.5 mm diameter is fixed in the wooden frame that is specially made to hold the specimens. The wooden frame along with the specimen is held 5cm away from the blasting tip and blasting of the surface is done on both sides for 10 minutes at 80 Lb pressure**.(Fig.2.)**

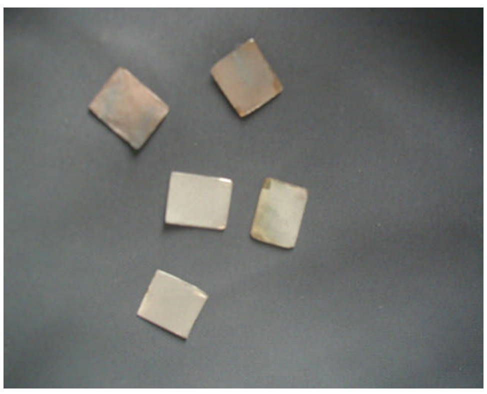


Fig.1. Titanium sheets of 4X4.5 mm

Fig.2. Blasting procedure

Fig.3. Acid etching procedure

2. **Blasting the surface of the titanium with Biphasic material (combination of Tricalcium phosphate and Hydroxyapatite[6]**

Sandblaster is cleaned thoroughly and filled with Biphasic material (150 microns). Titanium sheet of 0.2mm-thickness and 4×4.5 mm diameter is fixed in the wooden frame. The wooden frame along with the specimen is held 5cm away from the blasting tip and blasting of the surface is done on both sides for 10 minutes at 80 Lb pressure.

3. **Blasting the surface of the titanium with commercially pure Tricalcium phosphate. (TCP)[6]**

Sandblaster is cleaned thoroughly and filled with commercially available pure Tricalcium phosphate (120 microns). Titanium sheet of 0.2mm-thickness and 4×4.5 mm diameter is fixed in the wooden frame. The wooden frame along with the specimen is held 5cm away from the blasting tip and blasting of the surface is done on both sides for 10 minutes at 80 Lb pressure.

4. **Blasting the surface of the titanium with conventionally made Hydroxyapatite[6]**

Sandblaster is cleaned thoroughly and filled with Hydroxyapatite (120microns). Titanium sheet of 0.2mm-thickness and 4×4.5 mm diameter is fixed in the wooden frame. The wooden frame along with the specimen is held 5cm away from the blasting tip and blasting of the surface is done on both sides for 10 minutes at 80 Lb pressure.

II. Chemical treatment group:

1. **Acid treatment with Hydrofluoric acid:[7]**

2% of Hydrofluoric acid is prepared by diluting 2ml of concentrated acid with 98 ml of distilled water. Titanium sheet of 0.2mm-thickness and 4×4.5 mm diameter is fixed in the wooden frame and etched on the both the sides by placing it in the beaker containing 2% of hydrofluoric acid for 10 minutes. **.(Fig.3.)**

2. **Acid treatment with Hydrochloric acid and Sulfuric acid: [8]**

20% of Hydrochloric acid and sulfuric acid is prepared by mixing equal amount of 10% of HCL and H2SO4. Diluting 10 ml of concentrated acid in 90 ml of distilled water individually makes 10% of the acids. Titanium sheet of 0.2mm-thickness and 4×4.5 mm diameter is fixed in the wooden frame and etched on the both the sides by placing it in the beaker containing 20% of Hydrochloric acid and sulfuric acid for 10 minutes.

Fig.4. Surface profilometer

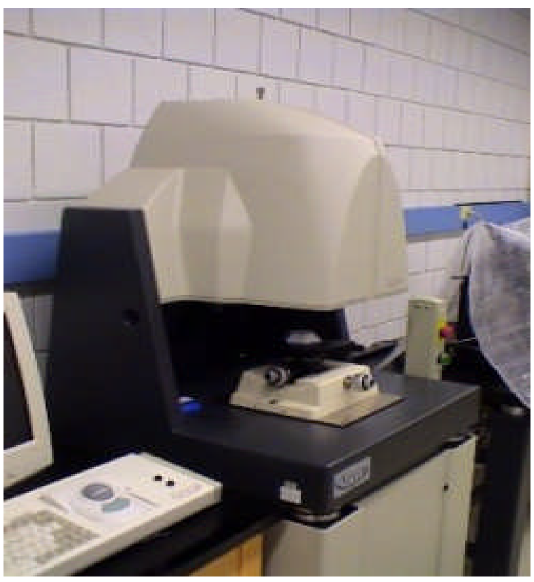


Fig.5. Surface analyzer

Fig.6. contact angle measured with optical microscope is shown on the computer screen attached to it

3. **Acid treatment with heat-treated Hydrochloric acid and Sulfuric acid[8]:**

20% of Hydrochloric acid and sulfuric acid is prepared by mixing equal amount of 10% of HCL and H2SO4. 10% of the acids are made by diluting, 10 ml of concentrated acid in 90 ml of distilled water individually. Heating the test tube does heat treatment of the acid, containing the acid and Titanium sheet of 0.2mm-thickness and 4×4.5 mm diameter on the direct flame intermittently for 10 minutes.

Methods of Measuring Surface Roughness[9]

Surface Profilometry[6]: Contact profilometry is method of measuring the surface texture of a material**.** MAHR Perthometer (S2) a surface textures measuring and recording instrument is used for this purpose**. (Fig.4.)**

Parts:

1. Stylus
2. Tracing head
3. Block made of metal
4. Microprocessor

The titanium sheets are positioned in the flat block made of metal, and stylus is attached to the tracing head.

All the samples were cleaned with distilled water in an ultrasonic cleaner for this study. The stylus is kept in contact with the long axis of the titanium sheets with various surface treatments and recordings were made for average 3.8mm length of all the sheets and microprocessor gives calculations and recordings of the surface roughness. Average Roughness (Ra): is the arithmetic mean of all values of the roughness profile 'R' with the measuring length lm**. (Graph.1)**

Surface Analysis[6]:

It is a non-contacting method of recording the surface of the substrate. Ultrasonically cleaned samples were placed on the plat form and surface topography is measured under 10^{-9} magnification and the computer image of the surface is made. The measurements of the roughness parameters are calculated by the microprocessor**. (Fig.5). (Graph. 2)**

Scanning Electron Microscopy[4]

The surface topography of all the surface modified samples is studied by coating it with gold and scanning them under the scanning electron microscope at high magnifications (500x, 2000x).

IV.. Method of Measuring Surface Wettability

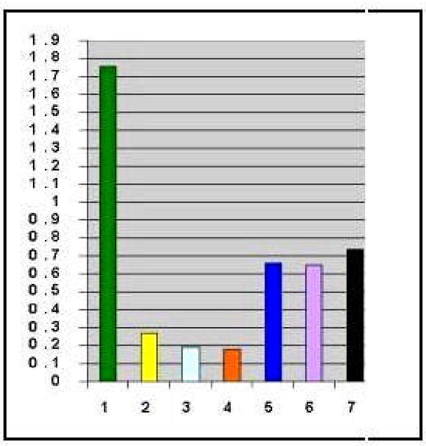
Contact Angle Measurement[7]:

One drop of distilled water was deposited on the surface of the modified sample, with the help of optical microscope **(Fig.6.)** two observers measured and calculated the

Table-I. Results for surface roughness measurements using surface profilometer

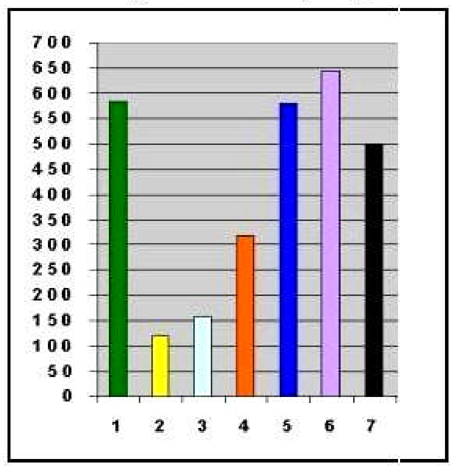
Surface Modified Samples	Sample 1 Ra	Sample 2 Ra	Sample 3 Ra	Sample 4 Ra	Sample 5 Ra	Mean Ra
GROUP 1	1.821µm	1.805µm	1.798µm	1.787µm	1.810µm	1.7568
GROUP 2	1.805µm	1.795µm	1.764µm	1.810µm	1.798µm	0.2722
GROUP 3	1.821µm	1.805µm	1.764µm	1.686µm	1.650µm	0.1940
GROUP 4	1.752µm	1.826µm	1.650µm	1.870µm	1.686µm	0.1806
GROUP 5	0.446µm	0.795µm	0.964µm	0.820µm	0.668µm	0.6630
GROUP 6	0.694µm	0.456µm	0.663µm	0.640µm	0.810µm	0.6526
GROUP 7	0.795µm	0.686µm	0.592µm	0.630µm	0.612µm	0.7386

Graph – 1
Roughness Measurement
(Surface Profilometer)



1 – AL_2O_3 blasted with 100 µ and 80 psi pressure
2 – Biphasic (TCP + HA) blasted 80 psi pressure
3 – Commercially pure Tricalcium phosphate(TCP) blasted
4 – Hydroxyapatite(HA blasted)
5 – Hydrofluoric acid 2% for 10 minutes
6 – HCL + H_2SO_4 20%
7 – Heat treated HCL + H_2SO_4 20%

Graph – 2
Roughness Measurement
(Surface Analyzer)



1 – AL_2O_3 blasted with 100 µ and 80 psi pressure
2 – Biphasic(TCP + HA)blasted 80 psi pressure
3 – Commercially pure Tricalcium phosphate(TCP) blasted
4 – HA blasted
5 – Hydrofluoric acid 2% for 10minutes
6 – HCL + H_2SO_4 20%
7 – Heat treated HCL + H_2SO_4 20%

Table-II. Results for surface roughness measurements using surface analyzer

Modification of the surface	Sample 1 Ra	Sample 2 Ra	Sample 3 Ra	Sample 4 Ra	Sample 5 Ra	Mean Ra
GROUP 1	649.59ηm	652.56ηm	470.12ηm	560.10ηm	586.85ηm	583.844
GROUP 2	106.02ηm	111.04ηm	114.12ηm	130.14ηm	140.56ηm	120.376
GROUP 3	124.08ηm	164.09ηm	148.36ηm	156.54ηm	196.04ηm	157.822
GROUP 4	259.02ηm	436.02ηm	400.22ηm	186.03ηm	312.12ηm	318.682
GROUP 5	649.59ηm	620.60ηm	570.50ηm	498.10ηm	560.12ηm	579.782
GROUP 6	649.67ηm	614.72ηm	716.82ηm	826.82ηm	416.12ηm	644.830
GROUP 7	543.62ηm	496.34ηm	642.68ηm	402.12ηm	416.13ηm	500.178

contact angles of three drops of water for each sample. The contact angles are obtained by following equation.

$$\theta = \tan^{-1}(2h/d)$$

Total specimens were divided in to 7 groups according to the surface modification. And 5 samples were done for each group.

Group 1: AL_2O_3 blasted with 100µ and 80-psi pressure
Group 2: TCP + HA blasted 80 psi pressure
Group 3: Commercially pure TCP blasted
Group 4: HA blasted
Group 5: Hydrofluoric acid 2% for 10 minutes
Group 6: HCL + H_2SO_4 20%
Group 7: Heat treated HCL + H_2SO_4 20%

Roughness average (Ra) and contact angle was totally measured for 60 samples.

Statistical Analysis

The statistical package SPSS-PC+ (Statistical package for social science, version 4.0.1) was used for statistical analysis. Mean was estimated for all the five samples for each study group. The mean values were compared by One way analysis for variance. Mean value is calculated by using this formula:

$$\text{Mean} = \frac{\sum x}{n}$$

$\Sigma\chi$= Sum of total readings for group
n= number of specimens

Results

Results for surface roughness measurements using surface profilometer and surface analyzer are tabulated. **(Table-1 and Table-2.)**. Results for surface wettability measurements using contact angle measurement are tabulated . Contact angle measurement will indicate the surface wettability of the samples.**(Table-3 and Graph.3)**

The surface roughness measurements with the help of surface profilometer revealed that samples treated with blasting with100µ alumina and showed highest mean roughness values **(Fig.7.).** The surface roughness measurements with the help of surface analyzer revealed that samples treated dual etching with hydrochloric acid and sulfuric acid showed highest mean roughness values. **(Fig.8.)**. The contact angle measurement revealed that samples blasted with biphasic material (TCP +HA) and treated with 2% hydrofluoric acid a showed lowest contact angle measurement. **(Table-3 and Graph.3)**

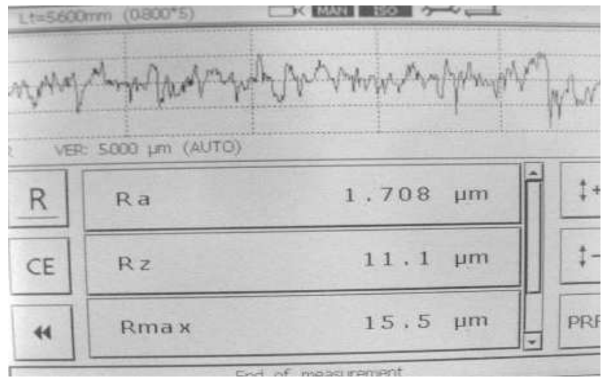


Fig.7.Samples treated with sand blasting showing higher roughness average (Ra) values

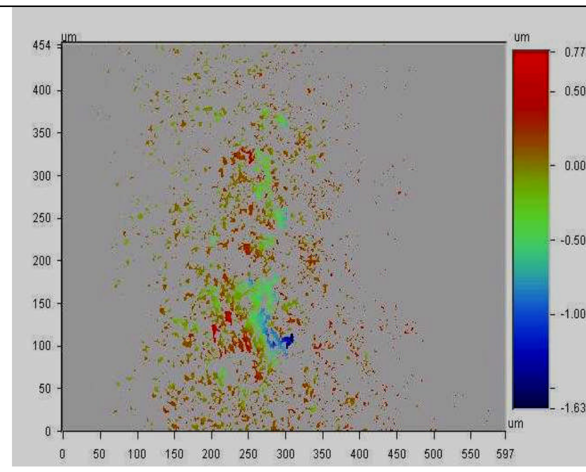


Fig.8. The image of sample treated with sand blasting revealing the deeper red and shallow green depressions and blue elevations on the surface

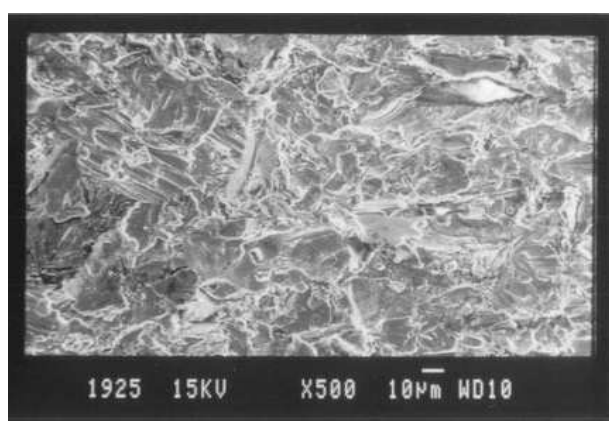


Fig.9. Scanning electron pictomicrograph of titanium surface blasted with alumina showing an uniform rougher configuration of the surface

Table-III. Results for surface wettability measurements using contact angle measurement

Modification of the surface	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Mean Contact angle
GROUP 1	105°	105°	109°	101°	98°	103.60
GROUP 2	65°	65°	60°	80°	64°	66.80
GROUP 3	90°	90°	85°	85°	80°	86.00
GROUP 4	90°	85°	85°	95°	80°	87.00
GROUP 5	76°	65°	74°	75°	68°	71.60
GROUP 6	85°	75°	80°	72°	80°	78.40
GROUP 7	77.5°	86.5°	78.2°	82°	74°	79.64

Discussion

Endosseous dental implants are available with various surface characteristics ranging from relatively smooth machined surface to rougher surfaces created by blasting with various substances, by acid treatments or combinations.

The objective of this study is evaluating two different methods of modification of the titanium surfaces, by mechanical and chemical procedures and comparing the roughness value, and surface wettability of variously treated samples.

Advantages of increased surface roughness on commercially pure titanium surfaces: [16]

1. Increased surface area of the implant adjacent to bone
2. Improved cell attachment to the implant surface
3. Increased bone present at the interface
4. Increased biomechanical interaction of the implant with the bone (surface area reduces stress next to the implant)

The above claims inspired us to investigate on different methods on surface modification and comparison of different surface treated samples of titanium. Changes in topography affect cell adhesion to the surfaces of similar chemistry. Types of cells that adhere to the surfaces are red blood cell and plate lets with in fibrin rich matrix. Platelet serves as an important role as carrier of abundant growth factors to direct wound healing. Davies hypothesized that the improved wettability and increased clot retention was measured at acid etched implant surfaces resulted in improved osseointegration.

The surface roughness and wettability can be altered or modified by modifying the surface of the titanium. There are two ways to modify the surface layer. Creation of convex texture, or concave texture.

This research project dealt with mainly with concave surface modification. Various methods of surface modifications of the titanium surface: [17]

I. **Mechanical treatment group:**

a. Blasting with alumina
b. Blasting with commercially pure Tricalcium phosphate:
c. Blasting with Hydroxyapatite
d. Blasting with Biphasic material (Tricalcium phosphate + Hydroxyapatite)

II. Chemical treatment group:

1. Hydrofluoric acid 2% for 10 min
2. Hydrochloric acid and Sulfuric acid 20% for 10 min
3. Heat activated Hydrochloric acid and Sulfuric acid 20% for 10 min (Dual etching)

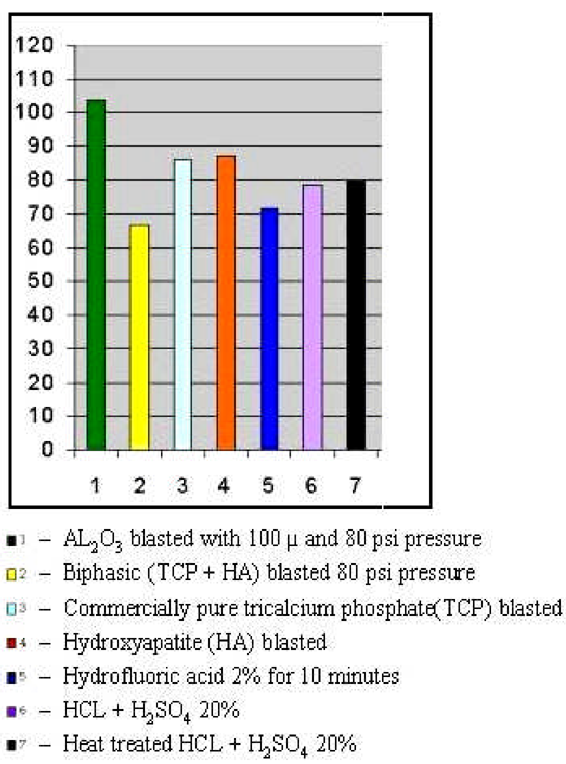
The surface modification was done in above-mentioned seven different ways for five samples each.

Tomas Albrektsson[15]studied on bone metal interface and stated that implant characteristics are very important for osseointegration. And Carl E Misch[18] stated that increase in surface area of implants would allow the use of shorter implants especially in posterior regions. Maurizio Piattelli[6] and coworkers studied the effect of blasting the surface of titanium with Resorbable blast material and concluded that there was increased implant contact for these surfaces when compared to machined surfaces.

In this study samples were blasted with hydroxyapatite, pure tricalcium phosphate and biphasic material (combination of H.A and T.C.P), the scanning electron microscopic studies of these samples showed a uniform thin coating of the material on titanium substrates **(Fig.9.).** Robert M London and [14]co workers determined that the dual etched surfaces achieved higher level of bone implant contact percentages; accordingly in this study, Samples were dual etched with heat-treated HCL and H_2SO_4 and profilometer studies showed good roughness values.

Young Jun Lim[17] and coworkers concluded that when the contact angles is greater than 45 degree contact angle increased linearly with roughness average (Ra) and when the contact angle is less than 45 degree it decreases linearly with Ra, to determine the relationship between the contact angle and roughness average, Contact angle of all the specimens were measured with distilled water and it is observed that contact angle decreased with the increase in roughness average. W. Aubreysoskolne[15] stated that cell adherence to rough titanium surfaces is greater than to the machines surfaces and Lyndon F.Cooper[14] stated that increased titanium surface topography improves the bone to implant contact and the mechanical properties of the enhanced interface, growing clinical evidence for increased bone to implant contact at altered implant surface confirms the advantages of the increased functional area.

Graph – 3
Contact Angle Measurement



The surface modifications of the titanium found to increase the surface area of titanium that would result greater surface coverage by bone. The contact angle representing the surface wettability also affects the bone implant contact.

Summary

This study evaluated different methods of surface modifications of the titanium and compared the surface roughness and surface wettability of variously treated surfaces of titanium. Titanium substrate with following treatments such as Blasting with alumina (100μ), and samples dual etched with HCL+H2SO4 Showed highest surface roughness values, Along with the above mentioned surface modified samples, surface blasted with biphasic material (combination of Hydroxyapatite and tricalcium phosphate) showed uniform rougher surface in scanning electron pictomicrograph. Measurement of the wettability of the surface is expressed by the contact angle. Samples blasted with biphasic material and those treated with Hydrofluoric acid 2% showed lowest contact angle Measurements.

CONCLUSION

1. The surface roughness measurements with the help of surface profilometer revealed that samples treated with blasting with100μ alumina and showed highest mean roughness values.
2. The surface roughness measurements with the help of surface analyzer revealed that samples treated dual etching with hydrochloric acid and sulfuric acid showed highest mean roughness values.
4. The scanning electron photomicrographs showed that samples blasted with alumina and biphasic material, showed uniform rough configurations of the surface.
5. The contact angle measurement revealed that samples blasted with biphasic material (TCP +HA) and treated with 2% hydrofluoric acid a showed lowest contact angle measurement.

Acknowledgement

We express our heartfelt gratitude and deep sense of indebtedness to **Prof. Dr. E. Munirathnam Naidu,** Principal and H.O.D, Prosthodontics. Meenakshi Ammal Dental College, Chennai.

References

1. Per -Ingvar Branemark, Osseo integration and its experimental background. Journal of prosthetic dentistry. 1983; 50: 399 – 409. http://dx.doi.org/10.1016/S0022-3913(83)80101-2
2. Triantafollis papadopoulas, Athena Tsetsekou abd George Eliades. E ffect of aluminium oxide sandblasting on cast commercially pure surfaces. E uropean journal of prosthodontic and restorative dentistry.1999;7:15-21.
3. Jhon B. Brunski, David A. Puleo, Antonio Nanci, Biomaterials and biomechanics of oral and

maxillofacial implants: current status and future developments. The internatioinal journal of oral and maxillofacial implants.2000;15:15-39.

4. Davies J.E.. Mechanisms of endosseous integration.the international journal of prosthodontics. 1998; 11:391-401.
5. Piattelli A,.Scarano A, Piattelli M , Calabrese L. Direct bone formation on sand-blasted titanium implants: an experimental study Biomaterials 1996: 17: 1015 – 1018. http://dx.doi.org/10.1016/0142-9612(96)84677-1
6. Maurizo Piattell, Antonio scarano, Micheal Paolantonio ,Criovanna Petrone, Adriano Piattelli, Bone response to machined and resorbable blast material titanium implants: an experimental study in rabbits. Journal of oral implantology 2002:XXVIII:2-7.
7. GiovannaOrisini,Batolomeo Assenza, Antonio Scrano,,Maurizio Piattelli, Adriano Piattelli. Surface analysis of machine versus sandblasted and acid etched titanium implants. The international journal of oral and maxillofacial implants 2000; 15: 779-784.
8. Dario De Leonardis, Arun K Garg, Gabriel E. Pecora, Osseointegration of rough acid etched titanium implants: 5-year follow-up of 100 minimatic implants. The international journal of oral and maxillofacial implants. 1994;14: 384-391.
9. Andreas E.Von Recum, Carolyn E.Brown, Clare E. Shannon and M artine Laberge. Surface topography. Handbook of biomaterial evaluation. 1999; 227-238.
10. Michael McCraken. Dental implant materials: commercially pure titanium and titanium alloys. Journal of prosthodontics. 1999: 8:40-43. http://dx.doi.org/10.1111/j.1532-849X.1999.tb00006.x
11. David L. Cochran. A comparision of endosseous dental implants surfaces. J.Periodontal 1999; 70:1523-1539. http://dx.doi.org/10.1902/jop.1999.70.12.1523
12. ,Victoria A. Marker, Gilbert Triplett, Ronald D. Woody Implant materials, designs and surface topographies; their effect on osseoinegration. A literature review. The international journal of oral and maxilla facial implants. 2000; 15: 675-685.
13. Tomas Alberktsson, and M.Jacobson, Bone metal interface in osseointegration. Journal of prosthetic dentistry 1987; 57:597-606. http://dx.doi.org/10.1016/0022-3913(87)90344-1
14. Robert M. London, Frank A. Roberts, David A. B aker, DDS, MSD, M icheal D. Roherer, MS Robert B.O.Neal, Historic comparison of a Thermal Dual-ethched implant surface to Machined , TPS, and HA surfaces; Bone contact in vivo in rabbits. International journal of oral and maxillofacial implants 2002; 17:369-376.
15. Aubrey W.Soskolne, Sarit Cohen, Lars S ennerby, Ann wenner berg, Lior Shapira. The effect of titanium surface roughness on the adhesion of monocytes and their secretion of TNF-X and PGE2 clinical oral implantology 2002; 13: 86-91.
16. Lyndon F Cooper. A role of surface topography in creating and maintain bone at titanium endosseous implants. Journal of prosthetic dentistry: 2000; 84: 522-534. http://dx.doi.org/10.1067/mpr.2000.111966
17. Young Jun Lim, Yoshiki Oshida, Carl J. Andres, Martin T.Barco, Surface charecterizations of variously treated titanium materials. International journal of oral and maxilla facial implants: 2001; 16:333-342.
18. Carl E. Misch, Functional surface area: shortVs long implants. Dentistry today. 1999;18:60-65.
19. Jhon B. Brunski, David A. Puleo, Antonio Nanci,. Biomaterials and biomechanics of oral and maxillofacial implants: current status and future developments. The internatioinal journal of oral and maxillofacial implants.2000;15:15-39.

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