Politecnico di Milano

Masking materials & Bio-inspired caps for chemical etching of Dental Implants

by

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Declaration of Authorship

I, Pavan Tejaswi Velivela, declare that this thesis titled, 'Masking materials & Bio-inspired caps for chemical etching of dental implants' and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a Master's degree at Politecnico di Milano.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.

Pavan Tejaswi Velivela

Date: 4th October 2018

यद भावं तद् भवति

యద్ భావం తద్ భవతి

English: "Yad Bhaavam Tad Bhavati"
meaning: your are what you believe

- Brihadaranyaka Upanishad 1.5.18

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Abstract

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English: Osseointegration is a process in which integration of the implant to the bone is improved to enhance the mechanical stability of the implant. This is done by micro-roughening the surface of the implant by various techniques such as sand-blasting followed by chemical etching. The micro-roughened surface, thus forms a strong interlock with the bone and improving the stability. However, only the surfaces that proceed towards the root of the tooth are needed to be micro-roughened and the upper surfaces of the implant are needed to be protected.

Currently, there is no literature about processes and materials that protect a part of the dental implant when subjected to SLA (Chemical treatment) process. This thesis is an experimentation to protect the upper portion of the implant, by using Low-surface energy (LSE) polymer tapes, chemically inert tapes and Bio-inspired design of caps. The experiments were carried out to see how Low surface energy polymer (LSE) tapes & chemically inert tapes would withstand the high corrosive nature of the acids and how Bio-inspired caps act as an effective sealing agent in protecting the surface of the implant. Also, on how "Claw inspired structures" can be used in a entirely different application, that is as a sealing agent.

Keywords: Dental Implants, Osseointegration, Super-hydrophobic surfaces, Nano-structures, Low surface energy polymers and Bio-inspired and Bio-mimetic structures.

Italian: L'Osteointegrazione è un processo che migliora l'integrazione delle protesi con l'osso, al fine di garantirne stabilità meccanica. Ciò viene ottenuto, eseguendo un micro-irruvidimento della superficie dell'impianto, tramite vari processi, quali la sabbiatura seguita da incisione chimica. La superficie micro-irruvidita funge in questo modo da congiunzione serrante con l'osso, migliorandone la stabilità. Tuttavia solo la superficie che penetra la cavità radicale del dente necessita un processo di micro finitura, mentre la superficie dell'impianto che resta esposta deve esserne esclusa.

Allo stato dell'arte non è presente alcuna letteratura riguardo processi e materiali atti a proteggere aree specifiche degli impianti, quando sono soggetti a trattamenti superficiali SLA (Trattamento chimico). Questa tesi è una ricerca sperimentale sulla protezione della porzione superiore nelle protesi dentali, tramite l'utilizzo di adesivi polimerici a bassa energia superficiale LSE (Low surface energy) e di capsule ispirate al bio-design. Gli esperimenti sono stati eseguiti per studiare come gli adesivi polimerici a bassa energia superficiale (LSE) possano essere in grado di resistere alla natura altamente corrosiva degli acidi e capire come le capsule dentali ispirate al bio-design possano fungere efficacemente da elementi sigillanti, proteggendo la superficie dell'impianto. Lo studio esplora l'utilizzo delle strutture ad artiglio in un'applicazione completamente diversa come quella di strutture sigillanti negli impianti dentali.

Parole chiave: Impianti dentali, odontotecnica, osteointegrazione, superfici superidrofobiche, nano-strutture, polimeri a bassa energia superficiale, strutture bio-ispirate e bio-mimetiche

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To my family I am particularly grateful

Thank you

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Abbreviations

LSE Low surface energy polymers

CVD Chemical Vapour deposition

ALD Atomic layer deposition

TPU Thermoplastic Polyurethane

Physical Constants

Surface Tension of water in contact with air	72 dyne/cm
Surface Tension of Sulphuric acid 98.5 percent conc. in contact with air	55.1 dyne/cm

Symbols

ϕ	contact angle	degrees
γ	Surface energy	mN/m
θ	contact angle	degrees

*Dedicated to my parents, Kalidas Velivela and Nagamani Velivela,
my grandparents, late Seshagiri Rao Damerla and Janaki Damerla
and to Sree. Sistla Rama Krishna Rao gaaru*

Chapter 1

Introduction

Dental implants are becoming more and more popular. These dental implants help in restoring diseased and traumatized teeth, neighbouring tooth structure and tissues [1].

Dental implant materials are divided into three categories
1) Metallic
2) Ceramic
3) Polymer based

Dental implants are more suitable for adults with good general health. These implants can be only used once the jawbone has stopped growing "The main aim during the placement of any implant is to achieve immediate close contact with the surrounding bone"[1]. Dental implants today are highly predictable and highly invasive. About 98 percent to 99 percent of the implants placed in the bone are used to integrate with

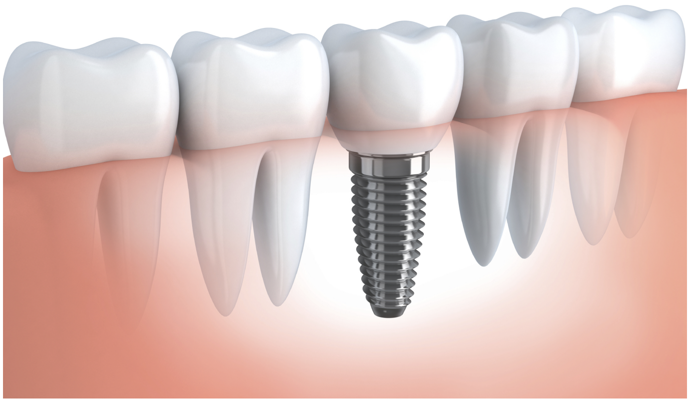


FIGURE 1.1: A graphic of the dental implant

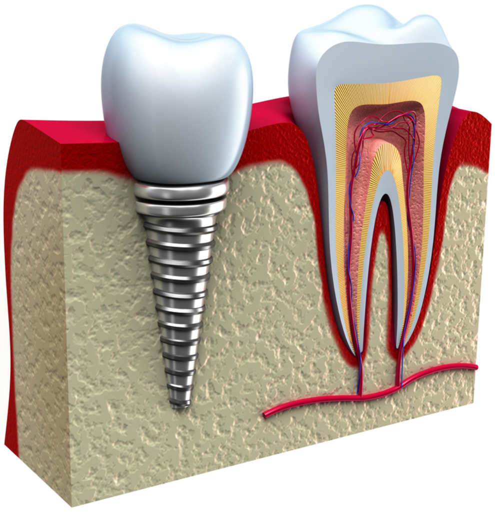


FIGURE 1.2: A graphic showing the implant with bone integration

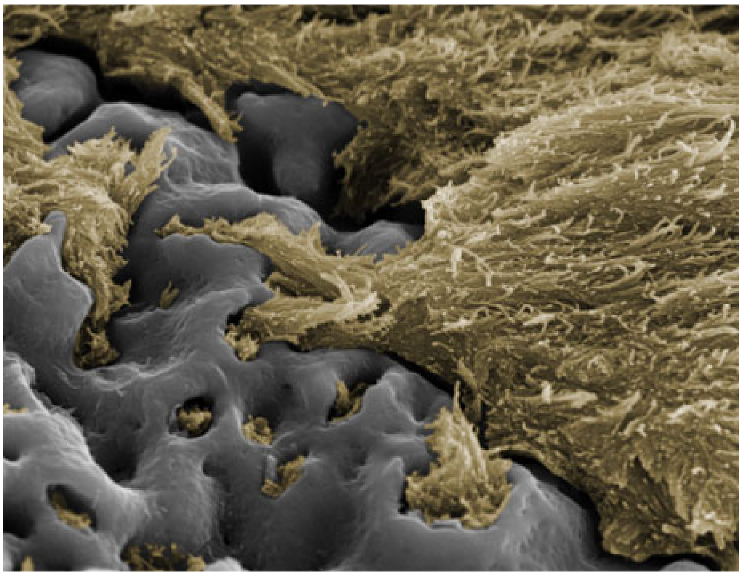


FIGURE 1.3: A graphic showing the bone growing on the implant

the bone. The implants need to be bio-compatible [1]. Originally implants were first introduced by Professor Branemark in the 60's.

Many implants are designed in such a way that they promote the Osseointegration. Osseointegration can be defined as a biological phenomenon which incorporates of the dental implant to the bone tissue [1]

1.1 Materials for Dental Implants

As mentioned earlier, the materials for the dental implants are categorized into three different types such as
1) Metallic
2) Ceramic
3) Polymer based

METALS

In the metallic category, Titanium metal is mostly used. These are titanium screws that can be anchored in the bone of the alveolar ridge and missing teeth. Statistics show that every year 12-14 million implants are planted annually Metallic implants have generally crystalline structure and the atoms are closely packed. General metallic properties include ductility, malleability, non-transparent, lustrous and hard. These metals are combined with other materials to form alloys to enhance their physical and chemical properties [1].

Name	**composition**
Commercial pure titanium	Titanium
Alloy (TiZr)	Titanium and Zirconia
Titanium with coating	Titanium with Hydroxy apatite

Table 1.1: Commercially available titanium implants

First generation of Titanium alloys [1].
General properties include
- Machined and smooth
- Minimally rough
- Osseointegration was possible with smooth surface

Second generation of Titanium alloys [1].
General properties include
- Micro-roughened
- Achieved a higher bone-to-implant contact and they also demonstrated signs of contact **Osteogenesis**

Osteogenesis: Bone is formed directly on the implant surface [1]. Below are the images showing the different types of implants during the first generation and second generation respectively.

The advent of micro surface roughness saw a tremendous improvement in the Osseointegration and the Osteogenesis. This showed a better understanding of the surface modification and its importance in the processing of implants. Further adding an insight on

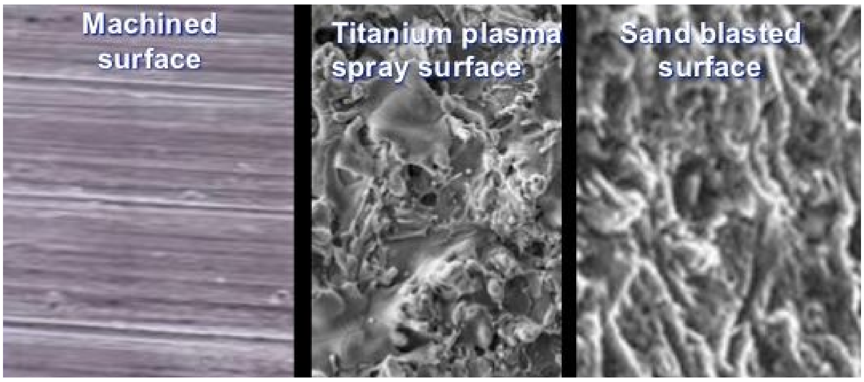


FIGURE 1.4: A graphic showing the surface modification techniques of first generation of dental implants and corresponding micro-structure

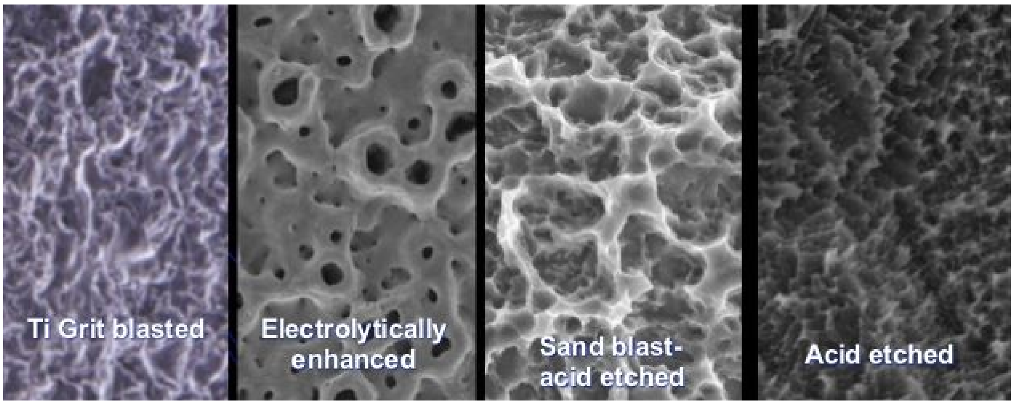


FIGURE 1.5: A graphic showing the micro-structural surface of the second generation of dental implant

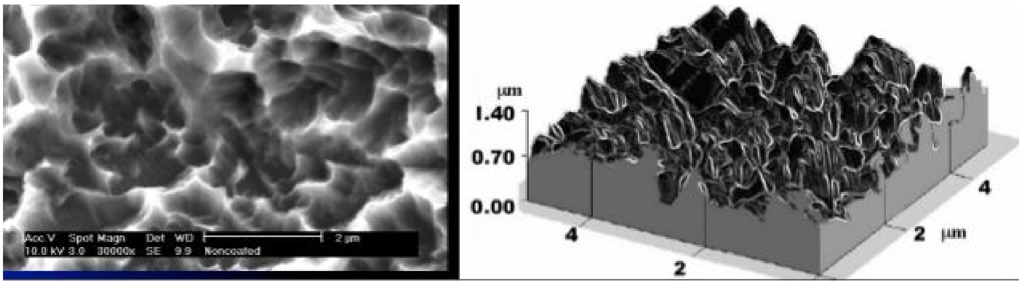


FIGURE 1.6: A graphic showing more predominant surface modification of second generation of dental implants

the advantages (Bruser D et.al 1991) performed experiments to compare the advantages of smooth surfaces and rough surfaces of the titanium implants. The results showed a significant advantage of rough surfaces over smooth surfaces in terms of bone-to-implant contact and the quantity of Osseointegration. Increasing the surface roughness of the implants resulted in smaller and thinner implants and placing the implants in an area, that was previously not possible [1].

Third Generation implants

General properties include

- Hydrophilicity
- Nano-roughness
- Use of Nano-particles or active molecules

Ceramics These are non-metallic solid materials made of certain metal oxides and formed by the firing process. These are used as a restorative material in the dentistry. Some of the general properties of ceramics include durability, aesthetic, bio compatibility, high melting temperature and low electrical and thermal conductance [1] A common material used in Ceramic industry include Zirconia or Zirconium dioxide (ZrO2), commonly called as "ceramic steel". However, Zirconia stabilised with other oxides such as Ceria (CeO2), Yttria (Y2O3), Allumina (Al2O3) etc [1] The main reason for the use of ceramics is that of its aesthetics of lookalike of natural teeth. Zirconia is chemically inert and has a week adhesion strength. It needs surface treatment to enhance the adhesion property. Grit blasting is one of the mainly used chemical treatment for surface modification [1]

Another main use of ceramics is the manufacture of the crown for the tooth. It is used to keep the metal structure underneath the ceramic for more strength. Examples are, ceramo-metal crown and porcelain fused to metal crowns.

Classification of dental ceramics (Gracis et al 2015 Int J prosthdont 28: 227-235) Dental ceramics can be classified into three types namely,

1) Glass matrix ceramics: Contains non-metallic inorganic ceramic materials that contain a glass phase

2) Poly-crystalline ceramics: Non-metallic inorganic ceramic materials that do not contain a glass phase.

3) Resin-matrix ceramic: Polymer matrices containing predominantly inorganic refractory compounds that may include porcelain, glasses, ceramics and glass-ceramics.

Polymers

Polymers are also some good materials that are widely used in the dental implants. Polymers consist of composite fillings that are mixed with a filler material to form a hard and durable substance and is build up in increments by light cure [1]. Some examples of plastic composites that are used in dental industry are: Fibre reinforced plastics/composites [1].

- These plastics exactly have the same mechanical properties compared to enamel and dentine.
- They can be tailored to different structures
- Easy to be shaped and polymerized to the oral cavity

Fibre reinforced matrix-FRC	**Metals**
No metal bleaching	Better adhesive properties

Table 1.2: FRC Vs Metals

Fibre reinforced matrix-FRC	**Ceramics**
Rough surfaces adhere more microbes and proteins	Better aesthetics and strength

Table 1.3: FRC Vs Ceramics

Fibre reinforced composites are made up of Glass, carbon fibre, polyethylene and aramid. In general, these composites are transparent in appearance with a silicone coating. The hydroxyl silicone coating adheres well to resin matrix [1].

In addition to the fibre reinforced polymers there is cement used in dental implant technology. Cement is classified into Water based, Oil based and Polymeric based resin cement respectively. For example, Luting cement is used in the dental cavity for pulp protection. Different uses of dental cement are as follows:

- Pulp protection
- Cavity Lining
- Insulation layer

1.2 Titanium and its alloys

As mentioned earlier that titanium is playing a prominent role in implant technology. The properties of Titanium are increased by the addition of Zirconia a ceramic material. This addition helps in increase in the bending moments and mechanical strength. This lead to the manufacture of smaller diameter implants. The main reason for the use of titanium is its bio compatible nature. The material is not recognized as a foreign material by the body. The following materials show a good bio-compatible property

- Niobium
- Tantalum
- Platinum
- Titanium
- Titanium and its alloys

Titanium has been one of the best materials because of the following properties:

1) Withstand conditions of the biological environment
2) Withstand oxidative mature of the interstitial milieu
3) Sufficiently inert
4) Not release toxic components or cause inflammation

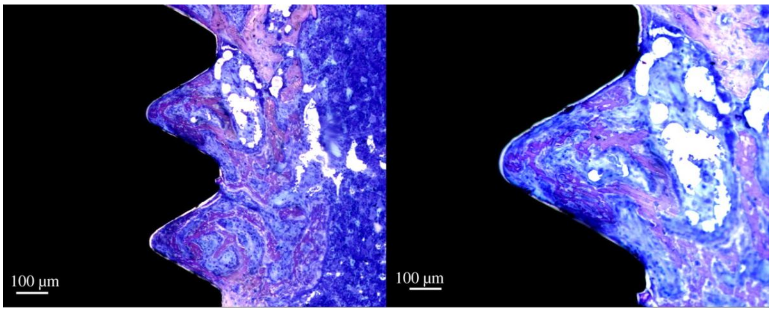


FIGURE 1.7: A graphic showing the starting of the growth of bone

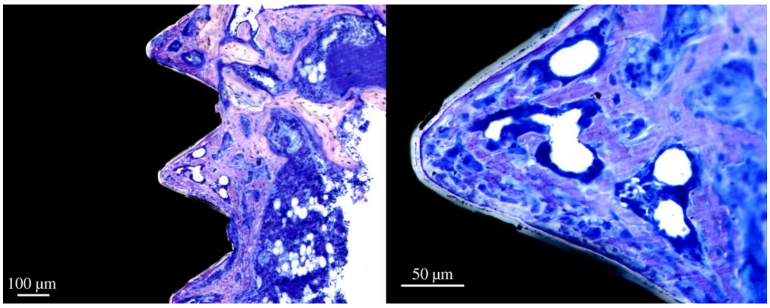


FIGURE 1.8: A graphic showing the growth of bone becomes more predominant on the dental implant

Pure titanium is a week and it needs the addition of materials to increase the strength

1.3 Need for surface treatment

The process for surface treatment includes

1) Cleaning

2) Removal of losing particles ad debris

3) Modification of surface The surface treatments alter the surface properties of dental restorations physically and chemically or both ways. This helps in bonding between tissue and the implants. The main purpose of surface treatment especially for the implants is that

1) To remove the debris.

2) To increase the surface free energy

3) To create special surface micro-structure for retention

4) To maximize the molecular interaction at the inter-facial layer between two different substrates.

5) Optimize the adhesion at the interface. Some of the common techniques of surface treatments include Grit blasting, Chemical wet etching etc. Chemical wet etching processes in which, high concentration acids are used to change the surface of the implant and thereby increasing the surface roughness and surface free energy. This process

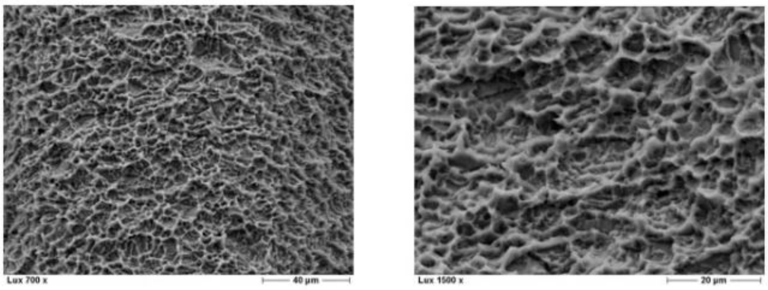


FIGURE 1.9: A graphic showing the chemically etched surface of the implant

helps in improving the adhesion property in different materials such as ceramics, metals and composites [1]. Adhesion is a molecular or atomic attraction between two contacting surfaces by the inter-facial forces of attraction from different molecules or atoms. For example, a common etching agent used is Hydrofluoric acid. In dental implants it uses HF gel is most commonly used. In porcelain surface treatment about 4-10 percent concentrated HF is used for 1-2 min to create a micro-porous structure of porcelain[1].

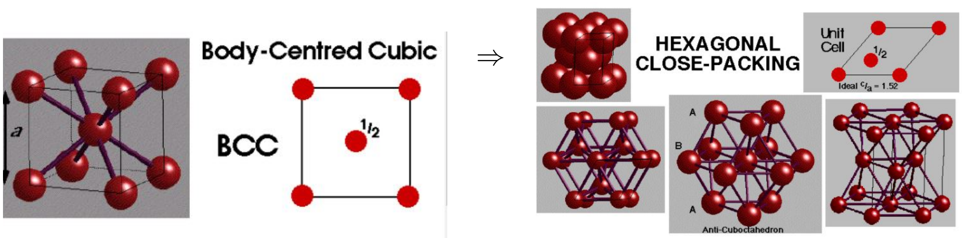
Finally, only the surfaces of the implant that are entering the bone area are need to be etched and the other surfaces are not required to be chemically etched.

Chapter 2

Literature Survey

One of the major reasons for the use of titanium in many medical and various other application is due to its high strength and low density (4.5g/cm3). The tensile and yield strength are comparable to that of a steel. Bio-compatibility is one the major reasons for the use of titanium in implant technology [2] Titanium is extensively used in chemical processing industry due to its outstanding resistance to aggressive chemical environment. Titanium exist in two phase crystal structure namely alpha and beta titanium [2]
The alpha phase – Hexagonal closed packed structure [HCP]
The beta phase – Body centred cubic [BCC]

Alloying elements such as aluminium and tin tend to stabilize alpha phase, whereas transition element vanadium is used often to stabilize beta phase. Titanium alloys that support both phases show improved physical properties than alloys containing only one phase stabilizes. The common one with both phase stabilizers are that contains 6 percent aluminium and 4 percent vanadium. Commonly called as **Ti-6Al-4V**(Grade 5 Titanium) [2]



(A) BCC (B) HCP

FIGURE 2.1: Titanium natural occurrence in two crystal states [2]

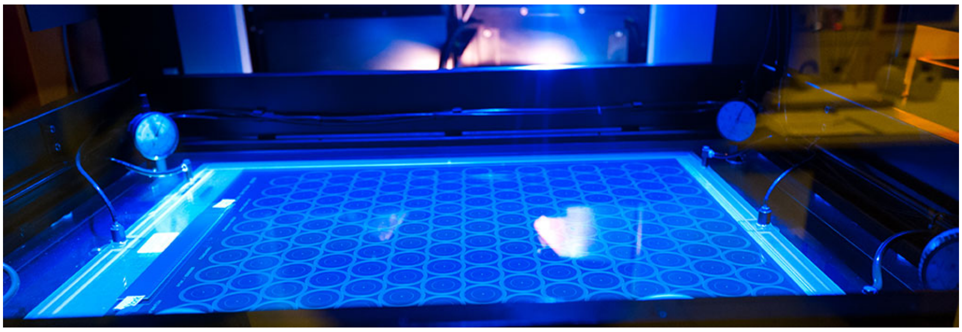


FIGURE 2.2: A graphic showing the photo chemical etching of Titanium

The protective layer [2]

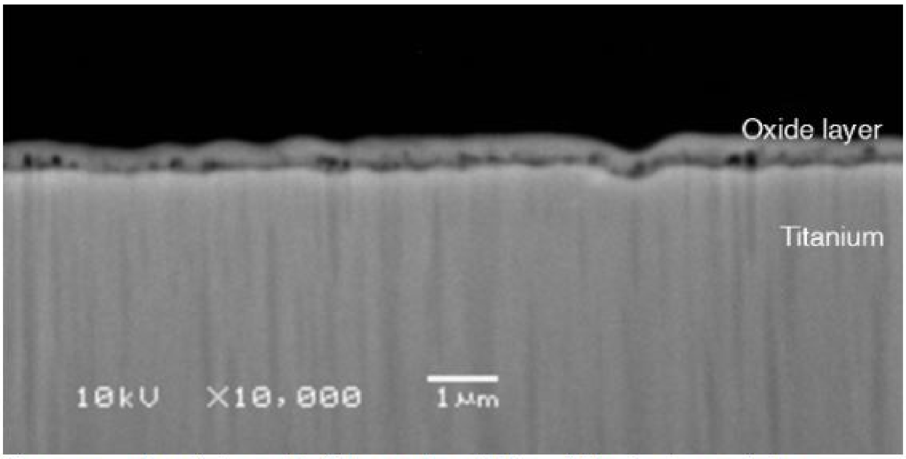
Titanium is very reactive metal, but the resistance comes from the protective oxide layer upon exposure to oxygen. The protective layer of titanium is only about a few Nano-meter thicknesses. This oxide layer is continuous, consistent and highly stable. This helps in insulating the base material from the external environment.

Photo-chemical Etching process

This process is used to produce patterns and features on metal sheets by selectively dissolving in oxidizing agents. The process of the Photo-chemical process in brief:
1) Patterns are drawn on a computer and are photo plotted on to a film (Black or Clear). Depending upon the type of photo resist either the black/clear images are used to produce the desired pattern.
2) Metal sheets are cut to match the size of the photo film created
3) Metal is cleaned to remove the residual acids.
4) Metal sheets are then coated with a photosensitive resist. These Photo-resist materials are sensitive to UV light and resistant to acid.
5) Now the coated metal sheets are placed in between the photo films and now are exposed to UV light. The areas/clear areas where the resist is exposed it becomes hardened. The black areas that are shielded by UV light remain soft.
6) After that the sheets are processed through a developer, where the sheets are rinsed, and the soft photo-resist material is washed away.
7) The hardened photo-resist material remains. Now the metal is removed by using an etchant and the metal that is protected by photo-resist material remains there.
8) The photo-resist is then removed by using a resist stripper which dissolves the resist
Conventional photo-chemical etching of titanium is performed using hydrofluoric acid or a mixture of hydrofluoric acid and Nitric acid.

Use of strong acids

Due to the ability of the titanium to form a protective oxide layer on the surface once



The cross section photograph of the anodic oxidation of titanium by an electron microscope

FIGURE 2.3: A graphic showing the formation of oxide layer formation on titanium implant

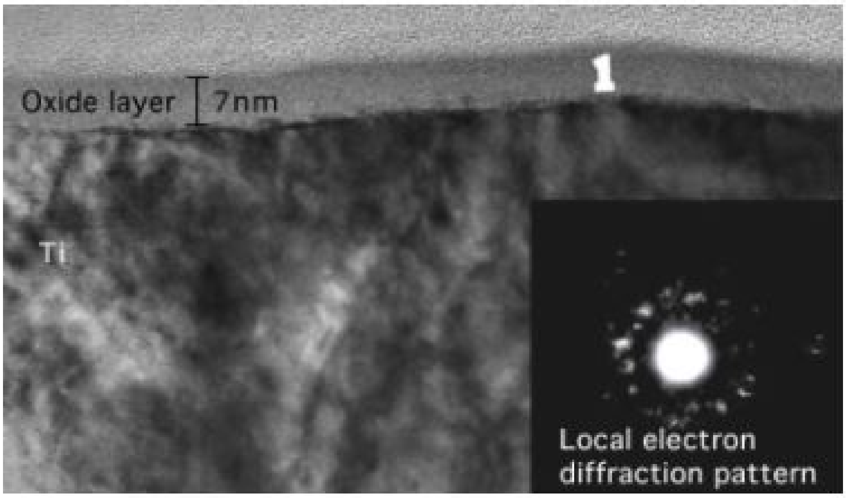


FIGURE 2.4: A graphic showing the formation of oxide layer of 7 nm on the surface Titanium

exposed to air, and removal of such oxide layers is very difficult. Hence there is need to use strong acids such as HF to remove the oxide layer. In the year 2013, researchers form Budapest university of technology and economics carried out an experiment to find an optimal parameter setting, where the irregularities (burns and grooves) caused my milling procedure would disappear. The research was carried on two samples one is an implant material Grade 2 titanium and the other is Nano-particulate titanium alloy[3]

Manufacturing process of Titanium alloys

Grade 2 Titanium alloy - **Traction of raw titanium into a bar**

Nano-particle Titanium alloy - **Equal Channel pressing**

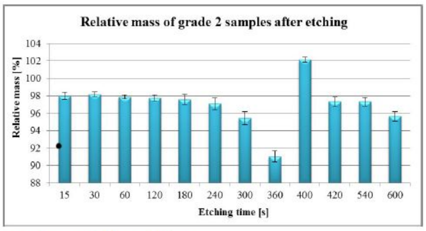


Fig. 3. Grade 2 titanium masses

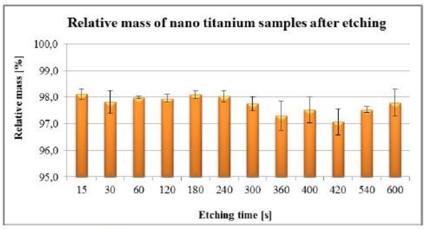


Fig. 4. Nano titanium masses

(A) Relative mass Vs Surface roughness - A

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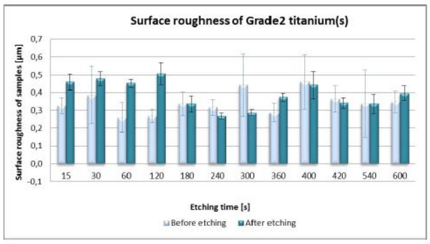


Fig. 7. Surface roughness of "s" side on Grade2 titanium samples

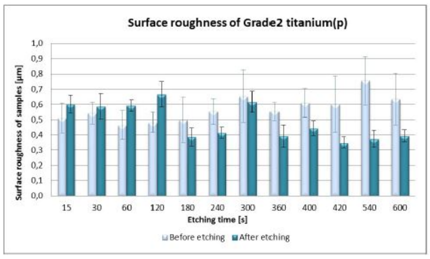


Fig. 8. Surface roughness of Grade2 titanium "p" sides

(B) Relative mass Vs Surface roughness - B

FIGURE 2.5: A graphic showing the relative mass Vs surface roughness of titanium [3]

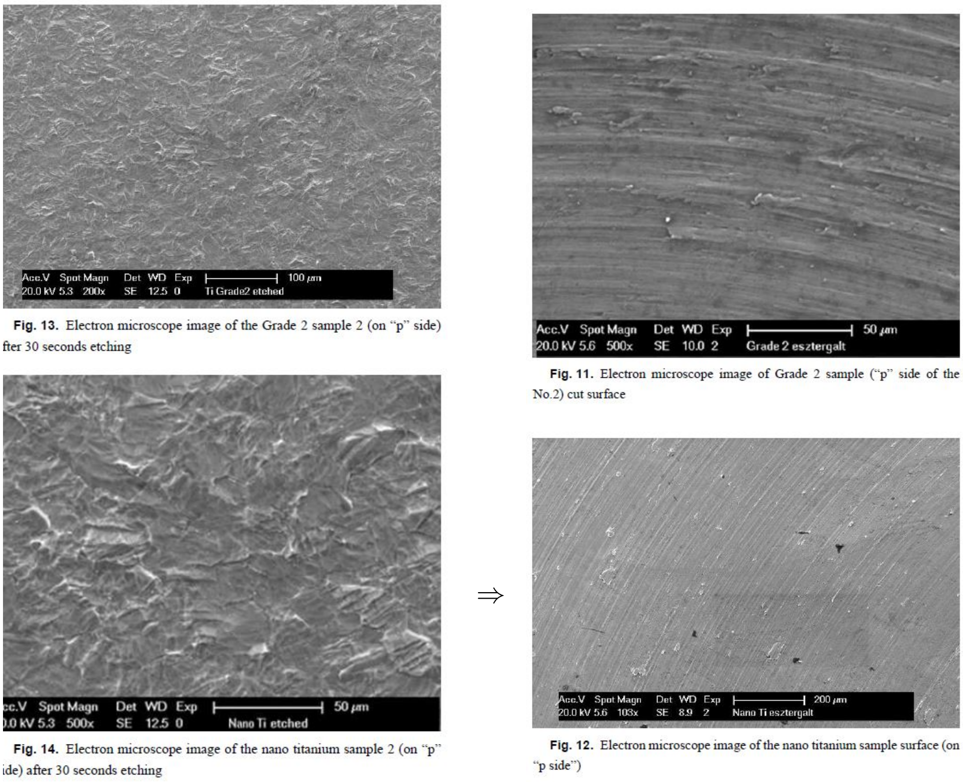
Results showed the following criteria:

1) Longer the etching time causes greater material loss.

2) The mass of the sample reduces continuously with longer etching time. It is not worth etching a material for a longer time more than 300 seconds (up to 5min) for both the materials. The side with higher surface roughness is labelled as "P-Side" (Pitted side) the side with lower surface roughness is labelled as "S-Side" or smooth side. The surface roughness distribution as a function of time for samples are as follows

Nano-Titanium Samples – 0.22 to 0.39 micro-meters

Grade 2 Samples – 0.27 to 0.60 micro-meters[3]



(A) Microscopic image of Surface - A (B) Microscopic image of Surface - B

FIGURE 2.6: A graphic showing the surface roughness of titanium [3]

2.1 Insights form previous studies

A research group from the department of dentistry, The University of Granada Spain in 2016, conducted to measure the effect of etching time on the typography, chemistry, wettability and cell adhesion. During their experiment, Titanium (Ti) surfaces were evaluated using HF acid for 0,2,3,5,7 and 10 minutes respectively.

The results showed that roughness and wetting increased with longer etching time except for 10 min. At 10 min the roughness increased, and the wettability decreased. Wetting and cell adhesion were reduced on the highly rough surfaces obtained after 10 min of etching time. Highest cell adhesion was observed for 5-7 min of etching time. Surface properties of the implant effect the bone formation at the interface.

Bio-material surfaces usually need to be hydrophilic in nature to favour cell attachment. The wettability of the solid surface can be quantified by the contact angle. Where, in this experiment the wettability is measured by measuring the dynamic contact angle[4]

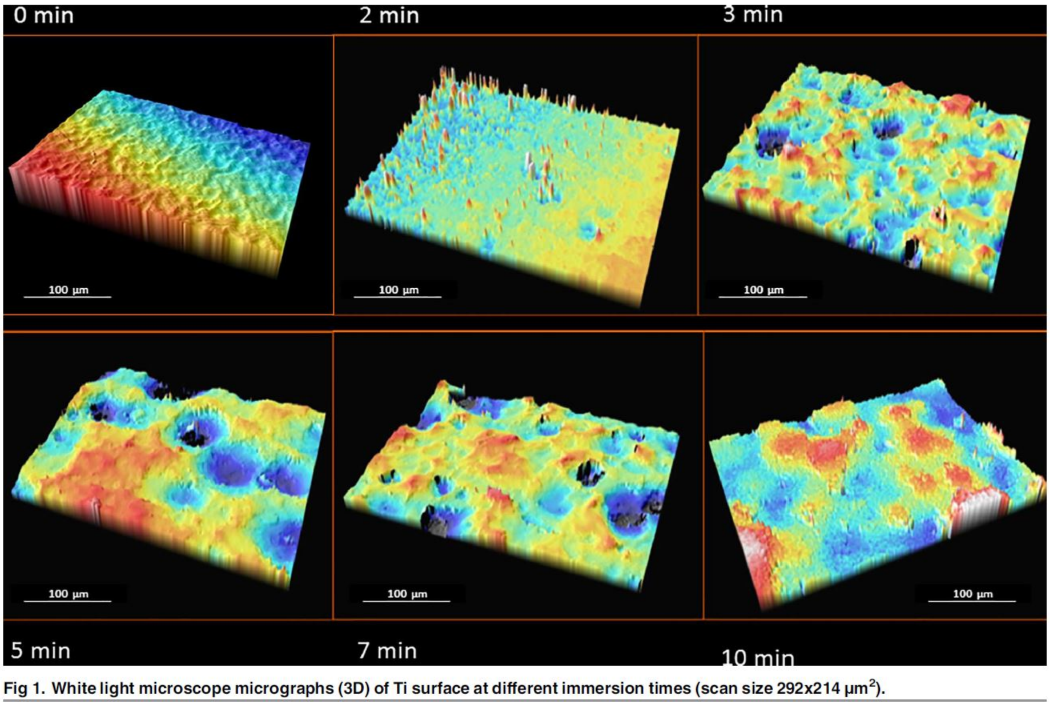


FIGURE 2.7: A graphic showing the 3D images of Titanium surface with different immersion times

Different surface topologies were taken into considerations such as arithmetic mean roughness (Sa), maximum relative height (Sp), Maximum relative depth (Sv), Root mean square roughness (Sq), Skewness (SSk), Kurtosis (Sku), Wenzel fraction (Sw) and Fractal dimension (Df)[4].

• Etching time of 5 and 7 min were found to achieve maximum cell attachment, which is crucial for rapid healing of bone-implant interface

• The layer of TiO2 is removed with longer etching time due to strong corrosive effect of HF acid on Titanium oxide

• Most influential parameters such as roughness are related to the form and distribution of peaks. With higher peaks the surface roughness increases which also increases the contact angle[4] Advanced contact angle is represented as

$$\theta_a$$

Receding contact angle is represented as

$$\theta_r$$

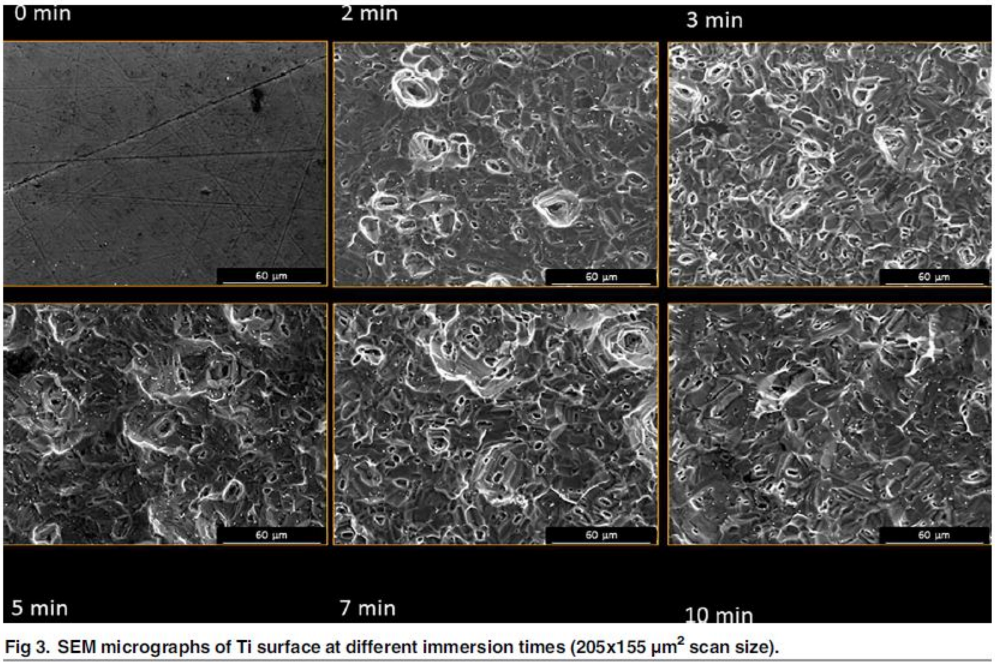


FIGURE 2.8: A graphic showing the SEM images of Titanium surface with different immersion times

The average of advanced and receding contact angle is represented as

$$\theta_A$$

. This angle is used to calculate Young's angle that is

$$\theta_r$$

The equation is as follows.

$$cos\theta_A = S_w * cos\theta_r$$

[4]
Another research group in 2015, from the material science and metallurgical engineering and centre for Nano-Engineering, Universitat Politecnica de Catalunya, also made experimentation on the effect of etching time on Zirconia implants, which is an important alloying element for titanium implants. The group has also tested the effect with respect to various concentration levels of the hydrofluoric acid[5] The parameters such as average roughness, RMS roughness, developed inter-facial area ratio, ten-point peak-peak height, mass loss etc. were compared with respect to etch time. All the parameters are compared with 5, 20 and 40 percent concentrated HF. The results show that etching with 40 percent HF leads to faster and most uniform etching. Mass loss and surface roughness increases with the time. The parameters such as average roughness (Sa) and root mean square roughness (Sq) increases until one hour of etch time and later decreases.[5]

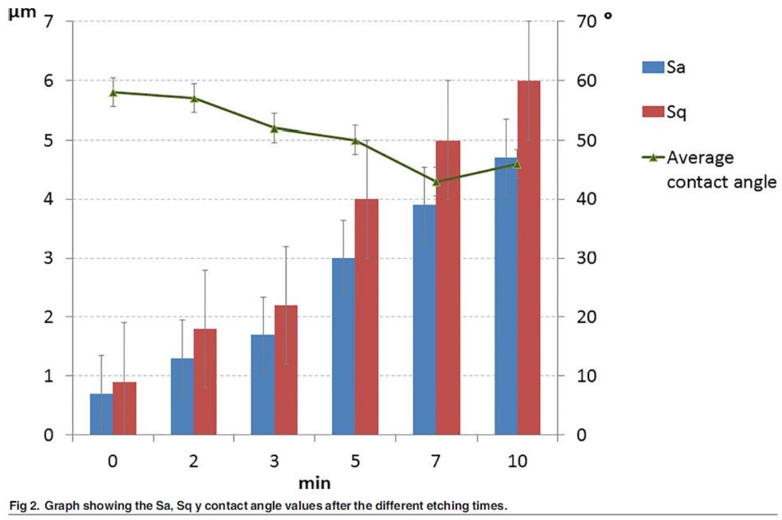


FIGURE 2.9: Graph showing arithmetic mean roughness (Sa) and Root mean square roughness (Sq) and Contact angle

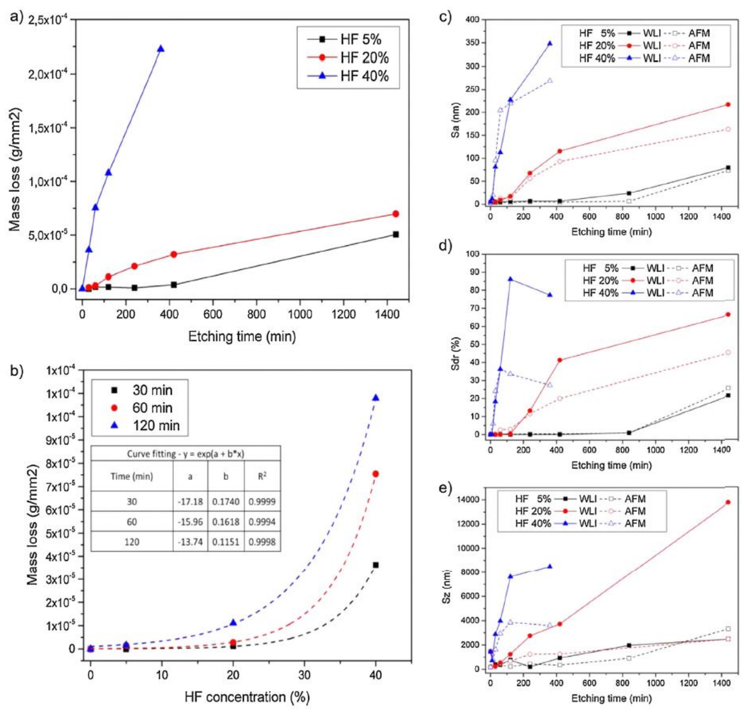


FIGURE 2.10: Graphs showing various parameters with respect to Etching time

2.1.1 Hydrophobic and Oleophobic surfaces

Micro-and Nano-structures on the silicone substrate help to repel water and other liquids making the entire surfaces as Superomniphobic. The research paper points that the construction of Nano-structures along with chemical coating with low energy surface molecules helps in achieving the Superomniphobic surface
Coating with Perfluorodeyltrichlorosilane (PFTS)- A low energy surface molecule that enhances the repellent nature of the surface. The wetting properties are characterized by static contact angle (CA) and contact angle hysteresis (CAH) [6] Liquids of various surface tensions were tested on the surface and their contact angle and contact angle hysteresis were measured. For a surface to be superhydrophobic it requires that the contact angle (CA) greater than 150 degrees and contact angle hysteresis (CAH) less than 10 degrees. The nature of the surface can be determined by the two states namely Wenzel and Cassie-Baxter states respectively. A comparison between silicon micropillars and silicon Nano-wires were established
• Silicone Micropillars (P-Si) were obtained by standard optical lithography and dry reactive ion etching (RIE). These micropillars were further subjected to metal assisted electroless etching presenting a double scale micro and Nano structuration (P-NanoSi).
• Silicone Nano-wires were synthesized via vapour-liquid-solid (VLS) growth mechanism. By varying furnace pressure and reaction two surface morphologies were obtained namely (P-SiNW-A) and (P-SiNW-B)
All the above-mentioned interfaces were coated with Perfluorodeyltrichlorosilane (PFTS). The results show that (P-SiNW-B) showed better repellent character due to extra nanolayer and it resembles to "Slippery liquid-infused porous surface (SLIPS)" [6]

Another group of researchers, tried to make surfaces super repellent even for most wetting liquids. Roughening a hydrophobic material can give us super-hydrophobic and super-oleophobic surfaces. However, no surfaces were able to repel extremely low energy liquids such as fluorinated solvents, these solvents wet even the most hydrophobic material. This research group suggest that use of double re-entrant structures would even repel the most wetting liquids. For example, the most wetting liquid such as fluorinated solvents have a surface energy or tension of less than 15 milliJoules per sq.meter. To repel, **Theta*** greater 90 degrees (Static contact angle), and the **Theta(Roll-off)**(Contact angle hysteresis) must be small. To super repel **Theta*** greater than 150 degrees (Static contact angle) and the **Theta(Roll-off)** (Contact angle hysteresis) less than 10 degrees [7] Liquid suspension by the surface structure (or resisting liquid wetting by surface topologies) with characteristic length smaller than the liquids capillary effect was proposed in 1960's. A re-entrant micro-structure is required to suspend the liquid and resist it from wetting the surface. The surface structure of a doubly re-entrant topology might

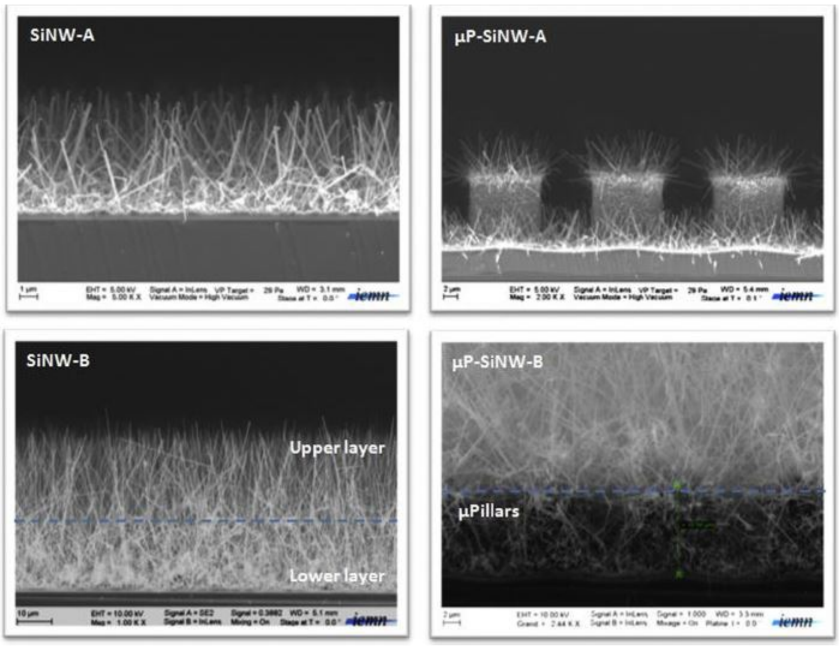


FIGURE 2.11: Pictures showing the SI Nano-wires grown on Micropillars

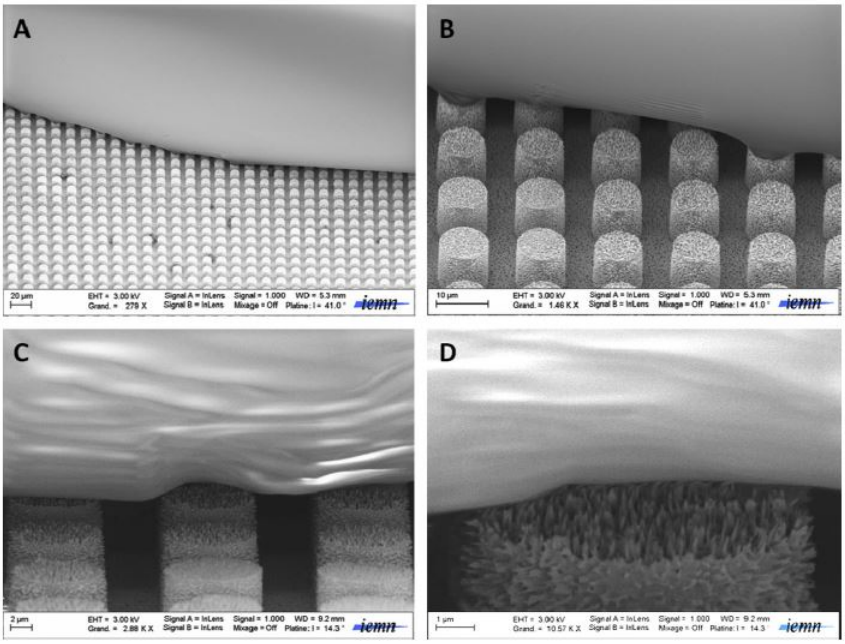


FIGURE 2.12: Pictures showing the SI Nano-wire growth on PFTS coated surfaces

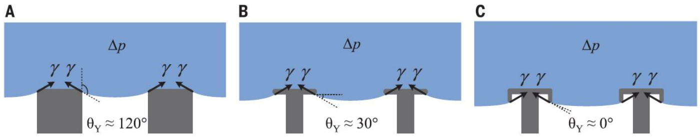


Fig. 1. Liquid suspension on surface structures of three different topologies. (**A**) Simple structures require $\theta_Y > 90°$ to suspend water. Δp, is the pressure difference between the liquid and air. (**B**) Reentrant structures allow $\theta_Y < 90°$ to suspend oils or solvents. They would fail if $\theta_Y \sim 0°$, as surface tension acts parallel to the horizontal overhangs with little vertical component to suspend the liquid. (**C**) Doubly reentrant structures allow $\theta_Y \sim 0°$ to suspend any liquid, as surface tension acts on the vertical overhangs with a substantial vertical component. If the liquid-solid contact fraction is small enough, the surfaces would also repel the liquids.

FIGURE 2.13: Pictures showing different topologies and suspension of the liquid on the structure

provide a stronger resistance against wetting and retain suspension. The major aspect to make a super hydrophobic surface is that to reduce the liquid-solid contact fraction. This group suggests that the air trapped inside the cavity created by the micro-structures would aid to the repellence. This state is typically called as Cassie-Baxter state The formulated equation is as follows,

$$cos\theta^* = f_s * (cos\theta^*) - f_g$$

[7] Where, the Liquid solid contact fraction or contact fraction. That is proportion of the liquid solid contact area to the projected area of the entire composite interface is represented as

$$f_s$$

and the gas fraction simply defined by liquid -vapour interface is represented as

$$f_g$$

Finally the relation between the liquid-solid contact fraction and gas fraction is as follows,

$$f_g + f_s >= 1$$

The ideal Cassie-Baxter state is as follows,

$$cos\theta^* = f_s * (1 + cos\theta_y) - 1$$

Which gives us an insight that as the component decreases, the **Theta*** increases. As a result, an array of doubly re-entrant structure consisting of micro-scale posts with non-overhanging were created. Tests were performed on the surfaces with 14 different liquids with different surface tensions or surface energies. Super-hydrophobic surfaces with vertical posts could not suspend liquids with surface tension less than 40 milli Newtons per meter. But, with re-entrant posts repelled liquids with lower surface tension ranging from 20-40 milli Newtons per meter. Doubly re-entrant posts with vertical overhanging's repelled all the 14 liquids (even without hydrophobic coating)[7] Another research group

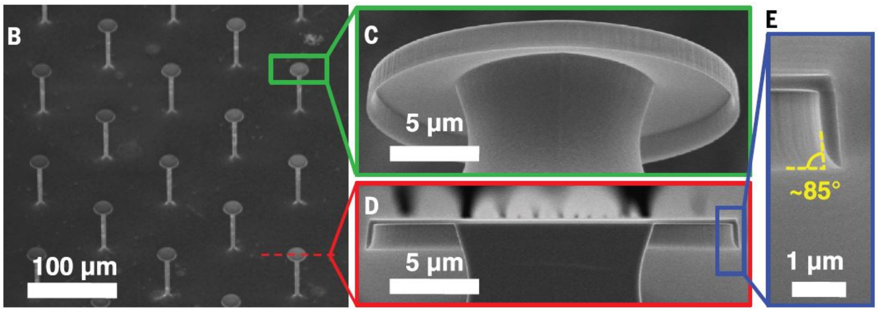


FIGURE 2.14: Pictures showing double re-entrant structure along with overhanging positioned at 85 degrees

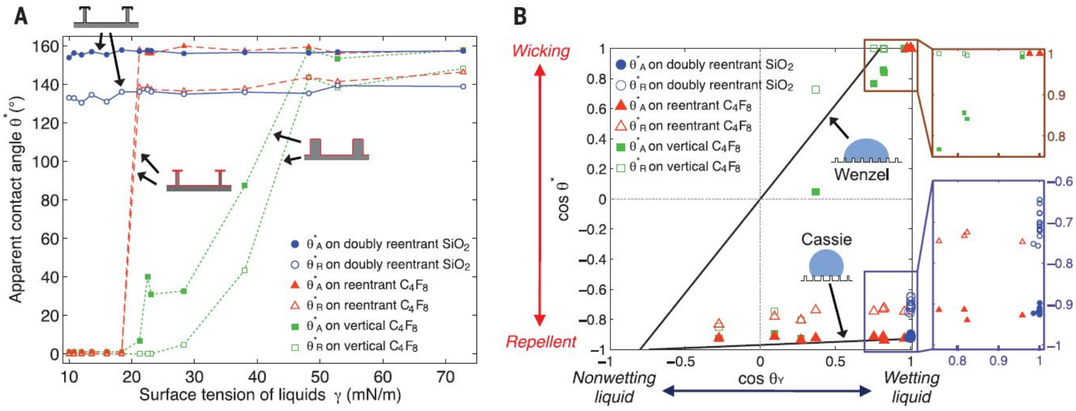


FIGURE 2.15: Pictures showing the graphs of different surface tensions of the liquid with respect to contact angle

from the Nanoprobe Laboratory for Bio and Nanotechnology and Biomimetics (NLBB), Ohio State University in 2015, experimented the layer-by-layer approach to fabricate mechanically durable, superomnipobic coatings for self-cleaning and anti-smudge[8] Their experiment involved in an adaptive layer-by-layer approach involving charged species with electrostatic interactions is combined with uncharged fluorosilane layer to result in a durable and superomniphobic coating. In this experiment materials such as polyelectrolyte binders, SiO2 Nano-particles and fluorosilane layers are deposited providing the combination of surface roughness and low surface tension. As discussed in the earlier studies, for a surface to be superomniphobic to liquids the static contact angle (CA) greater than 155 degrees and the contact angle hysteresis/Tilt angles less than 10 degrees[8] From the Young's equation,

$$cos\theta = \gamma(sv) - \gamma(sl)/\gamma(lv)$$

Where, the surface tension between solid-vapour is represented as

$$\gamma(sv)$$

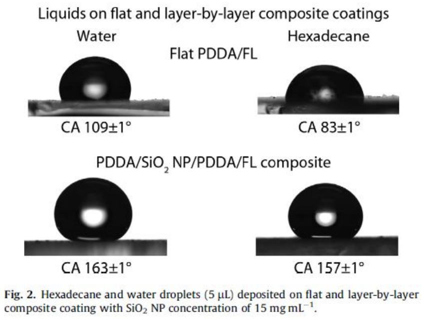


FIGURE 2.16: Pictures showing liquids on flat and layer-by-layer coatings

The surface tension between solid-liquid is represented as

$$\gamma(sl)$$

and the surface tension between liquid and vapour is represented as

$$\gamma(lv)$$

An important observation is that to make a non-repellent surface to repellent or super-repellent, we can increase the surface roughness, and this results in the formation of a composite air/solid interface. These rough surfaces can trap air in between and resulting in a composite interface called as Cassie-Baxter state. From this study it can be noted that fluorinated components provide low surface tension and o=roughness of the surface increase solid-liquid interactions[8] Many compounds such as fluorinated polyhedral oligomeric silsesquioxane has been used in numerous deposition techniques including electrospinning and coating re-entrant structures to create super-oleophobic coatings. Certain spray coatings do offer super-hydrophobic surfaces In this experiment, to enhance the repellence, roughness was introduced vi spray deposition of SiO2. As a result, this increase in roughness introduced an increase in oil/water contact angles (CA) due to composite air-solid interface, typically called as **Cassie-Baxter state**. The materials used are Glass substrate, followed by spray coating of PDDA binder and then SiO2 Nano-particles to increase the roughness and then again, a coating of PDDA binder. Finally, a low surface energy polymer fluoro-silane is vapour deposited at the end[8] Research group from School of materials from the University of Manchester in 2015, experimented the behaviour of titanium while being etched in Bromine-methanol electrolyte. Titanium and its alloys when they are exposed to aqueous electrolytes or air, they form a dense and compact oxide layer. With a thickness of few Nano-meters. This dense is called as titanium oxide TiO2. The results of the experiment were[9]

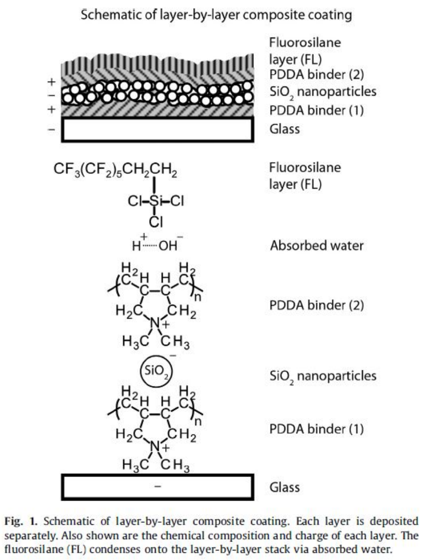


FIGURE 2.17: Pictures showing Layer-by-layer deposition of Fluoro-Silane

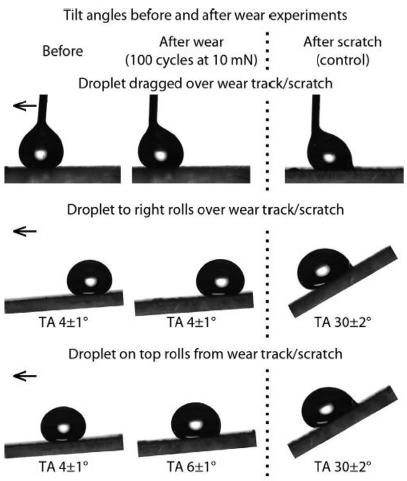


FIGURE 2.18: Pictures showing ascending and descending angles of Hexadecane droplets

• Without the air formed TiO2 film, pitting corrosion occurred on bare titanium substrate due to the attack of Bromine

• The corrosion continued from 10 to 300 seconds

• The surface roughness increased with the increase in the etch time[9] Furthermore, metal nanodot arrays were also used as a hard mask material in the fabrication of the silicone nanowires[10] Various Nano-fabrication methods such as electron beam lithography (EBL), allows well defined and well positioned nanodots. However, the most economical method in producing nanodots would be from the Nano-imprint technology or Hot embossing technique[11]

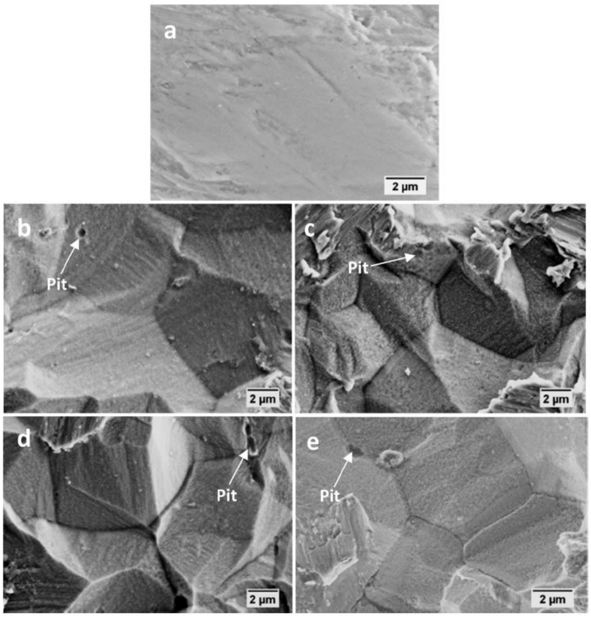


Fig. 2. Scanning electron micrographs of as-received (a) and titanium etched in the bromine-methanol electrolyte for 10 s (b), 30 s (c), 120 s (d) and 300 s (e) at ambient temperature.

FIGURE 2.19: Pictures showing Scanning electron microscopy images of etched Titanium in Bromine-methanol electrolyte for 10,20, 120 and 300 seconds receptively

2.2 Surface Morphology

2.2.1 Nano-Imprint Technology

This is a process in which heat and force are used to produce a master model onto a substrate. For example, the intended structure is printed on to a PMMA substrate when the PMMA is in its glass transition temperature[12] Some of the general parameters that are required for this technology are as follows:
1) Stamp material: Si, SiO2
2) Resist: Thermoplastic
3) Heat and Press, temperature of the mould reaching 100-200 degrees
4) Viscosity of the thermoplastic can be from

$$0.001 - 0.0000001 Pa - Sec$$

2.2.2 Vapour Deposition Technique

Electron beam Vapour deposition is a technique in which the source material is melted with the help of high energy electrons focused on to the source material. Thus, melted

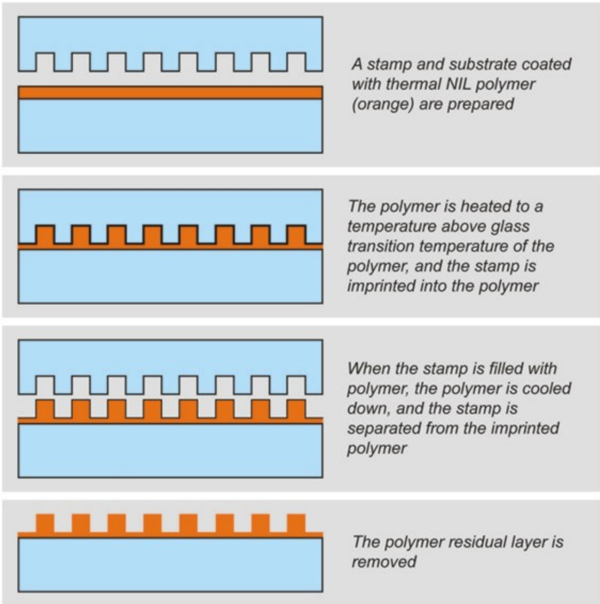


FIGURE 2.20: Pictures showing Nano-imprint lithography technique

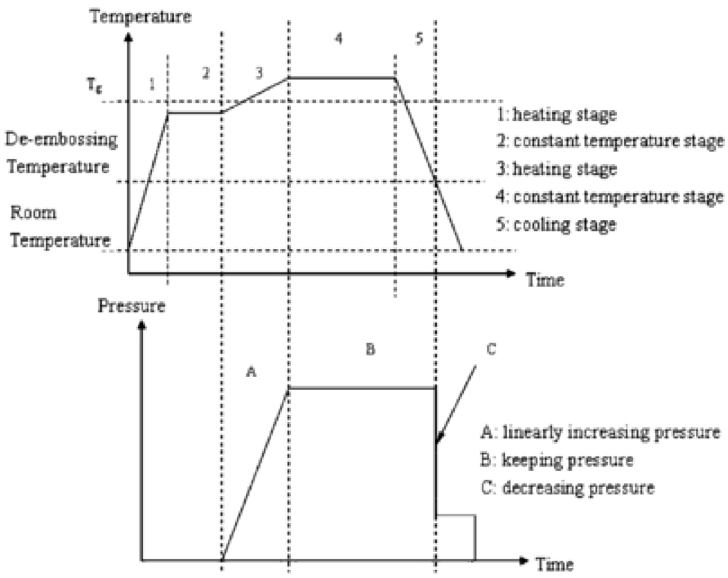


FIGURE 2.21: Pictures showing the graph for the hot embossing technique

material is then deposited on the substrate. This process involves an electron gun and a filament (the source of electrons) and magnets to direct the electron beam[12] There is another vapour deposition process called as chemical vapour deposition process. In this process directly, gasses are introduced into the vacuum chamber and the layer of the gas particles is formed on the surface of the substrate. One or more gasses can be introduced at the same time. With more then one gas introduction, the gasses react with each other and form a thin layer on the substrate[12] There are two different types of Gas introduced vapour deposition process. They are namely:

1) CVD – Chemical Vapour deposition: Gasses are introduced at the same time.

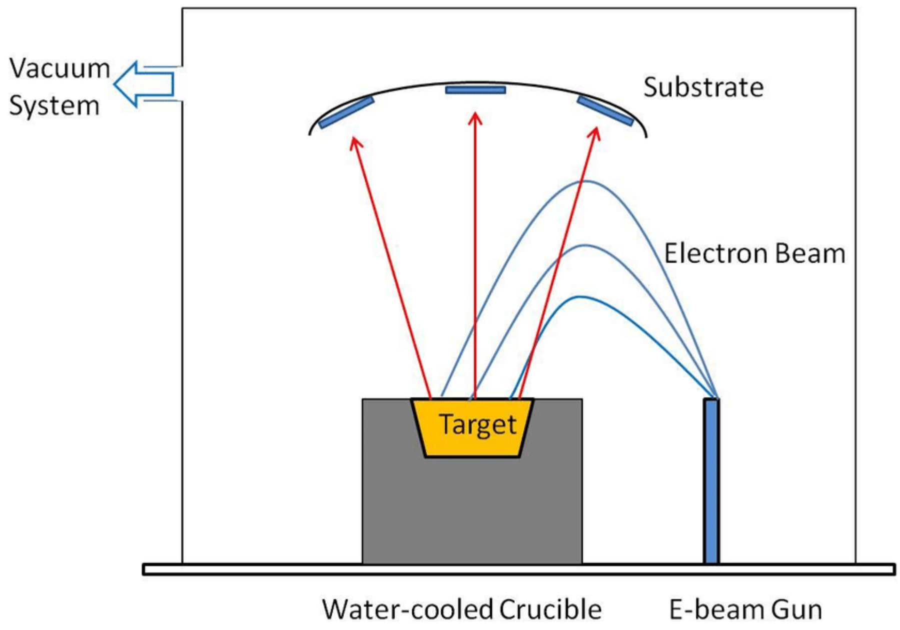


FIGURE 2.22: Pictures showing Electron beam vapour deposition process

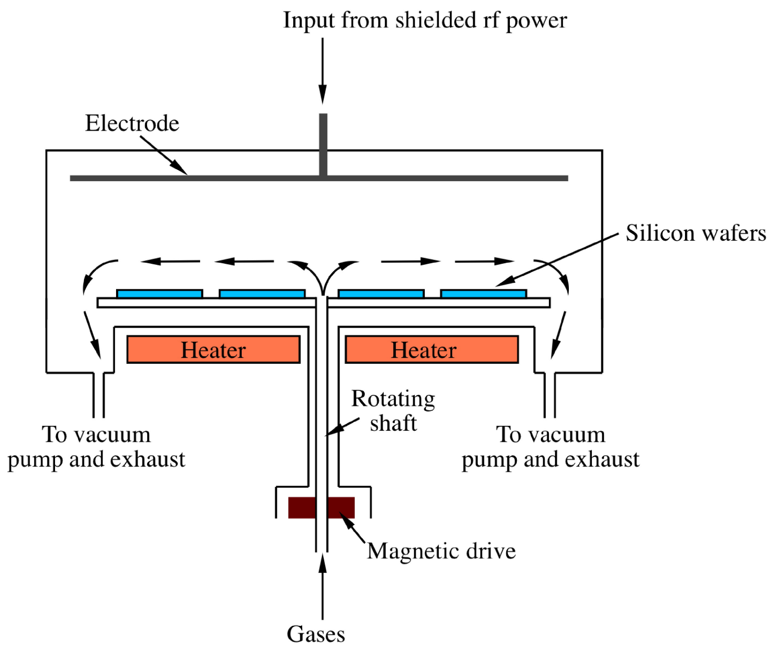


FIGURE 2.23: Pictures showing chemical vapour deposition process

2) ALD – Atomic Layer deposition: each gas is introduced sequentially that is one after another

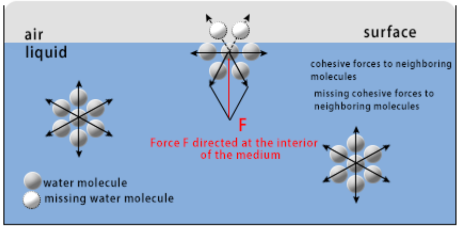


FIGURE 2.24: Pictures showing the surface tension of water

2.3 Surface Tension and Surface Energy

Surface is the main reason why the water droplets take the shape of the sphere. It is because of the cohesive forces that exists between the molecules of water. In between solid-liquid or liquid-gas interactions, adhesive and cohesive forces play a key role[13] Adhesive forces are those forces that exist between different types of molecules. Whereas, cohesive forces are the forces that exist between same type of molecules[13] The mathematical definition of surface tension is that the force per unit line (imaginary) drawn on a free surface of a liquid Let the length of the imaginary line is L. The surface tension is then

$$S = F/L$$

. Units are N/m or Dyne/cm Surface Energy of a liquid is defined as

$$W = S * A$$

. Units are J/m2 or erg/cm2[13]

Surface Energy The surface energy in the materials can be defined as work done per unit area to create a new surface of the material. The energy that is spent on creating a new surface is a combination of the energy required to break the bond and heat. So, while creating a new surface we are imparting some energy to the molecules on the surface and air molecules[14][15] So, the surface molecules of every material try to combine with other molecules to lower their energy state. For example, metals in reaction with surrounding oxygen form a thin oxide layer on the surface to lower their energy. Hence, more is the bond strength, more is the energy required to break the bond.[14][15] This explains that more is the surface energy of a material, more is the affinity to form new bonds with other materials. For example, the order of magnitude of energy for the metals is 1000 mJ/m2 and plastics such as polyethene has 30 mJ/m2 and Teflon has about 18 mJ/m2

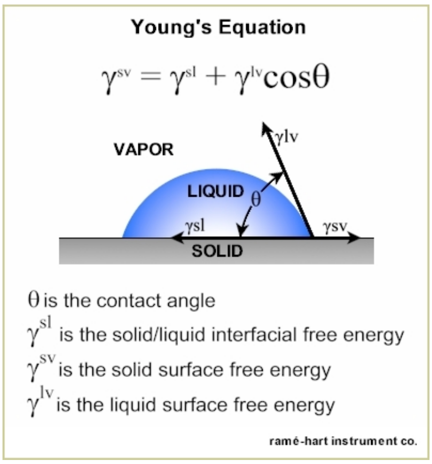


FIGURE 2.25: Picture showing surface energy and Young's equation

Another important factor to consider is the surface area to volume ratio. Which can be defined as follows:

$$N(Total) = N(Bulk) + N(Surface)$$

Where, N = number of atoms. In the same way, the energy associated with the individual atoms can also be defined as

$$E(Total) = E(Bulk) + E(Surface)$$

Where E = energy associated with individual atoms.[14][15]

Surface energy will be higher if we make the bulk material into chunks or fine powder. Hence, the bulk from has less number of surface molecules than in granulated form.[15][16]

$$(SurfaceArea)/(Volume)$$

This ratio determines the material behaviour and its reaction with other materials. For example,

$$(SurfaceArea)/(Volume)$$

ratio for bulk form is much less than the granulated form.[15][16]

2.3.1 Wenzel and Cassie-Baxter states

Each of the surfaces be it solid, liquid and gas every phase has its own surface energy [17] The surface energy of interaction between solid-liquid is represented as

$$\gamma(SL)$$

The surface energy of interaction between solid-vapour is represented as

$$\gamma(SV)$$

The surface energy of interaction between liquid-vapour is represented as

$$\gamma(LV)$$

Let us assume that all the energies are in equilibrium and we will balance the energies along the x-axis. We have,

$$\gamma(LV) * cos\theta = \gamma(SV) - \gamma(SL)$$

1) If **Theta** greater than 90 degrees we say it as hydrophilic, and if **Theta** is less than 90 degrees we say it as hydrophilic.
2) If **Theta** greater than 150 degrees then it is super-hydrophobic, if **Theta** is less than 50 degrees then it is super-hydrophilic.

Wenzel Model According to the Wenzel model, we see that the surface sticks completely on the surface [17] Let us say,

$$\gamma = (Surf.Area - (Real))/(Surf.Area - (Protected)$$

. Since every surface has some roughness and no surface is perfectly smooth,

$$\gamma > 1$$

So, the equation is,

$$cos\theta^* = \gamma * cos\theta_E$$

Cassie-Baxter Model In the case of Cassie-Baxter states, that is in the case of very rough surfaces, there is chance of air bubbles that are trapped in between the surfaces. Then the equation would become,[17]

$$cos\theta^* = -1 + \phi_s * (cos\theta_E + 1)$$

The percentage of solid that is in contact is defined as

$$\phi_s$$

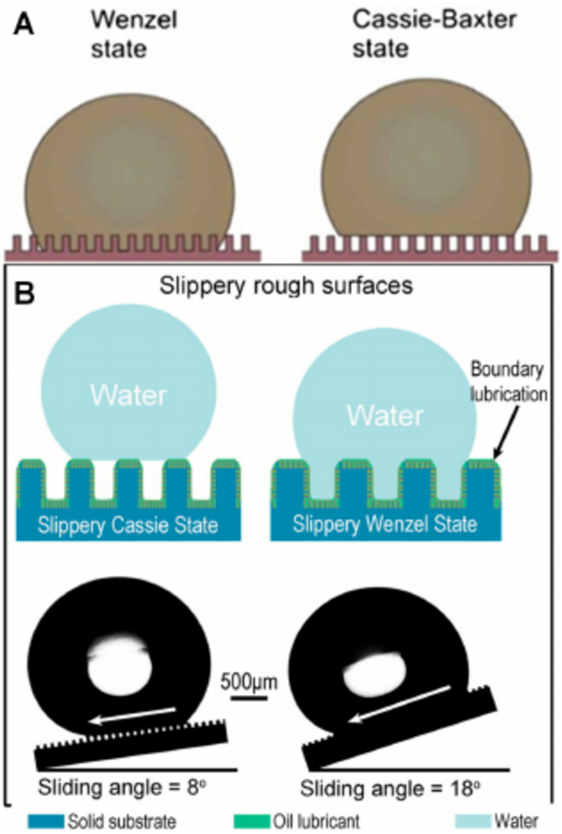


FIGURE 2.26: Picture showing Wenzel and Cassie-Baxter model

If,

$$\phi_s = 0$$

$$cos\theta^* = -1$$

then

$$\theta^* = 180 degrees$$

From the above research articles and a study on dental implants, the masking material to protect the titanium would be materials with very low surface energy and very high surface roughness

Chapter 3

Masking materials and Ideation Development

3.1 Masking materials - Polymers of Low surface energy

ADHESIVES Adhesives must spread over the solid surfaces displacing air and any other surface contaminants that are present.

• Adhesives contains oxygen, nitrogen and other electron rich atoms and are polar materials. Some of the example of industrial adhesives include cynoacrylate, epoxy, polyurethane and room temperature vulcanizing rubber. Structural adhesives examples:

1) 3M Scotch-Weld structural plastic adhesives DP8005 and DP8010. These adhesives cure at room temperature.

2) 3M Pressure sensitive adhesives. These are viscoelastic in nature, and they do not require further surface treatment or curing. These viscoelastic materials that exhibit both viscous (flow) and elastic (resistance) properties at the same time.

3) Acrylic pressure-sensitive adhesives provide the best balance of adhesion and performance properties for many applications. Bonding with acrylic pressure sensitive adhesives with low surface energies is often quite difficult and requires additional surface treatment.

4) Some tapes that are available for Low surface energy molecules are [18] **3M VHB 4932 and 3M VHB 4952 tapes**

1) Silicone

2) PTFE

3) Acetal and Polyolefin plastics (Polypropylene, PE) Considering the above mentioned

Material	Surface Tension mN/m
PTFE	18.5
Acetal	22
Silicone	24
Poly(Vinylidene Fluoride)	25
Polypropylene	29
Polyethylene	31
Polystyrene	35-37
Acrylic	39
PVC	39
PET	41
Poly carbonate	46
Nylon-6	46

TABLE 3.1: Surface tension values of various polymers

commercially available polymeric materials and their respective surface tensions, a further research on polymers with much less surface energy was made. Poly (dimethyl Siloxane) is one of such polymers, with very low surface energy. Properties of Poly (dimethyl Siloxane)

- Surface Tension (PDMS 60000 CS) at 180 degrees C = 12.1 mN/m
- Surface Tension (PDMS 1000000 and 60000 CS) at 150 degrees C = 13.6 mN/m

3.2 Bio-inspired sealing (Mask/Cap)

3.2.1 Adhesive mechanism of various insects

Since, all the dental implants are subjected to chemical etching, there is need for a proper sealing of the cap to prevent the acid to flow inside the protected area. Dental Implants consists of external thread like structure. The external protective cap must have a sealing structure may be within the cap or in the form of external component that is placed on the cap. "Bio-inspiration" is one of the best ways to find answers. Initial study resulted in looking at the different adhesive mechanisms such as Geckos and other organisms that attach and detach to a surface in a simple way. The gecko's feet are one of the examples of how it can attach and detach from any surface[19][20]

A better approach to stick to any rough surface is to look out for the adhesive mechanisms of insects. Insects usually when climbing vertical surface, they use claws, tibial spines or tarsal pads. For example, the cockroaches utilize claws and tibial spines to hook onto coarse substrate[21] These insects rely on interlocking mechanism. The claws, spines and hooks rely on compressive normal forces to generate traction against the surface. Analogy between the sand paper and claw tip is that, sharper the claw tip and

FIGURE 3.1: Picture showing Gecko's feet

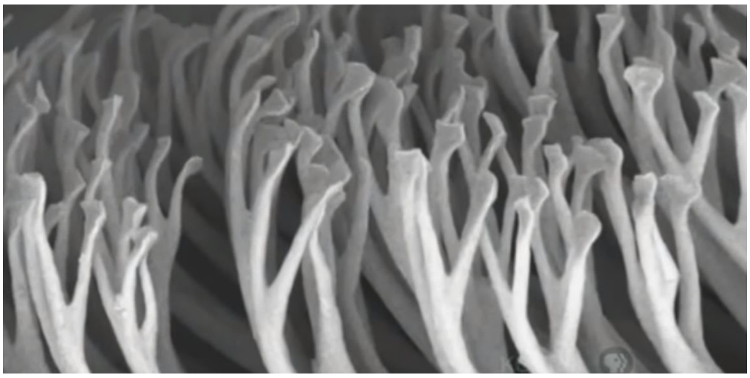


FIGURE 3.2: Picture showing microscopic adhesive hairs

rougher the substrate, the greater the effective friction coefficient. Geckos uses many microscopic hairs that provides weak Van-der Waal forces of attraction and thus providing the attachment. These Van-der Waals forces provide the principle for DRY ADHESION. On the other hand, crickets use surface conforming pads and these pads produce adhesive liquid.The attachment in flies and geckos make use of tangential contact forces. The important aspect lies in detachment of the leg with minimal force expenditure. This happens only when the attachment pad is peeled of the global scale. In geckos, the peeling force is generally 90 degrees normal to the surface[21]

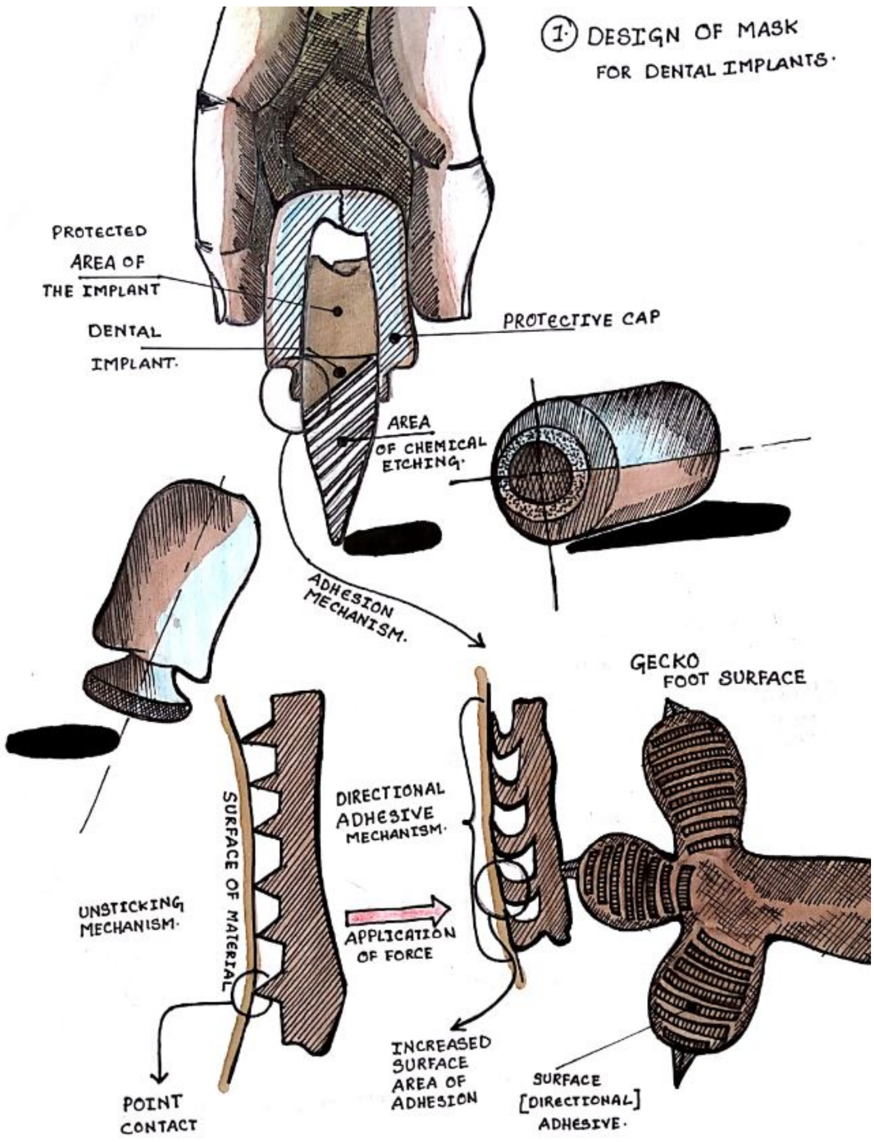


FIGURE 3.3: Gecko inspired adhesive sealing

3.3 Claw and Adhesive pad sealing effect and ideation

Many researchers made quite a lot of experiments about the adhesive mechanisms in various insects. Such an experiment was made on Asian Weaver ants. These ants have arolia pads which is an adhesive organ of these ants. These pads can be folded and unfolded with each step. Extension of the arolium pads would contact the surface and thus increases the contact area[22] **Attachment and Detachment**

Attachment

- Maximum attachment is achieved when adhesive pads are pulled towards the body.
- Pulling the tarsus towards the body.

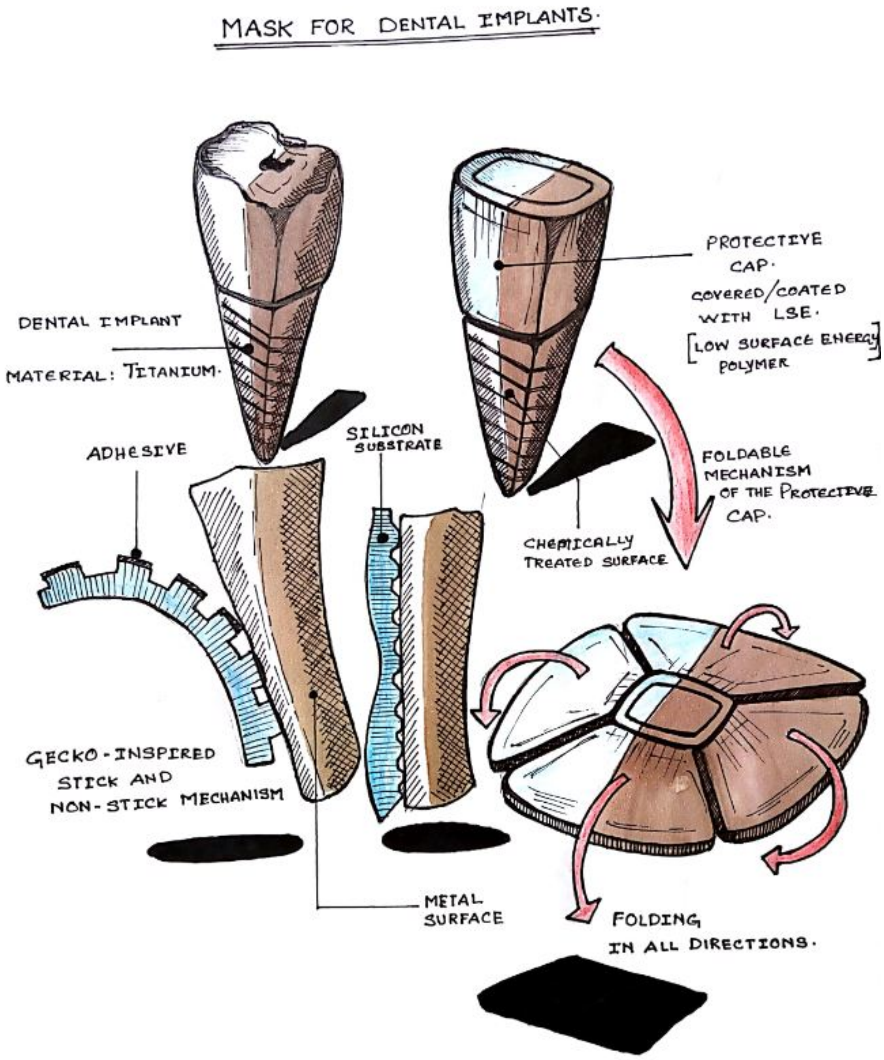


Figure 3.4: Concept 2

Detachment

- Detachment occurs when the pads are pulled away from the body.
- Folding back the arolium

The Claws are made up of stiff, and hard keratin and probably more wear resistant than adhesive pads. These claws have an advantage over the adhesive pads only if they are tither able to interlock with surface asperities, or if they significantly indent and /or penetrate the substrate.[23] Key factor: the ability of the claw to interlock depends upon the radius of the claw tip **R(ct)**[23]

Another experiment was conducted to measure the performance of both adhesive pads

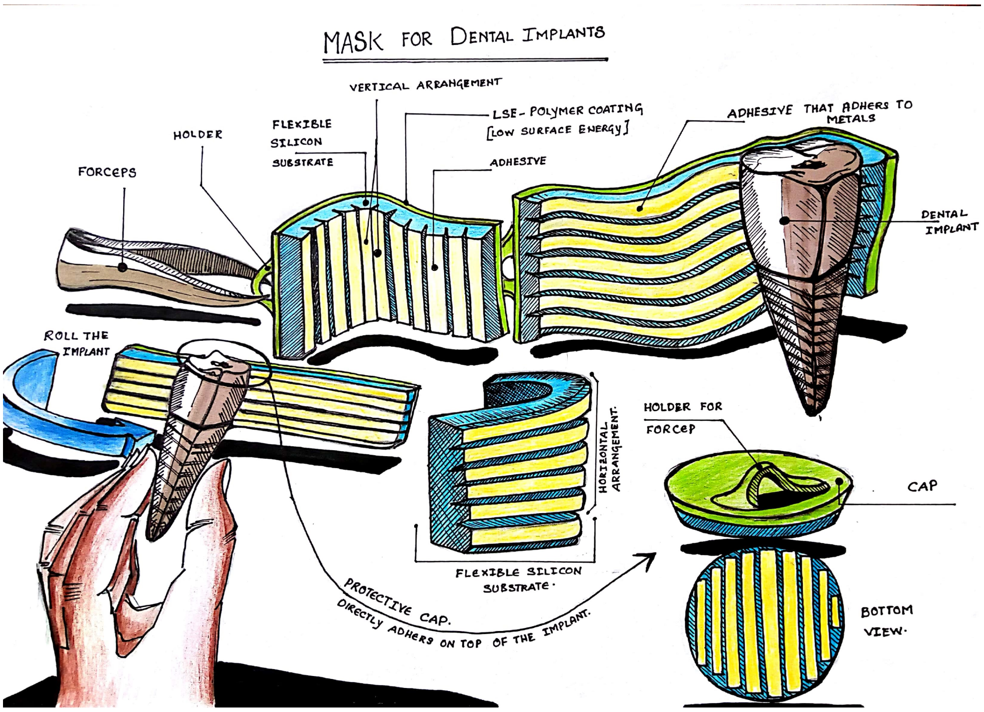


FIGURE 3.5: Concept 3

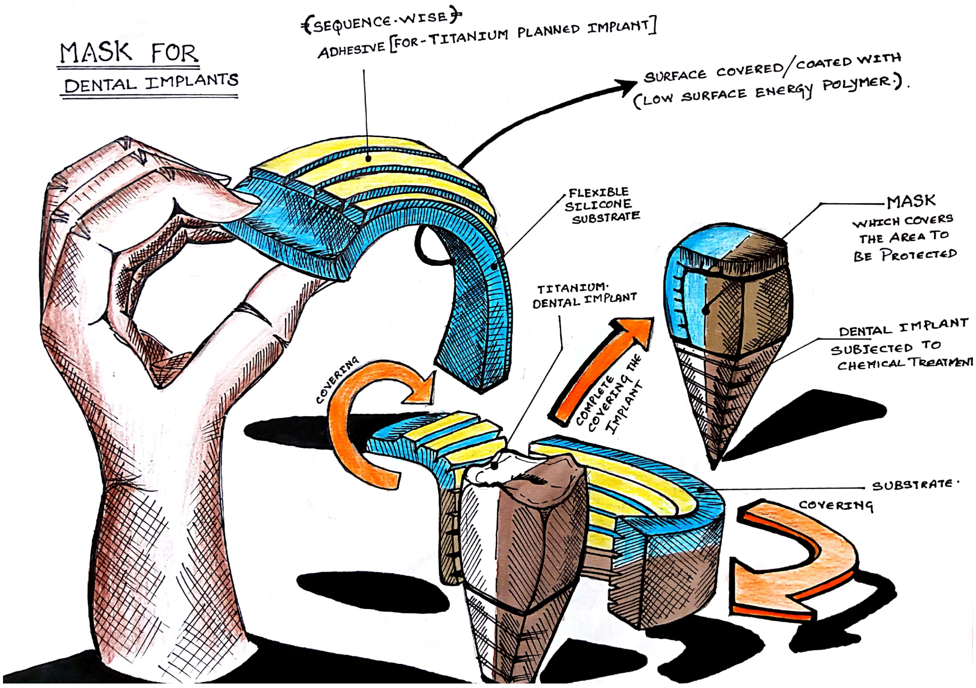


FIGURE 3.6: Concept 4

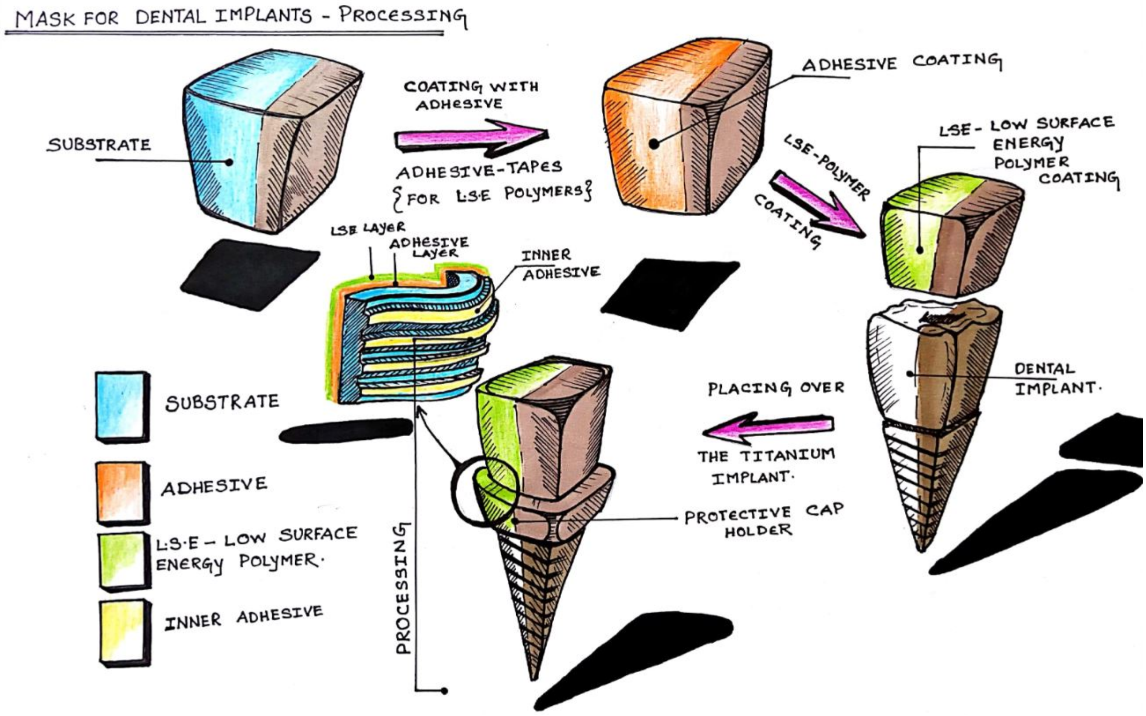


Figure 3.7: Concept 5

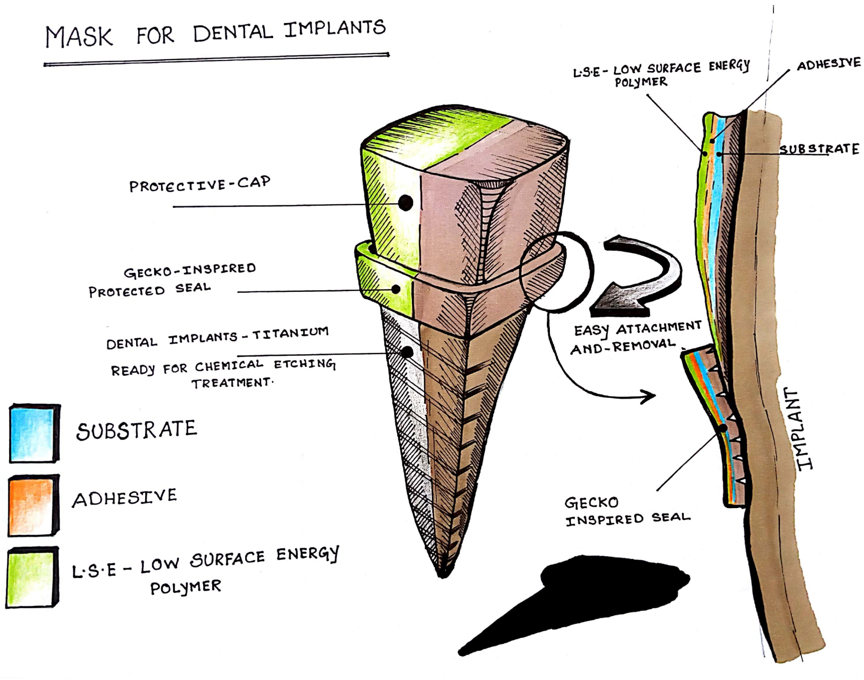


Figure 3.8: Concept 6

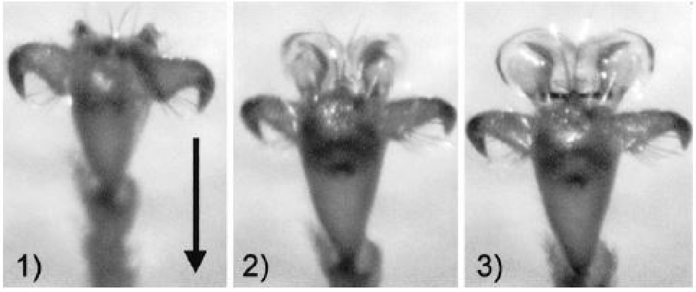


FIGURE 3.9: Claw movement

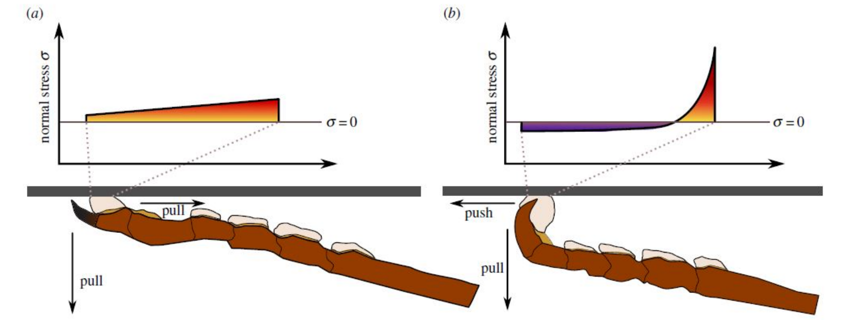


Figure 5. Shear forces may be used to control the normal stress distribution in the contact zone of adhesive pads. When legs are pulled towards the body, normal stresses may be relatively uniform, resulting in strong attachment. If pads are pushed away from the body, the chain-like tarsus may buckle, causing strong stress concentrations at the proximal edge of the pad, facilitating easy detachment. A more detailed discussion of the effect of pushing and pulling on the stress distribution is given in §7b. Note that the figure is not drawn to scale, and stress distributions are shown only schematically.

FIGURE 3.10: Stresses and adhesive nature

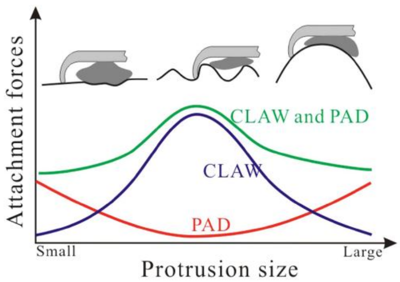


FIGURE 3.11: Adhesion levels claw and pad

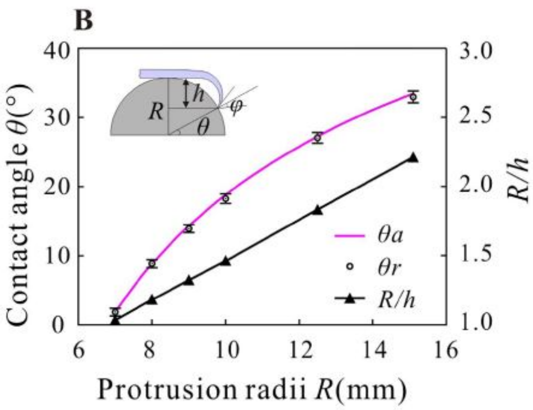


FIGURE 3.12: Contact angle and protrusion radii

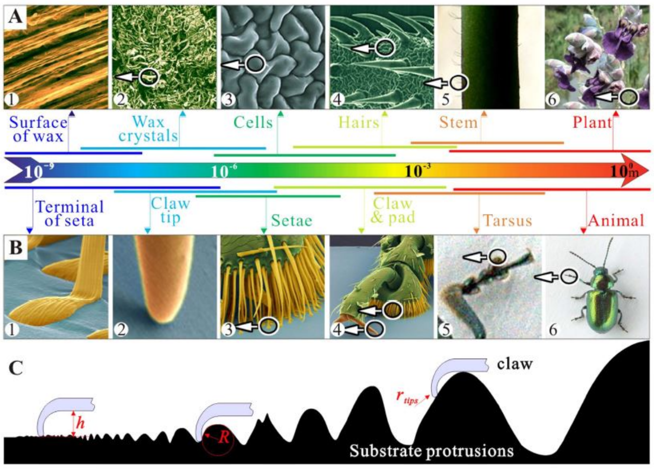


Figure 1. Comparison of different scales of biological devices and natural substrates. (A) Surfaces (plants) at different magnifications. The circles and arrows indicate detail views and the color bars indicate possible scale ranges. (B) Insect (leaf beetle) with attachment pads and claws at different magnifications. (C) Sketch of interactions between insects' claw and substrate protrusions, where, h is the size of the claws, R is the mean radius of substrate protrusions and r_{tip} is the radius of claw tips.

FIGURE 3.13: Radius to height ratio

and claws together. This experiment resulted that the synergy between adhesive pads and claws have much stronger attachment forces than compared to adhesive pads and claws when tested independently[24]

Dry Adhesive mechanism uses Van-der Waals forces or Capillary force. These are employed by flies, geckos and other insects. Wet Adhesive mechanism uses smooth soft pads and generate adhesive forces through capillary interactions. These are employed by frogs, ants and crickets[24] The design of the claw depends upon the substrate protrusion (R), usually not larger than the mean radius of the claw tip **R(tip)**. Important:

$$R/h <= 1$$

for the claw to never slip of the substrate[24] From the above graphs we see that the protrusion size and the claw tip radius are necessary to be near equal to attach to the profile [23] Let us assume that the R is the radius of the protrusion. The height of the claw tip from the protrusion or can be called as the claw tip radius. Thus, as mentioned above, for the claw tip to not to slip form the surface of the protrusion, we have the relation that

$$R/h <= 1$$

[24] Hence, the design of the claw tip depends upon the claw tip radius and radius of the protrusions. The idea here is to make a firm attachment with the surface of the implant, hence making a proper sealing condition.

This technique helped to come up with two possible designs namely, adaption of complete internal thread and separate cap with external sealing.

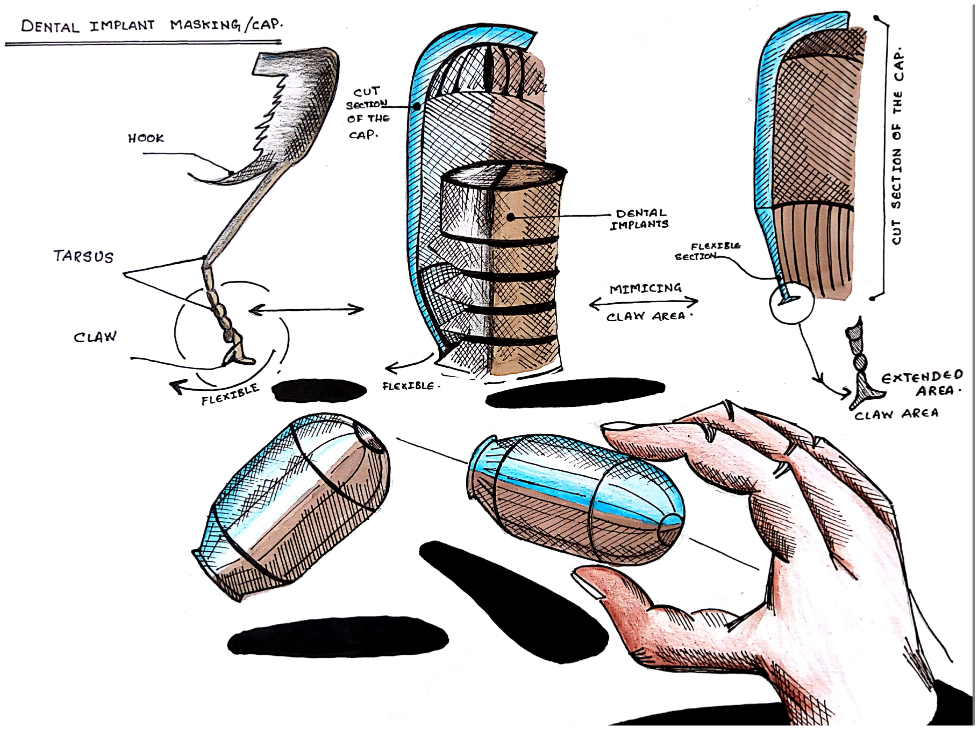


Figure 3.14: Concept 7

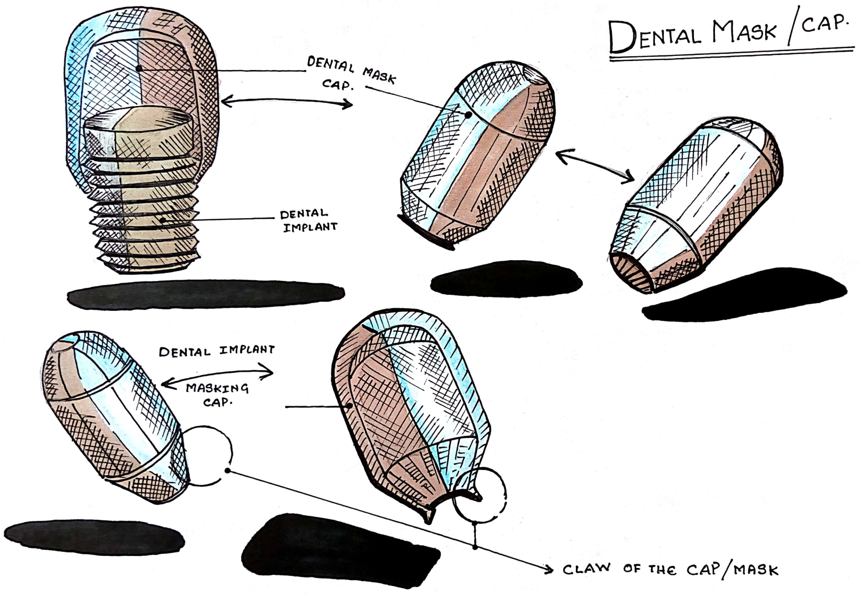


Figure 3.15: Concept 8

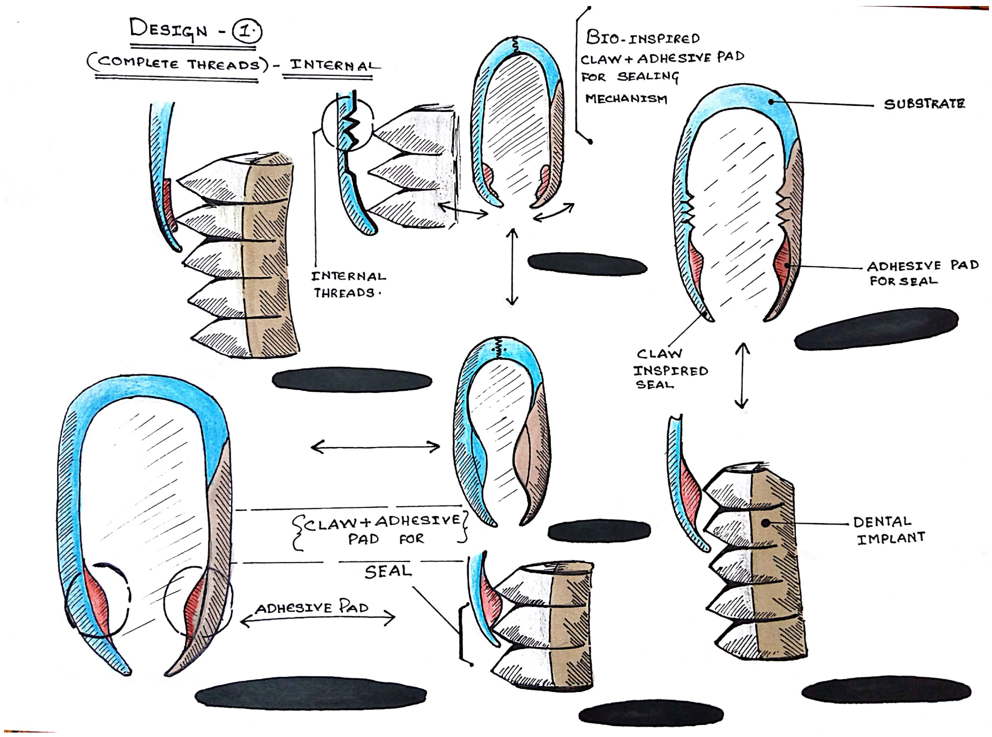


FIGURE 3.16: Concept 9

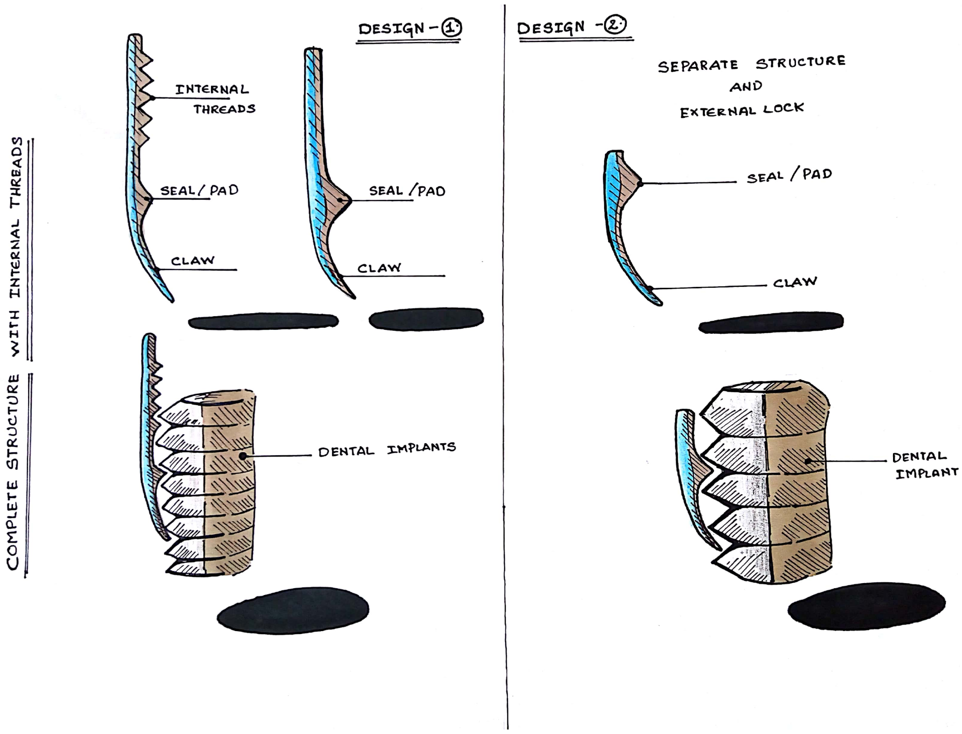


FIGURE 3.17: Concept 10

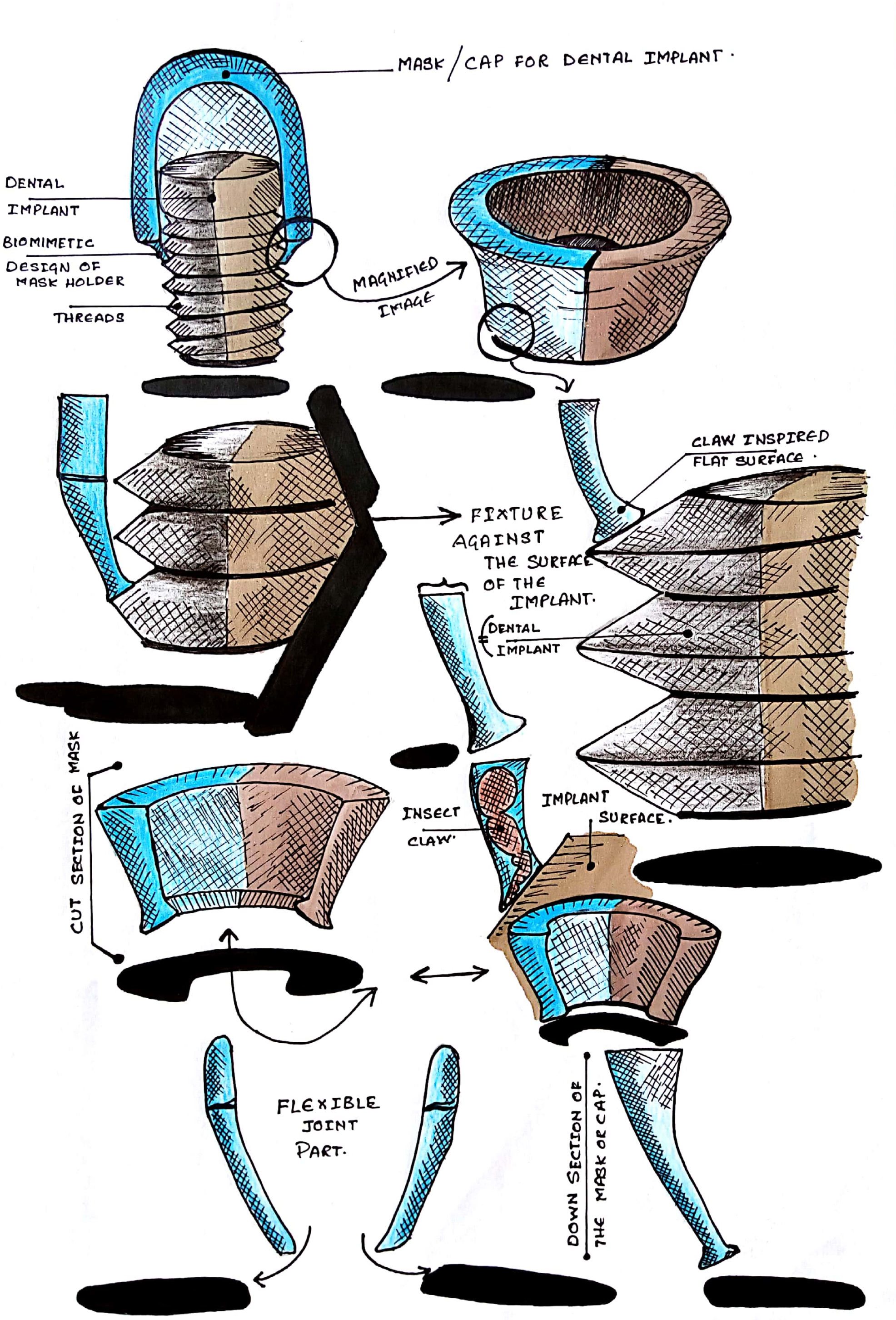


Figure 3.18: Concept 11

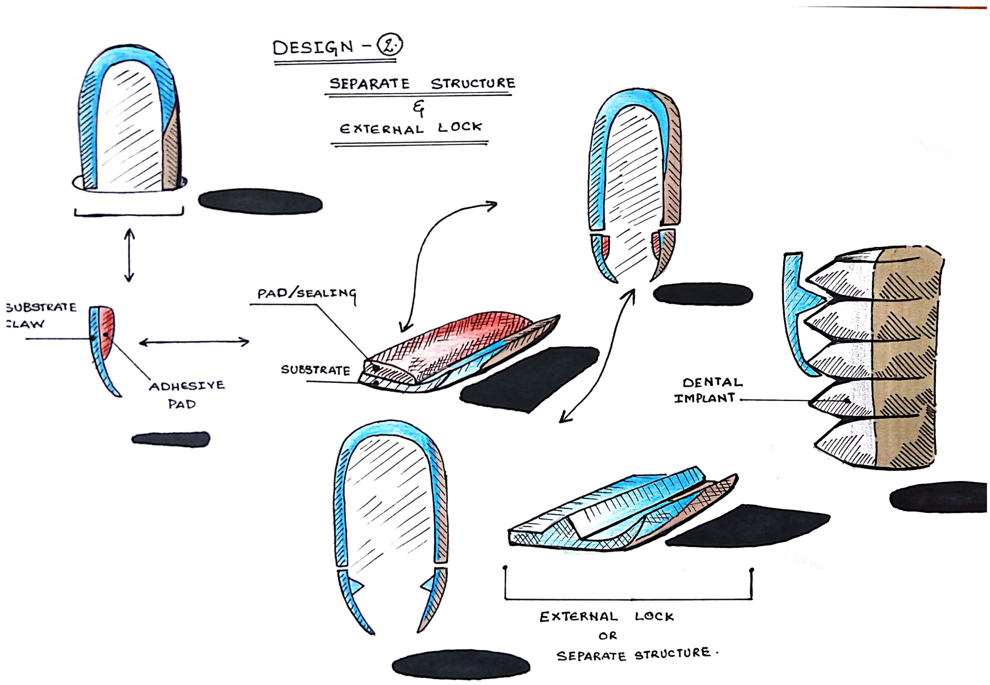


Figure 3.19: Concept 12

Final Designs-next page

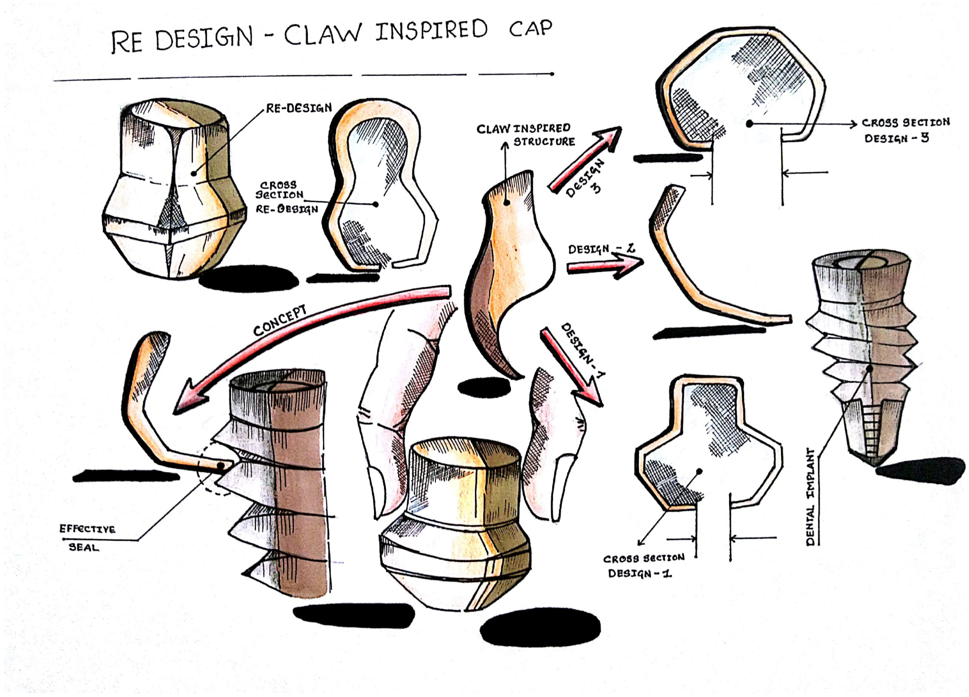


FIGURE 3.20: Final Concept

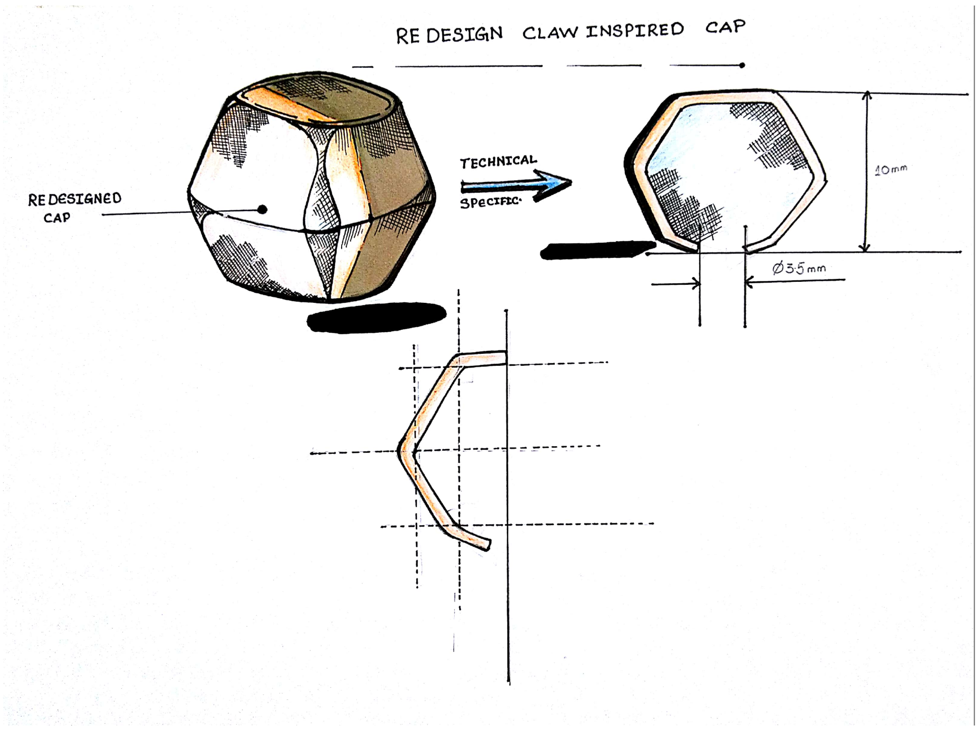


FIGURE 3.21: image showing the final design

Chapter 4

Methods and Experimentation

4.1 Experimentation with ABS

We have made a brief experimentation with the ABS plastic (Acrylonitrile Butadiene Styrene) to replicate the exact structure of the claw and pad design.

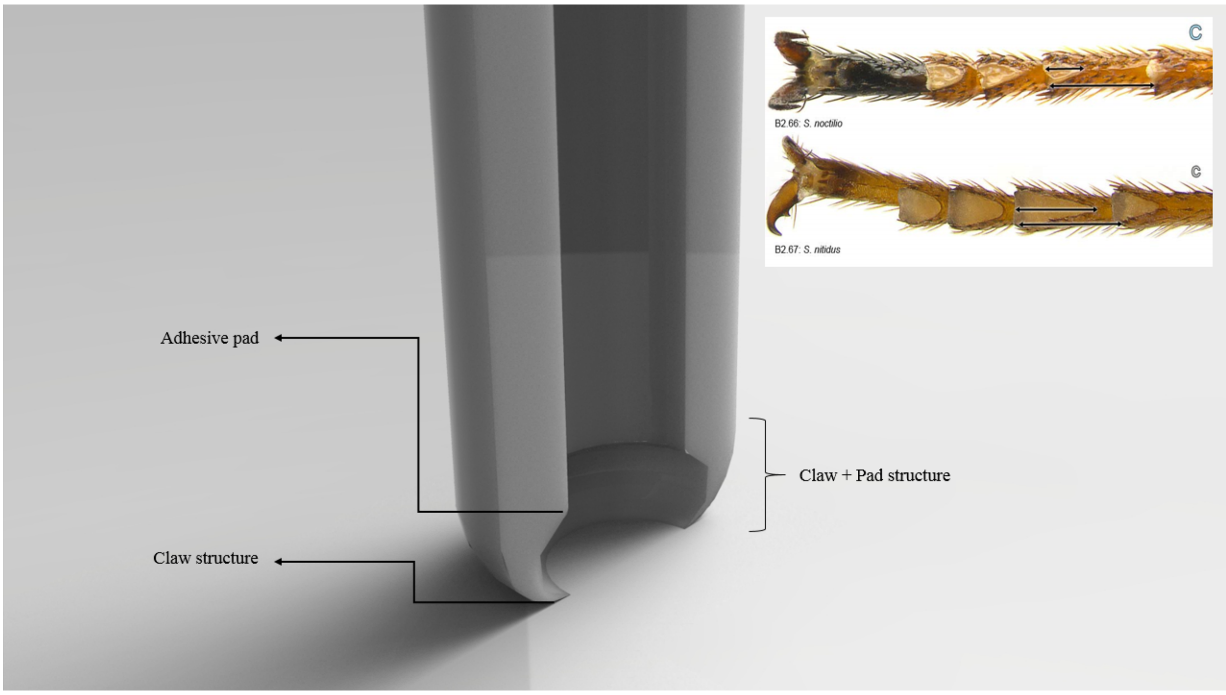


FIGURE 4.1: Image showing the render of the design of claw and pad

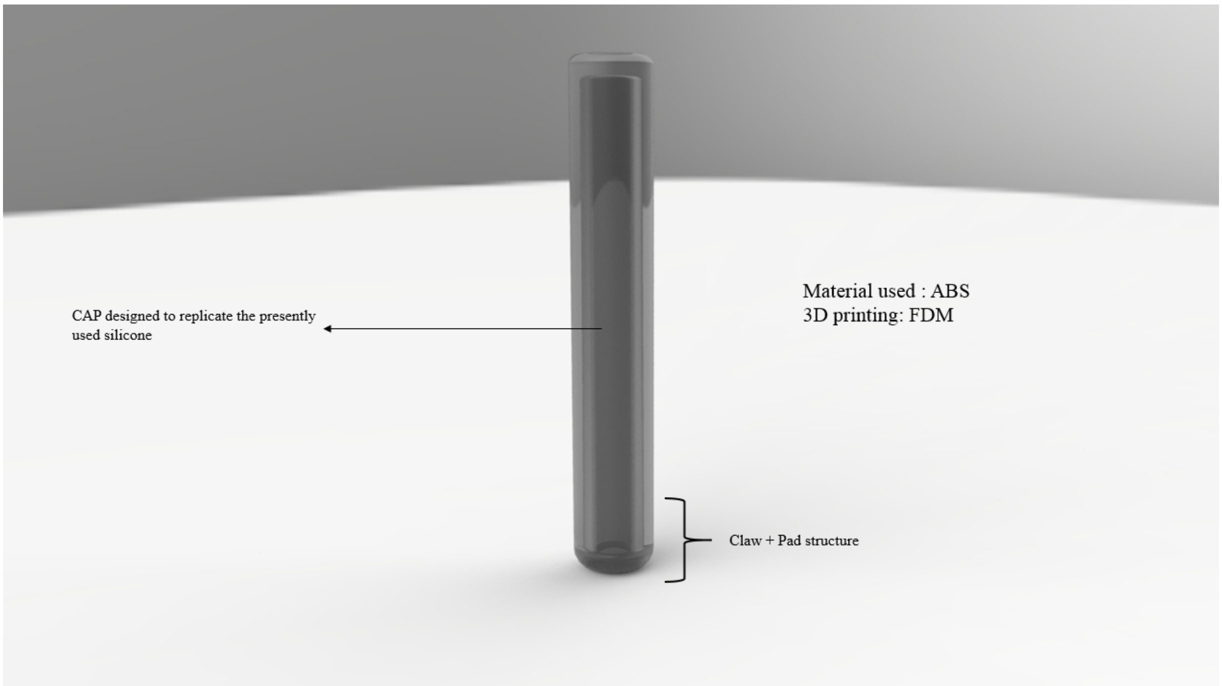


FIGURE 4.2: Image showing the render of the caps

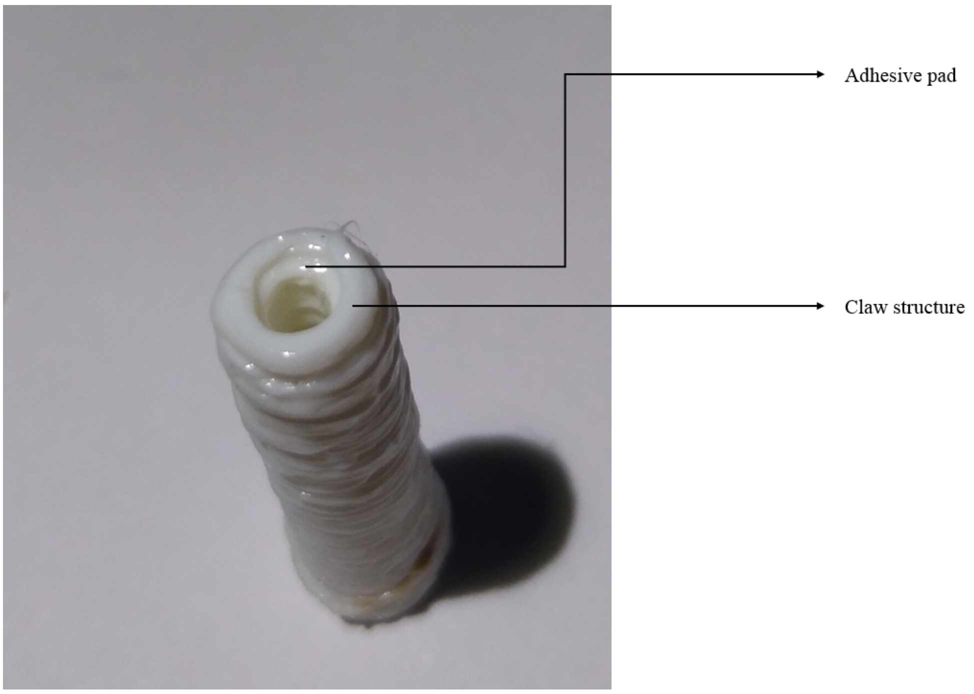


FIGURE 4.3: Image showing caps printed with ABS (sample 1)

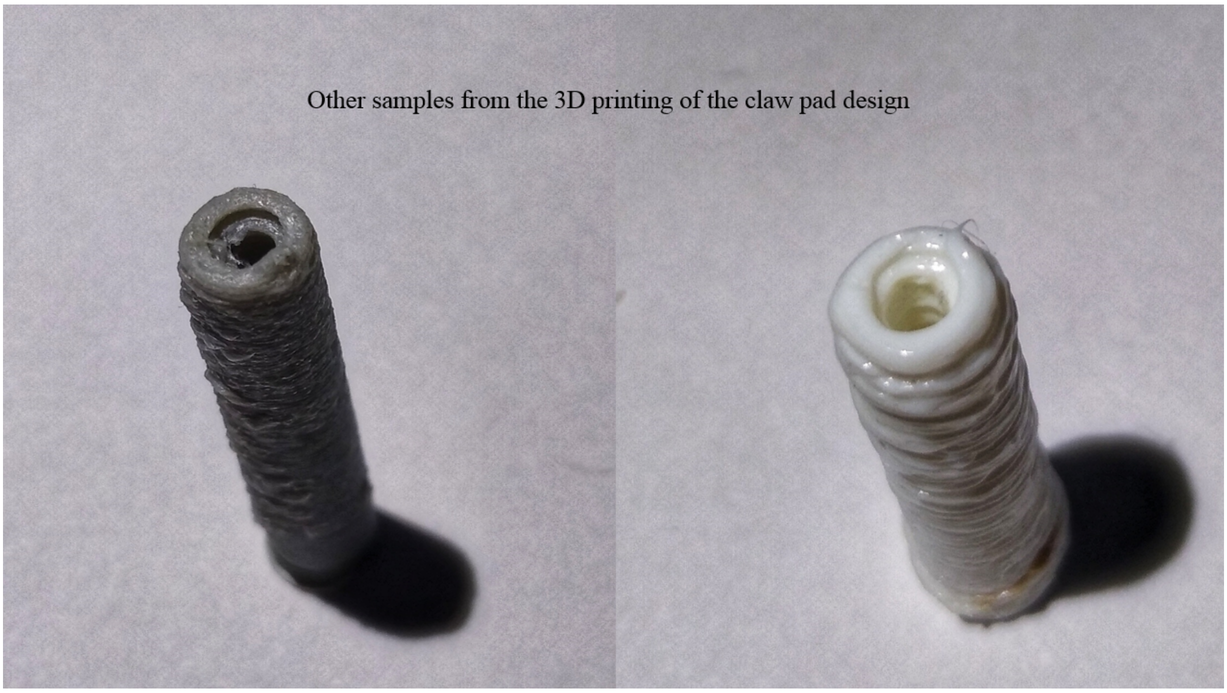


FIGURE 4.4: Image showing the caps printed with ABS (sample 2 and 3)

4.2 Experimentation with TPU

We have performed the experiments on TPU samples to see whether they can withstand the corrosive effect of the acids for a 30 min time period at 50 degrees centigrade. The results are as follows:

• The 3D printed PU sample is cut into 6 mm by 6 mm into 6 samples and was weighed before and after the acid treatment.

In this experiment, the material TPU is tested because this material is flexible and would mimic the flexibility of the insect claw.

Before acid treatment	**After acid treatment**
0.059 g	0.052 g
0.058 g	0.057 g
0.055 g	0.052 g
0.058 g	0.056 g
0.058 g	0.056 g
0.057 g	0.030 g

TABLE 4.1: Weights of the TPU samples before and after chemical treatment

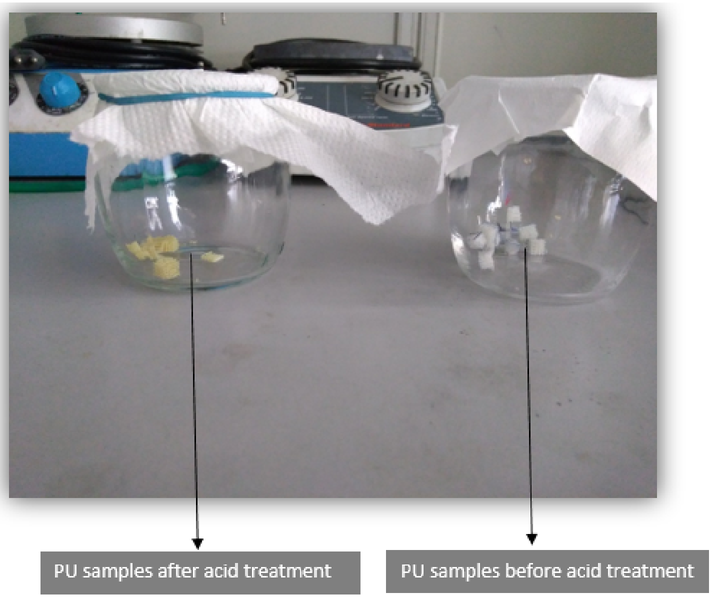


FIGURE 4.5: TPU samples before and after chemical treatment

FIGURE 4.6: Picture showing the weighing the TPU samples

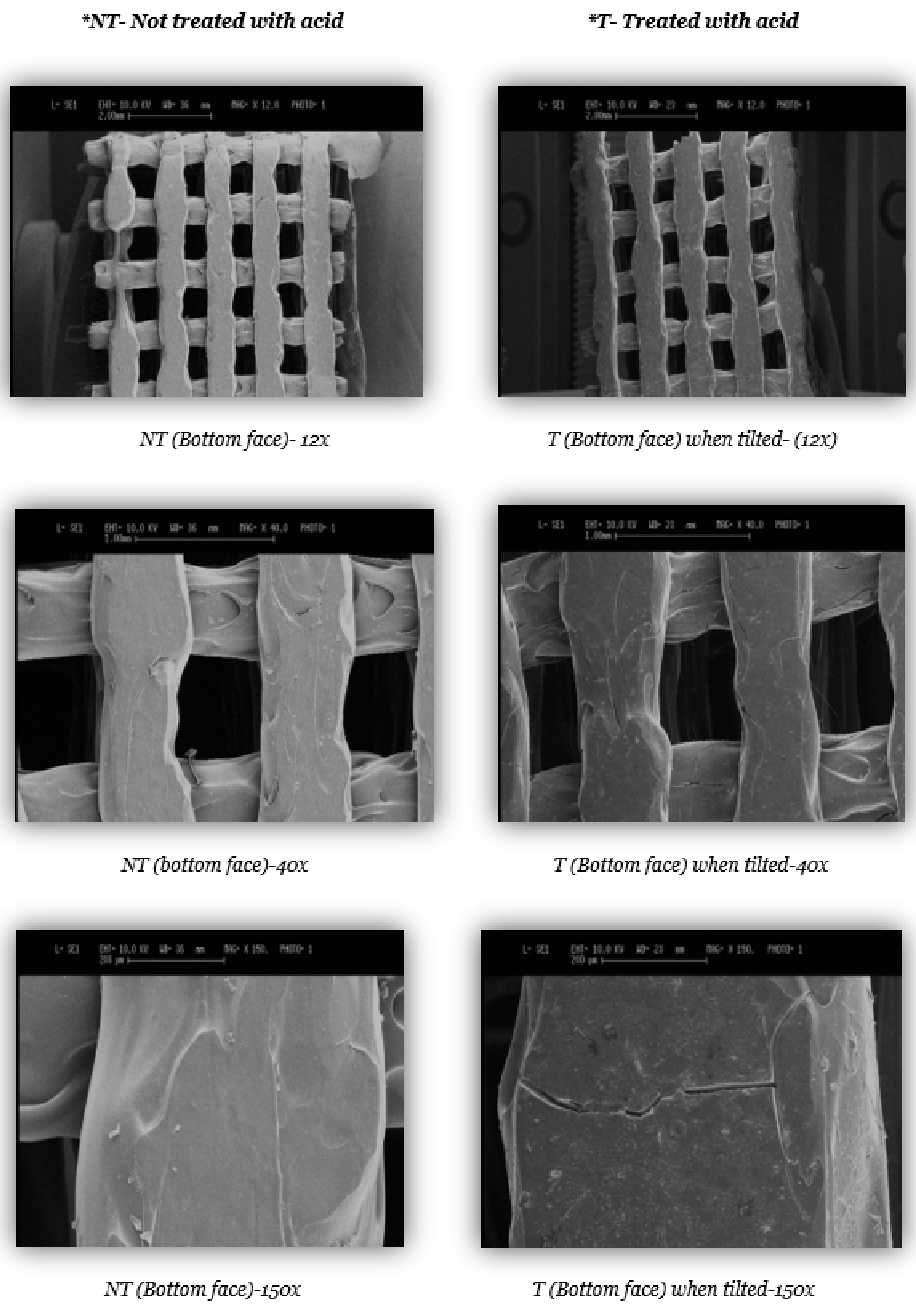


FIGURE 4.7: Picture showing the SEM images after chemical treatment for 30 min top surface

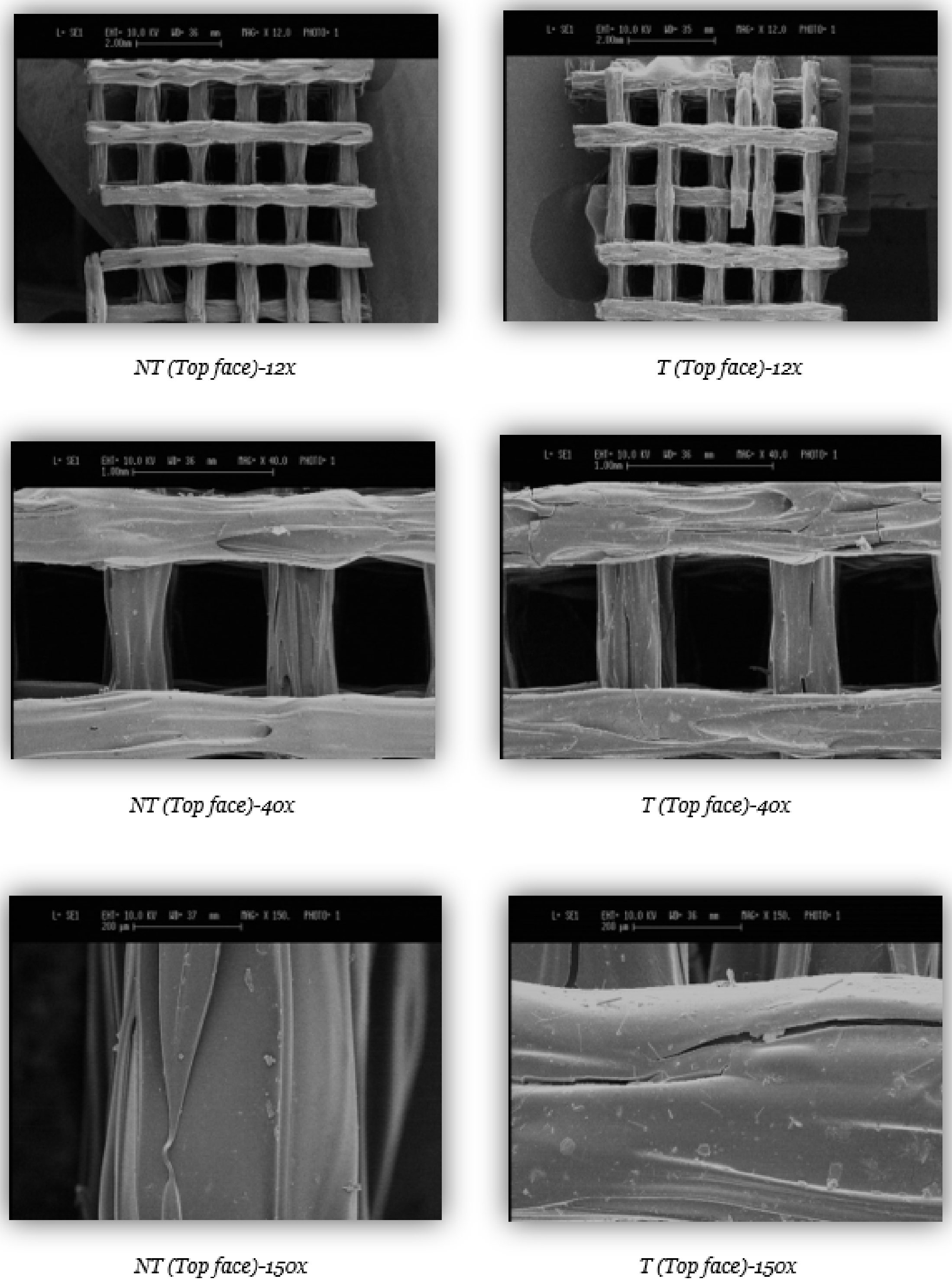
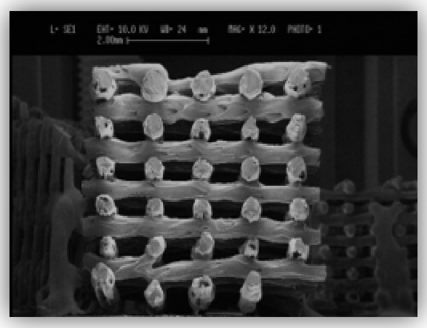
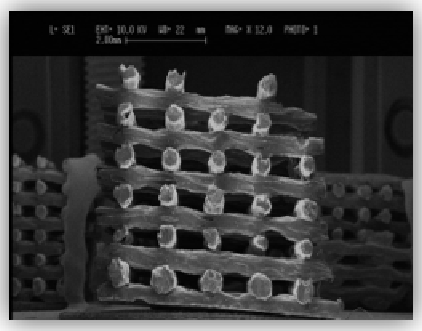


FIGURE 4.8: Picture showing the SEM images after chemical treatment for 30 min, to the left images of not treated samples and to the right images of treated samples

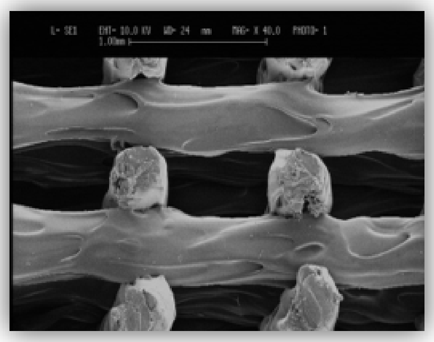
Observation Cross sections



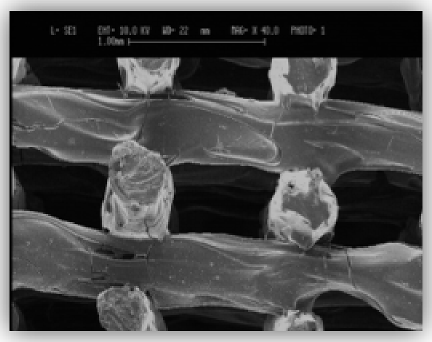
NT when tilted- 12x



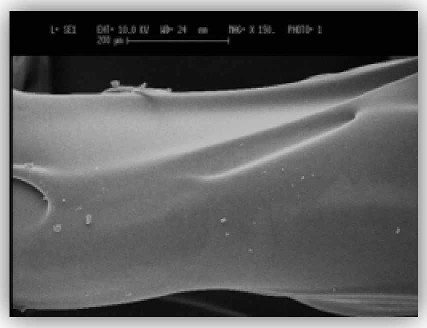
T when tilted- 12x



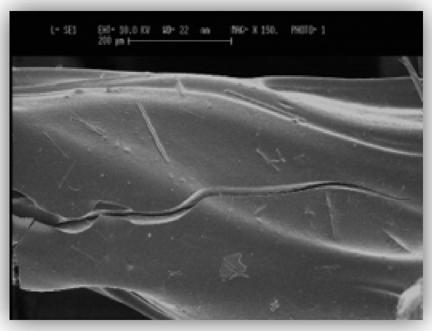
NT when tilted-40x



T when tilted- 40x



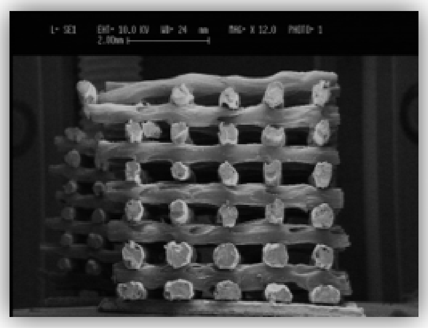
NT when tilted-150x

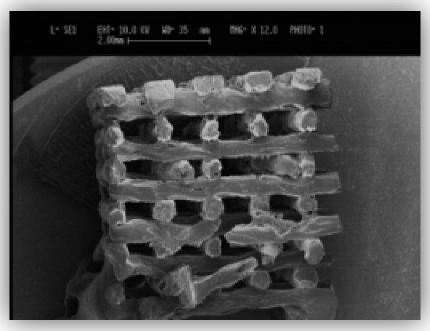


T when tilted-150x

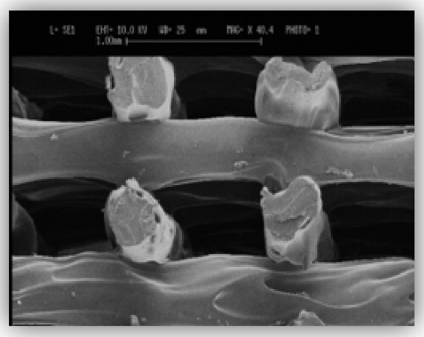
FIGURE 4.9: Picture showing the SEM images of filament cross-section after chemical treatment for 30 min,to the left images of not treated samples and to the right images of treated samples

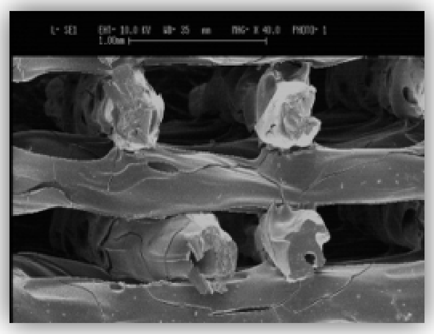
Observation Cross sections



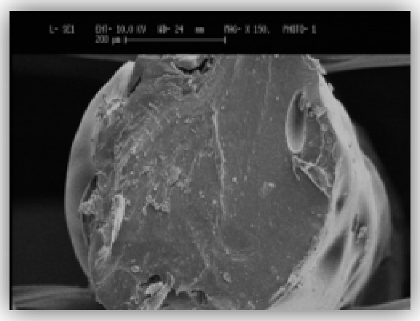


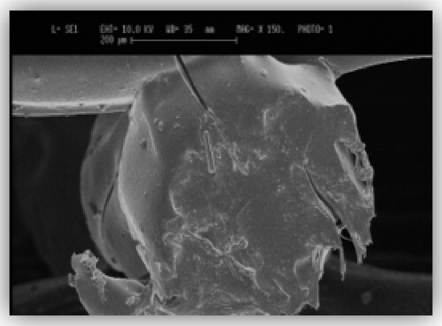
NT Cross section when tilted- 12x | *T Cross section- 12x*





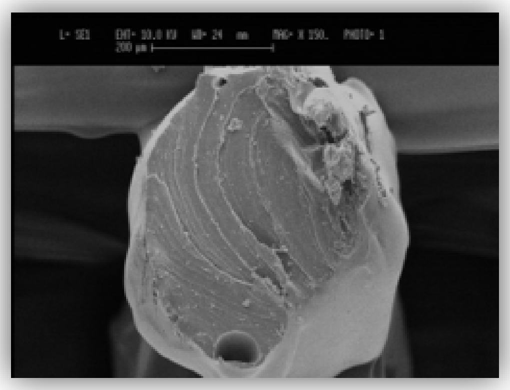
NT Cross section when tilted- 40x | *T Cross section-40x*



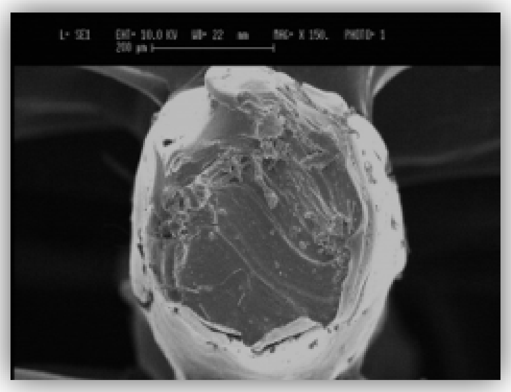


NT Cross section when tilted- 150x | *T Cross section- 150x*

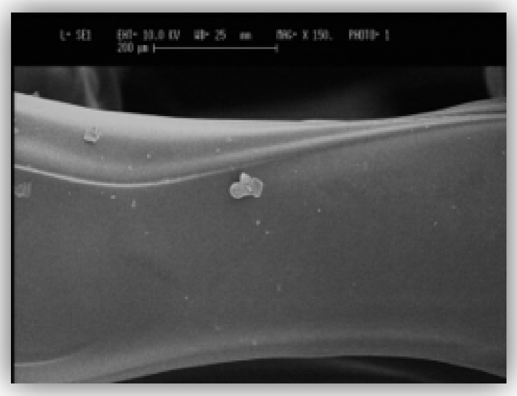
FIGURE 4.10: Picture showing the more detailed SEM images of filament cross-section after chemical treatment for 30 min,to the left images of not treated samples and to the right images of treated samples



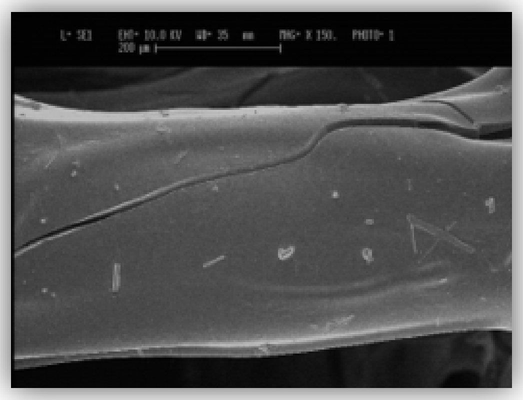
NT Cross section of strand when tilted- 150x



T Cross section of strand when tilted- 150x



NT filament- 150x



T filament-150x

FIGURE 4.11: SEM images of filament cross-section after chemical treatment for 30 min,to the left images of not treated samples and to the right images of treated samples

4.3 Bio-inspired caps printing & Experimental setup

The chemical treatment was done by preparing 100 ml solution of 10 percent V/V sulphuric acid and 20 percent V/V Hydrochloric acid. This is typically used in the SLA chemical etching process. The experiment was carried out at 50 degrees centigrade constant temperature. LSE-Low Surface Energy Polymer tapes used are

1) **3M Nastri vinilici**-Product code 471

2) **26BR High Temp RTV Red Silicone GASKET MARKER 3OZ**-Product NO: 81160

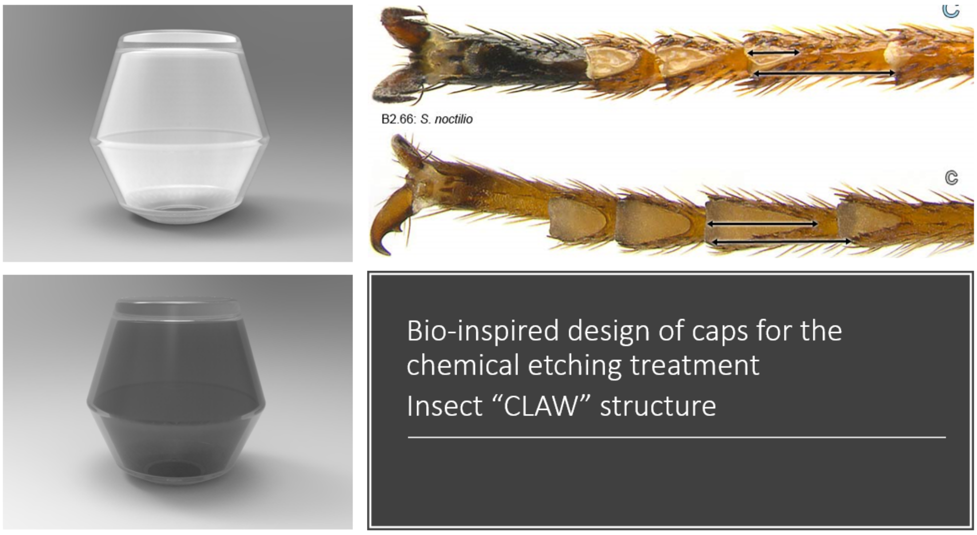


FIGURE 4.12: Image Bio-inspired caps design

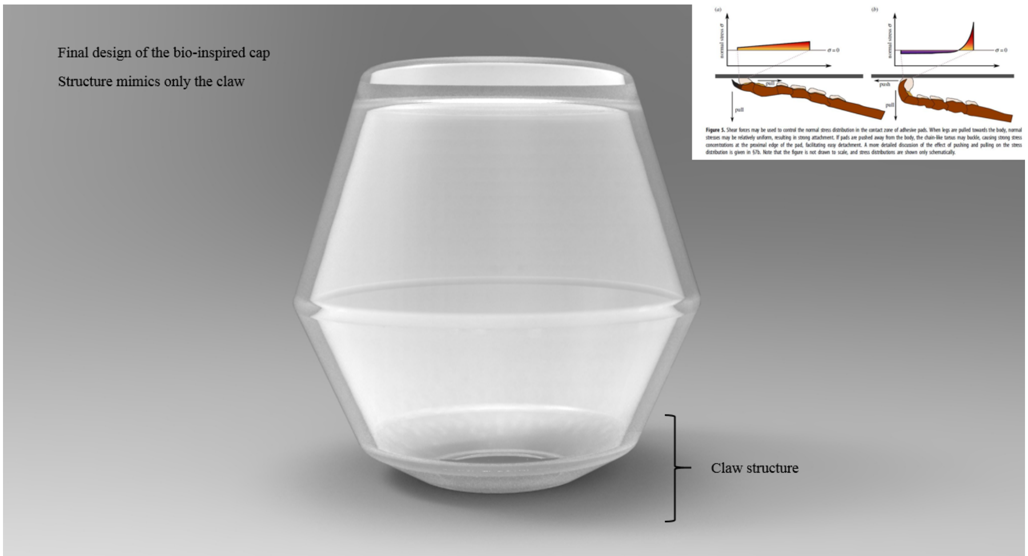


FIGURE 4.13: Image showing the render of the cap design 1

4.3.1 Why TPU material for Bio-inspired caps

The caps were 3d-printed using the **Slic3r** 3d-printing machine using the TPU filament. As mentioned earlier, the main reason for using TPU filament is that, it is very flexible and can imitate the flexibility of the claw structure. Even though TPU is not resistant to very high corrosive environments for example, strong acid environments, the main aim is to see whether the structure would protect the surface form such corrosive environments for up-to 30 minutes. As you can notice form the images taken by the Scanning Electron Microscopy (SEM), TPU samples could withstand such harsh environments for up-to 30 min. So, we have decided to use TPU to 3D print the caps that resemble the claw structure.

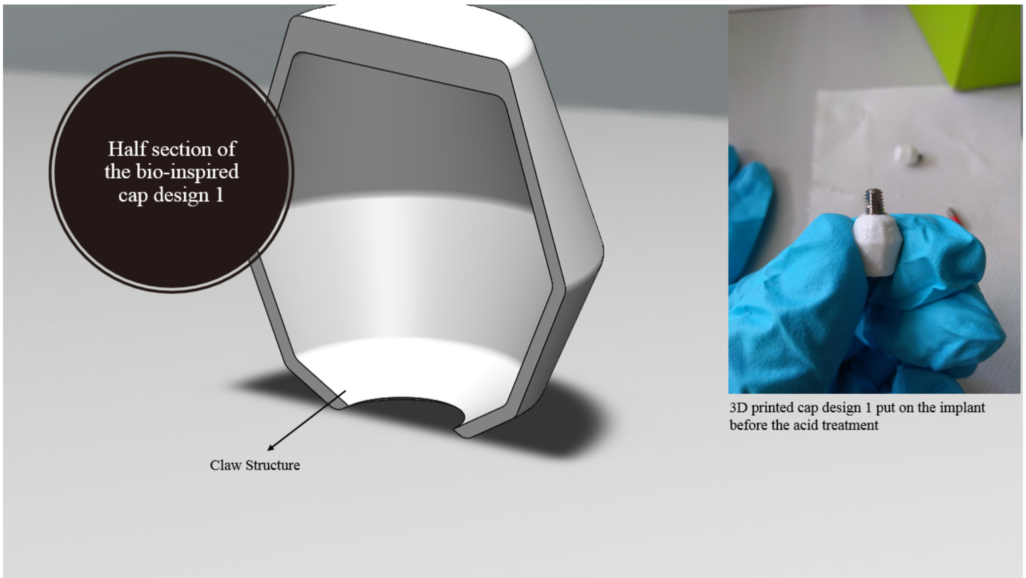


FIGURE 4.14: Image showing the half-section of the cap design 1

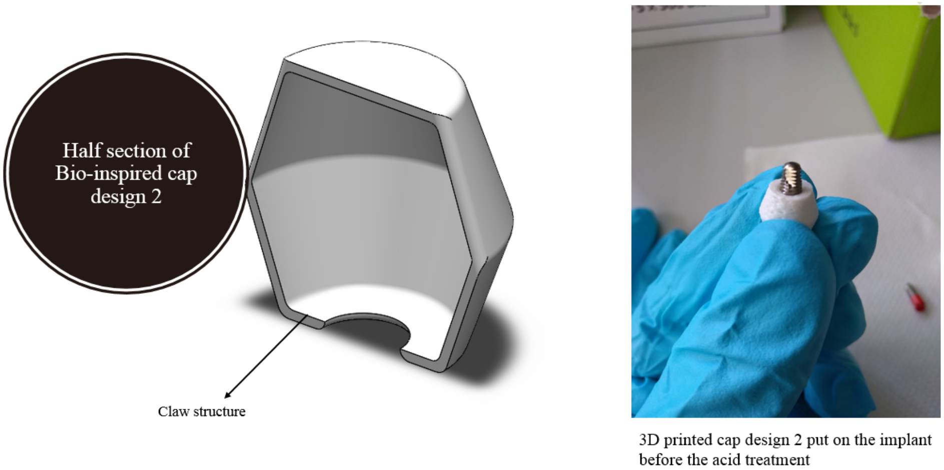


FIGURE 4.15: Image showing the half-section of the cap design 2

FIGURE 4.16: Solution preparation and setup of the chemical etching experiment

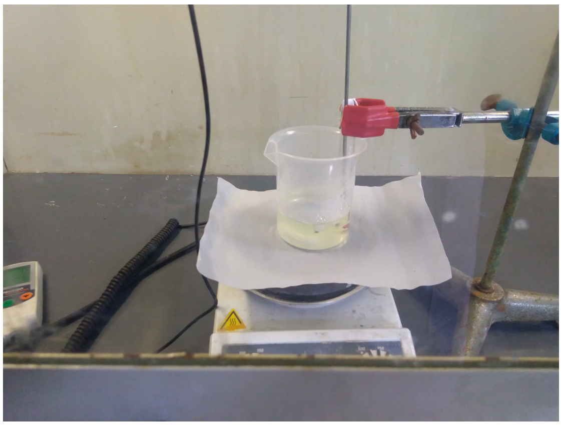


FIGURE 4.17: Image showing the experimental setup of the chemical etching experiment along with the thermometer and dental implant samples inside

FIGURE 4.18: Image showing the samples covered with different materials including the 3d printed caps

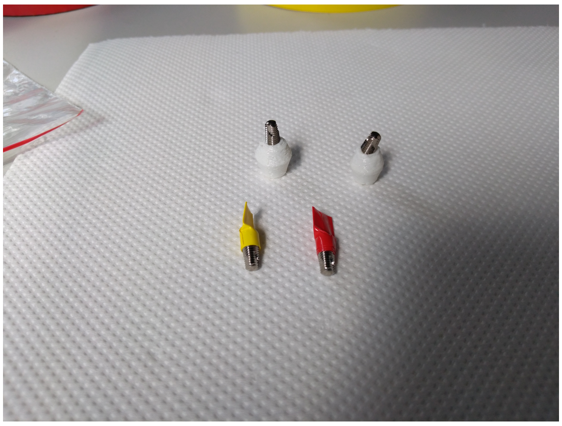


FIGURE 4.19: Image showing the samples ready for the experiment

FIGURE 4.20: Image showing the 3d printed bio-inspired cap design 1

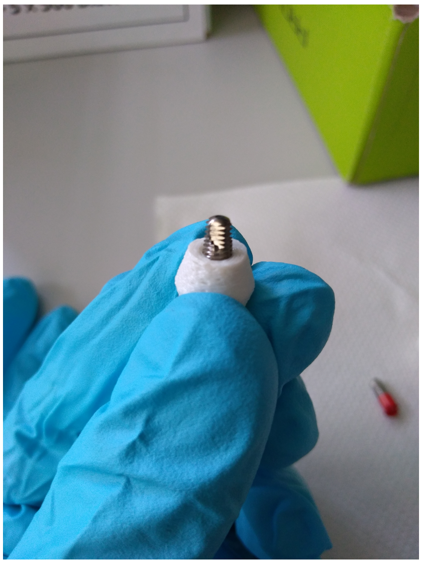


FIGURE 4.21: Image showing the 3d printed bio-inspired cap design 2

4.4 Sand-Blasting & Chemical etching of Dental Implants

As apart of the complete dental implant preparation, we have used the sand blasting technique, before the acid etching treatment. This treatment is done to remove the passivization layer of titanium oxide, and making it ready for the chemical etching process.

After the sand blasting treatment, the samples are stored in 37 percent concentrated HCL (Hydrochloric acid) to prevent the formation of titanium oxide layer on the surface.

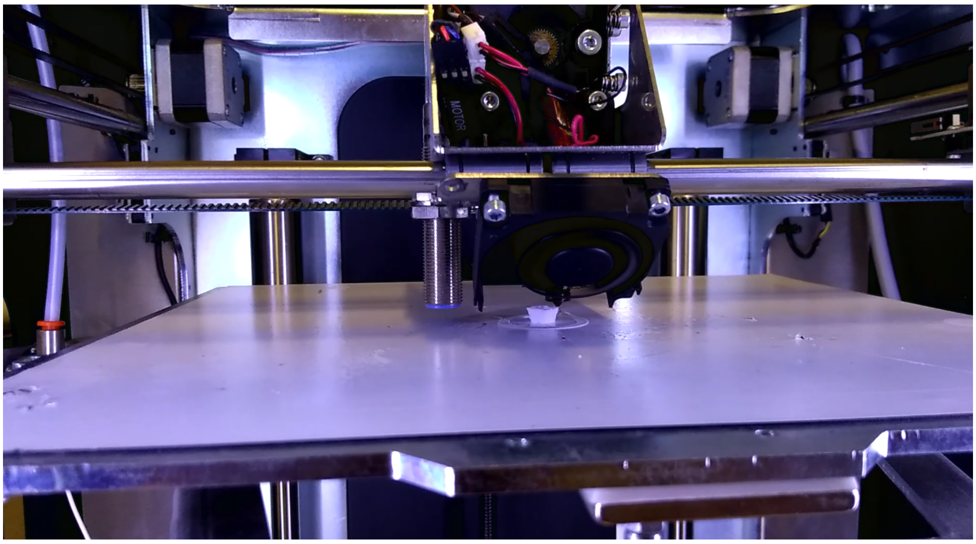


FIGURE 4.22: Image showing the 3d printing of the caps using the Slic3r machine

FIGURE 4.23: Image showing the samples before sand blasting

4.4.1 SLA solution preparation & testing

As mentioned in the previous section, the solution that we have used for this process is 1o percent V/V of Sulphuric acid and 20 percent V/V of Hydrochloric acid. We have used, 100 ml of solution to perform the experiment.

1) Sulphuric acid: 95-97 percent concentrated

2) Hydrocholric acid: 37 percent concentrated (The volume in 100 ml solution was calculated using stochiometry equations).

Figure 4.24: Image showing the samples after sand blasting

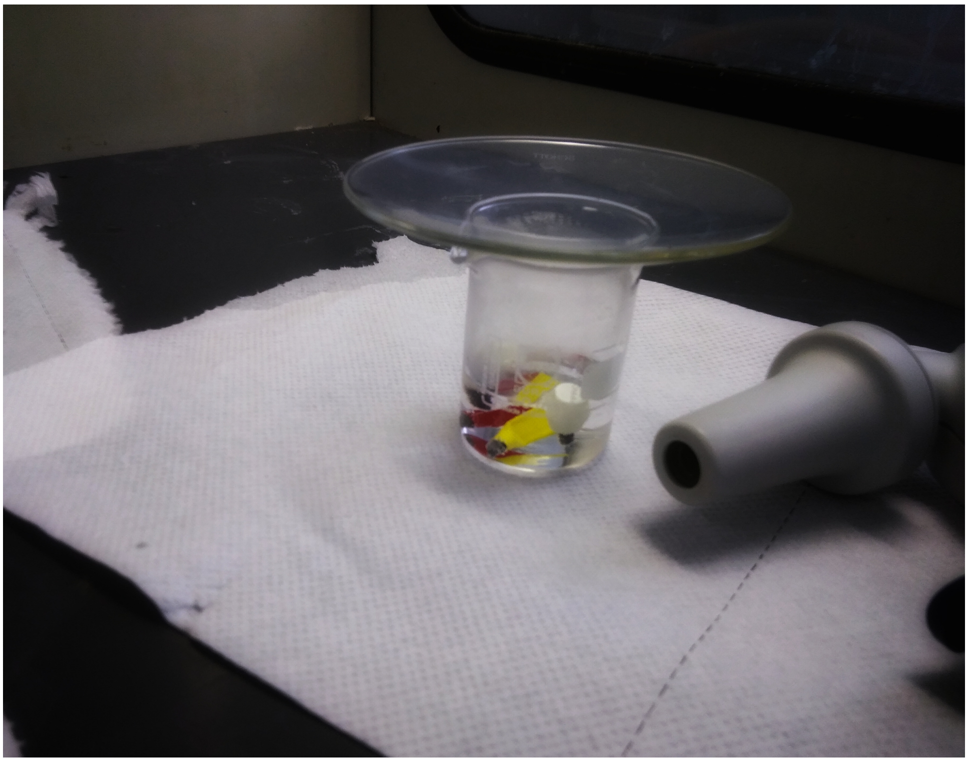


Figure 4.25: Image showing the samples are stored in HCL solution to prevent the formation of passivization layer

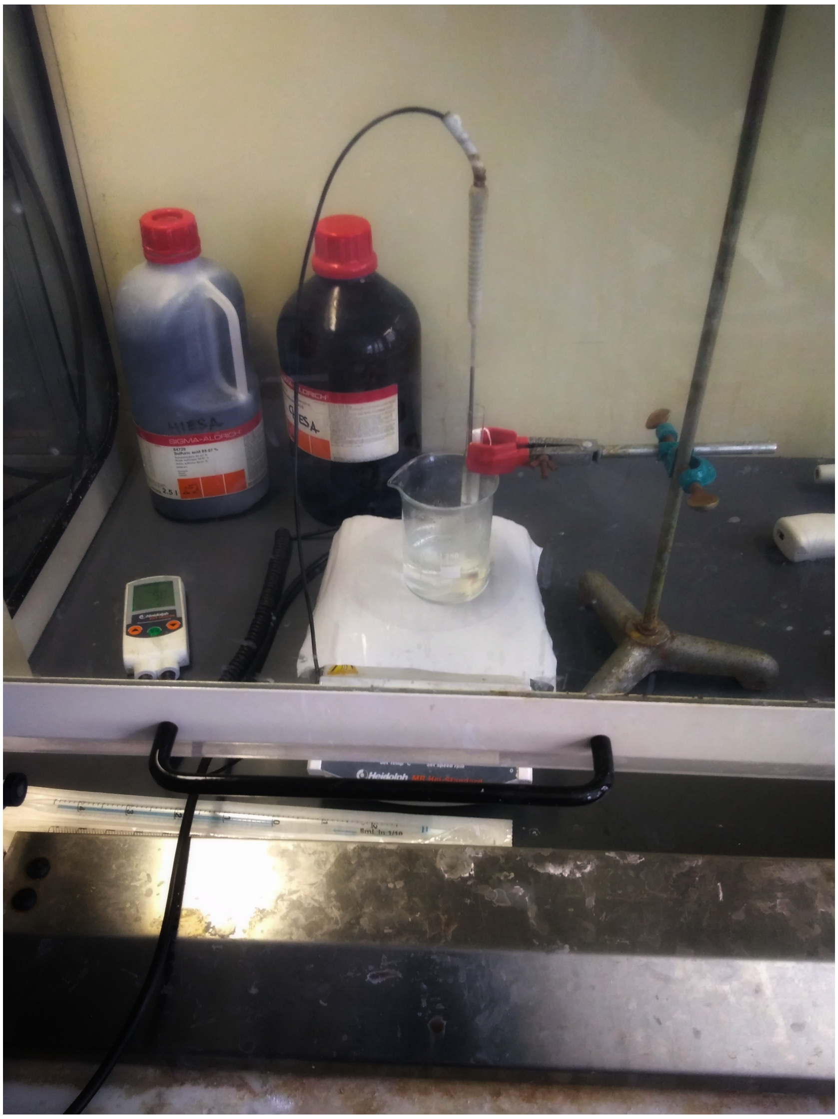


FIGURE 4.26: Image showing the prepared SLA solution and etching treatment

Chapter 5

Results and Conclusion

5.1 SEM-Scanning electron microscopy images & Optical distinguish between protected and unprotected surfaces (Without Sand-blasting technique)

The images of SEM, taken on the 4 samples that were subjected to chemical etching process. Those are cap desin 1, cap design 2, red tape and 3M Low surface energy tape.

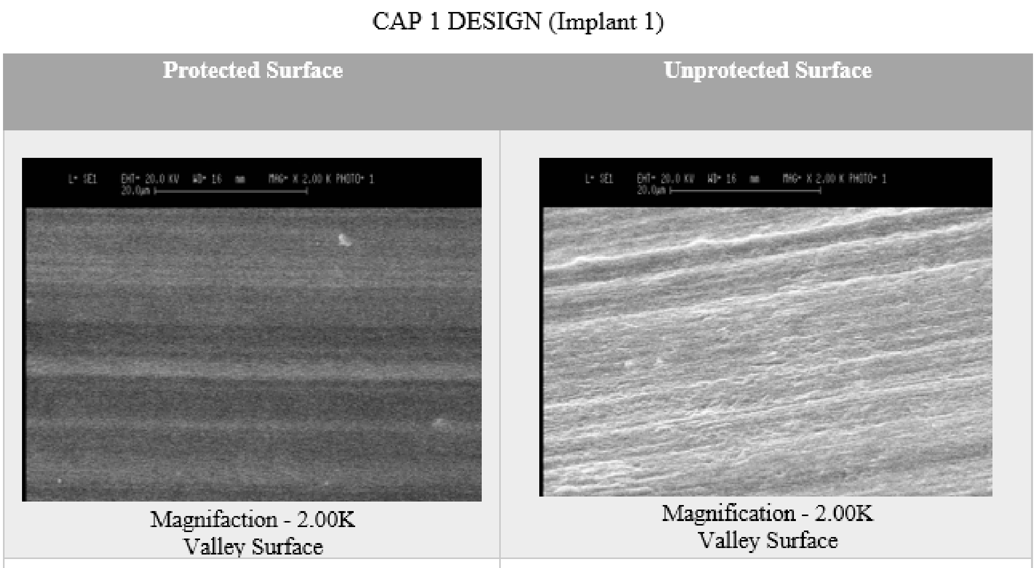


FIGURE 5.1: Comparison of protected and unprotected surfaces of cap design 1

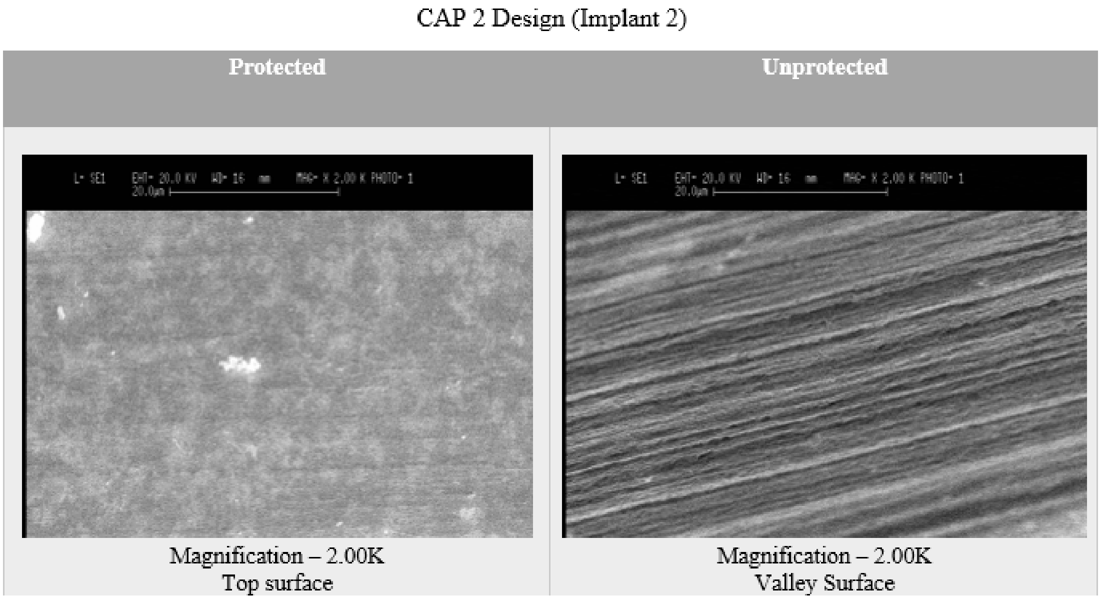


FIGURE 5.2: Comparison of protected and unprotected surfaces of cap design 2

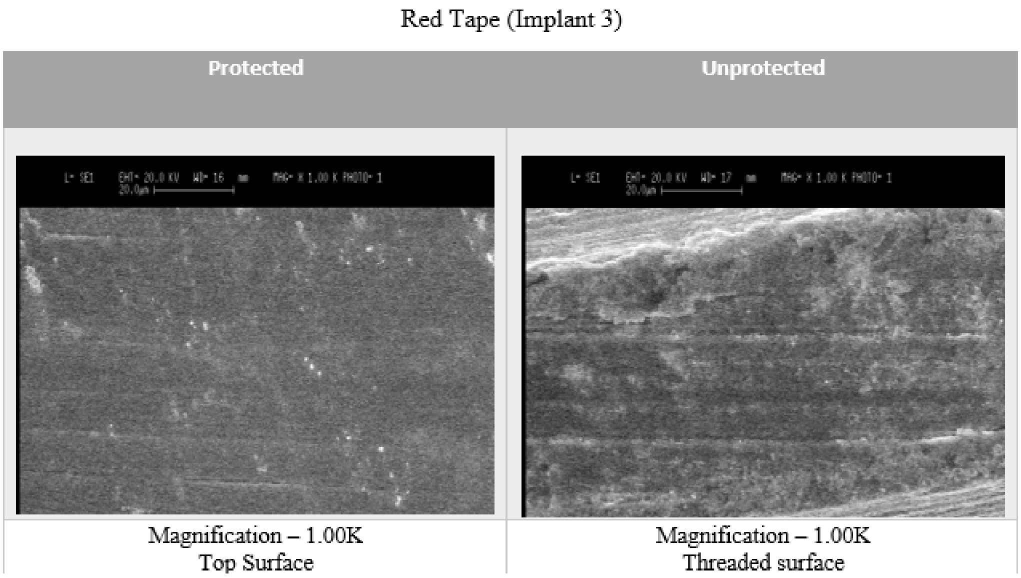


FIGURE 5.3: Comparison of protected and unprotected surfaces for red tapes

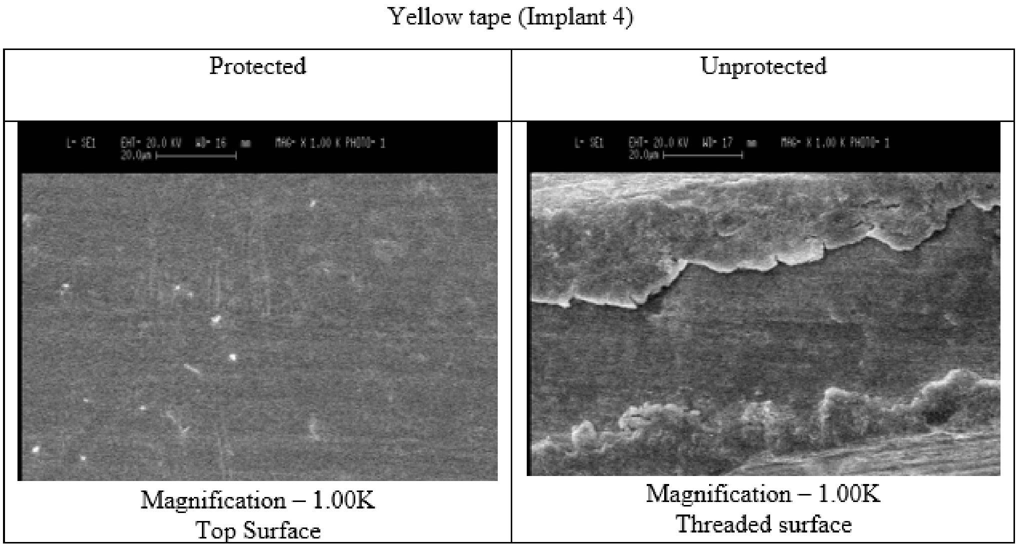


FIGURE 5.4: Comparison of protected and unprotected surfaces for 3M LSE tapes

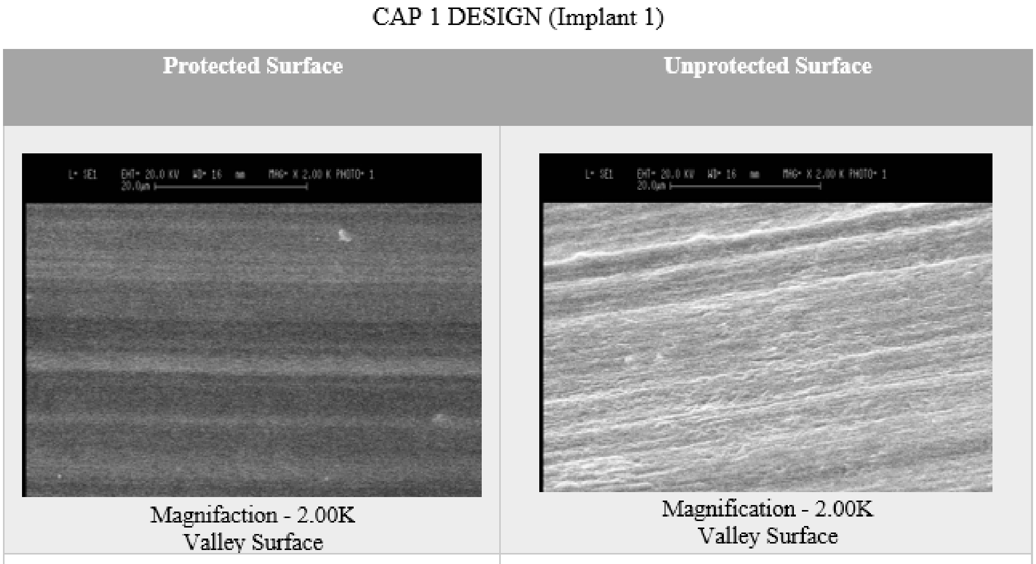


FIGURE 5.5: Comparison of protected and unprotected surfaces of cap design 1

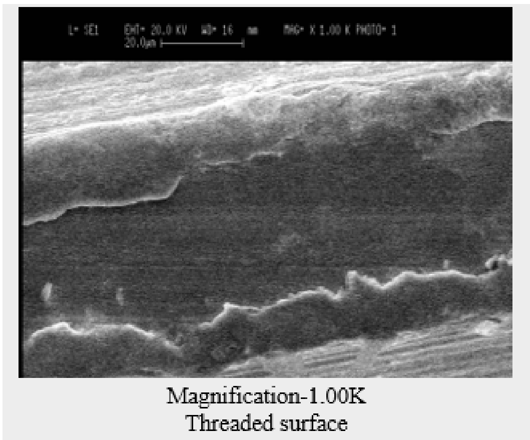


FIGURE 5.6: magnified image of unprotected surface for cap 1

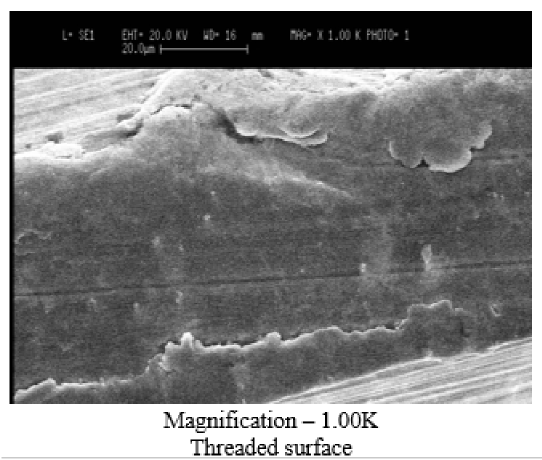


FIGURE 5.7: magnified image of unprotected surface for cap 2

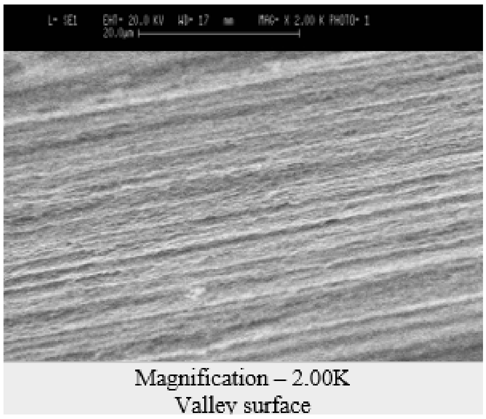


FIGURE 5.8: magnified image of unprotected surface for red tape

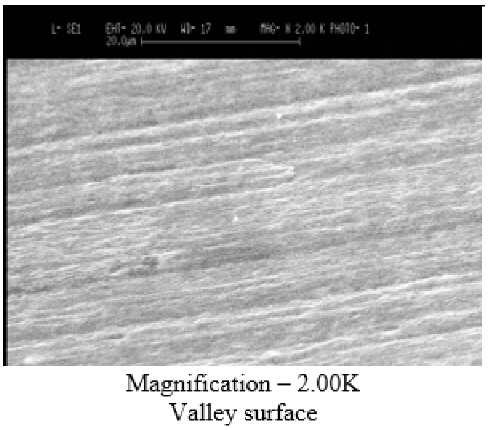


FIGURE 5.9: magnified image of unprotected surface for 3M LSE tape

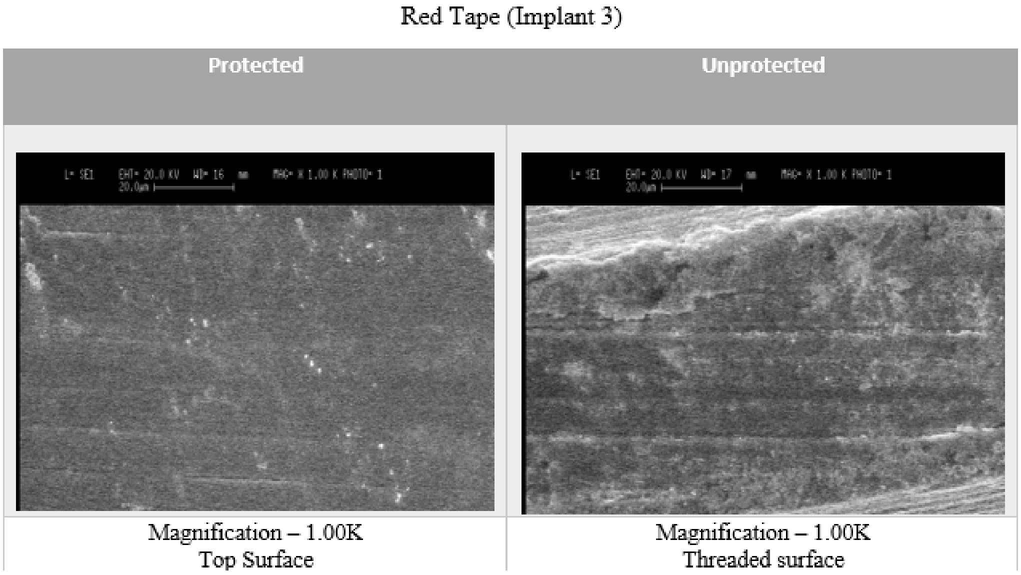


FIGURE 5.10: magnified image of protected surface for red tape

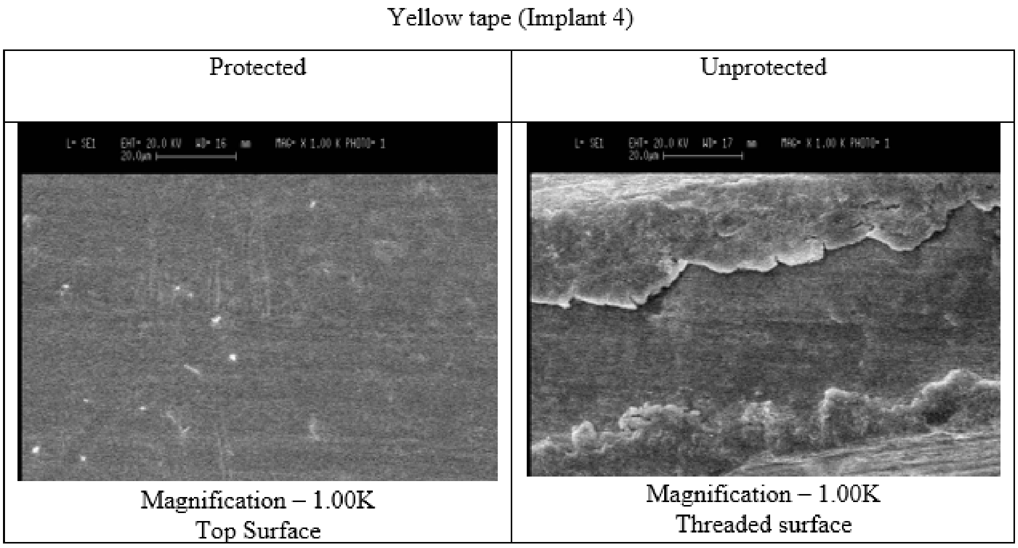


FIGURE 5.11: magnified image of protected surface for 3M LSE tape

5.2 SEM-Scanning electron microscopy images & Optical distinguish between protected and unprotected surfaces (With Sand-blasting technique)

The Implants are subjected to sand-blasting and chemically etching.The surface of the implant during the chemical etching is protected using the LSE tapes (3M and Red tapes) and Bio-inspired "Claw structured caps". The results are as follows:

FIGURE 5.12: Dental implants after chemical treatment (without sand-blasting)

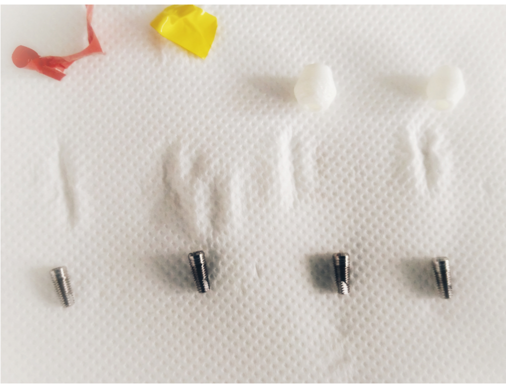


FIGURE 5.13: Dental implant samples after removal of the caps and tapes (without sand-blasting)

FIGURE 5.14: Image showing the distinguish between protected and unprotected surface when covered with 3M tape (without sand-blasting)

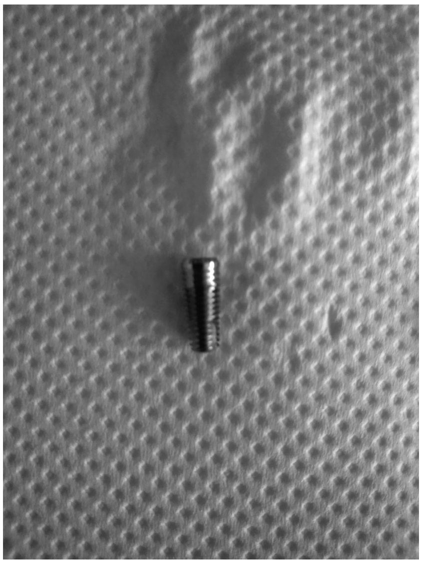


FIGURE 5.15: Image showing the optical difference between protected and unprotected surface when sealed with bio-inspired cap design 1 (without sand-blasting)

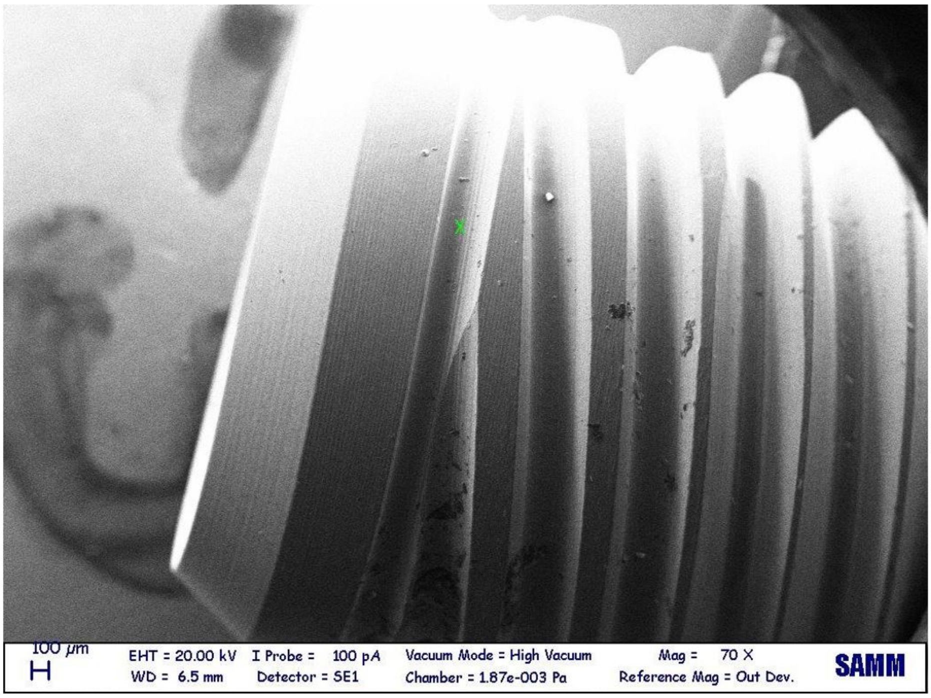
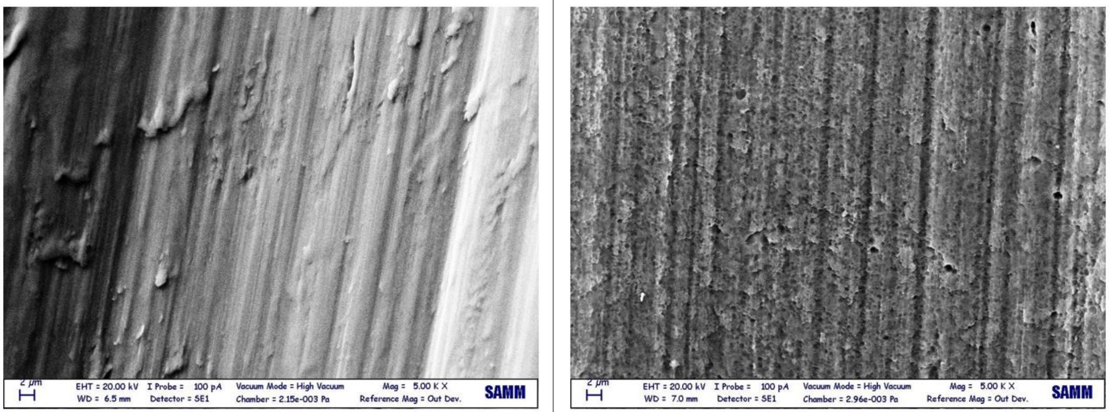


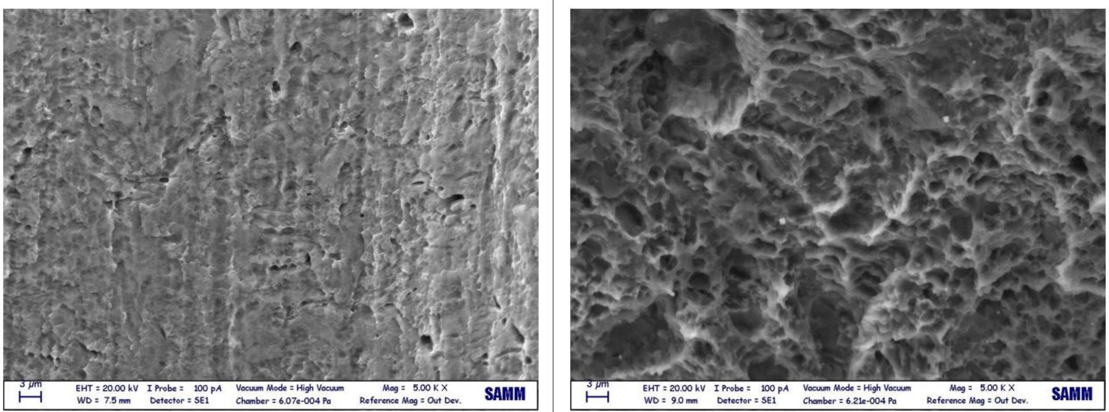
FIGURE 5.16: Image showing the SEM of the implant and portion on which image is generated (with sand blasting)-CAP 1



Protected surface (cap design 1)

Unprotected surface (cap design 1)
(chemically etched surface)

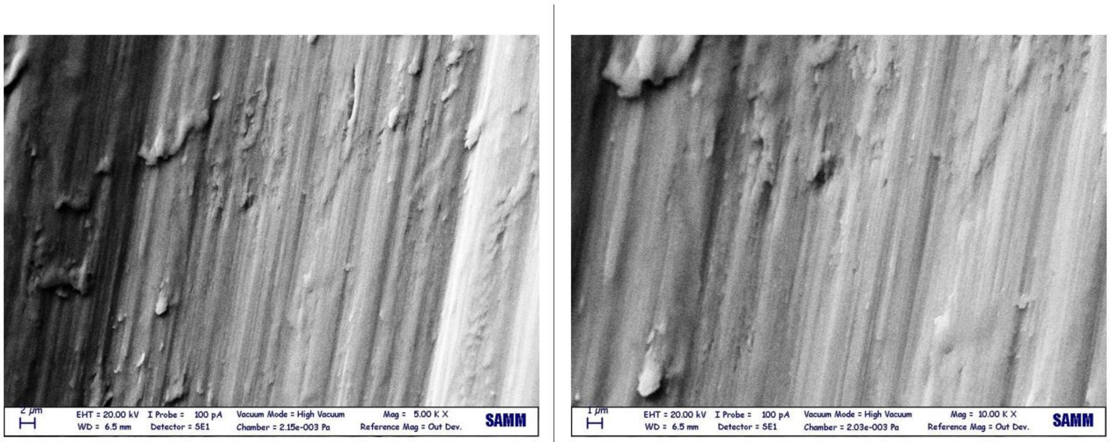
FIGURE 5.17: Image showing the difference between protected and unprotected surface when sealed with Cap design 1 (with sand blasting)



Chemically etched surface of implant
(Cap design 1)

Sand blasted + Chemically etched surface
(Cap design 1)

FIGURE 5.18: Image showing the difference between chemically etched surface and sand blasted + chemically etched surface -cap 1



Protected surface of the implant (Cap design 1)
(with magnification 5.00 K X)

Protected surface of the implant (Cap design 1)
(with magnification 10.00 K X)

FIGURE 5.19: Image showing the magnified portion of the protected surfaces-Cap design 1

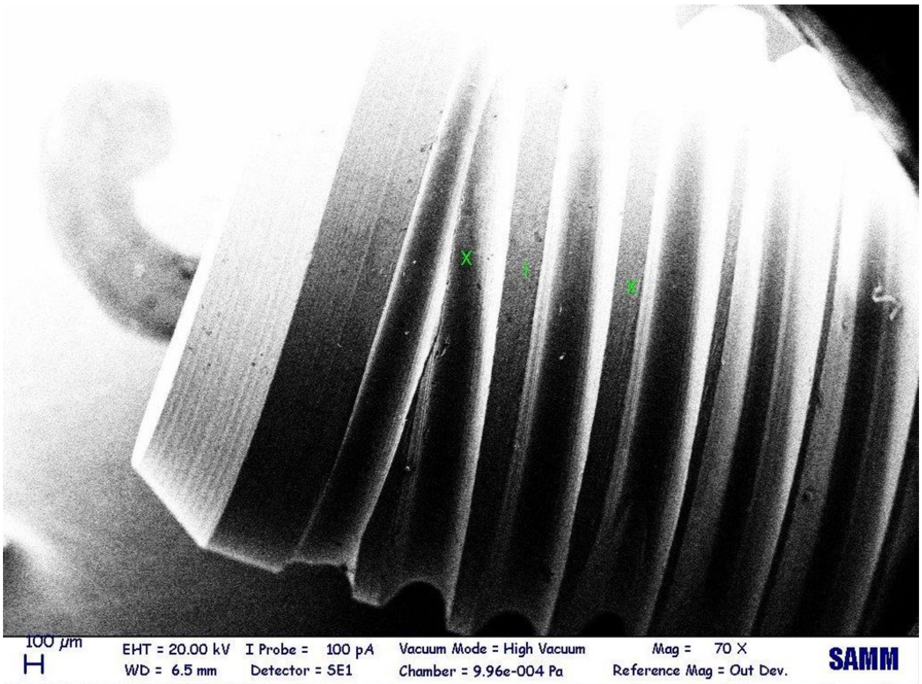


FIGURE 5.20: Image showing the SEM of the implant and portion on which image is generated (with sand blasting)-CAP 2

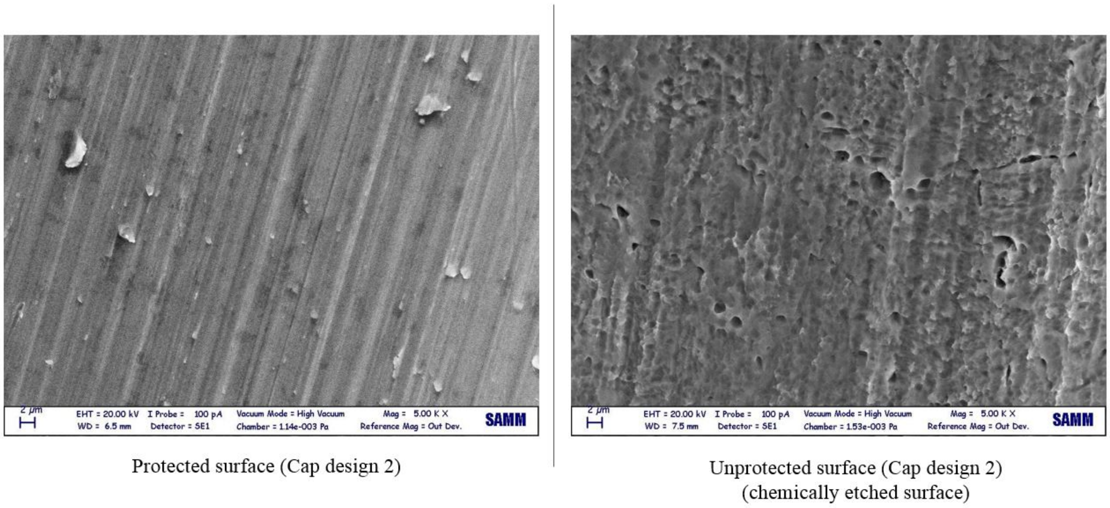


FIGURE 5.21: Image showing the difference between protected and unprotected surface when sealed with Cap design 2 (with sand blasting)

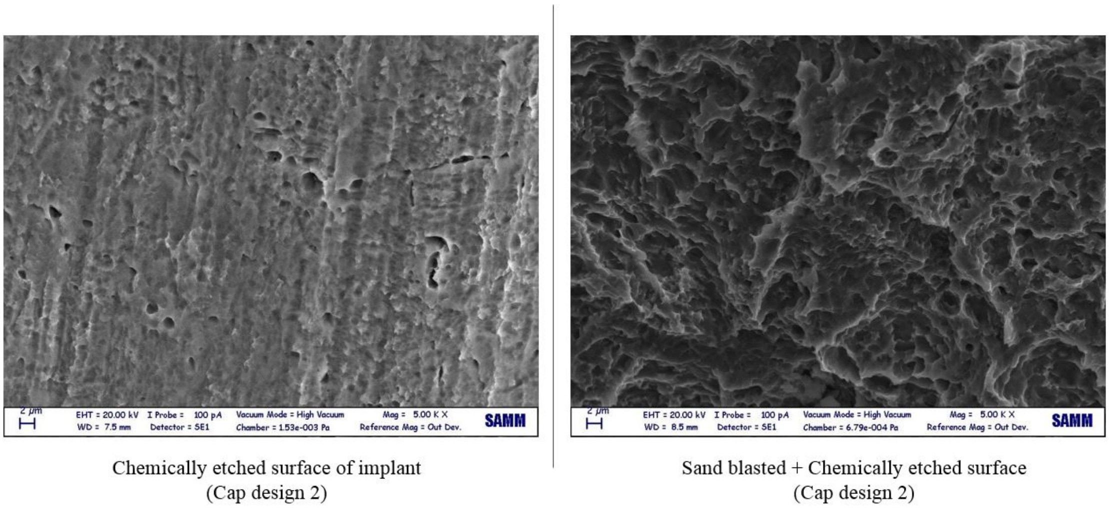
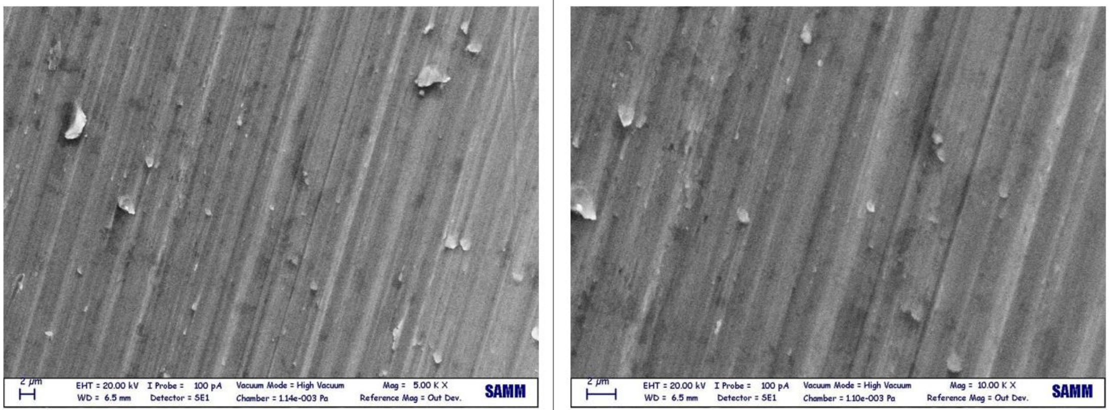


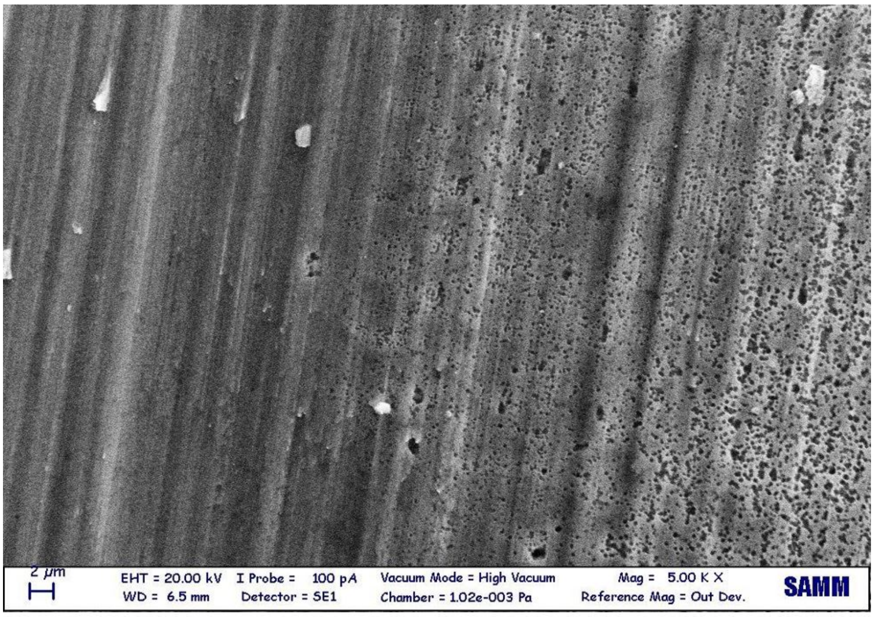
FIGURE 5.22: Image showing the difference between chemically etched surface and sand blasted + chemically etched surface-cap 2



Protected surface of the implant (Cap design 2)
(with magnification 5.00 K X)

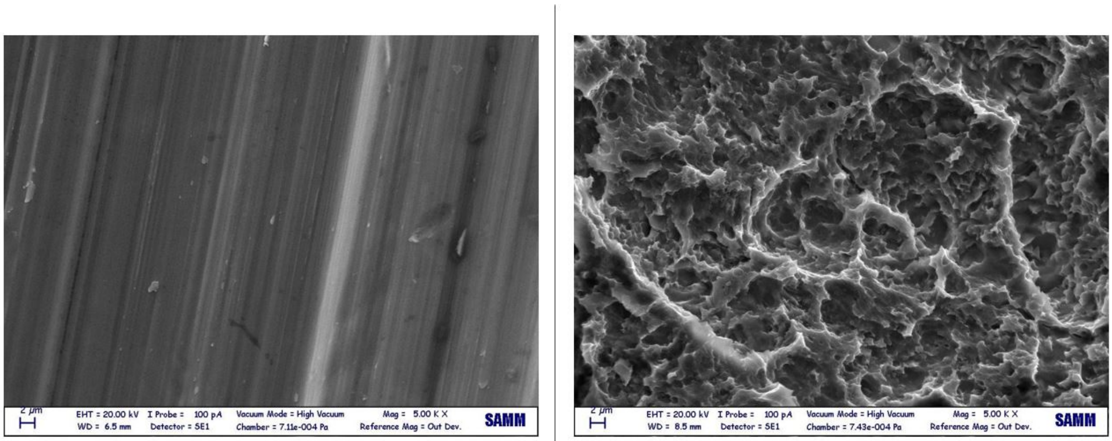
Protected surface of the implant (Cap design 2)
(with magnification 10.00 K X)

FIGURE 5.23: Image showing the magnified portion of the protected surfaces-Cap design 2



Showing the gradual difference between protected surface and unprotected surface
(Cap design 2)

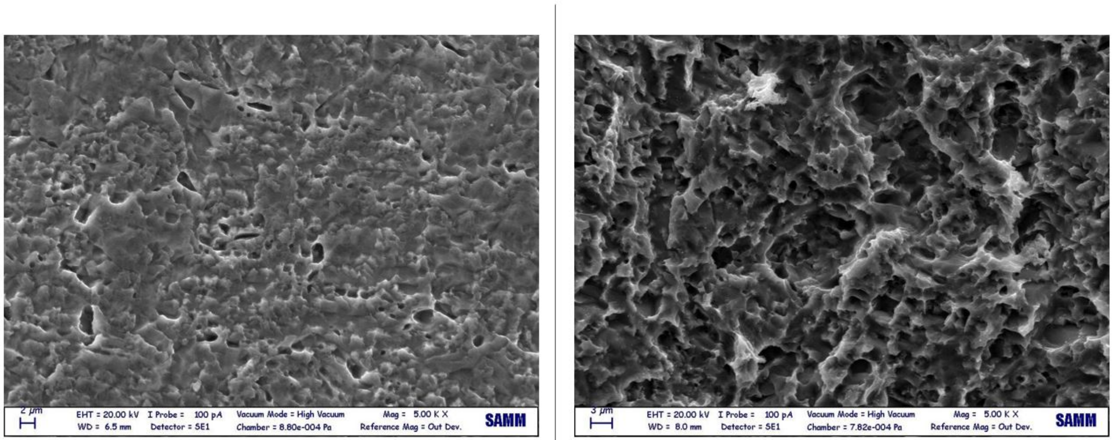
FIGURE 5.24: Image showing gradual difference between the etched and protected surface-cap 2



Protected surface of the implant (Red tape)

Sand blasted + chemically etched surface (Red tape)

FIGURE 5.25: Image showing difference between protected surface and unprotected surface-Red tape (with sand blasting)



Protected surface (3M yellow tape)

Sand blasted + Chemically etched surface (3M yellow tape)

FIGURE 5.26: Image showing gradual difference between protected and unprotected surface-3M yellow tape (with sand blasting)

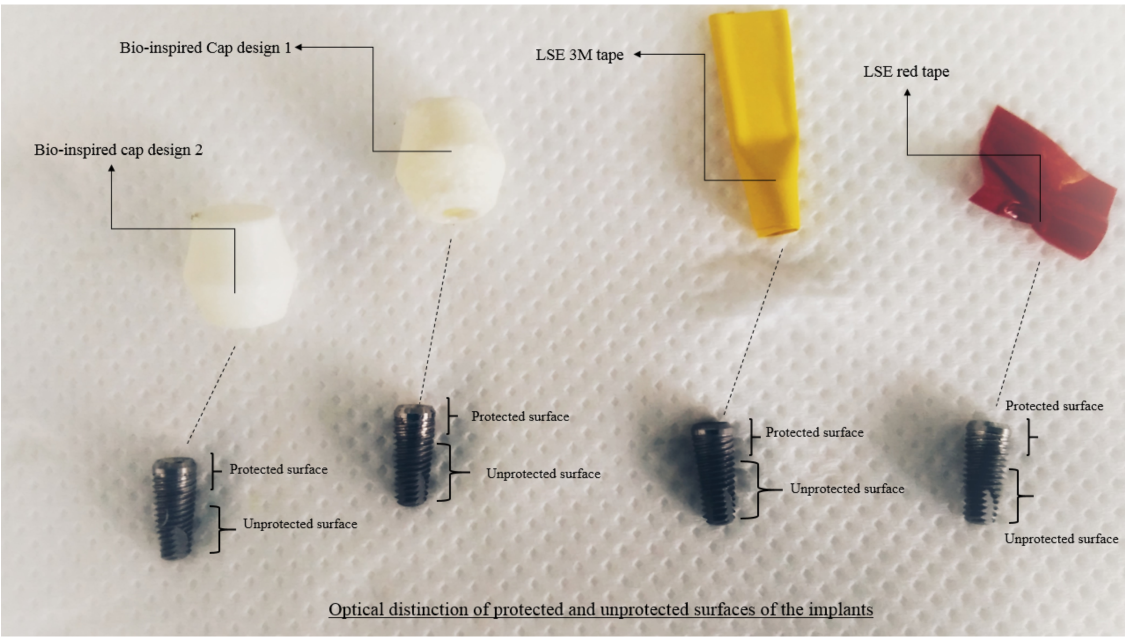


Figure 5.27: Image showing the difference between protected and unprotected surface when sealed with caps and protected with tapes (with sand-blasting)

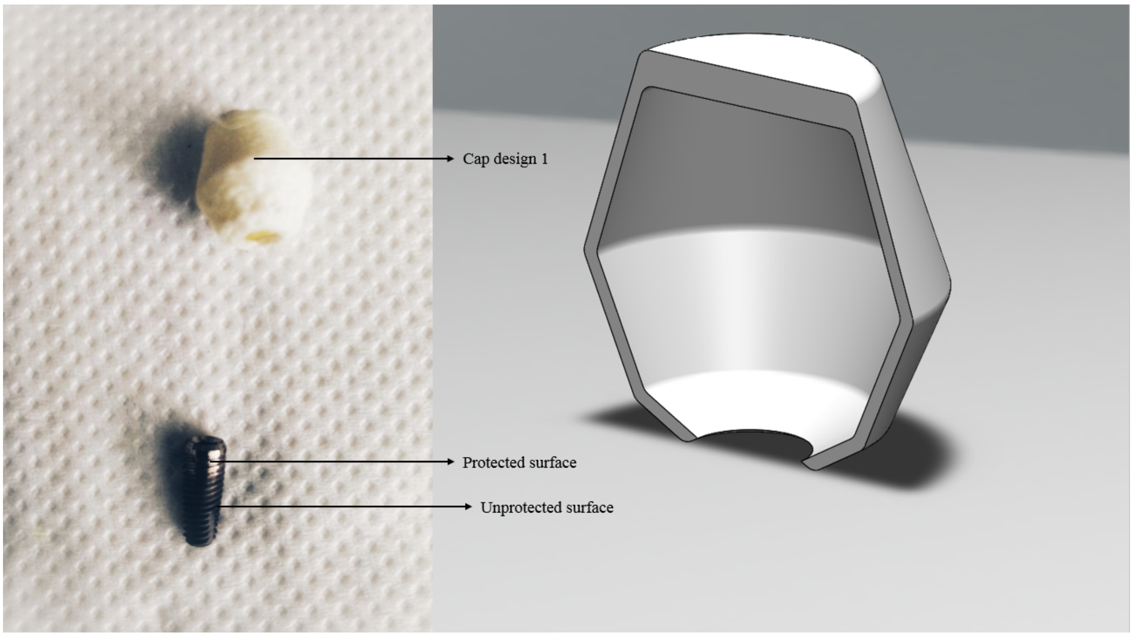


Figure 5.28: Image showing the difference between protected and unprotected surface when sealed with cap design 1 (with sand-blasting)

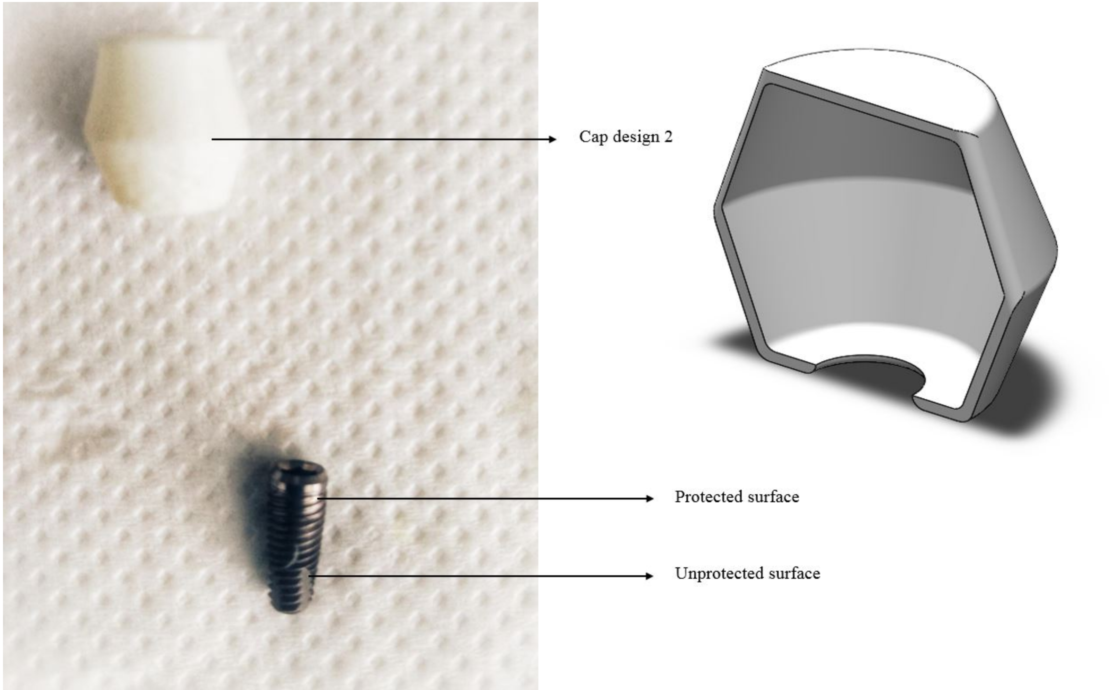


FIGURE 5.29: Image showing the difference between protected and unprotected surface when sealed with cap design 2 (with sand-blasting)

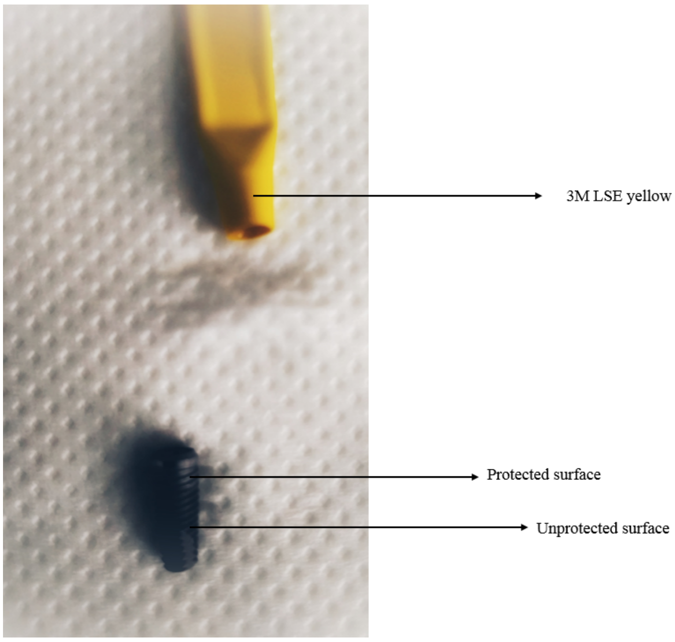


FIGURE 5.30: Image showing the difference between protected and unprotected surface when sealed with 3M tape (with sand-blasting)

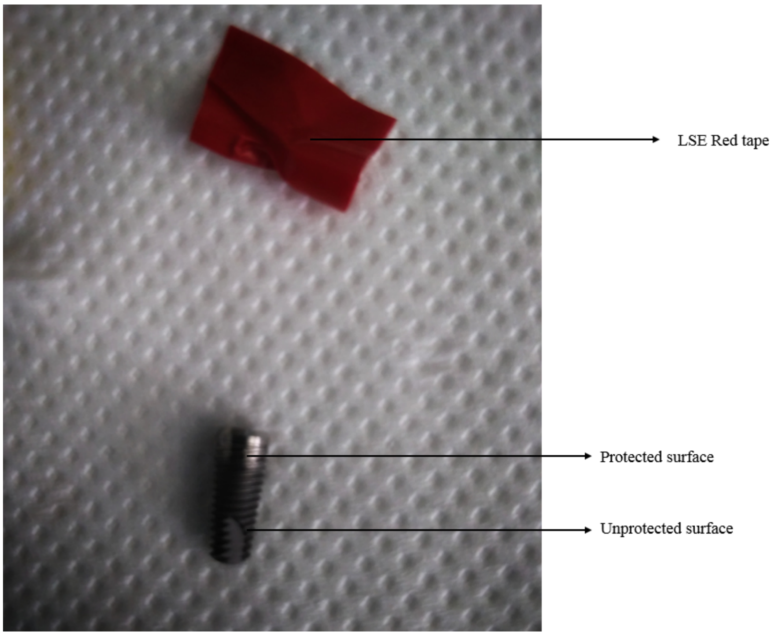


FIGURE 5.31: Image showing the difference between protected and unprotected surface when sealed with caps and protected with red tape (with sand-blasting)

5.3 Conclusion

From the images, we can state that the claw structured 3D printed caps and also the Low surface energy tapes were proved effective in protecting the upper surface of the dental implant. Thanks to the ever improving additive manufacturing (3D printing), which has opened the doors to explore and experiment complex shapes and designs. "Claw inspired structures" can be used in a entirely different application, that is as a sealing agent. The hypothesis that was made earlier were achieved. These are as follows:
1) LSE and chemically inert tapes were effective in protecting the required surfaces during the chemical etching process of the implant
2) Bio-inspired caps that is claw inspired 3D printed caps were effective in sealing the implant surface during the chemical etching process of the implant

Appendix A

An Appendix

3D printer used:

1) Name: Slic3r

Technical parameters of the printer used

3) Layer height: 0.2mm

4) Temperature of filament: 217 degrees

5) Loops : 5

6) Distance from the object : 4 mm

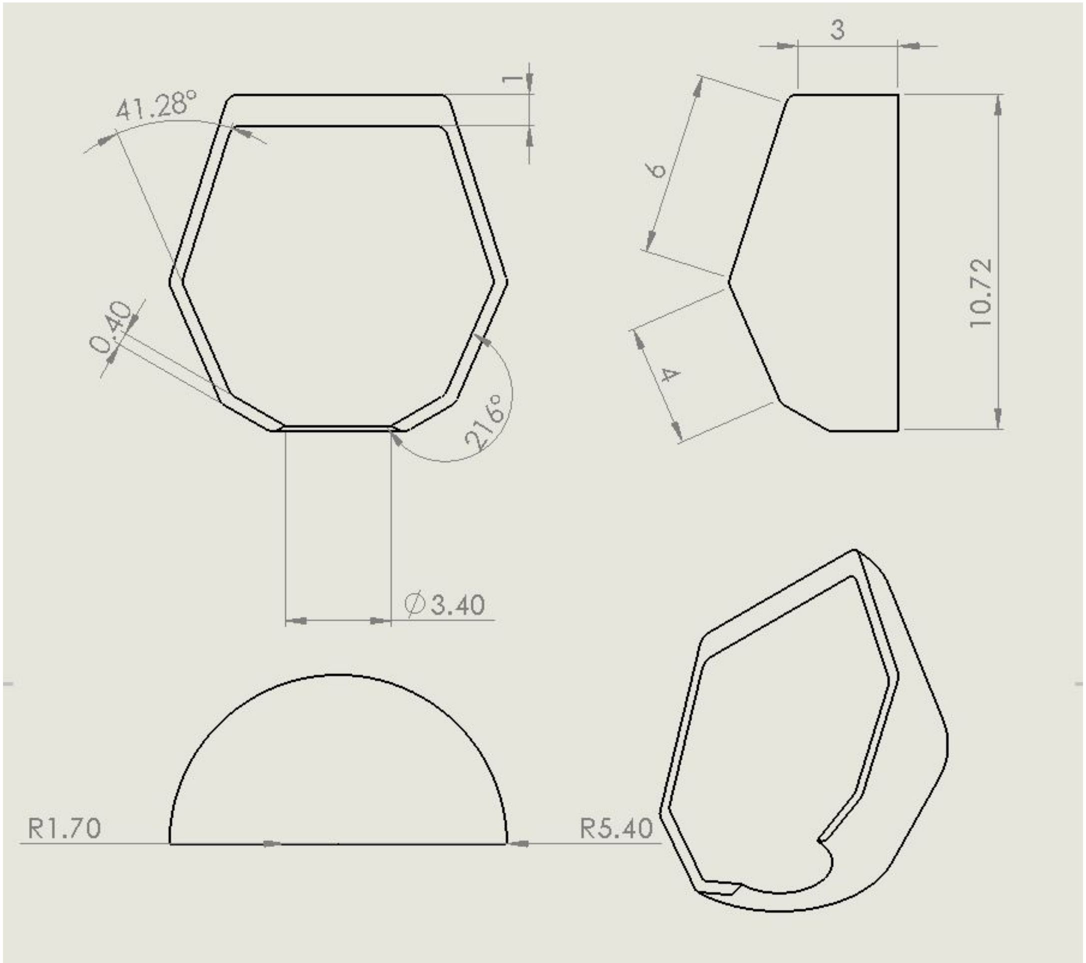


FIGURE A.1: Image showing technical details of cap design 1 - half section

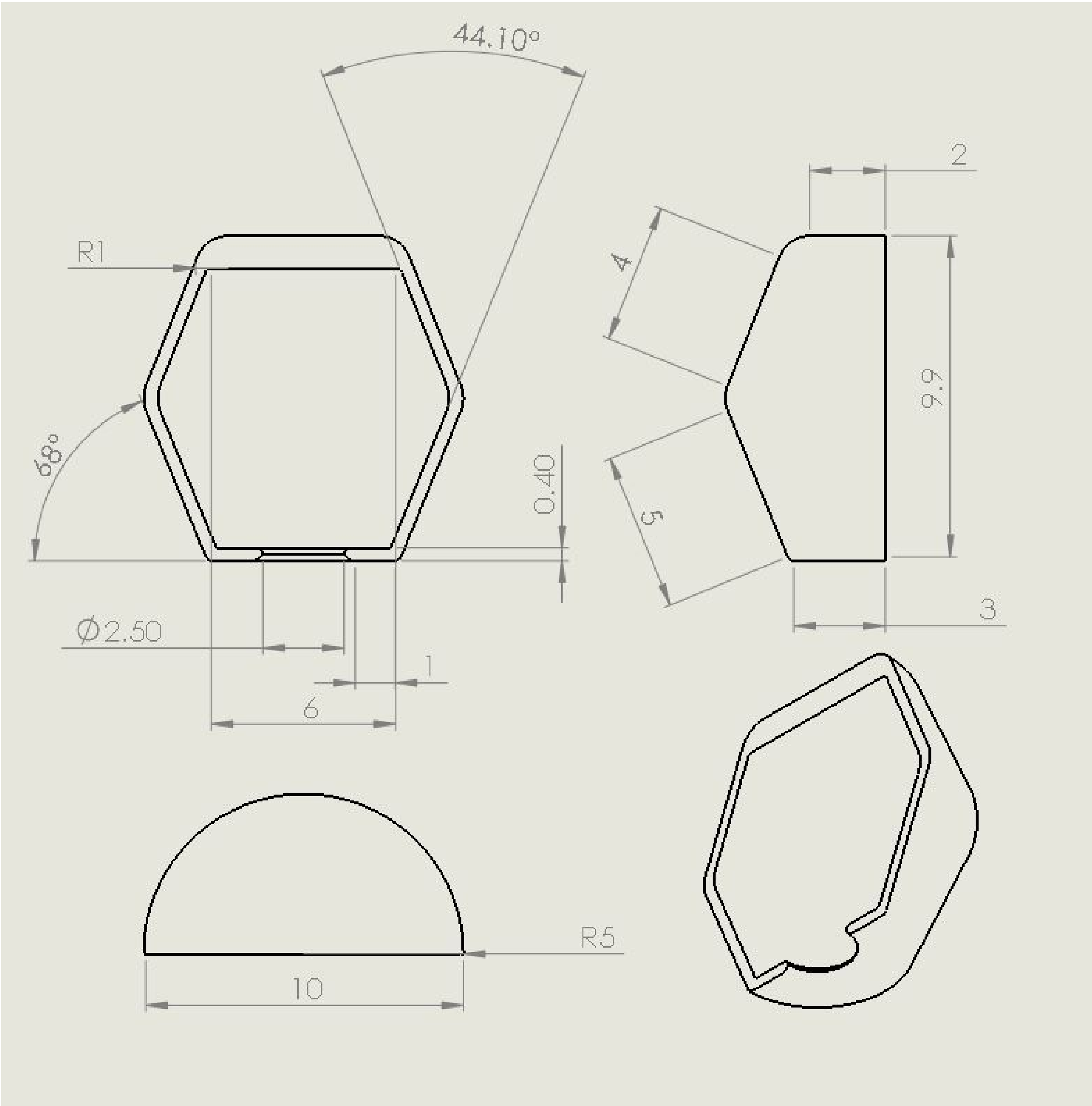


FIGURE A.2: Image showing technical details of cap design 2 - half section

Figure A.3: Render of cap design 1

Figure A.4: Render of cap design 2

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