EFFECT OF INCORPORATION OF FILLER PARTICLE ON PHYSICAL & MECHANICAL PROPERTIES AND CHEMICAL CHANGES IN MAXILLOFACIAL PROSTHETIC SILICONE ELASTOMER IN LOCAL MALAYSIAN WEATHER

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By

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TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

%	Percentage
°C	Degree Celsius
µm	Micrometer
ANOVA	Analysis of Variance
ATR-FTIR	Attenuated Total Reflectance Fourier Transform Infrared
CeO_2	Cerium oxide
Co.	Company
cPs	centiPoise
df	Degree of freedom
FTIR	Fourier Transform Infrared
g/cm^3	gram per cubic centimeter
h	Hour
HTV	Heat temperature vulcanized
ISO	International Standard Organization
km/h	kilometer per hour
MFPSE	Maxillofacial prosthetic silicone elastomer
mm	Millimeter
mm/min	Millimeter per minute

mm/s	Millimeter per second
MPa	MegaPascal
No.	Number
NY	New York
ppi	Pounds per inch
psi	Pounds per square inch
RTV	Room temperature vulcanized
SD	Standard deviation
SiO_2	Silicon dioxide
SPSS	Statistical Package for the Social Sciences
TiO_2	Titanium dioxide
$TiSiO_4$	Titanium silicate
USA	United States of America
UTM	Universal Testing Machine
UV	ultraviolet
Y_2O_3	Yttrium oxide
ZnO	Zinc oxide
ZrO_2	Zirconium oxide
$ZrSiO_4$	Zirconium silicate

LIST OF APPENDICES

KESAN KEMASUKAN PARTIKEL PENGISI TERHADAP SIFAT FIZIKAL DAN MEKANIKAL DAN PERUBAHAN KIMIA DI DALAM PROSTETIK MAKSILOFASIAL ELASTOMER SILIKON DALAM CUACA TEMPATAN MALAYSIA

ABSTRAK

Prostetik Maksilofasial Elastomer Silikon (MFPSE) adalah bahan yang dipilih untuk membikin semula struktur wajah yang hilang akibat kecacatan kraniofasial. Namun begitu, MFPSE masih ada kesan buruk yang mengehadkan jangka hayatnya. Dalam senario kehidupan sebenar, prostesis yang terdedah kepada pencuacaan semulajadi merosot lebih awal menyebabkan penggantian prostesis yang lebih kerap. Sebelum ini banyak kajian yang telah dilakukan untuk memperbaiki sifat-sifat MFPSE dalam pencuacaan buatan dengan menggunakan partikel pengisi. Oleh sebab itu, tujuan kajian ini adalah untuk meneroka kesan pengisi nano terhadap kekasaran permukaan, kekuatan tensil, peratusan pemanjangan dan perubahan kimia MFPSE yang dikenakan pencuacaan luaran. Sejumlah 90 sampel telah disediakan untuk kajian eksperimen perbandingan secara in-vitro. Dua jenis silikon tervulkan suhu bilik (RTV) yang berbeza (A-2006, A-103) telah digunakan untuk menghasilkan sampel dan 2% TiO_2 and 2% SiO_2 berdasarkan berat telah dimasukkan dalam kumpulan eksperimen. Semua spesimen telah didedahkan dalam cuaca luar selama empat bulan di dalam rak pendedahan yang ditempah khas. Selepas empat bulan, spesimen pun diuji. Kekasaran permukaan diuji oleh profilometer; kekuatan tensil dan peratus pemanjangan telah diukur oleh mesin pengujianan universal dan perubahan kimia telah diperiksa oleh spektrometer Inframerah Transformasi Fourier (FTIR). Ujian Kolmogorov-Smirnov telah dilakukan untuk menilai normaliti data. Untuk

analisis sifat-sifat, ANOVA dua-hala telah dilakukan. Perbandingan individu, perbandingan berpasangan dan kesan interaksi telah diteroka untuk kedua-dua kumpulan kawalan dan eksperimental. Dalam perbandingan individu kedua-dua faktor, perbandingan berpasangan dan kesan interaksi menunjukkan perbezaan yang tidak signifikan untuk kekasaran permukaan. A-103 dengan TiO_2 menunjukkan min kekasaran permukaan yang tertinggi. Untuk kekuatan tensil dan peratusan pemanjangan; kedua-dua faktor, perbandingan berpasangan dan kesan interaksi menunjukkan perbezaan signifikan ($P<.001$). A-103 menunjukkan kekuatan tensil yang bagus dengan kedua-dua pengisi dan A-2006 dengan TiO_2 menunjukkan min peratusan pemanjangan tertinggi. Spektra FTIR menunjukkan tiada penambahan atau kehilangan puncak antara kumpulan tidak berpengisi dan kumpulan berpengisi menandakan bahawa kemasukan pengisi nano tidak memberi kesan kepada struktur kimia MFPSE. Disebabkan tiadanya perbezaan struktur kimia yang dapat diperhatikan, maka dapat dicadangkan bahawa A-103 dengan pengisi nano mampu mengekalkan kelicinan permukaan dan kekuatan tensil dalam cuaca Malaysian dan A-2006 adalah lebih baik dari segi peratusan pemanjangan apabila dimasukkan dengan pengisi TiO_2 dan SiO_2 dalam keadaan pencuacaan semulajadi.

EFFECT OF INCORPORATION OF FILLER PARTICLE ON PHYSICAL & MECHANICAL PROPERTIES AND CHEMICAL CHANGES IN MAXILLOFACIAL PROSTHETIC SILICONE ELASTOMER IN LOCAL MALAYSIAN WEATHER

ABSTRACT

Maxillofacial prosthetic silicone elastomer (MFPSE) is the material of choice to refabricate the lost facial structure due to craniofacial defect. Still and all, MFPSE has some adverse effect which make the lifespan of the prosthesis limited. In the real-life scenario, the prosthesis which gets exposed in natural weather degrades earlier leads to replacement of the prosthesis frequently. Previously many researches had been conducted to improve the properties of MFPSE using filler particles in artificial weather. Therefore, the aim of this study is to explore the effect of nano fillers on surface roughness, tensile strength, percentage of elongation and the chemical changes of MFPSE subjected to outdoor weather. A total of 90 samples were prepared for this comparative in-vitro experimental study. Two different room temperature vulcanized (RTV) silicone (A-2006, A-103) were used to fabricate the samples and 2% TiO_2 and 2% SiO_2 by weight was incorporated with the experimental group. All the specimens were exposed in outdoor weather for four months in a custom-made exposure rack. After four months, specimens were tested. Surface roughness was tested by profilometer; tensile strength and percentage of elongation was measured by universal testing machine and the chemical changes was checked by Fourier-transform infrared (FTIR) spectrometer. Kolmogorov-Smirnov test was done to assess the normality of the data. For the property analysis two-way ANOVA was performed. The individual comparison, pairwise comparison and

interaction effect was explored for both control and experimental group. In the individual comparison both factors, pairwise comparison and the interaction effect showed non-significant difference for surface roughness. A-103 with TiO_2 showed the highest mean surface roughness. For tensile strength and percentage of elongation; both factors, pairwise comparison and interaction effect showed significant difference ($P<.001$). A-103 showed good tensile strength with both fillers and A-2006 with TiO_2 showed the highest mean percentage of elongation. The FTIR spectra showed no extra or diminished peak between non-filler induced group and filler induced groups indicated that incorporation of nano fillers did not affect the chemical structure of MFPSE. As there were no chemical structural differences observed, therefore it can be suggested that A-103 with nano fillers had the capability of sustaining the surface smoothness and tensile strength in Malaysian weather and A-2006 was better for the percentage of elongation when incorporated with TiO_2 and SiO_2 filler in natural weathering condition.

CHAPTER 1

INTRODUCTION

1.1 Background of the study:

Maxillofacial defects mainly occur due to congenital, traumatic or neoplastic incidences. Sometimes surgical removal is the only treatment option. As a consequence, it makes a large deformation in the facial region which affects patients regular, personal and social life. Proper rehabilitation is needed to improve their quality of life. Maxillofacial prosthesis is used for the rehabilitation of this kind of deformities.

For the fabrication of Maxillofacial prosthesis, various material can be used, but among of all medical grade silicone elastomer is the most widely used material. Medical grade silicone elastomer has lots of advantages like its high durability, stability, biocompatibility, clinical inertness and easy manipulation technique (Alsmael and Ali, 2018). Apart from all of this advantages, silicone elastomer has also some drawbacks.

Maxillofacial prosthesis made of silicone performs well initially, however, time passes, deterioration occurs either in degradation of mechanical properties or chemical changes. Reason of the degradation can be improper use of prosthesis, lower life span of prosthesis or effect of weathering also, thus it needs to be changed frequently. (Barman *et al.*, 2020) So, considering the aforementioned shortcomings, it is essential to improve the physical and mechanical properties and decrease the rate of chemical changes of silicones as well as increase the life span of prosthesis to lower the rate of refabricating of the prosthesis.

There were many researches had done to improve the properties of silicone and many filler particles was used by most of the authors to enhance the required properties. The effect of weathering pattern is one of the most important factors which influence the properties of silicone elastomer. Silicone prosthesis are prone to degradation by the climatic change of outdoor environment (Nguyen *et al.*, 2013). But the geographic condition, climatic pattern and the season around the world differs from one continent to another. So, there is a lack of proper information on the long period of outdoor weathering on properties of silicone elastomer incorporated with filler particles.

Therefore, it is very essential to evaluate the effect of incorporating filler particles on physical and mechanical properties and chemical changes of maxillofacial prosthetic silicone elastomer subjected to outdoor weathering.

1.2 Problem Statement:

Though silicone elastomer is an ideal material for prosthetic rehabilitation, it has some disadvantages especially low physical and mechanical properties like surface roughness, tensile strength, percentage of elongation. Due to inadequate strength of properties, the life span of silicone elastomer become shorten, therefore prosthesis needs to be refabricated frequently (Barman *et al.*, 2020), (Rashid *et al.*, 2020). There were several reasons present for the shorter longevity of silicone like failure to follow the instructions on how to handle the prosthesis properly, improper cleaning technique and effect of weather. Besides the patient's failure, the effect of exposure on the outdoor environment is one of the most important factors for degradation of the properties. Prosthesis which gets more exposure in the outdoor environment degrade earlier. Exposure to natural weather make the properties weaker due to heat, ultraviolet (UV) radiation, humidity, dust, sunlight etc. (Nguyen *et al.*, 2013). The average life span of silicone elastomer is six months to eighteen months according to previous literature (Lemon *et al.*, 1995), (Polyzois, 1999). The frequent change of the prosthesis creates trouble for the patients with lower economic condition. For the long-term use of prosthesis, improvement in the physical and mechanical properties of silicone elastomer is needed. The incorporation of nano particles with the silicone elastomer results increases physical and mechanical properties reported by several researchers (Han *et al.*, 2008). The outcome in physical and mechanical properties of silicone elastomer after incorporation of nano filler particles needed to be explored and compared with the non-filler incorporated silicone elastomer to find the actual difference in the strength of properties between non filler incorporated and nano filler incorporated silicone samples subjected to outdoor weathering.

Therefore, it is necessary to improve the properties of silicone with the incorporation of nano filler particles as well as make the service life of prosthesis long lasting against environmental factors to reduce the frequency of refabricating the prosthesis.

1.3 Justification:

The study intended to improve the physical (surface roughness) and mechanical properties (tensile strength, percentage of elongation) of silicone with the incorporation of nano filler particles due to lack of mechanical properties. The chemical changes evaluation is also important in order to analyze the inner chemical bond of a material to explore how the nano fillers interacts with silicone elastomer. Nano particles plays a very important role to enhance the required properties. There are variety of nano sized filler present in current market. But it is necessary to evaluate which filler can improve the properties most. There are many studies investigated the improvement of silicone with the reinforcement of nano particles in both artificial aging condition. Very few research was done in outdoor weathering and most of the studies were conducted in European weather rather than in Asian weather. There are many differences in the pattern of weather in different continents. Weathering pattern of Asia is different from Europe and America. To the best of our knowledge, there is no proper study being conducted in local Malaysian weather to compare the strength of the properties of silicone elastomer between the non-filler incorporated silicones and nano filler incorporated silicones.

Therefore, this study will aim to investigate and compare the effect of incorporation of filler particles in maxillofacial prosthetic silicone elastomer on physical, mechanical and chemical changes in local Malaysian weather.

1.4 Clinical Significance and Expected Outcome:

The expected outcome of this study will help to create a thorough understanding for the clinician and laboratory technicians how filler particles can effectively increase physical property (surface roughness), mechanical properties (tensile strength & percentage of elongation) and reduce the chemical changes as well as improve longevity of the silicone prostheses under natural weathering conditions.

1.5 Objectives:

1.5.1 General Objective:

To assess the effect of incorporation of filler particles on physical, mechanical properties and chemical changes in maxillofacial prosthetic silicone elastomer subjected to Malaysian weather.

1.5.2 Specific Objectives:

1. To determine and compare the surface roughness of silicone elastomers (A-2006, A-103) with and without incorporation of nano filler particles (TiO_2, SiO_2) subjected to outdoor weathering in Malaysia.
2. To determine and compare the tensile strength and percentage of elongation of silicone elastomers (A-2006 and A-103) with and without incorporation of nano filler particles (TiO_2, SiO_2) subjected to outdoor weathering in Malaysia.
3. To determine and compare the chemical changes of maxillofacial silicone elastomers (A-2006, A-103) with and without incorporation of nano filler particles (TiO_2, SiO_2) after outdoor weathering in Malaysia.

1.6 Research Questions:

1. Is there any changes in surface roughness of maxillofacial silicone elastomers with and without incorporation of nano filler particles after outdoor weathering in Malaysia?

2. Is there any changes in tensile strength and percentage of elongation of maxillofacial silicone elastomers with and without incorporation of nano filler particles after outdoor weathering in Malaysia?
3. Is there any differences in the chemical changes of maxillofacial silicone elastomers with and without incorporation of nano filler particles after outdoor weathering in Malaysia?

1.7 Research Hypothesis:

The null hypotheses that will be tested for factor silicone, factor filler and interaction effect are summarized as follows:

1. There is no significant difference in surface roughness for factor silicone (A-2006, A-103) with and without incorporation of factor filler and also no interaction between factor silicone and factor filler subjected to outdoor weathering in Malaysia.
2. There is no significant difference in tensile strength and percentage of elongation for factor silicone (A-2006 and A-103) with and without incorporation of factor filler and also no interaction between factor silicone and factor filler subjected to outdoor weathering in Malaysia.
3. There is no significant difference in chemical changes of maxillofacial silicone elastomers (A-2006, A-103) with and without incorporation of nano filler particles subjected to outdoor weathering in Malaysia.

CHAPTER 2

LITERATURE REVIEW

2.1 Historical Background

Maxillofacial prosthesis has been discovered among the Egyptians and Chinese for centuries. They used wax and resins for the construction of missing part of head and neck region. The Chinese's used wax, resins, gold, silver for making the missing part of nose and ear (Mitra *et al.*, 2014), (Alqutaibi, 2015). Alphonse Louis made a mask covering the whole left side of the maxillae and mandible using silver for a soldier. In 1541, Ambrose Pare has described the first obturator consisted of a simple disc connected with a sponge. Tycho Brache (1546-1601) made a nasal prosthesis for himself using gold. William Morton also made an artificial nose, but he used enameled porcelain to get the better complexion of patient (Beumer, Curtis and Marunick, 1996). In 1880, Kingsley discussed about a nasal prosthesis attached with an obturator. Vulcanite rubber was widely used in 19th century in dentistry as well as for fabrication of facial prosthesis and Upham discussed about nasal and auricular prosthesis made from vulcanite. In 1905, Ottofy, Baird and Baker all introduced black vulcanized rubber as a material for making prosthesis. In 1913, gelatin-glycerin compounds was described as another material for fabricating facial prosthesis for its softness and flexibility. Acrylic resin was introduced from 1940-1960 and variety of silicone elastomer was introduced from 1960-1970 in dental profession. In 1960, Barnhart first use silicone for making an extra oral prosthesis and silicone became very famous over other materials for the maxillofacial rehabilitation (Alqutaibi, 2015).

Jeevanandam et al (Jeevanandam *et al.*, 2018) discussed the history of usage of nanoparticles and its introduction to the healthcare: The Ancient Egyptians first introduce nano materials 4000 years back as a synthetic chemically processed hair color. The Egyptians had introduced blue pigment through the mixture of nanosized quartz and glass for the decoration purposes in 3rd century BC. The 14th to 13th century BC is known as the beginning of the new era when metallic nano particles were introduced in the form of glass using metals. The evaluation of making different colorful glass from metallic nano particles were noticeable from the late Bronze Age (1200 to 1000 BC) to mid-19th century for several purposes like decorations, reflection basis, kitchen appliances. After 19th century the scientific era of the nano particles started at 1857 by Michael Faraday synthesizing the colloidal silver nano particle solution. In 1940s, nano silicone di oxide (SiO_2) was manufactured for the reinforcement of rubber and currently nano materials showed its positive outcome in different sectors by its excellent physical, chemical and biological properties (Jeevanandam *et al.*, 2018).

In health sector nano particles are used in cosmetics and sunscreen products which act as an anti-reflectance and antioxidants. Silver nano particles are used in toothpastes, air sanitizing sprays, shampoos, food storage containers and wet wipes. In dentistry nano materials were used as permeant, temporary restorative material, cements, sealants, coating and adhesives because of its smaller particle size and anti-microbial activity (Hamouda, 2012). Since the last 15 years many research had been conducted to promote a new material which can be added with the silicone to improve its property. Nano particles are among the filler which can be incorporated with the silicone in certain amount to achieve its desired goal and service life (Ali and Tukmachi, 2017). Therefore, it can be stated that, there was always an urge of developing a new product with nano particles was noticed which can create a new era for the developing dentistry

2.2 Materials Used for Maxillofacial Prosthesis:

Maxillofacial prosthesis was made by ivory, wood, wax and metal in the earlier period of recorded history. Over time, materials such acrylic copolymers, acrylic resins, vinyl polymers, polyurethane elastomers and silicone elastomers were among the commonly used material for fabricating the prosthesis. At current, silicone elastomer becomes the choice of material and used widely in dentistry for prosthetic rehabilitation. (Beumer, Curtis and Marunick, 1996), (Chalian, 1971), (Moore, 1994), (Roberts, 1971).

Silicone becomes the first choice because of its desirable properties such as nontoxic, easily cleansable, lightweight and compatible with adhesives. The longevity of prosthesis is around 6 months. Moreover, silicone made facial prosthesis has restored the missing part of the facial region with acceptable texture, form, color and translucency by duplicating the lost tissues and structures. Characteristics of an ideal material for prosthetic material are as follows:

2.3 Characteristics of an Ideal Prosthetic Material:

According to Beumer et al, (Beumer, Curtis and Marunick, 1996)

2.3.1 Physical Properties:

- Dimensionally stable
- High elongation
- High resistance
- High strength

- High tensile strength
- Low friction
- Low surface tension
- Available adjusted thermal conductivity
- No water resorption
- Translucent
- Flexibility similar to human tissue
- Resistance to environmental discoloration
- Long shelf life
- The usable life of 2 or more years

2.3.2 Processing characteristics:

- Ease of intrinsic and extrinsic coloring with commercially available colorants
- Ease of mold fabrication
- Ease of processing
- Ease of handling
- Long operational time
- Short functional time

2.3.3 Patients Factor:

- Compatible with supporting tissue
- Non-toxic components
- No polymerization by-products
- Odorless

- Inert to solvents and skin
- Ease of adherence to living tissue
- Resistance to the growth of microorganisms
- Hygienic
- Cleansable with disinfectants
- Cleansable without loss of detail at surface or margins
- Softness compatible with tissue and maintained during use

2.4 Evaluation of the materials for prosthetic rehabilitation:

According to Mitra et al and Alqutaibi, (Mitra *et al.*, 2014), (Alqutaibi, 2015):

- **Acrylic resins**:

Both extra oral and intra oral prosthesis can be fabricated by acrylic resin. It consists of polymethylmethacrylate powder and methyl methacrylate liquid form. The polymerization of acrylic resin varies depending on temperature, activation method and purity of the chemicals. Acrylic resin is used for making the prosthesis of less movable part of face while functioning. Acrylic resin has lots of advantages like availability, good color stability, better service life, better strength, sufficient rigidity, enough absorbability as well as it can be relined and repaired however, duplication is not possible.

- **Acrylic co-polymer:**

Though acrylic copolymer is elastic and soft, it has several disadvantages like less durability, insufficient edge strength as well as it degrades when exposed to sunlight. Moreover, coloring process is difficult and complete restorations become tacky due to dust collection and staining.

- **Polyvinylchloride and copolymer:**

It is a combination of polyvinyl chloride and plasticizer which is colorless, odorless and tasteless in nature. Polyvinylchloride and copolymer is used for the fabrication of facial prosthesis because of its flexibility as well as it can adapt with any intrinsic and extrinsic color that makes the appearance of the prosthesis more acceptable. But polyvinylchloride and copolymer absorbs sebaceous secretions and degrade when exposed to UV light.

- **Chlorinated polyethylene:**

It is an industrial grade thermoplastic elastomer and had also been used for prosthesis fabrication because it is less irritating to human tissues, less toxic than thermosetting elastomer and it is non carcinogenic. It is an acceptable alternative to silicone for the construction of maxillofacial prosthesis.

- **Polyurethane elastomers:**

Calthane and Epithane-3 are the only polyurethanes currently available for making facial prosthesis. They have many advantages like flexibility, higher tear resistance, environmental stability, low modulus without use of plasticizers, good ultimate strength and elongation. However, the disadvantage of this material is poor color stability, poor compatibility with adhesive system and production of gas bubbles while processing.

- **Thermoset urethane elastomers:**

They are usually made of primary chemical crosslinks and it is greatly affected by aging and weathering.

- **Silicone:**

Silicone is a combination of organic and inorganic compounds and chemically they are termed as polydimethyl siloxane and considered as the most successful being commonly accepted material for the fabrication of facial prosthesis. The inorganic backbone makes the unique difference of this material as siloxane bonds Si—O—Si in the main chains, as well as Si—C bonds where side groups are bonded to silicone, are extremely flexible and have a great freedom of motion. This is reflected in their lower viscosity, lower surface tension, lower melting point and glass transition temperatures, and is responsible for the elastomeric behaviors of many poly siloxanes.

Silicone is a material with great advantages. It has good physical and mechanical properties, can be easily manipulated, can be stained with intrinsic or extrinsic color which make the prosthesis more real, chemically inert, less toxic and it has greater oxidative and thermal stability. Properly cured silicone elastomers are resistant against the bacterial growth, easy to clean as well as safer than other materials.

2.5 Classification of silicone:

2.5.1 According to the vulcanization reaction of silicones:

- **Heat temperature vulcanization (HTV):**

  HTV silicones are rarely used for the fabrication of facial prosthesis. It is an opaque material with high viscosity and putty like consistency. HTV silicones cured by heat and need a high curing temperature (30 min., 180°C). It is stronger than RTV silicones (Polyzois, Hensten-Pettersen and Kullmann, 1994). They have more stability, better mechanical property, biocompatibility and flexibility but main disadvantage is difficulty in manipulation and fabrication (Bell, Chalian and Moore, 1985) as well as it is less aesthetic and less elastic.

- **Room temperature vulcanization (RTV):**

RTV silicone is cured in the room temperature. The approximate curing time is 72 hours under room temperature for the full polymerization and RTV silicones are famous for use because of its easy manipulation and fabrication technique but it has low mechanical property.

2.5.2 Classification according to application:

- Implant Grade
- Medical Grade
- Food Grade
- Industrial Grade

2.6 Properties of Material used in this research:

According to manufacturer,

- **A-2006 Silicone Elastomer:**

It is also medical grade translucent RTV silicone (manufacturer: factor II Inc.) and curing time is 72 hours at room temperature. It bonds exceptionally with acrylic resin with using A-330 G primer. The value of individual properties of A-2006 are 12+/-3 for shore A hardness, 410 psi for tensile strength, 84 ppi for tear strength, 626% elongation, 130000 cPs for viscosity A and 16000 cPs for viscosity B.

- **A-103 Silicone Elastomer:**

It is a new medical grade RTV silicone (manufacturer: factor II Inc.) as well as it is pourable, clear to translucent, platinum cured, high strength in nature. It is cured in room temperature for 72 hours and no shrinkage occurs while curing and also can accelerate by heat. It has high elongation (500%), improved tear strength (90 ppi) and tensile strength is 650 psi, shore A hardness is 27, viscosity A is 70000 cps.

2.7 Materials used for the improvement of properties of silicone:

In 1980 Lewis and Castleberry (Lewis and Castleberry, 1980) published the desirable properties of maxillofacial silicone with their goal although the desirable surface roughness was not mentioned and reportedly there were no accepted standard surface roughness is present (Sarac *et al.*, 2006). Of the desirable properties, tensile strength, tear resistance, hardness, percentage of elongation, surface roughness, wettability, bond strength was effectively tested by many authors (Hatamleh *et al.*, 2011), (Hatamleh and Watts, 2010). Although silicone is material of choice, but the properties of silicone elastomer is not sufficient enough to fabricate long lasting prosthesis and thus needed to be changed frequently causing trouble for the patient with low income as maxillofacial prosthesis is expensive. So, there have been various instances where researchers have attempted to modify the silicone in different ways to improve the desirable properties. Many research has been conducted to figure out a solution for this problem. From numerous testing, incorporation of nano-particles had proven to produce the best result in achieving the desired goal of a more durable prosthesis (Han *et al.*, 2008).

Nano particles are basically small in size (1-100) nanometer and due to this small size, they have large surface area. They have incorporated into the silicone to increase the mechanical properties as well as to improve the life span of the prosthesis. The concentration of nano particles is a very important factor because it has been found that the mechanical properties of nanoparticle infused silicone exhibit an increased characteristic up to certain concentrations in which there is either no change or can be adversely affected when exceeded a certain amount of concentration (Han *et al.*, 2008). That is why it is essential to know in which concentration of nano particle needed to be incorporated and with which type of maxillofacial silicone. Different authors used different nano particles for their studies and evaluate the changes. In health sector, nano particles were also used in cosmetics and sunscreen products (Ali and Tukmachi, 2017) (Bishal *et al.*, 2019). There are several types of nano fillers used in dentistry. Carbon based nano materials, hydroxy apatite, iron oxide, zirconia, silica, silver and titanium are some commonly used nano particles used in dental practice (Priyadarsini, Mukherjee and Mishra, 2018).

2.8 Nano fillers used in this research with their properties:

- **Titanium dioxide (TiO_2):**

  It is the most common nano oxide used for the enhancement of the properties of silicone elastomer. It has strong ultraviolet protecting property. It is smaller in size so that it has large surface area. They are functionally active and has strong interfacial interaction with the organic polymer. TiO_2 exhibited with several advantageous properties like TiO_2 is non-toxic, chemically inert, inexpensive, high refractive index, antibacterial characteristic under a variety of spectrum, corrosion resistant and high hardness (Shirkavand and Moslehifard, 2014). It can increase the properties of silicone as well as can be added in coating, rubbers, plastics, sealants, fibers, textiles, and cosmetics (Han *et al.*, 2008).

- **Silicon dioxide/ Silica (SiO_2):**

  It is another common nano oxide incorporated with maxillofacial silicone to improve the properties of elastomer. It is the most common ingredient on earth's crust, and it can be found in both pure form and subjected to other metal oxides. It is resistant towards abrasion, chemical materials and heat as well as its coefficient of thermal expansion is low, its density is 2.65 to 2.70 g/cm^3 and its hardness is 7 on the Mohs scale (Cevik and Eraslan, 2017).

2.9 Properties research on maxillofacial prosthetic silicone elastomer:

Maxillofacial prosthesis is used to replace the missing part of the facial region. The material choose for the fabrication of prosthesis must have favorable properties that can adapt with human tissues and mucosa. In 1960 Barnhart (Barnhart, 1960) first used silicone elastomer as a prosthetic material and since, it has becomes the choice of material for fabricating facial prosthesis. Therefore, it is important that the raw materials used in the fabrication of the prosthesis must have certain ideal properties which will determine the ultimate properties of the finished prosthesis (Craig, Koran and Yu, 1980).

However, in 1980, Lewis and Castleberry conducted a research as well as described the processing characteristic and desirable performance properties of maxillofacial silicone with their goal (Lewis and Castleberry, 1980).

Table 2.1 Processing characteristic of maxillofacial silicone elastomer

Processing characteristics	Goal
Viscosity at ambient temperatures	< 75000 cPs
Color	Colorless
Solubility parameter	9-11 cal $^{1/2}$

Working time	15-60 minutes
Curing temperature	< 100 °C
Curing time	72 hours

Table 2.2: Desirable properties of silicone elastomer with their goal

Physical and mechanical properties	Desired range
Tear strength	30-100 ppi
Tensile strength	1000-2000 psi
Modulus at 100% elongation	50-250 psi
Elongation at break	400% to 800%
Hardness	25 to 35 Shore A scale
Water absorption	None

However, the disadvantage of silicone is its lower shelf-life due to insufficient strength of property over time. There were many researches done to evaluate the properties of silicone and how to improve them. Han et al (Han *et al.*, 2008) used nano-TiO_2, zinc oxide (ZnO), and cerium oxide (CeO_2) for their study and got the positive outcome. Among all, TiO_2 is commonly used and it is safe for the cosmetics products up to 25%. By adding TiO_2 reinforcement agents, nanocomposites with polymer-TiO_2 nanostructures can have amazing optical, electrical, and physiochemical properties at very low TiO_2 contents, making them a new class of materials that may prove to be very beneficial (Shirkavand and Moslehifard, 2014), (Bishal *et al.*, 2019). Shakir et al (Shakir and Abdul-Ameer, 2018) and Wang et al, (Wang *et al.*, 2014) both used TiO_2 as nano particle for their study but they are used in different concentration. Shakir et al used 0.25%-0.2% by weight and stated that TiO_2 improved tear and tensile strength where

Wang et al used 2%-6% by weight and found positive result. However, authors used TiO_2 in different concentrations, but they all agreed that TiO_2 increase the properties of silicone. Therefore, use of TiO_2 as filler particles may successfully give the positive result.

Several authors used SiO_2 as a filler material to improve the properties of silicone as SiO_2 is readily available. In 2014 Zayed et al (Zayed, Alshimy and Fahmy, 2014) tested 0.5% to 3% SiO_2 by weight as a potential filler particle for silicone and found the best results in 3% SiO_2 for tensile strength, tear strength and hardness. The author pointed out the benefits of SiO_2 as proven by their applications in biological & biomedical development. Andreopoulos et al (Andreopoulos and Evangelatou, 1994) used 30%-55% by volume silica as a reinforcement of silicone and got the best results on 35% for tensile strength and 50% for tear strength & hardness. But Cevik et al (Cevik and Eraslan, 2017) used silica and TiO_2 at the concentration of 10% by volume where they got the best results when they added TiO_2. Furthermore, Aziz et al (Aziz, Waters and Jagger, 2003) also experimented with silica at 0%-25% by weight and found 20% concentration to be the best for mechanical properties. Kalamarz et al (Kalamarz *et al.*, 2016) used silica at 10% and 15% by weight where they got the best result in 15% for tensile strength and hardness. They used it in different concentrations with different types of silicone elastomers but all of them found the positive feedback and came to the same point that SiO_2 can enhance the properties of prosthetic silicone in certain amount (Zayed, Alshimy and Fahmy, 2014), (Ali and Tukmachi, 2017).

Apart from the commonly used nano particles, Alsmael et al (Alsmael and Ali, 2018) used titanium silicate ($TiSiO_4$) nano particles for their study, Kareem et al (Kareem *et al.*, 2018) used zirconium silicate ($ZrSiO_4$) and Mohammad et al (Al-Mohammad and Abdul-Ameer, 2019) used yttrium oxide (Y_2O_3) as a filler for their study. However, from the usage of these uncommon filler it can be assume that researchers are still searching for a new material, not depending on the commonly used filler for the reinforcement.

2.10 Fourier Transform Infrared (FTIR) analysis for chemical evaluation:

FTIR spectroscopy is a tool for qualitative and quantitative analysis. FTIR spectroscopy is quite accurate, rapid in process, sensitive and non-destructive analytic technique. FTIR analysis has been done to evaluate the organic and inorganic component of a solid, liquid, paste or gaseous material as to see the chemical bond among them. There is an impact of infrared radiation on the atomic vibration of a molecule in the specimen which results the absorption or transmission of energy (Nandiyanto, Oktiani and Ragadhita, 2019).

The outcome of FTIR analysis comes as a graphical representation of the transmittance in percentages (%) versus infrared frequency in term of wavelength (cm^{-1}). FTIR spectrum generally consists of three wavelength regions: far infrared spectrum (<400 cm^{-1}), mid infrared spectrum (400 - 4000 cm^{-1}) and near infrared spectrum (4000 – 13000 cm^{-1}). Among the three regions the mid infrared spectrum is the most common and widely used spectrum for specimen analysis. The mid infrared spectrum again divided into four regions: fingerprint region (600 – 1500 cm^{-1}), double bond region (1500 – 2000 cm^{-1}), triple bond region (2000 – 2500 cm^{-1}) and single bond region (2500 – 4000 cm^{-1}) (Nandiyanto, Oktiani and Ragadhita, 2019), (Ţucureanu, Matei and Avram, 2016).

2.11 FTIR analysis on maxillofacial prosthetic silicone elastomer:

Many researchers have done FTIR spectroscopy for the chemical evaluation of the silicone elastomer. The FTIR spectrum of neat silicone elastomer showed peak at single bond region and fingerprint region which indicates the presence of methyl group. However, some researchers have also performed FTIR analysis on silicone elastomer incorporated with various filler particles. But no noteworthy changes were observed in the chemical structure of silicone elastomer after adding such filler particles (Jebur, Fatalla and Aljudy, 2018), (Al-Judy, 2019). As in this research two different types of nano particles were incorporated to reinforce the silicone elastomer, it was necessary to explore if there were any changes in the chemical structures or any new chemical bonds created. It was also necessary to evaluate if there was any reaction between TiO_2 and SiO_2 with the silicone structure.

Several authors agreed at the same point that incorporation of filler particles does not affect the chemical structure of silicone elastomer. The bonding of filler particles and silicone elastomer are physical interconnection instead of chemical bond. (Kareem *et al.*, 2018).

2.12 Weathering testing features to evaluate the properties of silicone:

Properties can be tested in artificial or natural weathering. In 2012, Kheur et al (Kheur *et al.*, 2012) conducted a research evaluated the main cause of degradation of silicone to be sunlight, pollutants, dust, moisture, temperature and wind as well as stated that degradation varies in climatic condition and environment in which the prosthesis is worn.

In 2009 Eleni et Al (Eleni *et al.*, 2009) conducted another study to evaluate the deterioration of the prosthesis and found that it was strongly depending's on the geographic location, season, time of day, cloud coverage and exposure orientation as well. The author also performed the research on the outdoor weathering in different climatic condition at least for one year. Farah et al (Farah, Sherriff and Coward, 2018) also agreed to this and preferred outdoor weathering, as it gives more accurate results for the life span of prosthesis But, Han et al disagreed and preferred artificial weathering as it is more accurate in terms of control provided by authors which has different impact on the properties of material (Han *et al.*, 2010).

However, many authors used artificial weathering for their research as they can predetermine the required temperature, environment and duration. Artificial weather can determine the outdoor performance and predict the lifetime of the prosthesis under service conditions however, accelerating weathering often can give the wrong estimation for the longevity of prosthesis (Eleni *et al.*, 2009).

CHAPTER 3

MATERIALS AND METHODS

3.1 Study design:

It is a comparative in vitro experimental study.

3.2 Source population:

Samples for the study were made from two different RTV silicone (A-2006, A-103) (Factor II, Inc., Lakeside, AZ, USA). For the reinforcement of silicone elastomer, two commonly used filler particles were selected namely Titanium dioxide (TiO_2) and Silicone dioxide/Silica (SiO_2) (Metal basis, Alfa/US).

3.3 Sampling frame:

3.3.1 Inclusion criteria:

The specimens of this study were made of according to the ISO specification for type II dumbbell shaped samples (Standard and ISO, 2005).

3.3.2 Exclusion criteria:

The specimens that were more than 20% different from the specifications of ISO for type-II dumbbell-shaped specimens were eliminated.

3.4 Sample size calculation:

For sample size calculation G-power v3.1.9.4 sample size calculation software were used.

For specific objective 1, 2:

To compare the properties between the experimental and control specimens within same type of silicone elastomer after outdoor weathering, the sample size calculation was carried out using the following parameters:

An effect size of 0.4 (Large effect, Cohen) with α=0.05 and power of 0.80 suggested a total 90 samples. Therefore, a size of 15 samples for each experimental and control groups were determined.

3.5 Research materials and tool's:

3.5.1 Materials:

Table 3.1 List of Maxillofacial prosthetic silicone elastomers used in this study

Name of silicone	**Type of silicone**	**Packaging**	**Base: catalyst By weight**	**Curing time**
A-2006	RTV	Two component gel	1:1	72 hours at room temperature
A-103	RTV	One component gel and one component fluid	10:1	72 hours at room temperature

* These materials are medical grade silicone elastomers from Factor II Inc, Lakeside, AZ, USA.