COLOR STABILITY OF PIGMENTED MAXILLOFACIAL PROSTHETIC SILICONE ELASTOMER WITH AND WITHOUT FILLER INCORPORATION SUBJECTED TO OUTDOOR WEATHERING - A DIGITAL EVALUATION

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by

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LIST OF ABBREVIATIONS

ΔE	Color difference
µm	Micrometer
2D	Two dimensional
3D	Three dimensional
ANOVA	Analysis of Variance
Avg	Average
AZ	Arizona
CIE	International Commission on Illumination
CAD-CAM	Computer-Aided Design & Computer-Aided Manufacturing
CBCT	Cone-Beam Computed Tomography
CeO_2	Cerium oxide
cm	Centimeter
Co.	Company
df	degree of freedom
FDI	Federation Dental International
g/cm^3	Gram per cubic centimeter
g/mol	Grams per mole
gm	Grams
GmbH	Gesellschaft mit beschränkter Haftung
h	Hour
HALS	Hindered Amine Light Stabilizer
HSV	Hue Saturation Value
HTV	Heat Temperature Vulcanizing silicone elastomer
Inc.	Incorporation
ISO	International Organization for Standardization
Lux	Luminous Flux per unit area
Max T	Maximum Temperature
MBPI	Mean Blue Pigment Intensity
MFPSE	Maxillofacial Prosthetic Silicone Elastomer

Min	Minute
Min T	Minimum Temperature
MJ/m^2	Millijoule per square meter
mm	Millimeter
NEF	Nikon’s Raw file format
oz	Ounces
PABA	Para-Aminobenzoic Acid
ppi	Pounds per inch
psi	Pounds per square inch
RGB	Red Green Blue
rpm	Revolutions per minute
RTV	Room Temperature Vulcanizing silicone elastomer
SD	Standard Deviation
Sdn. Bhd.	Sendirian Berhad
SiO_2	Silicon dioxide
SLR	Single-Lens Reflex
SPSS	Statistical Package for the Social Sciences
STL	Standard Tessellation Language
TiO_2	Titanium dioxide
TPU	Thermoplastic polyurethane
USA	United States of America
UV	Ultraviolet light
W/m^2 /nm	Watt per square meter per nanometer
ZnO	Zinc oxide

LIST OF APPENDICES

KESTABILAN WARNA PROSTETIK MAKSILOFASIAL ELASTOMER SILIKON BERPIGMEN DENGAN DAN TANPA PEMASUKAN PENGISI YANG TERDEDAH KEPADA PENCUACAAN LUARAN-SUATU PENILAIAN DIGITAL

ABSTRAK

Kejayaan klinikal prostesis berelastomer selalunya dicabar oleh kepelbagaian pencuacaan persekitaran dan pencahayaan tempatan, yang akan menyebabkan perosotan warna. Pelbagai kaedah, seperti kemasukan pengisi telah dilaksanakan untuk memperlahankan proses perosotan warna secara fizikal. Walau bagaimanapun, dengan peralihan kepada pendigitalan lengkap baru-baru ini, tanggapan maya dan penerimaan juga menjadi sepenting kejayaan klinikal sebagai pemulihan berfungsi tertakluk kepada ledakan dalam komunikasi digital melalui gambar foto dan rakaman video. Oleh yang demikian, fotografi digital sekarang memainkan peranan penting dalam perancangan rawatan, motivasi pesakit dan hasilan diagnostik dalam praktis pergigian seharian. Kajian ini bertujuan untuk menilai secara digital pengaruh pencuacaan luaran dan kemasukan pengisi terhadap kestabilan warna elastomer silicon berpigmen. Dua elastomer silicon prostetik maksilofasial (A-103 dan A-2006) telah diwarnakan dengan dua pigmen berasaskan minyak [blush (FI-SK13) dan honey (FI-SK09)] untuk meniru tona kulit menurut ‘skala Fitzpatrick’. 216 sampel silikon berpigmen [A-103(blush), A-103(honey), A-2006(blush), A-2006(honey)] telah dihasilkan daripada templat khas cetakan 3D. Pengaruh cuaca Malaysia terhadap perosotan warna elastomer silikon berpigmen telah dinilaikan berdasarkan pencuacaan 72 sampel. Pengisi nano partikel silikon dioksida (SiO_2) telah dimasukkan ke dalam tambahan 72 sampel berpigmen yang turut dicuacakan. Pencuacaan sampel dilakukan di atas rak pencuacaan luaran yang ditempah khas selama 4 bulan bawah cuaca Malaysia. 72 sampel lagi tidak dicuacakan dan diletakkan di dalam alat pelembap pada suhu 20ºC ±5 ºC dengan

kelembapan bandingan 70 ± 5 %. Sampel tersebut dirakamkan 2 kali; sekali sebelum pencuacaan (garis dasar) dan sekali selepas pencuacaan oleh kamera digital professional dalam tetapan studio terpiawai terbina khas. Gambar foto telah dikalibrasi warna secara electronik dengan menggunakan ‘carta warna Macbeth’ berkomputer dan nilai-nilai CIELAB telah diterbitkan secara digital dengan menggunakan Adobe-Photoshop Lightroom Classic CC. Perubahan Warna (ΔE) selepas pencuacaan telah dinilaikan untuk semua sampel. ‘Independent Sample t-test’ dan ‘Analisis Varians’ (2-hala and 3-hala) telah dilakukan untuk perbandingan statistik. A-103 (honey) dan A-2006 (blush) menunjukkan perbezaan warna yang tidak signifikan (P>.05) selepas pencuacaan dengan kesan interaksi yang signifikan (P<.001) diperhatikan antara semua kumpulan silikon dan pigmen. Kemasukan pengisi nano menunjukkan tiada perbezaan signifikan (P>.05) selepas pencuacaan tetapi mempunyai interaksi signifikan (P<.001) dengan kumpulan pigmen dan silikon. Hasil dapatan menyatakan, dalam keadaan pencuacaan tropikal, prostesis diperbuat daripada pigmen A-103 honey atau A-2006 dengan pigmen blush dapat menghasilkan ketahanan warna yang lebih dan SiO_2 hanya melindungi silikon sekiranya gabungan pigmen A-103 dan blush digunakan.

COLOR STABILITY OF PIGMENTED MAXILLOFACIAL PROSTHETIC SILICONE ELASTOMER WITH AND WITHOUT FILLER INCORPORATION SUBJECTED TO OUTDOOR WEATHERING - A DIGITAL EVALUATION

ABSTRACT

Clinical success of elastomeric prostheses is constantly challenged by local environmental weathering and lighting variations, which eventually leads to color degradation. Various methods, such as filler infusion have been implemented to slow down physical color degradation process. However, with the recent shift to complete digitization, virtual perception and acceptability have become just as important for clinical success as functional rehabilitation owing to a boom in digital communications via photographs and video recordings. Therefore, digital photography now plays a key role in treatment planning, patient motivation and diagnostic outcomes in everyday dental practice. The current study aims to digitally evaluate the influence of outdoor weathering and filler inclusion on the color stability of pigmented silicone elastomers. Two maxillofacial prosthetic silicone elastomers (A-103 and A-2006) were colored with two oil-based pigments [blush (FI-SK13) and honey (FI-SK09)] to simulate skin tone according to the 'Fitzpatrick scale'. 216 pigmented silicone samples [A-103(blush), A-103(honey), A-2006(blush), A-2006(honey)] were derived from custom 3D-printed templates. The influence of Malaysian weather on color degradation of the aforementioned pigmented silicone elastomers was evaluated by weathering 72 samples. Nano-filler particle silicon dioxide (SiO_2) was infused within an additional 72 pigmented samples that were also weathered. Weathering of the samples was done on a custom-made outdoor exposure rack for 4 months in Malaysian weather. 72 samples were not weathered and were subjected to a humidifier at a temperature of

20ºC ±5ºC with relative humidity of 70 ±5%. The samples were photographed 2 times; once before weathering (baseline) and once after weathering by a professional digital camera in a custom-made standardized studio setup. The photographs were electronically color calibrated by using a computerized 'Macbeth color chart' and CIELAB values were digitally derived by using Adobe-Photoshop Lightroom Classic CC. Color change (ΔE) after weathering was then evaluated for all samples. Independent Sample t-test and Analyses of Variance (2-way and 3-way) were performed to make statistical comparisons. A-103 (honey) and A-2006 (blush) exhibited no significant (P>.05) color differences after weathering with significant interaction (P<.001) effects observed between all silicone groups and pigments. Incorporation of nano-filler showed no significant (P>.05) difference after weathering but had significant interactions (P<.001) with pigment and silicone groups. The findings suggest that, in tropical weathering conditions, prosthesis made with A-103 honey pigments or A-2006 with blush pigments can produce more color resilience and SiO_2 only protect the silicone if A-103 and blush pigment combination was used.

CHAPTER 1
INTRODUCTION

1.1 Background of the study

Maxillofacial prosthodontics is the sub-speciality in maxillofacial prosthetics which opened an opportunity for the patients, who have the deformities from birth or any kind of extra oral defects which cannot be restored surgically (Kiat-amnuay *et al.*, 2009; Farah, Sherriff and Coward, 2018). Patients also might exhibit deformities due to trauma, malignancy, infection, and burns. Although, small facial defects can be restored surgically but for large facial defects combination of both surgical and prosthetic interventions are required. If not treated properly, such deformities not only affect the patient's quality of life, but also become a cause for their psychological imbalance (Cevik, Polat and Duman, 2016; Kheur *et al.*, 2016, 2017). The success of these prosthetic treatment mostly depends on many factors and one of this could be the material that are selected for that treatment purpose (Alqutaibi, 2015).

For rehabilitation of craniofacial defects different materials can be used but over the year's silicone is the material of choice for the fabrication of the maxillofacial prosthesis (Cevik, Polat and Duman, 2016; Bishal *et al.*, 2019)**.** Silicone has the properties such as biocompatibility, strength, durability, non-toxicity and most importantly it is compatible to mimic the color of natural human skin when mixed with different pigments and makes it esthetically more acceptable (Cevik, Polat and Duman, 2016; Bishal *et al.*, 2019). Though, prostheses are mainly used to restore such defects and by using it one can regain their lost structure but realistic coloration of the prosthesis has become the prime concern for both the patients and the clinicians (Rashid *et al.*, 2020). To obtain a color matched natural looking silicone prosthesis, there are various extrinsic and intrinsic coloring procedures available and those procedures includes different organic or inorganic coloring agents (pigments), which eventually makes the prosthesis visually more appealing (R. M. Kantola *et al.*, 2013; Anitha *et al.*, 2016; Kheur *et al.*, 2017).

According to the patients, a facial prosthesis is called perfect when it remains unnoticeable in public (esthetically acceptable) as well as if it retains its functional properties (color stability) over the years (Kiat-amnuay *et al.*, 2009). But it has been reported that, 29% of the patients have remade their prosthesis within one year because of its color degradation property (Bankoğlu *et al.*, 2013). While color degradation is an inevitable process, studies have shown that different filler particles such as ground quartz, glasses, sol-gel derived ceramics or metals & minerals can be incorporated into the silicone elastomer to effectively slow down its color degradation process (Akash and Guttal, 2015; Farah, Sherriff and Coward, 2018). Among all the filler particles, nano fillers are widely used in medical sciences because they are small in dimension with large specific area and exhibited a strong interfacial interaction while mixed with the silicone elastomer (Jeevanandam *et al.*, 2018). Studies have reported that, adding nano filler particles to the silicone elastomer, the particle could control both the mechanical and biological properties of silicone elastomer and also improved silicone’s optical function by reducing the color degradation process of the material (Akash and Guttal, 2015; Cevik, Polat and Duman, 2016).

There are many techniques available for collecting skin color information in such a reliable and constant way (Hu, Johnston and Seghi, 2010). Within the dental clinics, visual color matching with shade guides is the most frequently used shade selection technique, which exhibit an overall accuracy of 40-60% (Kim *et al.*, 2018; Liu *et al.*, 2019). This is because, most of the dentists are not well trained to carry out the shade selection procedures and also have lack of knowledge within the color sciences (Tam and Lee, 2012). Spectrophotometers and colorimeters were introduced in the 1970s to improve the reliability and consistency of color matching (Rashid *et al.*, 2020). But unfortunately, those devices are technique sensitive, expensive and have very poor inter-device reliability (Sampaio *et al.*, 2019). Regardless, these devices are considered standard and the color values are displayed in the CIELAB color spaces. (Hu, Johnston and Seghi, 2010)

'Color spaces or color models' is a method in which color is understood as a visually indistinguishable metameric lights that are represented by their spectral power distribution (i.e., illumination of per unit wavelength) (Logvinenko, 2009). There were 12 kinds of color spaces such as; RGB, HSV, YUV, YCbCr, XYZ, YIQ, L*a*b*, U*V*W*, L*u*v*, $I_1I_2I_3$, HIS and rgb but among them CIELAB color space is most commonly used, which was proposed by CIE (International Commission on Illumination) in 1931(Lazar *et al.*, 2019). Additionally, in the same year CIE also addressed the theory of color difference, where the color difference between two subjects can be calculated by using 'Euclidian' color differences, which is 'ΔE' (Mehl *et al.*, 2017; Mahn *et al.*, 2020). For the more details and definitions of all color spaces refer to **Appendix A**.

Undoubtedly, the current trend in dentistry has demonstrated a shift towards digitization and automated diagnostics. Perception and acceptability of esthetic treatment has become just as important as functional rehabilitation owing to a boom in social media influence and digital multimedia communications (Kaplan and Haenlein, 2010; Montero *et al.*, 2014; Labban *et al.*, 2017). In the past few decades, technology has brought upon a massive growth for making life simpler for a person. Within this technological advancement, photography has benefited mostly (Qutieshat, 2019). Now a days, digital cameras and smartphones are readily available tools in everyday dental practice and have reliably simplified esthetic dental treatment planning and digital diagnostics (Tam and Lee, 2012; Mulcare and Coward, 2019; Sampaio *et al.*, 2019). Studies have proved that digital photographic technique is a more suitable and reliable medium of shade analysis for both in vivo and in vitro cases (Hu, Johnston and Seghi, 2010; Lazar *et al.*, 2019).

Color degradation may vary due to multitude of factors; environmental problems especially the local environment has an adverse effect not only to the skin but also to the silicone prostheses as the patients wearing the prosthesis are mostly exposed to the outdoor weathering environment (Tran, Scarbecz and Gary, 2004; Kheur *et al.*, 2017). Nevertheless, many real-life usage conditions also affect the materials color and cause varying rates of color degradation (Han, Powers and Kiat-amnuay, 2013). However, there is a limited published data available for color stability of pigmented maxillofacial prosthetic silicone elastomer (MFPSE) with or without filler incorporation subjected to natural Malaysian weather using digital photographic technique.

1.2 Problem statement

Main drawback of the silicone elastomer was the need for frequent renewal of the prosthesis within a year because of its color degradation property (Farah, Sherriff and Coward, 2018; Bishal *et al.*, 2019; Rashid *et al.*, 2020).

Environmental factors including ultraviolet lights (UV), humidity, water, temperature, solar radiation can affect the MFPSE. Although, the use of different disinfectant solutions for cleaning and application of adhesives material can also change the mechanical properties (tensile strength, tear strength, hardness, and elongation of break) of the silicone elastomer (Cabral *et al.*, 2018; Barman *et al.*, 2020). It can be occurred due to the continuous polymerization of the silicone itself or alteration of the chromatic products and constant release of sub products during polymerization of the silicone elastomer. This subsequently reduces the bonding capabilities of silicone with different fillers and pigments (Kheur *et al.*, 2016, 2017). Additionally, Asian weather varies in terms of humidity and solar radiation and thus influence the color degradation of silicone prosthesis as opposed to cooler climates to the West (R. Kantola *et al.*, 2013).

For making a successful facial prosthesis, the color of the prosthesis should be matched with the surrounding structures of the patient's skin (Farah, Sherriff and Coward, 2018). While fabricating a prosthesis, clinicians face a big challenge because of the color matching procedure of the prosthesis. Conventional techniques like chair side visual trials, color evaluation with shade guides, instrumental colorimetric procedures are available, however they are technique sensitive, expensive, require special skill to perform and also they are time consuming, which results multiple modifications during the prosthesis fabrication hence increasing chairside time (Kim-Pusateri *et al.*, 2009; Hu, Johnston and Seghi, 2010; Sarafianou *et al.*, 2012; Gurrea *et al.*, 2016; Sampaio *et al.*, 2019). Along with the above-mentioned problem statements:

- There is a little evidence that, the color degradation of silicone incorporated with the skin color pigments have been evaluated or tested digitally in natural Malaysian / Asian weathering.
- Since almost all the studies experimented the color degradation have used an artificially controlled weathering chamber, thus a proper evaluation in natural outdoor weathering is still missing in local Malaysian environment.
- Nevertheless, from the best of our knowledge there is a lack of evidence available in which photographic color analysis technique was applied to

evaluate the color degradation property of pigmented silicone elastomer with or without filler incorporation under natural Malaysian outdoor weather.

So, the aim of the study is to evaluate the color stability of maxillofacial prosthetic silicone elastomer with and with-out filler incorporation subjected to outdoor weathering by using digital photographic technique.

1.3 Justification

To evaluate the true effects of the environmental factors (UV, solar radiation, temperature, and rain) on silicone elastomers a study conducted by Rahman (Rahman *et al.*, 2021) have introduced their samples within the dark chambers and made comparison with local Malaysian environment. However, that study neither used pigmented silicone elastomer nor the authors evaluated the color degradation property of silicone elastomer. So, there is a need to evaluate the baseline data of pigmented silicones, when they are subjected to both dark and outdoor weathering environmental condition in Malaysia. Apart from that, most of the studies evaluated color degradation of pigmented silicone have been conducted their studies in USA or Europe. However, the weathering parameters varies in terms of geographical location, season, and the amount of cloud cover upon the weathered exposed material (Nguyen *et al.*, 2013). Therefore, a proper evaluation of how pigmented silicone will act with or without any external environment needs to be assessed, so that which combination of silicone elastomer and pigment would be suitable under local Malaysian environment can be evaluated.

Furthermore, there are many kinds of silicone elastomer and pigment particles available in the market. Different silicone has different surface properties and also binds differently while mixed with pigments. However, selection of proper combination is necessary because there could be a chance that silicone itself or different pigment particle incorporation might instigate the color degradation property of MFPSE. Therefore, there is a need to investigate which element is mainly responsible for silicones color fastness under local Malaysian environment.

Additionally, to reduce the silicones color degradation property studies have incorporated nano-filler particles within the silicone elastomers. But from the best of our knowledge those studies were not conducted in South-East Asian region. As Asian weather exhibit greater variations, so there is a need to evaluate which combination of pigmented and silicone should be used with nano-filler so that, the combination might show some amount of color stability in natural weathering, especially in Malaysia.

Furthermore, during fabrication of the maxillofacial prosthesis, clinicians have found it difficult to perfectly match the color of the prosthesis by using traditional methods. But studies have proved that digital image provides an accurate esthetically acceptable skin color replicant prosthesis over traditional color analysis methods with minimal color adjustments and modifications. Nevertheless, this procedure can potentially reduce the treatment time (Jain *et al.*, 2010; Buzayan *et al.*, 2015). To the best of our knowledge, color analysis by using digital photographs has not been evaluated in Malaysian environment.

Thus, the aim of the study is to digitally evaluate the color stability of maxillofacial prosthetic silicone elastomer with and with-out filler incorporation subjected to outdoor weathering.

1.4 Clinical significance:

- Previously studies have successfully used filler particles for improving the mechanical and color degradation property of maxillofacial silicone elastomer

(Han *et al.*, 2008; Farah, Sherriff and Coward, 2018; Bishal *et al.*, 2019; Barman *et al.*, 2020; Rashid *et al.*, 2020). These filler particles incorporated silicone elastomer can become the material of choice for the clinicians to make a long-lasting prosthesis in local environment which will potentially reduce the frequency of the clinical follow-ups/re-fabrication.

- Nevertheless, the current generation is exposed to social media influence and currently 80% of the world population is active on a social media platform, so for them pictures and videos are important (Nielsen and Schrøder, 2014). As digital photographic technique is highly accurate, simple, less expensive, and easily available, it has become one of the necessary tools within the dental practices. The benefits of the photographs range from easier data capture, manipulation, color analysis, professional communication and patient education (Jarad, Russell and Moss, 2005; Montero *et al.*, 2014; Carney and Johnston, 2016; Rauber *et al.*, 2017). Without the need for any special training, such technology inherently aid in better clinical judgements (Luo *et al.*, 2017; Lazar *et al.*, 2019; He *et al.*, 2020), even in complex clinical cases such as evaluating the integrity and possible breakdowns of dental restoration (Rauber *et al.*, 2017; Lam *et al.*, 2018; Liu *et al.*, 2019).

1.5 General objective:

To digitally evaluate the color stability of pigmented maxillofacial silicone elastomers with and with-out filler incorporation subjected to local Malaysian environment.

1.6 Specific objective

1. To compare the color stability of 'indoor weathered' and 'outdoor-weathered' pigmented silicone elastomer samples [A103 (blush), A103 (honey), A-2006 (blush), A-2006 (honey)] by using digital photographs
2. To compare color stability of silicone elastomers (A103, A-2006) with different pigmentation (blush, honey) subjected to outdoor weathering by using digital photographs
3. To compare color stability between non-filler and filler-infused (SiO_2) pigmented maxillofacial silicone elastomers [A103 (blush), A103 (honey), A-2006 (blush), A-2006 (honey)] after outdoor weathering by using digital photographs

1.7 Research hypothesis:

1. There is no significant difference in color stability of 'indoor weathered' and 'outdoor weathered' pigmented silicone elastomer samples by using digital photographs
2. There is no significant difference in color stability of silicone elastomers with different pigmentation subjected to outdoor weathering by using digital photographs
3. There is no significant difference in color stability between non-filler and filler-infuse pigmented maxillofacial silicone elastomers after outdoor weathering by using digital photographs

1.8 Research question:

1. Is there any difference in color stability of ‘indoor weathering’ and ‘outdoor weathering’ pigmented silicone elastomer samples by using digital photographs?
2. Is there any difference in color stability of silicone elastomers with different pigmentation subjected to outdoor weathering by using digital photographs?
3. Is there any difference in color stability between non-filler and filler-infuse pigmented maxillofacial silicone elastomers after outdoor weathering by using digital photographs?

CHAPTER 2
LITERATURE REVIEW

2.1 Historical background of the maxillofacial prosthesis

Maxillofacial prosthodontics deals with the prosthetic rehabilitation of acquired and congenital disfigurement by birth or developed due to any disease or trauma (Hatamleh *et al.*, 2010). Such defects can be restored either surgically or by using some prosthetic approach or in some complex cases combination of both (Alqutaibi, 2015). In 1953, ‘Ackerman’ described maxillofacial prosthesis as the phase of dentistry that can repair and artificially replace the injured part of the face after any surgical intervention or trauma (de Caxias *et al.*, 2019).

Maxillofacial prosthesis includes both intra and extra oral prosthesis like nasal, auricular, ocular, palatal obturator, and tongue prosthesis. Even an artificial structure of cranial bone, maxilla-mandible and plate can also be provided by the maxillofacial surgeons (de Caxias *et al.*, 2019). Therefore, to rehabilitate the craniofacial defects there were many materials available such as acrylic resins and its co-polymer, polyurethane based elastomer, vinyl polymer and silicone elastomers. Previously, Chinese people used to make nasal and auricular prosthesis using waxes, resins as well as metals like gold and silver (Alqutaibi, 2015; Cevik, Polat and Duman, 2016).

Before 1600 A.D the first ever prosthesis constructed were made of wood, waxes, clay, and the insertion was done into the ‘Egyptian and Chinese’ mummies. At that time the ‘Romans and Greeks’ used to fabricate artificial eyes with silver and inserted into their statues (de Caxias *et al.*, 2019). Around 1510-1590, a ‘French’ surgeon called ‘Ambrose Pare’ proposed a silver nasal prosthesis and the prosthesis was attached with a metal string around the patient’s head. Apart from this, the surgeon also proposed some nasal and eye prosthesis which was made with leather, ivory, and gold. But unfortunately, those protheses were discontinued because of that metal string around the patient's head. Thus, for the contribution in the field of eye prosthesis rehabilitation 'Ambrose Pare' is called the 'Father of Facial Prosthesis'. But the clinical applicability of those prostheses are still questionable (de Caxias *et al.*, 2019). Only one recorded clinical evidence was present between 200AD and 1000AD for a golden nose, which was constructed by 'Byzantine Emperor Justinian II' (Chalian, Drane and Standish, 1972; McKinstry, 1995; Beumer, Curtis and Marunick, 1996; de Caxias *et al.*, 2019).

In 16th century, there were debates among 'Germany and France' doctors regarding the suitability of the use of glass and wood for constructing maxillofacial prosthesis. In 17th century, 'Pierre Fauchard' developed a palatal obturator with silver and concluded that, an obturator not only improved the esthetic condition but also can minimize the masticatory problems in patients with palatal defects. In 1880, 'W. Kingsley' combined the nasal and palatal prosthesis and also explained the advantages of the proposed technique. In 1889, 'Claude Martine' used ceramic for the construction of nasal prosthesis. Later on, in 19th century, 'William Morton' fabricated a nasal prosthesis which was attached with patient's glasses and used enamelled porcelain to match with the surrounding structure. At the end of the 19th century cellulose, metals, ceramics were replaced by vulcanite's and was frequently used during the time of 'World War I'. After that, in 20th century for the first-time, cleft palate reconstruction was done by using maxillofacial prosthesis (Moore, 1994; de Caxias *et al.*, 2019).

In the year 1913, Gelatine- Glycerine compound was used as a prosthetic material because of its softness and flexibility. In 1940 to 1960, as prosthetic material acrylic resins were used to rehabilitate different extra and intra oral defects. Clinicians mostly preferred to use acrylic resins because of its easy processing, color stability and translucency. But soon after, the clinical use of the acrylic resins were discoursed by the clinicians because of its rigidity (Chalian, Drane and Standish, 1972; Moore, 1994; McKinstry, 1995; Beumer, Curtis and Marunick, 1996).

Though the silicone was first introduced in 1946, but ‘Barnhart’ was the person who used silicone elastomer as maxillofacial prosthetic material in 1960 (Alqutaibi, 2015). From then to till now, over the last 50 years silicone is the material of choice for maxillofacial prosthesis fabrication, because it has several physical, mechanical, and optical properties which makes it best suitable for prosthetic reconstruction. Most importantly silicone can be perfectly matched with the surrounding structure of the skin, which makes it esthetically more acceptable and appealing for the patients (Cevik, Polat and Duman, 2016; Bishal *et al.*, 2019; Rahman *et al.*, 2021).

2.2 Expected properties of prosthetic material:

A prosthetic treatment is called desirable when it cannot be differentiated immediately from a certain distance by an observer (Farah, Sherriff and Coward, 2018). Therefore, for obtaining patient’s satisfaction and clinical success, a maxillofacial prosthodontist should have a detailed knowledge about the material to be used for repairing such defects (Chalian, Drane and Standish, 1972; Beder, 1974; Moore, 1994; McKinstry, 1995; Beumer, Curtis and Marunick, 1996). A prosthetic material needs to be flexible so that it can be used on the movable tissue beds and also should be strong enough so that any edge tearing can be prevented while removing the prosthesis (A C Roberts, 1971). But, most importantly the prosthesis should retain its color and does not degrade even under harmful exposure of UV radiation within six months (Artopoulou *et al.*, 2006; Babu, Manju and Gopal, 2018). According to Beumer

(Beumer, Curtis and Marunick, 1996), Moore (Moore, 1994) and Alqutaibi (Alqutaibi, 2015), the ideal properties of the maxillofacial prosthetic material should include some physical property, biological property and processing characteristics. List of such properties were given below:

Table 2.1: Ideal properties (physical properties, processing characteristic and biological properties) of MFPSE

Physical properties	**Processing characteristic properties**	**Biological properties**
• Translucent	• Facilitate intrinsic and extrinsic coloration techniques	• Color stability
• Low surface tension	• Easy Processing	• Non-toxic and non-irritant
• High elongation and tensile strength	• Do not change the color after setting	• Do not self-polymerized
• High resistance property	• Easy mold fabrication	• Odorless
• High peripheral edge strength	• Easy of handle	• Easy to adhere with living tissue
• Dimensionally stabile	• Chemically inert	• Hygienic, can be clean with the disinfectant solution
• Relative flexibility and softness	• Long working time	• Inhibit the growth of micro-organisms

• Long shelf life of 2 or more years	• Short setting time	• Cleansable without any loss of surface details
• Compatible to surrounding tissue		• Static to solvents and adhesives

2.3 Material used for the fabrication of maxillofacial prosthesis

According to the past literature reviews (Beumer, Curtis and Marunick, 1996; Alqutaibi, 2015), the materials that are commonly used for fabricating the facial prosthesis as follows:

1. Acrylic resins
2. Polyvinylchloride co-polymers
3. Chlorinated polyethylene
4. Polyurethane elastomer
5. Silicone elastomer

2.4 Acrylic resins and the reason their use was discontinued in facial prosthetic rehabilitation

Acrylic resins are the derivatives of ethylene and can be used for fabrication of both intra and extra-oral prosthesis. They consist of powder Poly (methyl methacrylate) and liquid (Methyl methacrylate). Poly (methyl methacrylate) is a transparent resin and does not discolor under UV lights. Coloration of the prosthesis can be done by both extrinsic and intrinsic coloration procedures by using acrylic base paints (Moore *et al.*, 1977; Alqutaibi, 2015). Acrylic resins can be used in those areas where minimum tissue movement occurred during functioning. Previously acrylic resins were used because, it has high durability and color stability, if required relining and repairing could be possible. Among the auto polymerized and heat polymerized acrylic resins, heat polymerized acrylic resins were preferred because it is free from any tertiary amine activator and more color stable (Alqutaibi, 2015). However, it is a rigid material and duplication of the prosthesis is not possible. The material also causes irritation to the tissues and patients mainly faced discomfort during the winter because it has high temperature conductivity and within the months, the shiny appearance of the prosthesis faded (Beumer, Curtis and Marunick, 1996).

2.5 Polyvinylchloride co-polymers and their challenges in making flexible prostheses

In the past, vinyl polymer and co-polymers were widely used for facial restoration because it has combination of polyvinyl chloride and plasticizer (Lemon *et al.*, 2005) The material have most of the desirable properties like flexibility, adaptability to extrinsic and intrinsic coloration and initially, it could able to show an acceptable appearance if manipulated adequately (Beumer, Curtis and Marunick, 1996). But unfortunately, under the UV lights, ozone and tetraethyl leads to plasticizer migration which eventually causes color degradation. Though, the material's expected life span is 6 months but can be extend to 9 to 11 months by reducing the amount of plasticizer (Beumer, Curtis and Marunick, 1996; Alqutaibi, 2015). Additionally, absorption of cosmetics and sweat might hamper the flexibility of the material. However, for curing the material high temperature with metal mold is required and this eventually makes the material darker (Lemon *et al.*, 2005).

2.6 Chlorinated polyethylene and their infrequent uses in fabricating maxillofacial prostheses

Based on the chemical composition and physical properties chlorinated polyethylene resemble the polyvinylchloride (Beumer, Curtis and Marunick, 1996). Their unique advantage is the molding procedure can be repeatable and the coloration of the prosthesis is done by using oil soluble colorant. However, while fabricating the samples, the material requires higher curing temperature and metal mold.

2.7 Polyurethane elastomer and their unfavourable physical properties as prosthetic material

Polyurethane elastomer is used in many commercial purposes but for facial prosthesis only Epithane-3 is used (Alqutaibi, 2015). They can be made as quite thin and elastic material without compromising the edge strength of the prosthesis. This material is suitable for the movable tissue beds because of its flexibility. Both extrinsic and intrinsic coloration can be done. But the disadvantages include; it's difficult to manipulate, have high moisture sensitivity, under UV lights its color degrades and also the material have poor adhesive property.

2.8 Introduction of silicone elastomer as an alternative

Silicones are mainly combination of organic or inorganic compound of polydimethylsiloxane (Mitra *et al.*, 2014). They are mainly consisting of alternative chains of silicone and oxygen atoms. Silicones can be modified by attaching different organic sub-groups or by crosslinking with different molecular chains (Alqutaibi, 2015). Therefore, by adjusting the silicone-oxygen chain length, silicones can be produced in the form of rubber, resins, or fluids and can be used as a lubricant, wax, electric insulator, or a non-sticky coating material. Many additives, vulcanizing agents and antioxidants were mixed during processing of silicone elastomer to transform the raw mass into rubbery resin. For obtaining additional strength fillers can also be incorporated with the silicone elastomers (Alan Clive Roberts, 1971; Chalian, Drane and Standish, 1972; Beder, 1974; Beumer, Curtis and Marunick, 1996).

Among the silicone materials, 'Polydimethylsiloxane' is commonly used for facial prosthesis. It forms a polymer by reacting with the water (Alqutaibi, 2015;

Cevik, Polat and Duman, 2016; Bishal *et al.*, 2019). It is a translucent, watery, white fluid polymer in which viscosity is determined by the polymeric chain length. It is advantageous because long chain polymers have property to provide protection against UV light (Beder, 1974; Beumer, Curtis and Marunick, 1996).

Though silicone has low surface tension, poor tear, and tensile strength but during oxidation reaction, the polymers provide resistance by increasing the strength to its silicone-oxygen bond, which makes it an ideal material for various purposes. Silicone can maintain their strength, elasticity, and flexibility within -78ºC to 300ºC temperature or sometimes more than that. Additionally, in health profession silicones were advantageous because they can be produced synthetically and therefore, has no chemical reactivity with the oxides (Alan Clive Roberts, 1971; Chalian, Drane and Standish, 1972; Beder, 1974; Beumer, Curtis and Marunick, 1996).

2.8.1 Classification of silicone elastomer

When the polymer chains bind individually is known as vulcanization reaction. The process usually based on cross linking and can occur with or without any heat. According to vulcanization reaction maxillofacial silicone can be classified into two groups: (Chalian, Drane and Standish, 1972; Moore, 1994; Beumer, Curtis and Marunick, 1996; Mitra *et al.*, 2014; Alqutaibi, 2015; Farah, Sherriff and Coward, 2018)

- Heat Temperature Vulcanizing silicone elastomer (HTV)
- Room Temperature Vulcanizing silicone elastomer (RTV)

And according to the application facial silicone can be classified into 4 groups: (Beumer, Curtis and Marunick, 1996; Alqutaibi, 2015)

- Class I: Implant grade
- Class II: Medical grade

- Class III: Food grade
- Class IV: Industrial grade

Table 2.2: Properties of different silicone elastomer

Classification	Name	Advantage and disadvantage
According to vulcanizing reaction	RTV	**Advantages:** • Gypsum mold was used • Required approximately 72 hours to get fully polymerized • It has flexibility for this it can be used in movable tissue beds • Extrinsic or intrinsic coloring agent can provide optimum esthetics without hampering the strength at the edges • In spite of having longer curing time but still RTV silicone elastomers are commonly used as prosthetic material **Disadvantages:** • The material is esthetically acceptable, but the material become fade over the time. Which leads to remake the prosthesis within a year
	HTV	**Advantages:** • White material with high viscus consistency • Has excellent tear strength • Highest tensile strength with color stability • Has excellent thermal conductivity **Disadvantages:** • It’s an opaque material • Technique sensitive • Required higher temperature 180ºC for 30 minutes with metal mold

		• Exhibit less elasticity and low edge strength for functioning in the movable tissue beds • HTV silicone reacts with the mold color and tend to displace the mold color within the silicone elastomer
According to the application	Class I: Implant grade	**Advantages:** • Synthesized pharmaceutically and has a successful previous history of implant on human and animals **Disadvantages:** • Did not meet the FDI (World Dental Federation) requirements
	Class II: Medical grade	**Advantages:** • If appropriate pigments were used, they remain color stable • Available as moldable putty, paste or liquid **Disadvantages:** • No adverse effect was reported to the human skin, for this reason it frequently used for making external prosthesis
	Class III: Food grade	Due to similarity in the compositions and properties with medical grade silicone elastomer recently food grade elastomers were used in maxillofacial prosthesis
	Class IV: Industrial grade	The silicones under this classification were mostly used for industrial purpose

2.9 Pigments that are used in maxillofacial prosthetic silicone elastomer (MFPSE)

Making a natural looking prosthesis was quite difficult because human skin is made of different layers of dermis, epidermis and subcutaneous tissues with varying thickness and compositions. Different pigments like melanin, beta carotene and haemoglobin were into the skin cells which altogether try to give the color of the skin towards the ambient lights (Anitha *et al.*, 2016). Silicone is the material of choice for maxillofacial prosthesis however, it needs frequent renewal (Kheur *et al.*, 2017; Farah, Sherriff and Coward, 2018). Farah (Farah, Sherriff and Coward, 2018) stated that non-pigmented silicone generally shows more color instability and change when subjected to both weathering chambers (artificial and outdoor weathering).

For the coloration of silicone various organic or inorganic pigments can be used like dry earth pigments or kaolin and rayon flocking's, artist's oil, thermochromic pigments and liquid cosmetics for making it visually more appealing (R. Kantola *et al.*, 2013; R. M. Kantola *et al.*, 2013; Kheur *et al.*, 2017). The application of color to a silicone can be done at the levels of internal coloration (during mixing of the silicone) or external coloration (superficial coating of color onto the silicone material) (Willett and Beatty, 2015).

Oil based pigments were used in coloration of maxillofacial prosthesis because they contain the 'linseed oil' which form a protective barrier on the particles of the pigments (dos Santos *et al.*, 2011). Among all the pigments, kantola (R. M. Kantola *et al.*, 2013) found that at lower temperatures, 0.2% thermochromic pigments exhibit better color stability than their 0.6% counterparts which tend to turn reddish. Thus, the author suggested that 0.2% pigment can be used for facial prosthesis while, if necessary, 0.6% can be used for ear prostheses. The author contradicted their own statement in another study where they stated that the previous concentrations are not suitable for facial prosthesis at higher temperatures. The authors explained that at higher temperatures, the ‘Leuco dyes’ present in thermochromic pigments sensitize the silicone to UV light and induce rapid color degradation. From this, an assumption can be made that 0.2% and 0.6% by weight of thermochromic pigments are more suitable for colder climates than more arid/humid conditions (R. Kantola *et al.*, 2013).

According to kheur (Kheur *et al.*, 2017) red and yellow color are more commonly used as a base color for skin color formulation. But author also stated that, red color degrades more during weathering than the yellow pigments because of its certain organic properties (Bankoğlu *et al.*, 2013). However, previously Anitha (Anitha *et al.*, 2016) mixed the basic pigments (red, yellow, blue) to create skin colors and the procedure was called ‘trial and error’ method. But the procedure was time consuming, increased chairside time, and most importantly required special skill to perfectly match the prosthesis color with the surrounding structure of the skin (Mulcare and Coward, 2019)**.** Therefore, in 1975, Thomas B. Fitzpatrick developed a numerical scheme to estimate the response of different types of skin under the UV lights and named as “Fitzpatrick Scale”. It is commonly used to analyse sun sensitivity on the human skin in the case-control studies related to UV exposure, tanning, skin cancer and protective behaviour (Sachdeva, 2009).

Therefore, instead of coloring the prosthesis, some authors also tested the effects of applying different colors into the cast in which the silicone was molded. The author found that amongst most of the colors used in the dental stone, only green showed no reaction or color displacement. All other colored casts; yellow, reddish brown & white displace their colors onto the silicone effectively producing a yellowish tint on the elastomer surface. Thus, the author recommended curing the silicone under room temperature when green colored cast is used (Cifter *et al.*, 2017).

2.9.1 Chemical interactions:

Organic pigments are brighter, but they tend to be affected by the ultraviolet in the sunlight. Upon exposure, the ultraviolet light can break covalent bonding in pigment molecules, which leads to visual fading of the color. On the other hand, inorganic pigments are usually based on metal oxides, and they have neither covalent bonding nor organic functional groups like carboxylic or hydroxyl, so they are considered to be more color stable than the organic pigments (Bankoğlu *et al.*, 2013; Kheur *et al.*, 2017).

2.10 Fillers used to improve the color fastness (resistance to fading) of MFPSE

As we know, color degradation of the prosthesis may vary on a multitude of factors. But, now a days many kinds of filler particles especially the nano particles were used to improve the mechanical, physical and color changing property of the silicone-based materials (Cevik, Polat and Duman, 2016). Not only nano-fillers but some studies (Gunay *et al.*, 2008; Fatalla, AlSamaraay and Jassim, 2017) also incorporated different macro fillers to evaluate the mechanical and physical properties of silicone elastomers. But, when macro fillers were compared with nano filler, it demonstrated that nano fillers gave 69.23% superior result than macro fillers (30.76%) (Barman *et al.*, 2020).

Filler particles can be obtained from grinding quartz, glasses, or sol-gel derived ceramics. They have barium or zinc, which provide radiopacity when exposed under the x-ray. (Sakaguchi and Powers, 2012) Nano particles are widely used in every sector of healthcare but primarily were used in cosmetics to provide sun protection to the skin while exposed under sun (Jeevanandam *et al.*, 2018) They are nano in size (1- 400 nm) with a large specific area and have a strong interfacial interaction with the polymers (Cevik, Polat and Duman, 2016; Randolph *et al.*, 2016). However, silicone elastomers and nanoparticles does not bond chemically, they interacted physically with each other (Kareem, Fatalla and Ali, 2018).

According to previous literatures the commonly used filler particles are; Titanium dioxide (TiO_2), Silicon dioxide (SiO_2), Zinc oxide (ZnO) and Cerium oxide (CeO_2) (Han *et al.*, 2010; Dos Santos *et al.*, 2012; Bishal *et al.*, 2019; Barman *et al.*, 2020). Most authors used TiO_2 in some forms (Kiat-amnuay *et al.*, 2006, 2009; Paravina *et al.*, 2009; Han *et al.*, 2010; Han, Powers and Kiat-amnuay, 2013; Cevik, Polat and Duman, 2016; Bishal *et al.*, 2019) like dry TiO_2 white pigment, though it appeared to be the most color stable and commonly used filler particle but it is difficult to use in the clinics because of its strong color intensity (Kiat-amnuay *et al.*, 2006). It has been demonstrated that, addition of 3% or 15% Silicon dioxide/Silica (SiO_2) as a filler particle can improve the mechanical and physical property of silicone elastomer. (Barman *et al.*, 2020)

Sherman's study (Sherman, 1950) used Para-aminobenzoic acid (PABA) with silicone which attach to the silicone-carbon bond and produce formaldehyde and formic acid. This reaction did not protect the silicone from degradation rather caused a large amount of discoloration. Therefore, Kheur (Kheur *et al.*, 2016) used the UV stabilizer (Chimassob81 & HALS) as filler and discovered that Chimassob81 soaks the harmful UV rays energy and prevent the formation of free radicals. On the other hand, Hindered Amine Light Stabilizer (HALS) neutralized the free radicals and then provide protection for a longer period. However, it is important to note that none of the aforementioned materials were proven to provide noteworthy protection to the