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The influence of halloysite nanotube addition on some properties of room temperature vulcanized maxillofacial silicone before and after simulated weathering

A Thesis
Submitted to the Council of the College of Dentistry at the University of Baghdad in Partial Fulfillment of the Requirement for the Degree of Master of Science in Prosthetic Dentistry

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Certification of the Supervisor

I certify that this thesis entitled "**The influence of halloysite nanotube addition on some properties of room temperature vulcanized maxillofacial silicone before and after simulated weathering**" was prepared by **Khalid Amjed Fadhil** under my supervision at the College of Dentistry/ University of Baghdad in partial fulfilment of the requirements for the degree of Master of Science in Prosthetic Dentistry.

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Dedication

To my family with love and gratitude for everything they have done for me.

To my lovely wife, thank you for being such a supporter and understanding companion in our journey.

KHALID

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All praise and thanks to **Allah** the exalted for his never-ending blessings and mercy upon me. This work cannot be accomplished without the help, encouragement, and guidance of family, colleagues and friends throughout my course of study.

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Abstract

Background: The commercially available silicone elastomers cannot fulfill all the ideal characteristics such as; color stability, high tear and tensile strength with acceptable surface hardness. Additionally, degradation upon aging is considered as one of the main drawbacks of silicone elastomer as maxillofacial material, as it may render the shelf life of prostheses shorter. Consequently, researches are being established continuously to improve silicone materials either by modifying their formulas or by incorporation of fillers.

Aim of the study: This study aimed to evaluate the impact of halloysite nanotube (HNTs) incorporation on selected properties, namely tear strength, tensile strength, elongation percentage, surface roughness and hardness, of VST-50F silicone before and after simulated weathering.

Materials and methods: First, a pilot study was conducted to determine the most suitable weight percentages of HNTs to be incorporated into VST-50F silicone. Accordingly, 1% HNTs and 1.5% HNTs weight percentages were chosen to be the experimental groups and compared with silicone without additives. The main study involved the preparation of 240 specimens divided equally into two main groups; group 1 (before weathering) and group 2 (after weathering) .Each main group was further subdivided into 3 subgroups: control with 0.0 wt % HNTs, experimental group with 1 wt % HNTs and experimental group with 1.5 wt % HNTs. These subgroups contain 40 specimen, 10 specimens for each test (i.e. tear strength, tensile strength, surface roughness and hardness). Meanwhile elongation percentage was concurrently measured with tensile test. Group 2 specimens were subjected to simulated weathering for 200 hour. After that, all the aforementioned mechanical tests were conducted for both group 1 and group 2 specimens. The research readings were collected and statistically analyzed using ANOVA, post-hoc and paired t-test tests.

Additional tests were also performed Including Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS).

Results: SEM test revealed a well dispersion fashion of HNTs within VST-50F silicone, while FTIR did not exhibit any chemical reaction between the silicone and HNTs. However, mechanical tests results before weathering showed significant rise in all tests readings except for roughness, where the change was non- significant. Meanwhile, the study results after weathering revealed a significant decline in tear strength, tensile strength and elongation percentages, yet roughness did not change significantly, but hardness increased remarkably. There were significant differences between group 1 and group 2 in all study groups of all the tested properties, except surface roughness results which did not change significantly.

Conclusion: Reinforcing VST-50F with HNTs improved some of its mechanical properties but did not protect it from aging consequences. However, the reinforced silicone after weathering still higher than the raw silicone in term of tears strength, tensile strength and elongation percentage.

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List of Abbreviation

Abbreviations	Meanings
ANOVA	Analysis of variance
ASTM	American society for testing and materials
$BaSO_4$	Barium sulfate
CAD	Computer aided design
CAM	Computer aided manufacture
CNC	Computer numerical control
CPE	Chlorinated poylethelyne
Df	Degree of freedom
EDS	Energy dispersive X-ray spectroscopy
ES	Effect size
FDA	Food and drug administration
FTIR	Fourier transform infrared spectroscopy analysis
HNTs	Halloysite nanotubes
HSD	Honestly significant difference
HTV	High temperature vulcanized
ISO	International organization for standardization
IU	Indentation unit
J	Joule
M	Mega
MPa	Mega pascal
N	Newton
OH^-	Hydroxyl group
PDMS	Polydimethylsiloxane

PHMS	**Polyhydromethylsiloxane**
RH	**Relative humidity**
RTV	**Room temperature vulcanized**
SD	**Standard deviation**
SEM	**Scanning electron microscope**
SiO_2	**Silicon dioxide**
SPSS	**Statistical package for the social sciences**
TiO_2	**Titanium dioxide**
UV	**Ultra violet**
W	**Watts**
ZnO	**Zinc oxide**

Introduction

Introduction

Maxillofacial anomalies (inherited or acquired) have a negative impact on normal living both physiologically and psychologically **(Alqutaibi, 2015)**. The available choices to reconstruct the defective parts include; surgery or prosthesis, the former is desirable and should be performed whenever possible, while prostheses are considered substitute to surgery when the latter is contraindicated **(Guiotti, 2010; Padmaja, 2015)**.

Regarding maxillofacial prostheses, the scientist utilized different materials in these appliances till the innovation of silicone, where great shift was made in this industry. This owns to many favorable properties of silicone such as; biocompatibility, durability, eases of manufacturing and chemical stability **(Aziz *et al.*, 2003)**.

Nevertheless, some properties, like tear and tensile, are not optimum and require improvements. Furthermore, noticeable physical and chemical changes might be encountered during silicone aging, where the cumulative effect of sunlight and oxygen (photo-oxidative attack) are considered as major causative factors for deterioration **(Dootz *et al.*, 1993)**.Therefore, the shelf life of maxillofacial prostheses made from silicone is short, and that would obligate prostheses replacement continually in a period ranging from 6 months to 1 year **(Al-Dharrab, 2013).** Consequently, different methods have been carried out to improve silicone elastomers, among them was the addition of fillers which would increase the elasticity of the material and improve its properties both physically and mechanically, making it more practical clinically **(Abdullah and Abdul-Ameer, 2018)**.

VST-50F maxillofacial silicone was used in this research as it has many encouraging properties, including good mechanical properties, ease of manipulation, short setting time and affordable prize **(Al-Judy, 2019).** Meanwhile, halloysite nanotubes (HNTs) had been chosen as a filler material due to their brilliant properties such as; biocompatibility, availability, low cost and ease of processing **(Pasbakhsh *et al.*, 2013; Abdullayev and Lvov, 2011).**

Simulated weathering was conducted in this study because it is more influential than outdoor weathering on clinical use (**Lemon *et al*., 1995; Tran *et al*., 2004**). Two hundred hour were chosen as a period of simulated weathering because this time is roughly equivalent to 6 months of clinical use, where the maxillofacial prostheses are expected to deteriorate after such period as a result of weathering **(Atta Allah and Moudhaffer 2017).** Therefore, the goal of this study is to improve some mechanical properties of maxillofacial silicone and increasing its shelf life by making it more resistance to aging consequences.

Aims of the study

This study aims to investigate the impact of reinforcement with halloysite nanotubes on VST-50F maxillofacial silicone before and after 200 hour of simulated weathering, regarding the following properties:

1-Tear strength

2-Tensile strength

3-Elongation percentage

4-Surface hardness

5-Surface roughness

Chapter One

Review of literature

Review of Literature

1.1 Maxillofacial prosthetics and maxillofacial prosthesis

Maxillofacial prosthetics: refers to that section of prosthodontics which deals with restoration and substitution of stomatognathic and craniofacial structures by utilizing artificial elements in fixed or removable form (**GPT 9, 2017)**.

Maxillofacial prosthesis: refers to the prosthesis that replace the lost structure of stomathognathic and/or craniofacial region either in part or as a whole **(GPT 9, 2017)**.

1.2 Objectives of Maxillofacial prosthesis

The objectives of such prosthesis involve the following points **(Deba *et al***, **2012**):

1- Appearance re-establishment.

2- Psychological rehabilitation.

3- Function restoration.

4- Tissue protection.

5- Therapeutic action.

1.3 Historical background of maxillofacial prosthetics

Although the starting date of such prosthesis is not clearly defined, but it had been invented and developed from the ancient history. In Egypt, for example, different facial structures had been found in Mummies, the ancient Egyptians made use of various elements in the fabrication of these prostheses like copper, precious stone and bronze (Figure 1-1). East Asia represents another example where wax, metal and resin have been used to restore nose and ear **(Deba *et al.,* 2012a)**.

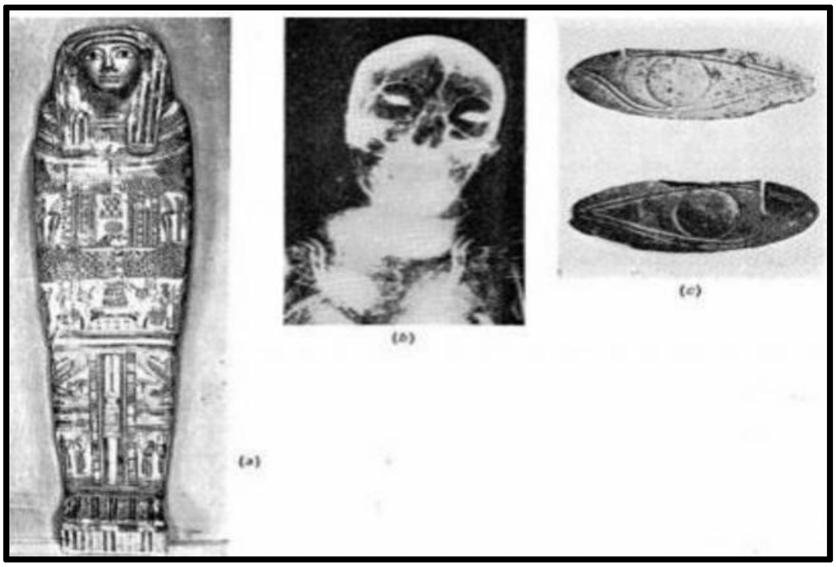

Figure 1-1: Orbital prosthesis found in Mummies (Roberts, 1971).

After these ancient era (from 1500 to 1800 AM), there was a few recorded attempts, like the case of Tycho Brahe's nose, an astronomer from Denmark, which has been lost in a fight; he use silver and gold to made an artificial nose which was fabricated precisely to a degree made it seem even better than the natural one **(Barhate *et al.*, 2015)**.

Another attempt was recorded during this period belong to Pierre Facular who used a cast mask made from silver to substitute some bone of mandible of French soldier. He also used oil paint to match skin color of the patient (**Maller *et al.*, 2010)**.

Furthermore, Ambroise Pare, a French surgeon, made a great progress in this field during the aforementioned period and some of his inventions are shown in (Figure 1-2) **(Beumer *et al.*, 1996).**

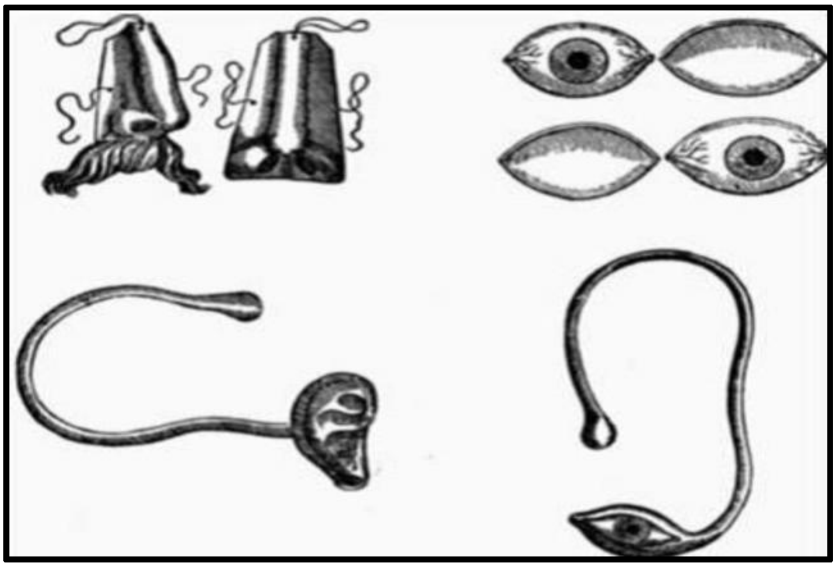

Figure 1-2: Nasal, auricular and orbital prostheses fabricated by Pare (Adopted from Roberts, 1971).

Following that, about 18th century, Kingsley developed prosthesis that have palatal portion (obturator) combined with nasal portion, so that the obturator became a primary component of nasal prosthesis. Meanwhile, Claude Martin incorporated ceramic material in the fabrication of nasal prosthesis **(Mahajan and Gupta, 2012).**

Nineteenth century experienced the incorporation of vulcanite rubber in maxillofacial prosthesis, which has desirable properties like translucency, ease of fabrication and coloring. However, it has some drawbacks concerning rigidity (**Zardawi, 2013).** Moreover, the excellent properties of acrylic resin encouraged the scientist to use it in head and neck prosthesis, despite its rigidity **(Mahajan and Gupta, 2012).** To overcome this rigidity, many scientists had made attempt to discover latex material for fabrication of head and neck prosthesis (**Deba *et al.*, 2012a**).

Thereafter the maxillofacial prosthetic witnessed the first use of silicone material in the fabrication and pigmentation of facial prosthesis, which done by Barnhart (**Zardwi, 2013).**

The incorporation of silicone elastomers in maxillofacial prosthesis made great shift in this field, and that’s because of the many desirable properties which characterize these materials **(Aziz *et al*., 2003).**

Regarding the processing, the prosthesis in the past was made by hand carving**.** Then after**, Wolfaardt *et al.*, (2003)** indicated the use of rapid prototyping technology, stereolithography and fused deposition modeling which would be a promise for implantation in facial reconstruction. Subsequently , evolution in computer technology make it possible to design facial prostheses digitally by utilizing 3D scanning, rapid prototyping and CAD/CAM, but it need further studies and development to be more feasible clinically also there are limitations concerning cost, safety and security issues **(Zardawi *et al*., 2015; Marro *et. al*., 2016)**.

In term of prosthesis retention, implant had been incorporated in this field , where better acceptance and success have been experienced in prosthesis retained by implant compared with those retained by adhesive, due to the ease of use and the retention of the former **(Chang et al., 2005**).

1.4 Requirements of maxillofacial materials:

The required features in maxillofacial materials include **(Gupta *et al*. 2017; Beumer *et al*., 2011):**

I) Esthetic requirements

It should have the ability to be reshaped according to the missing part.

II) Biologic requirements

a) Should have a chemical stability to maintain its structure when exposed to various weathering conditions.

b) Must have antimicrobial effect to resist microbial growth.

c) Ease of cleaning and disinfection are mandatory in such prostheses

d) Should be biocompatible i.e.; it must not have any toxic, carcinogenic or allergic effect.

III) Mechanical and/or physical requirements

a) The weight should be within the desired range.
b) Should have long service life i.e. durability.
c) Must be dimensionally stable.
d) Material should have good mechanical strength regarding tear and tensile with good elongation percentage.
e) Should be flexible to an acceptable degree, thus surrounding tissue could be freely mobilized.

IV) Processing requirements

a) It is desirable that the material set at low temperature, by this way the mold could be re –used.
b) It should have adequate working time.
c) Material processing in general must be simple.
d) Ability to be stained either intrinsically or extrinsically.
e) Maintenance of the color after setting.

1.5 Types of materials that are used in maxillofacial prostheses

1.5.1 Acrylic resins

The main use of acrylic in maxillofacial prosthesis is in the fabrication of obturator. According to curing system; acrylic may be heat cured, lighted cured or auto polymerized, but the former is more preferable due to its higher mechanical properties **(Van Noort, 2014)**.

This material can be utilized in area where the expected mobility of tissue surrounding the prosthesis is very limited, i.e. during function. Acrylic resins have a number of desired characteristic for example, its available widely, have an adequate service life, good mechanical properties, can be relined and repaired easily. However, there are some drawbacks concerning the rigidity and water sorption. Some generations of acrylic resin have a degree of elasticity but it also have disadvantages like insufficient edge strength, bad resistance to weathering condition, discoloration and inadequate durability **(Deba *et al*., 2012)**.

1.5.2 Polyurethane elastomers

These materials have a desirable flexibility with sufficient strength at edges; such properties make it possible to achieve higher esthetic by fabrication of thin margin. In addition, they have a good tear and tensile strength with low modulus of elasticity and good durability. However, there are some drawbacks concerning color stability, adhesive compatibility and moisture sensitivity, which in turn result in bubble formation (**Barhate *et al*., 2015)**.

These materials composed of two components, aliphatic segment and polyol segment. The proportion of the two groups to each other would determine the physical properties of the elastomer, so that it should be adjusted to give the desired flexibility for facial prosthesis. However, nowadays there are only two types of polyurethanes which can be utilized in maxillofacial prosthesis; Calthane and Epithane-3 **(Alqutaibi, 2015; Mitra *et al*., 2014)**.

1.5.3 Chlorinated polyethylene (CPE)

Lewis and Castleberry have produced this material which is resemble Polyvinylchloride both chemically and physically (**Barhate *et al*., 2015)**, but it requires a high temperature to be processed as a sheet in metal mold. It's considered as suitable substitute to silicone in facial prosthesis as it shows a good biocompatibility with less irritation to mucosa when compared with silicone. Beside that it has an affordable cost (**Mitra *et al*., 2014)**.

1.5.4 Thermoset urethane elastomers

These elastomers produced through primary chemical cross linking. The morphology of the material could be adjusted by controlling the proportion of the reacted components .The massive change that the material experienced during weathering remains the main disadvantage (**Gupta *et al.*, 2017**; **Yu *et al.*, 1980)**.

1.5.5 Polyvinylchloride and copolymer

A number of encouraging features, like sufficient flexibility and coloring feasibility, made the scientists incorporate such material in the fabrication of facial prostheses. Different additives have been merged in this material in order to improve its strength, stabilize its color or to obtain flexibility at room temperature **(Gupta *et al.*, 2017)**. Nevertheless, it have undesirable properties like color change, inadequate strength at the edges, plasticizer loss and absorption of tissue secretion which in turn negatively affect the mechanical strength **(Alqutaibi, 2015)**.

1.5.6 Silicones:

Barnhart, in 1960, had introduced silicones in such field for the first time **(Khindria et al., 2009)** .Nowadays, they are considered as the most favorite choice when dealing with facial prosthesis. Many researches have being overwhelmed in order to enhance silicones properties. The secret behind their popularity is their preferable characteristics (tensile and tear strength in particular). In addition, they are easy to manipulate, thermally and chemically stable, accept staining and have bacteriostatic effect **(Tyagi *et al.*, 2016)**.

Silicones are polymer consisting of repeated bonds of (Si-O) which represent its backbone**.** The structure of silicone composed of inorganic component represented by siloxane bonds (Si—O—Si) and the organic component attached to silicone atom (R—Si—R).The organic component may be vinyl, trifluoropropyl, phenyl or methyl group (where it called polydimethyl siloxane) **(Colas and Curtis, 2005)** (Figure 1-3)**.** The bond between organic and inorganic component is flexible and allow wide range of motion, and this interpret some of their characteristics compared with other material, such as lower values of viscosity, surface tension, melting point and glass transition temperature. Besides that, the flexible characteristic made silicone behave as an elastomeric material **(Mitra et al., 2014).**

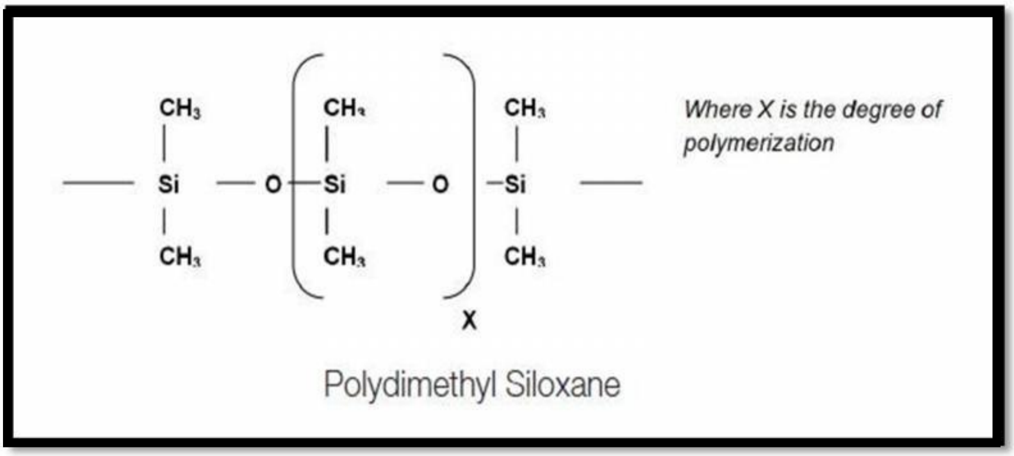

Figure 1-3: Polydimethyl siloxane (adopted from Chandra *et al*., 2015).

1.5.6.1 Curing reaction of silicone

A) Cross-linking with radicals

In such type of reaction, effective cross-linking cannot be achieved unless there are some vinyl groups available. The reaction will follow the mechanism shown in (Figure 1-4), where peroxide group is the source of free radicals and should be added before processing. This type of cross-linking reaction is adopted for silicone rubbers that have high viscosities **(Colas and Curtis, 2005).**

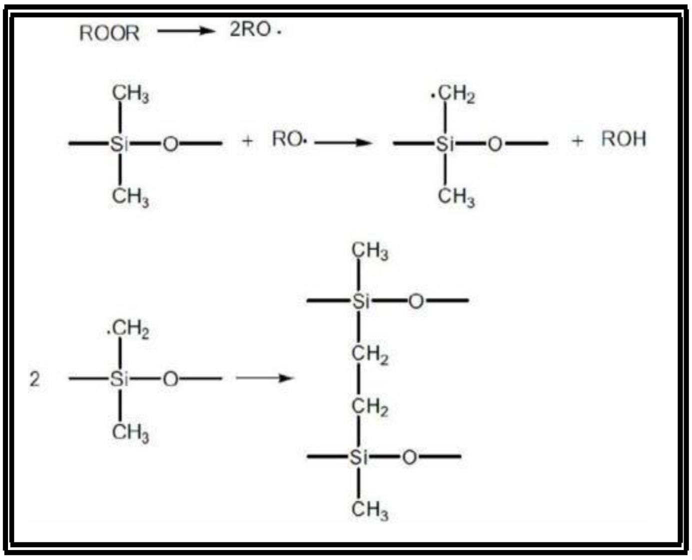

Figure 1-4: Cross-linking with radicals (adopted from Zardawi, 2013).

B) Cross-linking by condensation

Oligomeric poly hydromethylsiloxane (PHMS) act as cross-linking agent in such type of reaction. The process is established through the reaction of the Si-OH and Si-H, accelerated by tin octate or amine group and releasing hydrogen as a byproduct (**Taylor *et al.*, 2003)**. However, this reaction result in increased free volume due to excess unbounded PHMS together with leached PDMS which have low molecular mass. Such free volume will lead to increased surface permeability which result in turn in enhanced microbial growth and participate in discoloration and decreased service life **(Zardawi, 2013)**. Shrinkage is considered as another limitation, which results from releasing alcohol as a byproduct. So that, condensation silicone does not considered as a favorable choice for constriction of precise area **(Colas and Curtis, 2005)**.

Manufacturer may provide silicone following such kind of reaction in two systems: either one component system or two components system (Figure 1-5) .The difference between the two is that; in the former one the catalyst and cross-linker are provided with the base, whilst in the latter the base and catalyst are separated (**Deepthi, 2016**).

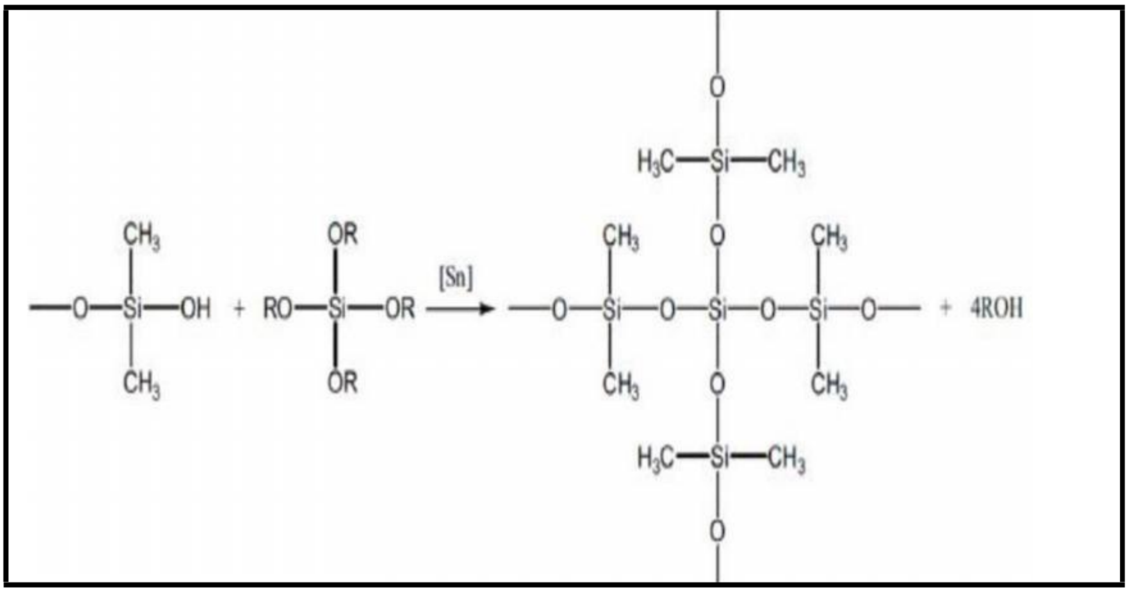

Figure 1-5: Cross-linking by condensation (adopted from Zardawi, 2013).

C) Cross-linking by addition

In this type of cross linking, silyl hydride (SiH) bind to vinyl end (CH2=CH—) of silicone. This reaction is assisted by a catalyst (usually palladium or platinum) **(Mitra *et al.*, 2014, Zardawi, 2013)** (Figure 1-6).

The major advantage of this vulcanizing reaction is no by-products are released. Thus, addition reaction overcomes shrinkage issue that found in condensation process. Anyhow, there is a disadvantage concerning the formation of inactive catalyst which retards curing process. Such sequel is clearly shown when platinum is used as a catalyst ,where it bind with electron giving substance, such as organo-sulfur or amine, resulting in inactive catalyst **(Stark *et al.*, 1982; Colas and Curtis, 2005)**.

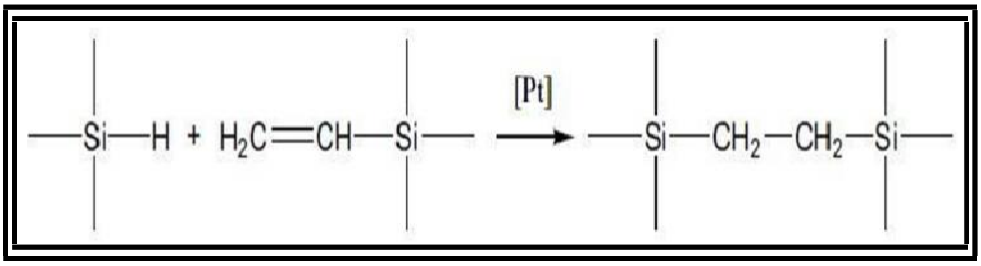

Figure 1-6: Addition cross – linking (adopted from Zardawi, 2013).

1.5.6.2 Silicone elastomer classification

Depending on their uses and application, silicones could be classified into four categories (**Alqutaibi *et al*., 2015**; **Nallaswamy *et al*., 2017)**:

a) Class I (Implant grade): used within body tissues, so it should fulfill FDA requirements .An example for such type is breast implant.
b) Class II (Medical grade): this type is used in maxillofacial prosthesis.
c) Class III (Clean grade): used for industrial applications.
d) Class IV (Industrial grade): used for industrial applications.

1.5.6.3 Maxillofacial Silicone classification

Such silicone can be classified into room temperature or heat temperature vulcanized, and this classification depends on whether the vulcanization process occurs with or without heating **(Deepthi, 2016)**.

A) Heat temperature vulcanized silicones (HTV)

White, opaque and highly viscous material found as putty consistency, presented as one or two-components system. Vulcanization process is obtained through addition reaction **(Mitra *et al.,* 2014)**. The structure of this type of silicone consists of polydimethyl vinyl siloxane with side chain of 0.5% vinyl dichlorobenzoyl peroxide act as vulcanizing agent , whereas platinum salt represents the catalyst for such reaction , in addition to silica fillers **(Chandra *et al.,* 2015)**. The favorable properties can be achieved by altering the ratio of fillers **(Maller *et al.,* 2010)**.

The heat required for HTV silicone range from 180° to 220°C, applied for 30 minutes under pressure. It will decompose the initiator, resulting in free radicals production which in turn will vulcanize the copolymer **(Anusavice *et al.,* 2012)**. HTV silicone is characterized by high tear and tensile strength with good elongation percentage, also HTV silicone is stable thermally and chemically, beside its excellent color stability (**Mitra *et al.,* 2014; Chandra *et al.,* 2015).** However, there are some drawbacks, such as; bad esthetics due to opacity which results in lifeless appearance .In addition, HTV is technique sensitive and has poor elasticity **(Zardawi 2013)**.

B) Room temperature vulcanized silicones (RTV)

It's available in variable viscosities depending on the intended applications. A clear solution is available, and that would enable intrinsic or extrinsic staining or otherwise keep the prosthesis translucent. Cross linking of such material is done by condensation or addition reaction and at room temperature (**Maller *et al.,* 2010)**.

There are some advantages of RTV silicone over HTV siliconelike; ease of fabrication and staining, furthermore it's inert biologically and highly esthetic. Nevertheless, there are some limitations concerning color stability and edge strength in comparison with HTV silicone **(Anusavice *et al*., 2012)**.

1.5.7 Substitutional materials

I) Silastic 386

It is a type of RTV that characterized by bubbles formation after base - catalyst mixing. This occurs due to gas release during the reaction. The bubbles will make the material larger in volume (about 7 times). Such property has the advantage of reducing the weight of the prosthesis. However, this type has a lower strength, and susceptible to stain **(Mitra *et al*., 2014; Chandra *et al*., 2015)**.

II) Siphenylenes

This type of material is a silicone copolymer which contains phenyl and methyl groups. It has greater edge strength, better color stability and lower modulus of elasticity when compared with other types of silicones **(Gupta *et al*., 2017)**.

III) Silicone block copolymers

They are blocks of polymers could be placed within siloxane polymer in order to improve physical properties of conventional silicone. An example of this; is the positioning of poly methyl methacrylate within siloxane polymer **(Barhate *et al*., 2015; Gupta *et al*., 2017)**.

1.6 Silicones reinforcement and the role of nanotechnology

Several researches have been already carried out to estimate the execution of silicone as a maxillofacial material. However, there is no ideal material that fulfills the entire requirement. Consequently, researchers are focusing on fillers as a method to reinforce silicones in order to optimize their efficacy **(Zayed *et al*., 2014)**.

Fillers are classified into two categories: reinforcing fillers and extending fillers. Reinforcing fillers utilized to improve a number of mechanical and physical properties like tear, tensile and abrasion. Meanwhile, the extending type used to produce specific characteristic, though it's called as semi-reinforcing materials **(Harkness and Taylor, 1999)**.

The degree of improvement achieved by fillers incorporation governed by the following factors (**Momen and Farzaneh, 2011)**:

1) Fillers concentration

This factor together with particle size will determine the inter particle distance which play a major role in fillers reinforcement **(Zhang *et al*., 2006)**.

2) Fillers morphology

Fillers have different shape (platelets, particle and tubes) (**Wang *et al*., 2003)**. Concerning the size, decreasing it will result in wider surface area, making it more reactive chemically **(Vaia, 2002)**.

3) Fillers dispersion

Higher physical properties are usually expected when the particle are distributed in polymer matrix in a wide and uniform way. However, inorganic fillers have a high surface energy that make them agglomerate when added as a fillers, rendering the polymer matrix weaker **(Han et al., 2008)**.

4) Fillers-polymeric matrix adhesion

Tight bond between fillers and polymeric matrix will produce a higher mechanical performance **(Deshmane *et al*., 2007)**.

Nanotechnology deals with tiny material with 1-100 nm size range. These fillers have superior polish with high flexural strength and elastic modulus. Additionally, they are characterized by good translucency and esthetic appearance **(Jhaveri and Balaji, 2005).**

This technology has been incorporated in various domains of sciences including the medical field, where nanotechnology had been employed in different implementations like malignancy treatment, pharmacology diagnosis of diseases etc. (**Massaro *et al.*, 2017**). Nanotechnology also had been used in dentistry, where its used in the diagnosis, prevention and treatment of disease, also it has been utilized in reinforcement of various material that used in dentistry **(Jasdeep *et al.*, 2016)** .**Shaker and Abdul-Ameer in 2018**, for example, reinforced two type of maxillofacial silicone with nano TiO_2 and they observed an improvement in some mechanical properties, like tear tensile and elongation. Furthermore, **Moudaffer and Fatalla (2018),** in their study concerning the impact of reinforcement of RTV silicone with zirconium silicate nanofillers, achieved significant enhancement in the studied mechanical properties, namely tear strength, tensile strength and elongation percentage. **Yeh H. in 2014** also obtained the same assumption when he reinforced silicone with silica fillers.

1.7 Halloysite nanotubes (HNTs)

HNTs were first described by Berthier in 1826 as a kaolin type clay mineral .After that, Belgian geologist Omalius d'Halloy analyzed the minerals. Such nano clays are exist naturally in rocks and soil (**Liu *et al.*, 2014)**. They are Nano-sized with 0.5–2.0 μm length and 50-200 nm diameters (**Pasbakhsh *et al.*, 2013)** (Figure 1-7).

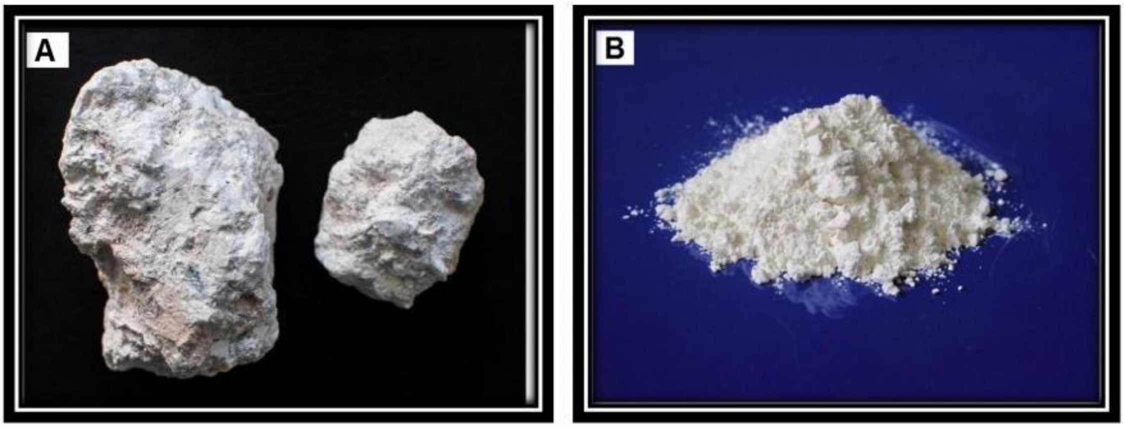

Figure 1-7: (A) Raw halloysite nanotubes, (B) Ground Halloysite nanotubes (Adopted from Liu *et al.*, 2014).

The chemical structure of HNTs is $Al_2Si_2O_5(OH)_4.2H_2O$ that similar to kaolinite, their wall composed of bilayers of aluminum and silicon oxide. Each layer consists of tetrahedral coordinated SiO_4, octahedral coordinated AlO_6 and alumina presents internally as shown in (Figure 1-8) (**Abdullayev and Lvov, 2013; Ferrante *et al*., 2015)**.

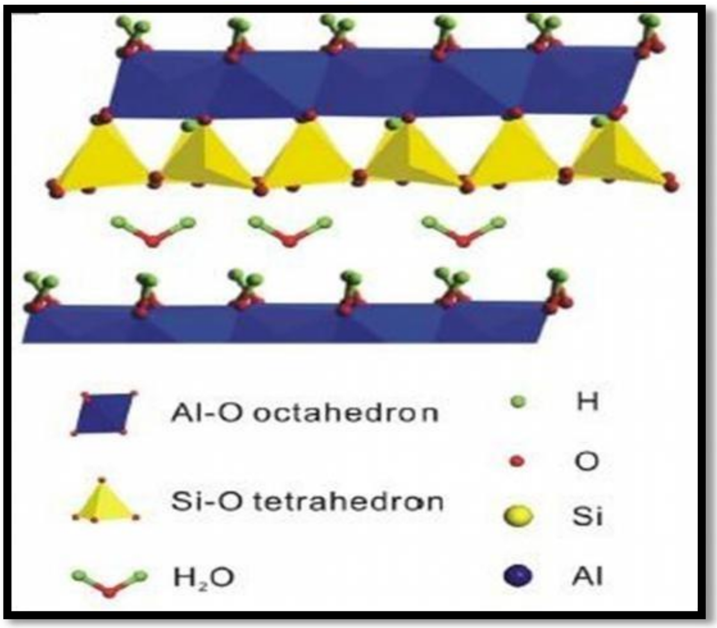

Figure 1-8: Crystalline structure of halloysite nanotubes (Adopted from Yuan *et al*., 2015).

HNTs have rolled structure and their morphology resample that of multi-walled carbon nanotubes **(Nazir *et al*., 2016**) (Figure 1-9) .Anyhow, it has some advantage over carbon nanotube especially in implementations where biocompatibility is of high priority. Furthermore, HNTs are not expensive and naturally available. Also it has different reactivity on their surfaces; the outer surface is predominated by silica layer, while alumina is prevalent on the inner surface (**Joussein *et al*., 2005; Yuan *et al*., 2015).**

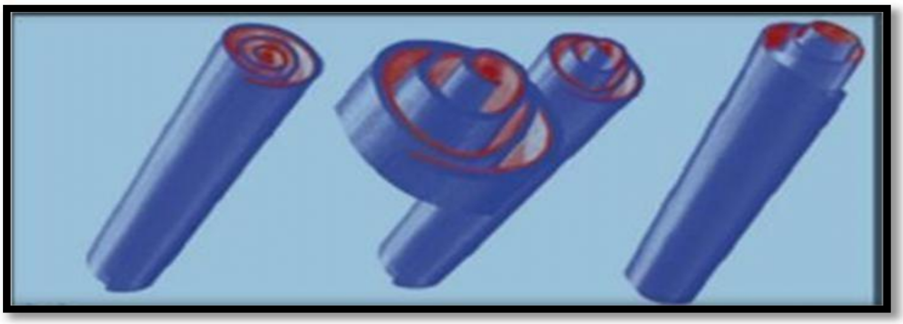

Figure 1-9: The rolled structure of hallosite nanotubes (Adopted from Massaro *et al*., 2017).

HNTs also characterized by quite low cell toxicity, also its biocompatible and harmless. However, HNTs cannot be degraded in human body, so it cannot be injected intravenously (**Massaro *et al*., 2016)**. Instead, HNTs can be used for external medical implication, such as oral tablets, spray etc. HNTs can be employed in drug delivery for tumor treatment (**Lvov *et al*., 2016b**).

HNTs had been incorporated in polymethyl methacrylate bone cement together with gentamicin antibiotic, and such addition revealed an enhanced structural integrity with sustained antibiotic release **(Wei *et al*., 2012, Lvov *et al*., 2016b)**. Additionally, it was reported that the incorporation of HNTs in composite resin would elevate its strength by 50%, beside that such reinforcement will result in a shade close to that of natural teeth **(Feitosa *et al*., 2015; Alkatheeri *et al*., 2015).**

Moreover, **Yaseen and Moudaffer in 2018** had incorporated HNTs in heat cured denture liner, and such addition improved the thermal conductivity of the soft liner. Also it markedly increased tear strength and shear bond.

1.8 Aging of maxillofacial prostheses

The durability of maxillofacial prosthesis is considered as an essential feature regarding the clinical applications **(Markt and Lemon, 2001).** Indeed, they have short service life and should be replaced frequently **(Hatamleh *et al*., 2011)**. Degradation and discoloration are considered as the main problems that associated with such prostheses (Figure 1-10). Environmental conditions (humidity, sunlight, air pollution and ultraviolet light) may be the main causes behind material deterioration. It was stated that maxillofacial prostheses made from silicone elastomers should be replaced periodically at 6-12 months intervals **(AL-Dharrab *et al*., 2013)**.

Figure 1-10: Discoloration of orbital prosthesis (adopted from Ariani, 2015).

1.8.1 Simulated weathering

As mentioned before, there are several environmental factors that affect the maxillofacial prosthesis when it is in use .These factors can be simulated by using different methods, like cleaning solution, natural day light and accelerated artificial weathering **(Hatamaleh *et al.*, 2016)**. The latter can predict the degradation that polymer undergo when the appliance is in service.

However, it cannot perfectly match what happen in natural aging conditions **(Pospisil *et al.*, 2006).** In this method natural day light reproduced artificially in weathering chamber (Weather- Ometer) that try to predict material durability **(Al- Dharrab *et al.*, 2013)**.

The artificial light source that used in such method may be fluorescent, filtered long arc xenon, carbon arc or metal halide lamps or carbon arc. In such test it is possible to adjust water exposure temperature and moisture to the desired degree or level, also the testing procedure can be conducted in continuous manner and without interruption, unlike natural weathering where there are many uncontrolled factors **(McGeer and Matthew, 2001**).

1.8.2 The Influence of simulated weathering on some properties of maxillofacial silicone

Polyzois and Frangou in 2002 stated that the maxillofacial material should have excellent properties, such as; high tear, and tensile strength with sufficient hardness. Therefore, measuring these properties considered a good clue for material selection and usage **(Rai and Guttal, 2013).**

The desirable material should match natural tissue in term of physical and mechanical properties with long service life. Tear and tensile strength of this material should be of sufficient degree while their surface hardness should be close to that of the skin **(Aziz *et al*., 2003; Eleni *et al*., 2011)**. In addition, surface roughness should be taken in consideration, since defect at the surface is considered as nucleation sites which would result in corrosion or cracks, leading to prosthesis failure and replacement **(Eleni *et al*., 2013; Al-Dharrab *et al*., 2013).**

Longevity is also a substantial characteristic in such prosthesis, since defect like cracks, discoloration and degradation might necessitate prostheses replacement **(Leonardi *et al*., 2008; Eleni *et al*., 2011)**.

18.2.1 Tensile strength

It's material force that induced internally and resists elongation which is directed in parallel way to stress **(GPT 9, 2017)**. When such property increase (together with tear strength), the prostheses durability will increase in turn **(Mohammad *et al*., 2010).** Furthermore, insufficient tensile and tear strength are responsible for material deterioration **(Udagama and Drane, 1982).**

Hauge *et al*. in 1992 had studied the properties of A-2186 material under 7 different environmental variables and they noticed slight rise in tensile readings after 6 months of natural aging. Following that, **Dootz *et al*. in 1994** studied the effect of weathering on the mechanical properties of three silicone materials, where they also reported a slight increase in tensile readings.

Meanwhile, **Eleni *et al*. in 2009** had figured out a remarkable decrease in the tensile strength when they subject three types of CPE and PDMS to 216 hours of artificial weathering at 1000 W/m2 irradiance. Furthermore, **Hatamleh *et al*. in 2011** exposed TechSil S25 silicone to variable weathering regimes, and the result showed substantial deterioration in tensile strength.

Wang *et al*. in 2014 studied the effect of weathering on mechanical properties of MDX4-4210 silicone elastomer after TiO_2 nanoparticle addition and the result showed an increase of tensile readings after 24 and 72 hours of weathering. **Al-Harbi *et al*. in 2015,** as well, studied the impact of 6 months of weathering on 3 silicone material and he found that there is no noticeable change in tensile strength of A-2186 platinum RTV silicone.

Later on, **Atta Allah and Moudhaffer in 2017** had reported a reduction in tensile strength of A-2186 silicone which is filled with 5% SiO_2 nanoparticle as a result of artificial weathering of (200 and 300) hours.

1.8.2.2 Elongation percentage

It is a deformation produced by the application of tensile force. It can be also defined as stretch degree that the material reaches before breaking **(GPT9, 2017).**

Hauge *et al*. in 1992 had studied the impact of different environmental variables on A-2186 silicone, and the results showed a decrease in elongation percentage after natural weathering. After that, **Dootz *et al*. in 1994** had reported a reduction in elongation percentage of A-2186 silicone after 900 hours of simulated weathering.

In addition, **Hatamleh *et al*. in 2011** had subjected TechSil S25 silicone elastomer to variable weathering conditions and he reported a reduction in elongation percentage. Furthermore, **Al-Harbi *et al*. in 2015** figured out a reduction in elongation percentage of A-2186 silicone after 6 months of weathering.

1.8.2.3 Tear strength

It's the resistance to rupture produced by elastomeric material when subjected to tensile strength **(Anusavice**, **2012**). High tear strength is favorable in maxillofacial prosthesis because it determines the marginal integrity and service life. Therefore, it's considered as a substantial property of material used in these prostheses **(Aziz *et al.*, 2003; Li *et al.*, 2007).**

Hauge *et al.* in 1992 reported a decrease in tear strength of A-2186 silicone when subjected to 6 months of weathering. While **Dootz *et al.* in 1994** reported an increase in tear strength of A-2186 silicone after 900 hour of weathering. Furthermore, **Mohite *et al.* in 1994** noticed fluctuated readings when they studied the effect of different environmental conditions on polyurthrane Epithane-3, MDX 4-4210 and Cosmesil. Epithane-3 was affected more than other materials, while MDX 4-4210 was the least affected.

Whereas **Hatamlah *et al.* in 2011** reported a decrease in tear strength of TechSill S25 silicone when subjected to 360 hours of artificial daylight weathering. Moreover, **Al-Harbi *et al.* in 2015** found a slight decline in tear strength of A-2186 platinum RTV silicone elastomer after 6 months of outdoor weathering. While **Nobrega *et al.* in 2016** stated that an increase in tear strength readings had been obtained when MDX4-4210 silicone (reinforced with $BaSO_4$, ZnO and TiO_2 nanoparticle) subjected to 1008 hour of simulated weathering.

1.8.2.4 Shore A hardness

It represents material resistance to any surface indentation or penetration. Shore A durometer is considered as a measure of elastomeric material hardness (**Sakaguchi and Powers, 2012**).The maxillofacial prosthesis should have a hardness value close to that of the part that it replace. Accordingly, silicone used in maxillofacial prosthesis should have a hardness readings range between 15- and 45(UI) (**Eleni *et al.*, 2013a**; **Wang *et al.*, 2014)**.

Hauge et al. in 1992 reported an increase in hardness readings of A-2186 silicone as a result of 6 months of natural aging. Furthermore, **Dootz *et al.* in 1994** also report upward incline of hardness readings after 900 hour of simulated weathering of A2186 silicone. **Eleni *et al.* in 2009** assured such increase in hardness value when they studied the effect of simulated weathering of 216 hour on 3 types of PDMS and CPE. Moreover, **Hatamlah *et al.* in 2011** studied the impact of 360 hour of artificial wreathing in their study on TechSill S25 silicone

And the result revealed a remarkable increase in hardness. **Al-Samaraay and Fatihallah in 2017** confirmed such findings when they study the effect of 100 and 200 hour of artificial weathering on A-2186 silicone.

1.8.2.5 Surface roughness

It represent the measurement of fine irregularities on material surface i.e.; surface texture**.** Such irregularities may lead to crack or corrosion. So that, roughness can gives an impression about material properties **(Al-Dharrab *et al*., 2013**). Defective surface might necessitate prosthesis replacement even though the bulk was intact. The rationale behind such replacement is that; bacteria accumulate on rough surface (**Eleni *et al*., 2013b)**, and this was proved by study done by **Kurtulmus *et al*. in 2010** who reported a widely spread growth of *Candida albicans* at the surface of VST-30 silicone which has rough surface, While the other two types of silicone (VST- 50, VST-50F) experienced merely localized clusters.

Goiato *et al*. in 2009 recorded a decline in roughness readings after 60 day of storage in their study which includes two materials (MDX4-4210 and Silastic 732 RTV). Meanwhile, **Al-Dharrab *et al*. in 2013** studied the impact of 6 months of storage (in acid, alkaine and sebum) on Cosmesil M511 silicone and he found remarkable increase in roughness readings.

Moreover, **Atta Allah and Moudhaffer in 2017** studied the effect of SiO_2 Nano filler addition on A-2186 silicone before and after weathering and they reported a significant increase in roughness value after 200 and 300 hour of simulated weathering.

Chapter Two

Materials and Method

2.1 Materials

The materials used in this study are mentioned in (Table 2-1).

Table 2-1: Materials used in the study

No	Material	Manufacturer	Source	Expire date
1	Cloroform material		china	2020
2	Silica gel	Avonchem Co.	UK	2022
3	Ethyl Alcohol	Abo teeba	Iraq	11/2019
4	VST-50F platinum silicone elastomer (Figure 2-1)	Factor II Inc	USA	Production date 2018, Valid for 5 years from production date
5	Halloysite nanotubes (HNTs)(Figure 2-2)	Nanoshell	USA	

Figure 2-1: VST-50F maxillofacial silicone.

Figure 2-2: Halloysite nanotube.

2.2. Equipment and instruments

The equipment and instruments utilized in this research is mentioned in (Table 2-2).

Table 2-2: **Equipment and instruments used in the study**

No	Equipment and Instrument	Company and Source
1	CNC-CO2 laser engraving machine	JL-1612, Jinan Link Manufacture and Trading Co., Ltd., China
2	Cooling box	Iran
3	Customized molds	Iraq
4	Digital caliper (0.01mm accuracy)	China
5	Digital electronic balance (0.001g accuracy).	China
6	Digital thermometer	China
7	FTIR spectrometer	Bruker, Germany
8	HS- A shore A durometer	Ezitown ,China
9	Mutivac 3 vacuum mixer	Germany
10	Pocket surf. profilometer tester	Mahr /Germany
11	Q-UV accelerated weathering tester	model QUV/spray, Q-Lab corp., USA
12	Scanning electron microscope (SEM)	Angstrom Advanced Inc, USA
13	Universal testing machine (computer controlled)	Laryee Technology Co., Ltd., China
14	Wax knife	china

2.3 Pilot study

A pilot study had been carried out in order to determine the proper percentages of halloysite nanotubes to be added into VST-50F silicone. Consequently, weight percentages of 0.5%, 1% 1.5% and 2% of HNT were added to VST-50F silicone and three specimens were prepared from each percentage, then a comparison were made with control specimens (contain wt%

HNTs) in term of hardness and tear strength. Accordingly, 1% and 1.5% weight percentages were chosen as they showed the best outcomes (Table 2-3).

Table 2- 3 pilot study results.

Tests Groups	Tear strength (N/mm)			Shore A hardness (IU)		
Control 0%	24.2	23.3	27.7	25.2	25.9	25.4
	Mean = 25.06			**Mean = 25.5**		
0.5% HNTs	26.6	25.5	26.04	26.8	26.5	26
	Mean = 26			**Mean = 26.4**		
1% HNTs	28.3	30.27	27.14	27	26.8	27
	Mean = 28.57			**Mean = 26.9**		
1.5% HNTs	30.6	27.8	30	27.6	27.5	27
	Mean = 29.4			**Mean = 27.3**		
2% HNTs	25.2	25.5	27.4	28.4	28.8	28.2
	Mean = 26.04			**Mean = 28.46**		

2.4 Methods

2.4.1 Study design

Two hundreds forty specimens had been prepared and divided into 2 main groups ; group 1 (before weathering) and group 2 (after weathering), with 120 specimen for each group . These two groups were further subdivided into 3 subgroups; Control with 0.0 wt% HNTs,1 wt % HNTs and 1.5 wt% HNTs, and each subgroup contain 40 specimens; 10 for each test(tear strength, tensile strength, surface hardness and surface roughness), while elongation percentage test was measured concurrently with tensile strength test (Figure 2-3).

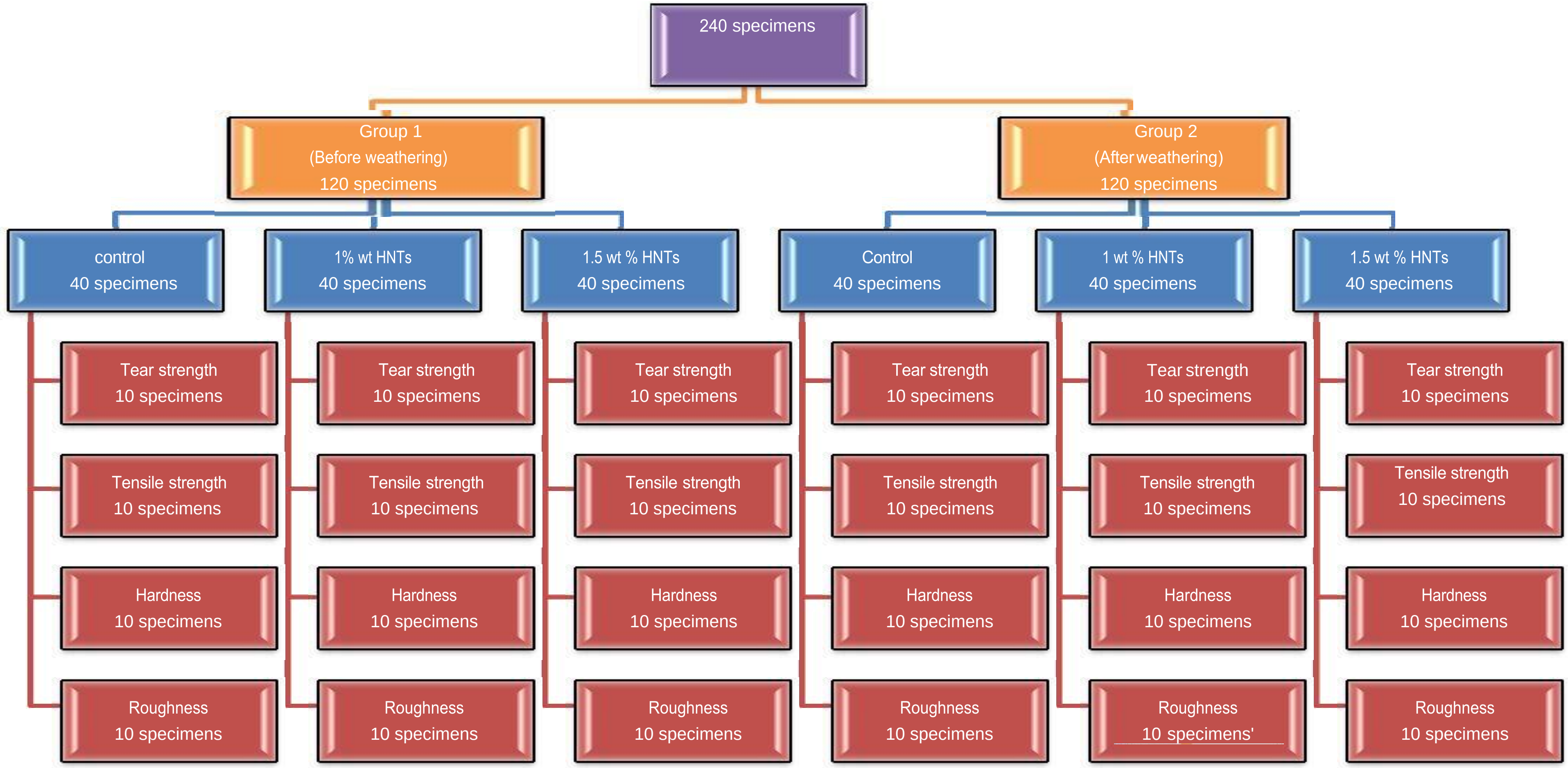

Figure 2-3: Study design.

2.4.2 Acrylic molds preparation

A laser engraving machine had been used to cut acrylic sheet of variable thickness (2 - 6 mm), and this cutting was performed according to specifications determined for each test (Figure 2-4).

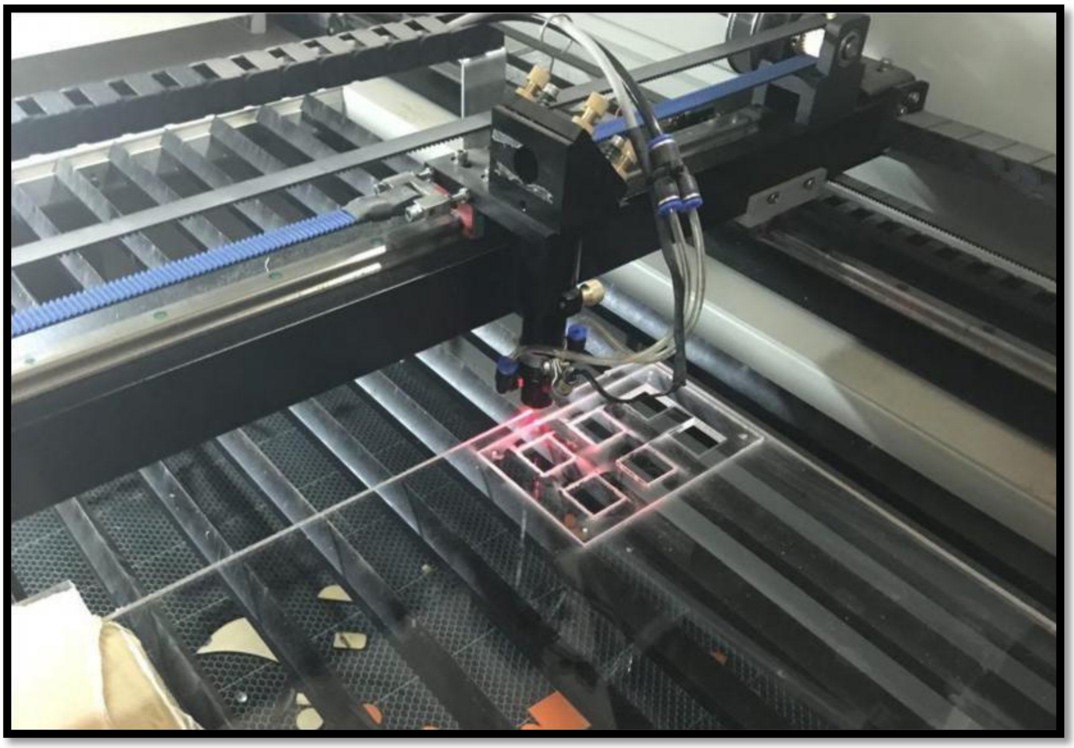

Figure 2-4: Laser engraving machine.

The mold consists of the following components:

1) The Matrix:

It is a sheet of clear acrylic having thickness of 2 or 6 mm according to the required specification of the chosen test. Four or more holes were made on each corner through which bolts would be inserted so as to fasten the mold parts together.

2) The cover and the base

They are clear acrylic sheets with dimensions similar to those of the matrix, also they have holes identical to these made in matrix. The base was attached to the matrix using a chloroform material, while the mold parts assembled all together using bolts through these holes.

3) Assembling and tightening parts

These include nuts and bolts which were used at each corner of the mold to fasten its parts. In addition, G-clamps were utilized at the margins to tighten the mold components so as to drain the excess material and reduce the chance of air bubbles formation (Figure 2-5).

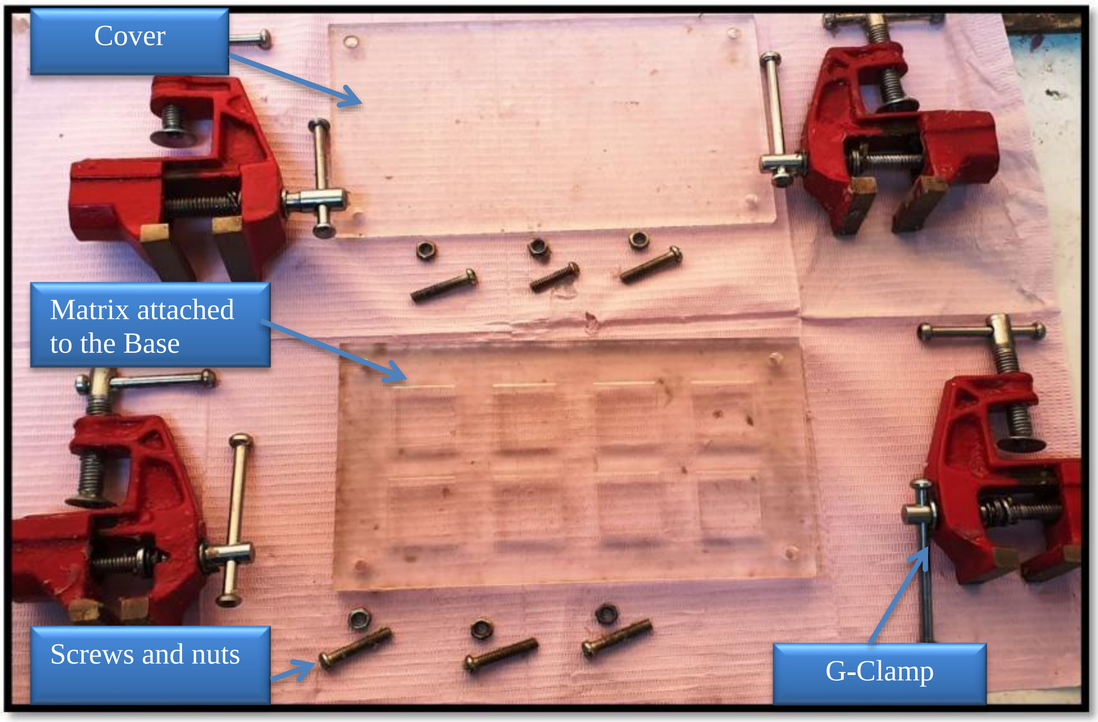

Figure 2-5: Mold parts.

2.4.3 Mixing procedure

The manufacturer's instructions reveal that; for each 10 parts of base: 1 part of catalyst by weight should be added. Besides that, the mixing should be done in a vacuum mixer in order to reduce the air entrapment which affects the material properties.

In order to add HNTs to silicone according to the chosen percentage (1% wt and 1.5 wt %), the weight of HNTs was subtracted from to the weight of the base. Table 2-4 shows the proper mixing calculation.

Table 2-4: Mixing calculation.

Groups	base	HNTs	catalyst	Total
control (0%HNTs)	50g	0g	5g	55g
1% wt HNTs	49.5g	0.5g	5g	55g
1.5% wt HNTs	49.25g	0.75g	5g	55g

For control group specimens ; the base and catalyst of VST-50F silicone were weighed properly using electronic balance , then they were mixed in vacuum mixer at 360 rpm speed under pressure of 10 bar for 5 minute so as to obtain bubble free mixture (**Tukmachi and Moudhaffer, 2017**) (Figure 2-6) .

While for the other experimental groups (1 wt % and 1.5 wt% HNTs) the chosen concentration of HNTs firstly weighed in the mixing bowel and the base then added in the desired weight, then after the base and the HNTs mixed together for 3 minute in the vacuum mixer without air evacuation (to avoid HNTs suctioning), followed by 7 minutes of vacuum mixing. Before the addition of the catalyst the mixture was left to cool down, doing so would reduce the chance of shortening the working time that may result from elevated temperature. After that, the catalyst was added and vacuum mixing was repeated for 5 minutes (**Tukmachi and Moudhaffer, 2017**).

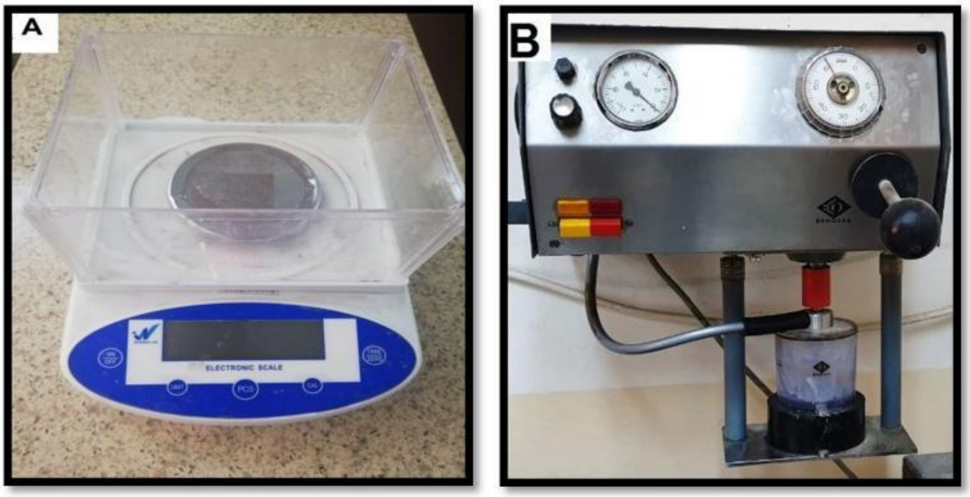

Figure 2-6: (A) Electronic balance, (B) Vacuum mixer.

2.4.4 Specimen fabrication

Silicone was applied to fill the mold gradually with the aid of wax knife. When the mold became completely filled, the cover was placed carefully and hand pressure was applied at the center of the mold. Then after, the mold parts fastened together using screws and nuts at the corners and tightened by G-clamp at the margins. The excess material and air bubbles were expected to be dispersed by mold closure and tightening (Figure 2-7).

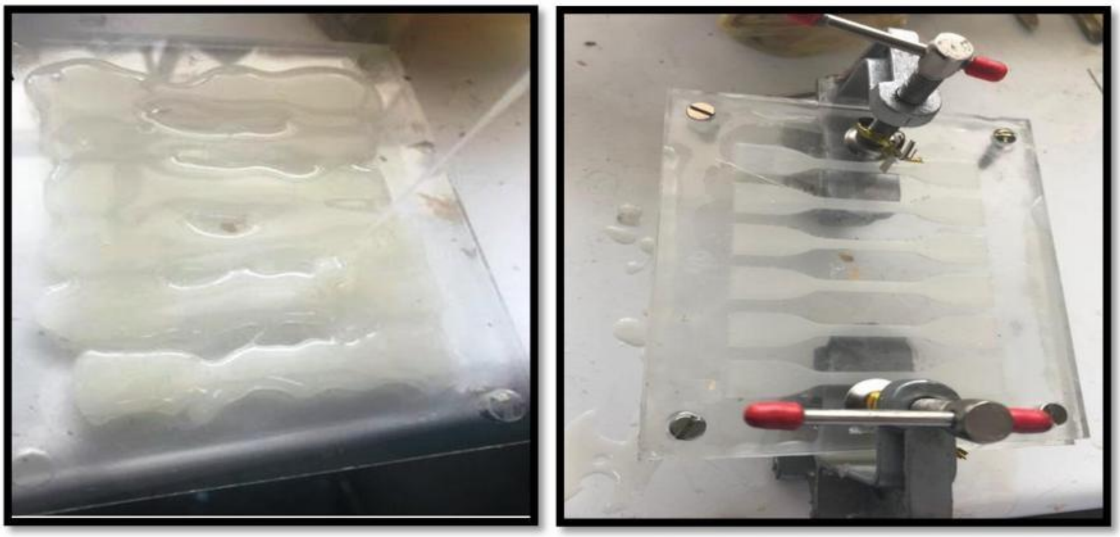

Figure 2-7: (A) Silicone pouring, (B) Mold securing.

2.4.5 Specimens' storage

Silicone specimens were stored at temperature of 23±2°C and relative humidity of 50 ±10% as directed by **ISO 23529:2016**. Accordingly, the specimens were stored in cooling box and silica gel was used to control the humidity. Meanwhile, temperature was monitored continuously using digital thermometer (Figure 2-8). By this way the impact of external conditioning factors (sun light, temperature and humidity) could be reduced (**Abdullah and Abdul-Ameer, 2018**).

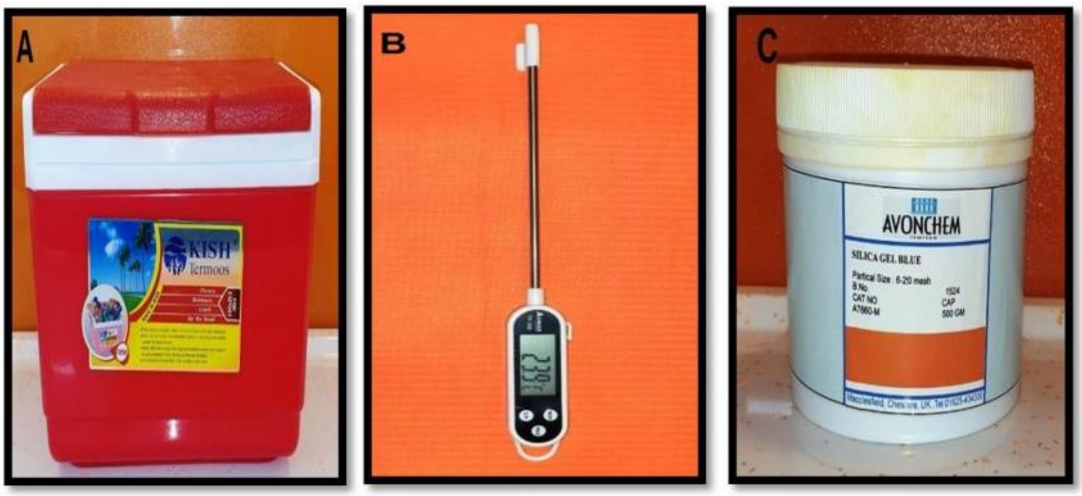

Figure 2-8: (A) Cooling box, (B) Digital thermometer, (C) Silica gel.

2.4.6 Fourier transforms infrared spectroscopy analysis (FTIR)

The purpose of such test was to discover if there was any chemical reaction between HNTs and VST-50F silicone before and after weathering. Therefore, this test was conducted for HNTs powder, reinforced and non-reinforced VST-50F silicone before and after weathering (Figure 2-9).

Figure 2-9: FTIR spectrometer.

2.4.7 Scanning electron microscopy (SEM):

SEM test was performed to evaluate the HNTs distribution pattern within VST-50F .Two specimens were tested, one for non-reinforced VST-50F and the other for 1.5 wt%VST-50F SILICONE (Figure 2-10).

Figure 2-10: Scanning electron microscope

2.4.8 Energy dispersive X-ray spectroscopy (EDS)

EDS test was performed to detect if there was any HNTs blending within VST-50F silicone or not. Such test provides chemical characterization or elemental analysis of a specimen. Two specimens were tested; one for non-reinforced VST-50F and the other for 1.5 wt % HNTs reinforced VST-50F.

2.4.9 Simulated weathering

One hundred twenty specimens had been arranged in panels and placed in accelerated artificial weathering tester for 200 hours (Figure 2-11). **ASTM G-154** cycle7 had been chosen, as it represents the most common system for UV light exposing, where the irradiation was set at 1.55W/m^2 and the temperature adjusted at (50-60 ^{o}C) range.

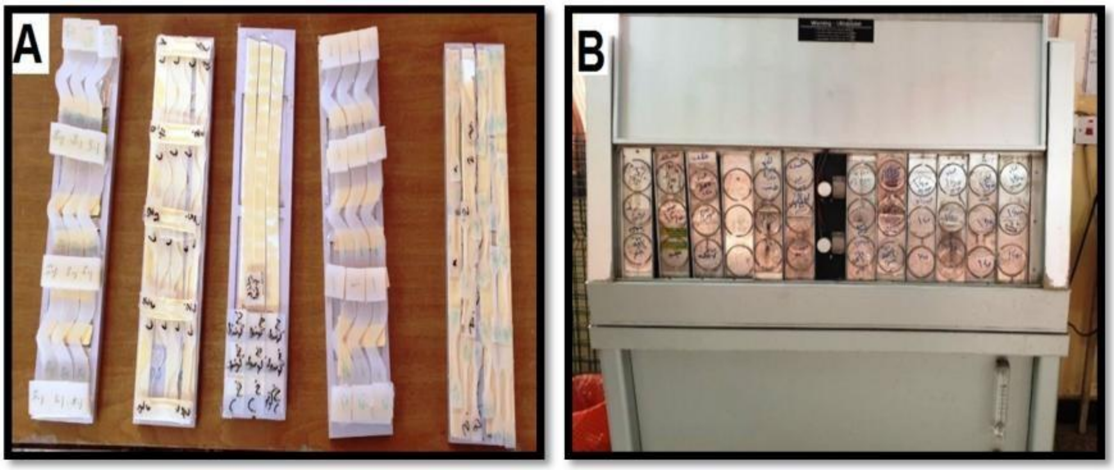

Figure 2-11: (A) Specimen arranged in panel, (B) Loading the specimens in artificial weathering tester.

2.4.10 Testing of mechanical and physical properties

2.4.10.1Tear strength test:

A) The design of the specimen:

The specimen design was based on **ISO 34-1:2015** specification. It has one apex and two tap ends, with thickness of 2±0.2mm (Figure 2-12).

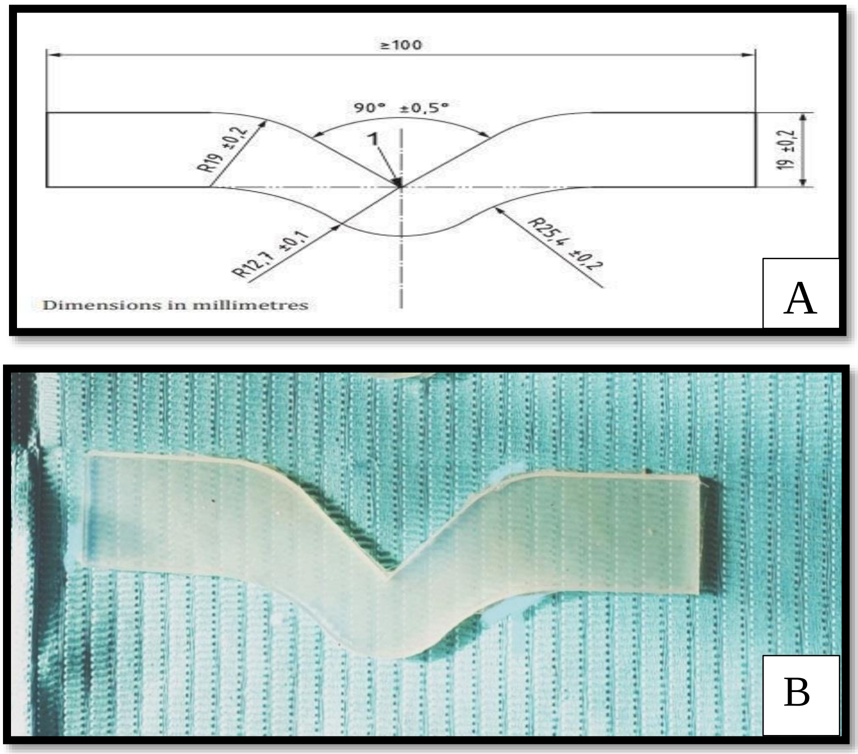

Figure 2-12: (A) Tear strength specimen dimensions according to ISO 34-1:2015, (B) The prepared tear specimen.

B) Specimen testing:

Testing procedure had followed **ISO 34-1:2015**. The thickness of the specimens were measured at the angled part (where the tear is supposed to be initiated) using digital caliper. A universal testing machine had been utilized to perform tear strength test. In order to distribute the force uniformly, the specimen ends should be mounted symmetrically through the machine grips. The speed was adjusted at 500mm/min and the maximum force at rupture was recorded (Figure 2-13).

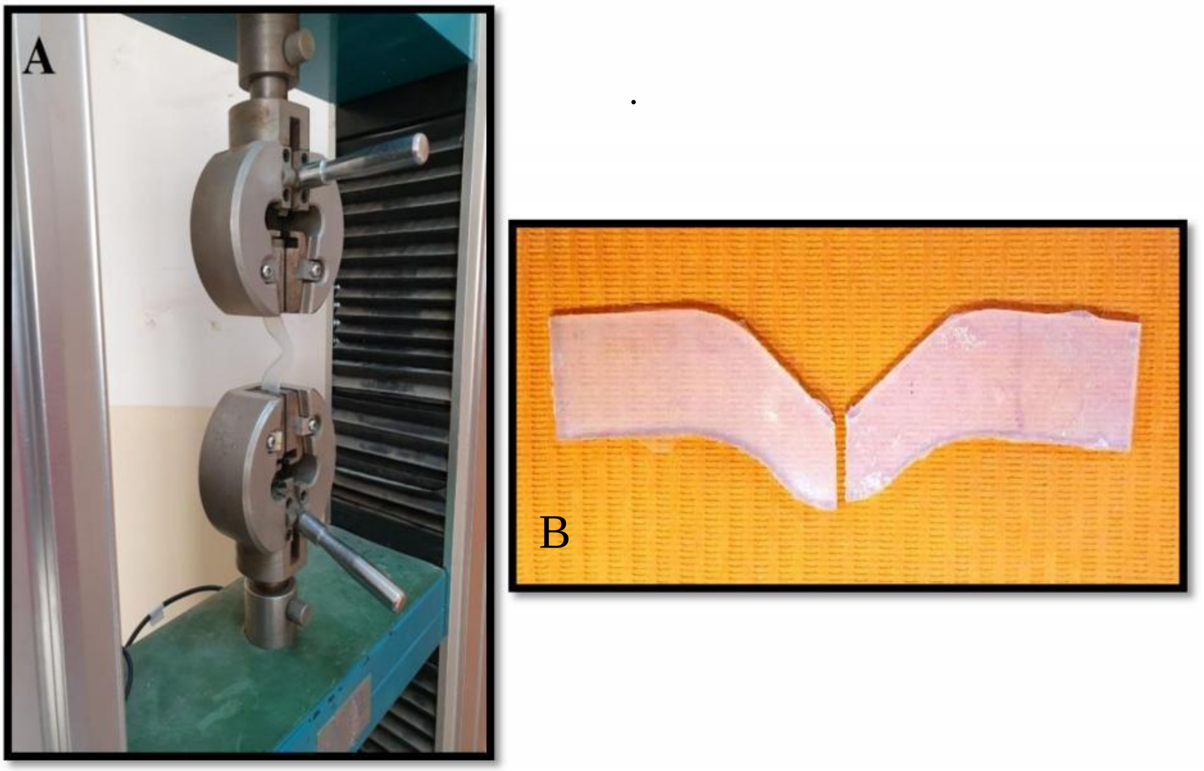

Figure 2-13: (A) Mounting of the tear specimen on universal testing machine, (B) Tear specimen after testing.

If the specimen ruptured at any part other than the supposed area (the angled part) then it was considered as anon-validand should be replaced.

Tear strength is calculated according to the following equation:

$$T = f/d$$

Where:

T represents tear strength (N/mm).

F represents the maximum force (newton).

D represents specimen's thickness (mm).

2.4.10.2 Tensile strength and elongation percentage tests:

A) specimen design:

The specimen designed according to **ISO 37:2017** specification (Figure 2-14).

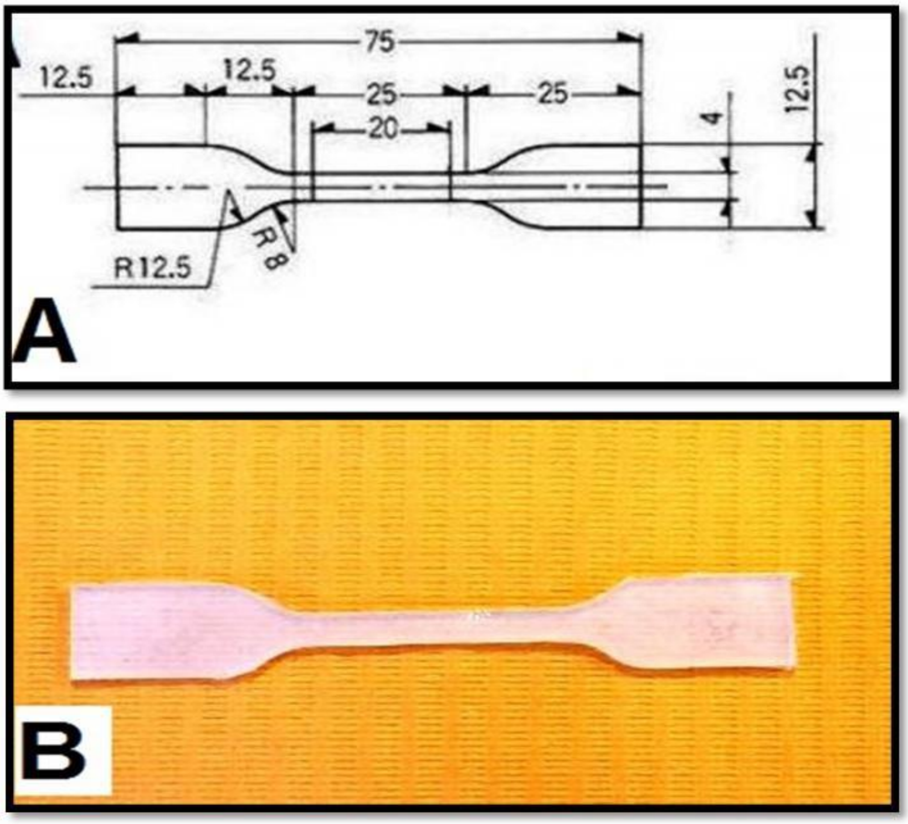

Figure 2-14: (A) Tensile strength specimen design dimensions as directed by (ISO 37:2017), (B) The prepared tensile specimen.

B) Testing procedure:

The test had been performed according to **ISO 37:2017** directions; the width and the thickness of the specimen were measured using digital caliper so as to calculate the cross sectional area of the testing length (the narrow part of the specimen). In term of thickness, three readings were recorded for each specimen (one at each end of narrow part and one at the center); the mean of them represented the specimen thickness.

This test had also been performed using universal testing machine, the specimen ends were mounted on the machine grips in symmetrical way in order to guarantee a uniform distribution of force. The machine run at 500mm/min speed and the maximum force and elongation at break were recorded (Figure 2-15).

If the specimen ruptured at areas other than the narrow portion, then it would be considered as a non-valid and should be replaced.

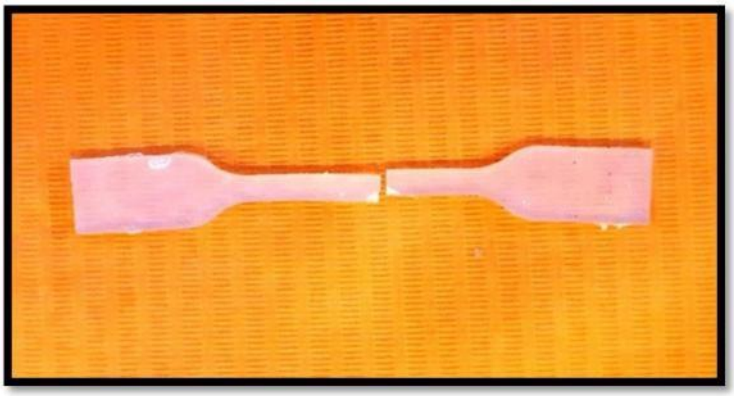

Figure 2-15: Tensile specimen after testing.

Tensile strength mmeasurement is obtained from the following equation **(ISO 37:2017)**:

$$Tc = F/Wt$$

Where

T_C represents tensile strength (N/mm).

W represents the width (mm).

t represents the thickness (mm).

The elongation percentage had been measured concurrently with tensile strength according to the equation below:

$$E\% = \frac{Lb - Lo}{Lo} \text{ X } 100$$

Where:

E% represents elongation percentage.

Lo represents the original length (mm).

Lb represents the length at breakage (mm).

2.4.10.3 Shore A Hardness test:

A) The design:

The design of hardness test was based on **ISO 7619-1:2010,** where **the** dimensions were dictated to be 25mm width, 25mm length and 6mm thickness (Figure 2-16).

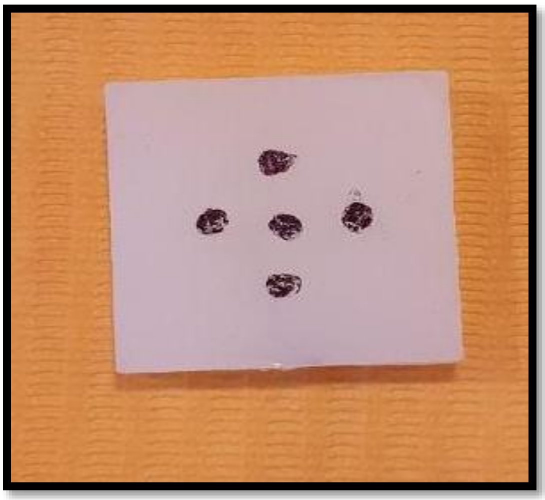

Figure 2-16: Hardness specimens.

B) Testing procedure:

This test had been performed in accordance to **ISO 7619-1:2010** specifications. Firstly, five points were marked on each hardness specimen; at least 6 mm should separate each point from the specimen center and from other points. Then shore A durometer was used to measure the hardness at the marked points and the mean of these five readings represent the hardness value of the specimen. Such device has a blunt indenter and gives the hardness results digitally (Figure 2-17).

Figure 2-17: Shore A durometer.

2.4.10.4 Surface roughness test

A) Specimen design:

The specimens were fabricated according to the directions of **ISO 7619-1: 2010,** where the dimensions were identical to shore A hardness specimens (**Mancuso *et al.*, 2009)**.

B) Testing procedure

A profilometer of 0.001 µm accuracy was used in this test (Figure 2-20). The specimen was placed on a rigid and stable surface, and then the device was applied in a manner where its stylus touches the specimen surface at three different points. The mean of the three readings were calculated and considered as roughness value of the specimen (Figure 2-18).

Figure 2-18: Prolifrometer.

2.5 Statistical analysis

The data had been analyzed using SPSS (statistical package for social sciences) software.

2.5.1 Inferential statistics

One-way ANOVA test (analysis of variance) had been used for comparison of mean values of tested groups.

Tukey HSD and Dunnett's T3 (post hoc test) had been utilized for the determination of the significance of difference between each two tested groups. Paired t-test was also conducted to compare group 1 specimens with group 2 specimens.

The *P* value (probability) had been calculated and if it was > 0.05 then it considered statistically non-significant (NS), whereas if it was ≤ 0.05: considered statistically significant (S) and if it was ≤ 0.01; considered as highly significant (HS).

Chapter Three

Results

Results

3.1 Fourier transform infrared spectroscopy analysis (FTIR)

FTIR test had been conducted for HNTs powder, non-reinforced VST50-F and reinforced VST-50F silicone before and after weathering (Figure 3-1, 3-2, 3-3, 3-4 and 3-5). The test results showed no impact on the spectra range of VST-50F silicone neither by HNTs addition nor by the artificial weathering.

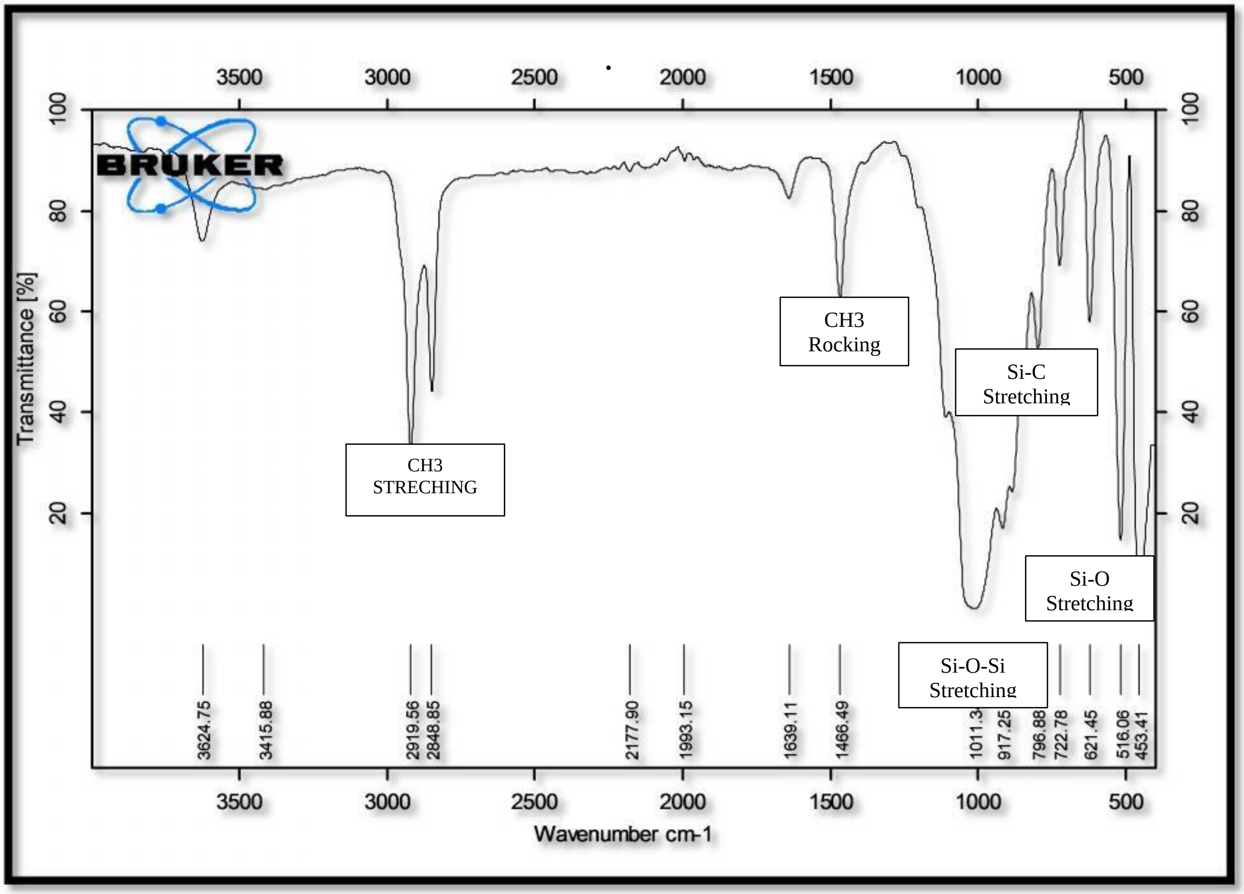

Figure 3-1: Fourier transform infrared spectroscopy analysis result of halloysite nanotubes.

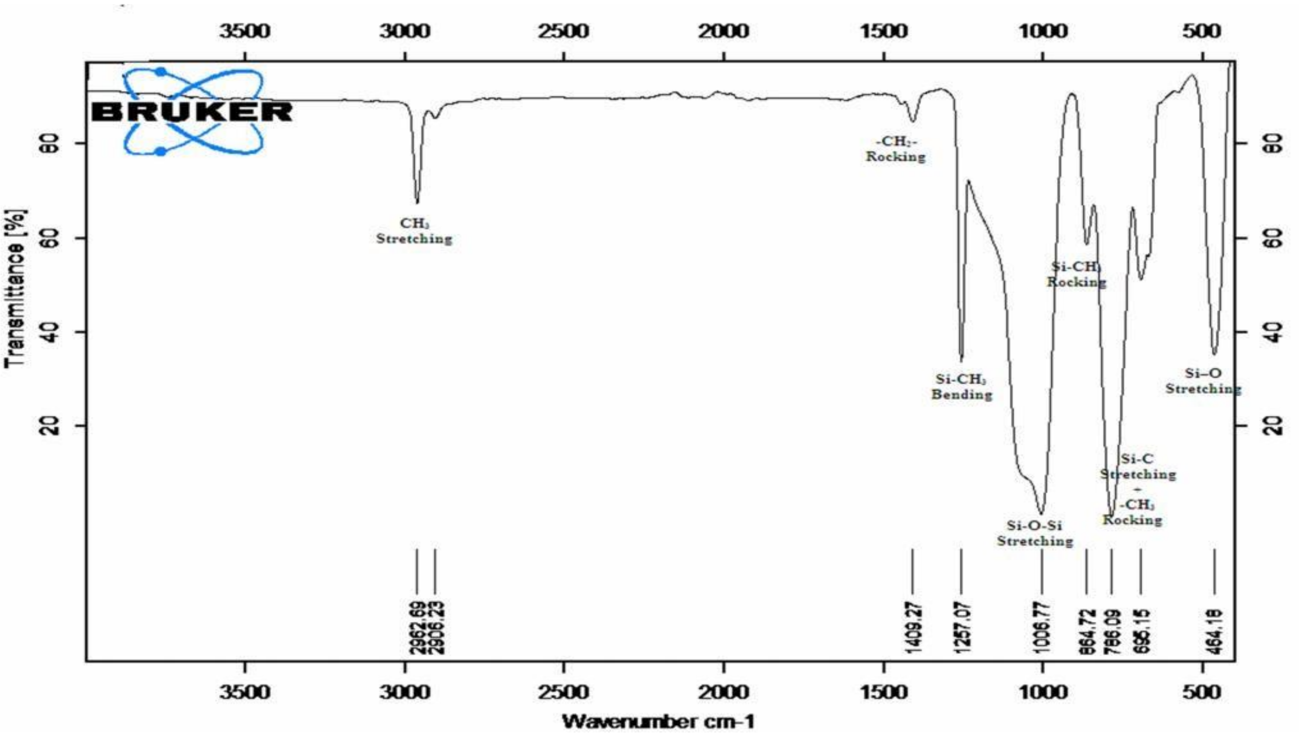

Figure 3-2: Fourier transform infrared spectroscopy analysis result of non- reinforced VST- 50F silicone before weathering.

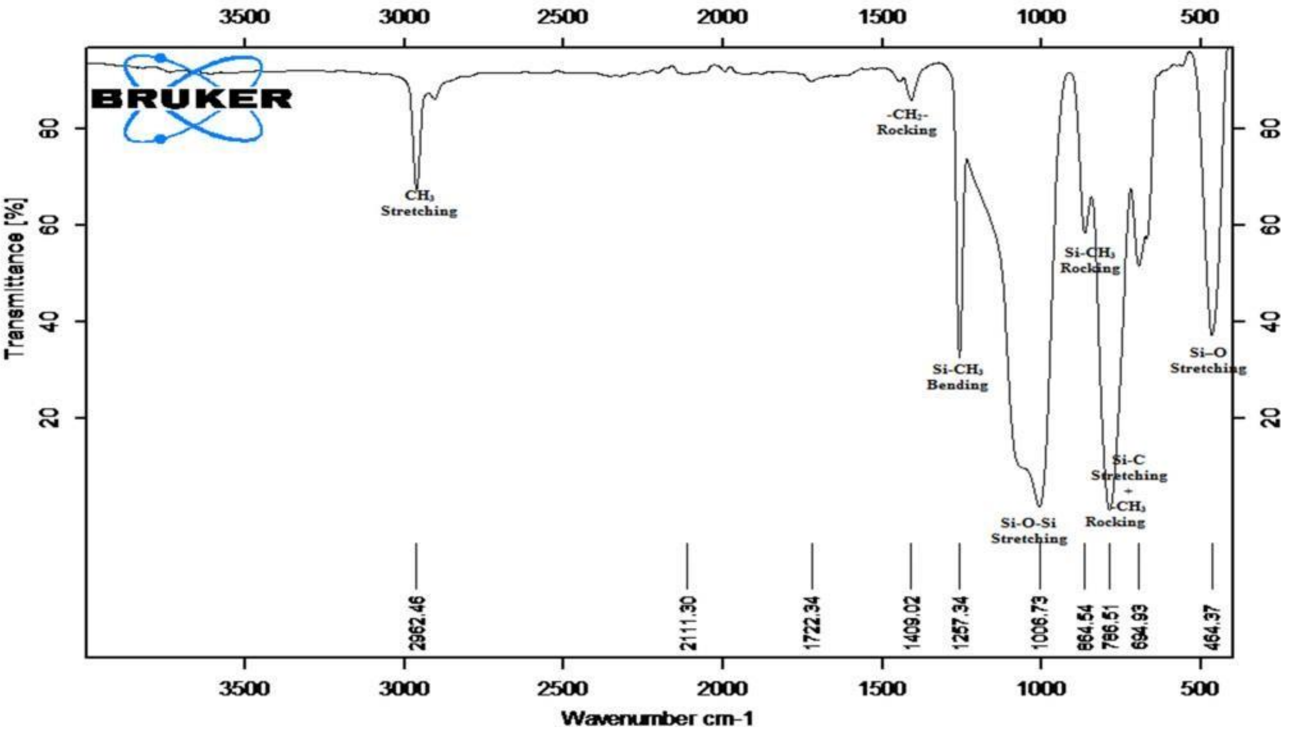

Figure 3-3: Fourier transform infrared spectroscopy analysis result of 1.5 wt % halloysite nanotubes reinforced VST- 50F before weathering.

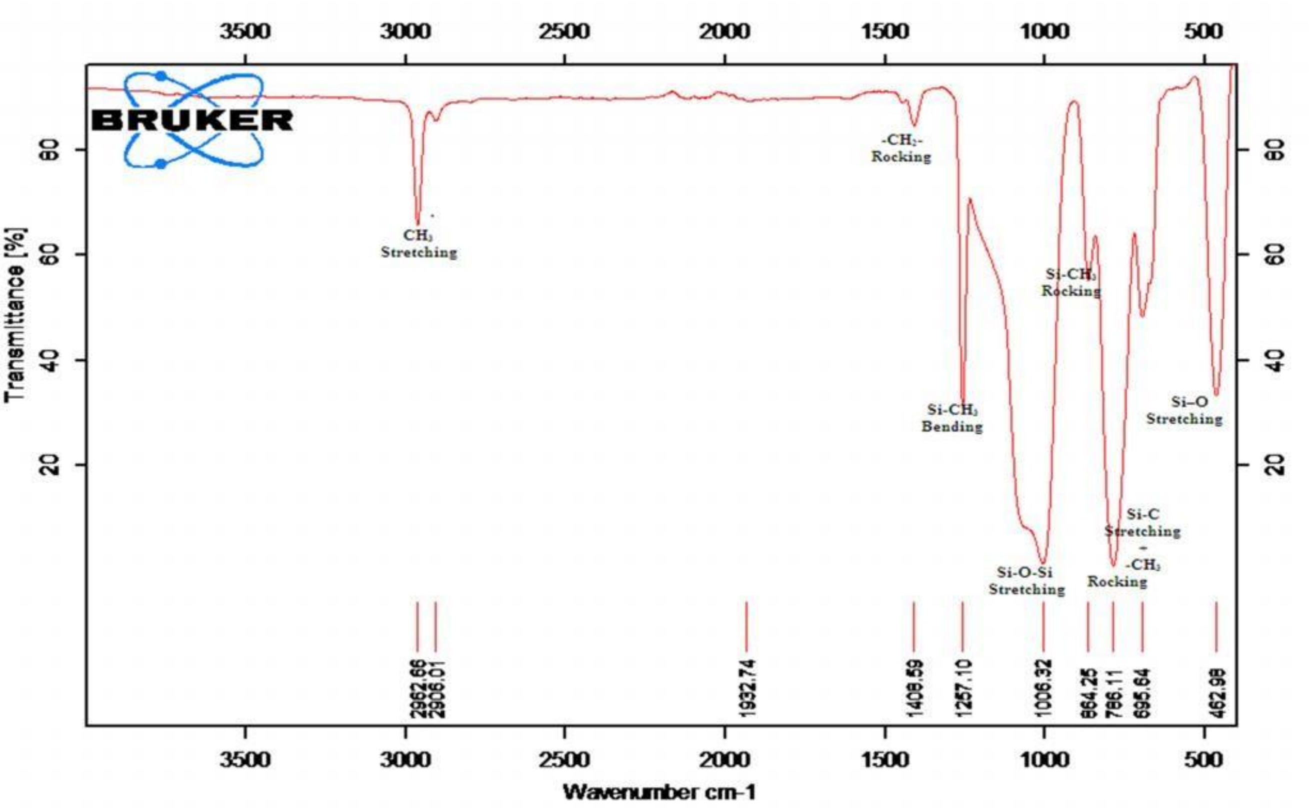

Figure 3-4: Fourier transform infrared spectroscopy analysis spectral result of non-reinforced VST-50F silicone after weathering.

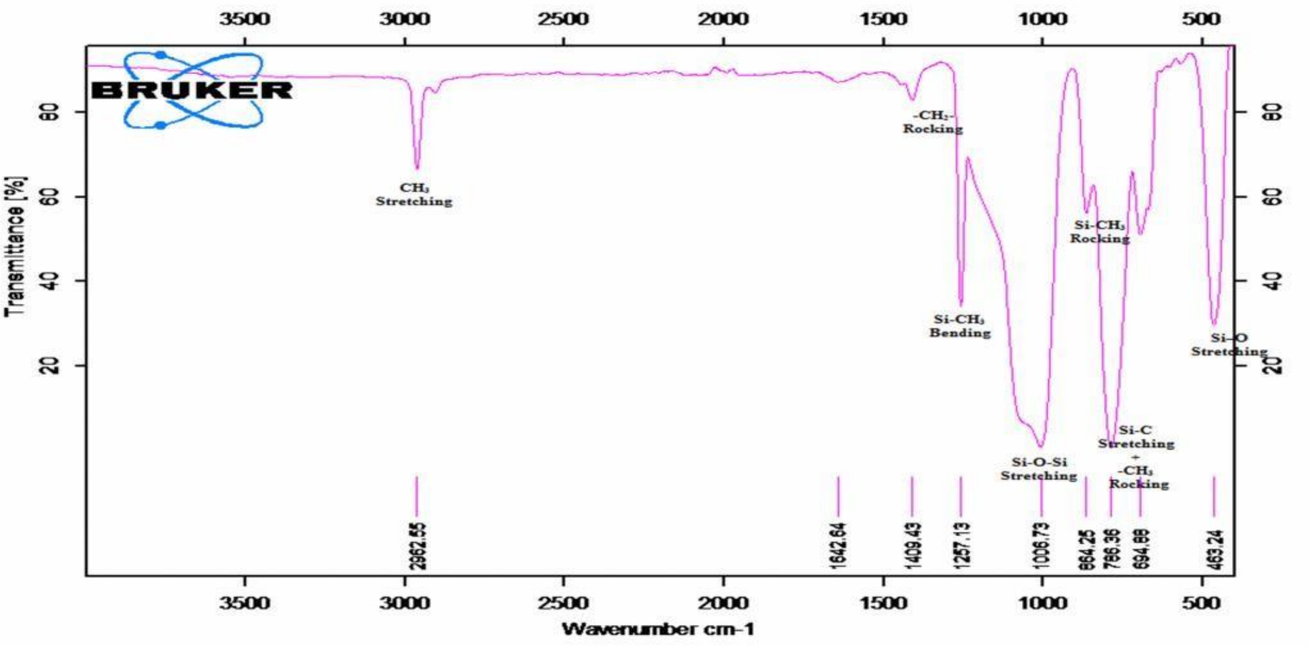

Figure 3-5: Fourier transform infrared spectroscopy analysis result of 1.5 wt % halloysite nanotubes renforcedVST-50F silicone after weathering.

3.2 Scanning electron microscope (SEM):

SEM test results of VST-50F maxillofacial silicone before and after the addition of 1.5% HNTs are shown in (Figure 3-6) and (Figure 3-7) respectively. The test result reveals a well dispersed fashion of HNTs within silicone polymeric matrix.

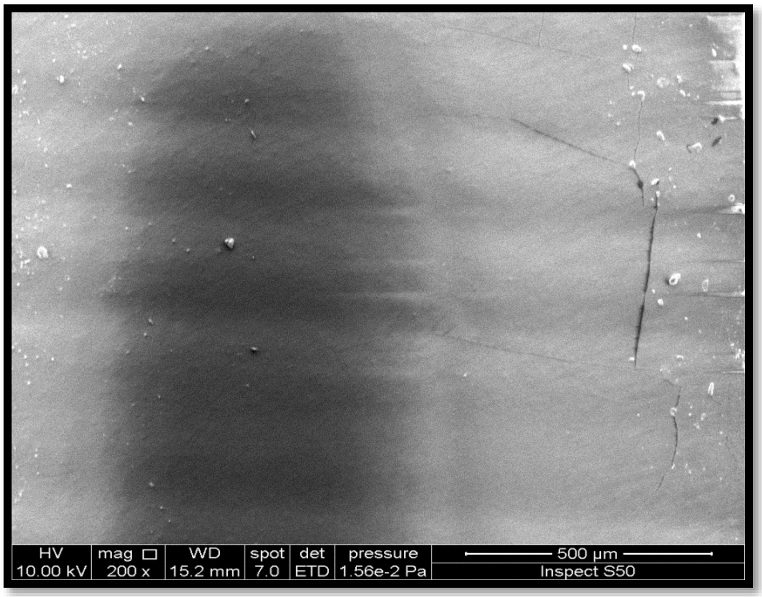

Figure 3-6: Scanning electron microscope image of VST- 50F silicone elastomer before the addition of halloysite nanotubes powder (at 500µm scale).

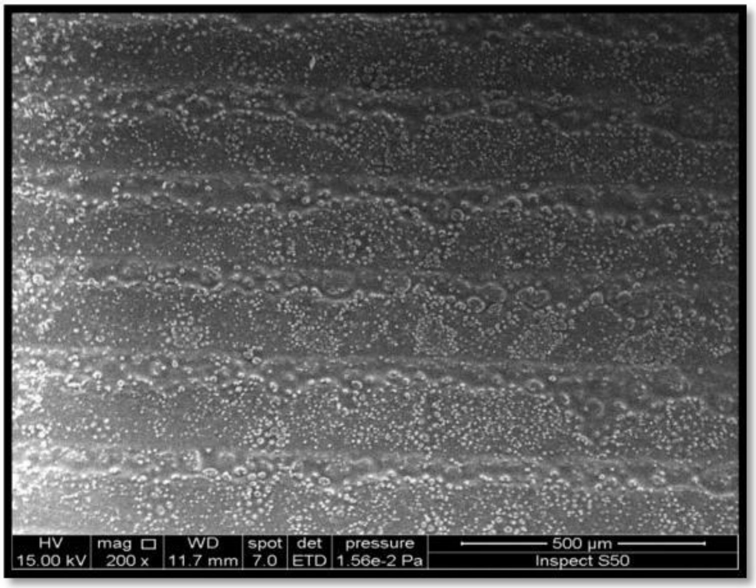

Figure 3-7: Scanning electron microscope image of VST- 50F silicone elastomer after the addition of 1.5 wt % halloysite nanotubes (at 500µm scale).

3.3 Energy dispersive X-ray spectroscopy (EDS):

EDS diagrams for VST-50F maxillofacial silicone before and after the incorporation of HNTs powder are shown in (Figure 3-8) and (Figure 3-9) respectively. The incorporated HNTs within VST-50F polymeric matrix create slight changes in EDS plot of VST-50F silicone.

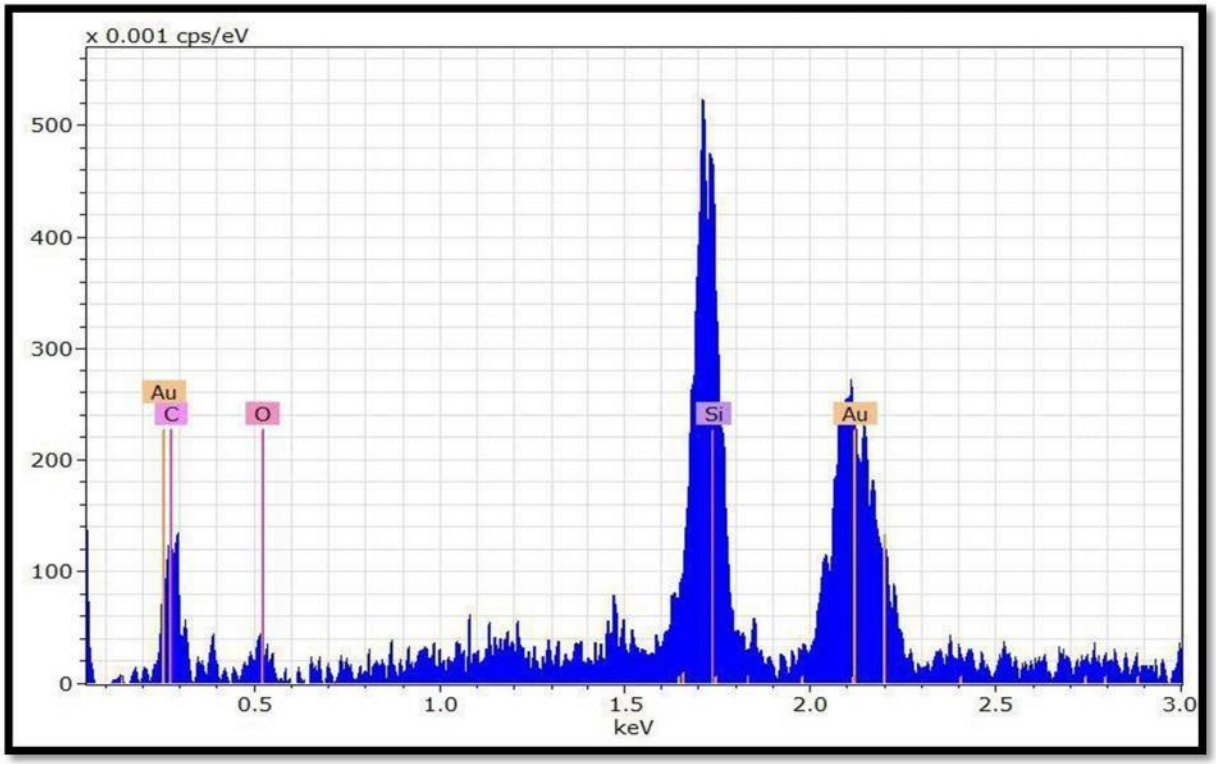

Figure: 3-8: Energy dispersive X-ray spectroscopy plot of VST-50F silicone before the addition of halloysite nanotubes.

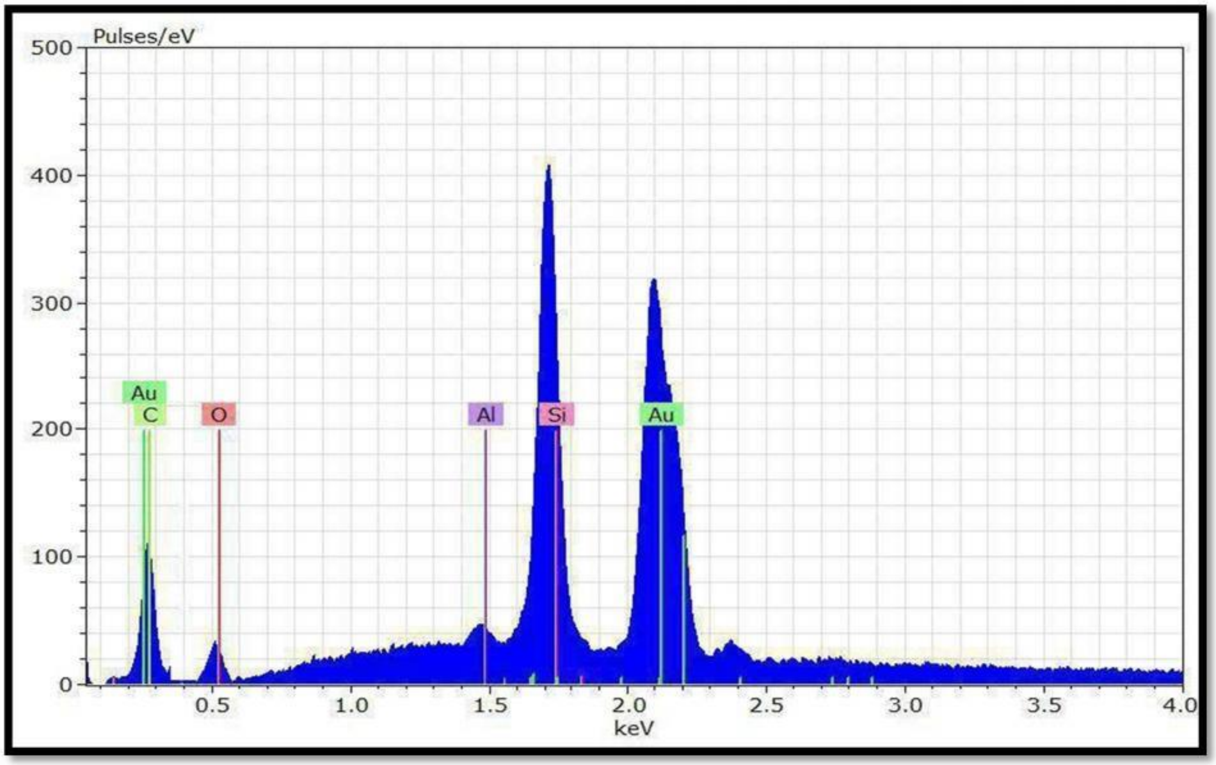

Figure: 3-9: Energy dispersive X-Ray spectroscopy plot of VST-50F silicone after the addition of 1.5 wt % halloysite nanotubes.

3.4 Results of descriptive and inferential statistics

By using shapiro-wilk test, all the variables are normally distributed at *P* > 0.05 (Table 3-1).

Table (3-1) Shapiro-wilk test.

Shapiro-Wilk						
Groups	**Control**		**1%HNTs**		**1.5%HNTs**	
Tests	**Statistic**	**Sig.**	**Statistic**	**Sig.**	**Statistic**	**Sig.**
Tear1	.920	.358	.954	.711	.896	.197
Tear2	.935	.496	.931	.458	.927	.421
Hardness1	.916	.328	.926	.412	.884	.144
Hardness2	.912	.294	.908	.265	.957	.750
Tensile1	.937	.515	.930	.443	.913	.301
Tensile2	.950	.664	0.853	.063	.952	.693
Roughness1	.956	.736	.962	.812	.968	.869
Roughness2	.973	.914	.852	.062	.856	.068
Elongation1	.967	.861	.955	.732	.948	.645
Elongation2	.849	.057	.948	.641	.882	.138

Where 1: before weathering and 2: after weathering.

3.4.1 Tear strength test:

For tear 1(before weathering), the two experimental groups (1 wt % and 1.5 wt % HNTs) had shown an increased mean values in comparison with control group, with the highest value recorded for 1.5 wt % HNTs. While in tear 2 (after weathering), there was a significant decline in all study groups, but the experimental groups still higher than the control (Figure 3- 10).

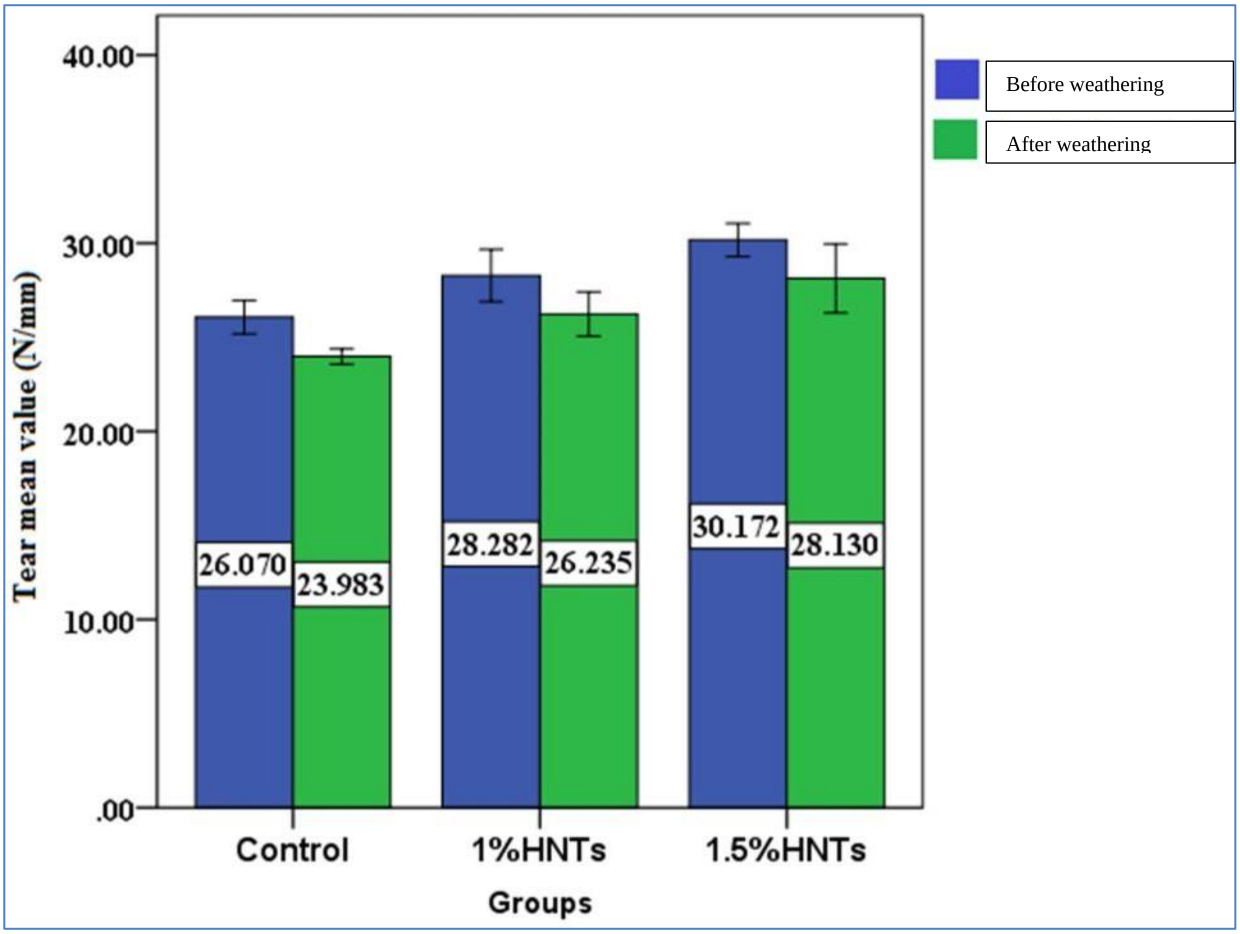

Figure 3-10: Bar chart shows the mean value of tear strength test results for all groups before and after weathering.

Descriptive and statistical test had been conducted for tear strength results and one- way ANOVA test had been performed to figure out if there was any significant difference among study groups within tear 1 and tear 2, and the results revealed a highly significant difference in both tear 1 and tear 2 (Table 3-2).

Table 3-2: Descriptive and statistical tests with one –way ANOVA test for tear strength variables.

	Groups	Minimum	Maximum	Mean	±SD	F	P value	Sig	ES
Tear1	Control	28.000	24.500	26.070	1.235	18.601	.000	HS	.579
	1%HNTs	31.000	25.200	28.282	1.938				
	1.5%HNTs	31.500	28.000	30.172	1.232				
Tear 2	Control	23.100	24.730	23.983	.567	13.432	0.002	HS	.499
	1%HNTs	24.200	29.000	26.235	1.643				
	1.5%HNTs	24.730	31.880	28.130	2.570				

Levene 1=0.117[NS], Levene 2=0.000[HS], DF=2

Then post -hoc test had been used so as to compare the mean values between each two groups. Depending on the result of levene's test, the types of post-hoc test was decided; either Tukey HSD test or Dunnet T3 test. Within tear 1; the control had shown a highly significant difference with both 1 and 1.5 wt % HNTs (*P*<0.01), also there was a significant difference between 1 and 1.5 wt %HNTs (*P* <0.05). While in tear 2; the control had also shown a highly significant difference with both 1 and 1.5 wt% HNTs (*P* <0.01), but there was a non-significant difference between 1% and 1.5% HNTs (Table 3-3).

Table 3-3: Post-hoc test of tear strength results.

Multiple Comparisons						Sig.
Dependent Variable		(I) Groups	(J) Groups	Mean Difference (I-J)	*P*	
Tear1	Tukey HSD	Control	1%HNTs	-2.212	.008	HS
			1.5%HNTs	-4.102	.000	HS
		1%HNTs	1.5%HNTs	-1.890	.024	S
Tear2	Dunnett T3	Control	1%HNTs	-2.252	.005	HS
			1.5%HNTs	-4.147	.002	HS
		1%HNTs	1.5%HNTs	-1.895	.183	NS

Finally, a paired t- test had been conducted to compare tear1 groups with their counterparts in tear 2, and the results showed a highly significant difference between the control groups((*P* <0.01), and a significant difference between the experimental groups (*P*<0.05), (Table 3-4).

Table 3-4: **Paired t-test for tear strength results**

Groups	Tear1		Tear2		T	df	P value	Sig.	ES
	Mean	±SD	Mean	±SD					
Control	26.070	1.235	23.983	.567	4.429	9	.002	HS	1.401
1%HNTs	28.282	1.938	26.235	1.643	3.040	9	.014	S	0.961
1.5%HNTs	30.172	1.232	28.130	2.570	2.531	9	.032	S	0.800

3.4.2 Tensile strength test

For Tensile 1 (before weathering), the two experimental groups (1 and 1.5 wt% HNTs) had shown a rise in the mean values when compared with control group, with highest value recorded for 1.5 wt% HNTs. Tensile 2 results (after weathering) showed a decrease in mean values in all groups in comparison with their counterparts in tensile 1 (Figure 3-11).

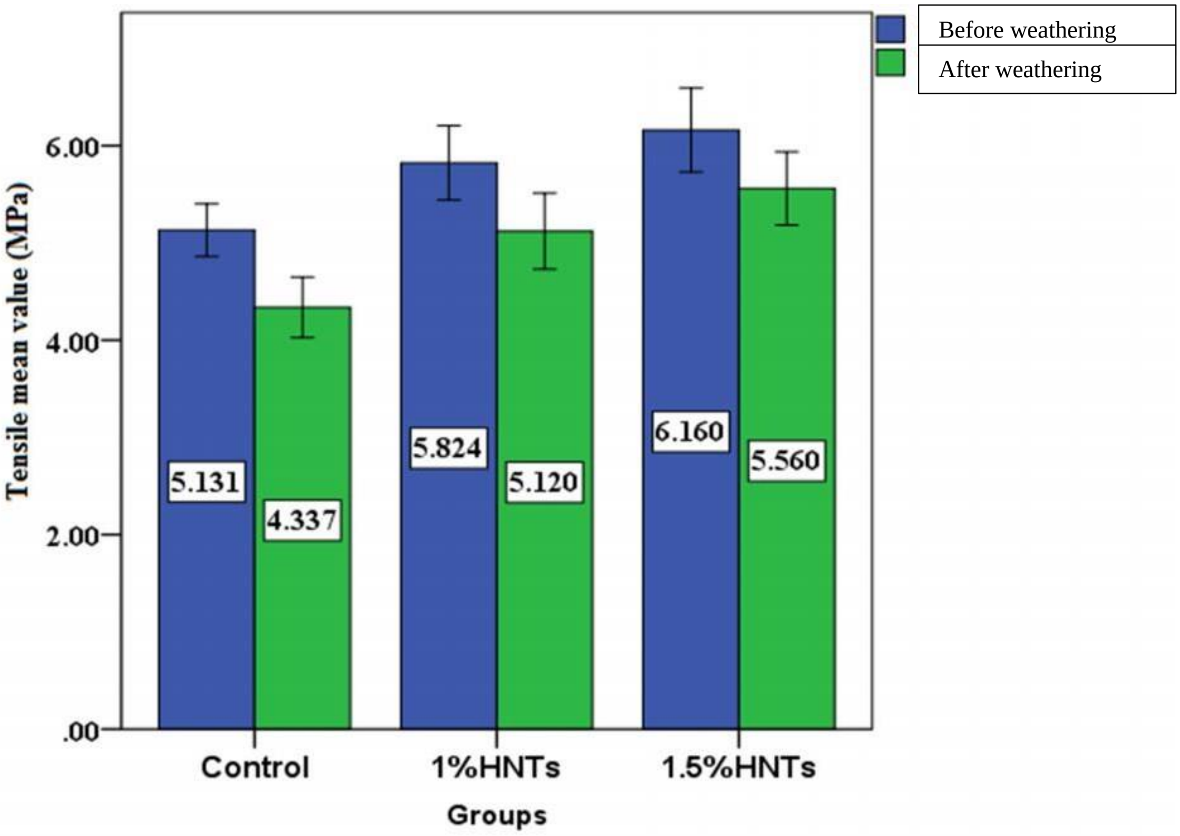

Figure 3-11: Bar chart shows the mean values of tensile strength test results for all groups before and after weathering.

Descriptive and statistical tests had been performed for tensile strength test results before and after weathering. One- way ANOVA test was conducted to see if there was any significant difference among groups in tensile 1 and tensile 2 and the results showed a highly significant difference for both tensile 1 and tensile 2 groups ($P < 0.01$), (Table 3-5).

Table 3-5: Descriptive and statistical tests with one way -ANOVA test for tensile strength results.

	Groups	Minimum	Maximum	Mean	±SD	F	P value	Sig.	ES
Tensile 1	Control	4.620	5.700	5.131	.377	10.415	.000	HS	.436
	1%HNTs	5.125	6.620	5.824	.536				
	1.5%HNTs	5.250	6.870	6.160	.603				
Tensile 2	Control	3.720	4.990	4.337	.435	15.016	.000	HS	.527
	1%HNTs	4.600	5.870	5.120	.547				
	1.5%HNTs	4.750	6.500	5.560	.527				

Levene 1=0.313[NS], Levene 2=0.559[NS], DF=2

In order to compare the mean values between each two groups in tensile 1 and tensile 2, post-hoc test had been performed (Tukey HSD). The results of tensile 1 showed a significant difference between control and 1 wt % HNTs ($P < 0.05$), and highly significant difference between control and 1.5 wt % HNTs ($P < 0.01$). While in tensile 2 the control had shown a highly significant difference with both 1 and 1.5 wt % HNTs ($P < 0.01$). However, there was no significant difference between the two experimental groups in both tensile 1 and tensile 2 (Table 3-6).

Table 3-6: Tukey HSD test for tensile strength results

Multiple Comparisons					
Tukey HSD					
Dependent Variable	(I) Groups	(J) Groups	Mean Difference (I-J)	*P*	Sig.
Tensile1	Control	1%HNTs	-.693	.015	S
		1.5%HNTs	-1.029	.000	HS
	1%HNTs	1.5%HNTs	-.337	.324	NS
Tensile2	Control	1%HNTs	-.783	.007	HS
		1.5%HNTs	-1.222	.000	HS
	1%HNTs	1.5%HNTs	-.439	.224	NS

In order to compare tensile 1 with tensile 2, a paired t-test had been conducted, and the results revealed a highly significant difference between the control groups (*P* <0.01) and a significant difference between the experimental groups (*P* <0.05) (Table 3-7).

Table 3-7: Paired t-test for tensile strength test results before and after weathering.

Groups	Tensile 1		Tensile 2		T	df	P value	Sig	ES
	Mean	±SD	Mean	±SD					
Control	5.131	.377	4.337	.435	5.113	9	.001	HS	1.617
1%HNTs	5.824	.536	5.120	.547	2.306	9	.047	S	0.729
1.5%HNTs	6.160	.603	5.560	.527	2.731	9	.023	S	0.864

3.4.3 Elongation Percentage:

The two experimental groups (1 and 1.5 wt % HNTs) had shown a higher mean values than the control in both elongation 1 (before weathering) and elongation 2 (after weathering), but the results of elongation 2 were lower than elongation 1 in all categories (control, 1 wt % HNTs and 1.5 wt % HNTs) (Figure 3-12).

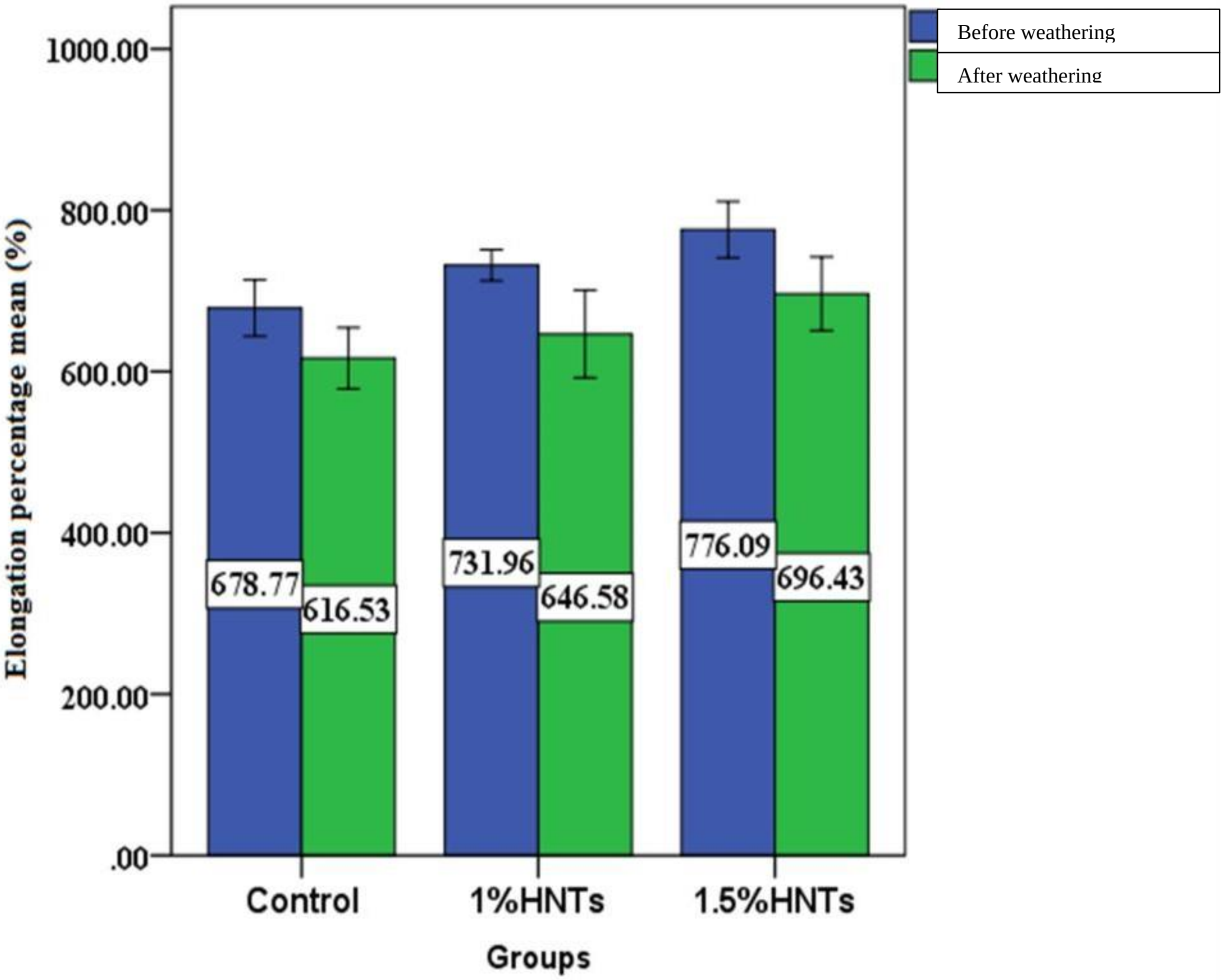

Figure 3-12: Bar chart shows the mean values of elongation percentage test results for all study groups before and after weathering.

Descriptive and statistical tests for elongation percentage results had been conducted and one- way ANOVA test was performed to find out if there was any significant difference among groups in elongation 1 and elongation 2. The results showed a highly significant difference among elongation 1 groups (*P* <0.01) and significant difference among elongation 2 groups (*P* <0.05) (Table 3-8).

Table 3-8: Descriptive and statistical tests with One- way ANOVA test for elongation percentage results.

	Groups	Minimum	Maximum	Mean	±SD	F	P value	Sig.	ES
Elongation 1	Control	611.100	768.500	678.770	48.692	13.042	.000	HS	0.491
	1%HNTs	675.500	771.100	731.962	26.906				
	1.5%HNTs	702.200	860.000	776.089	48.657				
Elongation 2	Control	488.000	677.700	616.530	52.959	3.877	.033	S	0.223
	1%HNTs	544.000	760.000	646.579	75.791				
	1.5%HNTs	622.200	786.600	696.428	63.654				

Levene 1=0.082[NS], Levene 2=0.182[NS DF=2

Post- hoc test (Tukey HSD) had been conducted to compare the mean values of each two groups in elongation 1 and elongation 2. The result showed a significant difference between control and 1 wt % HNTs (*P* <0.05) and a highly significant difference between control and 1.5 wt %(*P* <0.01), but there was a non-significant difference between 1% and 1.5% HNTs. Meanwhile in elongation 2, the control showed a non-significant difference with 1 wt % HNTs but it had a significant difference with 1.5% HNTs (*P* <0.05). Also, there was a non-significant difference between 1% and 1.5%HNTs (Table 3-9).

Table 3-9: Tukey HSD test for elongation percentages results.

Multiple Comparisons					
Tukey HSD					
Dependent Variable	(I) Groups	(J) Groups	Mean Difference (I-J)	*P*	Sig.
Elongation 1	Control	1%HNTs	-53.192	.025	S
		1.5%HNTs	-97.319	.000	HS
	1%HNTs	1.5%HNTs	-44.127	.071	NS
Elongation 2	Control	1%HNTs	-30.049	.561	NS
		1.5%HNTs	-79.898	.027	S
	1%HNTs	1.5%HNTs	-49.849	.216	NS

Paired t-test had been conducted to compare elongation 1 results with those of elongation 2 , and the results implied a significant difference between elongation 1 and elongation 2 in all study groups ($P < 0.05$),with exception for 1.5 wt % HNTs where the difference was highly significant ($P < 0.01$) (Table 3-10).

Table 3-10: Paired t-test for elongation percentage test results before and after weathering.

Groups	Elongation1		Elongation2		T	df	P value	Sig.	ES
	Mean	±SD	Mean	±SD					
Control	678.770	48.692	616.530	52.959	2.686	9	.025	S	0.849
1%HNTs	731.962	26.906	646.579	75.791	3.064	9	.013	S	0.969
1.5%HNTs	776.089	48.657	696.428	63.654	4.224	9	.002	HS	1.336

3.4.4 Shore A hardness test

The two experimental groups (1 wt % and 1.5 wt % HNTs) had shown a higher mean values than the control in both hardness 1 (before weathering) and hardness 2 (after weathering). However, the results of hardness1 were lower than hardness 2 in all study groups (Figure 3-13).

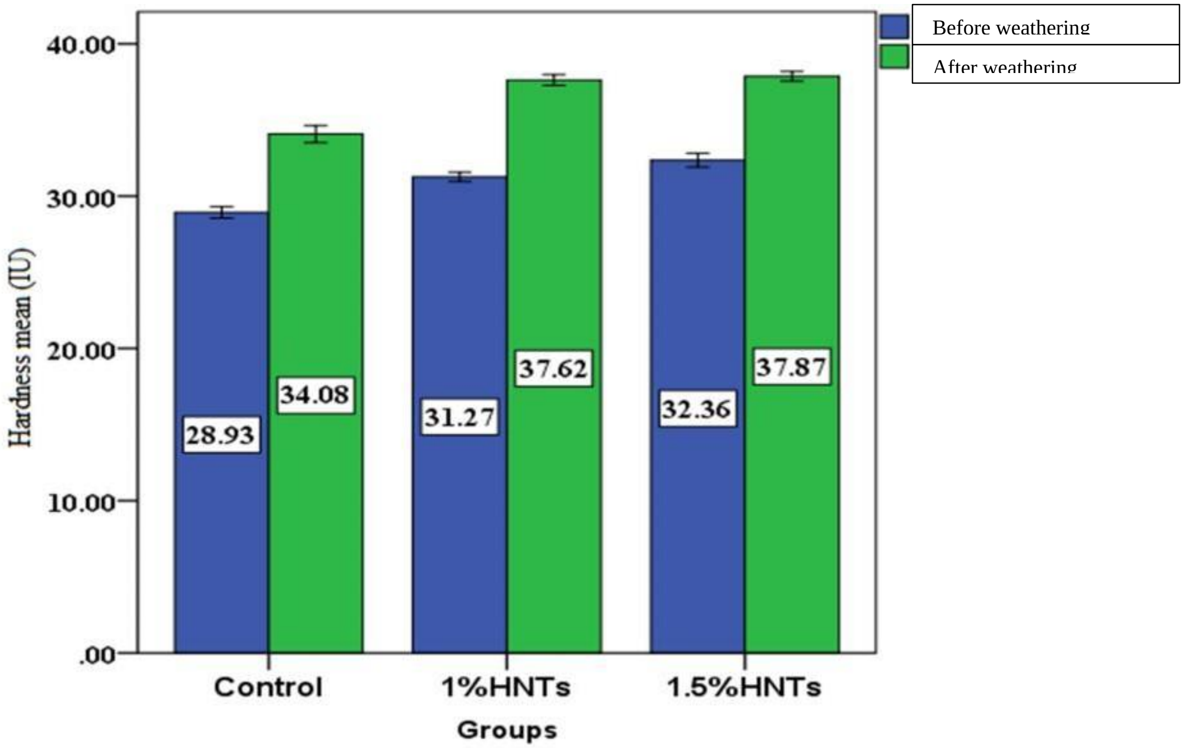

Figure 3-13: Bar chart shows the mean values of shore A hardness test results for all study groups before and after weathering.

Descriptive and statistical tests for shore A hardness results were performed and one - way ANOVA test had been conducted in order to reveal if there was any significant difference among groups within hardness 1 and hardness 2.The results showed a highly significant difference among study groups in hardness 1 and hardness 2 (*P* <0.01) (Table 3-11).

Table 3-11: Descriptive and statistical tests with one- way ANOVA test for shore A hardness results.

	Groups	Minimum	Maximum	Mean	±SD	F	P value	Sig.	ES
Hardness 1	Control	28.000	29.500	28.930	.531	105.696	.000[HS]	HS	0.887
	1%HNTs	30.600	31.800	31.270	.427				
	1.5%HNTs	31.700	33.600	32.360	.638				
Hardness 2	Control	33.000	35.800	34.080	.790	127.255	.000	HS	0.904
	1%HNTs	37.000	38.300	37.620	.489				
	1.5%HNTs	37.100	38.500	37.870	.442				

Levene 1=0.517[NS], Levene 2=0.574[NS], DF=2.

Post- hoc test (Tukey HSD) had been performed to compare the mean values among the study categories in hardness 1 and hardness 2. And the result revealed a highly significant difference between each two groups within hardness 1 and hardness 2 (*P* <0.01), except for the difference between 1%HNTs and 1.5%HNTs after weathering which was non-significant (Table 3-12).

Table 3-12 Tukey HSD test for elongation percentages results.

Multiple Comparisons					
Tukey HSD					
Dependent Variable	(I) Groups	(J) Groups	Mean Difference (I-J)	Sig.	
Hardness1	Control	1%HNTs	-2.3400	.000	HS
		1.5%HNTs	-3.4300	.000	
	1%HNTs	1.5%HNTs	-1.0900	.000	
Hardness2	Control	1%HNTs	-3.5400	.000	
		1.5%HNTs	-3.7900	.000	
	1%HNTs	1.5%HNTs	-.2500	.620	NS

Paired t-test was performed to compare hardness 1 and hardness variables, and the results implied a highly significant difference between the two groups in all categories (control, 1 and 1.5 wt %HNTs) (*P* <0.01) (Table 3-9).

Table 3-13: **Paired t -test for shore A hardness test results before and after weathering.**

Groups	Hardness 1		Hardness 2		T	df	P value	Sig.	ES
	Mean	±SD	Mean	±SD					
Control	28.930	.5314	34.080	.7899	18.674	9	.000	HS	5.905
1%HNTs	31.270	.4270	37.620	.4894	28.257	9	.000	HS	8.936
1.5%HNTs	32.360	.6381	37.870	.4423	27.216	9	.000	HS	8.606

3.4.5 Surface roughness test:

The two experimental groups (1 wt % and 1.5 wt % HNTs) had shown an increased mean value when compared with control group in both roughnesses 1 (before weathering) and roughness 2 (after weathering). However, the mean values of all study groups in roughness 2 were higher than their counterparts in roughness 1 (Figure 3-14).

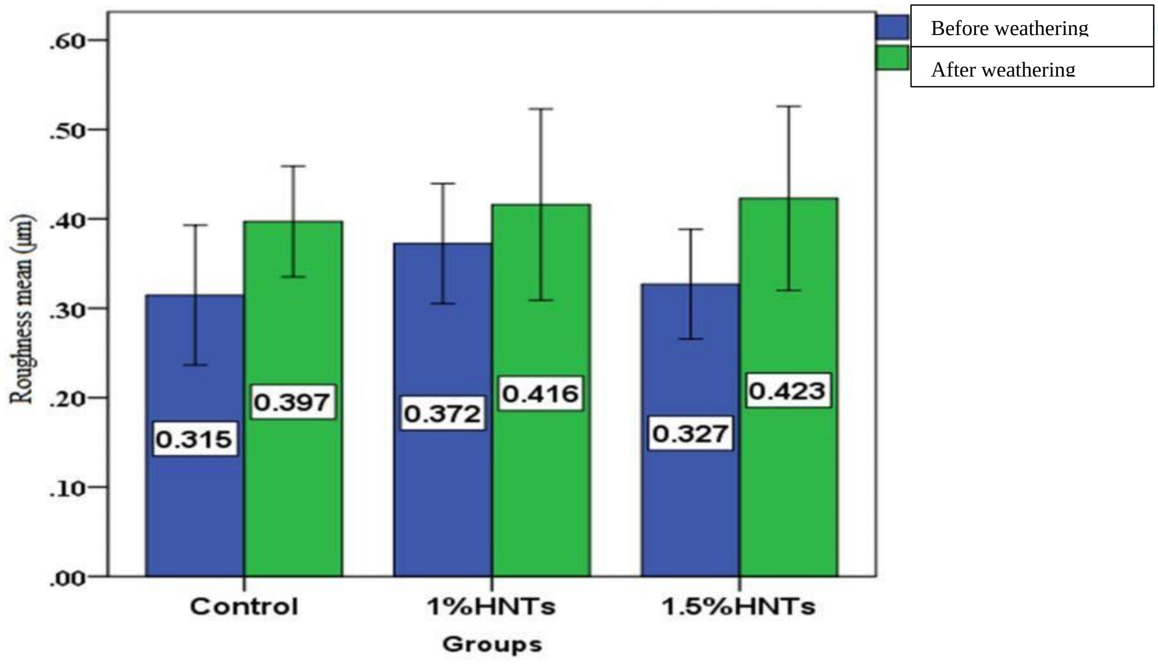

Figure 3-14: Bar chart shows the mean values of surface roughness test results for all study groups before and after weathering.

Descriptive and statistical tests for surface roughness variables were conducted and one- way ANOVA test had been performed so as to find out if there was any significant difference among the study groups of roughness 1 and roughness 2. The result revealed a non-significant difference among study groups within roughness 1 and roughness 2 (Table 3-14).

Table 3-14: Descriptive and statistical tests with One- way ANOVA test for surface roughness test results.

	Groups	Minimum	Maximum	Mean	±SD	F	P value	Sig.	ES
Roughness1	Control	.170	.490	.315	.109	.985	.386	NS	0.068
	1%HNTs	.200	.515	.372	.094				
	1.5%HNTs	.205	.500	.327	.086				
Roughness 2	Control	.230	.550	.397	.087	.107	.899	NS	0.008
	1%HNTs	.240	.790	.416	.150				
	1.5%HNTs	.260	.610	.423	.144				

Paired t-test was performed to compare roughness 1 and roughness 2 variables, and the results revealed a non- significant difference between roughness 1 and roughness 2 in all categories (control ,1%HNTs and1.5% HNTs) (Table 3-15).

Table 3-15: Paired t- test for surface roughness test results before and after weathering.

Groups	Roughness 1		Roughness 2		T	df	*P* value	Sig.	ES
	Mean	±SD	Mean	±SD					
Control	.315	.109	.397	.087	1.619	9	.140	NS	0.512
1%HNTs	.372	.094	.416	.150	.969	9	.358	NS	0.307
1.5%HNTs	.327	.086	.423	.144	1.662	9	.131	NS	0.526

Chapter Four

Discussion

Discussion

Maxillofacial materials should match natural tissue in terms of physical and mechanical properties. Tear and tensile strength of these materials should be of sufficient degree, while their surface hardness should be close to that of the surrounding skin (**Eleni *et al*., 2011; Aziz *et al*., 2003).**

Longevity is also a substantial characteristic in such prosthesis, since defect like cracks, discoloration and degradation might necessitate prostheses replacement **(Leonardi *et al*., 2008; Eleni *et al*., 2011)**.

Although silicone is the most commonly used material in maxillofacial prostheses, but none of the commercially available silicone elastomers can fulfill the aforementioned requirements **(Aziz *et al*, 2003).**

Moreover, maxillofacial prostheses made from silicone elastomers have short service life and need to be replaced periodically at 6-12 months intervals **(Al-Dharrab *et al*., 2013).**

Environmental conditions (humidity, sunlight, air pollution, ultraviolet light) may be the main causes behind material deterioration. These factors could be simulated by accelerated artificial weathering which can predict the degradation that polymer undergo when the appliance is in service **(Pospisil *et al*., 2006).**

In fact, it is difficult to determine the exact time of artificial weathering that equivalent to 6 months of clinical use ,and that is because such calibrations rely on a number of factors such as; the natural weather condition of study area ,type of material being studied and the properties of weather-ometer .However, , it can be roughly calculated depending on some information such as the mean of cumulative global radiation at Baghdad which is about (216 MJ/m^2 per year) **(Al-Riahi and Al-Kayssi in 1998; Al-Douri, 2016),** Also weather-ometer device can be adjusted in accordance with cycle 7 of ASTM G-154G, then the period is calculated according to the equation below **(Mcgreer M 2001)**:

$KJ/m^2=W/m^2\times3.6\times Hours$

Relying on the theses information; it can be assumed that every one year of clinical use equivalent to 387 hour inside the weathering device (**Atta Allah and Moudhaffer, 2017)**. Accordingly, 6 months period is equivalent to about 200 hour of simulated weathering.

4.1 Tear strength:

It is that quality of material which represents the resistance of tearing forces and acting as an indicator for material durability and marginal integrity during clinical use, particularly at prostheses-skin contact area **(Aziz *et al*., 2003; Sakaguchi and Powers, 2012**). Such quality is deemed to be the most valuable characteristic of maxillofacial prosthesis. That is because the prosthesis becomes thinner at the margin, making this area the weakest and the most susceptible to spoilage during clinical use (**Bibb *et al*., 2010**).

4.1.1 Tear strength test before weathering:

The test outcomes reveal an increase in tear strength in both experimental groups (1% and1.5% HNTs) when compared with control group, with the highest value recorded for 1.5%HNTs. Such improvement may be owning to well dispersion of HNTs (as revealed by SEM) and their physical interaction with VST-50F matrix.

Physically, nanoparticles have the ability to form three-dimensional meshes inside silicone polymer matrix and trapping some chains of polymer within such mesh. This interaction is supposed to have a role in prohibiting the movement not only of the trapped polymer chains, but also of the other polymer segments .Consequently, the matrix density might be changed leading to higher tear resistance **(Harper, 2002; Zhu and Sternstein, 2003**).

In fact, the high tear strength that characterizes the elastomer is attributed to their ability to dissipate the strain energy near the beginning of the propagated crack. Nanoparticle ,in turn fritter their energy within polymer matrix once the crack propagates ,resulting in increased tear strength of elastomers (**Sun *et al.*, 2009**).

The study outcomes before weathering agree with what achieved by **Cevik and Eraslan (2017)** in their study concerning the addition of 10% TiO_2, where they found an increase in tear strength readings after reinforcement .Also, this study agrees with **Shakir and Abdul-Ameer (2018)** who studied the influence of TiO_2 nanofillers on some mechanical properties of two different silicone materials, namely VST50F and Cosmesil M511.

However, the results disagree with **Nobrega et al. in 2016,** as they reported a fluctuated readings of incline and decline in tear strength when they added 1% and 2% concentrations of three nano-oxides (ZnO, $BaSO_4$, and TiO_2). The result also contradicts with **Ikram (2013)** research which revealed a non-significant change in tear readings after silicone reinforcement with CaCO3. This controversy might own to the difference in nano fillers or in their concentrations.

4.1.2 Tear strength after weathering

The result of tear after 200 hour of simulated weathering shows a significant decrease in all study categories (control, 1 wt % HNTs and 1.5 wt % HNTs) when compared with tear result before weathering. Such change may be explained as follow: weathering lead to chemical activation within polymer chains, this reaction is basically photo-oxidation accompanied by release of free radicals which in turn react with each other leading to continuous cross-linking .Beside that, they react with oxygen to form what called (peroxyradicals) that render the elastomer brittle and inelastic **(Rabek *et al.*, 2005; Paravina *et al.*, 2009).**

The study outcomes concerning tear results after weathering are in agreement with **Hatamleh *et al.* (2011)** in their study ,which was about the impact of out-door weathering conditions on TechSil S 25 silicone ,where the results revealed a significant decline in tear readings after weathering. Furthermore, **Zardawi *et al.* (2015)** also reported deterioration in tear strength of two different silicone materials as a result of simulated weathering. However, the study outcomes conflicted with **Polyzios *et al.* (2011)** as they reported a non-significant change in tears strength of Silasto30 and Premium 2 silicone material after one year of artificial weathering in dark. Meanwhile **Nobrega *et al.* (2016)** reported an increase in tear readings of MDX4-4210 silicone reinforced with different fillers after artificial weathering. Such conflict may be attributed to the difference in materials or in the weathering conditions.

4.2 Tensile strength and Elongation percentage:

Tensile strength refers to the largest stress that the material can bear just before the starting of failure (**Sakaguchi and Powers, 2012**). Through the daily use, the marginal parts of the facial device are submitted to larger tensile stress than other parts, particularly during prosthesis removal. Thus, tensile strength of material that was used in maxillofacial prosthesis is an influential property and detrimental factor in prosthesis shelf life (**Dhuru, 2004**).

4.2.1 Tensile strength and elongation percentage before weathering:

The result of these two tests before weathering reveals a significant rise in both experimental groups (1%HNTs and 1.5%HNTs) in comparison with control. These findings can be explained as follow; when tensile stress applied to reinforce silicone polymer, the polymer chains and the reinforcing fillers would undergo sliding movement over each other, thus the chains would be protected from breakage with the aid of fillers. Additionally, polymer matrix has the ability to dissipate the applied force energy to heat; hence the remaining energy is less than what required breaking polymer chains .Reinforcing fillers play a role in the dispersal of such energy **(Rajkumar *et al.* 2013; Wang *et al.*, 2014**).

The study outcomes regarding tensile and elongation percentage tests before weathering coincided with what obtained by **Mohamed Ali and Fatalla (2018)** in their study concerning the impact of reinforcement of RTV silicone with Zirconium Silicate nanofillers. Also, it agrees with **Yeh, H. (2014)** who studied the influence of silica fillers on silicone elastomer.

However, other studies have different findings, **Al-qenae (2010)**, for example, reported a decline in the readings of tensile and elongation when he reinforced RTV silicone with nano alumina ceramic fibers. **Ikram (2013)** also detected a non-significant change in these two properties after the addition $CaCO_3$. Such controversy may be attributed to the difference in types of the reinforcing fillers or in the reinforcement techniques.

4.2.2 Tensile strength and elongation percentage after weathering:

The study results of tensile and elongation percentage after weathering revealed a significant decline in the readings of these two properties in all study categories. Such decrease probably due to continual cross-linking that caused by accelerated ultraviolet light which is accompanied by volatile byproducts release, rendering the material inelastic and more susceptible to deformation under lighter force **(Hatamleh *et al*., 2010).**

The study outcomes concerning the weathering was coincided with **Nguyen *et al*. (2013)** in their study which was about the impact of opacifiers on MDX4-4210 silicone, where the results revealed a decrease in these two properties after weathering .Also, the study agreed with **Atta Allah and Moudhaffer (2017)** who studied the impact of weathering on SiO_2 reinforced Silicone polymer, where the tensile readings showed significant decrease.

Meanwhile, **Al-Harbi *et al*. (2015**) did not find significant change in tensile results of A-2186 silicone when it subjected to outdoor weathering. Such conflict may be due the difference in weathering conditions or difference in type of nano fillers.

4.3 Shore A hardness test

It refers to material resistance to plastic distortion that caused by indentation load, and it is considered as a determinant factor for degree of softness (**Liu *et al.*, 2015**). As material flexibility depend on its hardness, then it is regarded as an influential property and its value should be within the range of surrounding tissue hardness (**Hatamleh and Watts, 2010b**).

4.3.1 Shore A hardness before weathering

The hardness results before weathering revealed a highly significant increase in both experimental groups (1%HNTs and 1.5%HNTs) compared with control readings, with the highest value recorded for 1.5%HNTs. That’s mean the increase was gradual and directly proportional with HNTs increment.

Such findings could be explained as follow; the nano fillers are well dispersed within the polymer (as shown in SEM) and are capable of forming networks inside polymer progressively, reducing the inter-aggregate space consequently, making the material stiffer and harder **(Hasse *et al*, 2004)**.

In fact, the material elasticity relies on the internal forces (inter-atomic or inter-molecular). When such forces increase, the elastic modulus will increase as well, rendering the material stiffer **(Sakaguchi and Powers, 2012)**. Accordingly, increasing the nano fillers concentration will increase the amount of absorbed energy from the fillers, thus the intermolecular force increase and the hardness will increase as a consequence **(Hasse *et al*, 2004)**.

The study outcomes before artificial weathering was in agreement with **Tukmachi and Moudhaffer (2017)** as they reported an increase in hardness readings of VST-50 silicone after the incorporation of SiO_2 nano fillers in different concentrations**. Moudaffer and Al Smael (2018)** also obtain the same findings in their study which was about the effect of titanium silicate nano particles on VST50 silicone.

Whereas **Nobrega *et al.* (2016)** found that; the addition of three different nano oxides (ZnO, $BaSO_4$ and TiO_2) resulted in decline in hardness readings. Such controversy could be attributed to the difference in technique, in fillers types or in fillers concentrations.

4.3.2 Shore A hardness after weathering

The hardness readings after simulated weathering showed a significant increase in all study categories. These outcomes may happen as a result of continual polymerization which is attributed to the ultraviolet light exposure during simulated weathering period **(Nguyen *et al.*, 2013).** UV light absorption make the polymer network unstable, and the excess energy will be transmuted between the neighboring molecules, such events in turn will lead to degradation of these molecules as a result of photo-chemical reactions , making the material harder **(Dos Santos *et al.*, 2012)**..

The study outcomes concerning the hardness after weathering was in agreement with **Guiotti *et al*. (2016)** in their study, where the hardness readings of ZnO reinforced MDX4-4210 silicone increased significantly as a result of artificial weathering. Moreover, the result was in a line with the study of **Nobrega *et al*. (2016),** where weathering also increased the hardness of MDX4-4210 that was reinforced with different nano-oxides (TiO_2, $BaSO_4$, and ZnO).

On the other hand, **Nguyen *et al*. (2013)** found a decline in hardness results when they subjected MDX4 -4210 silicone to artificial weathering. This conflict probably due to the difference in weathering conditions or in study material.

4.3 Surface roughness

It represents the measure of fine irregularity of the material outer surface . It is considered as valuable indicator for material mechanical execution; as such surface irregularity might be a nucleation area for propagation of cracks or corrosion **(Al-Dharrab *et al*., 2013).**

The outcomes of study regarding roughness show a non- significant change not only between study groups before weathering but also with their counterparts after weathering. These findings may be due to the small concentration of HNTs that had been incorporated within VST-50F silicone. Besides that, HNTs are nano-sized and well distributed within polymer matrix (as revealed by SEM). All the aforementioned facts together make the amount and the effect of HNTs on the material surface insignificant, hence surface roughness readings did not change significantly as such test concern with outer surface irregularities.

Chapter Five

Conclusion and Suggestion

5.1 Conclusions

In the light of the results obtained ,the study concluded the following :

1- The incorporation of HNTs into VST-50F silicone resulted in remarkable improvement in some properties, namely tear strength, tensile strength, and elongation percentage, with the highest enhancement recorded for 1.5 wt % HNTs.

2- The incorporation of HNTs elevated the surface hardness significantly. Such elevation was directly proportionate with the HNTs concentration.

3- After 200 hour of simulated weathering there was a drop in the values of tear strength, tensile strength and elongation percentage of the HNTs reinforced silicone but they still higher than those of control group.

4- Simulated weathering for 200 hour caused a significant elevation in hardness values of both reinforced and non-reinforced VST-50F silicone, but the latter still lower than the former.

5- Surface roughness did not change significantly neither by HNTs addition nor by simulated weathering.

6- HTNs did not preserve VST-50F from weathering consequences.

5.2 Suggestions

After reviewing the outcomes of this study, additional researches might be required concerning the following issues:

1- The impact of HNTs incorporation on other properties of silicone material, like wettability, water sorption, solubility and shear bonding.
2- Color stability of HNTs reinforced silicone elastomer.
3- The impact of HNTs incorporation on HTV or on other types of RTV.
4- The effect of 500-1000 hour of artificial weathering on silicone material.
5- Fatigue life time of maxillofacial silicone before and after weathering.

References

References

(A)

- **ABDULLAH, H.A. & ABDUL - AMEER, F.M.** 2018. Evaluation of some mechanical properties of a new silicone elastomer for maxillofacial prostheses after addition of intrinsic pigments. Saudi Dent J. 30(4), 330-336.
- **ABDULLAYEV, E. & LVOV, Y.** 2013. Halloysite clay nanotubes as a ceramic skeleton for functional biopolymer composites with sustained drug release. J. Mater. Chem. B, 1, 2894-2903.
- **ABDULLAYEV, E., LVOV, Y.** 2011. Halloysite clay nanotubes for controlled release of protective agents. J Nanosci Nanotechnol., 11(11),10007-26.
- **AL-DHARRAB, A. A., TAYEL, S. B. & ABODAYA, M. H.** 2013. The effect of different storage conditions on the physical properties of pigmented medical grade I silicone maxillofacial material. ISRN Dent, 582051-582057.
- **AL-DOURI, Y. & ABED, F. M.** 2016. Solar energy status in Iraq: Abundant or not—Steps forward. J Renew Sustain Energy, 8(2), 025905.
- **AL-HARBI, F. A., AYAD, N. M., SABER, M. A., ARREJAIE, A. S. &MORGANO, S. M. 2015.** Mechanical behavior and color change of facial prosthetic elastomers after outdoor weathering in a hot and humid climate. J Prosthet Dent, 113(2), 146-151.
- **MOUDAFFER, M. & AL SMAEL, M.** 2018. The Effect of Nano Titanium Silicate Addition on Some Properties of Maxillofacial Silicone Material. J Res Med Dent Sci, 6. 127-132.

- **MOUDAFFER ,M. & FATALLA, A.** 2018. Effects of Zirconium Silicate Nanofillers on Some Properties of Room- Vulcanized Maxillofacial Silicone Elastomers. Res J Pharm Biol Chem Sci, 9. 1023-1031.
- **AL-JUDY, H.** 2019. Mechanical Properties of Chitosan Incorporated in Maxillofacial Silicone and its Anti Candidal Activity In Vitro. J Res Med Dent Sci, 6. 101-107.
- **ALKATHEERI, M. S., PALASUK, J., ECKERT, G. J., PLATT, J. A& BOTTINO, M. C.** 2015. Halloysite nanotube incorporation into adhesive systems—effect on bond strength to human dentin. *Clin.* Oral Investing, 19, 1905-1912.
- **AL-QENAE, N.** 2010. Nano ceramic fiber reinforced silicone maxillofacial prosthesis. M.Sc. Thesis; Indiana University School of Dentistry.
- **ALQUTAIBI, A. Y.** 2015. Materials of facial prosthesis: History and advance. Int J Contemp Dent Med Rev, 2015, 4.
- **AL-RIAHI, M. & AL-KAYSSI, A.** 1998. Some comments on time variation in solar radiation over Baghdad, Iraq. Renew Energy, 14(1-4), 479-484.
- **ALSAMARAAY, M. E., FATALLA, A. & JASSIM, R. K.** 2017. Effect of the Addition of Polyamide (Nylon 6) Micro-Particles on Some Mechanical Properties of RTV Maxillofacial Silicone Elastomer Before and After Artificial Aging. BPJ, 10, 1933- 1942.
- **ANUSAVICE, K.** (2012). Philips' science of dental materials, 12th ed. Missouri: Saunders Co.
- **ARIANI, N.** 2015. Microbial Biofilms on Silicone Facial Prostheses: A master thesis. UMCG,17-20.

- **ASTM G**154-06, 2006. Standard Practice for Operating Fluorescent Ultraviolet (UV) Lamp Apparatus for Exposure of Nonmetallic Materials. ASTM International, West Conshohocken, PA, USA.
- **ATTA ALLAH, A. & MOUDAFFER, M.** 2017. Influence of Artificial Weathering on Some Properties of Nano Silicon Dioxide Incorporated Into Maxillofacial Silicone. Int J Surg Res, 6(5), 423-428.
- **AZIZ, T., WATERS, M. & JAGGER, R.** 2003. Analysis of the properties of silicone rubber maxillofacial prosthetic materials. J Dent, 31, 67-74.

(B)

- **BARHATE, A., GANGADHAR, S., BHANDARI**, **A., &JOSHI, A**. 2015.Materials Used in Maxillofacial Prosthesis: A Review. Pravara Medical Review, 7(1). 5-8.
- **BEUMER, J., CURTIS, T.A., & MARUNICK, M.T.** 1996. Maxillofacial rehabilitation: prosthodontic and surgical considerations. Ishiyaku Euroamerica.
- **BEUMER, J., MARUNICK, M. T. & ESPOSITO, S. J.** 2011. Maxillofacial Rehabilitation: prosthodontic and surgical management of cancer-related, acquired, and congenital defects of the head and neck, Quintessence Pub.
- **BIBB, R., EGGBEER, D. & EVANS, P.** 2010. Rapid prototyping technologies in soft tissue facial prosthetics: current state of the art. Rapid Prototyp J, 16, 130-137.

(C)

- **CEVIK, P., & ERASLAN, O.** 2017. Effects of the addition of titanium dioxide and silaned silica nanoparticles on the mechanical properties of maxillofacial silicones. J Prosthodont, 26, 611-615.

- **CHANDRA, P., AHMAD, F., BHARATHI, S. S., NAIR, C. & KUMAR, A.** 2015. Present Trends in Maxillofacial Prosthetic Material: An Inclination toward Silicones. JDSOR, 6**,** 72-4.
- **CHANG, TL., GARRETT, N., ROUMANAS, E., & BEUMER. J.** 2005. Treatment satisfaction with facial prostheses. J Prosthet Dent, 94(3)**,** 275-280.
- **COLAS, A. AND CURTIS, J. 2005**. Silicone biomaterials: History and chemistry & Medical applications of silicones. 2nd Edition (Biomaterials Science).

(D)

- **DEBA, K., YUNUS. N., & TAMRAKAR, AK.,** 2012a. Oral & Maxillofacial Prosthetics-I Objectives & History. Healtalk, 4(6)**,** 18-20.
- **DEBA, K., YUNUS, N. & TAMRAKAR, A. K.** 2012. Oral & Maxillofacial Prosthetics-I: Objectives & History. Healtalk, 4, 18-20.
- **DEEPTHI, V. S.** 2016. Maxillofacial Prosthetic Materials-An Update. JIMD, 3, 02-11.
- **DESHMANE, C., YUAN, Q., PERKINS, R. S. & MISRA, R. D. K.** 2007. On striking variation in impact toughness of polyethylene–clay and polypropylene–clay nanocomposite systems: the effect of clay–polymer interaction. MSE: A, 458, 150-157.
- **DHURU, VB**., (2004). Contemporary Dental Materials. 1st ed.; Oxford University Press: USA.

- **DOOTZ, E., KORAN, A. R. & CRAIG, R.** 1994. Physical properties of three maxillofacial materials as a function of accelerated aging. J Prosthet Dent, 71(4), 379-383.
- **DOS SANTOS, D. M., GOIATO, M. C., MORENO, A., PESQUEIRA, A. A., DE CARVALHO DEKON, S. F. & GUIOTTI, A. M.** 2012. Effect of addition of pigments and opacifier on the hardness, absorption, solubility and surface degradation of facial silicone after artificial ageing. Polym Degrad Stab, 97(8), 1249-1253.

(E)

- **ELENI, PN., KROKIDA, MK., POLYZOIS, GL., GETTLEMAN, L.** 2013. Effect of different disinfecting procedures on the hardness and color stability of two maxillofacial elastomers over time. J Appl Oral Sci; 21(3): 278-83.
- **ELENI, PN., KROKIDA, MK., POLYZOIS, GL., GETTLEMAN, L., BISHARAT, G.I**. 2011. Effect of outdoor weathering on facial prosthetic elastomers. Odontology; 99: 68-76.
- **ELENI, P. N., KROKIDA, M. K. & POLYZOIS, G. L.** 2009b. The effect of artificial accelerated weathering on the mechanical properties of maxillofacial polymers PDMS and CPE. Biomed Mater, 4(3), 35001.
- **ELENI, P. N., KROKIDA, M. K., POLYZOIS, G. L. & GETTLEMAN, L.**2013a. Effect of different disinfecting procedures on the hardness and color stability of two maxillofacial elastomers over time. J Appl Oral Sci, 21(3), 278-283.
- **ELENI, P. N., PERIVOLIOTIS, D., DRAGATOGIANNIS, D. A., KROKIDA,M. K., POLYZOIS, G. L., CHARITIDIS, C. A., ZIOMAS, I. & GETTLEMAN, L.** 2013b. Tensile and microindentation properties of maxillofacial elastomers after different disinfecting procedures. J Mech Behav Biomed Mater, 28, 147-55.

(F)

- **FEITOSA, S. A., MÜNCHOW, E. A., AL-ZAIN, A. O., KAMOCKI, K‹. & BOTTINO, M. C.** 2015. Synthesis and characterization of novel halloysite-incorporated adhesive resins. J. Dent., 43, 1316-1322.
- **FERRANTE, F., ARMATA, N. and LAZZARA, G.** 2015. Modeling of the halloysite spiral nanotube. J. Phys. Chem. C, 119, 16700-16707.
- **FUJII, K., MINAMI, H., ARIKAWA, H., KANIE, T., BAN, S. & INOUE, M.** 2005. Mechanical properties and bond strength of silicone-based resilient denture liners. Dent mater, 24(4), 667-675.

(G)

- **GOIATO, M. C., PESQUEIRA, A. A., DA SILVA, C. R., GENNARI FILHO,H. & DOS SANTOS, D. M.** 2009a. Patient satisfaction with maxillofacial prosthesis. Literature review. J Plast Reconstr Aesth Surgy, 62(2) 175-180.
- **GPT 9**. 2017. The Glossary of Prosthodontic Terms.
- **GUIOTTI AM, GOIATO MC, DOS SANTOS DM** 2010. Evaluation of the shore a hardness of silicone for facial prosthesis as to the effect of storage period and chemical disinfection. J Craniofac Surg; 21: 323-27.
- **GUIOTTI,A. M., GOIATO, M. C., DOS SANTOS, D. M., VECHIATO-FILHO, A. J., CUNHA, B. G., PAULINI, M. B., MORENO, A. & DE ALMEIDA, M. T. G.** 2016. Comparison of conventional and plant-extract disinfectant solutions on the hardness and color stability of a maxillofacial elastomer after artificial aging. J Prosthet Dent, 115(4), 501-508.
- **GUPTA, A., RAJPUT, G.&AMINA.** 2017. Materials Used for Maxillofacial Prosthesis: A Review. IOSR, 16, 87-89.

(H)

- **HAN, Y., KIAT-AMNUAY, S., POWERS, J. M. & ZHAO, Y**. 2008. Effect of nano-oxide concentration on the mechanical properties of a maxillofacial silicone elastomer. J Prosthet Dent, 100, 465- 473.
- **HARKNESS, B. & TAYLOR, R.** 1999. Polymerization of cyclosiloxanes in the presence of fillers. 6001928.
- **HARPER, C. A.** 2002. Handbook of plastics, elastomers, and composites, McGraw-Hill New York.
- **HASSE A, WEHMEIER A & LUGINSLAND HD** (2004). Crosslinking and reinforcement of silica/silane-filled rubber compounds. J Rub World; 230(1): 22.
- **HATAMLEH, M. M. & WATTS, D. C.** 2010b. Mechanical properties and bonding of maxillofacial silicone elastomers. Dent Mater, 26, 185-191.
- **HATAMLEH, M. M., HAYLOCK, C., WATSON, J. & WATTS, D. C.** 2010. Maxillofacial prosthetic rehabilitation in the UK: a survey of maxillofacial prosthetists' and technologists' attitudes and opinions. Int J Oral Maxillofac Surg, 39(12), 1186-1192.
- **HATAMLEH, M. M., POLYZOIS, G. L., NUSEIR, A., HATAMLEH, K. &ALNAZZAWI, A**. 2016. Mechanical Properties and Simulated Aging of Silicone Maxillofacial Elastomers: Advancements in the Past 45 Years. J Prosthodont, 25(5), 418-426.
- **HATAMLEH, M. M., POLYZOIS, G. L., SILIKAS, N. & WATTS, D. C. 2011.** Effect of extra oral aging conditions on mechanical properties of maxillofacial silicone elastomer. J Prosthodont, 20(6), 439-446.
- **HAUG, S. P., ANDRES, C. J., MUNOZ, C. A. & BERNAL, G.** 1992a. Effects of environmental factors on maxillofacial elastomers: Part IV--Optical properties. J Prosthet Dent, 68(5), 820-823.

- **HAUG, S. P., ANDRES, C. J., MUNOZ, C. A. & OKAMURA, M.** 1992b. Effects of environmental factors on maxillofacial elastomers: part III—physical properties. J Prosthet Dent, 68(4), 644-651.

(I)

- **IKRAM, F.** 2013. Effect of calcium carbonate nano fillers on some properties of maxillofacial silicone elastomer. Ph.D, Hawler Medical University.
- **ISO 23529 STANDARDIZATION 2016**: Rubber -- General procedures for preparing and conditioning test pieces for physical test methods.
- **ISO 34-1 STANDARDIZATION 2015**: Rubber, vulcanized or thermoplastic -- Determination of tear strength -- Part 1: Trouser, angle and crescent test pieces.
- **ISO 37 STANDARDIZATION 2017**: Rubber, vulcanized or thermoplastic - Determination of tensile stress-strain properties.
- **ISO 7619-1 STANDARDIZATION** 2010: Rubber, vulcanized or thermoplastic -- Determination of indentation hardness -- Part 1: Durometer method (Shore hardness).

(J)

- **JASDEEP, K., KIRANDEEP, K., GEETA, A. and SL, K. H.** 2016. NANOTECHNOLOGY IN DENTISTRY. World J. Pharm. Pharm. Sci., 5(4),570-582.
- **JHAVERI HM AND BALAJI PR** (2005). Nanotechnology: The future of dentistry. J Ind Pros Soc; 5:15-17.
- **JOUSSEIN, E., PETIT, S., CHURCHMAN, J., THENG, B., RIGHI,D.& DELVAUX**, B. 2005. Halloysite clay minerals–a review. De Gruyter.Clay Minerals. 40, 383-426.

(K)

- **KHINDRIA, S., BANSAL, S. & KANSAL, M.** 2009. "Maxillofacial prosthetic materials. The J Indian Prosthodont Soc, 9(1), 2-5.
- **KURTULMUS, H., KUMBULOGLU, O., ÖZCAN, M., OZDEMIR, G. &VURAL, C.** 2010. "Candida albicans adherence on silicone elastomers: effect of polymerization duration and exposure to simulated saliva and nasal secretion". Dent Mater, 26(1), 76-82.

(L)

- **LEMON, J. C., CHAMBERS, M. S., JACOBSEN, M. L. & POWERS, J. M**. 1995 .Color stability of facial prostheses. J Prosthet Dent, 74(6), 613-618.
- **LEONARDI A, BUONACCORSI S, PELLACCHIA V, MORICCA LM, INDRIZZI E, FINI G** (2008). Maxillofacial prosthetic rehabilitation using extraoral implants. J Craniofac Surg; 19(2): 398-405.
- **LI, X. N., ZHAO, Y. M., LI, S. B., LIU, X. C., WU, G. F., ZHEN, L. L. &WU, N.** 2007. Comparison of mechanical properties of Cosmesil M511 and A-2186 maxillofacial silicone elastomers. J US-China Med Sci, 4(1), 34-37.
- **LIU, Q., SHAO, L., FAN, H., LONG, Y., ZHAO, N., YANG, S., ZHANG, X& .XU, J.** 2015. Characterization of maxillofacial silicone elastomer reinforced with different hollow microspheres. J Mater Sci, 50, 3976- 3983.
- **LVOV, Y. & ABDULLAYEV, E.** 2013. Functional polymer–clay nanotube composites with sustained release of chemical agents. Prog. Polym. Sci., 38, 1690-1719.
- **LVOV, Y. M., DEVILLIERS, M. M. & FAKHRULLIN, R. F.** 2016b. The application of halloysite tubule nanoclay in drug delivery. Expert Opin. Drug Deliv., 13(7), 977-986.

(M)

- **MALLER US, KARTHIK KS & MALLER SV** (2010). Maxillofacial prosthetic materials—past and present trends. J Indian Acad Dent Spec, 1(2), pp.42-44.
- **MAHAJAN H & GUPTA K** (2012). Maxillofacial prosthetic materials: A literature review. J Orofac Res; 2, 87–90.
- **MANCUSO, D. N., GOIATO, M. C. & SANTOS, D. M. D.** 2009. Color stability after accelerated aging of two silicones, pigmented or not, for use in facial prostheses. Braz Oral Res, 23(2), 144-148.
- **MARKT, J. C. & LEMON, J. C.** 2001. Extraoral maxillofacial prosthetic rehabilitation at the MD Anderson Cancer Center: a survey of patient attitudes and opinions. J Prosthet Dent, 85(6), 608-613.
- **MARRO A, BANDUKWALA T & MAK W** (2016). Three-dimensional printing and medical imaging: a review of the methods and applications. Curr Probl Diagn Radiol , 45(1), pp.2-9.
- **MASSARO, M., LAZZARA, G., MILITO, S., NOTO, R., RIELA‹S** 2017**.**Covalently modified halloysite clay nanotubes: synthesis, properties, biological and medical applications .J. Mater. Chem. B., 5 (16):2867-82.
- **MASSARO, M., RIELA, S., BAIAMONTE,C.,BLANCO, J., GIORDANO, C., MEO, P. L., MILIOTO, S., NOTO, R., PARISI, F& .PIZZOLANTI, G.** 2016. Dual drug-loaded halloysite hybrid-based glycocluster for sustained release of hydrophobic molecules. RSC Adv., 6, 87935-87944.
- **MCGREER, M.** 2001. Atlas weathering testing guidebook. Chicago: Atlas Material Testing Technology LLC,60-62.
- **MITRA, A., CHOUDHARY, S. & GARG, H.** 2014. Maxillofacial prosthetic materials-an inclination towards silicones. J Clin Diagn Res, 8, ZE08.

- **MOHAMMAD, S. A., WEE, A. G., RUMSEY, D. J. & SCHRICKER, S. R.** 2010. "Maxillofacial materials reinforced with various concentrations of polyhedral silsesquioxanes". J Dent biomech, 1, 701845-701851.
- **MOHITE, U. H., SANDRIK, J. L., LAND, M. F. & BYRNE, G.** 1994. Environmental factors affecting mechanical properties of facial prosthetic elastomers. Int J Prosthodont, 7(5), 479-486.
- **MOMEN, G. & FARZANEH, M.** 2011. Survey of micro/nano filler use to improve silicone rubber for outdoor insulators. Rev. Adv. Mater. Sci, 27, 1-13.
- **MUTLUAY, M. M. & RUYTER, I. E.** 2007. Evaluation of bond strength of soft relining materials to denture base polymers. Dent Mater, 23(11), 1373- 1381.

(N)

- **NALLASWAMY, D.** 2017. Textbook of prosthodontics, JP Medical Ltd.
- **NAZIR, M. S., KASSIM, M. H. M., MOHAPATRA, L., GILANI, M. A.,RAZA, M. R. & MAJEED, K.** 2016. Characteristic properties of nanoclays and characterization of nanoparticulates and nanocomposites. Nanoclay Reinforced Polymer Composites. Springer, 35-55.
- **NGUYEN C.T., CHAMBERS M.S., POWERS J.M., KIAT-AMMUAY S** (2013). Effect of opacifiers and UV absorbers on pigmented maxillofacial silicone elastomer, part 2: Mechanical properties after artificial aging. J Prosthet Dent; 109:402-10.

- **NOBREGA, A. S., ANDREOTTI, A. M., MORENO, A., SINHORETI, M. A.,DOS SANTOS, D. M. & GOIATO, M. C.** 2016. Influence of adding nanoparticles on the hardness, tear strength, and permanent deformation of facial silicone subjected to accelerated aging. J Prosthet Dent, 116(4), 623- 629.

(P)

- **PADMAJA, S.** 2015. An insight into the future beckons of maxillofacial prosthodontics: Anaplastology. JDRR, 2, 91.
- **PARAVINA, R. D., MAJKIC, G., DEL MAR PEREZ, M. & KIAT-AMNUAY S.** 2009. Color difference thresholds of maxillofacial skin replications. J Prosthodont, 18(7), 618-625.
- **PASBAKHASH, P., CHURCHMAN, G.J., KEELING، J.L. PLATT, J. A**. 2013.Characterisation of properties of various halloysites relevant to their use as nanotubes and microfibre fillers. Appl. Clay Sci., 74:47-57.
- **POLYZOIS GL, ELENI PN, KROKIDA MK.** 2011. Effect of time passage on some physical properties of silicone maxillofacial elastomers. J Craniofac Surg; 22(5): 1617-21.
- **POLYZOIS, G. L. & FRANGOU, M. J.** 2002. Bonding of silicone prosthetic elastomers to three different denture resins. Int J Prosthodont, 15(6), 535- 538.
- **POSPíŠIL, J., PILAŘ, J., BILLINGHAM, N., MAREK, A., HORAK, Z. & NEŠPŮREK, S.** 2006. Factors affecting accelerated testing of polymer photostability. Polym Degrad Stab, 91(3), 417-422.

(R)

- **RABEK, J. F.** 2005. Polymer photodegradation: mechanisms and experimental methods, New York: Chapman & Hall, 24-25.
- **RAI, S. Y. & GUTTAL, S. S.** 2013. Effect of intrinsic pigmentation on the tear strength and water sorption of two commercially available silicone elastomers. J Indian Prosthodont Soc, 13(1), 30-35.
- **RAJKUMAR, K., RANJAN, P., THAVAMANI, P., JEYANTHI, P.& PAZHANISAMY, P.** 2013. Dispersion studies of nanosilica in nbr based polymer nanocomposite. Rasayan. J. Chem., 6, 122-133.
- **ROBERTS AC.** 1971. Facial prostheses: the restoration of facial defects by prosthetic mean. Kimpton.

(S)

- **SAKAGUCHI, R. L. & POWERS, J. M.** 2012. Craig's Restorative Dental Materials-E-Book, Elsevier Health Sciences D. & CASTLEBERRY, D. 1980. An assessment of recent advances in external maxillofacial materials. J Prosthet Dent, 43(4), 426-432.
- **SHAKIR, D. A., & ABDUL-AMEER, F. M.** 2018. Effect of nano-titanium oxide addition on some mechanical properties of silicone elastomers for maxillofacial prostheses. J Taibah Univ Sci, 13(3), 281–290.
- **STARK, F., FALENDER, J. & WRIGHT, A.** 1982. Silicones in Comprehensive organometallic chemistry, 1st ed., Oxford: Pergamon Press, 305-363.
- **SUN, L., GIBSON, R. F., GORDANINEJAD, F. & SUHR, J.** 2009. Energy absorption capability of nanocomposites: a review. Compos Sci Technol, 69, 2392-2409.

(T)

- **TAYLOR, R. L., LIAUW, C. M. & MARYAN, C.** 2003. The effect of resin/crosslinker ratio on the mechanical properties and fungal deterioration of a maxillofacial silicone elastomer. J Mater Sci: Mater. Med, 14, 497-502.
- **TRAN, N. H., SCARBECZ, M. & GARY, J. J.** 2004. In vitro evaluation of color change in maxillofacial elastomer through the use of an ultraviolet light absorber and a hindered amine light stabilizer. J Prosthet Dent, 91(5), 483-490.
- TUKMACHI, M. AND MOUDHAFFER, M. 2017. Effect of nano silicon dioxide addition on some properties of heat vulcanized maxillofacial silicone elastomer. IOSR-JPBS, 12(3-4),37-43
- **TYAGI, S., SRIVASTAVA, S., DAHIYA, D. R. & SRIVASTAVA, R. K.** 2016. Maxillofacial Silicone: A Literature Review. Int J Sci Res, 5, 603-5.

(U)

- **UDAGAMA, A. & DRANE, J. B.** 1982. Use of medical-grade methyl triacetoxy silane crosslinked silicone for facial prostheses. J Prosthet Dent, 48(1), 86-88.

(V)

- **VAIA, R. A.** 2002. Polymer nanocomposites open a new dimension for plastics and composites. AFRL
- **VAN NOORT, R.** 2014. Introduction to Dental Materials-E-Book, Elsevier Health Sciences.

(W)

- **WANG, L., LIU, Q., JING, D., ZHOU, S. & SHAO, L.** 2014. Biomechanicalproperties of nano-TiO 2 addition to a medical silicone elastomer: the effect of artificial ageing. J Dent, 42(4), 475-483.
- **WANG, Z. L., LIU, Y. & ZHANG, Z.** 2003. Handbook of Nanophase and Nanostructured Materials: Materials systems and applications I.
- **WEI, W., ABDULLAYEV, E., HOLLISTER, A., MILLS, D. & LVOV، Y. M.** 2012. Clay nanotube/poly (methyl methacrylate) bone cement composites with sustained antibiotic release. Macromol. Mater. Eng., 297, 645-653.
- **WOLFAARDT, J., GEHL, G., FARMAND, M. &WILKES, G.** 2003. Indications and methods of care for aspects of extra oral osseointegration Int J Oral Maxillofac Surgy, 32(2)**,** 124-131.

(Y)

- **YASEEN, H. W. & MOUDAFFER, M**. 2018. Evaluation of Thermal Conductivity and Some Other Properties of Heat Cured Denture Soft Liner Reinforced by Halloysite Nanotubes. BPJ. 11. 1491-1500. 10.
- **YEH, H.-C.** 2014. Effect of Silica Filler on the Mechanical Properties of Silicone Maxillofacial Prosthesis.
- **YU, R., KORAN, A. & CRAIG, R. G.** 1980. Physical properties of maxillofacial elastomers under conditions of accelerated aging. J Dent Res, 59, 1041-7.
- **YUAN, P., SOUTHON, P. D., LIU, Z. and KEPERT, C. J.** 2012. Organosilane functionalization of halloysite nanotubes for enhanced loading and controlled release. Nanotechnology, 23, 375705, P.1-6.
- **YUAN, P., TAN, D., ANNABI-BERGAYA, F**. 2015. Properties and applications of halloysite nanotubes: recent research advances and future prospects. Appl Clay Sci, 112,75-93.

(Z)

- **ZARDAWI, F.M.** 2013. Characterisation of implant supported soft tissue prostheses produced with 3D colour printing technology. Ph.D Thesis, School of Clinical Dentistry, University of Sheffield.
- **ZARDAWI, F.M., XIAO K, VAN NOORT R & YATES JM** (2015). Mechanical properties of 3D printed facial prostheses compared to handmade silicone polymer prostheses. J European Sci, 11(12), 15-18.
- **ZAYED, S. M., ALSHIMY, A. M. AND FAHMY, A. E**. 2014. Effect of surface treated silicon dioxide nanoparticles on some mechanical properties of maxillofacial silicone elastomer. Int J Biomater, 750398-750405.
- **ZHANG, H., ZHANG, Z., FRIEDRICH, K. & EGER, C.** 2006. Property improvements of in situ epoxy nanocomposites with reduced interparticle distance at high nanosilica content. Acta Mater, 54, 1833-1842.
- **ZHU, A.-J.& STERNSTEIN, S.S.** 2003. Nonlinear viscoelasticity of nanofilled polymers: interfaces, chain statistics and properties recovery kinetics. Compos Sci Technol, 63, 1113-1126.

Appendices

Appendix I: Data representing tear strength readings before simulated weathering (N/mm).

#	Control	1% HNTs	1.5 % HNTs
1	24.5	31	30.5
2	26.5	29	30.952
3	24.7	29.5	31.5
4	27	25.78	31.5
5	28	30	30.47
6	27	28	29.47
7	25	30	30
8	27.3	27.5	28
9	25.5	25.2	28.33
10	25.2	26.84	31
AVG	26.14	28.66	30.172

Appendix II: Data representing tensile strength test readings before simulated weathering (MPa).

#	control	1% HNTs	1.5% HNTs
1	4.87	6.12	5.5
2	5.62	5.125	6.75
3	5.12	5.5	5.375
4	4.8	6	5.75
5	5.5	6.62	5.12
6	6	5.75	5.25
7	5.5	6.62	6.87
8	5.125	6.125	5.87
9	4.7	5.125	6.625
10	5.7	5.87	7
AVG	5.29	5.88	6.008

Appendix III: Data representing elongation percentage test readings before simulated aging.

#	Control	1% HNTs	1.5 %HNTs
1	722.2	762.22	824.22
2	675.5	744.4	860
3	777.7	722.2	806.6
4	622.2	675.5	817.77
5	768.5	737.7	753.3
6	688.8	742.2	702.2
7	644.4	771.1	760
8	704.4	713.3	733.3
9	611.1	720	748
10	704.4	731	755.5
AVG	691.9	731.97	777.962

Appendix IV: Data representing shore A hardness test readings before simulated aging (IU).

#	Control	1% HNTs	1.5% HNTs
1	29.5	30.6	31.7
2	28.3	31.4	33
3	28	30.7	31.8
4	28.9	31	32.1
5	29.5	31.8	32.2
6	29	31.5	33
7	29.3	31.7	33.6
8	28.7	31	31.7
9	29.5	31.3	32.3
10	28.6	31.7	32.2
AVG	28.93	31.27	32.35

Appendix V: Data representing surface roughness test readings before simulated aging (µm).

#	Control	1% HNTs	1.5%HNTs
1	0.2	0.45	0.25
2	0.32	0.2	0.4
3	0.17	0.43	0.26
4	0.256	0.255	0.385
5	0.49	0.515	0.35
6	0.29	0.38	0.295
7	0.21	0.36	0.205
8	0.36	0.44	0.305
9	0.45	0.343	0.32
10	0.4	0.35	0.5
AVG	0.3146	0.3723	0.327

Appendix V I: Data representing tear strength test values after artificial aging (N/mm) .

#	control	1% HNTs	1.5% HNTs
1	24	27.5	27.5
2	24.21	24.5	24.73
3	24.5	27.36	29.473
4	24.73	25.5	30.5
5	23.1	28.09	31.88
6	24.5	25	30.95
7	23.8	25.2	29
8	23.2	29	26
9	24.287	26	26
10	23.5	24.2	25.263
AVG	23.9827	26.235	28.1296

Appendix VII: Data representing tensile strength test readings after simulated weathering (MPa).

#	Control	1% HNTs	1.5 HNTs
1	4.14	5.375	5.625
2	3.902	5.125	5.125
3	3.94	4.75	5.75
4	3.72	4.662	6.5
5	4.52	4.6	5.1
6	4.99	5.75	4.75
7	4.28	4.6	5.87
8	4.761	4.62	5.125
9	4.87	5.85	5.75
10	4.25	5.87	6
AVG	4.3373	5.1202	5.5595

Appendix VIII: Data representing elongation percentage test readings after simulated aging.

#	Control	1% HNTs	1.5 % HNTs
1	646.6	544	746.66
2	595.5	666.6	713.3
3	660	602.22	786.6
4	646.6	740	760
5	624.4	622	622.2
6	628.8	595.5	751.1
7	597.7	700	691.1
8	488	548.87	631.1
9	600	760	640
10	677.7	686.6	622.22
AVG	616.53	646.579	696.428

Appendix IX: Data representing shore A hardness test readings after simulated aging (IU).

#	Control	1% HNTs	1.5 %HNTs
1	33	38	38.5
2	33.1	37.5	37.8
3	34	38	37.5
4	33.7	37.6	38.2
5	34.5	38.3	37.6
6	35.8	37.1	38
7	34	37.5	38.3
8	34.2	37	37.1
9	34.5	38.2	38.2
10	34	37	37.5
AVG	34.08	37.62	37.87

Appendix X: Data representing surface roughness test readings after simulated aging (µm).

#	Control	1% HNTs	1.5 % HNTs
1	646.6	544	746.66
2	595.5	666.6	713.3
3	660	602.22	786.6
4	646.6	740	760
5	624.4	622	622.2
6	628.8	595.5	751.1
7	597.7	700	691.1
8	488	548.87	631.1
9	600	760	640
10	677.7	686.6	622.22
AVG	616.53	646.579	696.428

الخلاصة

الخلفية: السليكون المطاطي المتوفر تجارياً لا يلبي كافة الخصائص المثالية مثل ؛ ثبات اللون ، قوة التمزق والشد مع صلابة السطح مقبولة. بالإضافة إلى ذلك ، يعتبر التدهور عند الشيخوخة أحد العيوب الرئيسية في السلكون المطاطي كمادة تستخدم في تعويضات الوجه والفكين ، لأنه قد يجعل عمر الاطراف الاصطناعية أقصر.الابحاث تقام باستمرار لتحسين مواد السليكون إما عن طريق تعديل الصيغ الخاصة بهم أو عن طريق تدعيمه بالاضافات .

الهدف من هذه الدراسة: تهدف هذه الدراسة إلى تقييم تأثير اضافة الأنابيب النانوية الهلوسيتية(HNTs) على الخصائص المختارة ، وهي قوة التمزق ، قوة الشد ، نسبة الاستطالة ، خشونة السطح ، والصلابة ، لسليكون VST-50F قبل وبعد التعرض للشيخوخة المحاكية .

المواد والطرق: أولاً ، أجريت دراسة تجريبية لتحديد النسبة المئوية الأنسب من HNTs التي سيتم دمجها في سليكون VST-50F. وفقا لذلك ، تم اختيار 1 ٪ HNTs و 1.5 ٪ نسبة الوزن HNTs لتكون المجموعات التجريبية ومقارنتها مع مجموعة المراقبة. تضمنت الدراسة الرئيسية تحضير 240 عينة مقسمة بالتساوي إلى مجموعتين رئيسيتين ؛ المجموعة 1 (قبل الشيخوخة) والمجموعة 2 (بعد الشيخوخة). تم تقسيم كل مجموعة رئيسية إلى 3 مجموعات فرعية: التحكم ، 1 HNTs٪ و 1.5٪ HNTs. تحتوي هذه المجموعات الفرعية على 40 عينة ؛ 10 عينات لكل اختبار (أي قوة التمزق ، قوة الشد ، خشونة السطح والصلابة). تم قياس نسبة الاستطالة في الوقت نفسه مع اختبار الشد. تم إخضاع عينات المجموعة 2 لشيخوخة محاكية لمدة 200 ساعة ، وبعد ذلك ، أجريت جميع الاختبارات الميكانيكية المذكورة أعلاه لكل من عينات المجموعة 1 والمجموعة 2. تم جمع قراءات البحث وتحليلها إحصائيا باستخدام اختبارات ANOVA ، post-hoc و paired t -test. وأجريت اختبارات إضافية أيضا بما في ذلك فورييه تحويل الطيف بالأشعة تحت الحمراء (FTIR) ومسح المجهر الإلكتروني (SEM).

النتائج: كشف اختبار SEM عن انتشار منظم لـ HNTs داخل سليكون VST-50F ، في حين أن FTIR لم يظهر أي تفاعل كيميائي بين السليكون و HNTs. ومع ذلك ، أظهرت النتائج الاختبارات الميكانيكية قبل الشيخوخة ارتفاع كبير في جميع قراءات الاختبارات باستثناء خشونة ، حيث كان التغيير غير كبير. في هذه الأثناء ، كشفت نتائج الدراسة بعد الشيخوخة عن انخفاض كبير في قوة التمزق وقوة الشد ونسبة الاستطالة ، وبقت خشونة السطح بدون تغير ملحوظ ، ولكن صلابة زادت بشكل ملحوظ. كانت هناك اختلافات كبيرة بين المجموعة 1 والمجموعة 2 في جميع مجموعات الدراسة من جميع الخصائص المختبرة ، باستثناء نتائج خشونة السطح التي لم تتغير بشكل كبير.

الاستنتاج: تعزيز VST-50F مع HNTs حسّن بعض خواصه الميكانيكية لكنه لم يحميه من عواقب الشيخوخة. ومع ذلك ، فإن السليكون المقوى بعد الشيخوخة لا يزال أعلى من السليكون الخام من حيث قوة التمزق وقوة الشد ونسبة الاستطالة.

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
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تاثيرات اضافة الأنابيب النانوية الهلوسيتية على بعض الخواص الميكانيكية للسليكون المستخدم في تعويضات الوجه والفكين قبل وبعد الشيخوخة المحاكية

رسالة
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كجزء من متطلبات نيل درجة الماجستير في التعويضات الاصطناعية

من قبل

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ماجستير في التعويضات الاصطناعية

2019 م **1441 هـ**