

EFFECT OF EXTRAORAL AGING CONDITIONS ON MECHANICAL PROPERTIES OF FACIAL SILICONE ELASTOMER REINFORCED WITH TITANIUM-OXIDE NANOPARTICLES (IN VITRO STUDY)

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ABSTRACT

INTRODUCTION: Investigators have been searching for ideal maxillofacial prosthetic materials in order to gain patient acceptance and can be fabricated easily in the dental setting.

OBJECTIVES: To evaluate the influence of adding different concentrations of titanium oxide nanoparticles (TiO₂ NPs) on the mechanical properties of facial silicone elastomer (SE) after different extra-oral aging methods.

MATERIALS AND METHODS: TiO₂ nanoparticles were mixed with MED-4210 maxillofacial silicone elastomer at 1.5 %, 2% and 2.5 % weight percentage (w/w). Unmodified silicone was served as control group. Each of the above groups were evaluated to mechanical properties before aging conditions. Control & 2.5% nano-TiO₂ silicone elastomers groups were subjected to six equal aging conditions groups as follow. Dry storage in dark for 6 months, storage in simulated sebum solution for 6 months, storage in simulated acidic perspiration for 6 months, accelerated artificial daylight weathering for 360 hours, storage in antimicrobial silicone-cleaning solution for 30 hours and mixed aging of sebum under UV light for 360 hours. After aging exposures, they were evaluated to the mechanical properties. Data were analyzed using the Kolmogorov-Smirnov test, F-test (ANOVA) and Post-hoc pair-wise test.

RESULTS: TiO₂ nanoparticles addition improved the mechanical properties in terms of tensile strength and percentage elongation, tear strength and shore A hardness of MED-4210 maxillofacial silicon elastomer before and after extra-oral aging conditions ($P < 0.05$). Pair-wise comparison between control group and 2.5% nano-TiO₂ silicone elastomers composite exhibited significant differences according to the mechanical properties after aging.

CONCLUSIONS: Reinforcement of MED-4210 maxillofacial silicon elastomer with TiO₂ nanoparticles introduces a favorable material with physical and anti-ageing properties in our in vitro study.

KEYWORDS: Nano-TiO₂, Silicone elastomer, mechanical properties, artificial ageing.

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INTRODUCTION

Despite the advances in plastic and reconstructive surgery, there are cases with extensive loss of tissues that cannot be surgically corrected because of lack of sufficient donor tissue, age and general condition of the patient (1). Maxillofacial prostheses are constructed to transform facial disfigurements into natural-appearing reproductions of the missing parts, restoring function and improving appearance (2). Silicone elastomer is a promising functional material used for the correction of maxillofacial defects. However, this material does have drawbacks, since natural or outdoor weathering of silicone elastomers can induce significant changes in its physical and mechanical properties (3).

Silicones have many desirable properties including biocompatibility, ease of manipulation, low viscosity, and patient accommodation properties. Moreover, they have high tensile strength, high elongation, and sufficient bonding to underlying substrates (4). Although silicone elastomers that may extend the service life of prostheses are available, poor tear resistance and staining remain significant problems. Most maxillofacial elastomers perform well initially; however, as time passes,

deterioration associated with either degradation of mechanical properties or changes in appearance occurs (5). Silicone materials almost always refer to polydimethylsiloxane (PDMS) because it is widely used as the material of choice for fabricating maxillofacial prosthesis. Beumer et al. who indicated that polydimethylsiloxane silicone elastomer that is vulcanized at room temperature is the most common silicone elastomer that has been used to fabricate maxillofacial prosthesis, because these materials are less time consuming, can be processed easily, are flexible and durable (6,7). Serviceability of extra oral maxillofacial prostheses ranges from 6 to 24 months mainly. However, silicone-based maxillofacial prostheses require replacement every 6 to 18 months, as they lose elasticity, resistance to tear, and color stability when exposed to environmental factors such as sunlight energy (solar ultraviolet radiation), heat, moisture, dust, air pollutants, and patient mishandling can affect mechanical and physical properties of facial prostheses (8,9).

Artificial aging (weathering) has been used to investigate the interaction of silicone elastomers to simulated conditions that affect silicone prostheses. It can

be in the form of accelerated artificial daylight aging. Most elastomers used in facial prostheses are not exposed to the wet environment that is used for part of the artificial aging process or thermal cycling under normal function (10-12). Weathering is the adverse response of a material to climate, often causing unwanted mechanical changes. Mohite et al (13) evaluated the tear propagation and resistance of Silastic MDX-4-4210, Cosmesil, and Epithane-3 after subjecting them to UV radiation, simulated sebum, ozone, chlorine, and nitrogen dioxide and there were a Statistically significant differences in the tear patterns of silicones and polyurethane after the artificially simulated environmental factors.

Nanoparticles (NPs) exhibit a number of special properties relative to bulk material. According to a survey of the literature, the addition of TiO₂ NPs and ZnO NPs to polymers can improve the mechanical and optical properties of polymers due to the small size, large specific area, and quantum effect of the NPs, as well as the strong interfacial interaction between the organic polymer and inorganic NPs. The NPs hardly scatter any visible light, being optically transparent, specially due to their nanometer scale and low content (14,15). Rutile-TiO₂ is known to have a high scattering effect that results in protection from ultraviolet light (16). Therefore, they can improve the physical and optical properties of the organic polymer, as well as provide resistance to environmental stress-caused cracking and aging (17). Wang et al (3) reported that addition of TiO₂ nanoparticles to MDX4-4210 maxillofacial silicone led to improving in tensile strength and Shore A hardness after artificial ageing. Dhuha et al (18) investigated two types of maxillofacial elastomers VST50F room-temperature-vulcanized (RTV) and Cosmesil M511 high temperature-vulcanized (HTV) for their mechanical properties after adding 0.25 wt% and 0.2 wt% TiO₂ nanofillers. The evaluated properties (tear strength, tensile strength, elongation percentage, and hardness) were enhanced with the selected concentrations.

Since the combination of nanoparticles/maxillofacial silicone elastomer showed great potential anti-aging properties and progression in mechanical properties. It would be interesting to verify whether a similar synergistic effects could be exist between TiO₂ NPs and MED-4210 maxillofacial properties and this triggered the interest to carry out this study. The proposed null hypothesis assumed that maxillofacial silicone elastomer properties after addition of nanoparticles are not affected by extra-oral aging conditions.

MATERIALS AND METHODS

This study was reviewed and accepted by committee of ethical scientific research, Faculty of dentistry, Alexandria University. Assessment the effect of human extra-oral and environmental aging conditions on the mechanical properties of maxillofacial silicon elastomer MED-4210 (Factor II Inc., Lakeside, AZ, USA) reinforced with different proportions of TiO₂ (US Research Nanomaterials, Inc.USA) nanoparticles. A total of 240 specimens were fabricated according to manufacturer's instructions and American society for testing and materials (ASTM) for recording mechanical properties (tensile strength & percentage elongation, shore A hardness and tear strength). Specimens were divided into four equal groups (15 specimens/ group) regarding TiO₂ NPs weight

percentage (w/w%). Un modified silicone elastomer (Blank silicone elastomer) was served as control group and nano-TiO₂ at 1.5%, 2% and 2.5% were mixed into the MED-4210 maxillofacial silicon elastomer. Each of the above groups were evaluated to mechanical properties before aging conditions (tensile strength & percentage elongation (n=5), tear strength (n=5) and shore A hardness (n=5)). For 0% (control group) and 2.5% nano-TiO₂ silicone elastomers composite were subjected to six equal aging conditions (30 specimens/group), dry storage in dark for 6 months, storage in simulated sebum solution for 6 months, storage in simulated acidic perspiration for 6 months, accelerated artificial daylight weathering for 360 hours, storage in antimicrobial silicone-cleaning solution for 30 hours and mixed aging of sebum under UV light for 360 hours. The mechanical testing was investigated on two stages, stage one, before aging conditions for the four groups (control, 1.5%, 2%, 2.5% TiO₂ NPs groups) and stage two after conditioning, for 0% (control group) and 2.5% nano-TiO₂ silicone elastomers composite only. The conditioning period selected simulated silicone prosthesis in service for 12 to 18 months (4).

Preparation of specimens

Test specimens were obtained by weighing specific proportions of the TiO₂ nanoparticles by the use of digital analytical balance (Sartorius CPA2245, Germany) then they were blended with the silicone cross linker in 50ml glass beaker under the mechanical stirrer (yellowline, OST Digital, IKA, Germany) for 10min and with mixing speed 150 to 200 rpm to achieve a homogenous mixture and dispersion of nanoparticles (3). Afterwards, the nanoparticles cross linker composite were added to the silicone elastomer base according to the recommended ratio 10:1 by weight (base: crosslinking agent), the composite was mixed for another 10min. Using the mechanical stirrer at the same mixing speed. The removal of incorporated air bubbles were done by placing the composition into the vacuum oven at pressure of 28inHg and for 30min. (according to manufacturer's instruction) (19,20). The composition was injected into the premade copper molds. Each specimen was evaluated for defects. Only specimens without visible defects were tested. All the specimens were saved in sterilization pouch and labeled according to each aging group and stored in plastic box to avoid variation in their properties.

Conditioning of specimens

The specimens were conditioned for 24 h prior to testing. They were conditioned at a standard laboratory temperature of 23±2 °C for a minimum of 3 h after flash removal. The flash was removed with a scalpel and a sharp #11 surgical blade (21,22).

Mechanical testing procedures

The mechanical properties of the untreated silicone and silicone reinforced with various concentrations of TiO₂ NP were evaluated using the following techniques:

A. Tensile strength & percentage elongation

ASTM D412 (2002) (23) standard test was used to determine the tensile strength properties. Eighty type 2 dumbbell-shaped specimens (Figure1.A) were prepared using a prefabricated copper molds to the dimensions of the type 2 standard test piece (N=80, n=5). The specimen was placed in the grips of a computer-controlled universal testing machine (Tinius Olsen, H10k, USA). The specimen was stretched at constant crosshead speed of 500 mm/min,

until the specimen was ruptured, and the maximum force after break was recorded by the computer software (Figure 2.A)

Ultimate Tensile strength, TS Mega Pascal (MPa), was calculated as follows:

Ultimate tensile strength (MPa) = F/A where F is the force recorded at break (N), and A is the original cross-sectional area of the samples (mm²).

The elongation at break, E_b (%), was calculated using the following equation:

Elongation percentage at break = $(L_b - L_0) / L_0 \times 100$ where L_b is the test length at break (mm) and L_0 is the initial test length (mm).

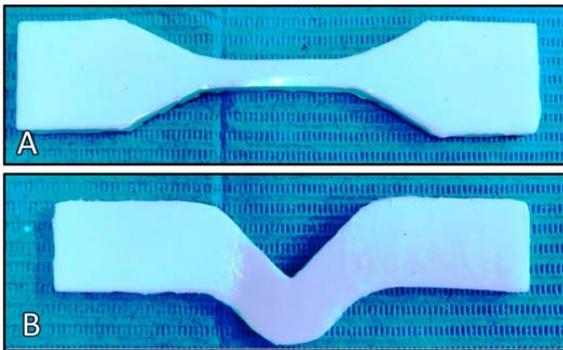


Figure (1): (A): showing tensile strength test specimen (B): showing tear strength test specimen

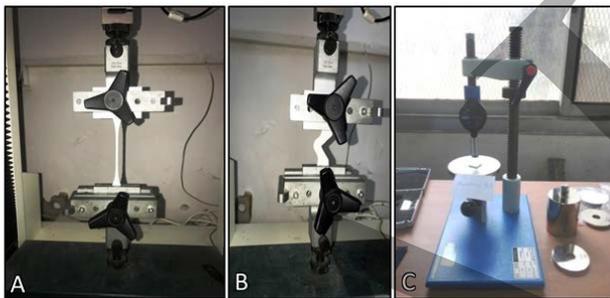


Figure (2): (A): showing specimen under tensile strength and elongation testing. (B): specimen under tear strength testing (C): Shore A durometer used to measure hardness of silicone test specimen

B. Tear strength test

ASTM D624 (24) standard test was followed for testing tear resistance. Specimen testing was conducted using a computer-controlled universal testing machine (Tinius Olsen, H10k, USA) (Figure 2.B). Type C specimens were used to measure the tear initiation strength (Figure 1.B). The following equation was used to determine the tear strength:

Tear strength = f/d where f is the maximum force required to break the sample (kN), and d is the median thickness of each sample (m).

C. Shore A hardness test

ASTM D 2240 (22) standard test was followed for hardness test. The test was performed on square specimens with dimensions of $25 \times 25 \times 6$ mm using a Type A Shore hardness digital tester (STD 226, SATRA, UK. RayRan/BS550). The hardness of the specimens was measured at five different points that were at a distance of 6 mm from each other and also from the border (Figure 2.C); the mean measurement values were considered to be the hardness of the specimen (25).

Aging Methods (4)

Specimens of control and 2.5% nanoTiO₂ silicone elastomer composite were exposed to six aging groups and values of mechanical properties were measured before and after aging conditions.

Group I: Storage in the dark (Time passage)

Dark storage was performed for silicone specimens at room temperature ($23 \pm 2^\circ\text{C}$) and $50 \pm 5\%$ relative humidity, which included suspending the specimens in a sealed glass container with stainless steel ligature wires and put them in the dark for 6 months.

Group II: Storage in sebum solution

Specimens were immersed in simulated sebum solution. The sebum solution was prepared according to International Organization for Standardization specification, using 10% palmitic acid and 2% tripalmitin dissolved in 88% linoleic acid (all wt %) and stirred vigorously in a hot water bath until the solution became clear. The flasks with specimens was stored in the incubator (MLW BST 5020 lap incubator) at 37°C for 6 months.

Group III: Storage in acidic perspiration solution

Specimens were immersed in simulated acidic perspiration solution for 6 months (PH=5.5), the solution was prepared according to International Organization for Standardization (ISO) specification ISO 105-E04:2013(26). The powders of the chemicals (El Gamhureya for Medicine Company, Alexandria, Egypt) were weighed using the digital analytical balance (Sartorius CPA2245, Germany) then dissolved in 1 liter of distilled water. The solution consisted of 0.5 g L-histidine monohydrochloride monohydrate, 5 g sodium chloride, and 2.2 g sodium dihydrogen orthophosphate dehydrate.

Group IV: Artificial accelerated daylight weathering

The accelerated daylight aging was done by the use of Xenon Weather Ometer (ATLAS Ci 3000 Xeno Weather-Ometer, USA) test chamber. The accelerated weathering standardization in this test was based on ASTM (G155) cycle no.1. (27) The specimens were exposed to 20cycles (equivalent to 360 hours) each cycle was accomplished in 18 h consisting of alternating intervals of 102 min. light only followed by 18 min. of light with water spray each cycle included irradiance of 340nm with a power of $0.35 \pm 0.02\text{W/m}^2$ and black panel temperature of Group V: Antibacterial silicone-cleaning solution.

A commercially antimicrobial silicone-cleaning solution (B-200-12, Daro Inc., Lakeside, AZ) was selected for cleaning and disinfection of the maxillofacial prostheses. Specimens were stored in that solution for 30 hours to simulate 1 year of (30 hours is 360 days) service assuming a 5 minute daily treatment.

Group VI: Mixed aging (Sebum storage under UV light)

Specimens were immersed in simulated sebum solution and stored in the climate test chamber under UV light for two weeks (360 hours), the chamber used ultraviolet lamp (UVA-340nm). $\pm 2^\circ\text{C}$ and the relative humidity was approximately 50%.

The values of mechanical testing before and after aging were tested.

Statistical analysis

Data of mechanical tests were collected and entered to the computer using SPSS program for statistical analysis (version 21) (28). The Kolmogorov-Smirnov test (29) was used to verify the normality of distribution. Quantitative data were described using range (minimum and maximum), mean, standard deviation and median. Comparisons were carried out between two studied groups that were normally distributed quantitative variables using Student t-test. As Student t-test was significant, Post-Hoc pair-wise comparisons was carried out using Tukey test for multiple comparisons with a significance level of P < 0.05.

RESULTS

There was a significant difference (p < 0.001) in the mean tear strengths between the control group MED-4210 maxillofacial silicone material and 1.5wt %, 2 wt% and 2.5wt% reinforced TiO₂ NPs concentrations groups, **Figure (3)**

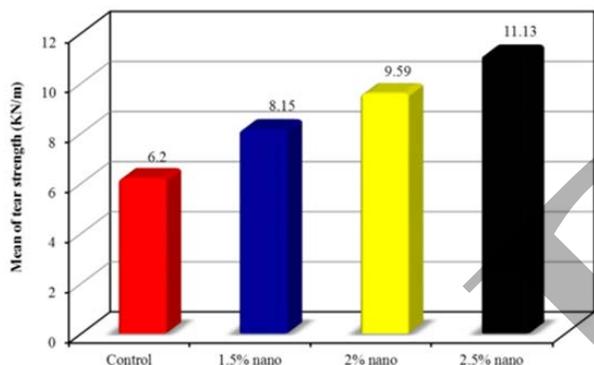


Figure (3): Comparison between the four studied groups regarding tear strength before aging.

There were a statistically significant difference (P=0.002 and P=0.026) in both control group and 2.5wt% TiO₂ group regarding tear strength before and after artificial daylight aging, **Figure (4)**

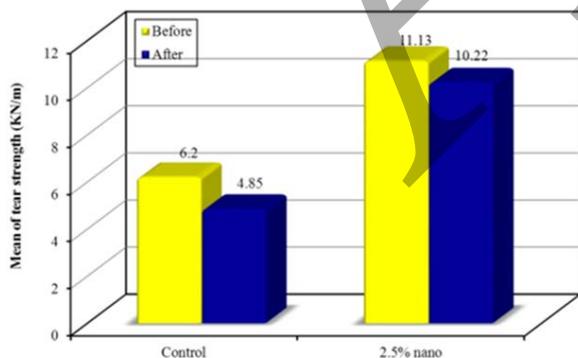


Figure (4): Comparison between the two studied groups regarding tear strength before and after artificial daylight aging.

There were a statistically significant difference (P<0.001 and P=0.003) in both control and 2.5wt% reinforced TiO₂ NPs group, respectively between the tear strength values before and after storage in the cleaning solution, **Figure (5)**

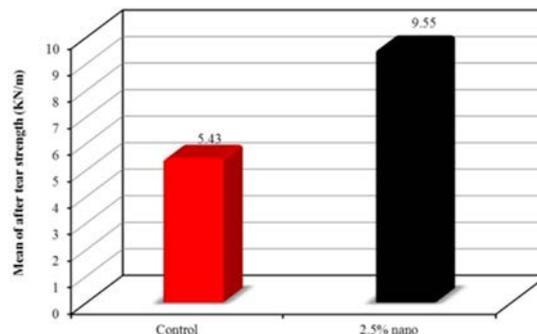


Figure (5): Bar chart presenting the mean values of tear strength between the two studied groups after storage in antibacterial silicone-cleaning solution.

Post-Hoc pair-wise comparison between the four studied groups (control group, 1.5wt %, 2 wt% and 2.5wt% reinforced TiO₂ NPs) using Tukey test to adjust the significant values, showed a significant difference (p < 0.001) in mean values of all mechanical properties before exposure to aging conditions, **Table (1)**

Table (1): Mean values (SD) of four studied groups regarding results of mechanical testing before aging.

Parameter	Contr ol group	SE- 1.5%(w/w)TiO ₂	SE- 2%(w/w)TiO ₂	SE- 2.5%(w/w)TiO ₂	P value
Tensile strength	2.57 (0.07)	2.77 (0.06)	3.13 (0.08)	3.42 (0.03)	<0.001*
Percentage elongation	551.80 (12.42)	672.80 (6.69)	737.0 (15.0)	746.80 (3.03)	<0.001*
Tear strength	6.20 (0.09)	8.15 (0.64)	9.59 (0.03)	11.13 (0.67)	<0.001*
Shore A hardness	27.64 (0.43)	29.39 (0.53)	33.14 (0.62)	35.57 (1.28)	<0.001*

Statically significant at p ≤ 0.05.

Comparing mean values of all mechanical properties using Student t-test of the two studied group (control and 2.5wt% TiO₂ group) after three aging conditions groups showed significant difference between the two studied groups (P<0.001), **Table (2)**

Table (2): Mean values (SD) of two studied groups regarding results of mechanical testing after three aging groups.

Parameter	Dark Storage		Sebum storage		Acidic perspiration	
	Control group	SE- 2.5%(w/w)TiO ₂	Control group	SE- 2.5%(w/w)TiO ₂	Contr ol group	SE- 2.5%(w/w)TiO ₂
Tensile strength	2.30 (0.04)	3.14 (0.13)	2.19 (0.05)	2.75 (0.06)	2.10 (0.07)	2.94 (0.04)
Percentage elongation	356.8 (8.87)	588.40 (11.08)	350.20 (37.53)	542.60 (36.54)	459 (14.46)	602.6 (7.09)
Tear strength	6.09 (0.09)	10.72 (0.42)	3.38 (0.34)	6.15 (0.08)	4.36 (0.21)	8.86 (0.27)
Shore A hardness	26.03 (0.05)	34.39 (0.45)	21.54 (2.24)	29.06 (0.63)	30.09 (0.75)	40.38 (0.42)
P value	<0.001*		<0.001*		<0.001*	

* Statically significant at p ≤ 0.05.

Comparing mean values of all mechanical properties using Student t-test of the two studied group (control and 2.5wt% TiO₂ group) after the other three aging conditions groups showed significant difference between the two studied groups $P < 0.001$, $P = 0.001$, $P = 0.014$, **Table (3)**

Table (3): Mean values (SD) of two studied groups regarding results of mechanical testing after three other aging groups.

Parameter	Accelerated daylight aging		Antibacterial cleaning solution		Mixed aging (sebum under UV light)	
	Control group	SE-2.5%(w/w)TiO ₂	Control group	SE-2.5%(w/w)TiO ₂	Control group	SE2.5%(w/w)TiO ₂
Tensile strength	2.34 (0.24)	2.90 (0.05)	2.52 (0.02)	3.21 (0.18)	1.57 (0.42)	2.34 (0.08)
Percentage elongation	560.60 (15.37)	641 (1.87)	757.80 (33.0)	931.60 (20.53)	500.80 (2.17)	665.40 (7.80)
Tear strength	4.85 (0.42)	10.22 (0.33)	5.43 (0.11)	9.55 (0.53)	1.57 (0.42)	2.34 (0.08)
Shore A hardness	26.16 (1.16)	31.25 (1.17)	27.41 (0.44)	32.94 (0.90)	22.48 (1.88)	30.78 (0.92)
P value	<0.001*		0.001*		0.014*	

* Statically significant at $p \leq 0.05$.

DISCUSSION

Maxillofacial prosthetic treatment allows many patients with orofacial defects to return to an active role in public. The results of prosthetic treatment are influenced by the nature of the defect, the skill of the prosthodontist, and the properties of the materials used (30). Elastomers have been used for almost 50 years to fabricate maxillofacial prosthetics and the success of any facial prosthesis depends on the physical and mechanical properties of the materials comprising the prosthesis (31,32).

MED-4210 maxillofacial silicone elastomer, it is a platinum-catalyzed RTV silicone elastomer, was chosen for the present study because of its texture, mechanical strength, durability, ease of handling and commonly used facial elastomers (33). TiO₂ (TiO₂ rutile, 99.9%, 10-30 nm) nanoparticles (NP) that tested are used as strengthening agents for maxillofacial silicones. They are characterized by their minute particle size, large specific area, active function, and strong interfacial interaction with the organic polymer. Therefore upon addition to silicone matrix it provide resistance to environmental stress cracking and aging, and also improve the physical and mechanical properties of the organic polymer (34,35). Titanium dioxide NPs are widely used as inorganic UV absorbers in nanotechnology applications. Their important role being that they do not migrate in a polymeric matrix and their thermal stability are acceptable and unaltered over decades.

Facial prostheses during their clinical lifetime and service are exposed to various environmental factors such as (solar radiation, temperature, moisture, pollutants, dust, and wind) and human conditions like (skin secretions, namely perspiration and sebum) as well as the deposition of microscopic residues in porosities on the material surface, and continuous handling of prostheses by the patient with utilization of cleansers and disinfectants (36) that can cause deterioration in physical and mechanical properties, discoloration, and delamination of the retentive substrate. A more recent study reported that a mean life

span of 14 months. So, the aging periods selected upon simulation of a silicone prosthesis being in service for 12 to 18 months. If we considered an average of 8 to 12 hours that patients wear their prosthesis daily, so 6 months exposure periods could be equivalent to 1 to 1.5 years of clinical usage. since the facial prosthesis remains esthetic and serviceable for only 1 to 2 years (37). The properties that are essential for maxillofacial silicone elastomers are high tear resistance, high tensile strength, good level of elongation at break, adequate hardness, and ideal color stability. As these properties define the resistance of a prosthesis to rupture during use and maintenance and its compliance to facial movement. Therefore, our study was based on measuring such properties due to their clinical significance in maxillofacial prosthesis fabrication (38).

The 2.5% concentration of TiO₂ NPs was chosen to be in comparison with control group throughout the aging conditions. This was based on a study by Han et al (2008) (5) who found incorporation of Ti, Zn, or Ce nano-oxides at concentrations of 2.0% and 2.5% improved the overall mechanical properties of the silicone A-2186 maxillofacial elastomer. Another explanation for that choice is 2.5% concentration of Ti nano-oxide group exhibited better values of mechanical testing than the other two groups (1.5%, 2%) before any exposure methods performed.

The results of the present study specifically before exposure to different aging methods indicated that tear strength test of MED-4210 maxillofacial silicone exhibit a highly statistically significant increase by the addition of TiO₂ nanoparticles in all concentrations (1.5%, 2% and 2.5%) compared to the control group. This improvement in tear strength values can be illustrated by ability of the polymer to dissipate strain energy near the tips of the growing cracks. As the tear propagates, nanoparticles will dissipate the energy within the polymer matrix, as making it highly resistant to tearing, therefore large load will be needed to break the polymer matrix (39).

The results of tensile strength and elongation at break tests also showed a highly significant increase after the addition of TiO₂ nanoparticles in all concentrations due to when polymer subjected to tensile forces, polymer chains and nanoparticles will slide over each other. So the presence of the NPs will prevent polymer chain from breakage (3). Ti nano-oxide particles act as multifunctional cross-links by formation of strong hydrogen bond between its surface hydroxyl group and PDMS chains; these multifunctional cross-links increase the overall cross-linking density of the polymer and make it more stiff and strong. Under tensional forces, these cross-links prevent the PDMS chains from breaking thus increasing its tensile strength (11). Shore A hardness results increases after the addition of titanium oxide nano-sized particles in all concentrations (1.5wt%, 2wt%, 2.5wt%) compared to the control group because through NPs loading as the concentration increases this will lead to binding between the particles each other, which will fill out the intermolecular spaces between the polymer chain, result in more rigid polymer with high elastic modulus and more resistance to permanent deformation by indentation or penetration (40). In this study, the Shore A hardness of nano-TiO₂ silicone elastomer was within the clinically acceptable range (25-55 units) indicating the same similarity with the soft tissue according to the defect site.

The effect of ageing can lead to falling of physical and mechanical properties of the silicone elastomer, reduction in the life of facial epitheses, which gradually leads to replacement (2,35). Comparison between results is much difficult due to diversity of maxillofacial prosthetic materials tested, experimental testing and parameters used to control simulated aging modes. Tensile strength and tear strength, elongation at break, and shore A hardness of MED-4210 maxillofacial silicone (control group) and MED-4210 maxillofacial silicone with addition of 2.5% TiO₂ NPs were evaluated after exposure to simulated aging methods. These properties changed according to the aging conducted. Variations in such properties are possibly due to differences in structural stability of the PDMS chains as a result of cross-linking densities and conditioning type (5,16). Quantitative results that obtained from specimens stored in the dark for 6 months showed non-significant difference between the control group (unmodified silicone elastomer) and 2.5wt% Ti nano-oxide group regarding the tear strength before and after dark storage. This can be attributed to absence of physical or mechanical conditioning, furthermore, these results silicone-type dependent as there are other materials that degraded by time and storage. However shore A hardness was significantly increased in 2.5wt%TiO₂ NPs group comparing to control group after dark storage because nano-oxide particles could increase the surface energy of silicone matrix, during the crosslinking reactions which will lead to reinforcement of matrix structure (10,12).

In our study, significant changes in the mechanical properties of both 2.5wt%TiO₂ NPs group and control group after immersion of specimens in simulated sebum solution. These changes are usually due to that sebum fatty acids tend to react with silicone, interrupting chain bonds and decomposing the elastomer, which result in softer and weaker elastomer (5). However, presence of nanoparticles develops much more of the mechanical properties compared to control group. This enhancement could be due to Ti nano-oxide particles possess high surface area which maximize polymer /NP interaction which enable the material greater deformation (17).

Our results from acidic perspiration storage showed significant changes regarding the two studied groups (2.5wt%TiO₂ NPs and control group). The acidic environment has a catalytic effect (i.e substance that increases the speed of chemical reaction) on the cross-linking reaction leads to the decomposition of polymer network junctions in the silicone, which break at lower forces (26). The common factors that affect the behavior of silicone elastomer materials are temperature, light, and mechanical force (14). Artificial accelerated daylight weathering was utilized in this study because the changes produced are greater than outdoor weathering. The 2.5% group of nano-TiO₂ silicone elastomers showed better performance than control group regarding the mechanical properties. This significance could be clarified as TiO₂ nanoparticles are a heat-resistant additives and can improve the cross-linking reaction temperature of polysiloxane side groups, which in turn improves the heat ageing properties of the silicone elastomer (5,33). Shihab et al (38) stated that enhancement of mechanical properties with weathering condition could be mainly due to photo oxidation of polymer chains and free radical formation and reaction of these radicals with each one another, leading to

further crosslinking. Additionally, this reaction with oxygen will result in brittle and inelastic material.

When silicone prostheses are made and given to patients, they are subjected to natural aging conditions and to disinfection procedures. Upon using the antimicrobial silicone-cleaning solution, it under goes decomposition which affects the mechanical properties of the silicone elastomer, as it leads to inhibition of the polymerization of silicone elastomer (1). In our study, significant results in terms of (tensile strength &percentage elongation, tear strength and shore A hardness) could be illustrated as slight addition of TiO₂NP reinforcing agent to a polymeric material affects the electrical, optical, chemical, and physical properties of the resulting hybrid material. The significant results in hardness values could be related to increase number of bonds between the polymeric matrix and NPs, which requires more energy to break these bonds (37).

Ultraviolet light is another aging method that shorten the longevity of maxillofacial prosthesis. This light with shorter wavelengths of higher energy that cause the greatest destructive effects (9,13). Our results before and after mixed aging of sebum under UV light regarding the untreated silicone elastomer (control group) showed significant decrease in both tensile &tear strength .This degradation could be related to structural modifications in the distribution of the polymer molecular masses which lead to polymer chain scission (i.e. chemical reaction resulting in the breaking of polymer skeletal bonds) (5,25) intensified cross-linking, or increased density causing the polymer to either become softer or harder. The UV irradiation could cause polymer chain disentanglement, through oxidizing deterioration of Si-C bonds together with depolymerization, which leads to shortening of the average length of the chains or to decrease in the network mesh size (3,4). It has been found that nano-TiO₂ has a strong ability to resist UV rays. Meaning that the nanoparticles can not only absorb, but also reflect and scatter UV rays due to their refractive index and optical activity. This was obviously noticed in 2.5%TiO₂ NPs silicone elastomer composite comparing with control group after mixed aging regarding the mechanical properties (9,17).

Within the limitation of the current study, it is evident that it could be assumed that the refinement in the mechanical properties of maxillofacial silicone elastomer was achieved by the addition of TiO₂ nanoparticles. This rejects the proposed null hypothesis of the present study. This novel composite material could have anti-aging properties against the human and environmental aging conditions. Further research is certainly warranted to determine whether other properties of this composite make it suitable for long-lasting and antibacterial facial epitheses.

CONCLUSION

Based on the results of the present study, the mechanical properties of MED-4210 maxillofacial elastomers are adversely affected by human and environmental factors. However, after addition of nano-TiO₂ nanoparticles which led to more improvement in mechanical properties after aging conditions.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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