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Article

Chitosan -TiO$_2$ Hybrid Nanocomposite Impregnated in Type A-2186 Maxillofacial Silicon Subjected to Different Accelerated Aging Conditions: The Color Stability Evaluation

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Abstract: This study explores the impact of Chitosan-TiO$_2$ nanocomposite incorporation on the color stability of pigmented Room Temperature Vulcanization maxillofacial silicone under varied accelerated aging conditions. Five hundred disk-shaped specimens were formed with silicone elastomer type A-2186, distributed into groups based on pigment types and nanoparticle treatments. The color difference (ΔE) was assessed using a Colorimeter within the CIELAB color system, pre- and post-exposure to aging conditions, including UV-accelerated aging and outdoor weathering. ANOVA, Dennett's T3, and Tukey HSD tests revealed significant color alterations across all silicon types, with the most pronounced in red-colored, 3% Chitosan specimens and the least in 2% TiO$_2$ specimens under UV-accelerated aging. Outdoor weathering consistently increased ΔE values across all categories. The study implies that, while nanoparticles may offer some resistance against accelerated aging, they fall short in adequately defending against UV radiation during outdoor weathering.

Keywords: synthesized Chitosan-TiO$_2$ nanocomposite; Core-Shell Method; Room Temperature Vulcanization (RTV) maxillofacial silicone; color stability; accelerated aging conditions

1. Introduction

The psychosocial consequences of visible esthetic differences in individuals' lives are determined by a combination of individual and social factors. These differences can render individuals temporarily or permanently vulnerable, depending on the nature of the impact. The utilization of surgery or prosthetics for rehabilitation serves as a crucial means of adaptation in addressing these challenges[1].

For nearly fifty years, elastomers have been utilized in the production of facial prostheses for individuals with missing facial features. In 1986, Factor II introduced A-2186, the first commercially available platinum-catalyzed silicone elastomer. A-2186 is a pourable silicone that is clear-to-translucent and consists of two parts (10:1 base-to-catalyst ratio). Among anaplastologists, maxillofacial prosthodontists, and dental technicians involved in fabricating facial prostheses, RTV silicone elastomer products were commonly used. The A-2186 silicone, specifically, was widely employed for intrinsic or base color packing due to its superior tensile strength, tear strength, and softer, more realistic skin-like surface texture[2].

Despite its widespread use in maxillofacial prostheses, silicone has certain limitations. One significant drawback is its short shelf life, primarily due to the rapid degradation of its physical properties and color stability. The overall appearance and esthetics of the prosthesis play a crucial role in determining the patient's well-being and social acceptance[3]. Clinical studies have indicated that the average lifespan of maxillofacial prostheses is approximately one and a half to two years, with many patients experiencing issues such as discoloration and decreased satisfaction within the first three years of use[4].

To achieve a lifelike appearance for facial prostheses, pigments are used as opacifiers and colorants for intrinsic and extrinsic coloring[2]. For creating the primary skin shade, basic colors like red, blue, and yellow are employed in maxillofacial prosthetic silicone elastomer. The amount of each color used depends on factors such as darker complexions, complex anatomy, and the desired skin tone. Red is used more for darker complexions, while blue is required more for lighter skin tones. Yellow is used to match moderate to substantial skin colors[5,6].

Previous studies have utilized dry earth pigments as opacifiers or intrinsic colors in their research. For instance, Beatty et al.[7] examined the color changes in dry-pigmented maxillofacial elastomer when exposed to ultraviolet light. They discovered that the red cosmetic dry earth pigment exhibited significant color changes after 400 hours of exposure, while the cosmetic yellow ochre remained color stable even after 1800 hours. Similarly, Kiat-amnuay et al.[8] investigated using dry earth cosmetic pigments mixed with silicone A-2186 and opacifiers. Their findings align with those of Beatty et al.[7], demonstrating that the red pigment groups experienced the most pronounced color change.

In recent years, significant research has been dedicated to developing a novel industrial process incorporating nanoparticles into a polymeric matrix. This advancement has led to the emergence of a new class of polymeric materials that combine the strength of nano-oxides with the flexibility of an organic polymer matrix. Adding nanoparticles to the polymeric matrix enhances its properties due to the particles' higher surface energy and chemical reactivity. This enables them to interact with the silicone elastomer matrix, forming a three-dimensional network within the polymer chain. By utilizing nanoparticles at the nanoscale, it becomes possible to fine-tune specific attributes of individual particles while exerting control over a range of properties such as biological, mechanical, electrical, magnetic, and optical characteristics. For example, researchers have discovered that nanosized rutile TiO_2 particles possess exceptional ultraviolet (UV) absorption and scattering capabilities, effectively safeguarding against UV light. These nanoparticles demonstrate diminutive dimensions, extensive surface area, active functionality, and robust interfacial interaction with organic polymers. Consequently, they enhance the polymer's physical and optical properties while fortifying its resilience against aging triggered by environmental stressors[9,10].

Nanoparticles serve as effective barriers against UV radiation due to their size being smaller than the wavelength of UV light. When exposed to UV radiation, the electrons in nanoparticles vibrate, leading to the absorption and dissipation of a portion of the light. Consequently, the smaller the nanoparticles, the more efficient they are at shielding against solar radiation. Maintaining an appropriate filler content is crucial when incorporating nanosized oxide particles into the silicone elastomer matrix. This is due to these particles' higher surface energy and chemical reactivity, which can lead to agglomeration if the content exceeds a certain level. The presence of agglomerated particles within the silicone elastomer matrix acts as stress-concentrating centers when subjected to external forces, decreasing the elastomer's mechanical strength[11].

Considering the findings of Han et al.[11] regarding the color stability of maxillofacial prostheses and previous studies on mechanical properties, it was determined that nano-TiO_2 at 2.0% and 2.5% content levels proved to be the most effective opacifier when used with A-2186 silicone maxillofacial elastomer. Also, with 2% nanosized TiO_2, an increased tendency to agglomerate, as an increase in particle size and concentration results in suboptimal dispersion of nano-oxides within the matrix. An augmented propensity for agglomeration further diminishes UV protective capabilities[9].

To overcome the limitations of nano aggregation, researchers have been investigating using TiO_2 support material composites. By combining TiO_2 nanoparticles (NPs) with chitosan coatings, nanocomposite films with enhanced properties such as mechanical strength, swelling properties, and thermal stability can be achieved. Chitosan is crucial in preventing agglomeration and facilitating the dispersion of metal oxide particles within the composite. This approach offers a potential solution to overcome the limitations associated with nano aggregation[12].

Chitosan, a natural polysaccharide derived from chitin shells of crustaceans, is highly valued for its effectiveness in various biomedical applications. It is obtained by treating chitin with alkaline substances like sodium hydroxide. Chitosan possesses several desirable qualities, such as biodegradability, biocompatibility, non-toxicity, and Antibacterial and hydrating properties. One of its unique features is its cationic nature, resulting from the presence of amino and hydroxyl groups in its structure. This cationic nature allows Chitosan to interact with other compounds through electrostatic forces, hydrogen bonds or by incorporating them into its polymeric matrix, enhancing its mechanical and biological properties. Furthermore, Chitosan exhibits a strong affinity for negatively charged compounds, particularly under low pH conditions. These exceptional properties, along with its biocompatibility, biodegradability, and lack of toxicity, have contributed to its widespread utilization in diverse fields[13–15].

Incorporating chitosan micro-particles into a matrix can provide strengthening properties as the micro-cracks between the matrix, and Chitosan can absorb energy. However, when the concentration of Chitosan exceeds a certain threshold of 3.0-3.5%, the particles tend to come closer or aggregate, transforming micro-cracks into macro-defects. Consequently, this results in a decrease in the material's tensile strength[16,17].

Over time, sweat and sebum can be absorbed into the extraoral silicone when the prosthesis is in contact with human skin. However, the presence of UV radiation can have detrimental effects. While it increases cross-linking, it also breaks down bonds within the polymer matrix, resulting in a slower polymerization rate and silicone degradation. These processes ultimately accelerate color changes and material deterioration[18].

Silicone elastomers have been subjected to controlled experiments to replicate the effects of environmental and human conditions experienced by prostheses during their use. These experiments involve exposing the elastomers to simulated conditions such as sebum solution or acidic perspiration, artificial daylight radiation for accelerated aging, outdoor natural weathering, and treatment with silicone cleaning solutions. By subjecting silicone elastomers to these conditions, researchers aim to closely mimic real-world scenarios and evaluate the performance and longevity of the materials used in prosthetic applications[19].

For the engineering of a color-stable prosthesis, thoroughly understanding the effects imposed by various environmental variables is of utmost importance. Although accelerated aging tests can offer indications regarding the outdoor performance of polymers and provide estimates of their service life, they can also impact the degradation mechanism and potentially yield inaccurate estimations of the actual lifespan of the polymers. Hence, it is essential to comprehensively comprehend the individual influences of environmental variables to effectively engineer a color-stable prosthesis with prolonged durability[20,21].

Although numerous research studies have focused on investigating the impact of incorporating different nanoparticles on the color stability of pigmented and non-pigmented maxillofacial silicone under various accelerated aging conditions [4,11,20,22–25], there is a notable absence of research exploring the effect of incorporating hybrid nanocomposites on the color stability of silicone. Specifically, no single study has examined the influence of hybrid nanocomposites on the color stability of silicone materials.

This study aims to investigate the impact of incorporating Chitosan-TiO_2 nanocomposite on the color stability of pigmented Room Temperature Vulcanization (RTV) maxillofacial silicone when exposed to various accelerated aging conditions. The null hypothesis posits that the color stability of pigmented maxillofacial A-2186 silicone elastomer would remain unaffected by the impregnation of Chitosan-TiO_2 nanocomposite, even after undergoing different accelerated aging procedures.

2. Materials and Methods

2.1. Materials

One hundred groups (n=5; five hundred specimens in total) of disk-shaped specimens were prepared (twenty-two-millimeter diameter, two millimeters thick) [8,9,26,27] using Room-Temperature-Vulcanized (RTV) maxillofacial silicon elastomer A-2186 (Factor II Inc., Lakeside, AZ, USA), the dimensions of samples were designed using Auto CAD 2013 and processed using the CNC (Computer Numerical Control) machine. Transparent acrylic sheets were used to fabricate molds;

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these plastic molds were made with the specified dimension suitable for digital Portable Colorimeter Devices. Each mold comprises the exact measurements' base, frame, and cover parts.

The Specimens were divided into four equal main groups (twenty-five specimens/group) regarding the pigments that had been combined with the silicon (brilliant red, blue, and yellow dry intrinsic pigments at 0.2% concentration by weight)[11] (Technovent Ltd., Bridgend, UK) and the fourth group without addition of pigment (Non-Pigmented group), each group was subdivided into five divisions representing the categories of silicon. Figure 1 illustrates the study design.

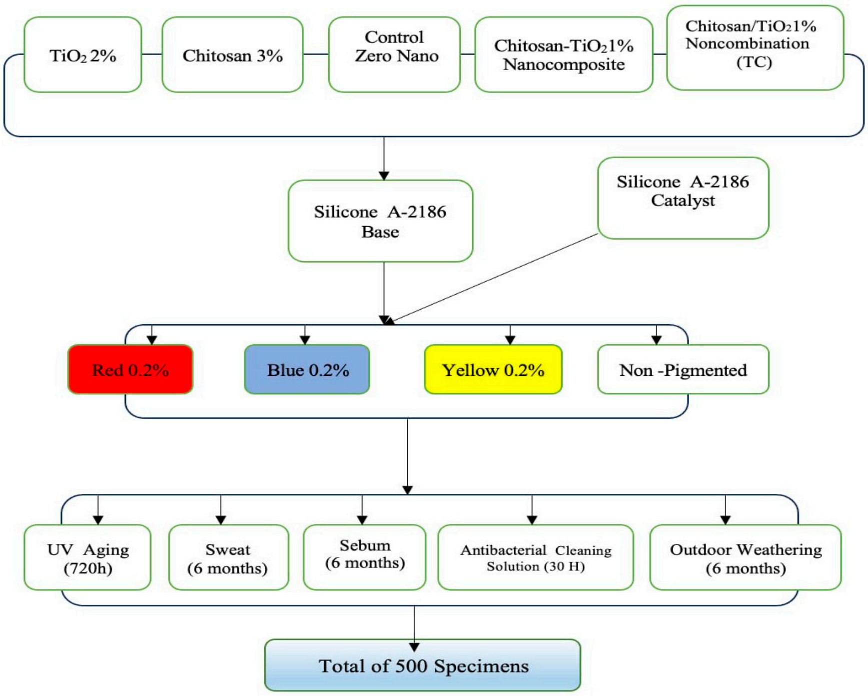

Figure 1. Study design.

Five categories of silicone were made, and the silicone without incorporation of any nanoparticles was considered as the Control; the second category was Titanium dioxide nanoparticle which was impregnated into silicone at a concentration of 2% by weight [11,28] and was obtained from Sigma-Aldrich (CAS Number 718467), twenty-one-nanometre primary particle size; the third category was the impregnation of Chitosan at a concentration of 3% by weight[16]and was obtained from Sigma-Aldrich (CAS Number 448869) with 75-85% degree of acetylation and low molecular weight; the fourth category was the reinforcement with hybrid nano combination of TiO_2 and Chitosan (TC) at a concentration of 1% (0.5% TiO_2 + 0.5% Chitosan) by weight; and the fifth category was the impregnation of silicone with synthesize nanocomposite of Chitosan -TiO_2 powder.

The absolute ethanol 99.5% (EM- PARTA ACS; Merck-KgaA) assisted the dispersion of nanocomposite TiO2- Chitosan powder in the silicon base[29].

2.2. Methods

2.2.1. pilot study

The pilot study was conducted to determine the most suitable concentration of synthesized nanocomposite of Chitosan-TiO_2 for use by evaluating its color stability after subjecting it to different accelerated aging media. At concentrations of 0.5%,1%.and 1.5% by weight of nanocomposite of Chitosan-TiO_2, they were impregnated into red color pigmented silicon (at 0.2% concentration by weight of brilliant red intrinsic pigment) and well dispersed by the assist of absolute ethanol. The de-achromatization of weathering conditions on red-pigmented silicone elastomers was at a higher rate than the ones with yellow pigments and the un-pigmented samples[6,8,26,30–35].

Based on the pilot study result, the most suitable percentage of nanocomposite of Chitosan-TiO_2 concentrations was 1%, which elucidates the least red color change of silicon after subjecting to accelerated aging conditions.

2.2.2. Preparation of Nanocomposite

In a typical experiment of the Core-Shell Method[36], Two grams of TiO_2 was dispersed in two hundred milliliters of 1% (v/v) acetic acid (was obtained from Merck (Cat. No. 100063)), sonicated for thirty minutes at room temperature (Q700 Sonicator; Qsonica LLC), where TiO_2 changed into Ti4 ions. Also, two grams of Chitosan were dispersed two hundred milliliters of 1%(v/v) acetic acid and sonicated for thirty minutes at room temperature. Then the (200 ml TiO_2 + 200 ml Chitosan) was mixed and stirred continuously until the clear sol was obtained at room temperature. NaOH solution (One Molarity) was added dropwise until the solution reached pH ten. The solution was then separated, and the residue was filtrated by the Buchner funnel and washed with excess distilled water thrice until pH seven was obtained from the Chitosan-TiO_2 solution. After that, the mixture was dried in a vacuum oven at 60 °C overnight. Furthermore, the composite was dried using a magnetic stirrer (LabTech LMS-1003; Daihan Labtech Co, Ltd) for two hours at 80 °C. The dried composite was then crushed using mortar to obtain a fine powder. Morphological Characteristics analysis was conducted with the FESEM system, XRD, and FTIR.

2.2.3. Preparation of control group specimens

According to manufactural instructions, the mixing ratio of RTV Silicone type A-2186 was the base to the catalyst ten to one. The control group's mixing began with adding the base to the electronic balance container, sensitive with 0,0001gram accuracy (Nimbus Analytical, Adam Equipment, USA). The catalyst was added and mixed for five minutes by the vacuum mixer (AX-2000, Aixin Medical Equipment Co., Ltd) with a speed of 360 rpm and under a vacuum of (−0.09 bar). For the intrinsic pigmented groups (brilliant red, blue and yellow), pigment powder at 0.2% of concentration[23] by weight was added to the electronic balance container, followed by the addition of the base, then mixed without vacuum for three minutes, followed by a vacuum mixing for seven minutes. Next, the catalyst was added and mixed with a vacuum for the remaining five minutes, and after that, placed in the vacuum chamber for fifteen minutes to eliminate air bubbles. Then the mixed material was left for three minutes in the chamber without a vacuum to allow the settlement of the material. Afterward, the mixed silicone was poured into the plastic molds. G-Clamps were used for tightening the mold so that the excess silicone material would flow outside the border of the mold. Then the material was left to cure at room temperature for twenty four hours.

2.2.4. Preparation of experimental group specimens

The experimental group specimens were fabricated by combining one type of nanoparticle ($TiO2$, Chitosan, and TiO_2-Chitosan hybrid nano combination (TC)) at 2%,3%, and 1%, respectively, either alone or with one of the three dry intrinsic pigments (brilliant red, blue and yellow) at 0.2% concentration[11] by weight with the base of silicon to be mix as same as the control specimens mixed and according to manufacturer instruction.

2.2.5. Preparation of experimental group specimens reinforced with Chitosan-TiO_2 synthesized nanocomposite

Chitosan-TiO_2 synthesized nanocomposite powder was combined with ethanol in weight percentages to fabricate the specimens. The volume of ethanol used depended on the amount of silicone base required for creating five specimens. The ethanol and Chitosan-TiO_2 nanocomposite mixture was subjected to sonication using a Q700 Sonicator from Qsonica LLC. The sonication process lasted for thirty minutes at room temperature with continuous cooling. A titanium alloy

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probe with a standard half-diameter of 136x13 millimeter was utilized, and an amplitude power of four hundred watts was employed with a pulse-on time of five seconds and a pulse-off time of two seconds.

Next, the synthesized Chitosan-TiO_2 nanocomposite with ethanol was added to the RTV Silicone type A-2186 base to prepare the experimental groups' specimens. The mixture was thoroughly mixed in a vacuum mixer for ten minutes. The vacuum mixer jar was placed on a magnetic hotplate stirrer (LabTech LMS-1003; Daihan Labtech Co, Ltd) and connected to a vacuum rotary pump (EuroVac; Thompson CSF) to evaporate the ethanol under a pressure of -0.075 MPa. The evaporation process took one hundred twenty minutes. To ensure homogeneous dispersion of Chitosan-TiO_2 synthesized nanocomposite within the silicone, the concoction was mixed every three minutes for one minute during the two-hour period. Subsequently, the mixture was cooled to room temperature before the catalyst was added. The mixture was mixed for an additional five minutes in the vacuum mixer. Finally, the prepared mixture was loaded into molds and transferred to a vacuum chamber for two minutes to eliminate any air bubbles. G-Clamps were used for tightening the mold so that the excess silicone material would flow outside the border of the mold. Then the material was left to cure at room temperature for twenty four hours. All the specimens were then trimmed and cut-marked to classify the groups.

2.2.6. Color stability test

The prepared specimens were subjected to a color stability test carried out using a Colorimeter (Portable Color Analyzer Precise Digital Colorimeter Color Meter Lab Tester four millimeter Measuring Aperture FRU WR10QC).

The evaluation of color differences was performed using the CIE L* a* b* (Commission Internationale de l'Eclairage) colorimetric system Figure 2. This system utilizes three parameters to define color: L*, a*, and b*. The L* axis corresponds to brightness, ranging from zero (black) to one hundred (pure white). The a* coordinate indicates the presence of red (positive values) or green (negative values), while the b* coordinate represents the amount of yellow (positive values) or blue (negative values).

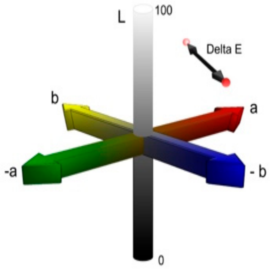


Figure 2. CIELAB color system[4].

The CIE colorimetric system allows for the calculation of the average ΔE (color variation) between two measurements using a specific formula:

$$\Delta E= [(\Delta L^*) +(\Delta a^*) +(\Delta b^*)]^{1/2} \quad (1)$$

This formula enables the determination of the mean color variation (ΔE) value by comparing the L*, a*, and b* values of two readings. Equation 1 was used.

Before weathering, all test specimens were washed, cleaned with distilled water, and gently dried with a clean paper towel. When readings were taken, a white card served as a background[37]. The L*, a*, and b* color coordinates for each sample prior to exposure to weathering were documented. Three measurements were taken and averaged, and the mean for each sample was determined using the CIELAB uniform color scale. L*, a*, and b* were the differences in the respective values before and after the aging condition.

In the context of LAB color space, the ΔE Lab measure, determined as the Euclidean distance between two LAB vectors, is commonly employed to assess color perception. A lower value suggests it's harder for an observer to differentiate between two colors, with 3.00 as the threshold value for human color discrimination.

The values of ΔE between zero and one represent unnoticeable color differences, whereas values between two and three represent color differences that are just noticeable. When ΔE values exceed or are equal to 3.3, the color difference is visually noticeable and clinically unacceptable.

Distinguishing between perceptible and acceptable color changes is common in various studies. The variation in acceptability thresholds among these studies can be attributed to the variations in pigments and silicones used. In the context of this study, alterations in coloration that are inferior to three units in magnitude are perceived to be detectable visually and are regarded as clinically tolerable[38].

2.2.7. Conditioning modes

The specimens were randomly assigned to five groups, each representing a different conditioning method. Testing the color stability of each five categories of silicon pigmented and non-pigmented were evaluated by the color difference before and after subjecting into five different accelerated aging conditions, first storage in Antibacterial silicone-cleaning solution (B-200-12, Daro Inc., Lakeside, AZ) for thirty hours which presented for the commercial sector. Second storage in simulated sebum solution for six months, the sebum was prepared by dissolving 10% palmitic acid with 2% Glyceryl Tripalmitate into 88% Linoleic acid (all w/w)[28,38–40]. Third storage in simulated acidic perspiration (sweat) for six months, the sweat was prepared according to International Organization for Standardization specification, ISO 105-E04:96, and was comprised of the following components (per liter of distilled water): 0.5-gram L-histidine monohydrochloride monohydrate, five-gram sodium chloride, and 2.2-gram sodium dihydrogen orthophosphate dehydrate[28,38,40]. The specimens were subjected to a fourth exposure of accelerated artificial Ultraviolet (UV) radiation weathering for 720 hours. This was facilitated using an accelerated UV aging chamber equipped with two bulb light fixtures positioned directly above the specimens. These fixtures provided an ultraviolet light exposure equivalent to 720KJ/m2/hour. In addition, the aging chamber maintained a consistent temperature of 60°C and relative humidity of 80%[20,30], and lastly, after Outdoor weather conditioning for six months.

The environmental exposure of the samples to atmospheric conditions was conducted in accordance with the standards set forth in the American Society for Testing and Materials Designation G7-8.3.1. The specimens for the natural outdoor weathering were meticulously suspended from stainless steel racks using ligature wire. The entire assembly was deliberately positioned on the roof of the College of Dentistry/University of Sulaimani for six months[28,38,41,42] from (February 2022 to August 2022). The monthly average high and low temperature and climatic data were documented during the outdoor weathering in Table 1. The specimens were left uncovered and exposed to environmental conditions during the weathering exposure. They were suspended in such a way there was no barrier or walls from the back, front, right and left side. Ensuring optimal exposure to environmental conditions. The specimens were checked daily to ensure that their position was not changed. Before specimens were evaluated, they were cleaned for ten minutes in distilled water, wiped dry, and tested.

Table 1. Monthly average climate data during outdoor weathering for the 2022 year in Sulaimani City / Kurdistan region / northern Iraq.

Date	Temperature C°			Average Humidity %	Pressure(mbar)
(2022)	Max	Min	Average		
February	15.2	5.4	10.3	64.0	917.4
March	15.3	6.4	10.8	59.6	915.9
April	26.2	14.6	20.4	43.5	914.5
May	28.2	17.3	22.8	41.8	913.2

June	37.4	24.6	31.0	28.3	910.1
July	40.7	26.8	33.7	24.2	906.4
August	42.1	28.0	35.0	23.9	908.5

The conditioning durations were chosen to mimic the use of silicone prostheses over a period of twelve to eighteen months. Typically, patients use their prosthetic for eight to twelve hours a day; during this time, the prosthesis is anticipated to be exposed to one to three hours of daylight, regular environmental conditions, and constant sebum and sweat when worn on the defect site. Furthermore, patients typically dedicate around five minutes to cleanse their prostheses before bedtime. Hence, the duration of one month of service corresponds to approximately thirty to ninety hours[29] of daylight aging, along with ten to fifteen days of storage in sebum or acidic solutions (sweat) and one hundred fifty minutes of storage in cleaning solutions[38].

2.3. Statistical Analysis

A comprehensive statistical analysis was carried out to concisely summarize the findings related to each variable studied. Descriptive statistics were calculated and presented for continuous variables, including the mean and standard deviation. A one-way analysis of variance (ANOVA) was utilized with a significance level of $p<0.05$ to evaluate significant differences among the five accelerated aging conditions across five categories of silicon specimens.

Since ANOVA operates on the assumption of equal variances across specimens, Levene's test of homogeneity of variance ($\alpha = 0.05$) was applied to all data, assuming equal variances. Consequently, when the equal variance assumption was rejected, Dennett's T3 multiple comparison test was used to compare the groups ($p<0.05$). On the other hand, when the assumption of equal variance was accepted ($p<0.05$), Tukey HSD multiple comparison tests were used to compare the groups.

A one-sample t-test was performed within each accelerated aging condition to examine the effect of modes on color change, with a significance level of $p<0.05$ being used.

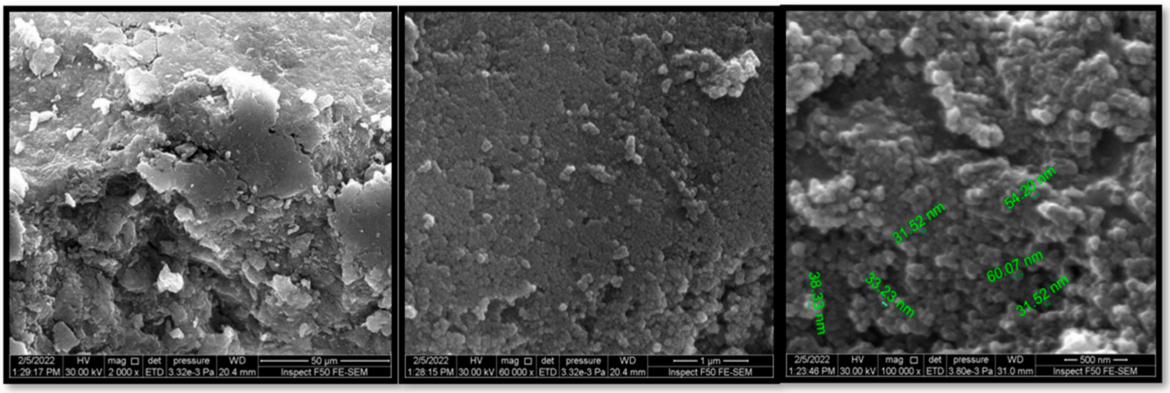
The implication that the variable in this analysis is normally distributed was given by applying the Shapiro–Wilk and Kolmogorov–Smirnov tests. Then assumption of using a t-test and One-way ANOVA was achieved, and version 27.0 of the SPSS program for Windows (SPSS for Windows) was utilized.

3. Results

3.1. Morphological Characteristics

3.1.1. Scanning Electron Microscope (SEM)

SEM was used to study the surface morphology of various coatings nanoparticles; SEM analysis revealed that the average particle size of the synthesized Chitosan-TiO_2 nanocomposite was from (31.52 - 60.07 nm), Figure 3. Field Emission Scanning electron microscopy (FESEM) helped acquire information about the external morphology of the Nanocomposite. In this research, FESEM confirmed the adequate homogenous distribution of nanosized and less aggregated TiO_2 particles within the Chitosan (CS) matrix. The irregular spherical morphologies were due to the interlocking interaction between TiO_2 and CS, which consequently improves the homogeneity of the two.

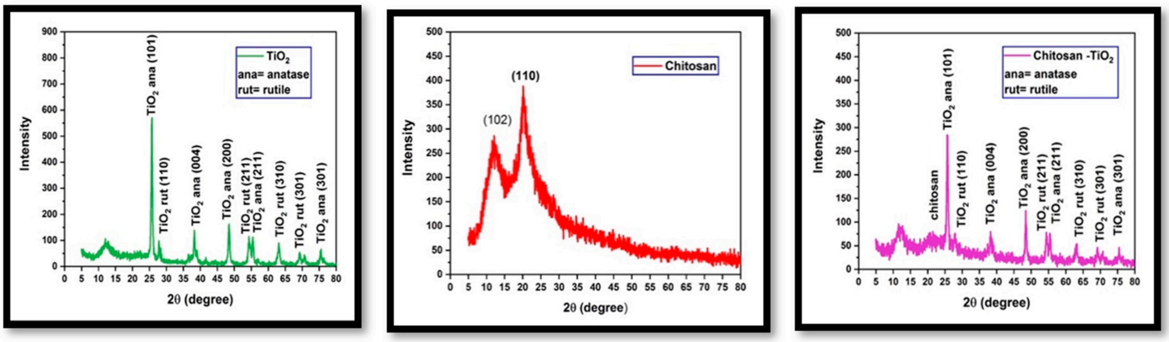


(a) (b) (c)

Figure 3. SEM of synthesizing nanocomposite Chitosan-TiO_2. (a) 50µm resolution; (b) 1µm resolution; (c) 500 nm resolution.

3.1.2. X-ray diffraction (XRD)

The crystalline structure of the synthesized nanocomposites was analyzed by XRD. XRD patterns of the synthesized Chitosan- TiO_2 nanocomposite, pure TiO_2, and Chitosan are demonstrated in Figure 4. The XRD pattern of Chitosan displayed a small, broad peak at 19.77°, indicating its amorphous nature. This suggests that the incorporation of TiO_2 into the chitosan matrix predominantly takes place in the amorphous region of Chitosan. In contrast, both Chitosan and TiO_2 exhibited distinct diffraction peaks in the XRD pattern of the nanocomposite. The TiO_2 nanoparticles displayed the presence of anatase and rutile forms, as evidenced in Figure 4(c). The coexistence of these mixed phases of TiO_2 is advantageous in minimizing the recombination of photogenerated electrons and holes, thereby enhancing the photocatalytic activity of titanium.



(a) (b) (c)

Figure 4. X-Ray Diffraction: (a) XRD of TiO_2 (b) XRD of Chitosan (c) XRD of Chitosan-TiO_2.

3.1.3. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis of the nanocomposite Figure 5 revealed the presence of characteristic bands corresponding to both Chitosan and TiO_2. The band in the 400-700 cm-1 range was attributed to the Ti-O bond, indicating the immobilization of TiO_2 onto the Chitosan matrix.

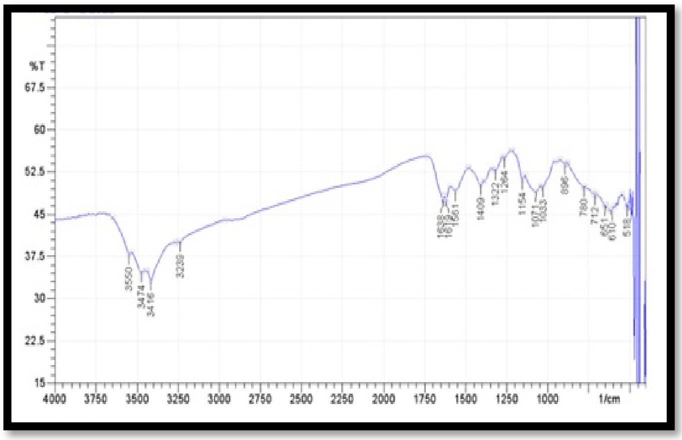


Figure 5. FTIR of the Synthesize Nanocomposite of Chitosan-TiO_2.

3.2. Pilot study

Mean, slandered deviation, and p-value of ΔE of the pilot study were listed in Table 2; the red color pigmented experimental silicon specimens, modified with Chitosan-TiO_2 1% and Chitosan-TiO_2 1.5% nanocomposites, exhibited a significantly lesser color change ($p<0.05$) than the Chitosan-TiO_2 0.5% specimens when exposed to Outdoor weather for six months.

Moreover, upon statistical analysis, the ΔE of red color in the Chitosan-TiO_2 1% specimens was found to be significantly lower ($p<0.05$) than in the Chitosan-TiO_2 0.5% and Chitosan-TiO_2 1.5% specimens when subjected to sebum. These findings led to the selection of the 1% Chitosan-TiO_2 nanocomposite as the percentage for use in the subsequent experimental group specimens.

Table 2. Mean values and standard deviations of (ΔE) brilliant red pigmented Silicon Categories with different conditions (pilot study).

Groups	**Brilliant Red ΔE (Pilot Study)**			
	Chitosan-TiO_2 1%	**Chitosan-TiO_2 1.5%**	**Chitosan-TiO_2 0.5%**	**p-value**
Sweat (6 months)	6.66 ± 3.60	5.20± 0.36	4.12± 0.87	0.305
Antibacterial Cleaning Solution (30 h)	3.31 ± 1.67	2.99 ± 2.02	1.28 ± 0.64	0.179
Outdoor weather (6 months)	16.62 ± 6.32^{b}	17.59 ± 1.68^{b}	24.64 ± 0.68	0.035
UV Weather 1 month (720h)	27.92 ± 1.24	26.45 ± 1.11	25.61 ± 2.64	0.162
Sebum (6 months)	6.24 ± 1.66^{a,b}	10.09 ± 2.96	11.14 ± 0.92	0.01
p-value	0.000*	0.000*	0.000*	

a: Compare to Chitosan-TiO_2 1.5%; b: Compare to Chitosan-TiO_2 0.5%; Different superscript letters in the same row indicate the only significant differences presented in ΔE ($p < 0.05$) after applying one-way ANOVA and (Dennett's T3 and Tukey HSD) multiple comparison tests.*There are overall significant differences in the color change of all silicon specimens between conditions.

3.3. Color stability results

The Mean, Standard Deviation, and Significant differences (P-value) of brilliant red, blue, yellow, and non-pigmented ΔE among all silicon categories after subjecting to different conditions were demonstrated in Tables 3,4,5, and 6, respectively.

3.3.1. The red color

For brilliant red pigments, within all silicon specimens, the UV Weather (720h) induced the prominence alteration in color (ΔE = 27.93, 31.38, 27.36, 41.19 and 40.84) ($p < 0.05$) with greatest ΔE to

Chitosan 3% silicon specimens (ΔE 41.19), in contrast, the lesser color changes were observed in all silicon specimens after immersion in Antibacterial cleaning solution (30h) with the lesser color changes for TiO_2 2% and TC 1% (ΔE 1.03 and 1.35) respectively.

According to statistical analysis, all conditioning modes provoked visually detectable color change (ΔE >3) to categories Chitosan- TiO_2 1%, Chitosan 3%, and Control (zero nano) silicon specimens. The color change of all specimens was significantly lesser ($p < 0.05$) than that of Control (zero nano) specimens when they were exposed to sebum. Consistently, ΔE of TC1% and TiO_2 2% categories were significantly lesser ($p<0.05$) than that of Chitosan 3% and Control (zero nano) silicon specimens when exposed to the Antibacterial cleaning solution.

Table 3. Mean values and standard deviations of (Brilliant Red ΔE) of Silicon Categories with different conditions.

Groups	**Brilliant Red ΔE**					
	Chitosan- TiO_2 1%	**TC 1%**	**TiO2 ₂%**	**Chitosan 3%**	**Control (Zero Nano)**	**P-value**
Sweat (6 months)	6.66±3.60	6.14 ± 0.38	5.45 ± 0.58	5.01 ± 2.02	5.15 ± 1.43	0.561
Antibacterial Cleaning Solution (30 h)	3.31 ± 1.67	1.35 ± 0.49^{c,d}	1.03 ± 0.98^{c,d}	4.62 ± 2.39	4.66 ± 1.11	0.000
Outdoor weather (6 months)	16.61 ± 6.32	21.19 ±1.70	19.74±2.95	20.87±1.03	18.91 ± 9.90	0.695
UV Weather 1 month (720h)	27.93 ± 1.24^{a,c}	31.38 ± 0.6^{b,c}	27.36±0.71^{c}	41.19 ± 2.6	40.84±7.15	0.000
Sebum (6 months)	6.24 ± 1.66^{d}	7.48 ± 1.66^{d}	6.25±2.34^{d}	9.26 ± 1.85^{d}	14.44±2.36	0.000
P-value	0.000*	0.000*	0.000*	0.000*	0.000*	

a: Compare to TC 1%; b: Compare to TiO2 2%; c: Compare to Chitosan 3%; d: Compare to Control (zero Nano). Different superscript letters in the same row indicate the only significant differences presented in ΔE ($p < 0.05$) after applying one-way ANOVA and (Dennett's T3 and Tukey HSD) multiple comparison tests.*There are overall significant differences in the color change of all silicon specimens between conditions.

3.3.2. The blue color

Significant color changes (ΔE = 9.08, 8.92, 10.65, 7.73, and 5.71) ($p<0.05$) were most remarkable in blue pigment specimens across all silicon categories when subjected to outdoor weather for six months. Specifically, the TiO_2 2% category specimens exhibited the highest color change (ΔE 10.65). However, when these TiO_2 2% specimens were exposed to sweat for six months and an Antibacterial cleaning solution for thirty hours, they displayed significantly lesser color changes (ΔE 0.96 and 0.74, respectively).

However, when exposed to all tested conditions, the Chitosan-TiO2 1% and Chitosan 3% specimens showed visually detectable color change (ΔE>3) except for the Antibacterial cleaning solution.

Statistically, the color change, as indicated by the ΔE value, of the Chitosan-TiO_2 1% specimen was significantly greater ($p<0.05$) than the Control (zero nano) specimens when exposed to UV weathering for 720 hours. Similarly, the color change in the Chitosan 3% category specimens was significantly greater ($p<0.05$) than the Control (zero nano) category specimens when exposed to sweat, outdoor weathering, and UV weathering for 720 hours.

On the other hand, TC 1% and TiO_2 2% category specimens displayed significantly lesser color changes ($p<0.05$) than Chitosan 3% category specimens when exposed to both sweat and sebum.

Table 4. Mean values and standard deviations of (Blue ΔE) of Silicon Categories with different conditions.

Groups	Blue ΔE					
	Chitosan-$TiO_2$1%	**TC 1%**	**TiO_2 2%**	**Chitosan 3%**	**Control (Zero Nano)**	**P-value**
Sweat (6 months)	3.49±2.57	1.18±0.82^{c}	0.96±0.26^{c}	3.46±1.02^{d}	1.50±0.55	0.001
Antibacterial Cleaning Solution (30 h)	1.21±0.67	1.37±0.93	0.74±0.43^{c}	2.94±1.39	1.32±0.31	0.001
Outdoor weather (6 months)	9.08±1.44^{d}	8.92±0.59^{d}	10.65±0.25^{d,c}	7.73±0.66^{d}	5.71±1.57	0.000
UV Weather 1 month (720h)	3.73±0.89^{d}	2.67±0.58	2.67±0.37	3.63±0.93^{d}	1.88±0.86	0.005
Sebum (6 months)	4.21±1.79	2.84±1.34^{c}	3.09±1.36^{c}	5.76±2.19	4.85±1.26	0.018
P-value	0.000*	0.000*	0.000*	0.000*	0.000*	

a: Compare to TC 1%; b: Compare to TiO_2 2%; c: Compare to Chitosan 3%; d: Compare to Control (zero Nano). Different superscript letters in the same row indicate the only significant differences presented in ΔE ($p < 0.05$) after applying one-way ANOVA and (Dennett's T3 and Tukey HSD) multiple comparison tests. *There are overall significant differences in the color change of all silicon specimens between conditions.

3.3.3. The yellow color

Among all the silicon categories specimens with yellow pigment, the most significant color change was observed when they were subjected to outdoor weather for six months. The Control (zero nano) specimens recorded the highest ΔE value of 3.04. Conversely, the TiO_2 2% category specimens displayed the least color change with a ΔE value of 0.48 after being subjected to sweat.

Upon statistical analysis, it was found that most condition modes, excluding sweat, didn't result in a significant color change in all specimens when compared to each other. However, when exposed to sweat, a significantly greater color change ($p<0.05$) was seen in the Chitosan-$TiO_2$1% and TC1% category specimens than in the TiO_2 2% category specimen. In contrast, under the same sweat exposure, the TiO_2 2% category specimen showed a significantly lesser ΔE value ($p<0.05$) compared to both the Chitosan 3% and Control (zero nano) category specimens; the observed color changes were within the clinically accepted limits, with ΔE < 3.

Table 5. Mean values and standard deviations of (Yellow ΔE) of Silicon Categories with different conditions.

Groups	Yellow ΔE					
	Chitosan-$TiO_2$1%	**TC 1%**	**TiO_2 2%**	**Chitosan 3%**	**Control (Zero Nano)**	**P-value**
Sweat (6 months)	1.34 ± 0.48^{b}	1.69 ± 0.85^{b}	0.48 ± 0.23^{c,d}	1.5 ± 0.60	2.21 ± 1.24	0.006
Antibacterial Cleaning Solution (30 h)	1.84 ± 0.50	1.14 ± 0.35	0.86 ± 0.38	1.41 ± 0.74	1.45 ± 0.78	0.103
Outdoor weather (6 months)	2.61 ± 0.56	2.64 ± 0.63	2.72 ± 0.74	2.72 ± 0.40	3.04 ± 0.61	0.803
UV Weather 1 month (720h)	0.95 ± 0.26	0.7 ± 0.26	1.02 ± 0.16	0.89 ± 0.32	1.13 ± 0.43	0.267
Sebum (6 months)	1.07 ± 0.36	1.49 ± 0.87	1.38 ± 0.50	1.32 ± 0.40	1.6 ± 1.29	0.788
P-value	0.000*	0.002*	0.000*	0.000*	0.035*	

a: Compare to TC 1%; b: Compare to TiO2 2%; c: Compare to Chitosan 3%; d: Compare to Control (zero Nano). Different superscript letters in the same row indicate the only significant differences presented in ΔE ($p < 0.05$) after applying one-way ANOVA and (Dennett's T3 and Tukey HSD) multiple comparison tests.*There are overall significant differences in the color change of all silicon specimens between conditions.

3.3.4. The non-pigmented

In the non-pigmented group, the most substantial color change across all silicon categories occurred when the specimens were exposed to sebum, with the control (zero nano) specimens showing a ΔE value of 9.02. On the other hand, the UV weathering for 720 hours resulted in significant color changes across all categories when compared with each other. Interestingly, the Antibacterial cleansing solution induced the least color change across all silicon categories, with the TiO_2 2% silicon variant recording a low ΔE value of 0.76.

From the statistical analysis, it emerged that the Chitosan 3% category silicon specimens had a significantly greater color change ($p<0.05$) compared to the Control (zero nano) category when exposed to sweat for six months and UV weathering for 720 hours. However, when exposed to Outdoor weathering for six months, the Chitosan-$TiO_2$1% category specimens exhibited a significantly higher ΔE value (7.77) ($p < 0.05$) compared to all other silicon categories.

Moreover, when exposed to sebum, the color change in the Chitosan-$TiO_2$1% and TC1% categories was significantly higher ($p<0.05$) compared to the TiO_2 2% silicon category. Yet, when exposed to the same condition, the TiO_2 2% category recorded a lower ΔE value ($p<0.05$) compared to the Control (zero nano) silicon category. Additionally, under exposure to sweat, the ΔE of all specimens was significantly lower ($p<0.05$) compared to the Chitosan 3% silicon category.

Table 6. Mean values and standard deviations of (non-Pigmented ΔE) of Silicon Categories with different conditions.

Groups	Non-Pigmented ΔE					
	Chitosan-TiO_2 1%	**TC 1%**	**TiO_2 2%**	**Chitosan 3%**	**Control (Zero Nano)**	**P-value**
Sweat (6 months)	1.12 ± 0.41^{c}	1.70 ± 0.99^{c}	1.26 ± 0.59^{c}	7.63 ± 3.5^{d}	1.39 ± 0.46	0.000
Antibacterial Cleaning Solution (30 h)	1.24 ± 0.48	1.10 ± 0.37	0.76 ± 0.37	1.17 ± 0.32	0.95 ± 0.39	0.294
Outdoor weather (6 months)	$7.77 \pm 0.36^{a,b,c,d}$	3.42 ± 0.45	4.11 ± 0.93	3.13 ± 1.61	4.67 ± 2.54	0.000
UV Weather 1 month (720h)	$3.81 \pm 0.35^{a,b,d}$	2.00 ± 0.51^{c}	1.8 ± 0.34^{c}	5.04 ± 1.21^{d}	1.88 ± 0.99	0.000
Sebum (6 months)	4.81 ± 0.92^{b}	4.84 ± 0.92^{b}	2.55 ± 0.52^{d}	5.5 ± 4.28	9.02 ± 3.96	0.009
P-value	0.000^{*}	0.000^{*}	0.000^{*}	0.014^{*}	0.000^{*}	

a: Compare to TC 1%; b: Compare to TiO2 2%; c: Compare to Chitosan 3%; d: Compare to Control (zero Nano). Different superscript letters in the same row indicate the only significant differences presented in ΔE ($p < 0.05$) after applying one-way ANOVA and (Dunnett's T3 and Tukey HSD) multiple comparison tests.*There are overall significant differences in the color change of all silicon specimens between conditions.

4. Discussion

In this study, all silicon categories, whether pigmented or non-pigmented, underwent different amounts of color changes regardless of aging conditions. The results of this study support the rejection of the null hypothesis that the color stability of pigmented maxillofacial A-2186 silicon elastomer was affected by the impregnation of Chitosan-TiO_2 nanocomposite after subjecting to different accelerated aging conditions.

The deterioration of color in facial prostheses can be attributed to environmental factors such as solar radiation, temperature, and water. Solar radiation consists of ultraviolet (UV), visible, and infrared radiation, with UV radiation significantly impacting color stability. The depletion of the ozone layer since the 1970s has raised concerns about the effects of UV radiation on facial prostheses[11].

Additionally, routine cleaning and disinfection procedures can lead to color alterations in maxillofacial silicone prostheses due to the high permeability of silicone. While various cleansing agents, such as water, neutral soap, and chlorhexidine, are recommended, they should be used cautiously to prevent adverse effects on the material's physical properties[43].

In alignment with Hatamleh et al. study[38], the findings of this research also demonstrated that the Antibacterial cleaning solution ensured the most color stability across all silicon categories, regardless of whether they were pigmented or not.

This study introduced the development of a novel three-phase composite by merging nanoparticles with polymeric silicon, a technique not previously employed. This composite was created successfully by meticulously integrating two different particles - nanoparticles (TiO_2) and microparticles (Chitosan) - in specific proportions. As a result, the overall qualities of silicone polymers saw significant enhancements. This progressive development is a substantial stride toward endowing maxillofacial prostheses with ideal properties and realistic attributes.

Hybrid nanoparticles, such as Chitosan-TiO_2 composites, have generated significant interest as they merge the properties of organic and inorganic components, resulting in novel materials with enhanced and unique characteristics[44,45].

The core-shell mixing method was effectively employed in this study to prepare a TiO_2-supported Chitosan nanocomposite. Comprehensive morphological characterization utilizing scanning electron microscopy(SEM) Figure 3, X-ray diffraction (XRD) Figure 4, and Fourier-transform infrared spectroscopy (FTIR)Figure 5. Confirmed the successful adsorption of TiO_2 nanopowder into the chitosan matrix with excellent dispersion. These findings demonstrate the meticulous preparation and integration of the TiO_2 and chitosan components within the nanocomposite.

Achieving proper dispersion of Chitosan-TiO_2 nanopowder in a polymer matrix, such as silicon, poses a significant challenge in nanocomposite production due to nanoparticle aggregation. However, achieving uniform dispersion is crucial for polymer/nanocomposites requiring enhanced color stability. Ethanol, as a polar solvent possessing hydroxyl (OH) groups, exhibits strong reactivity with ions, resulting in a prolonged dispersion effect. Its use as a stabilizer facilitates the sustained dispersion of the nanopowder within the ethanol solvent, thereby enabling a more uniform dispersion within the polymer matrix[45].

An unacquainted method was employed in this study to achieve improved dispersion of synthesized Chitosan-TiO_2 nanocomposite powder within a silicone matrix. The nanocomposite powder was dispersed in ethanol through sonication and subsequently mixed with the silicone base. The silicone mixture was subjected to heating and vacuuming to remove the ethanol. This approach aimed to achieve a higher level of dispersion without the need for any additional third-party materials that could potentially compromise the properties of the silicone. According to Abdalqadir et al.[29], ethanol was found to have no detrimental effects on the structure and integrity of silicone elastomers.

Based on the current study's findings, the red-colored samples across all silicon categories showed drastic color alterations after undergoing 720 hours of UV-accelerated aging. The most substantial change was observed in the Chitosan 3% samples (41.19) and the least in the TiO_2 2% samples (27.36). Similarly, outdoor weathering over a period of six months led to a steep increase in ΔE values, exceeding (21.19).

From a visual perspective, the pigments transitioned from a brilliant red to a lighter pink, and the pigmented elastomers indicated near-total color depletion. The findings are analogous to the prior research conducted by Beatty et al.[7] ,and Kiat-Amnuay et al.[8].

Subsequently, the brilliant red pigment ΔE values for all silicon categories exhibited discernible color shifts ($\Delta E>3$) in each instance of accelerated aging processes, apart from the ΔE values of TiO_2 2% and TC1% which demonstrated the minimal color transformation after being submerged in an Antibacterial solution for thirty hours, registering values of (1.03) and (1.35) respectively.

These observations align with earlier research by Beatty et al. [7] and Kiat-amnuay et al.[31], which pointed out that using intrinsic red pigment in the study may contribute to color degradation. This could be due to the organic nature of the red pigment, which is more susceptible to irradiation effects. Organic colorants, depending on double and triple bonds for color provision, tend to be relatively reactive and less stable. Conversely, inorganic pigments usually offer greater color stability.

However, they're often not favored due to their lower brightness compared to organic pigments, presenting a challenge in achieving a good color match.

Silicone is a polymer commonly available in the form of a moderately viscous liquid characterized by weak molecular interactions and difficulties in incorporating pigments. This property leads to chromatic alterations in the material, as smaller pigment particles tend to aggregate while larger particles tend to separate from the polymer. Moreover, the polymerization process of silicone elastomers can be influenced by organic materials like makeup powder. Consequently, the presence of pigments may delay the polymerization process and exacerbate the effects of accelerated aging on the materials[10].

Among the various pigments, the cosmetic powder displayed the greatest degree of color alterations. This phenomenon could be attributed to factors such as the incorporated particles' magnitude or the aging impacts. Silicone, known for its lower cohesive energy, exhibits weaker molecular interactions. Consequently, diminutive particles have a propensity to cluster, while their larger counterparts often disengage from the polymer, providing no reinforcement to the material's structure. The particulate components of the cosmetic powder, possibly larger sized, are more prone to separation from the polymer chain, which could contribute to the increased color instability within these materials. Additionally, pigments derived from organic sources, such as makeup powder, undergo amplified degradation with aging, often dissolving upon interaction with ultraviolet light[46]. Also, due to their larger size, dry earth pigments, which bear a structural similarity to cosmetic powders, tend to remain dispersed instead of becoming integrated within the polymer matrix. This characteristic potentially increases their vulnerability to UV degradation[43].

The susceptibility of polymeric biomaterials to deterioration under environmental conditions stems from their inadequate resistance to significant thermal changes and sunlight. Elements of weather, such as temperature, solar radiation, and moisture, can impact the properties of silicone elastomers by triggering chemical alterations. These changes, in turn, result in modifications to the functional features of these materials. The effective performance of silicone elastomers in response to extraoral factors can be ascertained by conducting tests that accurately simulate the conditions associated with outdoor exposure[41].

This study revealed that both outdoor weathering and UV-accelerated artificial weathering had a notable impact on the color of all types of silicon, irrespective of whether they were pigmented or not. Silicon, as a polymer, possesses aromatic rings and C=C bonds, which can be susceptible to the effects of UV light, resulting in color instability. When these functional groups in a polymer absorb UV light, they become energetically unstable. However, this excess energy can be mitigated through various means, such as transferring the excitation to other molecules for stabilization. The excited groups can then return to their original state by releasing the excess energy in the form of longer wavelength light or heat. Failure to dissipate the excess energy can lead to photochemical degradation, causing detrimental effects like color or brightness loss, reduced opacity, and material stiffness. Consequently, the presence of aromatic rings and C=C bonds in polymers allows UV light-induced degradation, leading to adverse changes such as altered color and brightness, decreased opacity, crack formation, and increased rigidity[20,47].

As demonstrated by the findings of this study, the samples that underwent artificial aging showed more considerable color changes (ΔE) compared to those exposed to outdoor weathering. In outdoor weathering, samples are subjected to natural conditions, yet this approach lacks the ability for precise control and is deemed subjective. In such weathering experiments, accurate regulation cannot be achieved for factors contributing to degradation, including geographic location, seasonal changes, specific weather conditions, time of day, and exposure duration[20].

The observed outcome could be attributed to the occurrence of post-polymerization cross-linking triggered by light irradiation, which leads to alterations in the structure of the polymer network. These modifications may involve changes in the polymer chain length, intermolecular bonding, and spatial arrangement of the polymer chains. Consequently, these changes affect light transmission through the maxillofacial material and contribute to the polymer's color shade degradation[20,47].

This study declared that integrating nanosized particles, whether utilized independently or as a composite, exhibited insufficient efficacy in safeguarding silicone against color degradation. The influence of all types of weathering on silicone color, particularly during outdoor weathering conditions, was notably significant.

Nano-TiO_2 is commonly used as an inorganic UV absorber due to its high thermal and photostability, unlike organic UV absorbers that tend to migrate within the polymeric matrix and are less stable. When nanoparticles are exposed to UV light, their electrons vibrate, leading to a combination of scattering and absorption of UV radiation. The UV shielding ability of nanoparticles is a result of this combined effect. Smaller particle sizes and lower nano-oxide concentrations enhance their dispersion within the elastomer matrix, thereby improving UV shielding[9,11,48].

According to Bangera et al.[49], aggregates of nano-oxide particles typically range between 30 and 150 nm, representing the most minor units in sunscreen formulations. These aggregates are formed by clustering primary particles, creating tightly bound structures larger than the individual building blocks. Increased particle size and concentration result in poor dispersion and a higher tendency for particle agglomeration, reducing the effectiveness of UV shielding. This is supported by studies conducted by Akash et al., Bishal et al., and Han et al.[9,11,48].

The decline in color stability observed in this study, following exposure of the elastomer to outdoor conditions, can be attributed to incorporating a nanosized composite comprising Chitosan-TiO_2 particles with sizes ranging from 31-60 nm. The aggregation of these particles played a significant role in this reduced stability. These findings align with the research conducted by Bangera et al.[49], further supporting the notion that particle aggregation negatively impacts color stability in silicone elastomers subjected to outdoor conditions.

All silicon categories, whether pigmented or non-pigmented, demonstrated considerable color alterations upon exposure to outdoor weathering. Notably, the highest color modification was detected in the pigmented blue silicon with a ΔE value 10.65, specifically in the 2% TiO_2 variant. Similarly, significant color shifts were observed in the yellow-pigmented silicon, with the control variant registering a maximum ΔE value of 3.04. Furthermore, non-pigmented silicon was not immune to these changes; the Chitosan-TiO_2 variant showed the most substantial color change, with a ΔE value 7.77. These findings underline the broad impact of outdoor weathering on color stability across all silicon types.

The exposure of elastomers to outdoor conditions leads to a slight whitening and yellowing phenomenon. This is caused by the photo-oxidative degradation of the polymer, which occurs due to the combined action of oxygen and sunlight. The process involves forming free radicals, reactions with oxygen, and the subsequent production of polymer oxy- and peroxy-radicals, resulting in chain scission. Additionally, cross-linking can occur through reactions between different free radicals or bonding between existing monomers and chains. When a polymer molecule absorbs ultraviolet light, it becomes molecularly unstable. Excess energy can be transferred between molecules, allowing the molecule to regain stability. However, the release of excess energy leads to photochemical degradation, contributing to the deterioration of the polymer molecule. This degradation process causes modifications in the polymer network structure, affecting the number of polymer chain units, their bonding, and spatial arrangement. Consequently, it affects light transmission through the maxillofacial material and degrades the polymer's color shade. These findings are supported by research conducted by Malavazi et al.[50] and Hatamelh et al.[38], which emphasizes the significance of photochemical degradation and cross-linking in the color changes observed in polymers exposed to outdoor environments.

As well as facial prostheses are in direct contact with human skin for extended periods, and during this time, they can absorb perspiration and sebum. The absorbed secretions can potentially cause changes in the structure of the deteriorating elastomer, ultimately contributing to the overall deterioration of the prosthesis[4,38].

During six months of exposure to artificial sebum aging conditions, non-pigmented silicone specimens exhibited a notable increase in ΔE values across all categories of silicone. The control category, which lacked nanoparticles, experienced the most significant shift, reaching a delta E value of 9.02. These findings suggest that incorporating nanoparticles, either alone or as composites, can potentially serve as a protective measure against color degradation in silicone materials when subjected to immersion in sebum.

Furthermore, the presence of fatty acids from sebaceous skin secretions, combined with environmental factors, can partially decompose silicone polymers by breaking down the bonds within the polymer chains. This degradation process may result in the continuous release of byproducts and alterations in the chromatic properties of the silicone. These observations are supported by the studies conducted by Hatamleh et al. and Al-Harbi et al. [38,41].

The color change (ΔE) of yellow-pigmented silicon specimens with zero nano (Control) was significantly higher when exposed to sweat compared to other silicon categories. Additionally, the color change of Chitosan-$TiO_2$1% and TC 1% specimens was significantly greater than that of TiO_2 2% specimens. On the other hand, the ΔE value of TiO_2 2% specimens was significantly lower than that of Chitosan 3% and Control. However, all ΔE values of yellow-pigmented silicon were within the clinically accepted limit of ($\Delta E<3$).

This finding suggests that immersion in acidic sweat may catalyze the cross-linking reaction, leading to the formation of an additional polymer network in the silicone[39]. This contradicts the findings of Han et al.[11], who discovered that yellow silicone pigment mixed with nano-oxides significantly impacted the color stability of A-2186 silicone elastomer.

The observed color changes in silicone materials may have been triggered by various factors, as Haug et al.'s [51] study suggested. These factors could include impurities introduced during the manufacturing process, reaction byproducts, initiators, or other mechanisms. Understanding the underlying cause of these transformations could contribute to developing more stable silicone formulations. By advancing the longevity of prosthetic devices, this research could extend their service life.

Additionally, Kiat-amnauy et al. [31] study highlighted that both the duration of exposure and the specific type of silicone elastomer employed significantly influenced color stability. This implies that the length of time the silicone elastomer was exposed to particular conditions, along with its specific formulation, played crucial roles in determining its color stability.

Considering these factors is critical when creating a maxillofacial prosthesis. The environmental conditions of the Middle East, specifically in the Kurdistan region / northern Iraq, are characterized by intense heat, dryness, strong sunlight during the summer, and significant climate shifts in winter. These conditions present challenges to the longevity and color stability of maxillofacial silicones. Extreme environmental conditions, such as elevated temperatures and ultraviolet radiation, can alter silicone elastomers' mechanical properties and color stability. Further research is urged to delve into the other impacts of incorporating the Nanocomposite Chitosan -TiO_2, such as its antimicrobial capabilities and potential allergenicity through cytotoxicity tests, on various types of maxillofacial silicone elastomers over a span of one year. Given the crucial role of mechanical properties in dental and maxillofacial materials, an all-encompassing examination of the investigated maxillofacial elastomers should consolidate both a color stability assessment and rigorous mechanical evaluations. A multidimensional approach of this nature would yield a more holistic view of the material's comprehensive performance and appropriateness for deployment in a demanding therapeutic context.

5. Conclusion

1. The core-shell mixing method is proven to be one of the methodologies of synthesizing Chitosan-TiO_2 nanocomposite, resulting in novel material with enhanced and unique characteristics.

2. The addition of nanosized particles, whether used alone or as a composite, effectively protected the silicon elastomer from accelerated aging conditions, with the exception of outdoor weathering. The significant color changes observed were primarily induced by UV radiation during outdoor exposure.

3. The remarkable alteration in color was predominantly observed in the brilliant red dry pigments. The substantial color change can be attributed primarily to post-polymerization cross-

linking caused by the effects of UV radiation from the irradiated lighting. Conversely, yellow and blue pigments exhibited color stability across various conditions. Nevertheless, the degree of color degradation can vary based on several factors, including the specific silicone elastomer, pigment types, opacifier concentration, and the specific aging method employed.

4. Compared to artificial weathering, outdoor weathering induces the most significant changes in ΔE values across all categories of silicon, regardless of whether they are pigmented or non-pigmented.

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