Effect of Nano Titanium Oxide Addition on Color Stability on Two Types of Maxillofacial Silicone Materials

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Abstract: Background: After 4-14 months of clinical use silicone elastomers may subjected for degradation, despite of they have a desirable properties like, easy coloration, easy manipulation, and biocompatibility. The purpose of this study: was to evaluate the effect of addition TiO₂ nanofiller on the color stability of VST50F (RTV) and Cosmesil M511(HTV) maxillofacial silicone elastomer. Materials and methods: 60 samples were fabricated by addition of 0.25wt% TiO₂ nanofiller with 0.25 wt.% of intrinsic pigment (cream) for VST50F and 0.2 wt% of nano TiO₂ with 0.25 wt.% of intrinsic pigment (cream) for M511 maxillofacial silicone elastomer. According to pilot study, 0.25wt % and 0.2wt% of nano TiO₂ with 0.25 wt.% intrinsic pigment reinforcement revealed superior properties (tensile strength, and hardness shore A). The main study samples were divided into three (3) groups for both silicone material, which were divided into (A: control pure silicone without nano TiO₂, B: silicone incorporated with nano TiO₂ and C: silicone incorporated with nano TiO₂ and intrinsic pigment). The main study samples with three (3) groups of each silicone material were divided into (A: control pure silicone without nano TiO₂, B: silicone incorporated with nano TiO₂ and C: silicone incorporated with nano TiO₂ and intrinsic pigment). The samples were tested before and after artificial ageing the data were analyzed with a descriptive statistical analysis, three-way ANOVA. Results: The addition of 0.25 wt% of TiO₂ nanofiller into VST50F maxillofacial elastomer and 0.2wt% of TiO₂ nano filler into cosmesil M511 and the addition of intrinsic pigment with nano TiO₂ resulted in a highly increase in mean values of the color change, after subjected to artificial ageing for both silicone elastomer materials. Conclusion: Reinforcement of nano TiO₂ with specific concentrations for each VST50F and Cosmesil M511 maxillofacial silicone materials were increase the service life of the prosthesis, but did not protect the silicone matrix from artificial aging degradation of both VST50F and Cosmesil M511 maxillofacial silicone materials.

Keywords: Maxillofacial silicone elastomer, VST50F silicone elastomer, Cosmesil M511silicone elastomer, nano TiO₂ intrinsic pigments,artificial ageing

1. Introduction

Surgical reconstruction may not be possible owing to size or location of the facial disfigurement can be the result of a congenital anomaly, trauma or tumor surgery, The patient's medical condition or personal desires may also preclude reconstructive surgery. In such cases, prosthetic rehabilitation is indicated (¹). As a natural need of human to repair or hide their facial defect maxillofacial prostheses were introduced. It is a skill and the knowledge of cosmetical, anatomics and restore function which is enquire through synthetic substitution of craniofacial structures that are missing or defective due to oncological surgery, facial trauma or congenital and developmental anomalies (²). In the past several materials have been utilized to fabricate maxillofacial prosthesis include wood, wax, ivory, metal and recently polymers such as silicone elastomer, polyurethane elastomers, and acrylic resins (³). For manufacturing maxillofacial prosthesis silicone elastomer has been utilized as the material of decision since the introduction of it by Barnhart in 1960, because of its chemical inertness, durability, ease of manipulation and biocompatibility (⁴, ⁵, ⁶).

The most common reason for refabrication is the expected half-life of silicone maxillofacial prosthesis and degradation of color and mechanical properties of the prosthesis (⁷). Some unpleasant property of silicone elastomer material; the most important one has small tear and tensile strength, deficient elasticity and degradation of physical and color properties (⁸).

2. Materials and Methods

Two types of maxillofacial silicone elastomers had been used, room temperature vulcanized VST50F RTV (Factor II Inc., USA) and heat temperature vulcanized Cosmesil M511 HTV (Factor II Inc., USA), nano titanium oxide particles (TiO₂) (Sky spring nano materials, Inc., USA), cream pigment (functional intrinsic FI) (Factor II Inc., Lakeside, USA) incorporated into each materials with selected concentration according to pilot study. About 60 specimens were prepared: 30 specimens for RTV silicone elastomer material and others 30 specimens for HTV silicone elastomer material that shared into 3 groups according to the conducted test with 10 specimens for each group that divided into (A, B, and C). Group (A) include control group without nano TiO₂, group (B) silicone material incorporated with nano TiO₂ and group (C) silicone material incorporated with nano TiO₂ and intrinsic pigment.

Pilot study

A pilot study was made to determine the best concentration for nano TiO₂ and intrinsic pigment to be used in the main study by testing its effect on tear strength and hardness. For RTV silicone elastomer the best concentration of nano TiO₂ was 0.25 wt.% concentration and for intrinsic pigment 0.25 wt.% concentration, while for HTV silicone elastomer nano...
TiO$_2$ was 0.2 wt.% concentration and for intrinsic pigment was 0.25 wt.% concentration.

**Mold making**

Specimens dimensions were designed by use Auto CAD 2013 (Autodesk Inc, San Rafael, CA, USA) then processed utilizing computer numerical control machine to form the matrix part of the mold that the material was poured into it\(^{(9)}\) (Figures 1 and Figure 2).

**Pouring the mixture into the molds**

The matrix and the bottom parts and the cover of the mold were previously coated with petroleum jelly\(^{(12, 16)}\) for HTV silicone elastomer molds and separating medium for RTV silicone elastomer molds, then the matrix parts and bottom parts were securely attached for the two types molds (metal molds for HTV silicone elastomer and acrylic molds for RTV silicone elastomer) and placed on the vibrator for RTV silicone elastomer with the mold spaces coated with separating medium. The material was injected from the syringe into the mold and a cover (RTV silicone molds) and a glass slab (HTV silicone molds), was laid onto the matrix filled with the material. Lying of the cover part, the glass slab was started from one side by resting the bottom edge of the slab and holding the top edge, while the covers, the glass slab was carefully and slowly lowered onto matrix to force excess material and air out ahead of it. Then a constant load of (1Kg) was placed over the acrylic molds to ensure that all bubbles were disappeared (Figure 3), after that remove the load and tighten the molds securely with nuts and G-clamps and left it for setting (2-4hrs) as recommended by manufacturer's instructions, while for the metal molds after the glass slab was laid the molds were tightly secured with nuts and apply a constant load (1Kg) over it and placed into hot dry oven (Figure 4).

**Demolding and storage of samples**

According to manufacturer’s product description the RTV silicone elastomer material sets in about 2-4 hrs. and for HTV silicone elastomer material sets in hot dry oven for one hr, then the samples were removed carefully from the mold\(^{(18)}\). Samples that had visible defects (to the same operator) were discarded before testing\(^{(19)}\). The samples were stored in a custom-made lightproof box in an air-conditioned room. During storage, the temperature was 10-30°C and RH did not exceed 80%\(^{(20)}\).

**Mixing of the silicone base with nanoTiO$_2$**

As recommended by manufacturer’s instructions, the mixing of VST50F and Cosmesil M511 silicone elastomers were in a proportion 10:1 of the base and catalyst for VST50F, and the base with thinner for Cosmesil M511. NanoTiO$_2$ and intrinsic pigment were hand-mixed with the base for 1 minute±1 second by a clean stiff flat ended spatula followed for 2 minutes±1 second mixing by a mechanical mixer in a mixer container without vacuum\(^{(10,11)}\), then mixing for 7 minutes±1 second by a mechanical mixer with vacuum to prevent air bubbles formation\(^{(12)}\). The vacuum pressure was 28 inches Hg as recommended by the manufacturer\(^{(13)}\).

Before adding catalyst, the mixture was left for 2 minutes because the rotation of the mixer create heat and this lead to decrease the working time of the material according to pilot study and other studies\(^{(14)}\). Then pouring the mixture into syringe to be ready for injected into the molds.

**Adding the catalyst**

Mixing of the base and catalyst for RTV silicone elastomer and mixing of the base with thinner for HTV silicone elastomer were made at 50±10% RH (relative humidity) and 23±2°C (controlled temperature). A metal spatula of flat ended was used for mixing the base with catalyst or thinner recommended by the manufacturer. The base and catalyst or thinner were mixed by mechanical mixer with vacuum for 5 minutes±1 second in order to remove all the air bubbles entrapped during mixing with the catalyst, the mixing was done by the same operator in one direction\(^{(10,15,16)}\).
Conditioning of samples
Samples were conditioned for 24 hours prior to testing (21). Then, samples were conditioned at a standard laboratory temperature of 23±2°C for a minimum of 3 hours after removal of flash (43). The flash was removed with a scalpel and sharp surgical blade #11 (12).

Physical testing procedure

Vita easy shade test
The samples were subjected to initialized chromatic analysis through a Visible Ultraviolet Reflection Spectrophotometer. The CIE L*a*b* system was used for calculating the color alterations, constitute by the "Commission Internationale de l’Eclairage - CIE". This system permits the rate of ΔΕ (color variation) in the middle of two scanning to be measured through the formula:

\[ΔE = [(ΔL)^2 + (Δa)^2 + (Δb)^2]^{1/2}\]

Spectrophotometer light transmission test
The amount of light transmitted through the sample was measured by using a spectrophotometer as a function of wavelength. The sample was located over the light opening of the device and then subjected to light. The percentage and the reading of transmitted light, was then acquired from the screen of the computer attached with the device.

Artificial aging
After measuring the color alteration and the amount of light transmission of the samples with vita test and spectrophotometer test The Samples were assessed in Weather-Ometer device (QUV) model (Xenon Arc Ci4000, Atlas Material Testing Technology, USA). According to the most popular aging standardization ASTM G-154 under cycle 7 (13). This cycle is primarily exposing the samples to cycles of (5) hours of UVA light source at 340nm with high temperature of 60°C, then followed by 4 hours (spray for 0:15minutes) and condensation (dew) at 50°C for 3:45minutes.

Statistical analyses
For analyzing the data of this study the statistical package for the social science software (version 23) (SPSS) was used, and the statistics below were performed:

1) Descriptive statistic: Graphical display by bar chart.
2) Inferential statistic: Two-way ANOVA (Two-way analysis of variance) and MC (Multiple Comparison) as a post-hoc were used with these significance levels:
   P > 0.05 NS Non-significant
   0.05 ≥ P > 0.01 S Significant
   P ≤ 0.01 HS Highly significant

3. Results
The mean value of color change for RTV is higher than mean value of color change for HTV before and after artificial aging and there is highly significant change of color when compare each time period with other period (p<0.01). Result found that there is highly significant change of color with time (color decrease when the time increase) (p<0.01) for each group with test at material.
infiltration factors involve with alterations in the matrix. The instability occurs both VST50F and Cosmesil M511, elastomer materials. Common factors that affect in the performance of silicone properties. Temperature, light, and mechanical force in the surrounding environment presented a sharp decline in decreased initial performance, than the silicone exposed to Hatamleh et al., in 2011 structure and sunlight, photo materials weathering of polymers, which cause alteration in their chemical cases cause color changes of the pigments.

Aging and environmental factors that effect on the silicone these studies. General degradation of polymers result from use of disinfectants or additives substitution, which regrettably occurs due to aging process, of mutilated patients is the main objective of prosthetic restoration and reestablishment of self-esteem in prosthetic rehabilitation of facial defects (25). Color is the most important parameter utilized by patient in the assessment of facial prostheses. Change in color is one of the requests of substitution, which regrettably occurs due to aging process, use of disinfectants or additives (15;16;17).

The primary physical property studies of maxillofacial elastomers are the color stability which acts as a part of these studies. General degradation of polymers result from aging and environmental factors that effect on the silicone elastomer, which cause changes in color itself, and in several cases cause color changes of the pigments. Alteration in chemical and physical characteristics can occur from the weathering of polymers, which cause alteration in their mechanical properties. The main source for most polymeric materials deterioration is the integration activity of oxygen and sunlight, photo-oxidative attack, on their chemical structure (18;19;20).

Hatamleh et al., in 2011 (21) showed that silicone elastomer stored for 6 months in a dark environment get a little decreased initial performance, than the silicone exposed to the surrounding environment presented a sharp decline in properties. Temperature, light, and mechanical force are the common factors that affect in the performance of silicone elastomer materials.

According to the results obtained in this study, color instability occurs both VST50F and Cosmesil M511, whether pigmented or not, presented (AE > 0), regardless of the senescent stage. It is recognized that both intrinsic and extrinsic factors may be caused chromatic alteration (24). The discoloration of the material itself result from intrinsic factors involve with alterations in the matrix (23). While the absorption and adsorption of substances represent extrinsic factors, also cause discoloration (24). Other factors correlated with this, can produce color insecurity, such as accumulation of stains, surface roughness, dehydration, water absorption, infiltration, degradation from use, chemical degradation, oxidation during double carbon reactions to produce peroxide compounds, and continuous formation of pigments due to degradation of products (25).

The vita easy shade test show that the last value of color changes following 150 hours of senescent for VST50F and Cosmesil M511 maxillofacial silicone elastomers were got by the colored test specimens (group C) and the highest value was obtained by group B for VST50F and by group A for Cosmesil M511 (Table 1). The spectrophotometric analysis revealed that the lowest values of color changes after 150 hours of aging for VST50F and Cosmesil M511 were got by the un-pigmented test specimens (group A) (Table 1).

For materials VST50F silicone elastomer revealed that the highest mean value of color change than CosmesilM511 maxillofacial silicone elastomers because of the curing procedure of Cosmesil M511 subjected to heat for setting and when subjected to artificial aging exposed for more heat and humidity which may be increase the color change of it.

For tests vita easy shade test show the highest mean value of color change than spectrophotometer test this could be due to the procedure of vita device differ from the spectrophotometer which measure a*b*L that represent (Hue, chroma and value of color) while the spectrophotometer device measure the translucency of a material (27).

Reduction of light transmission may be recognized to the scattering effect of nano TiO2 filler. Because the index of refraction of nano TiO2 is different from that of silicone

### Table 1: Descriptive statistics of color change results 3-way ANOVA repeated measure of color change arrange material, test times A, RTV material and B, HTV material

| Material | Test | Group | Control | 15hr | 25hr | 50hr | 100hr | 150hr |
|----------|------|-------|---------|------|------|------|-------|-------|
| RTV VT.  | A    | 36.03 | 3.048   | 37.45| 227  | 35.48| 421   | 11.55 |
|          | B    | 35.00 | 1.191   | 36.57| 275  | 35.91| 841   | 11.43 |
|          | C    | 34.80 | 1.012   | 36.99| 202  | 37.35| 852   | 8.02  |
| RTV ST.  | A    | -11.59| .027    | -11.79| .009 | -11.96| .055  | -9.61 |
|          | B    | .29   | .001    | .41  | .001 | .61  | .002  | .18   |
|          | C    | .37   | .002    | .67  | .002 | 1.16 | .001  | .79   |

4. Discussion

The aesthetic restoration and reestablishment of self-esteem of mutilated patients is the main objective of prosthetic rehabilitation of facial defects (19). Color is the most important parameter utilized by patient in the assessment of facial prostheses. Change in color is one of the requests of substitution, which regrettably occurs due to aging process, use of disinfectants or additives (15;16;17).

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elastomer light scattering occurs. The scattering effect will cause the material appear more dark\(^29, 30\).

Result indicates that both VST50F and Cosmesil M511 introduce acceptable color solidity and are suggested for clinic use because the accelerated ageing of UV, which was carried out for 24, 48, and 72 hours, is approximately equal to 0.5, 1 and 1.5 years of clinical wear, respectively\(^31, 32\). This results were agree with other study\(^33, 34, 35, 3, 36\). And according to the addition of pigments some physical and mechanical property, such as color stability, may be modify. For mixing groups, group B presented the highest color alteration values and group C presented the lowest values for vita easy shade test of both VST50F and Cosmesil M511 because of the silicones materials comprising pigments of yellow, orange yellow, white or light orange exhibited the largest color modification when subjected to accelerate ageing, which leads to loss of the color\(^37\). While for spectrophotometer test group C presented the highest values and group B show the lowest values (Figures 5, 6, 7 and 8). This would be depending on the dimension particle add ion or even to senescent. Also the cohesive energy of silicone was a low and, for that reason, a weak molecular interaction. So, mini subatomic lean towards aggregation, while the bigger ones detached from the polymeric, and do not back to the augmentation of the materials\(^38\). Also because of scattering activity of nanoTiO\(_2\) that reduce the light transmission and make the material appear dark.

The highest mean value of color change for group A of VST50F maxillofacial silicone elastomer in vita test than the other two groups in all period of time this is due to non colored silicone itself, color modification occur with time and even without subjection to UV irradiation\(^7\) except in the time period (150 hr.) the group B have the highest mean value than other two groups with highly significant difference. Because of the strong ability of nano-TiO\(_2\) to resist UV rays. And due to their refractive index and optical activity that, can absorb, reflect and scatter UV rays\(^39, 40, 41\). So, modification of silicone elastomer material with TiO\(_2\) nanoparticles can also improve resistance to environmental UV irradiation. The highest mean value of color change of group C for Cosmesil M511 maxillofacial silicone elastomer of spectrophotometer test than the other two groups. According to (Haug et al., in 1999)\(^3\) accomplished that the effect of weathering on color can be altered by the addition of pigments. The addition of inorganic pigment had the best color stability.

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