Color stability of maxillofacial silicone with nanoparticle pigment and opacifier submitted to disinfection and artificial aging

Marcela Filié Haddad
Marcelo Coelho Goiato
Daniela Micheline dos Santos
Amália Moreno
Nuno Filipe D’almeida
Aldiéris Alves Pesqueira
Color stability of maxillofacial silicone with nanoparticle pigment and opacifier submitted to disinfection and artificial aging

Marcela Filiê Haddad,a Marcelo Coelho Goiato,a Daniela Micheline dos Santos,a Amália Moreno,a Nuno Filipe D’almeida,b and Aldíeris Alves Pesqueiraa

aUNESP, Araçatuba Dental School, Department of Dental Materials and Prosthodontics, Rua José Bonifácio, 1193. CEP 16015-050. Araçatuba, SP, Brazil
bSanto Amaro University, School of Dentistry, Rua Professor Enéas de Siqueira Neto, 340. CEP 04829-300. São Paulo, SP, Brazil

Abstract. The purpose of this study was to evaluate the color stability of a maxillofacial elastomer with the addition of a nanoparticle pigment and/or an opacifier submitted to chemical disinfection and artificial aging. Specimens were divided into four groups (n = 30): group I: silicone without pigment or opacifier, group II: ceramic powder pigment, group III: Barium sulfate (BaSO₄) opacifier, and group IV: ceramic powder and BaSO₄ opacifier. Specimens of each group (n = 10) were disinfected with effervescent tablets, neutral soap, or 4% chlorhexidine gluconate. Disinfection was done three times a week during two months. Afterward, specimens were submitted to different periods of artificial aging. Color evaluation was initially done, after 60 days (disinfection period) and after 252, 504, and 1008 h of artificial aging with aid of a reflection spectrophotometer. Data were analyzed by three-way ANOVA and Tukey test (α = 0.05). The isolated factor disinfection did not statistically influence the values of color stability among groups. The association between pigment and BaSO₄ opacifier (GIV) was more stable in relationship to color change (ΔE). All values of ΔE obtained, independent of the disinfectant and the period of artificial aging, were considered acceptable in agreement with the norms presented in literature.

Keywords: spectrophotometer; elastomers; nanoparticle; disinfection; color stability; artificial aging.

1 Introduction

The prosthetic rehabilitation of facial defects has, as an objective, the aesthetic restoration and reestablishment of self-esteem of mutilated patients. Color is the most important parameter used by patients in the evaluation of facial prostheses. Color change is one of the needs of substitution, which unfortunately occurs in a short period of time.

Silicone prostheses are considered color effective for about six months up to one year, and afterward must be redone. The instability of observed color is attributed to the constant exposition to ultraviolet (UV) light, air pollution, pigment additions, and the use of cleansing products.

Literature has shown that intrinsic addition of opacifiers to facial silicones promoted longer color maintenance. Among the opacifiers commercially available, Barium sulfate (BaSO₄) is mentioned. It consists in a white powder, insoluble in water and organic fluids, used in the industry to achieve the white color in paints, glass, and photographic papers. In dentistry, it is used as an opacifier of endodontic cement and in medicine as radiographic contrast. It is also added to sunscreens due to the physical capacity of UV shielding and to obtain an enhanced appearance in cosmetics. However, literature is scarce about the interrelation of opacifier addition to facial silicones, mainly when the material is submitted to the process of chemical disinfection and artificial aging.

The present study had the purpose to verify color stability of Silastic MDX-4-210 facial silicone alone, with the addition of ceramic nanoparticles associated or not to a BaSO₄ opacifier submitted to several chemical disinfection procedures and latter submitted to artificial aging.

The null hypotheses were that the studied factors have no significant influence over the values of specimen color changes.

2 Materials and Methods

Specimens were made using a metallic cylindrical flask, with 10 cavities with a diameter of 30 mm and 6 mm in height. The silicone Silastic MDX-4-210 Silicone (Dow Corning Corporation, Midland, Michigan) was handled in agreement with the manufacturer’s instructions, at a controlled room temperature 23 ± 2°C and relative humidity of 50 ± 10%. One hundred twenty specimens were made, and according to the experimental condition, divided into four groups of 30 specimens each, named as GI: Plain silicone – no pigment or opacifier; GII: silicone pigmented with ceramic powder; GIII: silicone with the addition of BaSO₄; GIV: silicone pigmented with ceramic powder and the addition of BaSO₄.
For groups that received the addition of nanoparticle pigments and/or opacifier (GII, GIII, and GIV), pigments were weighed with a precision digital scale, equivalent to 0.2% by weight of the necessary silicone to fill up the space of the metallic flask. Each pigment was mixed into the silicone on a glass plate with the aid of a stainless steel spatula to obtain a homogeneous mixture.

All silicone combinations were inserted inside the flask and leveled on the surface with a metal spatula to maintain the uniform thickness. Each silicone combination was confined inside the flask with the external surface exposed to the environment for 72 h. After that period, each specimen was carefully separated from the metallic flask.

Initial color for all specimens was registered. All color values were obtained using a UV reflection spectrophotometer (Model UV-2450, Shimadzu, Kyoto, Japan), according to the previously described method, with the color changes calculated by means of the CIE L*a*b* system. The “L” axis is known as brightness and extends from 0 (black) to 100 (perfect white). The coordinate “a” represents the amount of red (positive values) and of green (negative values), while the coordinate “b” represents the amount of yellow (positive values) and of blue (negative values). This system calculates the value of ΔE (color change), between two readings, by means of the formula:

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

Ten specimens of each group were disinfected with one of the following substances: Efferdent alkaline peroxide effervescent (Ef) tablets (Pfizer Consumer Healthcare, Morris Plains, New Jersey), neutral soap (Ns) (Johnson & Johnson, São José dos Campos, SP, Brazil), and 4% solution of chlorhexidine (Cl) (Naturativa, Araçatuba, SP, Brazil).

The process of chemical disinfection was accomplished three times a week for 60 days. For disinfection with Efferdent, specimens were immersed for 15 min in a container containing an effervescent tablet dissolved in 250 mL of warm water with an initial temperature of 37°C and afterward rinsed in running water. Specimens washed with neutral soap were thoroughly scrubbed with it by hand friction for 30 s and rinsed in running water. Specimens disinfected with chlorhexidine were immersed in the solution for 10 min and rinsed in running water. After each disinfection procedure, all specimens were stored in a lightproof black box (no incidence of natural or artificial light), with controlled conditions of temperature (23 ± 2°C) and relative humidity (50 ± 10%), to avoid the occurrence of possible color changes.

After the 60-day disinfection period, new color readings were accomplished and specimens were subsequently submitted to an artificial aging process for nonmetallic bodies (Ultraviolet B/condensation – ASTM). For the artificial aging, specimens were positioned in the artificial aging chamber (Equilam, Diadem, SP, Brazil) and submitted to alternated periods of ultraviolet light and darkness with condensation of distilled water saturated in oxygen. Each aging cycle was accomplished in 12 h. In the first 8 h, ultraviolet light irradiance was at a temperature of 60 ± 3°C. In the following 4 h, a dark condensation period was at a temperature of 45 ± 3°C. In this way, 1008 artificial aging hours were accomplished simulating deterioration caused by rain, dew, and UV light (both direct and indirect sunlight irradiance). Specimens were removed for more color readings in the intervals 252, 504, and final 1008 h of artificial aging totaling five readings.

The values of color change (ΔE) were submitted to the variance analysis (ANOVA) for three factors, followed by the Tukey test (p < 0.05).

### Table 1

Results of three-way repeated-measures ANOVA. [*P < 0.05 denotes statistically significant difference.]

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disinfectant</td>
<td>2</td>
<td>0.118</td>
<td>0.059</td>
<td>0.851</td>
<td>0.430</td>
</tr>
<tr>
<td>Pigment</td>
<td>3</td>
<td>24.455</td>
<td>8.152</td>
<td>117.648</td>
<td>&lt;0.0001*</td>
</tr>
<tr>
<td>Disinfectant × pigment</td>
<td>6</td>
<td>18.375</td>
<td>3.063</td>
<td>44.200</td>
<td>&lt;0.0001*</td>
</tr>
<tr>
<td>Between subjects</td>
<td>108</td>
<td>7.483</td>
<td>0.069</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Period</td>
<td>3</td>
<td>17.242</td>
<td>5.747</td>
<td>118.892</td>
<td>&lt;0.0001*</td>
</tr>
<tr>
<td>Period × Disinfectant</td>
<td>6</td>
<td>1.153</td>
<td>0.192</td>
<td>3.974</td>
<td>0.001*</td>
</tr>
<tr>
<td>Period × Pigment</td>
<td>9</td>
<td>5.087</td>
<td>0.565</td>
<td>11.692</td>
<td>&lt;0.0001*</td>
</tr>
<tr>
<td>Period × Disinfectant × Pigment</td>
<td>18</td>
<td>17.946</td>
<td>0.997</td>
<td>20.625</td>
<td>&lt;0.0001*</td>
</tr>
<tr>
<td>Within subjects</td>
<td>324</td>
<td>15.663</td>
<td>0.048</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

Journal of Biomedical Optics 095004-2 September 2011 • Vol. 16(9)
Table 2 Mean values (SD) of $\Delta E$ for Silastic in the groups with different chemical disinfections. [Ns = Neutral soap; Ef = efferdent evervescent tablets; Cl = 4% clorexidine. Averages followed by the same capital letter in the column and for the same letter in lower case in the line did not significantly differ ($p < 0.05$).]

<table>
<thead>
<tr>
<th>Period</th>
<th>Disinfectant</th>
<th>GI</th>
<th>GII</th>
<th>GIII</th>
<th>GIV</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 days</td>
<td>Ns</td>
<td>1.07 (0.23) Aa</td>
<td>1.26 (0.18) Aa</td>
<td>0.43 (0.13) Ab</td>
<td>0.25 (0.08) Ab</td>
</tr>
<tr>
<td></td>
<td>Ef</td>
<td>0.55 (0.10) Ba</td>
<td>1.21 (0.12) Ab</td>
<td>1.22 (0.10) Bb</td>
<td>0.33 (0.13) Aa</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>1.14 (0.22) Aa</td>
<td>0.77 (0.17) Bab</td>
<td>0.93 (0.29) Bab</td>
<td>0.53 (0.17) Ab</td>
</tr>
<tr>
<td>252 h</td>
<td>Ns</td>
<td>2.04 (0.33) Aa</td>
<td>1.69 (0.27) Aa</td>
<td>0.65 (0.21) Ab</td>
<td>0.45 (0.11) Ab</td>
</tr>
<tr>
<td></td>
<td>Ef</td>
<td>1.39 (0.11) Ba</td>
<td>1.22 (0.26) Ba</td>
<td>1.29 (0.24) Ba</td>
<td>1.00 (0.23) Ba</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0.99 (0.26) Ba</td>
<td>0.81 (0.15) Ba</td>
<td>1.74 (0.32) Cb</td>
<td>1.16 (0.17) Ba</td>
</tr>
<tr>
<td>504 h</td>
<td>Ns</td>
<td>1.97 (0.23) Aa</td>
<td>0.94 (0.17) Ab</td>
<td>1.12 (0.23) Ab</td>
<td>0.93 (0.24) Ab</td>
</tr>
<tr>
<td></td>
<td>Ef</td>
<td>1.41 (0.30) Ba</td>
<td>1.38 (0.23) Ba</td>
<td>0.91 (0.20) Ab</td>
<td>0.74 (0.21) Ab</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>1.17 (0.22) Bab</td>
<td>0.93 (0.25) Ab</td>
<td>1.45 (0.32) Ba</td>
<td>1.13 (0.25) Aab</td>
</tr>
<tr>
<td>1008 h</td>
<td>Ns</td>
<td>2.07 (0.49) Aa</td>
<td>0.76 (0.19) Ab</td>
<td>1.27 (0.29) Ac</td>
<td>0.71 (0.11) Ab</td>
</tr>
<tr>
<td></td>
<td>Ef</td>
<td>1.57 (0.24) Ba</td>
<td>1.50 (0.28) Ba</td>
<td>1.36 (0.27) Aab</td>
<td>1.08 (0.27) Ab</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>1.63 (0.23) Ba</td>
<td>1.39 (0.34) Bab</td>
<td>1.30 (0.16) Aab</td>
<td>1.07 (0.14) Ab</td>
</tr>
</tbody>
</table>

In the present study, neutral soap (chemically inert) was considered as a control disinfection product. The disinfection of specimens with this product is done through digital friction, what is considered a negative point; because this technique can remove nanoparticles (pigments) on the superficial layer of the material. This fact can justify the highest color change presented in specimens of groups GI and GII after 60 days of disinfection with neutral soap (Table 2).

As seen in Table 2, disinfection alone did not significantly influence the value of $\Delta E$. It can be assumed that the color change presented by group GI (Table 2) is a consequence of a small but continuous liberation of by-products during the silicone polymerization seen after 60 days of disinfection and during the different periods of artificial aging. This could cause not only the dimensional change of silicone (contraction) but also changes in its chromatic pattern. The amount of each one of those factors, as well as the different types of solar irradiation, different degrees of humidity, and temperature variations, have an effect on these materials.

In this study, neutral soap was used as a control disinfection product. The disinfection of specimens with this product is done through digital friction, which is considered a negative point because this technique can remove nanoparticles (pigments) on the superficial layer of the material. This fact can justify the highest color change presented in specimens of groups GI and GII after 60 days of disinfection with neutral soap (Table 2).

As seen in Table 2, disinfection alone did not significantly influence the value of $\Delta E$. It can be assumed that the color change presented by group GI (Table 2) is a consequence of a small but continuous liberation of by-products during the silicone polymerization seen after 60 days of disinfection and during the different periods of artificial aging. This could cause not only the dimensional change of silicone (contraction) but also changes in its chromatic pattern. The amount of each one of those factors, as well as the different types of solar irradiation, different degrees of humidity, and temperature variations, have an effect on these materials.

However, when the BaSO$_4$ is added to specimens (groups GIII and GIV), the color change is lower than specimens disinfected with other substances (Table 2).

Physical sunshields, as Barium sulfate (BaSO$_4$), Titanium dioxide (TiO$_2$), and Zinc oxide (ZnO) present the advantages of safety, effectiveness, and blockage of ultraviolet rays. Due to their capacity of solar light reflectance and dispersion, in function of the size of their particles and their film thickness formed on the skin, Opacifiers consist of inorganic particles that remain in suspension when incorporated in sunscreen formulas. The size of...
these particles is extremely important for solar blockage effectiveness of the sun tan lotion and for the aesthetic appearance of the cosmetic product. As BaSO$_4$ is composed by nanoparticles, it has the capacity to accomplish strong union to the polymeric chain of the silicone. This also occurs when it is associated to ceramic pigments avoiding pigment removal through the repeated execution of the disinfection technique with neutral soap for 60 days.

In Table 2, group GII presents a significant reduction of color change after 504 and 1008 h of aging when compared to the changes shown after 60 days of disinfection with soap and after 252 h of artificial aging.

In the first moment, it seemed that specimens returned to the initial color have a tendency for color stabilization on part of the ceramic. In that case, it can be thought that during the aging period of 252 h, nanoparticle pigments not united to the polymeric molecular chain suffered oxidation by the action of UV light, leaving the color of the material more unstable. In 1008 h, those nanoparticles were removed by the action of the artificial aging and the polymeric organic matrix began degradation, which disguised the results.

Group GIV was the most stable for all of the aging periods when disinfected with neutral soap (Table 2). Once again, this proves that the association of opacifier and pigment favors their connection to the silicone polymer, without their removal during disinfection and also protects the material of degradation promoted by the exposure to UV rays of the artificial aging chamber.

In group GII, specimens disinfected with 4% chlorhexidine presented the lowest $\Delta$E values for all artificial aging periods, except for 1008 h.

The 4% chlorhexidine solution is biocompatible and the immersion disinfection technique is considered the most favorable in treating facial silicone prostheses. The lowest significant values of $\Delta$E presented by the different groups disinfected with chlorhexidine (Table 2), was noticed for group GIV after 60 days of disinfection with chlorhexidine and 1008 h of artificial aging. These values were even lower when compared to group GI and reinforce the concept that the association of ceramic nanoparticles and BaSO$_4$ opacifier hinder their removal by the repeated chemical disinfection process and protects the silicone and the ceramic powder of deterioration promoted by artificial aging.

Specimens with BaSO$_4$ addition and disinfected for 60 days with chlorhexidine presented $\Delta$E values statistically higher after 252 h of artificial aging when compared to other disinfection periods, but this change was not significant after 1008 h (Table 2).

When the different disinfectants are compared for each group (Table 2), it can be seen for group GI that those specimens disinfected with Efferdent presented the lowest value of $\Delta$E, which indicates a silicone polymeric matrix degradation that occurred independently of the nanoparticle addition. Group GIII specimens disinfected with neutral soap exhibited the lowest $\Delta$E values after 60 days of disinfection, sustaining the hypothesis that the BaSO$_4$ opacifier constituted by nanoparticles accomplishing a strong union with the silicone polymeric matrix were not removed by digital friction. After 1008 h of aging, group GII statistically presented a significant difference when disinfected with neutral soap.

The Efferdent effervescent tablets are alkaline peroxides, which can be used for cleaning both intra- and extra-oral prostheses. This product basically acts by means of oxygen liberation, with the objective of loosening fragments and removing light stains. By this method, it is reasonable to think that the oxygen-based cleansers, although they remove small stains, also cause prostheses whitening as already cited in other studies.

In group GI, the color change presented by specimens after 60 days of disinfection with Efferdent was significantly lower than specimens submitted by other disinfection methods (Table 2).

The low change observed for group GI specimens when disinfected with Efferdent is more specifically due to the composition of the silicone, originally clear without color, not presenting, therefore pigment degradation with the continuous procedure of disinfection.

After the artificial aging periods, there was no statistically significant difference among values of $\Delta$E among specimens of group GI disinfected with Efferdent and with Chlorhexidine. However, these values were significantly lower than the values obtained for specimens disinfected with neutral soap (Table 2). This may suggest that the effervescent tablets did not expose the pigment or create porosities in the materials, which might facilitate color degradation, as all other groups had the same behavior as group GI. In other words, the color change that occurred after the aging cycles is due to the structural alteration presented by the silicone when exposed to temperature variations and light. As a result of aging, the silicone presents color change caused by intrinsic and extrinsic factors.

The intrinsic factors involve the fading of the colorless silicone. Usually, this intrinsic fading occurs with the material aging due to several physiochemical conditions, such as thermal changes and humidity. Extrinsic factors such as absorption and adsorption of substances can also cause fading.

Other associated factors are responsible for color instability, such as accumulation of stains, dehydration, infiltration, superficial roughness, chemical degradation and usage, oxidation during the carbon double reactions producing peroxide compounds, and the continuous formation of pigments due to the material degradation.

In the evaluation of each group disinfected with Efferdent after 60 days and submitted to different periods of artificial aging (Table 2), there was a noticed an increase of color change after 252 h of artificial aging for all groups, however, this increase was statistically significant for only groups GI and GIV. This fact can be justified by silicone degradation, once all groups presented the same behavior as group GII.

Several studies have mentioned the use of artificial aging chambers in the evaluation of color stability of maxillofacial materials. The device exposes specimens to similar conditions of accelerated weather such as radiation, temperature, and humidity.

When values of $\Delta$E in the different aging periods were compared for each group (Table 2), it was observed that artificial aging promoted color change in all experimental groups. For some authors, the adverse effect caused by the artificial aging in the tested materials is due to the action of three factors that take place during the artificial aging: solar irradiation (light energy), temperature, and water (humidity). The exposure to ultraviolet light is known to considerably change the color of elastomers. This color change may be caused by...
intrinsic chemical alterations of the silicone or by the loss of certain color pigments that are not UV-resistant[26,27].

Other authors[28,29] also found similar results and affirmed that opacifiers can protect facial silicones from color degradation, by blocking the ultraviolet light, and consequent degradation of nanoparticle pigments and also of the own elastomeric structure through the same action observed when they are added to sun shielding lotions[22,23].

In agreement with NBS, a color change is considered very low when ΔE < 1. The situation is clinically acceptable if 1 < ΔE < 3; and it is considered clinically perceptible if ΔE > 3[22,23]. In the present study, the observed color change ranged from 0.435 to 2.044 (Table 2), therefore, it was not clinically perceptible.

These results are in agreement with Mancuso et al[30], who affirmed that the color change presented by colorless specimens of silicone and specimens pigmented with ceramic powder were not clinically perceptible even after 1000 h of artificial aging, demonstrating success in the color maintenance of facial prostheses with inorganic nanoparticle ceramic.

It is also possible to affirm, that the association between the ceramic pigment and the BaSO4 opacifier results in lower values of color change rather than when only the pigment is separately added to the silicone, because the opacifier promotes the reflection of the ultraviolet rays protecting the silicone and the pigments against color degradation[22,23].

Nevertheless, all of the associations accomplished in this study can be clinically applied, as they are in agreement with previously described literature norms[22,23,24].

5 Conclusion

Within the limitations of the study and based on the obtained results, the following conclusions in relation to the facial silicone were drawn:

1. Color changes occurred in all experimental periods, for all studied associations.
2. The association between ceramic nanoparticles and BaSO4 opacifier was the most stable condition in relation to color maintenance, without considering disinfection and the aging period.
3. All ΔE values obtained in the present study, independent of the disinfectant and of the period of artificial aging, were considered clinically acceptable.

References