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RESEARCH AND EDUCATION

Color stability of maxillofacial prosthetic silicone functionalized with oxide nanocoating

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ABSTRACT

Statement of problem. Maxillofacial prostheses made of silicone elastomers undergo undesirable color degradation over time. How this color change can be prevented is unclear.

Purpose. The purpose of this in vitro study was to evaluate the ability of an oxide nanocoating to prevent color degradation of maxillofacial silicone elastomers after artificial accelerated aging.

Material and methods. A silicone elastomer with functional intrinsic pigment was tested. Specimens (N=20) were fabricated, and half of them were coated with a nanolayer of titanium dioxide (TiO_2) using atomic layer deposition. Both coated and noncoated specimens (control) were exposed to artificial aging at 450 kJ/m^2 of total energy. Changes in the color of all the specimens with and without TiO_2 nanocoating were measured before and after the atomic layer deposition coating and before and after aging. The obtained color data were analyzed by using independent *t* tests and the 1-sample *t* test (α=.05).

Results. Color change (ΔE1=3.4 ±1.4) was observed for the silicone elastomers after the specimens were surface coated with TiO_2 nanofilm, although this change was not statistically significant (P=.369) compared with the acceptability threshold (ΔE=3.0). Upon exposure to artificial aging, the noncoated control specimens underwent color change (ΔE2=2.5 ±0.7, P=.083 compared with the acceptability threshold). The specimens with TiO_2 nanocoated surface experienced the least color change (ΔE3=1.4 ±0.6) when subjected to artificial aging, and this change was significantly lower (P<.001) than the established acceptability threshold of ΔE=3.0. In addition, the chemical analyses confirmed that the TiO_2 nanocoating remained on the surface after exposure to artificial aging.

Conclusions. TiO_2 nanocoating was shown to be effective in reducing color degradation of the silicone elastomer exposed to artificial aging for 120 hours with 450 kJ/m^2 of total energy. (J Prosthet Dent 2019;121:538-43)

Silicone, known as polydimethylsiloxane, is a widely used polymer in the biomedical industry.[1] It is popular for its inertness, high thermal stability and usability,[2] unique flexibility,[3] high gas permeability and compressibility, and nontoxic nature.[4] In medicine, it is used as a biomedical implant and in devices such as catheters and for artery regeneration.[5-9] For over 50 years, silicone elastomers have been used in the fabrication of extraoral maxillofacial prostheses to rehabilitate patients with craniofacial defects.[5-9] However, the longevity and maintenance of silicone prostheses are of concern.[5-7,9] The mean life span of silicone-based facial prostheses ranges from 14.5 to 36 months.[10-13] The most common reason behind the replacement of facial prostheses is discoloration of the silicone elastomers.[6,14-17] Color deterioration is primarily caused by exposure to weather conditions and external environmental factors such as solar radiation, temperature, and moisture,[5,6,18-22] with ultraviolet (UV) radiation having a large impact.[8]

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Clinical Implications

A nano-oxide coating on silicone elastomer surfaces may lessen color degradation of maxillofacial prostheses subjected to weathering or aging.

A psychophysical sensation in the eyes provoked by visible light and interpreted by the brain is the most pronounced appearance attribute for facial skin color.[23] Color notations are frequently defined using the CIE-Lab system developed by the Commission Internationale de L'Eclairage, (CIE), where the overall color difference attributed to all the color coordinate differences is denoted as ΔE^*.[24] For maxillofacial prosthetic silicone with light skin color, the perceptibility threshold is reported to be a ΔE of 1.1 and the acceptability threshold to be a ΔE of 3.0.[23]

In dentistry, nano-oxides such as titanium dioxide (TiO_2) and cerium oxide (CeO_2) are widely used as inorganic UV absorbers because their particle size is smaller than the wavelength of UV light (290 to 400 nm). These nano-oxides are capable of reducing harmful damage from UV rays by absorbing and scattering the incident UV light.[22] Ultraviolet A (UVA) can lead to absorption of harmful UV radiation and its dissipation as heat; a hindered amine light stabilizer (HALS) can act as a free-radical scavenger, thereby preventing polymer degradation.[22] The effects of nano-oxides, UVA, HALS, and opacifiers in protecting the color of silicone facial prosthesis materials subjected to accelerated artificial aging and involving different environmental factors and especially UV have been studied.[8,25,26] However, the safety of using these UVA and HALS in maxillofacial silicone prostheses for prolonged contact with skin and mucous membrane has not yet been established through clinical research.[22] In those previous studies, nano-oxide particles were directly incorporated into bulk materials during fabrication, while the surface of a material first faces all challenges of weathering-induced degradations.

The authors are unaware of studies on the effect of atomic layer deposition (ALD)–mediated nanocoating that could prevent color degradation on a pigmented silicone elastomer subjected to artificial aging. The present investigation focused on the study of a surface nano-oxide coating deposited using ALD and on the color stability of a pigmented silicone elastomer A-2000. ALD offers unique approaches to conformal, uniform, and very thin (a few nanometers thick) film deposition of metal oxides on 3-dimensional, complex, porous, nanostructural materials at a relatively low process temperature.[27-30] It provides precise control of the chemical composition and thickness of the nanocoatings.[27-30] A commercial modified ALD system that can accommodate several specimens at one time currently costs between US $110 000 and 240 000. Additional advantages of ALD include independence of line of sight and facilitation of chemical bonding between the coating material and specimen.[27-31] Disadvantages include slowness of this ALD reaction process (although spatial ALD can remedy this) and the availability of a suitable precursor. For this study, the null hypotheses tested were that the color difference between coated and noncoated silicone specimens would be below the perceptibility threshold and that no difference would be found between their baseline color before aging and their color after aging.

MATERIAL AND METHODS

A platinum-catalyzed, vinyl-terminated poly (dimethyl siloxane) elastomer (A-2000; Factor II, Inc) combined with functional intrinsic pigments (FI-SK: Functional Intrinsic Skin Colors - Silicone Coloring System; Factor II, Inc) were used for this study. The elastomer was combined with a polymethyl hydrogen siloxane cross-linking agent at a 1:1 ratio by weight. Once the elastomer components were thoroughly mixed, the pigments were added to resemble human skin color. The elastomer-pigment combination was placed under 0.667 Pa vacuum for 10 minutes to remove air from the system; it was then poured into 3 disk-shaped, 34-mm-diameter molds. The molds were placed in a convection oven and held at 98°C for 1 hour to achieve complete polymerization. The molds were removed and allowed to cool to room temperature; a biopsy punch was used to core the 20 specimens (5 mm diameter, 2 mm thickness). After the color $test_0$, 20 specimens were randomly divided into 2 groups for the coating process (10) and the control (noncoated, 10). The experimental diagram is shown in Figure 1.

A thin film of TiO_2 was deposited on the specimen surface using the ALD technique in a custom ALD reactor described previously.[32] The specimens were pretreated with oxygen plasma by using a compact benchtop plasma cleaning system (PE-50; Plasma Etch, Inc) for 1 minute at 400 W power to make the surface hydrophilic before the ALD process.[33] The sequence of the ALD experiment is shown in Figure 2. The deposition was carried out at 70°C reactor temperature, 50°C precursor bubbler temperature, and a deposition pressure of 66.7 Pa. Tetrakis(dimethylamino)titanium was used as the titanium (Ti) source, and ozone (1000 ppm in oxygen) was used as the oxidizer source for this TiO_2-ALD process. This ozone-based ALD process facilitates chemical bonding between the TiO_2 nanocoating and specimen surfaces.[31] A reference silicon (Si) wafer sample was used during the deposition on the silicone elastomer specimens, and the thickness of the deposited oxide was measured on the reference Si-wafer using a spectral ellipsometer (model M44; J.A. Woollam Co, Inc).

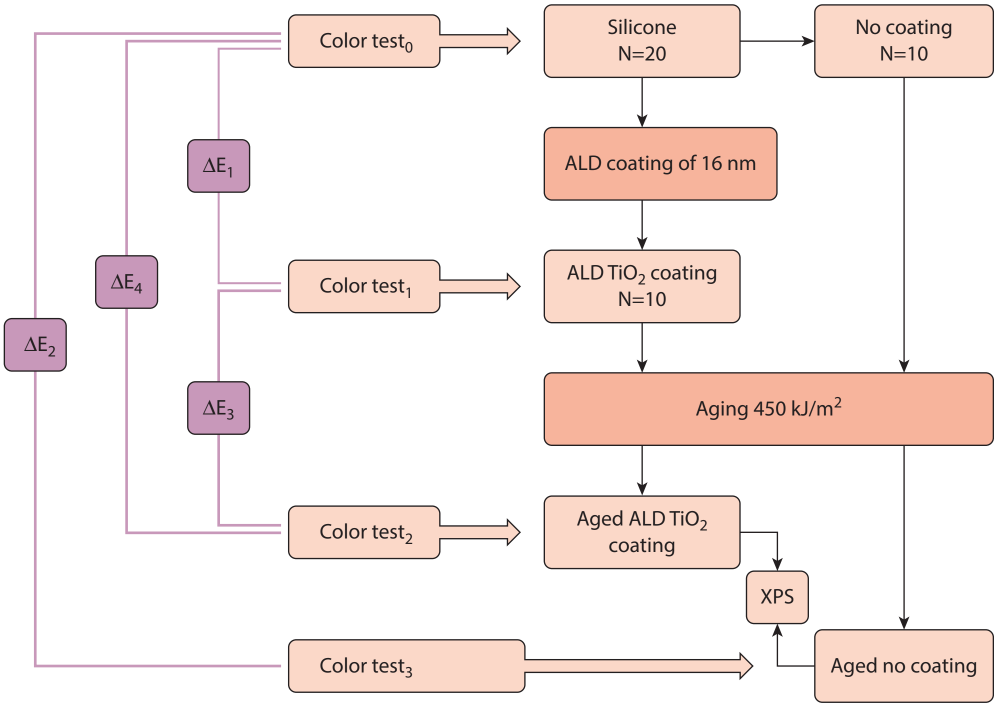

Figure 1. Experimental design involving TiO_2-ALD coating and artificial aging; color test$_0$ signifies color measurements of baseline or control specimens; color test$_1$ indicates color measurements of specimens after TiO_2-ALD coating; and color test$_2$ and color test$_3$ color measurements after artificial aging performed for TiO_2-ALD coated and noncoated specimens, respectively. ALD, atomic layer deposition; TiO_2, titanium dioxide.

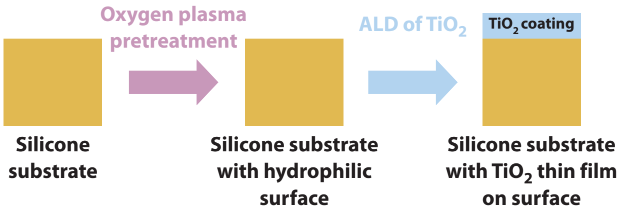

Figure 2. TiO_2-ALD coating process on silicone elastomer surfaces. ALD, atomic layer deposition; TiO_2, titanium dioxide.

Color measurements were performed before (color test$_0$) and after (color test$_1$) ALD coating and after the aging of coated (color test$_2$) and noncoated (color test$_3$) specimens. A spectroradiometer (PR 650; Photo Research, Inc) and 1 illuminator (FO-150; Chiu Technical Corp) were positioned with an optical configuration of 0-degree observance and 45-degree illumination to the specimen without any aperture between the specimen and light/sensor.[34,35] Color measurements (2.4-mm-diameter measurement area) were performed after 15 minutes of warming up and calibration with a white standard (Reflectance Standard SRS-3; Photo Research, Inc) from a 380 to 780 nm spectral reflectance with a 5-nm interval (SpectraWin2; Photo Research, Inc). The data were converted to CIELab values using D65 illumination and 10-degree observer. These L*, a*, and b* values were used to calculate the color change (ΔE^*) using the formula $\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$, where ΔL^*=lightness difference (light or dark), Δa^*=difference in a* values (green to red coordinate), and Δb^*=difference in b* values (blue to yellow coordinate).

Specimens were aged according to the American Society for Testing and Materials G154 specification[36] with 450 kJ/m^2 total exposure.[8] An artificial aging chamber (EQUV; Equilam) containing a UV-A lamp (340 nm of wavelength) with a typical irradiance of 1.55 W/m^2/nm was used. Each exposure cycle was 8 hours of UV at 70 ±3°C black panel temperature and 4 hours of condensation at 50 ±3°C black panel temperature. Ten cycles were carried out to provide a total exposure of 450 kJ/m^2, which is the adequate energy to verify the color stability of silicone materials.

A high-resolution X-ray photoelectron spectrometer (XPS; VSW HA100; Vacuum Scientific Workshop) equipped with an Al Ka (1486.6 eV) X-ray source operating at 12 kV and 15 mA was used to study the chemical composition of the specimen surface.

Data were analyzed by using independent *t* tests to compare the potential color difference among groups. One-sample *t* test was used to compare the potential difference between the recorded color difference with the perceptibility threshold (ΔE=1.1) and acceptability threshold (ΔE=3.0).[23] The estimate effect size was tested by using partial eta squared (η_p^2). With a minimum of 8 specimens per group, a large size effect ($\eta_p^2>0.26$) was obtained for ΔE ($\eta_p1^2=0.292$, *P*=.027), ΔL ($\eta_p^2=0.790$,

Table 1. Mean ±SD values of L*, a*, and b* of noncoated and TiO_2-coated specimens before and after aging

Specimens	L	a	b
No coating	73.3 ±0.5	10.5 ±0.4	22.3 ±0.8
ALD TiO_2 coating	70.7 ±0.7	11.7 ±0.5	23.8 ±0.7
Aged no coating	71.4 ±0.4	10.5 ±0.3	23.8 ±0.7
Aged ALD TiO_2 coating	70.5 ±0.8	11.3 ±0.3	24.8 ±0.7

ALD, atomic layer deposition; TiO_2, titanium dioxide.

Table 2. Statistical analysis (*t* test) of color difference (ΔE) values with respect to perceptibility threshold[22]

Specimens	ΔE	Perceptibility threshold = 1.1[22] *P*
No coating	ΔE_1=3.4 ±1.4	.001
ALD TiO_2 coating		
No coating	ΔE_2=2.5 ±0.7	.001
Aged no coating		
ALD TiO_2 coating	ΔE_3=1.4 ±0.6	.167
Aged ALD TiO_2 coating		
No coating	ΔE_4=3.8 ±1.3	<.001
Aged ALD TiO_2 coating		

ALD, atomic layer deposition; TiO_2, titanium dioxide.

P<.001), Δa (η_p^2=0.508, *P*=.001), and Δb (η_p^2=0.741, *P*<.001). All statistical analyses were performed by using statistical software (IBM SPSS Statistics, v22.0; IBM Corp) (α=.05).

RESULTS

A nanocoating of TiO_2 was deposited successfully on silicone specimens using 300 ALD cycles. This resulted in approximately 16-nm-thick TiO_2, as measured on the reference Si-wafer specimen surface exposed to the same process conditions as those of the ALD on the silicone specimens.

The means and standard deviation of the L*, a*, b* coordinates for the 4 groups are listed in Table 1. Statistical analysis of color difference (ΔE) with respect to the perceptibility threshold[22] is presented in Table 2. All evaluated specimen groups experienced a chromatic alteration (ΔE>0) from oxide coating and exposure to artificial aging. A significant color difference (ΔE_1=3.4 ±1.4) was observed between the noncoated and TiO_2-coated silicone specimens when compared with the perceptibility threshold of ΔE of 1.1 (*P*=.001). Nevertheless, this color difference after TiO_2 coating was less (*P*=.369) than the established acceptability threshold of ΔE=3.0. The noncoated specimens underwent a significant color change (ΔE_2=2.5 ±0.7) after aging. This color change was significantly higher (*P*=.001) than the perceptibility threshold (ΔE=1.1). However, the TiO_2-coated silicone specimen group showed the least color change (ΔE_3=1.4 ±0.6) after aging compared with the other specimen groups. This color change was higher (*P*=.167) than the perceptibility threshold, but significantly lower (*P*<.001) than the acceptability threshold (ΔE=3.0). The TiO_2-coated specimens had statistically significant (*P*=.005) less color difference after aging (ΔE_3=1.4 ±0.6) compared with noncoated specimens after aging (ΔE_2=2.5 ±0.7).

Figure 3 shows the XPS spectra of noncoated and TiO_2-coated silicone specimens after artificial aging with 450 kJ/m^2. Both specimens had 4 distinct peaks. These peaks are attributed to oxygen (O 1s: 532 eV), carbon (C 1s: 285 eV), and silicon (Si 2s: 149.7 eV and Si 2p: 99.4 eV), which are the basic chemical components of silicone elastomers. In addition to the O, C, and Si peaks, a distinct titanium peak (Ti 2p: 455 eV) was observed on the silicone specimens that were surface coated with a TiO_2 nanolayer.

DISCUSSION

The color difference between ALD TiO_2-coated and noncoated silicone specimens was found to be significantly higher than the perceptibility threshold of ΔE of 1.1. In addition, there was a significantly less color change in coated-aged compared with noncoated-aged specimens. Therefore, both null hypotheses were rejected.

A color change was also observed between the noncoated and TiO_2-coated groups. Although most of these color changes from TiO_2 coating (ΔE_1=3.4) were significantly higher than the perceptibility threshold of 1.1,[22] these color differences were not significantly higher than the acceptability threshold (3.0).[22] This implies that the color change of the coated silicone specimens in the present study is not clinically significant. The perceptibility threshold is defined as the color difference that is noticeable by the human eye, while the acceptability threshold is considered the color difference that is acceptable in terms of esthetics.[37] In a clinical setting, the color alteration of the material can be above the perceptibility threshold but below the acceptability threshold. This means that the color change of a material can be perceived clinically but still be acceptable esthetically. A future study evaluating the effect of different coating thicknesses on the color perceptibility threshold is warranted.

All specimen groups, irrespective of nano-oxide coating, showed color instability (ΔE>0) when exposed to artificial aging. Both the intrinsic (self-discoloration of the material) and extrinsic factors (adsorption or absorption of different substances) might cause color degradation.[17] Among contributing environmental factors such as solar radiation, temperature, and moisture, UV radiation was reported to have the greatest impact on color degradation of facial prostheses.[8] TiO_2-coated specimens showed approximately 44% less color change when compared with the noncoated specimens upon

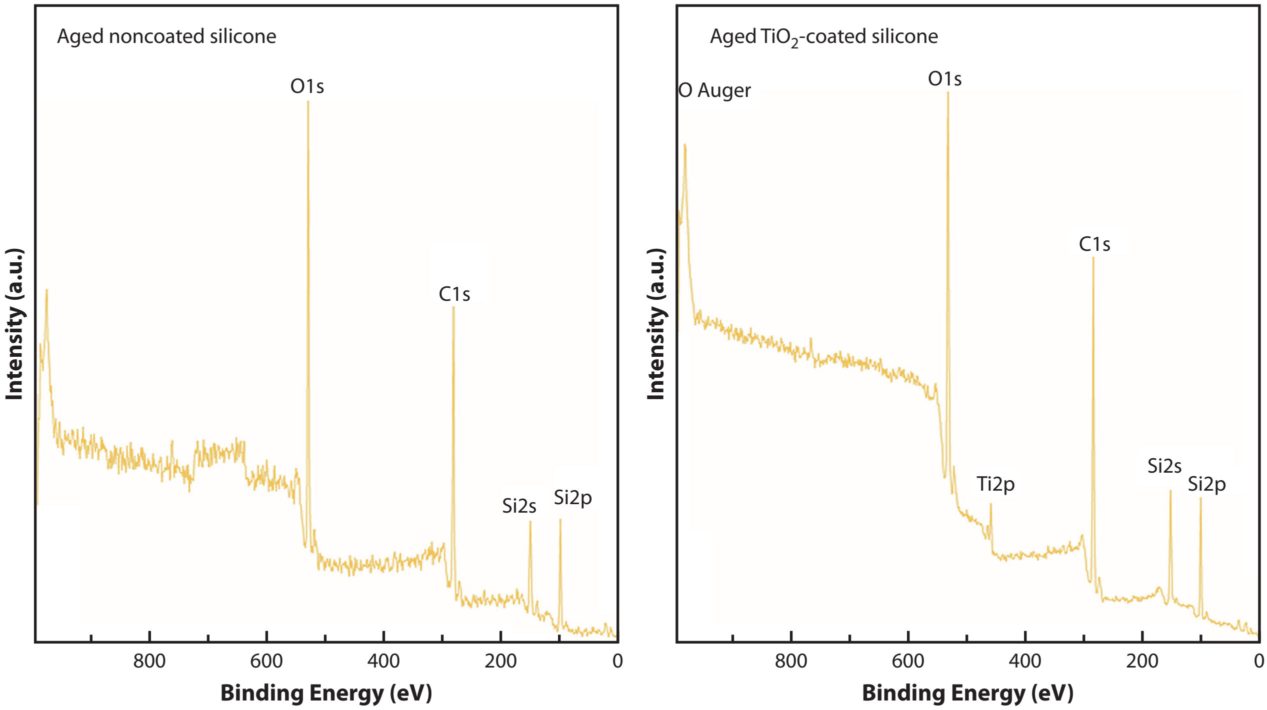

Figure 3. X-ray photoelectron spectroscopy spectra showing surface chemical composition of noncoated and TiO_2-coated specimen after subjecting to artificial aging at 450 kJ/m^2 for 120 hours. TiO_2, titanium dioxide.

exposure to artificial aging. The findings indicated that a TiO_2 nanocoating was able to protect the silicone elastomer from color degradation induced by artificial aging.

Nano-oxides are widely used as inorganic UV absorbers because of their high thermal and photo stability over decades, unlike organic UV absorbers, which are unstable as they migrate from the surface into a polymeric matrix.[25] When electromagnetic radiation such as UV light interacts with the nanoparticle surface, part of this UV light is scattered and absorbed by the nanoparticles. Owing to its high refractive index and semiconductive properties, TiO_2 could offer similar UV protection based on both scattering and absorption of UV rays.[27] These physical principles might contribute to interpreting the color stability of TiO_2-coated specimens presented in this study. Han et al[8] reported that color changes due to artificial aging were least for silicone prostheses with 2% to 2.5% nano-oxide of TiO_2 by weight as a opacifier. However, the color stability of their specimens containing TiO_2 nano-oxide was approximately 29% better than their control. These nano-oxides were inorganic white powder added directly to bulk during specimen preparation. Also, it was reported that 67 nm of ALD-TiO_2 coating (deposited at 80°C and 100 Pa) could almost completely protect biaxially oriented polypropylene polymer during 6 weeks of UV exposure by preventing the formation of UV-induced photodegradation products in the film.[27]

The XPS was used to investigate the inorganic-organic bonding between TiO_2 nanocoating and a silicone elastomer. The XPS results (Fig. 3) confirmed the presence of Ti peak for the TiO_2-coated silicone specimens after the artificial aging test was used. This finding revealed that the protective TiO_2 nanocoating could withstand artificial aging. The vapor phase surface chemical reactions during the ALD process resulted in chemical bonding between the coating material and the surface groups of the ALD substrate.[31]

There were limitations to this in vitro study. The color stability of the specimens was tested using artificial aging and not using natural outdoor aging. In addition, only 1 type of silicone elastomer was studied. Finally, the color of the silicone was measured with a neutral backing. Ideally, it should be measured with both a black and white backing, and the true color should be determined by using the Kubelka-Munk theory.[35]

Further in-depth studies are warranted to investigate the influence of other oxide or inorganic nanocoatings on the color stability of different types of pigmented silicone elastomers commonly used in the fabrication of maxillofacial prosthetic silicone in clinical practice. The intervention of coating in vivo with maxillofacial prosthetic silicone should be examined in a clinical setting. In addition, the range and time needed for color change should be evaluated.

CONCLUSIONS

Within the limitation of this in vitro study, the following conclusions were drawn:

1. All specimens underwent color changes when subjected to artificial aging at 450 kJ/m^2 for 120 hours.
2. Color changes (ΔE_1=3.4) of silicone specimens due to the TiO_2 nanocoating on the surface was clinically acceptable.
3. This nanocoating was stable after aging exposure because chemical analyses confirmed the presence of TiO_2 on the surface after the artificial accelerated aging used.
4. Upon exposure to artificial aging, the nanocoating of TiO_2 was able to reduce color degradation of the evaluated silicone elastomers compared with the noncoated silicone specimens. This indicated that the silicone elastomer with a surface nanocoating of ALD TiO_2 was a color-stable novel material to be used potentially in extraoral maxillofacial silicone prostheses.

REFERENCES

1. Curtis J, Colas A. Chapter II.5.18 - Medical applications of silicones A2. In: Ratner BD, Hoffman AS, Schoen FJ, Lemons JE, editors. Biomaterials science. 3rd ed. Waltham: Academic Press; 2013. p. 1106-16.
2. Van Krevelen DW, Hoftyzer PJ. Properties of polymers: correlations with chemical structure. Amsterdam: Elsevier Pub. Co.; 1976. p. 152.
3. Clarson SJ, Semlyen JA. Siloxane polymers. Englewood Cliffs: Prentice Hall; 1993. p. 478-649.
4. Lötters J, Olthuis W, Veltink P, Bergveld P. The mechanical properties of the rubber elastic polymer polydimethylsiloxane for sensor applications. J Micromech Microeng 1997;7:145.
5. Ariani N, Visser A, van Oort RP, Kusdhany L, Rahardjo T, Krom BP, et al. Current state of craniofacial prosthetic rehabilitation. Int J Prosthodont 2013;26:57-67.
6. Brandão TB, Vechiato Filho AJ, de Souza Batista VE, Ribeiro ACP, Nary Filho H, Chilvarquer I, et al. Assessment of treatment outcomes for facial prostheses in patients with craniofacial defects: a pilot retrospective study. J Prosthet Dent 2017;118:235-41.
7. Chang T-L, Garrett N, Roumanas E, Beumer J. Treatment satisfaction with facial prostheses. J Prosthet Dent 2005;94:275-80.
8. Han Y, Zhao Y, Xie C, Powers JM, Kiat-amnuay S. Color stability of pigmented maxillofacial silicone elastomer: effects of nano-oxides as opacifiers. J Dent 2010;38:e100-5.
9. Nemli SK, Aydin C, Yilmaz H, Bal BT, Arici YK. Quality of life of patients with implant-retained maxillofacial prostheses: a prospective and retrospective study. J Prosthet Dent 2013;109:44-52.
10. Jani R, Schaaf N. An evaluation of facial prostheses. J Prosthet Dent 1978;39:546-50.
11. Karakoca S, Aydin C, Yilmaz H, Bal BT. Retrospective study of treatment outcomes with implant-retained extraoral prostheses: survival rates and prosthetic complications. J Prosthet Dent 2010;103:118-26.
12. Visser A, Raghoebar GM, van Oort RP, Vissink A. Fate of implant-retained craniofacial prostheses: life span and aftercare. Int J Oral Maxillofac Implants 2008;23:89-98.
13. Watson RM, Coward TJ, Forman GH. Results of treatment of 20 patients with implant-retained auricular prostheses. Int J Oral Maxillofac Implants 1995;10:445-9.
14. Al-Harbi FA, Ayad NM, Saber MA, ArRejaie AS, Morgano SM. Mechanical behavior and color change of facial prosthetic elastomers after outdoor weathering in a hot and humid climate. J Prosthet Dent 2015;113:146-51.
15. Eleni PN, Krokida MK, Polyzois GL, Gettleman L. Effect of different disinfecting procedures on the hardness and color stability of two maxillofacial elastomers over time. J Appl Oral Sci 2013;21:278-83.
16. Hatamleh MM, Watts DC. Porosity and color of maxillofacial silicone elastomer. J Prosthodont 2011;20:60-6.
17. Mancuso DN, Goiato MC, Santos DM. Color stability after accelerated aging of two silicones, pigmented or not, for use in facial prostheses. Braz Oral Res 2009;23:144-8.
18. Andres CJ, Haug SP, Munoz CA, Bernal G. Effects of environmental factors on maxillofacial elastomers: part I—literature review. J Prosthet Dent 1992;68:327-30.
19. Polyzois GL. Color stability of facial silicone prosthetic polymers after outdoor weathering. J Prosthet Dent 1999;82:447-50.
20. Haug SP, Andres CJ, Moore BK. Color stability and colorant effect on maxillofacial elastomers. Part III: weathering effect on color. J Prosthet Dent 1999;81:431-8.
21. Hulterström AK, Eystein Ruyter I. Changes in appearance of silicone elastomers for maxillofacial prostheses as a result of aging. Int J Prosthodont 1999;12:498-504.
22. Kulkarni R, Nagda S. Colour stability of maxillofacial silicone elastomers: a review of the literature. Eur J ProsthodontRestor Dent 2014;22:108-15.
23. Paravina RD, Majkic G, Del Mar Perez M, Kiat-amnuay S. Color difference thresholds of maxillofacial skin replications. J Prosthodont 2009;18:618-25.
24. Paravina RD. Esthetic color training in dentistry. St. Louis: Elsevier Mosby; 2004. p. 245.
25. Tran NH, Scarbecz M, Gary JJ. In vitro evaluation of color change in maxillofacial elastomer through the use of an ultraviolet light absorber and a hindered amine light stabilizer. J Prosthet Dent 2004;91:483-90.
26. Kiat-amnuay S, Mekayarajjananonth T, Powers JM, Chambers MS, Lemon JC. Interactions of pigments and opacifiers on color stability of MDX4-4210/type A maxillofacial elastomers subjected to artificial aging. J Prosthet Dent 2006;95:249-57.
27. Lahtinen K, Maydannik P, Seppänen T, Cameron DC, Johansson P, Kotkamo S, et al. Protecting BOPP film from UV degradation with an atomic layer deposited titanium oxide surface coating. Appl Surf Sci 2013;282:506-11.
28. Hyde GK, Park KJ, Stewart SM, Hinestroza JP, Parsons GN. Atomic layer deposition of conformal inorganic nanoscale coatings on three-dimensional natural fiber systems: effect of surface topology on film growth characteristics. Langmuir 2007;23:9844-9.
29. Kemell M, Ritala M, Leskelä M, Groenen R, Lindfors S. Coating of highly porous fiber matrices by atomic layer deposition. Chem Vap Deposition 2008;14:347-52.
30. Spagnola JC, Gong B, Arvidson SA, Jur JS, Khan SA, Parsons GN. Surface and sub-surface reactions during low temperature aluminium oxide atomic layer deposition on fiber-forming polymers. J Mater Chem 2010;20:4213-22.
31. Rai VR, Agarwal S. Surface reaction mechanisms during ozone-based atomic layer deposition of titanium dioxide. J Phys Chem C 2008;112:9552-4.
32. Xu R, Tao Q, Yang Y, Takoudis CG. Atomic layer deposition and characterization of stoichiometric erbium oxide thin dielectrics on Si (100) using (CpMe) 3 Er precursor and ozone. Appl Surf Sci 2012;258:8514-20.
33. Bishal AK, Butt A, Selvaraj SK, Joshi B, Patel SB, Huang S, et al. Atomic layer deposition in bio-nanotechnology: a brief overview. Crit Rev Biomed Eng 2015;43:255-76.
34. Gozalo-Diaz DJ, Lindsey DT, Johnston WM, Wee AG. Measurement of color for craniofacial structures using a 45/0-degree optical configuration. J Prosthet Dent 2007;97:45-53.
35. Johnston W, Hesse N, Davis B, Seghi R. Analysis of edge-losses in reflectance measurements of pigmented maxillofacial elastomer. J Dent Res 1996;75:752-60.
36. Standard practice for operating fluorescent ultraviolet (UV) lamp apparatus for exposure of nonmetallic materials. ASTM International; 2012. Designation G: 154-06.
37. Khashayar G, Bain PA, Salari S, Dozic A, Kleverlaan CJ, Feilzer AJ. Perceptibility and acceptability thresholds for colour differences in dentistry. J Dent 2014;42:637-44.

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