

Colour Stability of Maxillofacial Silicone Elastomers: A Review of the Literature.

R.S. Kulkarni* and S.J. Nagda*

Abstract - Colour degradation is a serious limitation of maxillofacial silicone elastomers and most silicone facial prostheses have to be remade within 1 year due to colour deterioration. A comprehensive review of the literature was completed using MEDLINE and PubMed Library databases. This was supplemented with a manual search of selected journals and textbooks. English language articles published in peer-reviewed journals from 1966 to January 2012 in which colour stability of silicone elastomers was evaluated using standard research protocols were included. In all, 127 articles were identified and 23 met the inclusion criteria. Current literature reveals that average colour stability of maxillofacial silicone prostheses is 6-12 months, and inherent unstable nature of silicones is responsible for the color degradation. Opacifiers, oil pigments and inorganic colourants may have a protective effect on colour stability of prostheses. Organic colourants, ultraviolet (UV) light, cleansing solutions, dust and aging can adversely affect colour stability of silicone prostheses. A direct comparison between studies has not been possible, because of the differences in experimental set-up such as materials tested, colourants used, or method of aging. There appears to be a need for a standardised test protocol for colour stability of maxillofacial materials. Colour degradation limits the useful lifespan of maxillofacial silicones. Improvements in colour stability possible with the use of certain nano opacifiers, UV absorbers, photoprotective agents, and use of inorganic pigments and metal oxides.

KEYWORDS: maxillofacial silicones, color stability, pigments and opacifiers, and accelerated aging

INTRODUCTION

Barnhart introduced the use of silicone elastomers in the field of maxillofacial prosthodontics in 1960, and since then silicones have gradually become the most widely used materials for fabrication of extraoral prostheses¹⁻³. Even though silicones have many desirable properties for maxillofacial prosthetic applications such as clinical inertness, strength, ease of manipulation, and durability, a serious limitation of these materials is their lack of colour stability⁴⁻¹⁶. Ideally, a maxillofacial prosthesis should maintain its colour for a prolonged period. However, several studies indicate that average colour stability of a maxillofacial prosthesis is 6-12 months¹⁷⁻³². Discolouration of the prosthesis is the principal reason for its replacement, and causes of colour degradation include inherent chemical instability of silicones and pigments, exposure to cleansing agents and solutions, sunlight, dust and climatic conditions, smoking, human body secretions and oils³³⁻⁴⁶. This paper reviews the literature related to colour stability of maxillofacial silicones elastomers.

MATERIALS AND METHODS

PubMed and MEDLINE databases were accessed to search for pertinent peer-reviewed articles written in English published between 1966 and 2012. Keywords entered were "maxillofacial silicones", "colour stability", "pigments", "opacifiers" and accelerated aging; either individually or in

combination. The hand search of the *Journal of Prosthetic Dentistry*, *International Journal of Prosthodontics* and *Journal of Prosthodontics* was performed for the period from January 1990 to January 2012. The abstracts of the articles were reviewed, and articles were sorted based on the following inclusion and exclusion criteria. Articles published in English peer-reviewed journals, describing an original research, investigating colour stability of maxillofacial silicone elastomers were included. Clinical or technical reports, abstracts, personal communications, articles related to physical or mechanical properties of silicones, and theses were excluded.

RESULTS

A total of 127 articles were identified through the MEDLINE and PubMed searches. Abstracts were reviewed to confirm the articles met the inclusion criteria. A total of 56 articles published between 1966 and 2012 were identified and read in their entirety. Twenty - three articles were selected all of which were in vitro studies. Five studies evaluated the effect of opacifiers on colour stability, four studies employed oil based pigments, three studies evaluated the effect of cleansing solution/disinfectant, and one study assessed the effect of nano oxides. Commonly used silicone elastomers are listed in Table 1. Table 2 gives a brief description of studies examined for this review, and to avoid repetition in presence of similar studies, only representative study is included in the Table.

Bulbulian was the first to propose the essential requirements of maxillofacial materials in 1946⁸. Cantor *et al*⁹ first reported spectral measurements of human skin and facial prosthetic materials, whereas Sweeney¹⁰ was the first

* BDS, MDS (Prosthodontics)

to evaluate the colour stability of maxillofacial prosthetic materials in an artificial weathering environment. Researchers have commonly used contact measuring systems like reflection spectrophotometry or colorimetry to evaluate colour change, but the accuracy of these instruments may be affected by edge loss²⁹. Hu *et al* compared the accuracy of a non-contact measuring system to 4 contact colour measuring instruments and recommended that non-contact systems are reliable for colour measurement of maxillofacial prosthetic materials²⁹.

Measurement of the colour change

Studies evaluating colour stability usually involve fabrication of intrinsically or extrinsically coloured and unpigmented (control) silicone specimens, with or without additives like UV absorbers or opacifiers, conditioned via artificial or natural weathering, and observation of colour change by spectrophotometry using CIE L*a*b* system. This system offers an objective and reliable method of measuring the colour of an object. The CIE L*a*b* scale consists of a colour space in a similar arrangement to the Munsell colour space in which three dimensions, L*, a*, and b*, can define any colour in space^{4,46,47}. The L* represents a lightness-darkness scale, 0 is the theoretical black and 100 is theoretical white. The a* represents a red-green scale, plus is red, minus is green. The b* represents a yellow-blue scale, plus is yellow, minus is blue. Zero value in the a* and b* dimension refers to grey or the absence of chroma. A higher number, whether plus or minus, is a more saturated colour. The CIE L*a*b* colour difference formula $\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ can provide numeric data (ΔE) that quantifies the colour difference of two objects. ΔE is reported in units of just-noticeable differences (jnds). A ΔE of 1.0 is considered to be a colour difference that can be perceived by 50% of human observers^{41,48}, ΔE of 2.0 is the colour difference that can be perceived correctly 100% of the time by human observers⁴¹, and colour differences greater than 3 are considered visually perceptible by the naked eye. The thresholds for perceptible and acceptable colour difference of fair-skin-coloured silicone digit prostheses were reported to be 0.8 and 1.8, respectively²⁵, whereas perceptibility and acceptability thresholds for light-skin-coloured maxillofacial silicone specimens are 1.1 and 3.0, respectively⁴⁹.

Colourants, pigments and opacifiers

The organic or inorganic nature of colourants is important factor in determining colour stability of a prosthesis. The inorganic colourants, like dry earth pigments, consist of metal oxides which contain ionic bonds and are colour stable; while organic colourants contain more reactive double and triple bonds between carbon and hydrogen atoms, and have less colour stability⁵⁰. Inorganic colourants are often mixed with a vehicle like linseed oil, which protects the pigments and improves colour stability³⁹. Mancuso²² *et al* and Pesqueira³⁶ *et al* observed that ceramic colours are more stable than cosmetic (make-up) colours because of the small size of ceramic particles. These particles adhere to silicone and improve colour stability, whereas large sized make-up particles separate from silicones, leading to colour deterioration. Gary and Smith have presented a list of pigments approved by

Table 1. Information on commonly used maxillofacial silicone elastomers.

| Sr. no. | Name | Rubber catalyst ratio | Processing parameters | Manufacturer | Cross linking method | Representative studies |
|---------|----------------------------------|-----------------------|--------------------------------------|---|----------------------|-----------------------------|
| 1 | TechSil S25 | 9:1 | Heat cured for 2h at 100°C | Technovent Ltd, Leeds, UK | Addition | 33,35. |
| 2 | A-2186 | 10:1 | 1 h at 100 °C | Factor II, Lakeside, CA, USA | Addition | 27, 38, 17, 40, 28, 34, 16. |
| 3 | Silastic Medical Adhesive Type A | 1 part | Room-temperature cure | Dow Corning Corp, Midland, Mich. | Condensation | 15, 40. |
| 4 | Silskin | 10:1 | Heat accelerable | C.F.Thackery Ltd, Leeds, U.K. | Addition | 30. |
| 5 | Epsil | 1:1 | RTV/dry heat oven for 1 hour at 60°C | Dreye-Dentamid GmbH, Unna, Germany. | Addition | 44. |
| 6 | Silastic 4-4210 | 10:1 | 2hours at 55°C | Dow Corning Corp, Midland, Mich. | Addition | 40. |
| 7 | Ideal | 10:1 | Room-temperature cure | Orthomax, Bradford, U.K. | Addition | 30. |
| 8 | Elastosil M3500 | 1 part | Room-temperature cure | Wacker-Chemie GmbH, Munchen, Germany | Condensation | 30. |
| 9 | Silastic 732 RTV | 1 part | Room temperature cure | Dow Corning do Brasil Ltd., Hortolandia, SP, Brazil | Condensation | 31. |
| 10 | A-2000 | 1:1 | Room temperature for 24 h | Factor II Inc., Lakeside, AR. | Addition | 23. |
| 11 | MDX4-4210 | 10:1 | Heat accelerable RTV | Dow Corning Corporation, Midland, MI | Addition | 4, 15, 20, 22, 31, 36, 39. |
| 12 | 891 Type A adhesive | 10:1 | 3 hours at 75°C. | Dow Chemical Co, Midland, Mich. | Addition | 34. |

ASTM (American Society for Materials Testing) described by their common name, colour index name and number, ASTM light fastness, chemical type and formula¹⁸. Amongst various pigments investigated by researchers, cadmium yellow and cosmetic red^{17,19} alizarin red²⁸, titanium white oil colour and silicone intrinsic pigment white¹⁵, yellow silicone pigment²³ were found to be less colour stable than cosmetic yellow ochre, burnt sienna and mars violet^{17,19}. Haug *et al*⁴⁰ investigated colour stability of commonly used colourant-elastomer combinations exposed to natural weathering and storage in dark conditions. Silastic medical adhesive type A, Silastic 4-4210, and Silicone A-2186 with the dry earth pigments, rayon fiber flocking, artist's oil paints, kaolin and liquid cosmetics as colourants. The stored samples were sealed in glass containers and kept in the dark for 6 months while natural weathered samples were placed on the roof of a dental school for 6 months. They observed that colour changes occurred in many colourant elastomer combinations exposed to weathering, as well as in coloured specimens stored in the dark. Furthermore, colour changes were seen in non-coloured specimens under both conditions (weather exposure and dark storage). This suggested that the inherent nature of silicones was responsible for the colour changes and that silicones are not as stable as assumed by the profession. Colour change in some coloured and weathered specimen groups (e.g. dry earth pigmented Silicone A-2186) was less than the corresponding non-coloured specimens exposed to weathering, which indicated that colourants may have a protective effect on colour stability of silicones.

Exposure to ultraviolet (UV) radiation and effect of UV absorbers

UV radiation has a damaging effect on the colour of facial prostheses, since it may lead to degeneration of certain UV light-susceptible pigments and degradation of elastomer. Beatty *et al*¹⁹ evaluated 5 dry pigments (titanium white, cadmium yellow medium, mars violet, cosmetic red, and cosmetic yellow ochre) and 1 maxillofacial elastomer (A-2186) for colour changes resulting from 400, 600 and 1800 hours exposure to UV-A (315-400 nm) and UV-B (290-315 nm) and dark storage. Control specimens consisted of unpigmented elastomer specimens and pigment only specimens. Changes in colour were measured with a reflectance spectrophotometer (CM2002, Minolta Co., Ramsey, N.J.). Pigmented and unpigmented elastomer specimens underwent significant colour changes ($\Delta E > 2$) for all treatments at all time intervals. Titanium white pigment remained colour stable in pigment only specimens, but produced little resistance to colour change in elastomer specimens, signifying that pigment and pigment-elastomer colour stability may vary considerably. UV-B exposure caused greater colour change than UV-A exposure after 1800 hrs. They concluded that early colour changes in a prosthesis may result from degradation of certain UV light-susceptible pigments, whereas long term changes may reflect degradation of elastomer by UV light. The effect of various UV absorbers like para-aminobenzoic acid (PABA)⁴, sunscreens⁴, benzotriazole compound²⁰, hindered amine light stabilizer (HALS)²⁸, nano oxides³⁸ has been studied by researchers. Chu and Fischer⁵¹ evaluated the effects of 11 additive UV light absorbers and one antioxidant in nonpigmented polyurethane elastomers exposed to UV

light in an aging chamber. They found that the UV light absorbers made from the benzotriazole or amine group at 1.5% concentration were most effective in reducing visible yellowing of the elastomer. Bryant *et al*⁴ evaluated the efficacy of 3 commercially available sunscreens and para-aminobenzoic acid (PABA) in improving colour stability of intrinsically pigmented Silastic MDX 4-4210. The sunscreens were externally applied to half of the silicone specimens, whereas Para-aminobenzoic acid was mixed (5% by weight) in half of the specimens as an ultraviolet light absorber. Samples were irradiated with UV light for 300 hours, and control samples were placed in the dark for the same time. The colour measurement of samples was carried out at time 0 and at 300 hours in both groups. They observed that sunscreen and PABA photoprotective agents failed to provide ultraviolet radiation protection for silastic MDX 4-4210. Lemon *et al*²⁰ evaluated the effectiveness of a benzotriazole compound, a broad range (260-390nm) intrinsic UV light absorber (Spectra-sorb UV-5411; American Cyanamid Co.), on the colour stability of a pigmented room temperature-vulcanized (RTV) silicone elastomer (mixture of MDX4-4210 and type A medical adhesive, Dow Corning Co.). The oil base pigments yellow ochre, cadmium red, and burnt sienna were combined to produce a common Caucasian base colour, and specimens were exposed to natural and artificial weathering. It was observed that the addition of a UV light absorber UV-5411 did not protect samples from colour changes. Tran²⁸ evaluated effect of ultraviolet light absorber (UVA) (Tinuvin 213) and hindered amine light stabilizer (HALS) (Tinuvin 123) on colour stability of an RTV silicone (A-2186), pigmented with organic (hansa yellow and alizarin red) and inorganic pigments (burnt sienna). UVAs absorb the harmful UV radiation and dissipate it as heat, whereas HALS act as free-radical scavenger and prevent degradation of the polymer by UV light. Both have a synergistic effect when used together, and they were added at a 1:1 ratio at a concentration of 0.75% by weight. Specimens were exposed to natural weathering for 3 months, and L*, a*, b* readings were obtained before and after weathering with a spectrophotometer. It was observed that UVA and HALS improved colour stability of specimens containing burnt sienna and hansa yellow but had no effect on alizarin red. However, clinical research is required to establish safety of Tinuvin 213 and Tinuvin 123 for prolonged contact with skin and mucous membrane, as occurs with a maxillofacial prosthesis.

Effect of opacifiers, nano oxides and method of colouring

Nano-oxides of TiO₂, ZnO, CeO₂ are widely used as industrial inorganic UV absorbers. Nano oxide particles are smaller than the wavelength of UV light (290-400nm) so some of the incident UV light is scattered whereas some is absorbed by the nano particles, which reduces harmful effects of UV rays. Han *et al*³⁸ evaluated the effects of these nano-oxides on the colour stability of pigmented silicone A-2186. They observed that the nano oxides at optimum concentrations (particularly 1% nano-CeO₂ and 2% and 2.5% nano-TiO₂ by weight) protected silicone A-2186 material from colour changes. The most pronounced colour changes were observed with yellow silicone pigment at all nano-oxide combinations, a finding also observed by Kiat annuay *et al*²³, which indicates that these pigments should

Table 2. Synopsis of studies related to colour stability of maxillofacial silicone elastomers.

| <i>Author, year and reference</i> | <i>Sample size</i> | <i>Silicones†</i> | <i>Colourants#</i> | <i>Experimental conditions/ research hypothesis</i> | <i>Relevant findings</i> |
|-----------------------------------|----------------------|---|---|---|--|
| Haug SP. 1999. (40) | n=5 (Total 270) | Silastic Adhesive A, Silastic 4-4210, and A-2186. | Dry earth pigments, rayon fibers, oil paints, kaolin, liquid cosmetics, no pigment. | Storage in dark for 6 months versus exposure to sunlight and natural weathering. | Colour changes occurred in coloured and uncoloured specimens in dark storage and weathering conditions. Colourants tended to "protect" the silicones from weathering. |
| dos Santos DM.2011. (39) | n=10 (Total 60) | MDX4-4210 | Ceramic powder, oil paint | An opacifier (barium sulfate); accelerated aging for 1008 hours. | Opacifier protected facial silicone against colour degradation, and oil paint remained stable even without opacifier. |
| Mancuso DN. 2009. (22) | n=6 | MDX4-4210. Silastic 732. | Cosmetic, Ceramic, Iron oxide. | Exposure to 1,000 hours of accelerated aging. | Both pigmented and nonpigmented specimens presented colour instability, and the latter presented the least colour alteration. |
| Kiat amnuay S. 2009. (23) | n=5 (Total 375) | A-2000 | Silicone pigments Red, Yellow, Burnt sienna, and a mixture of them. | Effect of dry earth opacifiers -Georgia kaolin, calcined kaolin, Artskin white, and Titanium white; and 1 silicone pigment white. | Both 10% and 15% Artskin white and titanium white opacifiers protected silicone from colour changes. Calcined kaolin opacifier and Yellow silicone pigment exhibited most pronounced colour changes. |
| Polyzois GL.1999. (30) | n = 10 | Silskin 2000, ElastosilM3500, Ideal | - | Outdoor weathering for 1 year. | All silicone elastomers showed visually detectable, mean colour differences ($\Delta E^* > 2.0$). Silskin 2000 showed highest colour changes. |
| Gary JJ 2001. (16) | n=10 (Total 80) | A2186 | Burnt sienna, Hansa yellow, Alizarin red. | Outdoor weathering in two different sites(Arizona and Florida). | Mean colour changes that occurred in Arizona (desert) were significantly larger than those in Florida in all but alizarin red specimens. |
| Kiatamnuay S. 2002. (17) | n = 5 (Total 300) | A-2186 | Inorganic pigments red, yellow ochre, burnt sienna, and a mixture of these. | Various concentrations of opacifiers Georgia kaolin, calcined kaolin, Artskin white, and titanium white. | Any opacifier combined to mixed group (all pigments) did not improve colour stability. 10% concentration of Artskin white, titanium white, and calcined kaolin; and 5% concentration of Georgia kaolin presented smallest colour changes($p < 0.05$). |
| Beatty MW 1995. (19) | n=3 | A2186 | Titanium white, cadmium yellow, mars violet, cosmetic red and yellow ochre. | Pigment only, elastomer only, and pigmented elastomer specimens were exposed ultraviolet A (UVA) and UVB light for 1800 hrs. | It was observed that early colour changes in prosthesis may result from degradation of UV light susceptible pigments, while long term changes may occur due to changes within elastomer. |
| Tran N 2004. (28) | n=10 (Total 160) | A-2186 | Burnt sienna, Hansa yellow Alizarin red. | Effect of ultraviolet light absorber (UVA) and hindered amine light stabilizer(HAL). | UVA and HAL improved colour stability of specimens containing burnt sienna and hansa yellow, but had no effect on alizarin red. |
| Kiatamnuay S 2006. (15) | n=5 (Total 375) | MDX4-4210, Silastic Medical Adhesive Type A | Oil pigments cadmium-barium red, yellow ochre, burnt sienna, and mixture these. | Interactions of oil pigments and dry earth opacifiers Georgia kaolin, Calcined kaolin, Artskin white, Titanium white, Ti white artists' oil colour. | Majority of colour changes in all groups were below 1.0 ΔE units, i.e.non-perceptible. Oil pigments combined to opacifiers protected the silicones from colour degradation. |
| Beatty MW 1999. (34) | n=5 | 70:30 ratio of 891 Type A Adhesive and A-2186 | Titanium white. Cadmium red and yellow. Yellow ochre. Mars violet. | Intrinsic versus extrinsic staining of specimens. Pigment only and elastomer only specimens were controls. | Incorporation of pigments into a surface-applied adhesive layer(extrinsic) in higher concentrations improved the colour stability. Intrinsically pigmented and nonpigmented specimens underwent significant colour changes after exposure to UV radiation. |
| Bryant AW 1994. (4) | n=9 | MDX4-4210 | Talc and nylon flock. | Effect of photoprotective agents viz. sunscreens and para-aminobenzoic acid (PABA). UV exposure and dark storage. | PABA and two sunscreens(Photoplex, and Native Tan) increased the discolouration even more than UV light. One sunscreen(Faces Only) had no effect on colour stability. |

| | | | | | |
|---------------------------|-------------------|--|--|---|--|
| Lemon JC 1995. (20) | n=6 | 3:1 ratio of Adhesive type A and MDX4-4210. | Yellow ochre, burnt sienna and cadmium red in oil base. | UV light absorber (SpectraSorb) added to specimens in concentration 0.1 and 0.25 wt %. | UV light absorber did not protect silicone from colour changes. |
| Ying Han. 2010. (38) | n=5 (Total 230) | A-2186 | Silicone pigments Red, Yellow, Blue, and a mixture of these. | Nano-sized particle oxides of TiO ₂ , ZnO, CeO ₂ at various concentrations. | Overall, CeO ₂ groups had the most colour change, and TiO ₂ groups the least. The smallest colour changes were recorded at: CeO ₂ at 1%, and TiO ₂ at 2% and 2.5%. Yellow pigments most severely affected colour stability. |
| Hatamleh MM. 2010. (35) | n=8 (Total 112) | TechSil S25 | Intrinsic rose-pink skin shade (P409, Principality Medical) | Effect of dark storage (control), sebum solution, acidic perspiration, light aging, outdoor weathering, cleaning solution, and mixed effect of sebum storage and light aging. | Simulated sebum under light aging induced the greatest colour changes. TechSil S25 has unacceptable colour stability ($\Delta E = 6.17$ for unpigmented specimens stored in dark). Pigments failed to protect silicones during outdoor weathering. Negligible colour changes caused by cleaning solution. |
| Polyzois GL 2000. (44) | n=5 | Episil | - | Immersion in simulated sebum and perspiration (37°C ;6 months). | Perceptible colour changes were recorded in all groups. Greater colour changes in perspiration than sebum. |
| Kiat amnuay S. 2005. (27) | n=5 (Total 25) | A-2186 silicone + 10% titanium white opacifier | Cosmetic dry earth pigments: Red, Yellow ochre, Burnt sienna, and a mixture these. | Simulated 1.5-year period of microwave sterilization. | Yellow ochre and burnt sienna groups remained the most colour stable ($\Delta E < 0.35$), while Red had most adverse effect on colour stability. Unpigmented elastomer showed no visually perceptible changes ($\Delta E < 0.35$). |
| Pesqueira A A. 2011. (36) | n = 10 (Total 60) | MDX4-4210. | Makeup powder, Ceramic powder. | Efferdent denture cleanser (15 minutes 3 times a week) neutral soap and water washing (30 seconds) Both for 60 days. | Ceramic pigment presented significantly greater colour stability than makeup pigment. Neutral soap caused more discolouration than Efferdent in both pigment types. |
| Goiato MC. 2009. (31) | n=7 (Total 28) | Silastic 732 RTV and MDX 4-4210 | | Disinfection three times a week with Efferdent and daily with neutral soap. | Disinfection acts as a bleaching agent in silicone materials. Efferdent caused less discolouration than and neutral soap and water. |
| Hatamleh MM. 2011. (33) | n = 8 (Total 64) | TechSil S25 | A preblended intrinsic rose-pink shade. | Manual mixing versus mechanical mixing under vacuum. Sebum storage and accelerated daylight aging. | Pores affected the colour reproducibility as well as colour stability, hence mechanical mixing under vacuum recommended. |

† For information on manufacturers of Silicones, please refer to table I.

A detailed description of commonly used colourants for maxillofacial prostheses has been presented by Gary and Smith (18).

be used with caution. This study supported the hypothesis that opacifiers can protect silicone elastomers from colour degradation. Kiat amnuay¹⁷ evaluated the effect of opacifiers used at different ratios on the colour stability of pigmented A-2186 silicone maxillofacial elastomers. Georgia kaolin powder neutral, kaolin powder calcined, Artskin white, and dry pigment titanium white at concentrations of 5%, 10%, and 15% were tested with dry earth cosmetic pigments - red, yellow ochre, burnt sienna, a mixture of all pigments and no pigment (control). Specimens were placed in an aging chamber (Ci35 Weather-Ometer; Atlas Electronics, Chicago, IL) and exposed to light, water spray, fluctuating temperatures, and humidity. It was observed

that adding all pigments (mixed group) to any opacifier group produced ΔE values more than 2, and thus did not protect silicone A-2186 from colour degradation over time. This group may be considered as a suitable guide for selecting opacifiers. At all concentrations, none of the opacifiers tested enhanced the color stability of the silicone A-2186 elastomer in any of the all-pigment groups compared with control. It was observed that red pigment mixed in all opacifier groups increased ΔE^* values significantly at all times and yellow ochre remained the most colour-stable pigment over time, which agrees with the work of Beatty *et al*¹⁹. In another similar study, Kiat amnuay¹⁵ investigated the combined effect of dry earth opacifiers

Georgia kaolin, calcined kaolin, Artskin white, titanium white dry pigment, or titanium white oil color and oil pigments cadmium-barium red deep, yellow ochre, burnt sienna at various concentrations on the colour stability of an MDX4-4210/medical adhesive type A maxillofacial elastomers. They observed that oil pigments combined with opacifiers protected the silicones from colour degradation. Titanium white opacifier was found to be the most colour stable, but because of its high intensity, Kaolin powder (calcined) and Georgia kaolin may be recommended as a substitute. Titanium white oil colour was found to be the least colour stable at different concentrations. In a recent study, Kiat amnuay S *et al*²³ found that a combination of the silicone pigments red, yellow, burnt sienna, and a mixture of pigments, with opacifiers like Georgia kaolin, Artskin white and titanium white dry pigment protected silicone A-2000 elastomer from colour degradation. However, silicone intrinsic white pigment could not improve the colour stability despite its similar composition to silicone. Yellow silicone pigment markedly affected the colour stability of all opacifiers, hence this pigment should be used cautiously with A-2000 silicone. Similarly, dos Santos³⁹ observed that barium sulfate opacifier at 0.2% weight protected MDX4-4210 facial silicone from colour change after 1008 hours of accelerated aging. Beatty³⁴ tested the effect of intrinsic or extrinsic colouring on stability of silicone elastomers (mixture of 891 Type A adhesive with A-2186 base elastomer). Samples were coloured by either incorporating pigments in the base, or as surface tints; control specimens consisted of pigment only and silicone only discs. After exposure to UV light for 1800 hrs, control samples and elastomers coated with pigments as concentrated surface tints underwent minimum colour changes, whereas samples containing oil pigments as base colourants demonstrated a wide range of susceptibility to ultraviolet radiation. They concluded that chemical interaction or chemical incompatibility between pigments and elastomer resulted in colour changes, and recommended application of pigments into a surface-applied adhesive to improve colour stability.

Effect of disinfectants and body secretions

Researchers have evaluated the effect of different environmental factors and conditioning methods such as simulated perspiration and sebum, disinfectant and cleansing solutions, lipids, microwave energy, on colour stability of silicones. Such conditioning of silicones can cause propagation of crosslinking, or lysis of polymer chains, or increased density, increase in opacity, which may affect colour⁵. Even though outdoor weathering may be more realistic than accelerated aging, the latter does offer certain advantages like repeatability and comparability between studies, elimination of geographic and environmental variables, increased speed of degradation, and reduction in time and cost of testing¹⁷. Yanagisawa observed significant color change in two silicone elastomers which were immersed in a lipid medium for 24 hours and irradiated with ultraviolet light for another 24 hours. The cause of the colour changes may have been the result of lipid absorption by the silicone and its oxidation resulting in degradation of the silicones. Polyzois *et al* evaluated⁴⁴ changes in Episil silicone elastomer after immersion in simulated sebum and acidic and alkaline perspirations for

6 months at 37°C. They found visually perceptible colour changes after all 3 treatments, and color change in sebum was lesser than that in simulated perspirations. Hatamleh³⁵ evaluated colour stability of TechSil S25 silicone under 7 conditions like artificial sebum, acidic perspiration, cleaning solution, outdoor weathering, dark storage, natural weathering, and for first time in simulated sebum under continuous artificial daylight exposure. They reported that colour changes in specimens occurred primarily due to inherent colour instability of TechSil S25, because non-pigmented specimens stored in a sealed dark chamber showed significant colour change. Another intrinsic factor responsible for chromatic alteration is continuing chemical polymerization of the silicone. Among the different test conditions used, the greatest colour changes occurred in silicone samples stored in simulated sebum solution under artificial daylight exposure. There was a negligible effect on the colour of TechSil S25 from cleaning solution. Pigmented specimens exposed to natural weathering exhibited greater changes when compared to the equivalent nonpigmented specimens. Time was a significant variable affecting color stability under the above conditions. Maintenance routines of maxillofacial prostheses may involve use of cleansing agents like hypochlorites, peroxides, enzymes, acids which may have variable effects on prostheses³¹. Peroxides like Efferdent (Pfizer Consumer Healthcare, Morris Plains, NJ) liberate nascent oxygen that loosens debris and removes light stain. Goiato³¹ *et al* evaluated the effect of peroxide (Efferdent) disinfection on silicones (Silastic MDX 4-4210, and Silastic 732 RTV) and observed that Efferdent had a bleaching effect on silicones and caused colour degradation. Pesqueira³⁶ *et al* evaluated changes in MDX4-4210 silicone following two methods of disinfection, viz. Efferdent and neutral soap (Johnson & Johnson), and observed that neutral soap solution caused more colour alteration than Efferdent, probably due to removal of surface pigments by the soap solution. Microwave sterilization may be considered a potential method in maintenance of silicone prostheses, as it is a standard method for sterilization of many medical appliances²⁷. Kiat amnuay²⁷ assessed the effect of microwave energy exposure on colour stability of silicone A-2186 opacified with titanium white dry earth opacifier and pigmented with the cosmetic dry earth pigments red, yellow ochre, burnt sienna, and mixtures of these. Silicone specimens were exposed to multiple microwave exposures simulating a 1.5 year period of use. They reported a lack of colour stability of red dry earth pigments ($\Delta E > 1$) compared with the control (no pigment) group, and good stability of yellow ochre and burnt sienna ($\Delta E < 0.35$).

Miscellaneous

The use of a cast titanium framework for supporting silicones in a maxillofacial prosthesis has been described by Wolf *et al*⁴⁵. They evaluated the effect of titanium reinforcement on silicone colour stability observing a negligible influence of titanium reinforcement on the colour of 2 mm thick silicones. Hatamleh³⁵ *et al* examined the effect of manual and mechanical mixing techniques on colour stability of a silicone (TechSil S25 silicone). Pigmented and unpigmented (control) specimens were exposed to simulated sebum treatment or exposure to accelerated daylight aging. They observed that mechanically mixed pigmented specimens were more colour stable than manually mixed,

pigmented specimens ($p = 0.003$); whereas manually and mechanically mixed unpigmented (control) specimens exhibited the same colour change ($p = 0.179$).

CONCLUSIONS

Although maxillofacial silicones have many desirable properties, including ease of fabrication, durability and strength, colour degradation is a serious limitation. Average colour stability of maxillofacial silicone materials is 6-12 months, and most extraoral silicone prostheses have to be remade within 1 year due to colour deterioration. Existing literature reveals that inherent unstable nature of silicones is responsible for colour changes in the silicone prostheses. Ultraviolet light, cleansing solutions, dust, time and body secretions can adversely affect the colour of silicone prostheses. Improvement in colour stability is possible through the use of certain nano opacifiers, UV absorbers, photoprotective agents, inorganic opacifiers and metal oxides.

ADDRESS FOR CORRESPONDENCE

Dr. Rahul S. Kulkarni, Associate Professor, Department of Prosthodontics, Nair Hospital Dental College, Dr A L Nair Road, Mumbai, Maharashtra, India. 400008. E-mail: drrahulprotho@yahoo.com

REFERENCES

- Barnhart GW. A new material and technic in the art of somato prosthesis. *J Dent Res* 1960;**39**:836-844.
- Montgomery PC, Kiat-amnuay S. Survey of currently used materials for fabrication of extraoral maxillofacial prostheses in North America, Europe, Asia and Australia. *J Prosthodont* 2010;**19**:482-490.
- Phoenix, RD. Denture base resins. In Anusavice, KJ. (Ed): Phillips' Science of Dental Materials. 11th ed., St. Louis, Elsevier, 2003; 755-756.
- Bryant AW, Schaaf NG, Casey DM. The use of a photoprotective agent to increase the color stability of a tinted extraoral prosthetic silicone. *J Prosthodont* 1994;**3**:96-102.
- Dootz ER, Koran A 3rd, Craig RG. Physical properties of three maxillofacial materials as a function of accelerated aging. *J Prosthet Dent* 1994;**71**:379-383.
- Koran A, Yu R, Powers JM, Craig RG. Color stability of a pigmented elastomer for maxillofacial appliances. *J Dent Res* 1979;**58**:1450-1454.
- Selik LW, Yu R, Koran A. Stability of ceramic pigments for maxillofacial applications. *J Oral Rehabil* 1987;**11**:309-313.
- Bulbulian AH. Problems of facial prosthesis. *Surg Clin North Am* 1946;**26**:846-858.
- Cantor R, Webber RL, Stroud L, Ryge G. Methods for evaluating prosthetic facial materials. *J Prosthet Dent* 1969;**21**:324-332.
- Sweeney WT, Fisher TE, Castleberry DJ, Cowperthwaite GF. Evaluation of improved maxillofacial prosthetic materials. *J Prosthet Dent* 1972;**27**:297-305.
- Lewis DH, Castleberry DJ. An assessment of recent advances in external maxillofacial materials. *J Prosthet Dent* 1980;**43**:426-432.
- Mancuso DN, Goiato MC, Dekon SFC, Gennari-Filho H. Visual evaluation of color stability after accelerated aging of pigmented and nonpigmented silicones to be used in facial prostheses. *Indian J Dent Res* 2009;**20**:77-80.
- Hanson MD, Shipman B, Blomfield JV, Janus CE. Commercial cosmetics and their role in the coloring of facial prostheses. *J Prosthet Dent* 1983;**50**:818-820.
- Leow ME, Ow RK, Valiyaveetil S, Lee MH, Pho RW. Colorfast pigments in silicone hand and maxillofacial prostheses. *Prosthet Orthot Int* 2002;**26**:124-134.
- Kiat amnuay S, Mekayarajjanononth 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**:249-257.
- Gary JJ, Huget EF, Powell LD. Accelerated color change in a maxillofacial elastomer with and without pigmentation. *J Prosthet Dent* 2001;**85**:614-620.
- Kiat-Amnuay S, Lemon JC, Powers JM. Effect of opacifiers on color stability of pigmented maxillofacial silicone A-2186 subjected to artificial aging. *J Prosthodont* 2002;**11**:109-116.
- Gary JJ, Smith CT. Pigments and their applications in maxillofacial elastomers: A literature review. *J Prosthet Dent* 1998;**80**:204-208.
- Beatty MW, Mahanna GK, Dick K, Jia W. Color changes in dry-pigmented maxillofacial elastomer resulting from ultraviolet light exposure. *J Prosthet Dent* 1995;**74**:493-498.
- Lemon JC, Chambers MS, Jacobsen ML, Powers JM. Color stability of facial prostheses. *J Prosthet Dent* 1995;**74**:613-618.
- Craig RG, Koran A, Yu R, Spencer J. Color stability of elastomers for maxillofacial appliances. *J Dent Res* 1978;**57**:866-871.
- 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**:144-148.
- Kiat-amnuay S, Beerbower M, Powers JM, Paravina RD. Influence of pigments and opacifiers on color stability of silicone maxillofacial elastomers. *J Dent* 2009;**37**:45-50.
- Hulterstrom AK, Ruyter IE. Changes in appearance of silicone elastomers for maxillofacial prostheses as a result of aging. *Int J Prosthodont* 1999;**12**:498-504.
- Leow ME, Ow RK, Lee MH, Huak CY, Pho RW. Assessment of color differences in silicone hand and digit prostheses: perceptible and acceptable thresholds for fair and dark skin shades. *Prosthet Orthot Int* 2006;**30**: 5-16.
- Takamata T, Moore BK, Chalian VA. Evaluation of color changes of silicone maxillofacial materials after exposure to sunlight. *Dent Mater J* 1989;**8**:260-270.
- Kiat-amnuay S, Johnston DA, Powers JM, Jacob RF. Color stability of dry earth pigmented maxillofacial silicone A-2186 subjected to microwave energy exposure. *J Prosthodont* 2005;**14**:91-96.
- 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**:483-490.
- Hu X, Johnston WM, Seghi RR. Measuring the color of maxillofacial prosthetic material. *J Dent Res* 2010; **89**:1522-1527.
- Polyzois GL. Color stability of facial silicone prosthetic polymers after outdoor weathering. *J Prosthet Dent* 1999;**82**:447-450.
- Goiato MC, Pesqueira AA, dos Santos DM, et al. Color stability comparison of silicone facial prostheses following disinfection. *J Prosthodont* 2009;**18**:242-244.
- dos Santos DM, Goiato MC, Sinhoreti MAC, et al. Color stability of polymers for facial prosthesis. *J Craniofac Surg* 2010;**21**:54-58.
- Hatamleh MM, Watts DC. Porosity and color of maxillofacial silicone elastomer. *J Prosthodont* 2011;**20**: 60-66.
- Beatty MW, Mahanna GK, Jia W. Ultraviolet radiation-induced color shifts occurring in oil-pigmented maxillofacial elastomers. *J Prosthet Dent* 1999;**82**:441-446.
- Hatamleh MM, Watts DC. Effect of extraoral aging conditions on color stability of maxillofacial silicone elastomer. *J Prosthodont* 2010;**19**:536-543.
- Pesqueira AA, Goiato MC, Santos DM. Effect of disinfection and accelerated aging on color stability of colorless and pigmented facial silicone. *J Prosthodont* 2011;**20**:305-309.
- Eleni PN, Katsavou I, Krokida MK, Polyzois GL. Color stability of facial silicone prosthetic elastomers after artificial weathering. *Dent Res J* 2008;**5**:71-79.
- Han Y, Zhao YM, Xie C, Powers JM, Kiat-amnuay S. Color stability of pigmented maxillofacial silicone elastomer: Effects of nano-oxides as opacifiers. *J Dent* 2010; **38**: 100 - 105.
- dos Santos DM, Goiato MC, Moreno A, Haddad MF. Influence of pigments and opacifiers on color stability of an artificially aged facial silicone. *J Prosthodont* 2011;**20**:205-208.
- 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**:431-438.
- Seghi RR, Hewlett ER, Kim J. Visual and instrumental colorimetric assessments of small color differences on translucent dental porcelain. *J Dent Res* 1989;**68**:1760-1764.

42. Moore DJ, Glaser ZR, Tabacco MJ, *et al.* Evaluation of polymeric materials for maxillofacial prosthetics. *J Prosthet Dent* 1977;**38**:319-326.
43. Lontz JF. State-of-the-art materials used for maxillofacial prosthetic reconstruction. *Dent Clin North Am* 1990;**34**:307-325.
44. Polyzois GL, Tarantili PA, Frangou MJ, *et al.* Physical properties of a silicone prosthetic elastomer stored in simulated skin secretions. *J Prosthet Dent* 2000;**83**:572-577.
45. Wolf B, Reitemeier B, Schmidt A, Richter G, Duncan G. In vitro testing of the bond between soft materials used for maxillofacial prostheses and cast titanium. *J Prosthet Dent* 2001;**85**:401-408.
46. Hatamleh MM, Haylock C, Watson J, *et al.* Maxillofacial prosthetic rehabilitation in the UK, a survey of maxillofacial prosthetists and technologists attitudes and opinions. *Int J Oral Maxfac Surg* 2010;**39**:1186-1192.
47. Commission Internationale de l'Eclairage – CIE. Colorimetry, Official Recommendations of the International Commission on Illumination. 2nd ed. Publication CIE No. 15.2 (TC-1.3). Paris, France: Bureau Central de la CIE; 1985.
48. Kuehni RG, Marcus RT. An experiment in visual scaling of small color differences. *Color Res Appl* 1979;**4**:83-91.
49. Paravina RD, Majkic G, Del Mar Perez M, *et al.* Color difference thresholds of maxillofacial skin replications. *J Prosthodont* 2009;**18**:618-625.
50. Haug SP, Andres CJ, Munoz CA, Okamura M. Effects of environmental factors on maxillofacial elastomers: part III—physical properties. *J Prosthet Dent* 1992;**68**:644-651.
51. Chu CC, Fischer TE. Evaluation of sunlight stability of polyurethane elastomers for maxillofacial use. *Int J Biomed Mater Res* 1978;**12**:347-359.