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RESEARCH ARTICLE

Effects of the addition of titanium dioxide and silaned silica nanoparticles on the color stability of a maxillofacial silicone elastomer submitted to artificial aging

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ABSTRACT

Objectives: Silicone elastomers require replacement due to degradation of mechanical properties and deterioration in color over time. Recently, various nanoparticles have been incorporated into the silicones to reinforce their physical and mechanical properties. The purpose of this study was to evaluate the effect of nanosized particle addition on the color stability of a commercial RTV maxillofacial silicone elastomer submitted to an accelerated aging.
Materials and Methods: The nanosized particles (titanium dioxide and silaned silica) were added, 10% by volume, into a maxillofacial elastomer. The samples (n=10) were polymerized in an oven according to the manufacturer's recommendations. Color measurements were performed using digital spectrophotometry according to the CIE L*a*b* color system. The samples were subsequently placed into an aging chamber for 168 h. The second color measurement of the samples was performed after the aging process. Data obtained from the measurement was recorded and assessed by (ANOVA) (α=0.05).
Results: The highest color stability was obtained with the silica and the TiO_2 group samples; the lowest color stability was obtained with the control group samples in this study. However; no statistically significant difference in discoloration was observed in the ΔE values between the groups ($p > 0.05$).
Conclusions: The results of this pilot study revealed that the addition of nanosized TiO_2 and silica particles used as reinforcing agents did not cause any color degradation of an A-2000 silicone during the first 2 months. Further studies should be done on the effect of such nanoparticles in long term aging procedures on the color stability of maxillofacial elastomers.

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INTRODUCTION

Maxillofacial deformities and defects that occur due to trauma, congenital disorders, or pathological effects of diseases on the surrounding tissues generate physical and psychological trauma among patients.[1,2] Maxillofacial prostheses are used to restore acquired or developmental defects of the head and neck.[1,3]

Physical and mechanical properties of materials used for facial prostheses should be similar to the surrounding tissues. Moreover, maxillofacial prostheses should maintain the existing mechanical properties at least for one year.[4-6] Various materials such as acrylic resins, acrylic copolymers, polyvinyl chloride and copolymers, and polyurethane-based elastomers have been used for the fabrication of maxillofacial prostheses.[4] Silicone rubber materials [poly(dimethylsiloxane) rubbers] introduced in the 1960s have been the most widely used materials to date[2] because of their biocompatibility, chemical inertness, strength, lower thermal conductivity, and durability.[7,8] Silicones allow the construction of facial prostheses with natural appearance and enable replication of the natural color of human skin with internal and external painting processes.[4,7] Color stability of the silicone-based facial prostheses may be affected by sunlight, ultraviolet (UV) light, air pollution, humidity, human body secretions, cosmetics, and the use of strong solvents.[3,6,9-11] Poor tear resistance, ruptures on the thin edges during usage, and dimensional variations may decrease physical and mechanical properties.[7,12]

Recently, different types of additives have been reported as fillers to increase the physical and mechanical properties of silicone-based elastomers.[2,5,13-15] Nano sized particles used as reinforcing agents are rigid, and have a higher shear modulus, compared to pure silicone elastomers. They are also characterized by their small size, large specific area, active function, and a strong interfacial interaction with the organic polymer.[2,13] The enhanced properties of polymeric matrices reinforced with nanoparticles may be caused by the high degree of cross linking between polymer chains.8 The higher surface energy and chemical reactivity of the particles provide enhanced interaction with the silicone elastomer matrix and form a three-dimensional network within the silicone polyethylene backbone.[2,13] Nano sized particles may control the electrical, magnetic, biological, and optical characteristics of silicones.[2]

Andreopoulos et al.[15] stated that the tensile strength of a silicone elastomer improved with addition of silica up to 35% by weight. Aziz et al.[5] reported that addition of silica to a silicone enhanced the properties of the elastomer. Han et al.[2] reported that Ti, Zn, or Ce nano-oxides at concentrations of 2.0 and 2.5% by weight improved the overall mechanical properties of the silicone A-2186 maxillofacial elastomer.

Rutile -TiO_2 inserted in an elastomer reportedly provided protection against UV light.[2,16] Addition of TiO_2 to facial elastomers was determined to promote color stability over time and protection against the chromatic alterations caused by UV-B radiation.[6,10,17] However, little is known about the effect of the addition of nanoparticles on the mechanical properties of maxillofacial elastomers.[2]

The color analysis of materials used in dentistry is measured visually or by instrumental color devices. Visual color analysis is generally practical for in vivo studies, but it has limitations. Color perception of an object depends on the emotional considerations of observers.[18,19] Many factors have a direct effect on the selection of color, including the position, opacity, transmittance, and reflectance of the object, the color properties and intensity of the light, and the experience, gender, age, eye fatigue, etc. of the observer. Therefore, visual analysis of an object may not an objective and reliable method.[18-20]

Instrumental color measurement devices have been developed in order to minimize the potential errors while measuring color. Spectrophotometers and colorimeters are often used for color analysis. However, spectrophotometers are accepted as objective and quite successful for in vitro studies to determine color and color differences.[20,21] In this method, it is possible to calculate ΔE ab* values using color parameters in the CIE L*a*b* color system and obtain color differences.[20-22] Measurements made with a spectrophotometer yield accurate and highly reproducible results under standard conditions. Metamerism can be evaluated by spectrophotometers; however, they are expensive, impractical, and difficult to standardize.[19,20-22]

The CIE L*a*b* system used for color measurement was derived from the Commission Internationale d'Eclairage (CIE) Standard Color Table by transforming the original three colorimetric coordinates (color values) x, y, and z into the three reference values of L*, a* and b*.[17,21,22] In the CIE L*a*b* system, the L* parameter represents the degree of lightness and darkness. The coordinate "a" represents the amount of red (positive values) and green (negative values), while the coordinate "b" represents the amount of yellow (positive values) and blue (negative values). The intersection of these three coordinates yields the value of the color. Furthermore, color change can be defined by a single value in this system.[21,22] This system allows for calculating the mean ΔE value (variation of color) between two readings by Eq. 1, which is further defined in Eq. 2.

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

$$\Delta E = [(L1^* - L2^*)^2 + (a1^* - a2^*)^2 + (b1^* - b2^*)^2]^{1/2} \quad (2)$$

Most studies indicate a perceptible color change to consist of 1 [9,11,17] or 2 units of ΔE.[3,9,23] A ΔE value smaller than 3 units is considered visually perceptible and clinically acceptable. The thresholds for perceptible and acceptable color differences of fair-skin-colored silicone specimens were reported to be 0.8 and 1.8, respectively.[9,24] However, a recent study indicated that the CIE L*a*b* perceptibility and acceptability thresholds for light-skin-colored maxillofacial silicone specimens were 1.1 and 3.0, respectively.[9,25]

The aim of this study was to evaluate the color change of a commercial A-2000 silicone-based maxillofacial elastomer reinforced with nano sized particles (TiO2 and surface-treated silica) after an artificial aging process. The null hypothesis was that the color properties of a silicone A-2000 elastomer submitted to accelerated aging would not be affected by the addition of nano sized particles.

MATERIALS AND METHODS

The present study evaluated the color stability of an A-2000 Pt RTV silicone elastomer (Factor II Inc., Lakeside, AZ, USA) proposed for maxillofacial prosthetics. Surface-treated nano-silica and TiO2 nanoparticles (Imicryl Diş Malzemeleri San.ve Tic.Ltd, Türkiye) were used to evaluate color degradation of a pure silicone elastomer subjected to short-term artificial aging.

A disk-shaped metallic mold 18 mm in diameter and 2 mm thick was used to obtain the silicone specimens. Compression molding and wax melting processes were applied for producing the samples. The specimens were divided into three groups: the control group composed of pure silicone, the silica group, and the TiO2 group. Each group consisted of 10 specimens (n=10).

The pure silicone and the nanoparticles were adjusted by using a scaled container for the fabrication of the specimens. The nanoparticles corresponded to 10% by volume of the silicone. Each additive was mixed with the silicone using a spatula on a metal plate to obtain a homogenous structure. The specimens of A-2000 silicone elastomer were maintained in a dry oven for thirty minutes in 135°C according to the instructions of the manufacturer. Subsequently, the specimens were submitted to an initial color analysis using a clinical digital spectrophotometer (Vita Easyshade Advance 4.0; Vita Zahnfabrik, Bad Sackingen, Germany) and the CIE L*a*b* system. After the initial color measurement, all samples were exposed to an artificial aging process for approximately 168 h using the Atlas UV2000 accelerated air conditioning tester (Atlas Electric Devices Co, Chicago-, USA). During the aging process, the samples were exposed to moisture, temperature, and UV light. The secondary color measurement was performed following the artificial aging process. All calculated ΔE values were analyzed using a one way analysis of variance (ANOVA) and Tukey tests at a 5% level of significance.

RESULTS

The data were homogeneous and normally distributed according to the Levene test ($p = 0.484$) and the Shapiro-Wilk test ($p > 0.05$). ANOVA results revealed no significant differences among study groups ($p > 0.05$) (Table 1). Table 2 presents the results of the color variations on specimen groups.

Table 2 shows the mean values and standard deviations (SDs) of ΔE* at the 10% concentration of nanoparticles. The highest color stability was obtained in silica (3,2±1,2) and titanium dioxide (3,4±1,5) groups while the lowest color stability was obtained in control (4,5±1,6) group. However, the analysis of variance of the ΔE* values were conducted no significant differences between study groups ($p > 0.05$) before and after artificial aging.

DISCUSSION

The nano materials examined in this study are used as strengthening agents for maxillofacial silicones. TiO_2 is used as a dry white pigment. Han et al.[2] reported that incorporation of Ti at a concentration of 2% by weight improved the mechanical properties of a Pt silicone elastomer. Silica is also used as a filler to reinforce silicone elastomers. Surface-treated hydrophobic silica may enhance the mechanical properties of a silicone elastomer.[8] Surface-treated transparent hydrophobic silica was used in this study.

The improved properties realized upon adding nanoparticles into a polymeric material may be attributed to the chemical reactivity of the particles interacting with the silicone elastomer matrix.[13] Mirabedini et al.[26] reported that a concentration of 10 wt% silica increased the tensile properties of silicone elastomer coatings. Karayazgan[27] reported the elongation percentage of maxillofacial silicone elastomer were increased by addition of 10% fumed silica; however, the addition over 20% were altered the mechanical properties of silicone.

The results of the present study demonstrated that the addition of nanoparticles at a concentration of 10% by volume did not affect the color of the elastomer and that the color existed in the same range between the control and the study groups before and after artificial aging. The greatest color stability was obtained with the silica and the TiO_2 group samples; the lowest color stability was obtained with the control group samples in this study. No statistically significant difference was observed in ΔE values between the groups regarding discoloration ($p > 0.05$). Following 168 h of

Table 1. Anova results revealed no significant differences between groups

	Sum of squares	df	Mean square	F	Sig.
Between groups	10,083	2	5,041	2,315	,117
Within groups	60,970	28	2,177		
Total	71,053	30			

Table 2. Means of color variations (AE) and standard deviations

Groups	N	ΔE mean±SD
Control	10	4,5±1,6[a]
Silica	10	3,2±1,2[a]
Titanium	10	3,4±1,5[a]

Note: Means followed by the same letter do not differ statistically ($p<0.05$) by Tukey's test

artificial aging, which is clinically equivalent to two months, no color degradation was observed in silicone elastomer specimens. Thus, the null hypothesis was accepted by the researchers.

Haug et al.[11] reported that pigments and opacifiers can help to protect color degradation of silicone elastomers over time. Previous studies investigated the effect of pigments and opacifiers, separately and in combination on the color stability of a maxillofacial silicone elastomer.[11,17,28,29] However, the results from this experiment cannot be compared directly with other studies, because no data exists in the literature concerning the effect on color stability of adding both TiO_2 and silica filler agents to a Pt silicone elastomer. The results of this research indicate that these materials, if used as a filler agent, could increase the color stability of silicone elastomers over time.

Most elastomers used in experimental studies are subjected to artificial aging because the process causes faster color changes than under natural conditions. The artificial aging process can yield an estimation concerning polymer degradation in the outdoors. Nevertheless, an artificial aging mechanism is different from natural aging conditions. Artificial aging may also provide information regarding the degradation mechanisms of maxillofacial elastomers.[30,31] Future long-term studies may examine natural outdoor weathering and the correlation between natural and artificial conditions.

A Pt catalyst is incorporated into silicones by a hydroxylation reaction. Thus, chemically, vinyl-terminating siloxane functional groups are converted into cross-linked silicone groups with the aid of the Pt catalyst. Pt silicones that are affected by organic materials are commonly used by clinicians in maxillofacial prosthodontics. Therefore, studies made with Pt silicones are used only with dry earth fillers and pigments. In addition, no data currently exists regarding the clinical perceptibility of visual color changes for maxillofacial elastomers.

Certain limitations of this study are noted. Nano-oxide Ti and silica nano particles may have adverse effects on some mechanical properties of the elastomer. In this study, all fillers were added at a constant concentration of 10% by volume. Moreover, specimens were subjected to 168 h artificial aging; this period may be a short time over which to examine the clinical usage of silicone elastomers.

By improving mechanical and physical properties of facial silicone elastomers The data indicate that surface-treated silica was the most color stable over time, followed by TiO_2 and pure silicone. Inserting such additive particles with different proportions may lead to different results in mechanical properties as well as on color stability of silicones. Further in vitro studies should be investigated on long term color stability and mechanical properties of silicone elastomers.

CONCLUSIONS

Under the limitations of this study, the following conclusions were drawn:

1. Nanoparticles added to silicone elastomers could help to protect Pt RTV-type A-2000 silicone elastomers from color degradation over time.
2. The color degradation of an A-2000 type of silicone elastomer may not be evaluated properly by a short-term aging process.

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