Clinical and Experimental Health Sciences

Effect of Ultraviolet Protective Agents and Plasma Applications on the Color Stability of Maxillofacial Silicones

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Received: February 12, 2024 **Accepted:** March 4, 2025

ABSTRACT

Objective: The purpose of the present study was to evaluate the color stability of maxillofacial silicones after applying plasma and ultraviolet protectives.

Methods: Six different color specimen groups (clear, white, yellow, red, blue, and mixed) from additional polymerized maxillofacial silicone elastomer were prepared. The surface of the polymerized silicone was modified with argon and oxygen plasma. Then, five UV protective agents (benzophenone-3, 2-ethylhexyl salicylate, titanium dioxide, Ethylhexyl methoxycinnamate, and TiO2-ZnO) were applied to the modified silicones. Specimens of each color and UV group were aged with an accelerated aging and thermocycling device. The color difference (ΔE) of maxillofacial silicones was statistically analyzed by 4-way ANOVA (α=0.05).

Results: The silicone specimens coated with 2-ethylhexyl salicylate (UV-ES) showed the lowest ΔE values in all color groups and aging regimes. The red color generally showed the highest ΔE values, and the white color showed the lowest ΔE values. When the silicone surfaces were modified with oxygen and argon plasma, oxygen plasma exhibited significantly higher ΔE values than the argon plasma in red color groups, whereas in yellow color groups, argon plasma exhibited higher ΔE values than the oxygen plasma.

Conclusion: Coating the silicone surface with UV-ES followed by oxygen or argon plasma revealed a positive impact on the color stability of silicone elastomer. Plasma treatment and UV-ES coating may be used to enhance the clinical lifetime of silicone facial prostheses.

Keywords: Color; maxillofacial silicone; UV Protective, plasma, thermocycling

1. INTRODUCTION

All over the world, there are a considerable number of patients with maxillofacial defects resulting from cancer, trauma, or congenital diseases. These patients anticipate high-quality prosthetic reconstructions depending on advanced technology (1,2). A maxillofacial prosthesis with a natural appearance and comfortable facial tissues improves quality of life (3). The esthetic result of a maxillofacial prosthesis is relevant to many patient concerns, while color was the most important determinant of the esthetics of these prostheses (4,5).

Silicone elastomers have been considered favorable materials for maxillofacial prostheses for over 50 years because of their biocompatibility, adequate strength, flexibility, and suitability for intrinsic coloration. Initially, intrinsically colored silicone prostheses can successfully reproduce individual skin color and translucency when manipulated by an experienced and skilled prosthodontist. However, silicone maxillofacial prostheses cannot preserve initial physical properties during clinical use. Deterioration in mechanical and physical properties, discoloration, and retentive substrate delamination frequently occur (6-9). Color change of the prosthesis during usage is the most prominent problem among these complications. After the color change gets through to a recognizable level, the replacement of a maxillofacial prosthesis is required. Clinical observations revealed that the mean lifetime of silicone facial prostheses is up to 2 years (3,10,11).

Color degradation of maxillofacial silicones has been caused by environmental factors, including ultraviolet (UV) light, air pollution, humidity, body secretions, and patients' daily habits, such as cleaning and disinfection processes or smoking. Previous research showed that UV

https://doi.org/10.33808/clinexphealthsci.1398224

light is the most important factor for the color change of maxillofacial prostheses (2-4). To prolonge the longevity of the maxillofacial prostheses by improving color stability, several studies have been performed. These studies include the addition of UV protective chemicals, namely nano-oxides, UV absorbers, UV filters, and hindered amine light stabilizers in the polymer structure (4,5,12-16). Considering previous research, incorporating UV protectives in bulk silicone elastomer during prosthesis fabrication may result in unfavorable material properties. As the material surface is primarily exposed to environmental factors, modifying the surface layer of polymerized material with UV protectives might be a reasonable attempt. Bishal et al. (12) developed and investigated the effectiveness of a technique including coating the surface of a maxillofacial silicone with TiO_2 thin film to enhance the color stability of the material. It was reported that TiO_2 nano-coating reduced discoloration of the maxillofacial silicon compared with non-coated specimens after artificial aging. Furthermore, TiO_2-coated specimens showed clinically acceptable color change.

The purpose of the present study was to investigate the effect of 5 different UV protective agents on the color change of surface-modified maxillofacial silicones after artificial aging procedures. The null hypothesis of the study was that; coating the silicone surfaces with 5 UV protectives following both oxygen and argon plasma treatments would similarly decrease the color change after aging.

2. METHODS

A high-temperature curing platinum-catalyzed maxillofacial silicone (M511; Technovent Ltd, Newport, UK) was used in the present study. For specimen fabrication, the base and the catalyzer of the silicone elastomer were mixed at a ratio of 10:1 according to the manufacturer's instructions. To fabricate 6 color groups, pigments were mixed into silicone 0.2% by weight, and unpigmented, white, red, yellow, blue, and mixture (red, yellow, and blue) groups were obtained. Each group was mixed on a glass plate until the color was evenly distributed. Air bubbles in the silicone mixture were removed using a vacuum chamber and placed into disk-shaped stone molds (15 mm in diameter and 2 mm in thickness). The molds were kept in an oven for 1 hour at 100 ° C for polymerization. Polymerized specimens were evaluated under magnification (Dental Loupe opt-on; Orange Dental GmbH & Co KG, Osnabrück, Germany) for defect and porosity. Excess material at the edges of the specimens was trimmed, and specimens were cleaned in an ultrasonic cleaner (Eurosonic Energy; Euronda SpA, Vincenza, Italy) for 10 minutes to remove the stone mold residue. Before modifying the surfaces of specimens with plasma and UV protectives, parameters that provide the optimum roughness on the silicone surface were investigated for oxygen and argon plasma. For this purpose, 7 disc-shaped silicone specimens (1 was for control without plasma treatment, and 6 were for plasma treatments) were fabricated as described for specimen fabrication. The surfaces of the specimens were cleaned with acetone and kept for 15 minutes for drying. Specimens were treated with oxygen or argon gas in the plasma device as described by Güngör et al. (17). Each plasma treatment was applied for 5, 10, or 15 minutes (18-21). Immediately after plasma treatment, the surface topography of each specimen was analyzed by atomic force microscopy (AFM) (Park Systems). Also, the surface topography of one specimen without plasma treatment was analyzed to investigate the effect of plasma on the silicone surface. Table 1 shows the surface roughness of the specimens after the plasma treatments. According to the AFM images and the mean surface roughness values of each specimen, 10 minutes of plasma treatment provided an optimum surface for both oxygen and argon gases (Fig. 1).

Table 1. *Surface roughness of specimens after plasma treatments*

Specimen	Plasma type	Time (minutes)	Surface roughness (µm)
1	No plasma	-	1.068
2	Argon	5	1.676 µm
3	Argon	10	3.320 µm
4	Argon	15	1.637 µm
5	Oxygen	5	0.368 µm
6	Oxygen	10	3.073 µm
7	Oxygen	15	1.393 µm

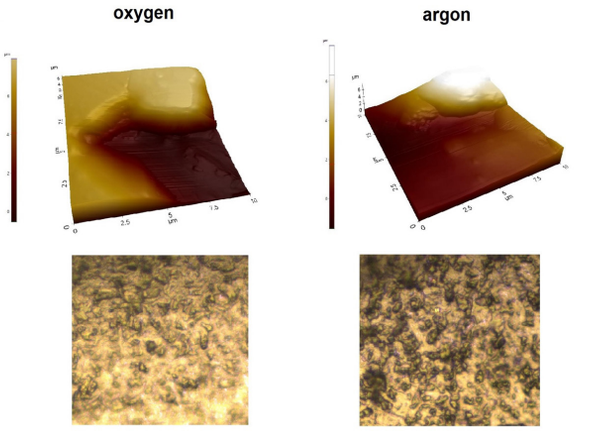

Figure 1. *AFM images of oxygen and argon plasma coated (10 minutes) silicone surfaces.*

Five UV protective agents; benzophenone-3 (UV-BP), ethylhexyl methoxycinnamate (UV-EM), titanium dioxide (UV-TD), 2-ethylhexyl salicylate (UV-ES), and sunscreen including titanium dioxide and zinc oxide (UV-SS) were applied onto the silicone specimens of 6 color (unpigmented, white, red, yellow, blue, and a mixture of red, yellow, and blue) groups. Control groups without UV protective coating were also prepared to evaluate the color change of the silicon material, and control groups were subjected to similar aging procedures with UV protective added groups. Table 2 shows the materials used in the study.

Table 2. *Materials used in study*

Material	Composition	Brand and Manufacturer	Lot no
Maxillofacial silicone, Part A	Platinum catalyzed, adding curing heat-temperature-vulcanized silicone elastomer	M511; Technovent Ltd	B16AJ
Maxillofacial silicone, Part B			
Yellow pigment	Dry pigment	Yellow P206, Technovent Ltd	12A
White pigment	Dry pigment	White 205, Technovent Ltd	12B
Blue pigment	Dry pigment	Blue P216, Technovent Ltd	12A
Red pigment	Dry pigment	Brillant Red, Technovent Ltd	12A
UV-BP	Benzophenone-3	Tokyo Chemical Industry Co	GVUTM-AD
UV-EM	Ethylhexyl methoxycinnamate	Sigma-Aldrich	BCBN1923V
UV-TD	Titanium dioxide	Sigma-Aldrich	SZBD03300V
UV-ES	2-ethylhexyl salicylate	Sigma-Aldrich	MKBX8153V
UV-SS	Sunscreen including titanium dioxide and zinc oxide	Kiehl's	

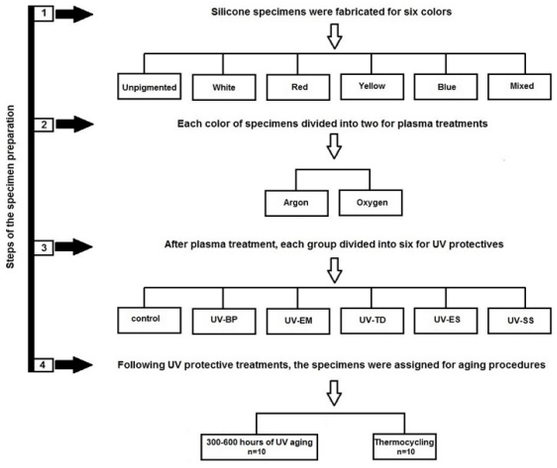

Figure 2. *Study design and number of specimens in each group.*

The powdery UV protectives UV-BP and UV-TD that were dissolved in the liquid silicone, UV protectives in liquid form (UV-ES and UV-EM) and sunscreen were applied onto the prepared surfaces as a film layer immediately after plasma treatment. The surfaces of control specimens were cleaned with acetone before UV protective application. Then, specimen surfaces were coated with a liquid silicone layer approximately 0.01 mm in thickness. The specimens were stored in a light protective box for 24 hours. They were subjected to accelerated aging procedures namely weathering (UV light-heat-humidity) and thermocycling. A different specimen was fabricated for the thermocycling procedure of each group. In total, 144 groups were prepared including 6 UV groups (5 UV protectives and control), 6 colors, 2 plasma treatments, and 2 aging (n=10). The study design is stated in Figure 2. Color measurements were performed initially and after 300 hours and 600 hours of UV aging on the same specimen. The UV aging procedure was performed as described in the previous studies.[21,22] After 300 aging, the specimens were dried and kept in a dark room for 24 hours. Within 48 hours, color measurements were made, and the aging procedure proceeded. After 600 hours color measurements were repeated. The color parameters including L∗, a∗, and b∗ were measured using a spectrophotometer (CM-2300d; Konica Minolta, Inc).

The color change (Delta-E: ΔE) of a specimen was calculated using the equation:

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

(ΔL*: difference in lightness, Δa*: difference in a value, and Δb*: difference in b value).

The ΔE results were analyzed in terms of the normality by the Kolmogorov-Smirnov test (P>.05). The data was tested regarding homogeneity of the variances using the Levene test. The mean and standard deviation of the ΔE data were calculated as descriptive statistics. Statistical analysis of the ΔE data was performed by 4-way analysis of variance (ANOVA) with UV protective, surface treatment, aging, and color as independent variables to evaluate the effects of all factors. Mean values were compared by Tukey HSD test at the 0.05 significance level using the statistical software SPSS v25 (IBM Inc.).

3. RESULTS

A statistically significant interaction was found among UV protectives, surface treatment (plasma gas type), aging, and color (P<0.001) according to the results of 4-way ANOVA (Table 3). The mean values, standard deviations, and comparisons for ΔE data are shown in Table 4.

Table 3. *4-way ANOVA results for ΔE*

Source	df	Adj SS	Adj MS	F-value	*P*-value
UV protective	5	93965	18793.0	1797.91	<.000
Surface treatment	1	2285	2284.6	218.57	<.000
Aging	2	2150	1075.0	102.85	<.000
Color	5	107104	21420.7	2049.30	<.000
UV protective×Surface treatment	5	5654	1130.7	108.18	<.000
UV protective×Aging	10	18588	1858.8	177.83	<.000
UV protective×Color	25	64858	2594.3	248.19	<.000
Surface treatment×Aging	2	2961	1480.3	141.61	<.000
Surface treatment×Color	5	5878	1175.7	112.48	<.000
Aging×Color	10	6256	625.6	59.85	<.000
UV protective×Surface treatment×Aging	10	2372	237.2	22.70	<.000
UV protective× Surface treatment ×Color	25	14605	584.2	55.89	<.000
UV protective×Aging× Color	50	8615	172.3	16.48	<.000
Surface treatment×Aging×Color	10	6261	626.1	59.89	<.000
UV protective×Surface treatment×Aging×Color	50	6930	138.6	13.26	<.000
Error	1944	20320	10.5		
Total	2159	368799			

Table 4. *Mean values, standard deviations (±), and comparisons for ΔE data*

UV protective	Surface treatment	Aging	Unpigmented	White	Yellow	Red	Blue	Mixed
Control	Argon	300 hours of UV aging	6.13 (±0.7) $Ca1^{A}$	4.08 (±0.3) $Cab1^{AB}$	15.31 (±0.6) $Aa1^{B}$	9.78 (±1) $Bb2^{D}$	14.14 (±0.5) $Aa1^{AB}$	14.45 (±0.8) $Aa1^{BC}$
		600 hours of UV aging	7.25 (±0.8) $Ca1^{AB}$	4.52 (±0.3) $Da1^{C}$	13.39 (±0.6) $ABa1^{C}$	5.39 (±0.4) $CDc2^{C}$	12.37 (±0.6) $Bab1^{BC}$	15.32 (±0.6) $Aa1^{BC}$
		Thermocycling	5.79 (±1.4) $Da1^{B}$	2.08 (±0.4) $Eb1^{B}$	10.17 (±4.4) $BCb1^{D}$	14.12 (±7.9) $Aa2^{E}$	11.24 (±2.1) $Bb1^{D}$	8.4 (±2.3) $Cb1^{D}$
	Oxygen	300 hours of UV aging	7.13 (±1.7) $Da1^{BC}$	3.06 (±0.3) $Ea1^{BC}$	14.45 (±1.6) $Ba1^{B}$	18.9 (±2.6) $Ab1^{C}$	9.77 (±0.9) $Ca2^{D}$	14.59 (±0.6) $Ba1^{CD}$
		600 hours of UV aging	6.66 (±1.1) $Da1^{C}$	3.82 (±0.5) $Ea1^{BC}$	12.2 (±1.7) $Cb1^{CD}$	25.09 (±1.9) $Aa1^{C}$	11.78 (±1.6) $Ca1^{D}$	14.89 (±1.5) $Ba1^{C}$
		Thermocycling	7.1 (±1.8) $CDa1^{B}$	2.34 (±0.5) $Ea1^{B}$	9.28 (±11.9) $BCc1^{C}$	19.43(±10.9) $Ab1^{C}$	10.41 (±2.1) $Ba1^{CD}$	5.54 (±2.7) $Db2^{DE}$
UV-BP	Argon	300 hours of UV aging	8.1 (±0.7) $CDa2^{A}$	5.96 (±0.6) $Da1^{A}$	13.84 (±1) $Aa1^{B}$	11.59 (±1.5) $ABb2^{D}$	10.07 (±0.7) $BCb2^{C}$	11.33 (±1.1) $Ba2^{D}$
		600 hours of UV aging	7.99 (±0.8) $Ba1^{A}$	7.55 (±0.9) $Ba1^{A}$	13.56 (±0.8) $Aa1^{C}$	6.05 (±1.2) $Bc2^{C}$	11.63 (±2.2) $Aab2^{C}$	12.87 (±1.1) $Aa2^{C}$
		Thermocycling	4.56 (±0.5) $Cb1^{B}$	2.03 (±0.5) $Db1^{B}$	13.34 (±5.4) $Ba1^{C}$	27.02 (±5.9) $Aa1^{C}$	13.01 (±1.5) $Ba1^{D}$	11.08 (±3.3) $Ba1^{C}$
	Oxygen	300 hours of UV aging	10.28 (±1.9) $Ca1^{A}$	4.88 (±2) $Dab1^{B}$	8.97 (±3.1) $Cab2^{C}$	19.32 (±1.7) $Ab1^{C}$	15.13 (±1.9) $Ba1^{C}$	16.07 (±1) $Ba1^{C}$
		600 hours of UV aging	9.41 (±2.1) $Ca1^{AB}$	4.99 (±1.2) $Da2^{B}$	9.75 (±3) $Ca2^{D}$	25.27 (±1.7) $Aa1^{C}$	14.62 (±1.5) $Ba1^{C}$	15.11 (±0.4) $Ba1^{C}$
		Thermocycling	5.18 (±0.7) $CDb1^{B}$	2.95 (±0.8) $Db1^{B}$	7.03 (±2.2) $BCb2^{C}$	8.74 (±4.9) $ABc2^{D}$	10.53 (±2) $Ab2^{CD}$	7.28 (±1) $BCb2^{CD}$
UV-EM	Argon	300 hours of UV aging	6.15 (±0.4) $Cab1^{A}$	4.39 (±0.5) $Ca1^{AB}$	15.44 (±2.4) $Aa1^{B}$	4.74 (±1) $Cb2^{E}$	14.34 (±0.8) $ABa1^{A}$	12 (±0.7) $Ba1^{CD}$
		600 hours of UV aging	6.73 (±0.3) $Ca1^{AB}$	4.91 (±0.4) $Ca1^{BC}$	16.95 (±10.8) $Aa1^{B}$	5.57 (±0.7) $Cb2^{C}$	13.72 (±0.7) $Ba1^{BC}$	13.71 (±0.7) $Ba1^{BC}$
		Thermocycling	4.11 (±0.9) $Cb1^{B}$	1.34 (±0.4) $Db1^{B}$	10.18 (±2.1) $Bb1^{D}$	21.32 (±9.9) $Aa1^{D}$	10.83 (±9.5) $Bb1^{D}$	3.28 (±1.1) $CDb1^{E}$
	Oxygen	300 hours of UV aging	6.73 (±0.9) $Da1^{C}$	3.60 (±0.7) $Ea1^{BC}$	13.74 (±2.4) $Ba1^{B}$	16.92 (±2.1) $Ab1^{C}$	10.65 (±1.2) $Cb2^{D}$	12.35 (±1.1) $BCb1^{D}$
		600 hours of UV aging	6.91 (±1.2) $Da1^{C}$	3.53 (±0.7) $Ea1^{BC}$	15.02 (±0.8) $BCa1^{B}$	25.57 (±0.8) $Aa1^{C}$	12.69 (±1.3) $Ca1^{CD}$	15.50 (±1.1) $Ba1^{C}$
		Thermocycling	5.04 (±0.4) $Ba1^{BC}$	2.59 (±0.3) $Ba1^{B}$	3.78 (±2.2) $Bb2^{D}$	4.10 (±1.9) $Bc2^{E}$	8.22 (±5.1) $Ac2^{D}$	3.75 (±1.7) $Bc1^{E}$
UV-TD	Argon	300 hours of UV aging	6.04 (±0.8) $Da1^{A}$	2.89 (±0.4) $Eab1^{B}$	28.49 (±1.3) $Bc1^{A}$	37.43 (±1.7) $Ab2^{A}$	12.86 (±1) $Cb2^{AB}$	15.23 (±0.9) $Cb2^{B}$
		600 hours of UV aging	5.41 (±0.4) $Da1^{B}$	3.29 (±0.4) $Da1^{C}$	30.58 (±1.7) $Bb1^{A}$	38.45 (±1.6) $Ab2^{A}$	14.30 (±0.6) $Cb2^{B}$	16.11 (±0.9) $Cb2^{B}$
		Thermocycling	4.69 (±0.8) $Ea1^{B}$	0.93 (±0.3) $Fb1^{B}$	40.73 (±2.5) $Ca1^{A}$	62.53 (±3.4)$Aa2^{A}$	49.33 (±7.1) $Ba1^{A}$	37.99 (±3.8) $Da1^{A}$
	Oxygen	300 hours of UV aging	6.05 (±0.4) $Ea1^{C}$	2.31 (±0.3) $Fa1^{C}$	22.78 (±5.3) $Db2^{A}$	61.6 (±2.6) $Ab1^{A}$	45.27 (±1.8) $Bb1^{A}$	35.6 (±4.0) $Cab1^{A}$
		600 hours of UV aging	6.26 (±0.9) $Ea1^{C}$	2.39 (±0.5) $Fa1^{C}$	22.34 (±5.9) $Db2^{A}$	60.7 (±4.5) $Ab1^{A}$	48.64 (±2.3) $Ba1^{A}$	34.83 (±4.6) $Cb1^{A}$
		Thermocycling	2.6 (±0.8) $Db2^{C}$	2.11 (±0.4) $Da1^{B}$	37.43 (±1.8) $Ca2^{A}$	68.88 (±2.2) $Aa1^{A}$	44.06 (±5.3) $Bb2^{B}$	37.05 (±4.1) $Ca1^{A}$
UV-ES	Argon	300 hours of UV aging	6.2 (±0.8) $CDa1^{A}$	3.85 (±0.6) $Da1^{AB}$	7.41 (±0.9) $Cb2^{C}$	20.91 (±1.3) $Ab1^{B}$	11.72 (±0.8) $Bb1^{BC}$	10.27 (±0.3) $Bb1^{D}$
		600 hours of UV aging	6.6 (±0.3) $Ca1^{AB}$	4.77 (±0.8) $Ca1^{C}$	9.66 (±0.4) $Ba2^{D}$	14.68 (±1.2) $Ac1^{B}$	12.8 (±0.3) $Ab1^{BC}$	15.26 (±0.4) $Aa1^{BC}$
		Thermocycling	6.44 (±0.8) $CDa1^{B}$	1.63 (±0.7) $Eb1^{B}$	5 (±1.8) $Dc2^{E}$	25.12 (±3.7) $Aa1^{C}$	18.21 (±3) $Ba1^{C}$	8.04 (±1.2) $Cc1^{D}$
	Oxygen	300 hours of UV aging	7.51 (±0.5) $BCa1^{BC}$	2.88 (±0.6) $Dab1^{BC}$	13.86 (±1) $Aa1^{B}$	5.1 (±0.8) $CDb2^{D}$	6.77 (±1.2) $Cb2^{E}$	9.26 (±0.7) $Bb1^{E}$
		600 hours of UV aging	7.85 (±1) $Ca1^{BC}$	3.59 (±0.3) $Da1^{BC}$	12.86 (±1.6) $Ba1^{BC}$	16.71 (±1.2) $Aa1^{D}$	10.52 (±1.2) $Ba2^{D}$	15.92 (±0.2) $Aa1^{C}$
		Thermocycling	5.88 (±0.9) $Ca1^{B}$	1.10 (±0.3) $Db1^{B}$	8.93 (±2) $ABb1^{C}$	6.53 (±1.7) $BCb2^{DE}$	11.16 (±2.6) $Aa2^{C}$	8.13 (±2.3) $BCb1^{C}$
UV-SS	Argon	300 hours of UV aging	6.43 (±0.6) $Db2^{A}$	6.16 (±0.5) $Da1^{A}$	16.12 (±1.9) $Bb1^{B}$	15.47 (±1.4) $Bb2^{C}$	11.93 (±1.8) $Cc2^{ABC}$	21.44 (±0.5) $Ac2^{A}$
		600 hours of UV aging	7.61 (±0.5) $Cab2^{AB}$	7.27 (±0.8) $Ca1^{AB}$	17.48 (±1.7) $Bb1^{B}$	15.03 (±0.8) $Bb2^{B}$	22.61 (±0.8) $Ab2^{A}$	23.73 (±0.5) $Ab2^{A}$
		Thermocycling	9.09 (±0.7) $Da2^{A}$	6.93 (±0.3) $Da1^{A}$	34.73 (±11.5) $Ba1^{B}$	41.1 (±3.6) $Aa2^{B}$	30.04 (±16) $Ca2^{B}$	32.62 (±5) $Ba1^{B}$
	Oxygen	300 hours of UV aging	9.26 (±2.1) $Cb1^{AB}$	8.03 (±0.9) $Ca1^{A}$	8.28 (±2.8) $Cc2^{C}$	38.17 (±3.7) $Ab1^{B}$	23.48 (±4.6) $Bc1^{B}$	23.65 (±3.7) $Bc1^{B}$
		600 hours of UV aging	10.36 (±1.4) $CDb1^{A}$	7.89 (±0.2) $Da1^{A}$	11.23 (±0.6) $Cb2^{CD}$	38.64 (±5.4) $Ab1^{B}$	26.4 (±3.8) $Bb1^{B}$	26.75 (±2.2) $Bb1^{B}$
		Thermocycling	14.14 (±0.3) $Ea1^{A}$	6.58 (±1.5) $Fa1^{A}$	33.36 (±15.2) $Ca1^{B}$	56.3 (±8) $Aa1^{B}$	48.8 (±8.6) $Ba1^{A}$	29.57 (±4.8) $Da2^{B}$

UV-BP, benzophenone-3; UV-EM, ethylhexyl methoxycinnamate; UV-TD, titanium dioxide; UV-ES, 2-ethylhexyl salicylate; UV-SS, sunscreen.Same uppercase letters indicate that ΔE values of silicone color groups were not significantly different in same protective agent, surface treatment, and aging groups (P>0.05). Same lowercase letters indicate that the ΔE values of aging groups were not significantly different in same protective agent, surface treatment, and silicone color groups (P>0.05). Same numbers indicate that ΔE values of surface treatment groups were not significantly different in same protective agent, aging, and silicone color groups (P>0.05). Same superscripts indicate that ΔE values of protective agent groups were not significantly different in same surface treatment, aging, and silicone color groups (P>0.05).

After UV aging for 300 hours, white, yellow, and mixed color groups of argon-treated and UV-ES-coated specimens resulted in lower ΔE compared with control groups with no UV protection and the differences were significant in yellow and mixed groups (P<0.05). Also, blue and mixed groups (argon treated and UV-BP covered) showed significantly lower ΔE values than control groups. Comparing UV protective coated groups after oxygen treatment, yellow color groups of UV-BP and UV-SS revealed lower ΔE than control groups. Also, red, blue, and mixed colors of UV-ES coated groups showed significantly lower ΔE values than control groups. Following UV aging for 600 hours, the highest color changes were noted for all groups regardless of surface treatment and UV protective coating. In all aging procedures, the highest color change (ΔE) was generally observed in the red groups than other color groups within each surface treated and coated group. The lowest ΔE values were found in white groups. In control groups (with no coating), the lowest ΔE values were detected in unpigmented, white, and yellow groups after 300 hours, and the red, blue, and mixed colors showed the lowest ΔE values after thermocycling. UV protective coated groups showed significantly highest and lowest ΔE values after 600 hours and thermocycling, respectively (P<0.05).

4. DISCUSSION

In the present study, the surfaces of a maxillofacial silicone elastomer were modified with plasma application. Then they were coated with 5 different UV protectives to decrease the color change of silicone elastomers. The null hypothesis of coating the silicone-colored surfaces with 5 UV protectives following both oxygen and argon plasma treatments would similarly decrease the color change of the material after aging was rejected because of the significant differences among the experimental groups.

Particularly UV light and environmental effects cause discoloration on the silicone facial prostheses (2,4) UV light causes continuing polymerization of the silicone chains. During this prolonged polymerization process, subproducts are released. Thereby decomposition of color pigments and disruption of the chains of polymer occur (4,7,10). This process resulted in the discoloration of the material. Previous literature includes experimental studies on protecting the maxillofacial silicones against the damaging effects of UV light. In these studies; opacifiers, UV protectives, and thermochromic pigments were incorporated into the silicone (2,4,5,9-11,15,16). The addition of opacifier powders as a white pigment in silicones enhanced optical and mechanical properties (2,4,5,15,16). However, the long-term effects of these protectives on the mechanical properties, optical properties, and biocompatibility of silicone are unknown when incorporated into the bulk material. Therefore, in the present study, coating the surface of polymerized silicone elastomer with UV protectives was planned. Previously only one study by Bishal et al (12) used a similar approach. They coated the surface of intrinsically pigmented silicone with a nanolayer of TiO_2. TiO_2 was found to be effective in reducing the color change of the silicone elastomer after artificial aging. In this study, reduced color changes in some UV-protective coated groups after artificial aging have been observed. These findings may address further research on the surface modification of polymerized maxillofacial silicone elastomers instead of intrinsically modifying the material before polymerization to provide color stability.

In the present study, oxygen or argon plasma treatments were applied to the specimen surfaces with the aims of cleaning, enhancing surface energy and wettability, and providing a chemical bonding between the coating material and the specimen. This study revealed that coating the silicone elastomer with UV-ES followed by oxygen or argon plasma treatments revealed significantly lower color difference values for each color group after aging than the control group (P<0.05). No characteristic difference was noted between the values of groups those oxygen and argon surfaces treated before UV-ES coating except for the red group. In the red-colored specimen group, ΔE value of argon-treated and UV-ES coated specimens was higher than un-coated control specimens and color change of oxygen-treated and UV-ES coated specimens. This finding may have resulted from chemical reactions of 3 components, namely argon-treated silicone surface, red pigment, and UV-ES. Plasma is an ionized form of a gas. Ions are negatively and positively charged particles of atoms. When the ions have adequate energy, they break covalent bonds on the surface layer of the material (18-20). Thus, hydrophilicity and wettability properties of the polymer surface can be improved by plasma application (18,20). The AFM analyses of the plasma-treated silicone surfaces revealed that argon plasma created more surface roughness than oxygen plasma. Differences in surface topographies of oxygen and argon plasma-treated specimens can result from different reactive properties of oxygen and argon atoms. Beyond surface topography, the chemical reactive potential of the silicone surface with pigments and UV protectives may differ by ionized oxygen and argon.

As previously reported, the type of pigment plays an important role in silicone discoloration (4,9). Red-pigmented silicone showed the highest discoloration under different aging conditions (9,11). UV protectives that reduce discoloration with maxillofacial silicone elastomers would be valuable, especially for reddish prostheses. Coating the colored and cured silicone surface with UV-ES would also be functional because it is a clear liquid and does not change the color and translucency of the final prosthesis, unlike opacifiers.

In the present study, one type of maxillofacial silicone (M511) was evaluated for the effectiveness of coating the silicone surface with UV protectives. Different maxillofacial silicone elastomers should be evaluated in terms of color stability after surface coating with UV protective agents, especially UV-ES. In future studies, the color change of different types of maxillofacial silicones can be investigated. Furthermore, silicone surface coating methods might be improved.

Artificial aging is a fast method of evaluating the long-term properties of clinical materials. Two aging procedures were applied in the present study. One is accelerated weathering which includes temperature, UV light, and humidity to test materials (22,23). UV light has been reported as responsible for the degradation of polymers and colorants (8,11). Therefore, a similar aging procedure is widely used to test silicone elastomers (2,4,6,11). However, differences in climate around the world cause the maxillofacial prosthetic material to be exposed to various factors. (1) Although accelerated aging with weathering devices is a fast and effective method for prosthetic materials, other factors affecting prostheses during daily use such as air pollution, hygiene procedures, and patient habits cause color degradation (15). In this study, thermocycling aging was additionally applied to a specimen group for simulating water cleaning of the prostheses using warm or cold water. Depending on the findings of the current study thermocycling also affected the color difference values. This result may reveal that intrinsically colored maxillofacial prostheses can show a color change when they are exposed to a wet environment at varying temperatures.

The study includes some limitations. First, the thickness of the UV protective and liquid silicone layer was not precisely measured and was not objectively standardized. In this study, the hypothesis was that only the surface of the coating of a colored and cured silicone with UV protectives would protect the silicone from discoloration. Thereby, the material would be enhanced without changing its optimally developed polymer formulation. Further studies are needed for more precious surface coating, especially for UV-ES. Another limitation of the present study is the M511 silicone elastomer coated with UV protectives. In clinical practice, various silicone elastomers and pigments were used. Other commercially available maxillofacial silicones should be tested in terms of color stability when coated with UV-ES. In the present study, the color differences after aging procedures were calculated with the CIELab formula to compare the results with the previous studies that used mostly the CIELab values. However further studies evaluating the color stability of UV-protective coated maxillofacial silicone elastomers by using the CIEDE2000 formula is required.

5. CONCLUSIONS

Within the limitations of this study, it can be concluded that; UV aging of 600 hours was the aging procedure that caused the highest ΔE values and thermocycling caused the lowest ΔE values. After aging procedures, the highest color change (ΔE) was generally observed in the red color groups than other groups while the lowest ΔE values were noted in white colors. Coating the silicone surface with UV-ES followed by oxygen or argon plasma revealed significantly lower ΔE for each color group after aging compared to the control groups. UV-ES coating might be a promising approach to prolong the clinical lifetime of silicone maxillofacial prostheses.

Funding: *The author(s) received no financial support for the research.*

Conflicts of interest: *The authors do not have any financial interest in the companies whose materials are included in this article.*

Peer-review: *Externally peer-reviewed.*

Author Contributions:

Research idea: BTB

Design of the study: SKN

Acquisition of data for the study: SKN, BTN, MBG, ND, MET, YKA

Analysis of data for the study: YKA

Interpretation of data for the study: SKN, BTN, MBG, ND, MET, YKA

Drafting the manuscript: MBG

Revising it critically for important intellectual content: SKN, BTB, MBG

Final approval of the version to be published: SKN, BTN, MBG, ND, MET, YKA

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How to cite this article: Karakoça Nemli S, Turhan Bal B, Bankoğlu Güngör M, Dilsiz N, Eskitoros Togay M, Kasko Arıcı Y. Effect of Ultraviolet Protective Agents and Plasma Applications on the Color Stability of Maxillofacial Silicones. Clin Exp Health Sci 2024; 14: 69-75. DOI: 10.33808/clinexphealthsci.1398224