Color Stability of Elastomers for Maxillofacial Appliances

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The color stability of polyvinyl chloride, polyurethane, and silicone polymers for maxillofacial applications was determined after accelerated aging using reflectance spectrophotometry. On the basis of color stability after accelerated aging, and ease of processing, several silicone materials were the most promising.

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Maxillofacial appliances allow many patients with oral-facial defects to return to an active role in society. For the thousands of patients who require maxillofacial reconstruction, suitable materials can represent the difference between a normal life or a life of fear and disfigurement. Maxillofacial appliances fail in two distinct ways: (1) degradation of static and dynamic physical properties of the elastomers, and (2) color instability in a service environment.

The objective of this study was to determine which available maxillofacial elastomers exhibited the best color stability under conditions of accelerated aging in an effort to understand the reasons for failure in a service environment.

There are few scientific investigations in the dental literature concerning maxillofacial materials, although there are many articles dealing with techniques. There are no studies on the degradation of color of maxillofacial elastomers and how these changes affect the life expectancy of appliances. A brief review of pertinent literature concerning the color of maxillofacial materials will demonstrate the urgent need for research.

Sweeney and associates[1] in 1972 reported an extensive study of the physical properties of maxillofacial materials. A proposed specification for maxillofacial materials was also presented. Included in this specification was a weathering test using a Weather-Ometer* to test color stability. It was proposed that acceptable maxillofacial materials should demonstrate no visible change after 2000 hours in the Weather-Ometer. In this test procedure, the results were evaluated visually by a trained observer.

Cantor *et al.*[2] reported on methods for evaluating prosthetic maxillofacial materials. A polyvinyl chloride, a plasticized poly-(methyl methacrylate), and silicones were evaluated. Reflectance spectrophotometry was used to evaluate the color of maxillofacial elastomers. By studying the color of human skin and pigmented maxillofacial materials, they suggested that isometrically matched maxillofacial materials could be developed that would match the color of human skin.

Firtell[3] described a method and material for external facial prostheses that would permit the duplication of the prosthesis without the patient being present. He used earth pigments and a silicone system to produce standard stock colors from which base shades and surface tints could be compounded by formula. A custom formula was then recorded for each patient and used whenever a new appliance was required.

Ouellette[4] described a method for spray coloring of silicone elastomers. Of interest in this article was the preparation and formulation of pigments. Following a spray coating of the pigmented elastomer on an appliance, a spray containing a catalyst was then applied and allowed to polymerize. This method might have application if a clinician wished to refinish a discolored appliance.

Schaaf[5] reported on the use of tattooing to achieve a more life-like appearance of maxillofacial appliances. In this technique, standard artist's oil paints were blended to produce the desired shade for the patient. The paint was placed on the surface of the appliance and tattooed into the surface

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*Model 25 WR, Atlas Electric Devices, Chicago, Ill. 60613.

to produce simulated freckles, blood vessels, or general shading. This technique is important since it is probably the best means available today to individually characterize maxillofacial appliances.

Sproull[6] published an article dealing with color in dentistry. He described the parameters of color as hue, value, and chroma. Hue is the basic color – for example, green, blue, or red. Value is the means by which an observer can distinguish between a light or a dark color. Chroma, the third dimension of color, is the way one distinguishes a strong color from a weak one. The Munsell Color Order System was described as a means of fulfilling the requirements of ideal color using these parameters. Again, the drawback of a color matching system of this design is the dependence upon the human eye for differentiation. In two later articles[7,8] a spectrophotometer was used in the analysis of color of dental structures.

In the present study, the color stability of a wide range of commercially available maxillofacial materials was evaluated under conditions of accelerated aging using a spectrophotometer to measure, quantitatively, changes in color. Using this method, it was possible to determine the color stability of each elastomer.

Materials and methods.

Three categories of maxillofacial materials were evaluated: a plasticized polyvinyl chloride,* polyurethane,† and four silicones. Three room-temperature-vulcanized silicone elastomers‡ and one heat-vulcanized silicone§ were evaluated. All materials were processed according to the manufacturers' instructions. Samples used were 3.5 mm x 4 cm x 6 cm. Five samples were made for each material studied. The polyvinyl chloride and silicones were processed in an aluminum mold, and the polyurethane was produced in a polytetrafluoro-ethylene mold.

Prior to accelerated aging, all materials were evaluated by reflectance spectrophotometry with a double-beam, ultraviolet-visible spectrophotometer and integrating sphere.* In this method of color analysis, the amount of light reflected at each wavelength in the visible spectrum (400 - 700 nm) is measured and recorded. The luminous reflectance, dominant wavelength and excitation purity are calculated for each test specimen by using a computer program† based on the C.I.E. Chromaticity diagram, 1931 and Source A.[9] Luminous reflectance is a measure of the total amount of light reflected by the specimen and is a measure of lightness or darkness. It is similar to value in other color systems. Dominant wavelength is the actual color of the specimen when compared to a standard observer and is similar to hue. Excitation purity is a measure of the amount of color present in the sample and is similar to chroma.

In order to evaluate the opacity or translucency of each material, the samples were evaluated with both a white and a black background. By comparing the luminous reflectance of the specimen with a white‡ and then a black background§, an index of opacity could be calculated for that material. The ratio of luminous reflectance with a black to a white background is called the contrast ratio, with zero representing a transparent sample and one representing a completely opaque sample. After determining these color parameters for all materials after processing, the samples were then placed in a weathering chamber# for accelerated aging. A 2500 watt xenon light source with borosilicate glass filters was used in the weathering chamber. The xenon light with the borosilicate glass filters produces a spectral distribution very similar to natural sunlight.[9] During the aging cycles, the light was left on constantly, and distilled water was sprayed on the specimens for 18 minutes every 102 minutes. The relative humidity was maintained at 90% RH, and the temperature of the chamber was 43°C or a black panel temperature of 63°C.

*Prototype III, Sartomer Industries, Inc., Essington, PA 19029.

†Epithane, Daro Products, Inc., Box 224, Butler, Wis. 33007.

‡Silastic 382, Silastic 399, and Silastic 44210, Dow Corning Corporation, Midland, MI.

§Silastic 44515, Dow Corning Corp., Midland, MI.

*Acta CIII Spectrophotometer with integrating sphere, Beckman Instruments, Inc., Irvine, CA 92634.

†Available from author upon request.

‡Part No. 104384, Beckman Instruments, Inc., Irvine, CA 92634.

§Part No. 375287, Beckman Instruments, Inc., Irvine, CA 92634.

#Weather-Ometer, Model 25WR, Atlas Electric Devices, Chicago, IL 60613.

TABLE 1
LUMINOUS REFLECTANCE OF MAXILLOFACIAL POLYMERS FOR A BLACK AND WHITE BACKGROUND AFTER 0 TO 900 HOURS OF AGING

		Hours of Aging					
Material	Background	0	100	300	600	900	Tukey Interval
Polyvinyl Chloride	Black	7.1 (0.4)*	9.2 (0.4)	9.4 (0.4)	10.2 (1.2)	10.3 (1.2)	1.6
	White	66.7 (3.5)	65.5 (6.6)	66.4 (5.1)	63.8 (7.0)	62.9 (7.2)	N.S.
Polyurethane	Black	6.2 (0.4)	6.5 (0.3)	6.3 (0.1)			N.S.
	White	79.6 (4.1)	79.5 (1.3)	69.6 (3.1)			N.S.
Silicone 382	Black	59.4 (0.2)	60.4 (0.2)	60.4 (0.2)	60.3 (0.4)	60.4 (0.3)	0.6
	White	60.6 (0.3)	61.4 (0.2)	61.5 (0.2)	61.0 (0.2)	61.5 (0.3)	0.4
Silicone 399	Black	30.9 (0.8)	35.0 (1.2)	38.1 (1.0)	39.7 (2.0)	42.5 (4.3)	4.2
	White	60.0 (3.6)	63.9 (1.4)	66.5 (1.7)	67.1 (1.3)	69.0 (2.2)	3.0
Silicone 44210	Black	6.7 (0.2)	7.0 (0.1)	6.9 (0.3)	6.7 (0.3)	6.7 (0.3)	N.S.
	White	69.9 (1.2)	78.9 (1.2)	78.5 (1.1)	78.4 (1.2)	78.3 (1.3)	N.S.
Silicone 44515	Black	8.9 (0.5)	9.6 (0.5)	9.6 (0.5)	9.5 (0.5)	9.5 (0.5)	N.S.
	White	60.4 (1.1)	62.1 (0.8)	63.5 (1.3)	64.1 (0.6)	64.5 (0.8)	1.8

*5 samples for each mean value, standard deviation in parentheses.
N.S. means no significant differences among means.

The spectral reflectance of all materials except the polyurethane was evaluated after 100, 300, 600, and 900 hours in the weathering chamber. The weathering of the polyurethane was stopped after 300 hours because of severe degradation. Means were calculated, and luminous reflectance, contrast ratio, dominant wavelength, and excitation purity were compared for each material at the specified times by analysis of variance[10] at a 95% confidence level. Comparisons of means were made by calculation of Tukey's intervals[11].

Results.

Luminous reflectance, contrast ratio, dominant wavelength, and excitation purity of the original and aged maxillofacial polymers are presented in Tables 1-4. The values for the Tukey intervals are also listed.

The polyurethane and silicone 44210 showed no significant changes in luminous reflectance with aging (Table 1). The silicones 382 with a white and a black background and 44515 with a white background and the polyvinyl chloride with a black background experienced only slight changes, and these

TABLE 2
CONTRAST RATIO OF MAXILLOFACIAL POLYMERS AFTER 0 to 900 HOURS OF AGING

	Hours of Aging				
Material	0	100	300	600	900
Polyvinyl Chloride	0.11 (0.01)*	0.14 (0.02)	0.14 (0.02)	0.16 (0.04)	0.16 (0.04)
Polyurethane	0.08 (0.01)	0.08 (0.00)	0.08 (0.00)		
Silicone 382	0.98 (0.00)	0.98 (0.01)	0.98 (0.00)	0.99 (0.01)	0.98 (0.00)
Silicone 399	0.53 (0.03)	0.55 (0.01)	0.57 (0.01)	0.59 (0.03)	0.61 (0.05)
Silicone 44210	0.08 (0.01)	0.09 (0.00)	0.09 (0.01)	0.08 (0.01)	0.09 (0.01)
Silicone 44515	0.15 (0.01)	0.15 (0.01)	0.15 (0.00)	0.15 (0.01)	0.15 (0.01)

*5 sample pairs for each mean, standard deviation in parentheses.

TABLE 3
DOMINANT WAVELENGTH, NM, OF MAXILLOFACIAL POLYMERS FOR A BLACK AND A WHITE BACKGROUND AFTER 0 TO 900 HOURS OF AGING

		Hours of Aging					
Material	Background	0	100	300	600	900	Tukey Interval
Polyvinyl Chloride	Black	581.4 (1.0)*	506.4 (5.2)	500.8 (1.3)	501.2 (1.9)	501.4 (2.2)	5.2
	White	584.0 (0.0)	584.2 (0.5)	584.0 (0.0)	584.0 (0.1)	583.8 (0.5)	N.S.
Polyurethane	Black	545 (28)	572 (8)	573.2 (1.6)			†
	White	583.2 (0.5)	583 (0.5)	584.0 (0.0)			0.6
Silicone 382	Black	582.2 (0.5)	582.2 (0.5)	582.2 (0.5)	582.8 (0.6)	582.2 (0.5)	N.S.
	White	583.0 (0.0)	583.0 (0.0)	583.0 (0.0)	583.0 (0.0)	583.0 (0.0)	N.S.
Silicone 399	Black	493.4 (0.6)	494.0 (0.0)	493.6 (0.6)	492.0 (0.0)	492.4 (0.6)	0.8
	White	570.8 (1.3)	562.0 (4.3)	531 (15)	501.2 (0.8)	500.8 (1.8)	†
Silicone 44210	Black	487.0 (0.0)	487.0 (0.0)	487.4 (0.6)	487.6 (0.6)	487.8 (0.5)	N.S.
	White	586.0 (0.0)	586.0 (0.0)	586.0 (0.9)	585.4 (0.6)	585.6 (0.6)	N.S.
Silicone 44515	Black	490.2 (0.5)	490.0 (0.0)	489.6 (1.3)	489.2 (0.5)	489.0 (0.0)	0.7
	White	585.8 (4.3)	585.8 (0.5)	585.8 (0.5)	586.0 (0.0)	586.0 (0.0)	N.S.

*5 samples for each mean value, standard deviation in parentheses.
N.S. means no significant differences among means.
†The means were not compared because the variances were not equal.

changes occurred mainly before 300 hours of aging. The largest change in luminous reflectance was seen for silicone 399, which changed 11.6 with a black background and 9.0 with a white background.

A contrast ratio is calculated by dividing the luminous reflectance with a black background by the luminous reflectance with a white background. A sample with a contrast ratio of 1 would be completely opaque, and a sample with a contrast ratio of 0 would be completely translucent. The values of the contrast ratio (Table 2) showed that silicone 382 was the most opaque, followed by silicone 399. The remainder of the materials had much lower values of opacity. Most of the materials did not change in opacity with aging up to 900 hrs. except silicone 399, which increased in opacity with aging about 10 percent. The contrast ratio for polyvinyl chloride increased about 6 percent with aging.

The dominant wavelengths of the maxillofacial polymers as a function of aging are presented in Table 3. No significant changes in dominant wavelength with a white background were observed on aging for polyvinyl chloride, or silicones 382, 44210 and 44515. A very slight change of 0.8 was seen with the polyurethane. The dominant wavelength with a white background for silicone 399 decreased from 570.8 to 501.2 nm after 600 hours of aging, indicating a decrease in yellow and an increase in green. In this instance the means were not compared statistically, since the variances were not equal. More changes in dominant wavelength with aging were observed with measurements made with a black background, with only silicone 382 and 44210 showing no significant change. For the polyvinyl chloride, the dominant wavelength with a black background decreased from 581.4 to 506.4 nm after 100 hours of aging and to 500.8 nm after 300 hours or more of aging; this change indicates a bleaching of the yellow on aging. The dominant wavelength (black background) for polyurethane changed from 545 to 572 nm after 100 hours or more of aging, indicating a change toward yellow. The means were not compared statistically, since the variances were not equal. Aging of polyurethane was not measured at 600 and 900 hours because of physical degradation of the samples, presumably because of hydrolysis. A slight change occurred in dominant wavelength (black background) for silicone 44515 after 600 hours of aging.

The excitation purity as a function of aging of the maxillofacial polymers is listed in Table 4. Excitation purity indicates the chroma or intensity of the color, with higher numbers representing more chroma. The excitation purity values emphasize the low intensity of the color of maxillofacial

TABLE 4
EXCITATION PURITY OF MAXILLOFACIAL POLYMERS FOR A BLACK AND A WHITE BACKGROUND AFTER 0 TO 900 HOURS OF AGING

		Hours of Aging					
Material	Background	0	100	300	600	900	Tukey Interval
Polyvinyl Chloride	Black	0.252(0.03)*	0.010(0.00)	0.014(0.01)	0.020(0.00)	0.020(0.00)	0.022
	White	0.552(0.05)	0.208(0.02)	0.190(0.05)	0.198(0.02)	0.198(0.02)	0.060
Polyurethane	Black	0.008(0.01)	0.014(0.01)	0.026(0.01)			0.013
	White	0.112(0.01)	0.124(0.01)	0.164(0.02)			0.020
Silicone 382	Black	0.100(0.00)	0.080(0.00)	0.080(0.00)	0.082(0.00)	0.080(0.00)	0.004
	White	0.110(0.00)	0.090(0.00)	0.090(0.00)	0.090(0.00)	0.092(0.00)	0.004
Silicone 399	Black	0.040(0.00)	0.036(0.01)	0.036(0.01)	0.036(0.01)	0.034(0.01)	N.S.
	White	0.034(0.01)	0.013(0.00)	0.010(0.00)	0.010(0.00)	0.010(0.00)	0.006
Silicone 44210	Black	0.096(0.01)	0.090(0.00)	0.090(0.00)	0.090(0.00)	0.090(0.00)	0.005
	White	0.076(0.01)	0.092(0.00)	0.100(0.00)	0.106(0.01)	0.106(0.01)	0.009
Silicone 44515	Black	0.102(0.00)	0.110(0.01)	0.110(0.00)	0.118(0.00)	0.120(0.00)	0.008
	White	0.252(0.02)	0.220(0.02)	0.202(0.02)	0.178(0.01)	0.178(0.02)	0.033

*5 samples for each mean value, standard deviation in parentheses.
N.S. means no significant difference among means.

polymers, and in most instances only small changes occurred with aging. The decrease in the excitation purity of polyvinyl chloride at 100 hours of aging emphasizes that the intensity of the color was reduced early in the aging, and no significant change occurred between 100 and 900 hours. The excitation purity of polyurethane increased slightly between 100 and 300 hours of aging, indicating an increase in the intensity of the dominant wavelength. All of the silicones showed slight changes in excitation purity on aging. Only silicone 399 with a black background showed no change in excitation purity after 900 hours of aging.

Discussion.

The four parameters – luminous reflectance, contrast ratio, dominant wavelength, and excitation purity – were used to evaluate the color stability of maxillofacial polymers during aging. Although statistically significant changes were observed on aging of one or more of these parameters for all materials, the changes were surprisingly small considering the problems with maintaining esthetics of maxillofacial appliances. The slight changes in color probably resulted from the incorporation of antioxidants and/or ultraviolet light stabilizers by the manufacturer.

The polyvinyl chloride was processed according to recommended directions at 175°C. The results indicate that the pale yellow color of the processed polyvinyl chloride decreased markedly during the first 100 hours of aging, after which it remained quite stable. The change in color is probably a result of leaching out of colored byproducts in the ultraviolet light-water spray aging test. Later experimenting with processing variables indicates that 150°C is the optimum processing temperature, since these samples are only slightly yellow and have nearly as good mechanical properties as those processed at 175°C. The critical nature of the processing variables for polyvinyl chloride could present problems in the control of color of maxillofacial appliances processed under dental laboratory conditions.

The color of the polyurethane polymer increased in intensity during 300 hours of aging, as indicated by the increase in the values for the excitation purity. Values were not reported for aging at 600 or 900 hours because of severe degradation of the mechanical properties indicated by loss of form of the samples. The polyurethane is prepared with a diisocyanate and a polyol which suffer from degradation as a result of hydrolysis. This product would appear to be a poor candidate as a maxillofacial material. However, aliphatic polyurethane maxillofacial materials developed by Goldberg *et al.*[12] are inherently more color stable without added antioxidants and are highly resistant to hydrolysis. Therefore, polyurethanes, in general, should not be eliminated as possible maxillofacial materials.

The silicones showed very slight changes in color, with aging with 44210 having the least change overall. Silicone 382 was the most opaque, followed by 399, 44515 and 44210. The concentration of opacifier in silicone 382 resulted in minimal differences in the color parameters when examined with a black and a white background. The lower filler content in silicone 399 resulted in larger differences in the color parameters when examined with a black and a white background. Silicones 44515 and 44210 were nearly transparent and thus had large differences in the color parameters when examined with a black and a white background. All of the silicones are polymerized at room temperature except silicone 44515, which requires heat and a metal mold for processing. On the basis of color stability with aging and ease of processing, silicones 382 and 44210 appear to be the most promising polymers for a maxillofacial appliance.

Conclusions.

The color stability of polyvinyl chloride, polyurethane, and silicone polymers for maxillofacial applications was determined by reflectance spectrophotometry. The color of the original samples and samples aged up to 900 hours in a Weather-Ometer was evaluated by determining the luminous reflectance, contrast ratio, dominant wavelength, and excitation purity.

The polyvinyl chloride material was slightly yellow after processing and became lighter in color after 100 hours of aging. Variation in processing conditions resulted in variation in the intensity of the color. This can be a significant problem in controlling the final color of a maxillofacial appliance.

The polyurethane material increased slightly in intensity of color. The main problem with the polyurethane, however, was the severe degradation of mechanical properties with aging in the ultraviolet light-water spray environment, which terminated the color study for this material after 300 hours of aging.

The silicone elastomers all showed good color stability, although 44210 appeared to have the best overall properties. The selection of a particular silicone would depend on the opacity desired, the physical and mechanical properties of the polymer, and whether heat or chemically-initiated polymerization is desired.

All color changes observed were small, considering the problems with maintaining the esthetics of maxillofacial appliances in a service environment. Other factors, such as the color stability of pigments and the stain resistance of the elastomers, may be partly responsible for the color degradation experienced in clinical situations.

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