Physical Properties of Maxillofacial Elastomers Under Conditions of Accelerated Aging

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The stability of the physical properties of various commercially available maxillofacial prosthetic materials was evaluated with the use of an accelerated aging chamber. The tensile strength, maximum percent elongation, shear strength, tear energy, and Shore A hardness were determined before and after accelerated aging. Results indicate that silicone 44210, a RTV rubber, is a promising elastomer for maxillofacial application.

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Introduction.

Advances in polymer technology have made possible the development of more durable and esthetic materials to replace lost facial tissues. For thousands of people who suffer facial disfigurement as a result of cancer surgery, birth defects, or accident, a maxillofacial prosthesis may allow them to return to normal life styles and active roles in the society.

Until recently, maxillofacial prostheses prepared from various existing commercial materials were less than adequate, since they had a rather short life expectancy in a normal service environment. Currently, the most favorable materials can, at best, remain esthetic and serviceable for about one or two years. The requirement for frequent replacement is often beyond the financial capability of many patients. In general, maxillofacial appliances fail in two distinct ways: (1) degradation of static and dynamic mechanical properties, and (2) the instability of color under service conditions.

Although there are many articles on maxillofacial materials dealing with clinical techniques, scientific studies on the properties of these materials reported in the literature are sparse. Cantor and co-workers,[1] in 1969, published a study on methods for evaluating prosthetic facial materials. They evaluated a polyvinyl chloride, plasticized poly(methyl methacrylate), and various types of silicone elastomers. They concluded that plasticized poly(methyl methacrylate) was the best material with regard to the resistance to tear and the degree of elongation.

In 1970, Walter[2] reported on the physical properties of four elastomers. They were an acrylic ester resin, Palomed; a di-methyl polysiloxane, Molloplast B; a silicone rubber, Verone R.S.; and a pourable latex rubber, Qualitex P.V. The specific gravity, water sorption, thermal conductivity, strain in compression, and permanent deformation for each material were evaluated. The results of clinical trials indicated that the high compressibility and good tissue compatibility of Palomed were an improvement over other harder materials.

The physical properties of two room temperature vulcanized elastomers and one heat-cured silicone elastomer were reported by Roberts[3] in 1971. The results for all materials were: (1) Durometer (Shore A) from 45 to 55, (2) tensile strength from 300 to 1000 psi, (3) percent elongation from 100 to 350%, and (4) tear energy (PPI, die B) from 20 to 100.

Lontz *et al.*,[4] in 1974, reported on the modification of the stress-strain profiles of polysiloxane elastomers. The tensile modulus of the elastomers was changed to match the flexibility of various tissues of the body such as aorta and tendon. The stress-strain profiles were modified by using silicone oil and xylene in combination with the elastomers.

In 1972, Sweeney and his associates[5] published the results of a weathering test utilizing an accelerated aging chamber to investigate the color stability of various elastomers. The effects of accelerated aging on the physical and mechanical properties of these materials were not reported.

Studies were reported by Goldberg[6] in

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1977 on plasticized polyvinyl chloride, one silicone elastomer, several formulations of aliphatic polyether urethanes, and two aromatic polyester urethane systems. All materials were evaluated for physical-mechanical properties, as well as the environmental properties of hydrolytic stability, ultraviolet light stability, color stability, and stain resistance. The overall results obtained for aliphatic diisocyanate-based polyurethanes were favorable compared to their aromatic counterparts, and the results for the remaining materials appeared to be adequate for maxillofacial applications.

A review of the pertinent literature indicates that experimental investigations dealing directly with the physical and mechanical properties of maxillofacial materials as they are affected by aging are entirely lacking. The purpose of this study was to quantitatively evaluate the physical and mechanical properties of various commercial elastomers and to determine which maxillofacial materials exhibited the best stability under conditions of accelerated aging.

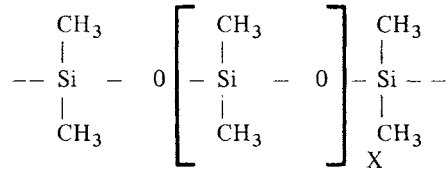
Materials and methods.

The maxillofacial materials chosen for this study were as follows: 1. Polyvinyl chloride – *Prototype III,*† 2. Polyurethane – *Epithane 3,*§ and 3. Silicones, a. RTV Elastomers – *Silastic 382, 399, and 44210,*‡ and b. Heat-Vulcanized Elastomer – *Silastic 44515.*‡

Although the exact formulation of these elastomers was not made available by the manufacturers, the fundamental polymer chemistry involved can still be described as follows: 1. In a pure state, conventional polyvinyl chloride has a high glass transition temperature of 80°C; 2. it is a partially syndiotatic polymer with sufficient irregularity of structure to exhibit a crystallinity that is quite low; 3. for maxillofacial applications, polyvinyl chloride is mixed with several other chemicals such as UV stabilizers to insure stability, and plasticizers are also added for elasticity; and 4. the polyvinyl chloride† was a complex system composed of an organic liquid plasticizer, a small quantity of crosslinking agent, catalyst, UV stabilizer, and finely dispersed polyvinyl chloride particles (this moderately viscous mixture was fused into an elastomer by heating at 170°C).

The polyurethane used was the only current commercially available polyurethane for maxillofacial applications. This material consists of three components. Part A was a prepolymer of high molecular weight polyester glycol; Part B was a low viscosity monomer of aliphatic diisocyanate,[7] and Part C was a catalyst of stannous octoate. Polymerization was achieved by direct mixing of the prepolymer, diisocyanate, and the catalyst at a temperature of 105°C.

Unlike most polymers, the silicones are unique synthetic materials because they have an inorganic backbone. The molecular structures of silicones are derived from a basic polydimethylsiloxane structure:



where X is the degree of polymerization.

As seen in this molecular chain, the inert inorganic polymer backbone of alternating silicon and oxygens is responsible for the unique characteristics of the elastomer.[8] However, this basic material does not possess high strength for many practical applications. To increase the strength, various types of fillers are added to reinforce the elastomers.[9,10] Fumed silica, precipitated silica, or aerogels are the most frequently used fillers with the silicones.

Samples were prepared for each test by following the manufacturers' instructions as outlined in a previous study.[11] When possible, vacuum was used to eliminate porosity from the materials prior to polymerization. The polyvinyl chloride and silicones were prepared in aluminum molds, and the polyurethane was processed in Teflon molds. Prior to accelerated aging, the ultimate tensile strength, maximum percent elongation, shear strength, tear energy, and Shore A hardness were determined for each material after processing, and additional samples

†Sartomer Industries, Inc., Essington, PA 19029
§Daro Products, Inc., Box 224, Butler, WI 53007
‡Dow Corning Corporation, Midland, MI 48640

were then placed in a Weather-Ometer.* A 2500 watt Xenon light source with borosilicate filters was used in the aging chamber. The light source and filter system produce a spectral distribution similar to that of natural sunlight.[12] During the aging process, the light was left on continuously and distilled water was sprayed on the samples for 18 minutes every 102 minutes. The humidity of the chamber was maintained at 90% RH and the temperature was 43°C, or a black panel temperature of 63°C.

In order to evaluate the maximum effects of accelerated aging, samples of each material were withdrawn from the weathering chamber for study after 600 and 900 hours. The weathering of polyurethane was stopped after 600 hours of aging because of severe physical degradation. The physical properties of the other elastomers were also determined at this time so that comparisons could be made with the polyurethane. Nine hundred hours of accelerated aging with the Xenon light and borosilicate filters is roughly equivalent to three years of clinical exposure. For example, if a person is exposed to one hour of direct sunlight a day for three years, the total exposure would be 1095 hours.

Several physical properties were tested to evaluate the elastomers before and after aging. Dumbbell-shaped samples with dimensions of 0.7x0.2 cm and gauge marks of 3.5 cm were used to test the ultimate tensile strength and maximum percent elongation. The samples were elongated in an Instron tester¶ at a constant strain rate of 10 cm/min. The ultimate tensile strength was expressed in terms of maximum load per unit area at which a sample ruptures, and the corresponding maximum percent elongation was calculated by dividing the ultimate separation between the gauge marks by the initial distance prior to sample elongation. Shear strength of each elastomer was determined as described by ASTM D732-46, the standard method for testing the shear strength of plastics.[13] The resistance to tear propagation was evaluated at room temperature with the Instron tester and a cross-head speed of 5 cm/min following the method outlined by Webber.[14] For this method, pant-shaped specimens 7.5 cm x 2.5 cm x 0.76 mm were torn in tension and the corresponding tear energies were calculated. Hardness was measured with a Shore A Durometer# on samples 1.0 cm in thickness. Readings were taken five seconds after indentation and recorded as hardness values for the materials. For each test, the means and the standard deviations were calculated for each material and at each time interval. The results were compared by Scheffe's or Tukey's multiple range analysis at 95% level of confidence.[15]

Results.

The ultimate tensile strength, maximum percent elongation, shear strength, tear energy and Shore A hardness were determined before and after aging. These results are tabulated in Tables 1, 2, and 3.

For the statistical analysis of data in Tables 1 and 2, Scheffe's multiple pairwise comparison test was adopted to compare results of unequal numbers of replications. In both tables, the vertical lines indicate no significant statistical difference at each time interval, and the corresponding Scheffe's intervals are listed in columns 4, 5, and 6. In Table 3, the means of the Shore A hardness were obtained from five measurements, and the calculated value for the Tukey interval is given in the footnote. Again, the vertical lines indicate no statistical difference between mean values.

The results of ultimate tensile strength shown in Table 1 indicate that silicones 382, 399, and 44515, and polyvinyl chloride were not affected at all by aging, while only a slight statistical difference was noted for silicone 44210 after aging to 900 hours. Prior to aging, silicone 44515 had the highest tensile strength of 59.8 kg/cm^2, and the polyurethane had the lowest of 8.5 kg/cm^2. Silicones 44210 and 44515 and the polyurethane demonstrated higher percent elongation ranging from 422 to 445%, while the remaining materials had lower values from 215 to 227%. No statistical difference in elongation was seen after 900 hours of aging for silicone 399 and polyvinyl chloride. Severe physical deterioration was observed

*Model 25WR, Atlas Electric Devices, Chicago, IL 60613

¶Instron Corporation, Canton, MA

#The Shore Instrument and Manufacturing Company, Jamaica, NY

TABLE 1
TENSILE STRENGTH AND MAXIMUM ELONGATION OF VARIOUS MAXILLOFACIAL ELASTOMERS

Material	Time of Aging hr	Ultimate Tensile Strength kg/cm²		Scheffe Interval 0-600	Scheffe Interval 600-900	Scheffe Interval 0-900	Maximum Elongation % *		Scheffe Interval 0-600	Scheffe Interval 600-900	Scheffe Interval 0-900
Silicone 382	0	34.2	(3.5)#	2.9	3.3	2.7	227	(13)	14	16	13
	600	36.9	(2.5)				225	(11)			
	900	35.1	(2.7)				254	(19)			
Silicone 399	0	28.1	(4.7)	4.0	4.4	3.6	221	(24)	22	24	20
	600	26.3	(4.5)				221	(24)			
	900	28.0	(2.4)				239	(18)			
Silicone 44210	0	42.8	(4.4)	3.1	3.0	2.3	445	(27)	23	22	17
	600	42.6	(1.8)				432	(15)			
	900	39.0	(2.2)				402	(24)			
Silicone 44515	0	59.8	(5.6)	7.3	8.0	6.7	441	(32)	43	47	40
	600	59.4	(8.7)				447	(59)			
	900	63.2	(5.0)				489	(19)			
Polyvinyl Chloride	0	40.7	(4.0)	4.3	5.5	5.2	215	(22)	22	28	26
	600	40.3	(2.0)				220	(5)			
	900	36.2	(2.4)				202	(10)			
Polyurethane	0	8.5	(1.1)	1.8			422	(51)	81		
	600	4.5	(0.6)				1330	(20)			
	900	----------				Disintegrated	----------				

*%Elongation = (Length of sample at break/initial length) x 100.
#Values in parentheses are standard deviations.
=No statistical difference at 95% level of confidence.

TABLE 2
SHEAR STRENGTH AND PANTS TEAR ENERGY FOR VARIOUS MAXILLOFACIAL ELASTOMERS

Material	Time of Aging hr	Shear Strength kg/cm²		Scheffe Interval 0-600	Scheffe Interval 600-900	Scheffe Interval 0-900	Pants Tear Energy dyne/cm		Scheffe Interval 0-600	Scheffe Interval 600-900	Scheffe Interval 0-900
Silicone 382	0	23.0	(3.2)*	3.2	3.5	3.1	605,000	(24,000)	40,000	47,000	36,000
	600	22.2	(1.0)				543,000	(17,000)			
	900	22.3	(2.7)				484,000	(9,000)			
Silicone 399	0	20.1	(1.6)	3.4	3.6	2.5	484,000	(24,000)	44,000	52,000	44,000
	600	21.0	(3.1)				454,000	(8,000)			
	900	20.1	(3.3)				430,000	(17,000)			
Silicone 44210	0	24.6	(1.7)	1.8	1.6	1.5	Does not tear but				
	600	24.7	(0.9)				stretched as in				
	900	24.5	(0.6)				tensile elongation.				
Silicone 44515	0	26.8	(1.0)	2.1	2.0	1.9					
	600	26.6	(1.1)				"				
	900	26.2	(1.8)								
Polyvinyl Chloride	0	20.4	(1.4)	1.9	2.1	1.7	4,283,000	(137,000)	251,000	290,000	251,000
	600	19.3	(0.6)				3,989,000	(71,000)			
	900	16.9	(0.8)				3,973,000	(42,000)			
Polyurethane	0	15.2	(0.9)	1.5			6,670,000	(260,000)			
	600	8.5	(0.2)				Too sticky & stretched				
							as in tensile elongation.				
	900	----------				Disintegrated	----------				

*Values in parentheses are standard deviations.
=No statistical difference at 95% level of confidence.

TABLE 3
SHORE A HARDNESS OF VARIOUS MAXILLOFACIAL ELASTOMERS

	Hours of Aging					
	0		600		900	
Silicone 382	47.6	(0.8)*	47.6	(0.9)	47.2	(0.7)
Silicone 399	46.6	(0.8)	46.8	(0.7)	47.0	(0.6)
Silicone 44210	32.4	(0.7)	32.6	(1.0)	33.0	(0.6)
Silicone 44515	44.8	(0.7)	45.0	(1.1)	44.8	(0.7)
Polyvinyl Chloride	53.4	(1.0)	56.0	(0.9)	57.2	(0.7)
Polyurethane	6.2	(0.7)	<1.0		DISINTEGRATED	

*5 Measurements for each mean; standard deviation in parentheses; Tukey interval for times = 0.7. Underline indicates no statistical difference at 95% level of confidence.

for polyurethane samples aged up to 600 hours. The percent elongation changed from 422 to 1,330%. This degradation proceeded further to total disintegration over 600 hours of aging. It should be noted that after 900 hours of aging, the percent elongation increased for silicones 382 and 44515, but decreased for silicone 44210. In Table 2, the shear strength of silicones 382, 399, 44210, and 44515 did not change over a period of 900 hours of weathering. Again, silicone 44515 had the highest shear strength value of 26.8 kg/cm^2, and the polyurethane at 15.2 kg/cm^2 was the lowest before aging. After 600 hours of exposure in the weathering chamber, the polyurethane became soft and the shear strength decreased to 8.5 kg/cm^2. Significant changes in shear strength on aging were also seen for the polyvinyl chloride samples with values decreasing from 20.4 to 16.9 kg/cm^2 after 900 hours.

The results of the pants tear test are listed in Table 2. The evaluation of the resistance to tear is crucial for a maxillofacial material because the prostheses are frequently feather-edged and are therefore more susceptible to tearing. Values of tear energy for silicones 44210 and 44515 were not reported because the specimens did not tear, but stretched as in tensile elongation, thus demonstrating excellent tear resistance. Prior to the aging experiment, the polyurethane exhibited good tear resistance at 6,670,000 dynes/cm, as did the polyvinyl chloride at 4,283,000 dynes/cm. However, the polyurethane samples failed to retain this strength after aging. Silicones 382 and 399 had considerably lower tear resistance; the values for these two materials were also found to be slightly altered on aging. The results of the Shore A durometer test are collectively tabulated in Table 3. Each mean value was calculated from the results of five samples, and the Tukey's intervals are listed in the footnote of the table. Prior to aging, comparison of values of Shore A hardness showed that the polyurethane at 6.2 Shore A units was the softest material, while the polyvinyl chloride at 53.4 units was the hardest. Among silicone materials, silicone 44210 with a value of 32.4 units was significantly softer than silicones 382 (47.6 units), 399 (46.6 units), and 44515 (44.8 units). This relationship remained unchanged on aging. Polyvinyl chloride was observed to be less stable on aging than the silicone elastomers as indicated by an increase in Shore A hardness from 53.4 to 57.2 units.

Discussion.

The physical properties of maxillofacial materials characterized by the tensile strength, maximum percent elongation, shear strength, tear energy, and Shore A hardness were determined before and after 600 and 900 hours of exposure in a Weather-Ometer. Evaluation of these results established the relative stability of each material under the conditions of accelerated aging.

The overall physical properties of various silicone elastomers demonstrated no change on accelerated aging. This stability is attributed to the unique characteristic of the inert inorganic backbone of the molecular chains. The wide range of ultimate tensile

strength, shear strength, and Shore A hardness for these four different types of silicones, along with the excellent tear resistance and high percent elongation for silicones 44210 and 44515, is probably a result of the chemical nature of fillers[10] and the configurations of crosslinkages[16,17] in the materials. Before vulcanization, silicone 44210 is a two component, moderately viscous fluid. It has a long setting time at room temperature, a quality that is convenient in the preparation of prostheses. Nevertheless, when fast or slow setting is needed, the polymerization rate can be conveniently manipulated by increasing or lowering the temperature. This characteristic offers great versatility in fabricating maxillofacial appliances.

The cured polyvinyl chloride was a highly plasticized material. It was observed to be less stable than the silicones. Prior to accelerated aging, syneresis of the plasticizer on the surface of processed polyvinyl chloride was noticed. Slight alterations in ultimate tensile strength, shear strength, and Shore A hardness were seen after 900 hours of aging. These noted changes are a direct result of leaching out of plasticizer from the elastomer. The degree of this exudation is controlled by the efficiency, compatibility, and miscibility of plasticizer and polyvinyl chloride in their molecular interactions.[18] Since polyvinyl chloride is readily susceptible to decomposition under the influence of UV light and the presence of an oxidant, the observed changes may also be due in part to ultraviolet irradiation.[19]

The least stable material studied was the polyurethane. This material suffered serious physical deterioration on aging, and it proceeded further to total disintegration after 600 hours of aging. This failure was probably a result of the hydrolytic degradation at the ester linkages of the polyurethane molecules when reacted with water under the influence of ultraviolet irradiation. It is because of this environmental instability that this particular polyurethane system is not recommended for maxillofacial applications. However, it would be unfair to label all polyurethane elastomers as inadequate, since there are several experimental materials which show great promise for maxillofacial applications.[6]

Based on the high degree of stability on aging and the varieties of physical-mechanical properties available to match the living tissues of specific facial-oral parts, the silicones are the most favorable materials for maxillofacial reconstruction at the present time.

The intention of the present study was to conduct a systematic evaluation of the various commercially available maxillofacial materials by laboratory technique, and not an attempt to establish clinical relevancy. Several physical property changes were small yet still statistically different. The changes may be insignificant in clinical application. The results do, however, indicate which materials have the potential for stability of physical properties in a clinical environment.

Conclusions.

The weathering effects on the physical properties of a polyvinyl chloride, a polyurethane, and several silicone elastomers used as maxillofacial materials were evaluated before and after intervals of aging in a Weather-Ometer. Comparisons of the results obtained for each material should enable clinicians to determine which materials are the most satisfactory candidates for specific oral-facial restorations.

Polyurethane was the only material that was greatly affected by aging. It demonstrated severe physical degradation and broke down completely after 600 hours of testing. This indicates that this particular polyurethane system may have deficiencies as a maxillofacial material.

The properties for the remaining materials did not vary to any great extent as a result of accelerated aging. The largest change after 900 hours was observed for the polyvinyl chloride, with a decrease in shear strength of 17%. The material that exhibited the best overall stability was the heat-cured silicone 44515. This material, however, is very viscous prior to vulcanization, and molding procedures are not within the capabilities of many laboratories. When the relative ease of processing is considered, such properties as the low viscosity of the prepolymer and the temperature at which the polymer can be vulcanized into a prosthesis are important factors. When these factors are considered, silicone 44210 is the best choice for maxillofacial prostheses among the products evaluated in this study.

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