

Hardness evaluation of prosthetic silicones containing opacifiers following chemical disinfection and accelerated aging

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Abstract: We evaluated the effects of disinfection and aging on the hardness of silicones containing opacifiers and intended for use in facial prosthetics. A total of 90 samples were produced using a cylindrical metal mold 3 mm in height and 30 mm in diameter. The samples were fabricated from Silastic MDX 4-4210 silicone in three groups: GI contained no opacifier, GII contained barium sulfate (Ba), and GIII contained titanium dioxide (Ti). The samples were disinfected using effervescent tablets (Ef), neutral soap (Ns), or 4% chlorhexidine (Cl) 3 times a week for 60 days. After this period the samples underwent 1,008 hours of accelerated aging. The hardness was measured using a durometer immediately following the disinfection period and after 252, 504, and 1,008 hours of aging. The data were statistically analyzed using 3-way ANOVA and the Tukey test ($p < .05$). The GIII group exhibited the greatest variation in hardness regardless of elapsed time. All groups displayed greater hardness after 1,008 hours of accelerated aging independent of disinfectant type. All of the hardness values were within the clinically acceptable range.

Descriptors: Maxillofacial prosthesis; Disinfection; Hardness.

Introduction

Deformities in the maxillofacial area can cause embarrassment for patients.¹ Plastic surgery is the first choice of treatment, but when surgery is inadvisable due to unfavorable conditions, rehabilitation with maxillofacial prostheses provides a means of improving patient aesthetics and self-esteem and facilitating their return to society.^{1,2}

Silicone is the most common material used to fabricate maxillofacial prostheses because of its texture, strength, durability, ease in handling and coloring, and patient comfort.^{2,3} However, silicone suffers from a rapid deterioration of physical properties and color instability and is difficult to repair, limiting its use in maxillofacial prostheses. After a few months of insertion, the prosthesis becomes unpleasant,⁴⁻⁶ and microorganisms colonizing the silicone^{7,8} may promote infection of surrounding tissues.^{1,2}

A recent method of silicone pigmentation involves adding opacifiers to the base material.⁹⁻¹⁰ This method reduces color instability¹¹⁻¹³ by blocking ultraviolet rays.⁹⁻¹⁰ However, changes to the physical properties

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(such as hardness) resulting from addition of these materials have not been investigated. We examined the effects of barium sulfate and titanium dioxide opacifiers on the hardness of Silastic MDX4-4210 following chemical disinfection and accelerated aging. Our hypothesis was that the opacifiers did not affect the physical properties of the silicone.

Material and Methods

The samples were fabricated by filling 30 mm diameter x 3 mm thick cylindrical metal molds⁶ with Silastic MDX4-4210 (Dow Corning Corporation, Midland, MI, USA). Barium sulfate (Wako, Osaka, Osaka, Japan) or titanium dioxide (Homeofar, Catanduva, SP, Brazil) were added to some of the samples as opacifiers. A total of 90 samples were fabricated in three groups (n = 30): the GI group contained no opacifier, the GII group was pigmented with 0.2 wt% barium sulfate (Ba), and the GIII group was pigmented with 0.2 wt% titanium dioxide (Ti). Both the pigments and the silicones were weighed using a precision digital scale (BEL Equipamentos Analítico, Piracicaba, SP, Brazil).^{4,14,15} The silicone was mixed according to the manufacturer's instructions. The opacifiers were mixed with the silicone and the mixture was placed in the mold. Excess material was removed to maintain a uniform thickness. The samples were cured in the molds for 3 days with the external surface left exposed.^{2,6,14,16}

After curing, an initial Shore A hardness test was performed on all samples using a digital durometer (Teclock, Osaka, Osaka, Japan) according to ASTM

procedures.¹⁷ The potency of the measurement was established between 0 and 100 Shore A, with $\pm 1\%$ of tolerance. The sample loading was 12.5 N for 10 seconds. Shore A hardness is a measure of material texture and flexibility and should be between 25 and 35 units for maxillofacial prosthetic materials.^{2,18-19}

The samples were disinfected 3 times a week for 60 days.^{6,16,20-21} Within each group, 10 samples were disinfected with Efferdent (Ef - Pfizer Consumer Health, Morris Plains, NJ, USA),^{6,20} 10 with neutral pH soap (Ns - Johnson & Johnson, São José dos Campos, SP, Brazil),^{6,20} and ten with 4% gluconate chlorhexidine (Cl - Naturativa, Araçatuba, SP, Brazil).^{2,21,22} After disinfection, the samples were again tested for hardness.

Accelerated aging tests were carried out using an aging chamber (Equilam, Diadema, SP, Brazil).⁶ The samples were subjected to alternating periods of exposure to ultraviolet light and distilled water.^{4,14} Hardness tests were repeated after 252, 504, and 1,008 hours of aging.⁸

The hardness values were analyzed using 3-way ANOVA and the means were compared using the Tukey test ($p < .05$).

Results

The mean hardness values are presented in Tables 1 and 2 and Graphs 1-3.

The opacifier, disinfection, and aging treatments were statistically significant with respect to hardness ($p < .05$). The GI and GII groups increased in hardness throughout the experiment. On the other

Table 1 - ANOVA results for hardness tests.

Source	df	SS	MS	F	P
Disinfectant	2	9.204	4.602	3.870	.025*
Opacifier	2	129.391	64.696	54.406	< .0001*
Disinf X Opac	4	17.582	4.396	3.696	.008*
Between subjects	81	96.320	1.189		
Aging	4	900.476	225.119	442.911	< .0001*
Aging X Disinf	8	56.484	7.061	13.891	< .0001*
Aging X Opac	8	320.831	40.104	78.902	< .0001*
Aging X Disinf X Opac	16	69.929	4.371	8.599	< .0001*
Within subjects	324	164.680	0.508		

* $p < .05$ denotes statistically significant difference. df: degrees of freedom, SS: sum of squares, MS: mean square.

Table 2 - Mean hardness values (SD) for Silastic silicones between chemical disinfectant groups.

Period	Disinfect	Groups		
		GI	GII	GIII
Initial	Ef	28.7 (0.82) ABa	28.6 (0.52) ABCa	29.6 (0.7) ABCa
	Ns	28.2 (0.79) Aa	28.2 (0.79) Aa	29.3 (0.48) ABCa
	Cl	29 (0.47) ABCa	28.5 (0.53) Aa	29.2 (0.63) ABa
60 days	Ef	29.8 (0.42) BCDA	28.7 (0.7) Aa	28.7 (0.48) ADA
	Ns	30.4 (0.52) CDEFa	30.7 (1.16) CDEa	28.7 (0.95) ADb
	Cl	30.1 (0.57) BCDEa	29.1 (0.57) ABa	27.6 (0.52) CDEb
252 hours	Ef	30.3 (0.95) CDEFa	29.3 (1.16) ABa	27.4 (0.52) DEb
	Ns	30.7 (0.95) DEFa	31.3 (1.06) DEFGa	27.5 (0.71) DEb
	Cl	30.4 (1.17) CDEFa	30.6 (0.97) CDEa	30.3 (0.7) Ba
504 hours	Ef	30.9 (0.88) EFGa	30.2 (0.92) BCDA	27.4 (0.7) DEb
	Ns	31.7 (0.95) FGHla	31.7 (1.16) EFGa	27 (0.47) Eb
	Cl	31.5 (1.08) EFGHa	30.8 (1.03) CDEFa	27.6 (0.95) DEb
1,008 hours	Ef	33 (0.82) la	32.7 (0.82) Ga	33.1 (0.74) Fa
	Ns	32.4 (0.84) Hla	32.4 (0.7) Ga	33.5 (0.71) Fa
	Cl	32.2 (0.92) GHla	32.7 (0.67) Ga	34 (0.67) Fa

Means followed by the same capital letter in column and same lowercase letter in line exhibit no statistical difference ($p < 0.05$) by Tukey test. Ef: Efferdent, Ns: neutral pH soap, Cl: chlorhexidine.

hand, GIII exhibited a significant decrease in hardness following disinfection and after 252 hours of accelerated aging (Graphs 1-3), except for samples disinfected with chlorhexidine. After 1,008 hours of aging, the hardness of the GIII samples increased independent of the disinfectant used (Graphs 1-3).

After 60 days of Ef disinfection, the GII and GIII samples exhibited lower hardness values than the GI group (Table 2). The hardness values of the GIII samples were lower than the GI and GII samples after 252 and 504 hours of aging regardless of disinfection procedure (Table 2). However, the GIII samples had the highest hardness after 1,008 hours (Table 2).

Chemical disinfection and accelerated aging did not statistically influence the mean hardness of the GI group, but when an opacifier was added both disinfection and accelerated aging produced significant changes in hardness (Table 2).

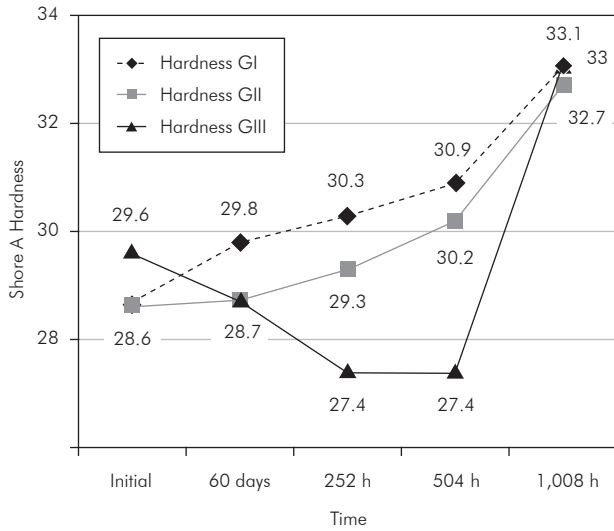
Discussion

All values obtained in the present study were within the acceptable range described in the literature (25-35 units)^{2,6,18,23} regardless of opacifier ad-

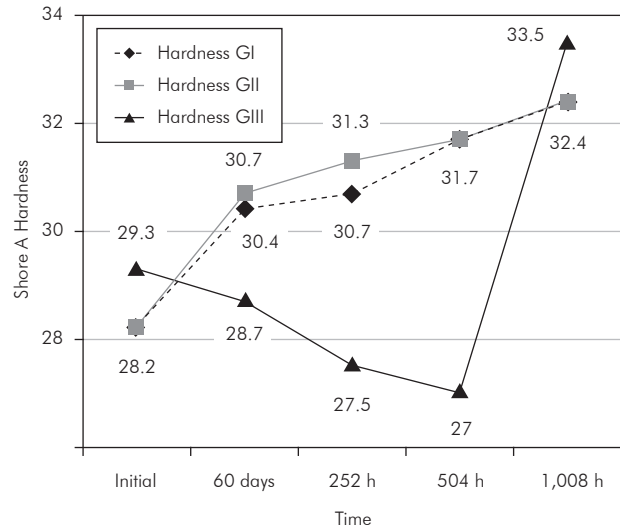
dition, disinfection, or aging (table 2). However, the hypothesis of the present study was rejected because when an opacifier was added both disinfection and accelerated aging produced significant changes in silicone hardness (Table 2).

In the present study, an increase in hardness was observed in the GI and GII groups both after disinfection and accelerated aging. The increases were only statistically significant after disinfection with neutral soup and accelerated aging (Graphs 1-3 and table 2), and could be the result of ongoing silicone polymerization with volatilization of formaldehyde,²⁴ which occurs during the aging process. The cross-linking system used in this material produces high temperatures, increasing the conversion rate, cross-linking density, and molecular weight of the silicone polymer^{6,25} to improve the hardness of the material.

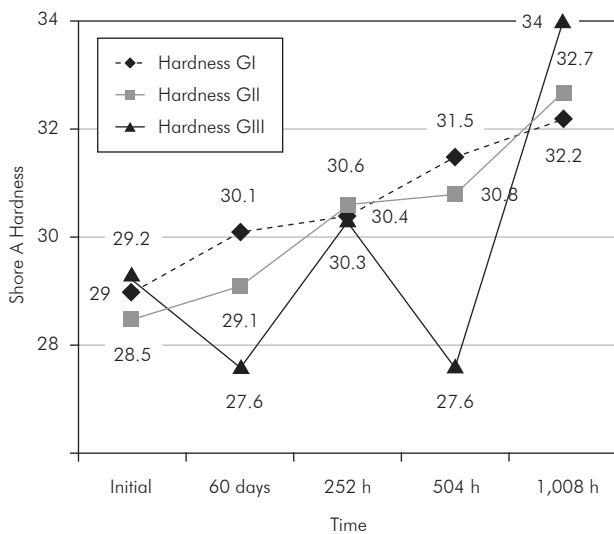
It is likely that Ba does not alter the silicone matrix since the behavior exhibited by Ba-containing samples was similar to the unmodified samples. In addition, Ba particles are capable of strongly associating with silicone chains even after disinfection. If the barium sulfate particles were removed during



Graph 1 - Mean hardness values of Silastic disinfected with Efferdent.



Graph 2 - Mean hardness values of Silastic disinfected with neutral soap.



Graph 3 - Mean hardness values of Silastic disinfected with chlorhexidine.

disinfection, an increase in porosity and reduced hardness would be expected.⁶

The GIII group displayed a decrease in hardness after 252 hours of accelerated aging, except for samples disinfected with chlorhexidine, and a significant increase in hardness after 1008 hours, regardless of the disinfection procedure.

After 60 days of disinfection with Ef, the GII and GIII groups exhibited lower hardness values than the GI group (Graph 1, table 2). The hardness

values of the GIII samples were also lower than the GI and GII groups after 252 and 504 hours of accelerated aging independent of the disinfection procedure (Graphs 1-3, Table 2).

Both the high hardness values in the initial period and the low hardness values after disinfection and accelerated aging (252 and 504 hours) are probably due to continuous polymerization of the silicone.^{4,6,19}

The polymerization process can be slowed by reaction between the disinfection products and the titanium dioxide opacifier. If the titanium dioxide particles are smaller than the barium sulfate particles, a portion of the titanium opacifier could have been removed during disinfection, resulting in more porous and softer samples.^{6,19}

One reason for the significantly lower hardness value observed in the GIII group after chlorhexidine treatment (Graph 3, Table 2) is absorption of the disinfection solution. The samples were immersed in Cl during the disinfection procedure, so a porous structure may have been formed. Mancuso *et al.*¹⁹ stated that additives to silicone materials may promote water absorption and lead to reduced hardness.

After 1,008 hours of accelerated aging, the hardness values of the GIII group were higher than those of the other groups (Table 2), suggesting that at the

end of the aging period the material reached a higher degree of polymerization for all samples.^{6,19}

Although hygiene is important in maxillofacial prostheses, there is no universally effective method for performing this maintenance. Brushing is not advisable because repeated washing may dissolve and remove some surface pigments. Rinsing with tap water is ineffective against calculus buildup and stains.⁶ Chemical soaking is the primary method of choice to disinfect maxillofacial elastomers. Patients are advised not to clean the prosthesis using solvents, such as isopropyl alcohol since this could cause dissolution of the pigments. The methods used in the present study included Efferdent tablets that employ saturation and oxidation using peroxides, neutral soap that acts through digital friction and is chemically inert,⁶ and 4% chlorhexidine, also chemically inert and acting through saturation.²²

None of the disinfectants used in the present study statistically affected the hardness value of the MDX4-4210 silicone, but when an opacifier was added, both the disinfection method and the aging process produced statistically significant changes in the material hardness. Only the GII samples disinfected with neutral soap experienced a significant increase in hardness. This result reinforces our previous supposition that the opacifier forms a strong link with the silicone chains, and this association is not broken even with digital friction during the disinfection procedure.⁶ The lower hardness values observed in the GII and GIII groups disinfected with

Cl (Table 2) can be explained by the disinfection method (immersion). According to the literature, long-term storage of silicone materials can promote water absorption, and the degree of absorption is dependent on the filler material (opacifiers) and the low level of adhesion between silicone polymers.²⁶

This trend was not observed in the GII and GIII samples disinfected with Ef (Table 2), which also acts by immersion. Prostheses disinfected with Ef have a tendency to change color because of the alkaline peroxides in the Ef tablets, which oxidize organic materials when released in solution. This tends to make the silicone more porous and consequently reduces the hardness.²⁰ Since the opacifiers used in this study were inorganic, the oxygen discoloration did not occur and the initial hardness was maintained.

According to the results of the present study, hardness values did not significantly differ with regard to disinfection process (Table 2), and all hardness values were within the acceptable clinical range (25 to 35 units).^{2,6,18-19} The samples were subjected to 1,008 hours of accelerated aging, equivalent to 1 year of clinical use.¹⁴

Conclusion

Within the limitations of this *in vitro* study, it can be concluded that the use of opacifiers and disinfection procedures in Silastic silicone prostheses is acceptable.

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