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A Comparative Evaluation of the Change in Hardness, of Two Commonly Used Maxillofacial Prosthetic Silicone Elastomers, as Subjected to Simulated Weathering In Tropical Climatic Conditions

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Abstract - *Silicone elastomers have become the materials of choice for fabrication of facial prostheses. However such prostheses need periodic replacement due to the degradation of their physical properties due to weathering of polymers. The effect of environmental factors, disinfection solutions and skin secretions on weathering of silicones has been reported. However, the literature does not report on the comparative evaluation on the change in hardness of two commonly used maxillofacial prosthetic silicone elastomers, cured by different techniques and subjected to tropical climatic conditions. This study provides improved insight and understanding into the behavior of such materials for better material selection and treatment results*

KEYWORDS: Maxillofacial prosthetic silicone, Elastomers, Change in hardness, Maxillofacial prostheses, Weathering of elastomers

INTRODUCTION

Maxillofacial prosthetics plays a key role in the overall rehabilitation of patients who have undergone extensive surgery following tumour resections, trauma or congenital malformation[1]. Over the past few decades developments in the area of maxillofacial surgery have dramatically increased the lifespan of patients. The need for the prosthetic rehabilitation has also proportionally increased[2]. Different types of materials are used to fabricate maxillofacial prostheses including poly methyl methacrylate, poly vinyl chloride, chlorinated polyethylene, polyurethanes, and silicones [3]. The ideal maxillofacial polymer should have physical and mechanical properties comparable to those of the human tissue to be replaced and should maintain these properties during patient use[4]. Silicone materials have over taken conventional acrylic resins and have become the materials of choice for fabrication of facial prostheses[5]. This is mainly because of their clinical inertness, strength, durability, ease of manipulation[2] and the comfort that they offer to patients, compared to the older materials. However such prostheses need to be periodically replaced. The main reason for replacement is the degradation of their mechanical and aesthetic properties due to weathering of polymers [2,6,7].

The main environmental characteristics that cause degradation are sunlight, temperature, moisture, wind, dust, and pollutants[2]. More precisely, deterioration is a result of a photo oxidative attack, that is, the combined action of oxygen and sunlight on a material's chemical structure [7]. The rate and amount of these changes can be variable depending on the climatic conditions and environment that the prosthesis is worn in. The changes could also occur in varying proportions depending upon whether the material is cured at room temperature or by the application of heat in a hot air oven. The effect of environmental factors on the weathering of silicones has been reported [2,3,5-11]. The survival of a prosthesis is strongly dependent on the method of retention used (implants, adhesives) [12]. Many studies have investigated the factors that affected the mechanical properties and colour changes of maxillofacial elastomers, such as weathering (irradiation, temperature, moisture, pollutants) [2,3,13-17], disinfection solutions [18-19], and skin secretions [20-21]. However, the literature does not report on the comparative evaluation on the change in hardness of two commonly used maxillofacial prosthetic silicone elastomers, cured by two different techniques as subjected to tropical climatic conditions. **T**his study was undertaken to provide improved insight and understanding in the behaviour of such materials to better material selection and treatment results.

MATERIALS AND METHODS

Two commonly used maxillofacial silicone elastomeric materials were tested in this study: a) M 511 – 10:1 platinum based system - Part A consists of the base and Part B the catalyst. They are mixed in the ratio 10:1; and b) Z004 – 1:1 platinum based system - Part A consists of the base and Part B the catalyst. They are manipulated in the ratio 1:1.

A total of 60 samples were fabricated for each material; 30 samples were denoted as Group A and 30 samples

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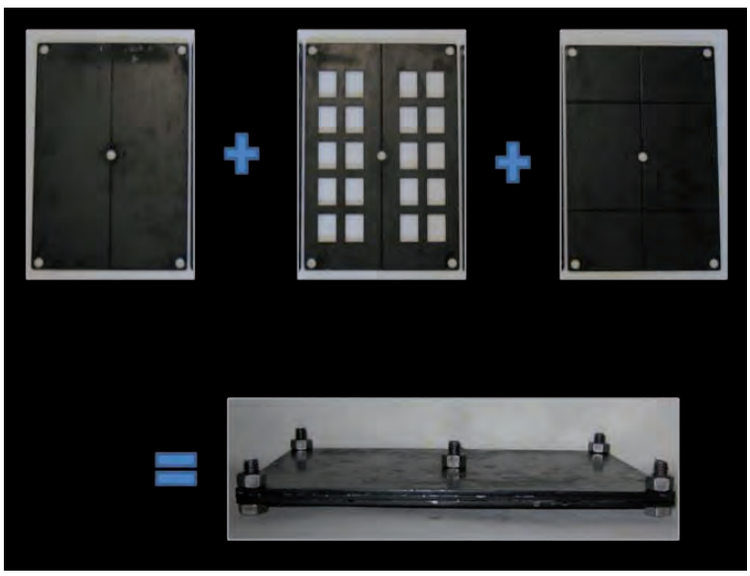

Figure 1. *Mould for fabrications of the samples.*

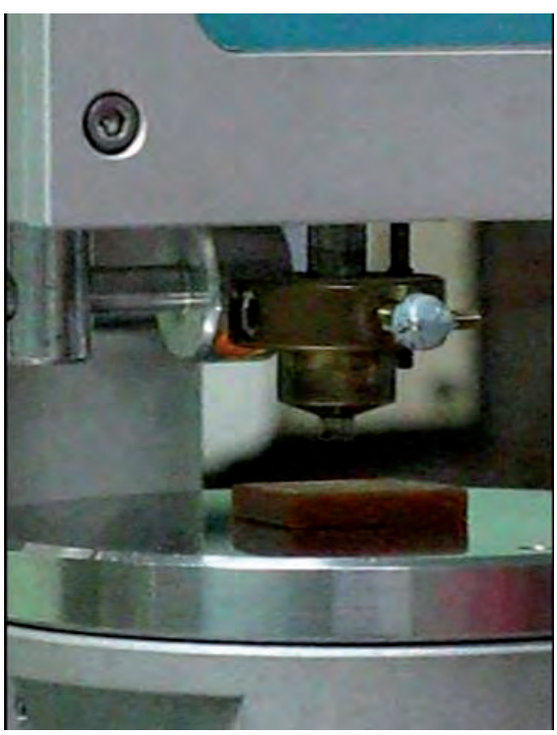

Figure 2. *Testing of samples for hardness*

as Group B. The Group A samples were cured at room temperature (A1 – M511 Room Temp and A2 Z004 Room Temp) and the Group B samples by heat application (B1 - M511 Heat Application and B2 Z004 Heat Application)

The Test Group comprised 23 samples each – Sub Groups A1, A2, B1, B2 and the Control Groups –7 samples each – Sub Groups A1, A2 , B1, B2.

The test group samples were subjected for simulated weathering

Standard, uniform sized silicone samples of 4cm X 3cm X 1cm thickness were fabricated by packing silicone elastomer in a Standardized Stainless steel mould (Figure1). Each of the materials were handled in strict compliance with the manufacturers instructions. To achieve maximum consistency among specimens within the same Group, all such specimens were processed together using the standardized protocol. The base and the catalyst were weighed using an electronic weighing scale and mixed by hand using a silicone mixing spatula. Each of the 200g of silicone were coloured using Dry earth pigments: Umber-0.1g, Dark yellow– 0.1g, Blue- 0.01 g, Red-0.01g. After mixing for 5 minutes, each mixture was de-aired under a vacuum of 30 inch mercury for 20 minutes. The mixed silicone was then poured into the moulds; the upper plate placed on the middle one on its matt surface and held under constant pressure providing by tightening the bolts at the end of the plates.

The Group A samples were left to cure at room temperature for 14 hours. The Group B samples were placed in a hot air oven at 90 deg Celsius for 1 hour as per manufacturers' instructions. After curing, the samples were recovered from the moulds and excess flash trimmed with sharp scissors. The samples in the Control group were stored in an airtight container free from exposure to light and at ambient room temperature throughout the duration of the study. The Test samples in the study groups A and B of each material type were suspended uncovered from wooden racks using stainless steel ligature wire, and the assembly was placed on the roof of the Dental Institute (simulated weathering). At the end of the treatment period, the specimens were removed, cleaned for 15 minutes in distilled water in an ultrasonic cleaner, wiped dry, stored for 24 hours at room temperature (23 ± 1°C), and then tested.

Testing of the samples, (for both control group and the test groups) was undertaken for the change in hardness.

Hardness of each sample was calculated by applying the International Rubber Hardness Durometer(IRHD) at 3 points on the surface of the sample (Figure 2). The mean was taken as the mean hardness of each sample and the change was calculated at each of the intervals as follows:

- Stage 1 - Immediately after curing. This time is used as 'the baseline time'.
- Stage 2 - 3 months from baseline.
- Stage 3 - 9 months from baseline.

STATISTICAL ANALYSIS

Values were shown as Median (Minimum-Maximum). Absolute comparison was done for baseline and 3-months values of hardness respectively. Relative comparison is done using relative percent change wherein relative percent change is calculated using the following formula:

$$\frac{100 \times [\text{Follow-up Hardness} - \text{Baseline Hardness}]}{[\text{Baseline Hardness}]}$$

Positive value of relative percent change indicated higher hardness at follow-up compared to the baseline hardness and vice-versa. P-values were obtained by using Mann-Whitney U test, a non-parametric test procedure to test the statistical significance of difference between two independent materials. P-value less than 0.05 were considered to be statistically significant. The entire statistical analysis was done using Statistical package for social sciences for MS Windows.

RESULTS

At Baseline, the Initial hardness of Material Z004 – 1: 1 platinum based system was greater than Material M 511 – 10: 1 platinum based system. While at 3 months interval, the change in hardness was more for M 511 as compared to Z004 (Figure 3). At 9 months interval from the baseline, the average change in hardness for material M 511 was lesser than Z004.

For material M511, the room temperature cured samples showed lesser change as compared to heat cured ones. While for material Z004, both room temperature and heat cured samples exhibited similar change in hardness. (Figure 4).

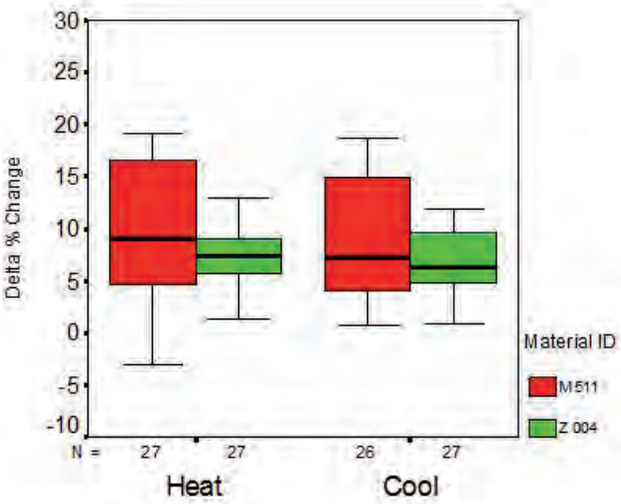

Figure 3. *Comparison of Two Materials for Change in Hardness at 3-Months (Box Plot) cured by two types of curing mechanisms.*

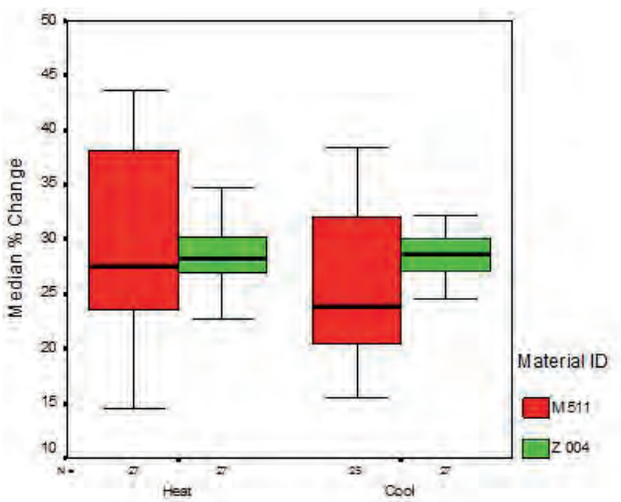

Figure 4. *Comparison of Two Materials for change in Hardness at 9-Months (Box Plot) cured by two types of curing mechanisms.*

DISCUSSION

Weathering of polymers leads to significant changes in their mechanical and physical properties. When a photo-oxidative degradation occurs the following steps might happen:

• *Initiation*: Formation of free radicals. The formation proceeds by a radical chain process initiated either by dissociation caused by the collision of a photon with sufficient energy with a polymer molecule, or as the result of some impurity present, for example trace metals from the polymerization catalyst

• *Propagation*: Reaction of free polymer radicals with oxygen, production of polymer oxy- and peroxy-radicals and secondary polymer radicals, resulting in chain scission.

• *Termination*: Reaction of different free radicals with each other resulting in further cross-linking.

The main structural modifications in irradiated polymers are changes in their molecular weight distribution – due to main chain scission, cross-linking and end linking – and the production of volatile degradation products. These phenomena tend to modify the material's physical properties[3]. The changes in physical properties affect the polymer structural network in different ways. The density of the structural network increases during cross-linking due to the formation of bonds between the existing monomers or between the chains [3]. Therefore, cross-linking leads to formation of harder materials. On the other hand, when chain scission is the dominant mechanism, the fracturing bonds within the main chain or between two different chains, incur a decrease in density of the structural network and the materials become softer [3]. In irradiated polymers both the above mechanisms take place; therefore it is critical to investigate which of them is dominant, in order to explain the structural analysis. The hardness of silicone elastomers is controlled by the surface characteristics of the polymer network and by the density of cross-links. Silicone elastomers undergo cross-linking once exposed to high-energy radiation, and the amount of cross-linking

is proportional to the radiation dose and duration[22]. Sebum fatty acids, perspiration tend to interact with silicone, breaking chain bonds and decomposing the elastomer by a phenomenon called as 'reversion' [20]. This degradation effect is accelerated with light radiation, leading to softer and weaker elastomer. Thus the actual performance of silicone elastomers under extraoral factors can be evaluated by exposure tests simulating conditions involving sterilization, hygienic maintenance procedures, biological skin fluid absorption, and outdoor exposure.

This study also evaluated the change in hardness when subjected to artificial ageing of two commercially available silicones elastomers cured using two different techniques. Control batch samples were stored in the dark to take into consideration the changes that may occur during the storage. The literature has reported data on silicone serviceability under storage in the dark, which have clinical relevance in both severity and duration for a maximum of 6 months of storage in the dark[23].

Weathering experiments in the present study lasted 9 months, to reduce the influence of seasonal weathering conditions. The city experiences seasonal variations in form of summer, rainy and winter seasons during a period of one year. The temperature of the city of Pune ranges between 12°C to 37°Cwith average rainfall recorded is 600 to 700 mm. Thus it is representative of Indian tropical environmental conditions. Hence it was selected as a location to study the effect of tropical climatic conditions on silicone samples when subjected to outdoor weathering.

The hardness of the maxillofacial material is a measure of its flexibility. The ideal hardness is similar to that of the missing facial tissue. Considering that facial features are composed of soft and hard texture, Lewis and Castleberry stated that 25–35 Shore-A indentation units are desirable[24].

The data obtained and evaluated in this study revealed interesting behaviour for the two silicone Elastomers, with appreciable clinical significance. When a comparison of method of curing was undertaken, for the room temperature cured silicone elastomers, the change in hardness for both materials was lesser as compared to the heat cured ones over the period of the study. The probable reason for more amount of change in hardness of the heat cured samples as compared to the cold cured ones may be that the initial polymerization is decreased and hence they undergo progressive polymerization/hardening with time. When a comparison of both materials is made, M511 (10: 1) initially showed greater increase in Hardness than the Z004 (1: 1). Overall, after 9 months, there was a progressive hardening of both materials, with Z004 (1: 1) hardening to a larger extent (though not statistically significant). Any difference could be attributed to its spatial distribution of catalyst radicals in the mix of both materials. The M511 (10:1) material would be having a more isolated pattern of catalyst distribution. Hence it would be assumed that it would show more complete initial polymerization by complete migration of catalyst during the overnight bench curing and thereby a reduced progressive polymerization /hardening. M511 (10: 1) showed lesser change in hardness as compared to Z004 (1: 1) when cured using the room temperature curing. While for Z004 (1: 1) the amount of change in hardness was approximately similar when subjected to either of the curing techniques.

CONCLUSIONS

The following conclusions can be drawn from the study

Over the period of the evaluation of both the materials showed hardening the differences between them were not significant.

Room temperature vulcanization of the maxillofacial silicone elastomer may produced lesser progressive hardening of the elastomer as compared to the heat vulcanization technique. This difference however was not statistically significant.

When M511 (10: 1 elastomer) is utilized, room temperature curing is possibly the preferred method of curing.

MANUFACTURERS DETAILS

- M511 and Z004 (Principality Medical, Technovent, UK)
- Dry Earth Pigments (Cosmesil pigments, Technovent Ltd UK)
- Statistical package for social sciences (SPSS Inc. Chicago, version 11.5) for MS Windows.

ADDRESS FOR CORRESPONDENCE

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