

The interpretation of thermal characteristics of pigmented silicone maxillofacial prosthetic material after artificial aging in different conditions

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Abstract: In recent decades several maxillofacial polymers are used in facial prosthesis. Silicones or polysiloxanes are popular material used for constructing maxillofacial prostheses. These materials represent unique polymeric materials that have a widespread application in health care. The longevity of maxillofacial prostheses is dependent on the prosthesis material and the patient's attitude toward the prosthesis. Pigmented color specimens of maxillofacial material were fabricated. They were divided into the following groups: Group (I): The specimens were aged only by exposure to accelerated artificial filtered xenon daylight UV-340 nm for 360 hours and subjected to DSC and TGA tests. Group (II and III): The specimens were aged in the simulated storage solutions (acidic, alkaline and sebum solution) and exposed to accelerated artificial filtered xenon daylight for 360 hours. Group II pigmented specimens were subjected to DSC test, while group III was subjected to TGA test. The results of DSC curve interpretation revealed that the glass transition (T_g) temperature between the groups were statistically significant ($F=88135.798$). TGA curve results revealed that aging of pigmented sample of cosmesil silicone maxillofacial material of group (I b) showed a % of weight loss more than pigmented sample of group (IIIb). We concluded from this study that Cosmesil M511 silicone used for maxillofacial prostheses showed a significant difference in the thermal behavior of pigmented samples aged by UV artificial day light and pigmented samples aged in simulated alkaline solution and UV daylight.

[Fahad H. Banasr. **The interpretation of thermal characteristics of pigmented silicone maxillofacial prosthetic material after artificial aging in different conditions.** *Life Sci J* 2015;12(5):79-84]. (ISSN:1097-8135). <http://www.lifesciencesite.com>. 9

Keywords: Silicones, Thermalanalysis, differential scanning calorimetry, glasstransition, Thermogravimetricanalysis, aging.

1. Introduction

Maxillofacial prostheses play a critical role in the rehabilitation of patients who have severe facial disfigurement (1).

Massive destruction of facial tissue frequently leaves large unsightly defects that cannot repaired by reconstructive surgical procedure and can be replaced by facial prostheses. In recent decades several maxillofacial polymers are used in facial prosthesis. The maxillofacial polymer should be nontoxic, non-allergenic, non-carcinogenic, cleansable, compatible with adhesives, resistant to outdoor weathering and body secretions (sebaceous, perspiration, nasal, and salivary) (2, 3).

Although polymeric materials are highly versatile, their performance is still far from ideal, since most of them have disadvantages such as low thermal stability and little resistance to solar radiation. The prostheses are colored with various pigment to provide a close match to the skin of a specific individual(4).

Silicones or polysiloxanes are popular material used for constructing maxillofacial prostheses. These materials represent unique polymeric materials that, have a widespread application in health care. Silicones

have many desirable properties including biocompatibility, low viscosity, easily cleansable, light weight, wide service temperature range and bi durability which can be expressed in terms of other material properties such as hydrophobicity (water-replant), low surface tension and chemical and thermal stability. The characteristics of a silicone rubber depend upon the type and amount of fillers - additives used and upon mixing, vulcanizing conditions and the glass transition temperature T_g . The value of the glass transition temperature T_g would be assumed to have fundamental importance of maxillofacial materials. These properties were the basis for silicone's initial use in the medical field (5-7).

The longevity of maxillofacial prostheses is dependent on the prosthesis material and the patient's attitude toward the prosthesis. Silicone based maxillofacial prostheses require replacement every 6 to 18 months, as they suffer deterioration in physical and mechanical properties and discoloration upon service (8, 9).

Facial prosthetics may absorb perspiration and sebum while resting on living human skin for extended periods. The absorption may cause changes in materials' structure, resulting in the deterioration of

prosthesis(10), also the increase in the temperature of the atmosphere will affect the maxillofacial prostheses that rest on the defect site and the adjacent tissues(11). Since this issue is really important for maxillofacial prosthesis so the purpose of this study was conducted to evaluate the influence of the environmental conditions on the thermal properties of pigmented maxillofacial silicone elastomer.

2. Material and Methods

A total eighty disc shaped specimens of pigmented maxillofacial silicone (cosmesil series maxillofacial rubber M511, Medical grade, Technovent, UK) with dimension (25mm in diameter and 3mm thickness (12) were fabricated, the materials were handled according to the manufacturer's instructions. To achieve maximum consistency, all the specimens were fabricated during one processing. A ratio of silicon elastomer 10gm of base was mixed with 1gm of catalyst to achieve 10:1. Colorant pigment (Colorants Intrinsic pigments-coloring agents) of 0.2% by weight was added and mixed until a homogenous mixture was obtained which close match to the skin of individual that found in clinical prostheses(13). Then the mixture was poured in dental stone mold and processed using dry heat oven for 1 hour at 100 °C. After polymerization, the specimens were carefully removed from the molds and flash was trimmed away with a sharp scalpel. All the specimens were left for 24 hours at room temperature after polymerization before grouping and testing.

The pigmented color specimens were divided into the following groups:

Group (1): Twenty specimens were aged only by exposure to accelerated artificial daylight for 360 hours. The aging machine used filtered xenon light of UV-340 nm, (Q Panel Lab, USA, Sun Xenon test chamber) for at least 1hr of day light for 360 hours.

Group (II and III) Sixty specimens were aged in the simulated storage solutions (acidic, alkaline and sebum solution) in the aging chamber of aging machine, and exposed to accelerated artificial filtered xenon light of UV-340 nm daylight for 360 hours. (patients wear their prosthesis 8-12 hrs during a day and expected to be exposed at least 1hr of day light. then 360 hrs exposure period could be equivalent to 3 years of clinical service). The different aging storage solutions included as follow; **Solution (a):** The pigmented specimens were stored in simulated acidic medium. The acidic perspiration was prepared by (PH 5.5) containing per liter of distilled water: 0.5g L-histidine monohydrochloride monohydrate, 5g sodium chloride, and 2.2g sodium dihydrogen orthophosphate dehydrate.

Solution (b): The pigmented specimens were stored in simulated alkaline medium.: Alkaline perspiration was

prepared (PH 8) containing the following per liter of distilled water: 0.5g L-histidine mono-hydrochloride monohydrate, 5g sodium chloride, and 5g disodium hydrogen orthophosphate dodecahydrate.

The solution (a and b) was prepared according to International Organization for Standardization (ISO) specification (10).

Solution (c): The pigmented specimens were stored in simulated sebum (skin secretions). Simulated sebum was prepared(14) using 10% palmitic acid and 2% tripalmitin dissolved in 88% linoleic acid (all wt %).

The pigmented specimen of the groups were subjected to the following tests:

Group (I): Twenty pigmented specimens were subdivided into two subgroup, each of ten specimens, which subjected to DSC and TGA test

Group (II): Thirty pigmented specimens were subdivided into three subgroup each of ten, which subjected to DSC test

Group (III): Thirty pigmented specimens were subdivided into three subgroup each of ten, which subjected to TGA test

Testing procedures:

Differential scanning calorimetry (DSC): DSC measurements were performed on 5-15-mg polymerized pigmented cosmesil M511 silicone samples with a Diamond DSC-60- instrument, (Shimadzu-60, Japan). The sample was placed in DSC aluminium pan and heated at a constant heating rate of 10°C/min and flowing nitrogen gas using liquid nitrogen to reach heating range from -140 °C-25⁰ C, DSC was calibrated with indium (m.p 156.6⁰C). In the DSC technique the thermal power is plotted as a function of temperature. The DSC thermograms exhibit the exothermic crystallizing peaks, the area under the peak represents the melting enthalpy, and a glass transition temperature T_g appears as a mid-point of inflection on the DSC curve during the heating run(15).

Thermogravimetric analysis (TGA):

TGA tests of polymerized pigmented cosmesil M511 silicone samples were performed using, thermogravimetric analyzer, (Shimadzu, TGA-50, Japan) The analysis was run with samples of 10 mg at a heating rate of 10 C²/min, from 25 to 300 C², under nitrogen flow. The flow rate of the carrier gas was fixed at 20 ml/ min (16).

Statistical analysis:

All statistical analysis were performed using Statistical Package for the Social Science software (SPSS, version 17, Chicago, IL, USA). Descriptive statistics as means and standard deviations were used.

Analysis of Variance (ANOVA) test of significance was performed for experimental data for comparison between the groups at 5 percent level.

3. Results

DSC of polymerized pigmentedcosmesil silicone maxillofacial specimens was measured in the temperature range between $-140^{\circ}\text{C} - 25^{\circ}\text{C}$. The DSC curve (Fig.1, group 1a) showed an exothermic crystallizing peak at about $-67.91^{\circ}\text{C} \pm 0.05$ with heat enthalpy $14.47 \pm 0.04 \text{ J/g}$. The glass transition (T_g) temperature is located at the point of inflection (mid-point) on the DSC curve at about $-111.51 \pm 0.05^{\circ}\text{C}$ (Table I).

The DSC curve of (Figs. 2, 3 and 4), groups (IIa, IIb and IIc) revealed an exothermic crystallizing peak at about $-70.47 \pm 0.04^{\circ}\text{C}$, $-71.93 \pm 0.03^{\circ}\text{C}$ and $-70.10 \pm 0.05^{\circ}\text{C}$ with heat enthalpy $12.54 \pm 0.03 \text{ J/g}$, $12.35 \pm 0.04 \text{ J/g}$ and $12.49 \pm 0.03 \text{ J/g}$ respectively. The glass transition (T_g) temperature of groups IIa, IIb and

IIc was $-119.37 \pm 0.03^{\circ}\text{C}$, $-107.84 \pm 0.04^{\circ}\text{C}$, $-106.92 \pm 0.04^{\circ}\text{C}$ respectively which was statistically significant at 5% level. ($F= 88135.798$) as shown in Table (I).

Fig.(5,1b) showed TGA curves of pigmented samples. It cleared that by increasing the temperature from ambient to 300°C , the sample lost 1.63% of the weight in the range of 184.84 to 299.78°C while for the samples of groups (III a and IIIc, figures 6,8) they showed no weight loss in the heating range. Group (IIIb, figure 7) showed a weight loss of 0.82% at temperature range of 140.22 - 172.69°C and by increasing the temperature from $172.69 - 299.43^{\circ}\text{C}$, the sample lost about 1.26% of the weight.

This loss refers to the decomposition of some component of the sample in this range of temperature.

Table (1) summarized the mean value of temperature, enthalpy and glass transition of the samples of each specimen group and the comparison of T_g between groups.

Glass transition (T_g) $^{\circ}\text{C}$	Enthalpy J/g	Peak temperature $^{\circ}\text{C}$	Parameter
Mean \pm SD			
-111.51 ± 0.05	14.47 ± 0.04	-67.91 ± 0.05	Group I,a
-119.37 ± 0.03	12.58 ± 0.03	-70.47 ± 0.04	Group II,a
-107.84 ± 0.04	12.35 ± 0.04	-71.93 ± 0.03	Group II,b
-106.92 ± 0.04	12.49 ± 0.03	-70.10 ± 0.05	Group II, C
F=88135.798			

F: (ANOVA) test of glass transition between groups

*: Statistically significant at $p \leq 0.05$

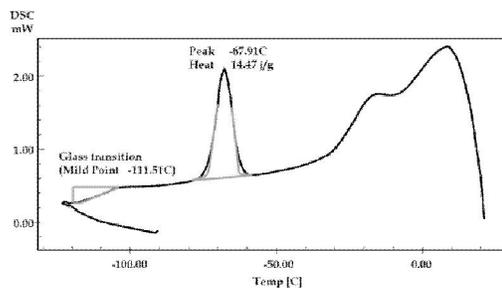


Fig. 1: Group (Ia)

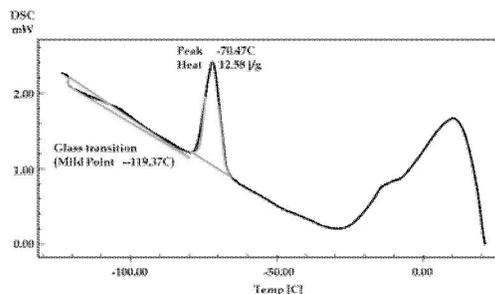


Fig. 2: Group (II a)

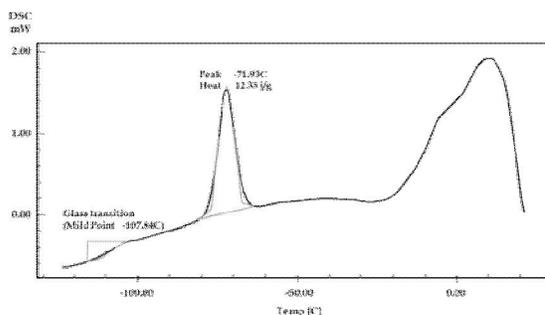
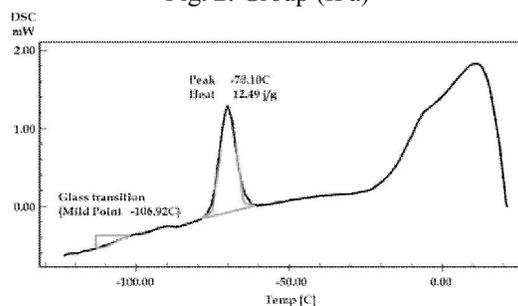


Fig.(3) group IIb



Fig(4) group IIc

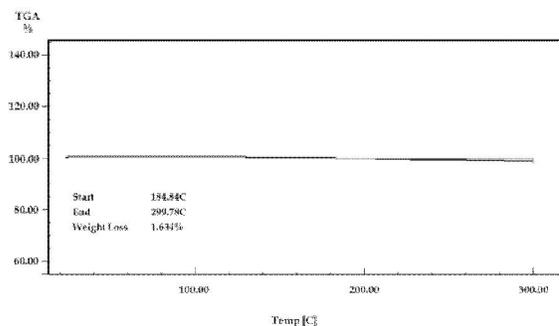


Fig. (5) group III b

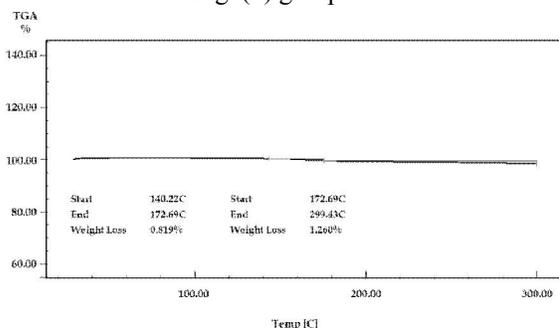


Fig.(7) group III b

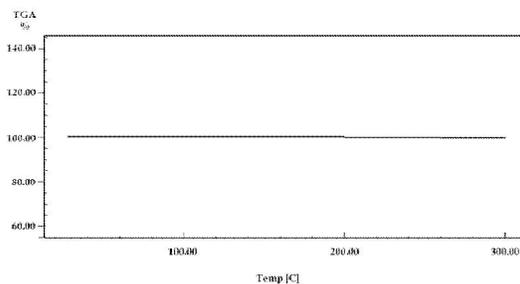


Fig.(6) group III a

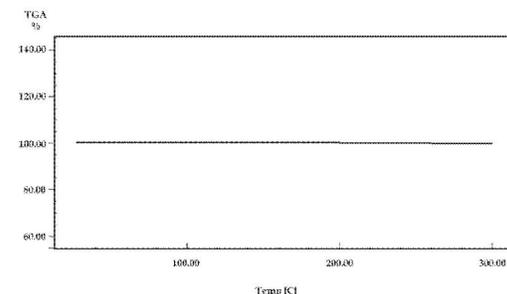


Fig.(8) group III c

4. Discussion

Static and dynamic mechanical properties of Silicone rubber depend on the glass transition temperature which is determined by both polymer composition and structure. The addition of clinical relevant pigments might affect the structural transformation process in silicone elastomer maxillofacial material(17).

Thermal analytical tests (DSC and TGA) was used in this study for the evaluation of pigmented specimens of cosmesil silicone M511 at the aging condition mode in simulated perspiration, sebum solution and artificial filtered xenon light. These tests were carried out because the facial prostheses are exposed to skin secretions (perspiration and sebum) and day light which may cause alteration in the functional properties of the materials, resulting in the deterioration of prosthesis(18). Xenon light was selected during aging because it have a light monitoring system produces a spectral distribution very similar to natural sunlight and can predict the lifetime of polymer under service(19).

Differential scanning calorimetry (DSC) used in this study, is reliable, sensitive technique for measuring the energy that provide the variation of enthalpy in the exothermic polymerization reaction. DSC can provide data with sharp peaks, low drift from baseline and a linear association between the area under the peak and the mass of the specimen. (DSC) curve also was used to locate the glass transition temperature (T_g), in elastomeric silicone. T_g

occurs when hard, rigid and glassy amorphous solid becomes a soft, flexible flowable, rubbery materials as the temperature increased during heating. The glass transition (T_g) value gives information about the viscoelastic properties of elastomer silicone (15, 17). DSC results revealed the T_g of group Ia, and group IIa, II band II c pigmented samples was below -120°C and heat enthalpy (67-71 j/g) which was in agreement with the reported glass transition temperature of polydimethylsiloxane maxillofacial prosthetic material (20). These results might be attributed to unique backbone polymeric organic and inorganic materials. Silicone is composed of chain of -Si-O- and two symmetric methyl group in the side chain of Si atom, allow a good solid stereo regularity of the chain and the crystallization to occur at low temperature (21). The low glass transition temperature rendering the silicone liquid at room temperature with high degree of flexibility. Cosmesil silicone also contain crystalline fumed silica filler and platinum catalyst which acts a material extender to reinforce, initiates the cross linked matrix, decreasing sticking and increasing hardness(22, 23).

TGA is a thermal technique used to determine changes in weight of a sample in relation to changes in temperature and to characterize the decomposition or thermal stability of materials under a variety of conditions. In this technique, the material upon heating its weight increases or decreased and the sample will released volatile material or generate combustion as it burns (24). In TGA the sample (mg size) is brought

up quickly to the desired temperature and the weight is monitored during thermal decomposition. TGA results revealed that aging of pigmented sample of cosmesil silicone maxillofacial material of group I b showed a % of weight loss more than pigmented sample of group IIIb which could be attributed to the artificial light which decrease the molecular weight of the aged samples due to formed chain scission. However the group IIIb aged in alkaline solution and artificial light showed a % weight loss less than group Ib might be due to decomposition of alkaline traces absorbed on the surface of the material. The TGA results of pigmented samples of group IIIa and group IIIc showed no weight loss % as the aging of these pigmented samples (similar to normal natural skin) did not affect the internal structure of silicone cosmesil maxillofacial material. Acid and sebum solution might be block daylight radiation and preventing it from acting within the entire elastomer mass(11). The catalytic effect of acidic solution assumed to propagate the cross linking reaction(10).

Conclusion

Thermal properties labs test help client to determine the material's suitability for specific intended usage. Cosmesila M511 silicone used for maxillofacial prostheses showed a significant difference in the thermal behavior of pigmented samples aged by UV artificial day light and pigmented samples aged in simulated alkaline solution and UV day light. The TGA curve interpretation showed a % of weight loss caused due to UV day light. The interpretation of DSC curve showed the T_g temperature of Cosmesila M511 silicone maxillofacial material was similar to the reported T_g temperature of fundamental polymer science principles of polysiloxanes.

Clinical Implication

The obvious effect of alkaline solution on this material necessitate that patients wearing maxillofacial prosthesis of Cosmesil silicone should use neutral cleansing agent. The decomposition of the material has not any prominent relationship with the service of years but it corresponds to the particular environments. To achieve good performance for the maxillofacial silicone prosthesis, it should be exposed intermittently to solar radiation

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4/26/2015