Impact of a mixture of nanofiller and intrinsic pigment on tear strength and hardness of two types of maxillofacial silicone elastomers

Faiza M. Abdul-Ameer

Department of Prosthodontics, College of Dentistry, University of Baghdad, Bab-ALmoadham, Baghdad, Iraq

ABSTRACT

Background: The ideal maxillofacial prosthesis should have fine and thin boundaries that bind with the surrounding facial structures and possess high tear strength. This study aims to determine the best percentages of nanofiller (TiO$_2$) and intrinsic pigment (silicone functional intrinsic) that could be mixed in as additives to improve the tear strength of Cosmesil M511 and VST50F silicone elastomers with the least effect on their hardness.

Materials and Methods: In this in vitro experimental study, a total of 80 samples, 40 for each elastomer, were fabricated. Each elastomer sample was split into two equal groups to test for tear strength and Shore A hardness. Each group consisted of 20 samples, including 10 control samples without additives and 10 experimental samples with additives (mixtures of 0.2 wt% nano-TiO$_2$ + 0.25 wt% intrinsic pigment and 0.25 wt% nano-TiO$_2$ + 0.25 wt% intrinsic pigment for the Cosmesil M511 and VST50F silicone elastomers, respectively). Two-way ANOVA and Tukey test were used for comparison; $P < 0.05$ was considered statistically significant.

Results: Significant differences in tear strength were found among all tested groups ($P < 0.05$). The tear strength of the experimental subgroups significantly increased compared with the control subgroups ($P < 0.05$). Significant differences in Shore A hardness were also observed among all tested groups ($P < 0.05$) except between the experimental subgroups of both materials, where a nonsignificant difference was obtained ($P > 0.05$).

Conclusion: Incorporation of select percentages of TiO$_2$ nanofiller and intrinsic pigment into Cosmesil M511 and VST50F silicone elastomers yields improvements in tear strength with a slight increase in hardness.

Key Words: Pigmentation, silicone elastomer, titanium dioxide

INTRODUCTION

Many patients are subjected to facial trauma or develop tumors that require surgical removal of an affected area. Other patients are born with congenital defects. These cases consistently result in facial defects requiring artificial maxillofacial prostheses, which are mostly made from silicone rubber. The average lifetime of such prostheses is 1.5–2 years.$^{[1]}$

Many studies deal with maxillofacial materials and attempt to improve the properties of these materials to promote their biocompatibility, employment, durability, and esthetics. Among the many different...
materials used to create maxillofacial prostheses, silicone is considered the most effective and widely used. Research to address the deficient strength of silicone has been conducted with the aim of obtaining an ideal maxillofacial prosthetic material.[2] Silicones are chemically known as polydimethylsiloxane (PDMS) and of two basic types depending on the vulcanizing process used: room-temperature-vulcanizing (RTV) silicone or heat-temperature-vulcanizing (HTV) silicone.[3]

The most clinically important property of silicone elastomer is its tear resistance, particularly at borders surrounding the maxillofacial prostheses that integrate the boundary of the prostheses with facial textures. A specific adhesive is used to paste the margins of prostheses to surrounding tissues, and these margins are prone to rupture when the patient removes his/her facial prosthesis for cleaning or at night.[4] The flexibility of the silicone elastomer used for maxillofacial prostheses is determined by its hardness, and using materials with a softness similar to that of the facial tissues surrounding the affected areas is preferred.[5]

Maxillofacial silicone elastomers are degraded when the facial prosthesis is removed, during pasting to the facial tissue, and upon exposure to ultraviolet rays.[6,7] Pigmentation is paramount in the successful and effective manufacture of maxillofacial prostheses. Extrinsic and intrinsic pigmentation are predominately utilized to obtain a natural maxillofacial prosthesis resembling human tissue. The environmental conditions and handling of prostheses exert some effects on intrinsic pigmentation, but the structure of the silicone mixture and its properties are more potentially affected by this type of pigmentation.[8,9]

A previous study was conducted to evaluate the effect of intrinsic pigmentation on two types of commercially available silicone elastomers, namely Cosmesil M511 silicone and Biomed silicone; this study proved that incorporation of intrinsic pigment results in improved tear strength in both types of silicone.[10]

Addition of dry opacifiers, such as CeO₂, TiO₂, and ZnO (nano-oxides), to silicone elastomers, improves most of their mechanical properties, leading to durable maxillofacial prostheses.[9,11] Incorporation of surface-treated (SiO₂) nanoparticles to A-2186 silicone elastomer at a concentration of 3% improved its mechanical properties.[12] Other authors also report that incorporation of nano-TiO₂ into Cosmesil M511 and VST50F silicone elastomers at concentrations of 0.2 wt% and 0.25 wt%, respectively, improved the properties of both materials.[13]

The present study evaluates the impact of addition of a nanofiller (TiO₂) and intrinsic pigment on the tear strength and Shore A hardness of Cosmesil M511, an HTV silicone elastomer, and VST50F, an RTV silicone elastomer. The null hypothesis is that incorporation of these additives would improve the tear strength of both elastomers without affecting their hardness.

MATERIALS AND METHODS

In this in vitro experimental study, a nano-TiO₂ powder (SkySpring Nanomaterials, Inc., Houston, TX, USA) and a silicone functional intrinsic pigment cream color (FI-SK07, Factor II Inc., Lakeside, USA) were added to Cosmesil M511 and VST50F, which were selected from Factor II, Inc., Lakeside, AZ, USA.

It was reported that incorporation of nano-TiO₂ into Cosmesil M511 and VST50F silicone elastomers at concentrations of 0.2 wt% and 0.25 wt%, respectively, improved the properties of both materials.[13] The improvement gated when this addition incorporated alone without any other important addition that always added to maxillofacial silicone to achieve the final appearance of a lifelike prosthesis through using silicone intrinsic pigments. Hence, this study conducted to determine the best percentage of intrinsic pigment that could be added as a mixture with nano-TiO₂ to maintain the improvement of the tear strength with minimal effect on the hardness for both materials. Mixtures of 0.2 wt% nano-TiO₂ + 0.25 wt% intrinsic pigment and 0.25 wt% nano-TiO₂ + 0.25 wt% intrinsic pigment revealed the best effects on the HTV and RTV silicone elastomers, respectively.

Eighty samples were fabricated for the main study: 40 samples for Cosmesil M511 and 40 samples for VST50F. Each elastomer sample was divided into two equal groups to test tear strength and Shore A hardness. Each group consisted of 20 samples, including 10 control samples without additives (coding: C HTV for the HTV elastomer and C RTV for the RTV silicone elastomer) and 10 experimental samples with nano-TiO₂ and intrinsic pigment addition (coding: E HTV for the HTV silicone elastomer and E RTV for the RTV silicone elastomer).
Mold creation for sample fabrication
A metal mold (Cast iron sheets, Iraq) for the HTV elastomer and an acrylic mold (Acrylic-Glass-Look, France) for the RTV elastomer were produced. AutoCAD 2013 (San Rafael, Autodesk Inc., CA, USA) was utilized to design the dimensions of the samples. Processing was performed on a computer numerical control machine to produce the parts of the matrix (mold) that were used for pouring of the silicone elastomeric material.[14]

Sample fabrication and conditioning
Samples were fabricated for each silicone elastomer and split into two subgroups, namely the control subgroup and the experimental subgroup. Samples in the control subgroup were mixed at a base: cross-linker ratio of 10:1 (w/w) following the manufacturer’s instructions. A vacuum mixer (Multivac 3, Degussa, Germany) was used for 5 min of mixing at a speed of 360 rpm and 10 bar.[15,16] Samples in the experimental subgroup were mixed in the same manner as the control samples using the same mixing ratio but with incorporation of a mixture of nano-TiO$_2$ and intrinsic cream color pigment. Mixing was performed by weighing 0.2 wt% nano-TiO$_2$ filler + 0.25 wt% intrinsic pigment and 0.25 wt% nano-TiO$_2$ filler + 0.25 wt% intrinsic pigment for the HTV and RTV elastomers, respectively. The base of the silicone elastomer was then added and mixed without vacuum for 2 min using the vacuum mixer (Multivae 3). The catalyst of the silicone elastomer was dispersed in several areas, and the mixture was completely mixed under vacuum for 5 min.[13,16]

Mixing and pouring were performed at 23°C ± 2°C (controlled temperature) with a relative humidity (RH) of approximately 50% ± 10% following the manufacturer’s instructions.[17] The Cosmesil M511 elastomer was placed in a dry and hot oven for approximately 1 h, whereas the VST50F elastomer was set for approximately 2–4 h. To avoid straining, the samples were carefully removed from their molds and stored in a lightproof box (custom-made) in an air-conditioned room. The temperature was maintained in the range of 10°C–30°C during storage, and the RH was approximately 80%.[18] Before testing, the samples were conditioned for 24 h at 23°C ± 1°C and 50% ± 10% RH.[19] Then, the samples were conditioned at 23°C ± 2°C (standard laboratory temperature) for 3 h after removal of flash from the samples[20] using a sharp surgical blade (#10) or scalpel.[12]

Procedures for the mechanical tests

Test for tear strength
The samples were tested according to ASTM D624.[17] A Type C sample was utilized to measure tear strength, and a computer-controlled universal testing machine (WDW-20, Laryee Technology Co., Ltd., Beijing, China) was used to test the samples.[17]
To estimate tear strength, the following equation was applied:

\[
\text{Tear strength} = \frac{F}{D}
\]

Where $F$ is the ultimate force required to break the sample measured in kilonewtons and $D$ is the average thickness for each sample measured in meters.[17]

Test for Shore A hardness
The Shore A hardness test was performed according to ASTM D2240 on square samples measuring 25 mm × 25 mm × 6 mm using a portable digital durometer (HT6510 Shore A) with an indenter (blunt and 1.25 mm in diameter).[20]

Five readings from five areas were obtained. The test areas were 6 mm away from each other and 6 mm from the edge of the sample. The average value is reported as the sample hardness.[21]

Statistical analysis
The data were evaluated using the R package “Shiny,”[22] and descriptive statistics were presented as bar charts and interaction plots. Two-way ANOVA and Tukey test were used to compare between groups and subgroups at $P < 0.05$ significance.

RESULTS

Subgroups C HTV and E HTV showed lower mean tear strengths (C HTV: 11.7412 kN/m; E HTV: 13.6804 kN/m) than subgroups C RTV and E RTV (C RTV: 24.6196 kN/m; E RTV: 27.2592 kN/m). For each elastomer, the experimental samples revealed greater tear strengths than the control samples [Figure 1].

In terms of hardness, C HTV revealed lower mean values than E HTV, C RTV, and E RTV, as shown in Figure 2. After addition of TiO$_2$ nanofiller and intrinsic pigment, an increase in hardness in both elastomers was observed with slight differences between E HTV and E RTV (28.5500 and 28.3000, respectively).

For tear strength test, two-way ANOVA and the Tukey test showed significant differences regarding the
comparison between materials groups and subgroups ($P < 0.05$) [Table 1]. The interaction between groups and subgroups for both materials regarding the effect of additives on tear strength shown in Figure 3.

In terms of hardness, two-way ANOVA and the Tukey test showed significant differences regarding comparisons between material groups and subgroups ($P < 0.05$) with exception between E HTV and E RTV, which showed nonsignificant differences ($P > 0.05$) [Table 1] and the interaction between groups and subgroups for both materials regarding the effect of additives on Shore A hardness shown in Figure 3.

**DISCUSSION**

The null hypothesis appears to be partially admissible, as the tear strength of the samples increased remarkably after addition of nanofiller + intrinsic pigment mixture; however, hardness also increased considerably.

The ideal prosthesis should feature fine and thin boundaries that bind with the surrounding facial structures and a high tear strength. The results of the current study show that subgroups E HTV and E RTV have higher tear strengths than subgroups C HTV and C RTV [Figure 1]; thus, incorporation of nanofiller and intrinsic pigments into the matrix of silicon improves the tear strength of the resulting materials.\[11,13,15,23\]

The highly significant improvement in tear strength of both elastomers ($P < 0.5$) may be due to the dispersion of strain energy adjacent to the ends of rising cracks through polymer ability. Nanofillers within the polymer matrix dissipate energy when tearing is propagated, thereby resulting in a greater tear resistance that requires more force for completely smashing of a polymer matrix.\[24\] The improvement in tear strength could also be due to the action of the liquid colorant, which acts as a plasticizer,\[16,25,26\] as well as may be due to contaminated the catalyst through the incorporation of intrinsic pigments that taken action as impurities and so lowering the degree of cure.\[27\] Thus, when the polymer matrix was slightly under cured, the tear resistance of silicone elastomer has improved since a reduction in curing time increases tear strength.\[28\]

Cosmesil M511 silicone elastomer has a lower tear strength (control and experimental samples) than VST50F silicone elastomer [Figure 1]. The
difference in tear strength between the two materials may be attributed to variations in their curing time and procedure. Cosmesil M511 was set in a hot and dry oven for 1 h, whereas VST50F was set at room temperature for about 2–4 h. Differences in curing procedure may result in dissimilar degrees of polymerization and cross-linking.

In the hardness test, subgroup C HTV showed significantly lower hardness than subgroup C RTV ($P < 0.5$) probably because of the low degree of polymerization and cross-linking of Cosmesil M511 compared with that of VST50F, which could decrease the density of the polymer and reduce its hardness. Both experimental subgroups (E HTV and E RTV) displayed highly significant increases in mean hardness after reinforcement with nanofiller and intrinsic pigment ($P < 0.5$) compared with the control samples, and a nonsignificant difference between experimental subgroups was found ($P > 0.5$). The hardness of maxillofacial silicone elastomer must be maintained at a suitable range (approximately 10–45). Shore A hardness relies on the region of facial tissue required to be replaced as the facial areas different in stiffness and hardness.\(^\text{[5,29]}\) Therefore, changes in the mean Shore A hardness in the experimental subgroups could be considered clinically favorable.

The difference in hardness between the two elastomers due to the amount of crosslinking depends on the percentages and type of thermal initiator, the additives, the fillers, the temperature required for curing, and the time required for polymerization.\(^\text{[30,31]}\)

The mechanism of reinforcement of the nanofiller can be explained by the nanoparticles working as multifunctional cross-links that form powerful bonds (hydrogen bonds) between a chain of PDMS and surface hydroxyl groups, resulting in an increase in polymer density and producing a stronger and stiffer material.\(^\text{[32]}\) The observed increase in hardness may also be due to the incorporation of more nanofillers, increases in the adsorption of polymer chains to the nanofiller surface, and increases in intermolecular forces, all of which cause the polymer to achieve a high modulus of elasticity, rigidity, and resistance to penetration.\(^\text{[33]}\)

Addition of intrinsic silicone liquid suspension pigment may also contribute to the increase in tear strength and hardness of the elastomers because the pigments may fully interfere with the matrix of the silicone elastomer.\(^\text{[10]}\)

Figure 3 interaction plots display the main effects of adding the nanofiller (TiO$_2$) and intrinsic pigment on the tear strength and hardness of RTV and HTV silicone materials. The observed steepest slope of the line graph indicates the effective interaction between groups and subgroups. Regarding the tear strength, interaction plots show fewer interaction effects as the plotting lines for RTV silicone materials. The observed steepest slope of the line graph indicates the effective interaction between groups and subgroups. This may be explaining by that profile plots thought of as two-dimensional projections may be three-dimensional response surface and part of the surface is hidden from view.\(^\text{[34]}\) In addition, the observed slope of the line graph in this interaction plots shows that the additive is slightly more effective on the tear strength for the E RTV subgroup than the other subgroup. It is observed that there is greater interaction between groups and subgroups for both materials as the plotting lines for hardness show that nonparallel line reveals a highly significant effect of additive on the material hardness and the effect more obvious on E HTV subgroup.

**CONCLUSION**

Incorporating mixtures of 0.2 wt% nano-TiO$_2$ + 0.25 wt% intrinsic pigment and 0.25 wt% nano-TiO$_2$ + 0.25 wt% intrinsic pigment into HTV and RTV silicone elastomers, respectively, improved the tear strength of both materials and slightly increased their hardness; these results are clinically favorable. Furthermore, the incorporation of nanofiller (TiO2) and intrinsic pigment displays significant interactive effects on the tear strength and the hardness of both materials.

---

**Table 1: Statistical analysis for the effects of additives on tear strength (kN/m) and hardness (Shore A unit) for both types of material groups and subgroups**

| Variable       | HTV C | HTV E | RTV C | RTV E | Groups | Subgroups | G × S |
|----------------|-------|-------|-------|-------|--------|-----------|-------|
| Tear strength  | 11.7±0.109$^a$ | 13.7±0.181$^a$ | 24.6±0.124$^b$ | 27.3±0.158$^b$ | <0.001 | <0.001 | 0.022 |
| Hardness       | 25±0.147$^a$ | 28.6±0.186$^a$ | 27±0.0687$^b$ | 28.3±0.134$^b$ | <0.001 | <0.001 | <0.001 |

Values are means±SEM, $n$=10 per treatment group. $^a$ Means in a row without a common superscript letter differ ($P<0.05$) as analyzed by two-way ANOVA and the Tukey test. $G × S$: Group × subgroup interaction effect; SEM: Standard error of mean; HTV: Heat temperature vulcanizing; RTV: Room temperature vulcanizing.
Abdul-Ameer: Impact of nano-TiO$_2$ and intrinsic pigment on maxillofacial silicone

Acknowledgment

The author wishes to thank the dean as well as the assistant dean for Scientific Affairs of the College of Dentistry, University of Baghdad, for their kind support in facilitating using the available resources and materials to accomplish this work.

Financial support and sponsorship

Nil.

Conflicts of interest

The authors of this manuscript declare that they have no conflicts of interest, real or perceived, financial or non-financial in this article.

REFERENCES

1. Visser A, Raghoebar GM, van Oort RP, Vissink A. Fate of implant-retained craniofacial prostheses: Life span and aftercare. Int J Oral Maxillofac Implants 2008;23:89-98.
2. Fatihallah AA, Alsamaray ME. Effect of polyamide (Nylon 6) micro-particles incorporation into RTV maxillofacial silicone elastomer on tear and tensile strength. J Bagh Coll Dent 2017;29:7-12.
3. Mitra A, Choudhary S, Garg H, H G J. Maxillofacial prosthetic materials – An inclination towards silicones. J Clin Diagn Res 2014;8:ZE08-13.
4. Aziz T, Waters M, Jagger R. Analysis of the properties of silicone rubber maxillofacial prosthetic materials. J Dent 2003;31:67-74.
5. Lewis DH, Castleberry DJ. An assessment of recent advances in external maxillofacial materials. J Prosthet Dent 1980;43:426-32.
6. Mohite UH, Sandrik JL, Land MF, Byrne G. Environmental factors affecting mechanical properties of facial prosthetic elastomers. Int J Prosthodont 1994;7:479-86.
7. Fouad M, Moudhaffer M. Effect of disinfection on some properties of heat-vulcanized maxillofacial silicone elastomer reinforced by nano silicon dioxide. J Bagh Coll Dent 2016;28:16-21.
8. Han Y, Kiat-amnuay S, Powers JM, Zhao Y. Effect of nano-oxide concentration on the mechanical properties of a maxillofacial silicone elastomer. J Prosthodont 2008;100:465-73.
9. Hu X, Pan X, Johnston WM. Effects of pigments on dynamic mechanical properties of a maxillofacial prosthetic elastomer. J Prostheth Dent 2014;112:1298-303.
10. Rai SY, Guttal SS. Effect of intrinsic pigmentation on the tear strength and water sorption of two commercially available silicone elastomers. J Indian Prosthodont Soc 2013;13:30-5.
11. dos Santos DM, Goiato MC, Moreno A, Pesqueira AA, Haddad MF. Influence of pigments and opacifiers on color stability of an artificially aged facial silicone. J Prosthodont 2011;20:205-8.
12. Zayed SM, Alshimy AM, Fahmy AE. Effect of surface treated silicon dioxide nanoparticles on some mechanical properties of maxillofacial silicone elastomer. Int J Biomater 2014;2014:1-7.
13. Shakir DA, Abdul-Ameer FM. Effect of nano-titanium oxide addition on some mechanical properties of silicone elastomers for maxillofacial prostheses. J Taibah Univ Med Sci 2018;13:281-90.
14. Chi YH. Effect of Silica Filler on the Mechanical Properties of Silicone Maxillofacial Prosthesis. MSc Thesis, Indiana University School of Dentistry, Indianapolis (MI); 2014.
15. Abdullah HA, Abdul-Ameer FM. Evaluation of some mechanical properties of a new silicone material for maxillofacial prostheses after addition of intrinsic pigments. Saudi Dent J 2018;30:330-6.
16. Shihab NM, Abdul-Ameer FM. Studying some mechanical properties of maxillofacial silicone elastomer before and after incorporation of intrinsic pigments and artificial aging. F D J 2018;4:244-52.
17. ASTM D624-00. Standard Test Method for Tear Strength of Conventional Vulcanized Rubber and Thermoplastic Elastomers. West Conshohocken, PA, USA: ASTM International; 2013.
18. Brown R. Physical Testing of Rubber. 4th ed. Spring street, New York, USA: Springer Science & Business Media; 2006.
19. ASTM D1349. Standard Temperature for Testing. West Conshohocken, PA, USA: ASTM International; 2014.
20. ASTM D2240-05. Standard Test Method for Rubber Property - Durometer Hardness. West Conshohocken, PA, USA: ASTM International; 2010.
21. Hatamlleh MM, Watts DC. Mechanical properties and bonding of maxillofacial silicone elastomers. Dent Mater 2010;26:185-91.
22. Assaad HI, Hou Y, Zhou L, Carroll RJ, Wu G. Rapid publication-ready MS-word tables for two-way ANOVA. Springerplus 2015;4:33.
23. Pesqueira AA, Goiato MC, dos Santos DM, Haddad MF, Ribeiro Pdo P, Coelho Sinhoreti MA, et al. Effect of disinfection and accelerated aging on color stability of colorless and pigmented facial silicone. J Prosthodont 2011;20:305-9.
24. Sun L, Gibson R, Gordianinejad F, Suhr J. Energy absorption capability of nanocomposites: A review. Compos Sci Technol 2009;69:2392-409.
25. Guiotti AM, Goiato MC, Dos Santos DM, Vechiato-Filho AJ, Cunha BG, Paulini MB, et al. Comparison of conventional and plant-extract disinfectant solutions on the hardness and color stability of a maxillofacial elastomer after artificial aging. J Prostheth Dent 2016;115:501-8.
26. Wypych G. Plasticizers Use and Selection for Specific Polymers. Toronto, Canada: Chem Tec Publishing; 2004.
27. Hu X. Analyses of Effects of Pigments on Maxillofacial Prosthetic Material. PhD Thesis. The Ohio State University; 2010.
28. Sreeja T. Studies on Short Nylon Fiber-Reclaimed Rubber/Elastomer Composites. PhD Thesis, Cochin, Cochin University of Science and Technology; 2012.
29. Eleni PN, Perivoliotis D, Dragatogianiss DA, Krokida MK, Polyzois GL, Charitidis CA, et al. Tensile and microindentation properties of maxillofacial elastomers after different disinfecting procedures. J Mech Behav Biomed Mater 2013;28:147-55.
30. Griniari P, Polyzois G, Papadopoulos T. Color and structural changes of a maxillofacial elastomer: The effects of accelerated photoaging, disinfection and type of pigments. J Appl Biomater Funct Mater 2015;13:e87-91.
31. Gunay Y, Kurtoglu C, Atay A, Karayazgan B, Gurbuz CC. Effect of tulle on the mechanical properties of a maxillofacial silicone elastomer. Dent Mater J 2008;27:775-9.
32. Andreopoulos AG, Evangelatou M. Evaluation of various
reinforcements for maxillofacial silicone elastomers. J Biomater Appl 1994;8:344-60.
33. Hasse A, Wehmeier A, Luginsland HD. Crosslinking and reinforcement of silica/silane-filled rubber compounds. Rub World 2004;230:22.
34. Trumbo BE. Minitab Notes for STAT 6305 Department of Statistics - CSU East Bay, Hayward CA, 94542, Unit 7: Two-Factor ANOVA Model with Interaction Term; 2010.