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# Effects of Zirconium Silicate Nanofillers on Some Properties of Room-Vulcanized Maxillofacial Silicone Elastomers.

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**ABSTRACT**

Silicone elastomers, as a maxillofacial material, require many improvements to simulate the lost parts and tissues of maxillofacial areas. Incorporation of nanofillers is one of these improvements. Different concentrations (0%, 0.5%, 1%, and 1.5%) of zirconium silicate nanopowder were added to room-vulcanized maxillofacial silicone. The cross linker was mixed according to the manufacturer's instructions. One hundred and sixty samples were constructed and divided into five groups to measure Shore A hardness, tear strength, surface roughness, tensile strength, and elongation. The results were statistically analyzed using one-way ANOVA and the least significant difference test ($P < 0.05$). Addition of 0.5% silicate nanopowder resulted in non-significant increases in shore A hardness, roughness, and tear strength, as well as significant increases in tensile strength and elongation. Addition of 1% silicone nanocomposite yielded significant increases in surface hardness, surface roughness, tensile strength, and elongation, as well as a non-significant increase in tear strength. Finally, addition of 1.5% of the nanopowder resulted in highly significant increases in all mechanical properties tested. Scanning electron microscopy showed good dispersion and distribution of nanofillers within the silicone matrix. Energy-dispersive X-ray spectroscopy was used to evaluate the chemical composition of the silicone nanocomposite, and Fourier transform spectroscopy was conducted to evaluate the interaction of nano-$ZrSio_4$ within the silicone.

**Keywords:** maxillofacial, mechanical properties, nanocomposite, room vulcanized, $ZrSiO_4$ nanofiller

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## INTRODUCTION

The face is a way to make contact with others and commonly considered a physical landmark for personal identification (1). The aesthetic appearance, comfort, confidence, and quality of life of patients after trauma or tumor removal can be enhanced by maxillofacial prostheses (2). Silicone materials are considered the material of choice when constructing maxillofacial prostheses because of their high strength, easy manipulation, durability, and comfort (3) (4). However, this material also presents some clinical problems, such as degradation of its mechanical and physical properties over time(5). A large amount of research has been dedicated to enhance and develop silicone materials by incorporating nanoparticles into the silicone matrix to form a nanocomposite with improved properties (6). An important feature of nanocomposites is that their small size leads to great changes in interfacial areas and a substantial volume fraction when combined with other polymers, resulting in properties that differ from those of conventional composites (7). Nanoparticles bring about optimal changes in particle characteristics and the control of biological, mechanical, electrical, magnetic, and optical characteristics of some materials (8). Composites with a small amount of nanofillers can show considerable enhancements in mechanical, electrical, thermal, and optical properties without a substantial increase in density (9).

Maxillofacial silicone reinforced with nanoparticles can be combined with titanium dioxide and silanized silica to achieve appreciable increases in tensile strength, tear strength, hardness, and elongation (10). Addition of nano-silicone dioxide to heat-vulcanized maxillofacial silicone results in a highly significant increase in hardness, tear strength, tensile, strength, and elongation; however, a marked decrease in the translucency of the material has also been observed (11).

Zirconium silicate ($ZrSiO_4$) nanoparticles are insoluble in water and inherently hard (7.5 in the hardness scale) (12). It has many applications as a reinforcement material in dentistry. Dental composites reinforced with $ZrSiO_4$ nanofibers, for example, demonstrate great increases in flexural strength (13). Reinforcement of heat-cured acrylic with $ZrSiO_4$ nanofillers also yields increases in transverse strength, surface hardness, and impact strength; a non-significant increase in surface roughness; and significant decreases in water sorption and solubility (14).

The aim of this study is to evaluate the effects of addition of 0.5%, 1%, or 1.5% (w/w) $ZrSiO_4$ on the Shore A hardness, tear strength, surface roughness, tensile strength, and elongation of room-vulcanized maxillofacial silicone.

## MATERIALS AND METHODS

Nano-$ZrSiO_4$ was added to a silicone base at concentrations of 0%, 0.5%, 1%, or 1.5% by weight. Mixing of the cross linker and curing of the material were done according to the manufacturer's instructions. One hundred and sixty specimens were fabricated and divided into 4 groups to test for tear strength, Shore A hardness, surface roughness, tensile strength, and elongation; here, a total of 40 specimens were used for each test. Each group was then divided into four subgroups according to the weight percentage of the nanofiller (control, 0.5%, 1%, or 1.5%).

### Mold preparation

Three plastic molds, one for each test, were prepared by cutting a plastic plate into the desired shape and dimensions using a laser cutting machine according to the required test. Each mold contained 12 specimen holes that were cut into specific dimensions for each test. The plastic mold used for the tear and tensile tests was 2 mm-thick, and the sheet used for the hardness and roughness tests was 6 mm-thick. For each plastic mold, two glass slabs were cut with the same outer dimensions of the mold. The glass slabs were used to sandwich the molds and confine the silicone during injection into the molds. Four holes were drilled through the corners of the glass slabs and plastic molds to secure them with screws and nuts.

### Mixing procedure

The proportions and mixing procedures of the silicone and nanofillers are listed in Table 1. Mixing was done using a Multivac 3 vacuum mixer (Degussa, Germany). For the control group, the base and cross linker

were weighed using a digital electronic balance (China) and then mixed in a vacuum mixer for 5 min at 360 rpm and a vacuum pressure of -10 bar. For the experimental groups, the base, cross linker, and nanofiller were weighed in a mixing bowl using a digital balance and then mixed in the vacuum mixer for 10 min. The vacuum was switched off after the first 3 min to avoid suction of the nanofiller then switched on for the next 7 min of mixing (15).

**Table 1: Percentages and amount of silicone base cross linker and ZrSiO4 nano-filler composite materials**

| Percentage of nano-filler | Amount of ZrSiO4 | Amount of base | Amount of cross linker |
|---|---|---|---|
| 0% | 0 g | 60 g | 6 g |
| 0.5% | 0.3 g | 59.7 g | 6 g |
| 1% | 0.6 g | 59.4 g | 6 g |
| 1.5% | 0.9 g | 59.1 g | 6 g |

**Mechanical and physical tests**

**Tensile strength**

Tensile strength was tested using a universal testing machine (H10 KT/Tinius Olsen, USA) with a separation of 20 mm between them at a cross-head speed of 500 mm/min. Prior to testing, the thickness of each specimen was measured by a caliper at the center and each end of the sample. The median thickness was used to calculate the cross-sectional area. Tensile strength was calculated as:

$$Ts = Fb/Wt$$

where *Fb* is the force recorded at breaking (N), *W* is the width of the narrow portion of the specimen (in mm), and *t* is thickness of the test length (in mm).

**Elongation percentage**

Elongation was obtained from the universal testing machine while testing specimens for tensile strength. Percentage elongation was calculated as:

$$\text{Percentage Elongation} = [(Lb - Lo)/Lo] \times 100\%$$

where *Lo* is the initial test length (in mm) and *Lb* is the test length at breaking (in mm).

**Tear strength test**

A universal testing machine was used to perform the tear test with a constant rate of jaw separation in the range of 500 ± 50 mm/min until the specimen broke. In this work, tear strength is defined as the maximum force required to break a specimen divided by the original thickness of the specimen:

$$Ts = F/d$$

where *F* is the force (N) applied to the specimen and *d* is the thickness (in mm) of the test piece.

**Shore A hardness test**

A digital Shore A durometer (HT–6510A, China) was used to test the specimens. The device was held in the vertical position and the presser foot was applied parallel to the surface of the specimens. Readings were obtained 1 s after firm contact was achieved. For each specimen, five readings were obtained, and a 6 mm-distance was maintained between each test point and the edges of a test specimen. The mean of five readings was calculated.

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**Surface roughness test**

The surface roughness test was performed using a profilometer (Time 3200/TR 200 China). The mean of three measurements per sample was computed.

## RESULTS

**Fourier transforms infrared spectroscopy**

Samples of the ZrSiO4 nanofiller, silicone, and silicone/nanofiller composite were examined by Fourier transform infrared spectroscopy (SHIMADAZU, Japan). The FT-IR spectra of the ZrSiO4 nanopowder group, the silicone group, and the silicone/nanocomposite group are shown in Figs. 1, 2, and 3, respectively.

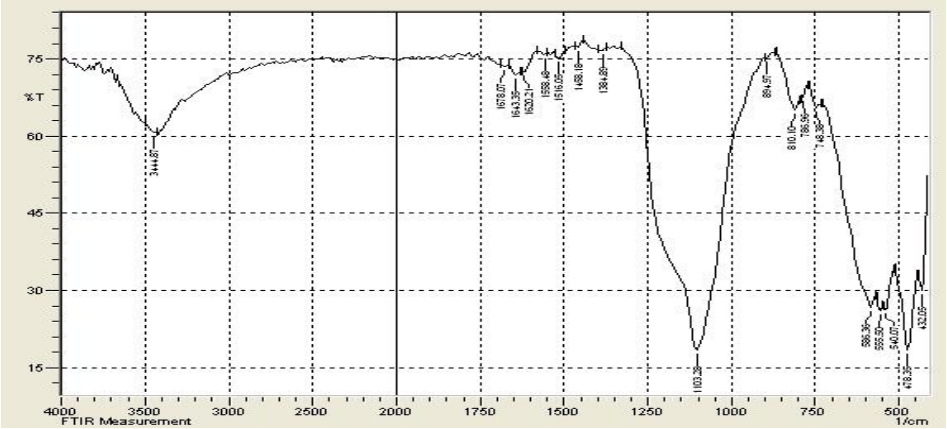


**Figure 1: FTIR for zirconium silicate nanofiller**

Comparing Figs. 2 and 3, minimal to no change in the peaks can be observed because of the small percentage of nanoparticles added to the composite material. These particles interact physically with the silicone matrix; no chemical reaction occurs between the nanoparticles and silicone (16).

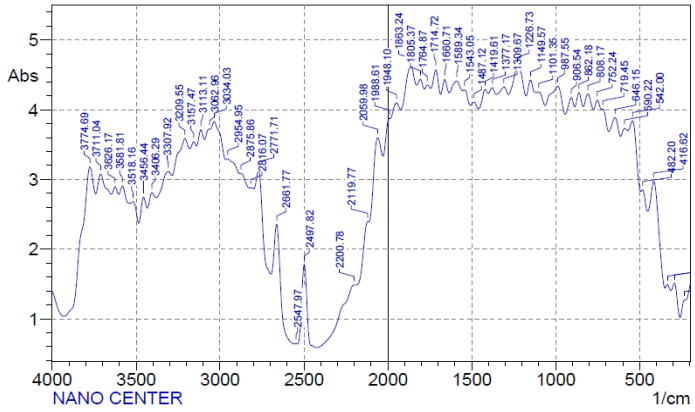


**Figure 2: FTIR for control sample of silicone.**

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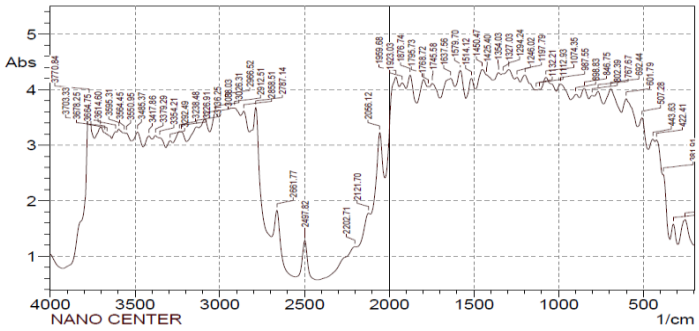


**Figure 3: FTIR of Silicone/nano-composite.**

**Scanning electron microscopy**

The dispersion and distribution of nanoparticles between the particles of the resin matrix of silicone was evaluated in a sample of the silicone nanocomposite using a scanning electron microscope (AIS2300 C USA). The test results showed that the nanoparticles were well dispersed in the matrix (Figs. 4 and 5).

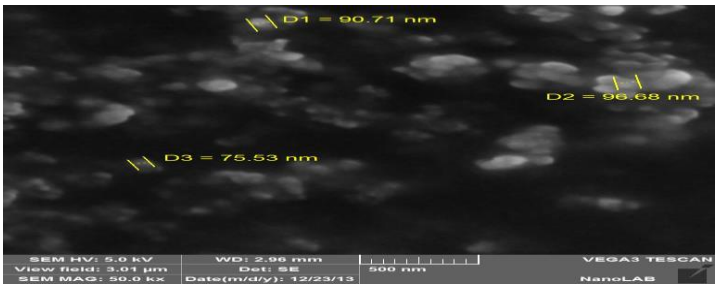


**Figure 4: Scanning electron microscope of zirconium silicate nano-powder.**

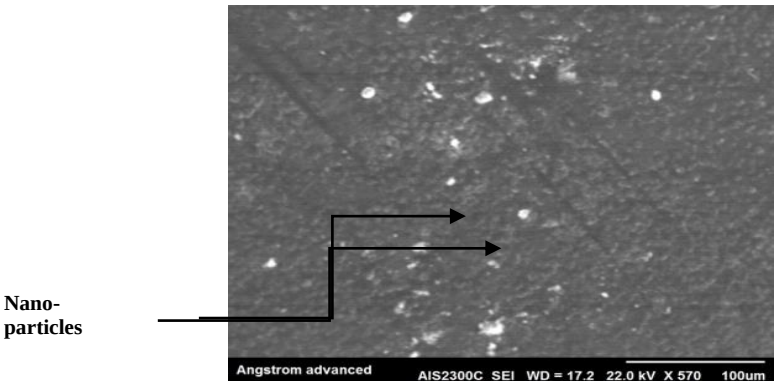


**Figure 5: Scanning electron microscope of silicone/nano-composite with 100um magnification showed dispersion of nanoparticles**

**Energy-dispersive X-ray spectroscopy:**

Chemical analysis of the samples was performed by energy dispersive X-ray spectroscopy. The results of this analysis depend on the interaction of x-ray excitation; each element has a unique atomic structure, allowing a unique set of peaks (17) (Figure 6).

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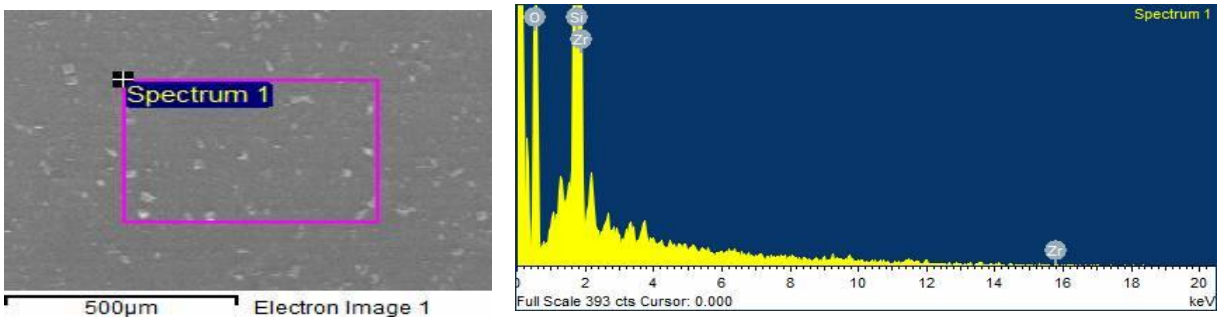


**Figure 6: Energy Dispersive Spectroscopy to sample of silicone/nanocomposite showing peaks of (O, Si, Zr) elements**

**Statistical analysis**

For descriptive statistical analysis, the results showed that the highest mean value found in 1.5% ZrSiO4 nano-filler by wt% addition to silicone material and the lowest one found in control group as shown in Table 2.

**Table 2 Descriptive data analysis of mechanical tests represented by mean, standard deviation, standard error, maximum and minimum**

| Test | percentage | N | mean | SD | SE | Max. | Min. |
|---|---|---|---|---|---|---|---|
| Shore A | 0% | 10 | 30.93 | 1.734 | 0.548 | 33.30 | 28.30 |
| | 0.5% | 10 | 31.25 | 1.712 | 0.541 | 33.60 | 28.40 |
| | 1% | 10 | 34.51 | 1.526 | 0.482 | 38.60 | 33.20 |
| | 1.5% | 10 | 34.86 | 1.317 | 0.416 | 37.00 | 33.20 |
| Tear strength | 0% | 10 | 20.75 | 0.978 | 0.309 | 22.00 | 19.50 |
| | 0.5% | 10 | 21.65 | 0.474 | 0.150 | 22.00 | 20.50 |
| | 1% | 10 | 21.66 | 2.995 | 0.947 | 24.30 | 14.64 |
| | 1.5% | 10 | 23.40 | 0.658 | 0.208 | 24.00 | 22.00 |
| Surface roughness | 0% | 10 | 0.309 | 0.063 | 0.019 | 0.380 | 0.237 |
| | 0.5% | 10 | 0.352 | 0.021 | 0.006 | 0.380 | 0.318 |
| | 1% | 10 | 0.449 | 0.045 | 0.014 | 0.515 | 0.402 |
| | 1.5% | 10 | 0.469 | 0.067 | 0.021 | 0.620 | 0.408 |
| Tensile strength | 0% | 10 | 3.887 | 0.109 | 0.034 | 4.00 | 3.75 |
| | 0.5% | 10 | 4.925 | 0.354 | 0.112 | 5.50 | 4.50 |
| | 1% | 10 | 4.937 | 0.497 | 0.157 | 6.13 | 4.52 |
| | 1.5% | 10 | 6.725 | 0.129 | 0.040 | 6.88 | 6.50 |
| Elongation percentage | 0% | 10 | 770.93 | 59.35 | 18.77 | 827.48 | 714.30 |
| | 0.5% | 10 | 994.74 | 84.02 | 26.57 | 1124.36 | 899.92 |
| | 1% | 10 | 1229.09 | 30.63 | 9.68 | 1278.00 | 1199.04 |
| | 1.5% | 10 | 1424.40 | 81.72 | 25.84 | 1544.00 | 1288.00 |

For inferential statistical analysis, the results show that comparing all groups by ANOVA table revealed a significance differences among them for all tests included in the study (Table 3).

**Table 3: One way ANOVA table for all tests included in the study**

| Mechanical test | F – test | P – value | Sig. |
|---|---|---|---|
| Shore A | 17.374 | 0.00 | S |
| Tear strength | 4.642 | 0.00 | S |
| Surface roughness | 21.334 | 0.00 | S |

| | | | |
|---|---|---|---|
| **Tensile strength** | **138.185** | **0.00** | **S** |
| **Elongation percentage** | **176.674** | **0.00** | **S** |

*Level of significance of P value < 0.05*

Further analysis was made among the groups within each test to show the significance level and better interpret the data as shown in table 4.

**Table 4: LSD test between groups**

| Mechanical test | Paired compare | P – value | Sig. |
|---|---|---|---|
| Shore A | Control - 0.5% | 0.66 | N.S. |
| | Control - 1% | 0.00 | S |
| | Control - 1.5% | 0.00 | S |
| | 0.5% -1% | 0.00 | S |
| | 0.5%-1.5% | 0.00 | S |
| | 1%-1.5% | 0.63 | N.S |
| Tear strength | Control -0.5% | 0.22 | N.S |
| | Control - 1% | 0.22 | N.S |
| | Control -1.5% | 0.00 | S |
| | 0.5% -1% | 0.99 | N.S |
| | 0.5%-1.5% | 0.02 | S |
| | 1% -1.5% | 0.02 | S |
| Surface roughness | Control - 0.5% | 0.08 | N.S |
| | Control - 1% | 0.00 | S |
| | Control - 1.5% | 0.00 | S |
| | 0.5% -1% | 0.00 | S |
| | 0.5%-1.5% | 0.00 | S |
| | 1% -1.5% | 0.39 | N.S |
| Tensile strength | Control-0.5% | 0.00 | S |
| | Control-1% | 0.00 | S |
| | Control-1.5% | 0.00 | S |
| | 0.5%-1% | 0.93 | N.S |
| | 0.5%-1.5% | 0.00 | S |
| | 1%-1.5% | 0.00 | S |
| Elongation percentage | Control-0.55 | 0.00 | S |
| | Control-1% | 0.00 | S |
| | Control-1.5% | 0.00 | S |
| | 0.5%-1% | 0.00 | S |
| | 0.5%-1.5% | 0.00 | S |
| | 1%-1.5% | 0.00 | S |

*Level of Significance P value < 0.05*

## DISCUSSION

Maxillofacial prostheses are subject to a variety of forces in every direction during muscle movement, including facial expression, chewing, speaking, and eye and nose movement. Therefore, prostheses must possess some degree of flexibility to withstand multiple tensile forces, prolong their life, and act as natural tissue without breakage (18, 19, 20). Good dispersion, distribution, and incorporation of nanofillers into a silicone matrix forms a three-dimensional network that allows energy dispersion of applied loads within the matrix and reduction of the mobility of nano-composite particles; thus, the resulting material is more resistant to tearing and features increased strength and elongation properties (21). When tearing is widespread, the energy of this action is dissipated by nanofillers, causing the silicone material to become more resistant to tearing and heavy loads (22). Increases in tear strength may be attributed to the small size of the nanoparticles, which enhances surface junctions between the nanofillers and silicone matrix and improves

mechanical properties (23). Dispersion of nanofillers in the resin matrix fills the spaces of the silicone matrix, increasing cross-sectional areas and forming a cross-linked nano-composite material with increased tensile strength (24). When silicone samples are subjected to a tensile force, the polymer chains slide over each other and over nanofillers, which present a large surface area per unit volume, causing increased contact between nanofillers and the resin matrix and reinforcement that prevents the breakage of silicone during stretching and elongation (25, 26).

The observed increase in surface roughness may be due to the presence of nanoparticles on the surface of the silicone specimens (27).

Substantial increases in surface hardness due to the dispersion of nanofillers within the silicone matrix lead to increased adsorption between nanofillers and polymer chains and increased intermolecular forces. These characteristics yield a more rigid mass of silicone, which features increased resistance to permanent deformation after penetration (28). ZrSiO4 has excellent hardness properties and a tetragonal structure, both of which make it a very durable material (29). Incorporation of this material into polymers results in increased hardness of the final nanocomposite (30).

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