Effect of addition ZrO$_2$-Al$_2$O$_3$ nanoparticles mixture on some properties and denture base adaptation of heat cured acrylic resin denture base material

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ABSTRACT

Background: The PMMA polymer denture base materials are low mechanical properties, adaptation of the denture base to underlying tissue is important for retention and stability of denture. The aim of the study was to evaluate the effect of mixture ZrO$_2$-Al$_2$O$_3$ nanoparticles on impact strength, transverse strength, hardness, roughness, denture base adaptation of heat cured acrylic resin denture base material.

Materials and methods: One hundred (100) specimens were prepared, the specimens were divided into five groups (20 specimens to each) according to the test type, each group was subdivided in to two subgroups (control and experimental) each subgroup consist of 10 specimens, the experimental group included mixture of 2% (ZrO$_2$- Al$_2$O$_3$ ratio 2:1) by weight. The impact strength was measured by Charpy's impact testing machine, the transverse strength was measured by Instron testing machine while the hardness was measured byshore D durometer and roughness was measured by Profilometer. Denture base adaptation was measured by digital microscope and evaluated by computerized tomography (CT).

Results: Highly significant increase of impact and transverse strength, non-significant increase of hardness, significant increase of roughness and reduction of denture base adaptation (measured at 3 point A, B and C) occurred in experimental group when compared to control group. CT evaluation, gap between the denture base and master cast (control and experimental groups) increased from the anterior to posterior side of palate and from the alveolar ridge to the mid palatal line.

Conclusion: The polymer nanocomposites had mechanical properties higher than neat PMMA at same time less denture base adaptation.

Keywords: Acrylic denture base, nano fillers, mechanical properties, denture base adaptation.

INTRODUCTION

Acrylic resin polymethyl methacrylate (PMMA) is the most extensively used material in fabrication of dentures. Although it is very popular, this material is still insufficient in fulfilling the ideal mechanical requirements of such appliances (1). Clinicians still encounter fracture of this material due to low resistance to impact, flexural, or fatigue stresses (2). In order to prevent fracture of the dentures, the thickness of acrylic resin in susceptible regions, such as the palatal midline, and the mandibular lingual and labial frenal attachments has been increased (3).

In addition, improvement on mechanical properties of denture base materials were tried to be achieved either by adding a polyfunctional cross-linking agent such as polyethylene glycol dimethacrylate (4) or by incorporating a rubber phase (5), metal oxides, metal wire (6,7), fiber (8). The reinforcement of polymers used in dentistry with metal-composite systems has been a prime interest. Addition of powdered Cu, Ag and Al into the PMMA resin and reported increased compressive strength but decreased tensile strength (9).

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Evaluation the changes in the mechanical properties of PMMA, polyethyl methacrylate (PEMA) and poly isobutyl methacrylate (PIMA) resin matrices by reinforcing with oxides of Al, Mg, Zr and pulverized E-glass particles (10). They suggested that 2% admixtures by volume in PMMA resin matrix resulted in better mechanical properties. Much attention has been directed toward the incorporation inorganic nanoparticles in to PMMA to improve its properties. The properties of polymer nanocomposites depend on the type of incorporating nanoparticles, their size and shape, as well as the concentration and interaction with the polymer matrix (11).

Nanoparticles were undergone surface treatment with silane coupling agent and embedded in to PMMA (12). Alumina nanoparticles were treated with trimethoxysilylpropylmethacrylate (TMSPM) to get PMMA/alumina Nano composite with improved properties over pure PMMA (13). Also, using modified ZrO$_2$ with trimethoxysilyl-propylmethacrylate to get PMMA/ ZrO$_2$ Nano composite to improve properties of PMMA (14). Furthermore, studying an experimental investigation of mixture HA/Al$_2$O$_3$ nanoparticles on mechanical properties of restoration materials (15). Also, evaluation of influence of mixture of ZrO$_2$-TiO$_2$ on mechanical and physical properties.
of heat-cured polymethyl methacrylate denture base resins \(^{(16)}\). Though the incorporation of fillers like rubber and fibers to heat-cured poly methyl methacrylate resin improves the impact strength and fatigue resistance, it may affect some of the properties of heat-cured poly methyl methacrylate resin such as fitness accuracy (denture adaptation), dimensional stability and the effect of water sorption \(^{(17)}\). Various investigators have compared the dimensional changes between different denture base materials \(^{(17,18)}\), palatal vault configurations \(^{(19)}\), methods of packing \(^{(18)}\), modes of polymerization \(^{(20)}\) and curing cycles \(^{(21)}\). This study was conducted to use inorganic mixture of ZrO\(_2\)-Al\(_2\)O\(_3\) Nano fillers that were added to heat cure PMMA and test the effect of this addition on the some mechanical properties and denture base adaptation of heat cured acrylic denture base material.

**MATERIALS AND METHODS**

Some of the materials used in this study are summarized in table (1).

<table>
<thead>
<tr>
<th>Material</th>
<th>ZrO(_2) nanofiller</th>
<th>Al(_2)O(_3) nanofiller</th>
<th>Trimethoxy silylpropyl methacrylate (TMSPM)</th>
<th>Heat-curing acrylic resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>HWNANO China</td>
<td>NS6130 01-123 Germany</td>
<td>2530-85-8 Germany</td>
<td>Vertex Netherlands</td>
</tr>
</tbody>
</table>

**Test specimens preparation**

Two different plastic patterns were constructed according to the required test. The pattern that was constructed for impact strength a bar shaped specimen (80mm X 10mm X 4mm) length, width, thickness respectively \(^{(22)}\). For transverse strength test: a bar shaped specimen was constructed (65mm X 10mm X 2.5mm) length, width, thickness respectively \(^{(23)}\) (Figure 1). Same specimen measurement was used to prepare hardness test and roughness test. For denture base adaptation test: prepare acrylic resin denture bases with their corresponding master casts by conventional denture flasking technique using a Biostar sheet as record base (2mm thickness) without teeth.

![Figure 1: Plastic patterns; A for transverse strength, B for impact strength](image)

**Surface modification of nanofillers (ZrO\(_2\), Al\(_2\)O\(_3\))**

The introduction of reactive groups to the fillers surface was achieved by reaction of 3-trimethoxy silylpropyl methacrylate (TMSPM) with zirconium oxide and aluminum oxide Nano fillersthrough salinization procedure \(^{(24)}\). For ZrO\(_2\), TMSPM was used in 5% wt. of nanofiller, toluene was used as a solvent to ZrO\(_2\) \(^{(12,14,24)}\), while Al\(_2\)O\(_3\), TMSPM was used in 75% wt. of Al\(_2\)O\(_3\), ethanol was used as a solvent to Al\(_2\)O\(_3\) \(^{(13)}\).

**Mould preparation**

**Addition of fillers**

This only for experimental group included mixture of 2% (ZrO\(_2\)-Al\(_2\)O\(_3\) ratio 2:1) by weight, electronic balance (Sartorius, Germany) with sensitivity of (0.0001g) was used to weigh then nanofillers powder weight in 2%wt. of the PMMA powder weight. The filler was added to the monomer of PMMA mixed by the probe sonifier apparatus (DANBURY, U.S.A.) for 3 minutes \(^{(15,14)}\) to disperse the nanoparticles in the monomer and reduce the possibility of particle aggregation.

**Mixing of the acrylic**

Acrylic material was mixed and manipulated according to manufacturer's instructions using a conventional water bath denture flasking technique for both groups (control and experimental). For experimental group the suspension of the monomer with nanofiller was immediately mixed with acrylic powder.

**Mechanical and denture base adaptation tests**

**1-Impact strength test.**

a- All the prepared specimens (20 specimens, 10 for each control and experimental groups) stored in distilled water inside incubator at 37°C for 48 hours before testing \(^{(22)}\).

b- Testing procedure: The impact strength test was carried out following the procedure recommended by the ISO 179 using impact testing device (Tmi, testing machine Inc. Amity Ville, New York, USA) \(^{(22)}\) (Figure 2). The specimen was supported horizontally at each end and strucked by free swinging pendulum of 2 Joules.
The scale readings give the impact energy in Joules. The charpy impact strength of un-notched specimen was calculated in Kilo-joules per square meter using the following formula:

\[
\text{Impact strength (kJ/m}^2) = \frac{E}{b} \times 10^3
\]

where E: The impact energy in Joules, b: Is the width of the specimens in millimeters, d: Is the depth of the specimens in millimeters.

2-Transverse strength test.
a. All the prepared specimens (20 specimens, 10 for each control and experimental groups) stored in distilled water inside incubator at 37°C for 48 hours before being tested (23).

b. Testing procedure: The test was performed using Instron universal testing machine (WDW-200 E, UK) (Figure 3), each specimen was positioned on the bending fixture which consist of two parallel supports (50 mm apart). The load was applied by a rod placed centrally between the supports with across head speed of 1mm/min applied making deflection until fracture occurs. The transverse strength was calculated using the following formula:

\[
\text{Transverse strength (N/mm}^2) = \frac{3PL}{2b^2}
\]

Where P: is the peak load, L: is the span length, b: is the sample width, d: is the sample thickness (25).

Figure 2: Impact strength testing device

Figure 3: Instron testing device

3- Measuring hardness property
a- All the prepared specimens (20 specimens, 10 for each control and experimental groups) stored in distilled water inside incubator at 37°C for 48 hours before being tested (23).
b- Testing procedure: Test was performed using durometer hardness tester (shore D hardness, TH210, Italy)which is suitable for acrylic material (23). The instrument consists of a blunt pointed indenter (0.8 mm in diameter) that present in a cylinder (1.6mm in diameter) .The indenter was attached to a digital scale that is graduated from 0 to 100 unit. The usual method was to press down firmlyand quickly on the indenter, a measurements were taken directly from the digital scale reading. Five measurements were recorded on different areas of each specimen and an average of these five readings was recorded.

4-Measuring surface roughness.
a- All the prepared specimens (20 specimens, 10 for each control and experimental groups) stored in distilled water inside incubator at 37°C for 48 hours before being tested (23).
b- Testing procedure: The Profilometer device surface roughness tester (TH 210, China) was used to test the micro geometry of the surface for experimental and control group. The device has surface analyzer (sharp stylus made from diamond) to trace the profile of the surface irregularities. It moves for maximum distance of 11 mm. The Profilometer records by its scale all the peaks and recesses which characterized the surface of the specimen under testing. The analyzer pass along the specimen surface for 11 mm distance. Three locations were selected in every specimen making 3 readings then the mean of these readings were recorded as a surface roughness value for each specimen.

5- Denture base adaptation testing
a- Microscopic measurement: The cast- denture base sets (20 specimens, 10 for each control and experimental groups)was sectioned to a horizontal line 5 mm away from the posterior end of the cast using a cutting saw device under water cooling (26,27). Three points were marked on the cast on transverse line at the posterior border of the cast specimens (deepest point of the left vestibule, left ridge crest and midline point which is marked according to the line bisecting the incisive papilla and extending posterior on the cast) as (A, B and C) respectively (figure 4) (26).

Figure 4: Denture base with its castshow position of 3 points: (1) point A, (2) point B and (3) point C
The gap between the cast and the denture base margin at these 3 points was measured with the use of digital microscope (Dino- Lite, Taiwan) of magnification 200x capability and accuracy of 0.001 mm. Two measurements were made, first one made immediately after deflasking and sectioning for all the samples. Second measurement was done after incubation in distilled water at 37°C for 14 days for all the samples (27), then each denture base was seated on its corresponding cast and measurement of the gap was done while a weight of 1kg was placed over the denture base to ensure a proper seating of the denture base over the cast (26).

b- To observe the overall gap formation of the denture base, All denture bases placed on their respective master cast for each group was scanned by computerized tomography (Light Speed, Philips, Netherland), (figure 5). The frontally-sectioned images of the denture-cast set and sagittal images obtained at the palatal midline were taken from the CT data (27).

**Figure 5: A- computerized tomography device, B- The casts with their corresponding denture bases under scanning**

**RESULTS**

Mean values, standard deviation, t-test, p-value and Significances of mechanical properties presented in table (2).

<table>
<thead>
<tr>
<th>Property</th>
<th>Tested groups</th>
<th>N</th>
<th>Mean</th>
<th>S.D.</th>
<th>T-test</th>
<th>P. value</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impact strength (KJ/m²)</td>
<td>Control group</td>
<td>10</td>
<td>7.94</td>
<td>0.25</td>
<td>-16.02</td>
<td>0.000</td>
<td>HS</td>
</tr>
<tr>
<td></td>
<td>Experimental group</td>
<td>10</td>
<td>9.63</td>
<td>0.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transverse strength (N/mm²)</td>
<td>Control group</td>
<td>10</td>
<td>88.50</td>
<td>0.77</td>
<td>-11.85</td>
<td>0.000</td>
<td>HS</td>
</tr>
<tr>
<td></td>
<td>Experimental group</td>
<td>10</td>
<td>93.48</td>
<td>1.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface hardness</td>
<td>Control group</td>
<td>10</td>
<td>84.64</td>
<td>1.12</td>
<td>-1.316</td>
<td>0.205</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Experimental group</td>
<td>10</td>
<td>85.35</td>
<td>1.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface roughness (μm)</td>
<td>Control group</td>
<td>10</td>
<td>1.29</td>
<td>0.08</td>
<td>-2.309</td>
<td>0.033</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>Experimental group</td>
<td>10</td>
<td>1.37</td>
<td>0.07</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mean values, standard deviation, t-test, p-value and Significances of the gap at three selected points (A, B and C) to measure denture base adaptation presented in table (3).

<table>
<thead>
<tr>
<th>point</th>
<th>Time</th>
<th>Tested groups</th>
<th>N</th>
<th>Mean</th>
<th>S.D.</th>
<th>T-test</th>
<th>P-value</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point A</td>
<td>Immediately After deflasking</td>
<td>Control group</td>
<td>10</td>
<td>0.122</td>
<td>0.018</td>
<td>-2.160</td>
<td>0.045</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Experimental group</td>
<td>10</td>
<td>0.160</td>
<td>0.054</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>After incubation 14 day</td>
<td>Control group</td>
<td>10</td>
<td>0.143</td>
<td>0.038</td>
<td>-2.266</td>
<td>0.036</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Experimental group</td>
<td>10</td>
<td>0.195</td>
<td>0.063</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point B</td>
<td>Immediately After deflasking</td>
<td>Control group</td>
<td>10</td>
<td>0.065</td>
<td>0.016</td>
<td>-2.61</td>
<td>0.018</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Experimental group</td>
<td>10</td>
<td>0.081</td>
<td>0.013</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>After incubation 14 day</td>
<td>Control group</td>
<td>10</td>
<td>0.088</td>
<td>0.035</td>
<td>-1.64</td>
<td>0.111</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Experimental group</td>
<td>10</td>
<td>0.113</td>
<td>0.036</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point C</td>
<td>Immediately After deflasking</td>
<td>Control group</td>
<td>10</td>
<td>0.244</td>
<td>0.040</td>
<td>-0.711</td>
<td>0.486</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Experimental group</td>
<td>10</td>
<td>0.257</td>
<td>0.033</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>After incubation 14 day</td>
<td>Control group</td>
<td>10</td>
<td>0.284</td>
<td>0.053</td>
<td>-0.524</td>
<td>0.607</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Experimental group</td>
<td>10</td>
<td>0.301</td>
<td>0.087</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Evaluation of denture base adaptation made by CT images (Figure 6) was at the mid sagittal line of denture bases on the respective master cast for all tested specimen (control and experimental groups), gap formation between the tissue surface of the denture base and master cast increased from the anterior to posterior side of palate and also from the alveolar ridge to the mid palatal line. However, the gap distance or volume could not be measured from the CT images due to the low resolution.

Figure 6: Computerized tomography images for denture-cast sets: A. control group, B. experimental group

DISCUSSION
The present study was conducted to evaluate and compare the effect of addition (ZrO$_2$:Al$_2$O$_3$-nano-fillers mixture) to PMMA on some mechanical properties and denture base adaptation of heat cured acrylic denture base. The introduction of nanofillers into PMMA produced highly significant increase in the value of impact strength when compared with control group. The increase in the impact strength could be due to the high interfacial shear strength between nanofiller and matrix resulted from the formation of cross-links or supra molecular bonding which cover or shield the Nano fillers which in turn prevent propagation of cracks. Also the crack propagation may be changed by good bonding between nanofiller and resin matrix resulted from interaction between the functional groups introduced by salinization process. The small size and high surface area and relatively low concentration may helped in a good distribution of these fillers that may cause a restricted motion of macromolecule chains and enhance mechanical properties, that means the PMMA nanocomposite has mechanical stability more than neat PMMA.

Also, the transverse strength test result showed highly significant increase with nanocomposite when compared with control group. This increase in transverse strength may be explained on the basis of transformation toughening, when sufficient stress develops and crack begins to propagate, a transformation of ZrO$_2$ and Al$_2$O$_3$ which depletes the energy of crack propagation, also, in this process expansion of ZrO$_2$ and Al$_2$O$_3$ crystals occurs and places the crack under a state of compressive stress and crack propagation is arrested.

Increase in transverse strength also could be due to transfer of stress from more flexible polymer to the higher modulus, more rigid and stiffer filler particles. The addition of nanofillers at 2wt.% to PMMA led to increase of surface hardness beyond that of pure PMMA, statistically was not significant, this could be due to the relatively low concentration of the nanofillers used in the study, although, this improvement may be attributed to the inherent characteristics of the nanoparticles. Nanoparticles possess strong ionic interatomic bonding, giving rise to its desirable material characteristics, that is, hardness and strength. On these bases it may be expected when nanoparticles disperse in a matrix, they increase its hardness and strength.

The surface roughness of modified PMMA with nanofiller was significantly increased when compared with control group. This is may be due to the difference in roughness of Nano particles and acrylic denture base matrix and also probably attributed to the difference in micro structural characteristics of the materials and the form of the particles.

With regard to this study, the significantly increase in surface roughness can be considered unimportant since microorganism colonization occurs when the roughness more than 0.2µm. The gap between denture base and cast was measured at 3 point (A, B, C) in two time to
evaluate denture base adaptation, where it mostly depend on polymerization shrinkage and water sorption of PMMA. So, in first measurement made immediately after deflasking showed a significant increase of gap in experimental group when compared to control group at point A and B, and non-significant increase of gap in experimental group at point C. This increase explained may be due to addition of nanoparticle lead to increase in thermal conductivity of acrylic resin, and degree of polymerization effected considerably by heat dissipation and thermal conductivity. (35) lead to contraction of denture base due to further polymerization shrinkage that occur due to exposure to high temperature with reduction in the spaces between the chain of the polymer this result in agreement with Ogawa and Hasegawa (36).

In second time after incubation 14 day showed in a significant increase of gap in experimental group when compared to control group at point A, and non-significant increase of gap in experimental group at point B and C. This result may be due to that the addition of nanoparticles to PMMA may decreased in water sorption when compared with unmodified PMMA. (13,30), So, decrease expansion of acrylic denture base which considered antagonist effect to polymerization shrinkage that occur in experimental group more than control group as discussed previously. (37).

The CT images of denture base-cast sets did show this tendency of gap formation in mediolateral and anterior-posterior areas (Figure 6). These findings are also predictable with the results reported by Consani et al. (38), who compared the posterior border gap of the denture base-cast sets sectioned transversally at each area of the canine, molar and posterior ends. Moreover, the magnitude of the posterior border gap generally increased medially along the palatal vault reaching a maximum at the midline of the palate.

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