The influence of adding of modified ZrO₂-TiO₂ nanoparticles on certain physical and mechanical properties of heat polymerized acrylic resin

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ABSTRACT

Background: The mechanical and physical properties of Polymethyl methacrylate (PMMA) don’t fulfill the entire ideal requirements of denture base materials. The purpose of this study was to produce new modified polymer nanocomposite (PMMA /ZrO₂-TiO₂) and assess its impact strength, transverse strength and thermal conductivity in comparison to the conventional heat polymerized acrylic resin.

Materials and Methods: Both ZrO₂ and TiO₂ nano fillers were silanized with TMSPM (trimethoxysilyl propyl methacrylate) silane coupling agent before being dispersed by ultrasonication with the methylmethacrylate (monomer) and mixed with the polymer by means of 2% by weight in (1:1) ratio. 60 specimens were constructed by conventional water bath processing technique and divided into 2 groups: 30 specimens for control group 0% nanofillers and 30 specimens for experimental group 2% of (1:1) ZrO₂ and TiO₂ nano fillers then each group was subdivided into 3 subgroups according to the test to be conducted with 10 specimens for impact, transverse and thermal conductivity test.

Results: The interaction of TMSPM silane and the nanofillers was confirmed by FT-IR (Fourier Transform Infra-red spectrophotometer). High significant increase in impact strength (9.838) Kj/m² and non-significant increase in thermal conductivity (0.286) W/m°C° of heat cured acrylic resin of the new polymer nanocomposite were observed.

Conclusions: The addition of 2 wt.% of ZrO₂:TiO₂ by means of 1:1 ratio considerably improved the impact and transverse strength and had a positive effect on the thermal conductivity.

Key words: Polymethyl methacrylate, nanofillers, polymer nanocomposite. (J Bagh Coll Dentistry 2015; 27(3):33-39).

INTRODUCTION

PMMA acrylic resin is the most extensively used material for the fabrication of dentures as it possess a combination of favorable characteristics such as easy laboratory manipulation, light weight, inexpensive fabrication, stability in the oral environment, lack of toxicity and appropriate aesthetic and color matching ability (1). However it’s not ideal in every aspect and have several drawbacks that need to be addressed including low impact resistance, fatigue failure, low thermal conductivity which compromises the patients appreciation of taste and palatability (2). Many attempts were advocated to overcome these drawbacks and improve the performance of PMMA denture base material mainly either by modifying the structure of PMMA by copolymerization with rubber (3) or reinforcement by incorporation of different forms and types of fillers like metallic wire (4), fibers (5-7) and the use of metallic oxides (8).

With the great development of nanotechnology and nano-phased materials, great attention is directed toward the use of nano-sized fillers to reinforce the denture base resins thus producing a polymer nanocomposite with improved mechanical and physical properties as compared to those filled with micro-scale particles. Furthermore the use of multiple nanofillers rather than single additive develops a high performance composite which cannot be achieved by using single filler (9).

The mechanical properties of the resultant polymer nanocomposite depend strongly on the dispersion and adhesion of the filler at the filler matrix interface thus surface treatment of the fillers with silane coupling agent is necessary to improve compatibility between the filler and matrix (10,11).

Both ZrO₂ and TiO₂ nanoparticles have interesting mechanical, physical and photocatalytic properties that make them suitable additives. Furthermore, many properties of this mixed nanostructured metal oxides (ZrO₂:TiO₂) were reported to be better than single additive mainly due to the size difference between titanium and zirconium (12).

This study is performed to produce a new modified polymer nanocomposite by adding surface treated ZrO₂:TiO₂ nanoparticles to heat polymerized acrylic resin and assess its impact strength, transverse strength, and thermal conductivity.

MATERIALS AND METHODS

The materials that were used in the current study are illustrated in table 1.
Table 1: Some of the materials that were used in the study

<table>
<thead>
<tr>
<th>Materials and Trade</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium oxide (ZrO₂) nanofiller 70-80 nm</td>
<td>HWNANO (China)</td>
</tr>
<tr>
<td>Titanium oxide (TiO₂) nanofiller &lt;50 nm.</td>
<td>Nanoshell (USA)</td>
</tr>
<tr>
<td>Trimethoxysilylpropyl methacrylate 98% Silane</td>
<td>No 2530-85-8. Sigma-Aldrich (Germany)</td>
</tr>
<tr>
<td>Heat-curing acrylic resin</td>
<td>Vertex-Dental B.V. Holand</td>
</tr>
</tbody>
</table>

**Surface modification of nanofillers**

Introducing the reactive groups onto the surface of nano fillers was achieved by the reaction of Tri(methoxysilylpropylmethacrylate) silane coupling agent with the nanofillers using 5% wt. of TMSPM for Surface modification of ZrO₂ nanoparticles (13) and 75% wt. of TMSPM for Surface modification of TiO₂ nanofillers (14).

**Preparation of test specimens**

Three plastic patterns were constructed according to the required test. For impact strength test, a bar shaped specimen with [(80mm x 10mm x 4mm) ± 0.2mm] length, width and thickness respectively (15) was used while for transverse strength test a bar shaped specimens with dimensions of [(65mm length, 10mm width, and 2.5mm thickness)± 0.2mm] (16).

Thermal conductivity test: disk with dimension of 40mm in diameter and 2.5mm in thickness according to instrument specification (Thermal constant apparatus) as shown in figure 1.

**Mold preparation**

The plastic patterns were coated with a thin layer of separating medium (Isodent. Spofa dental, Europe) and allowed to dry before being invested. Investing started by filling the lower half of the metal flask with type IV dental stone (Elite stone, Italy) mixed with the ratio of (powder to water was 100g/25ml) according to the manufacturer instructions, then plastic patterns were inserted incompletely into the stone and after the investing stone sets it was coated with separating medium and allowed to dry, then the upper half of the flask was fitted upon the invested one and filled with stone on the vibrator to avoid air babbles.

After complete setting of the stone the flask opened carefully to separate the two halves as shown in figure (2) and the plastic patterns were removed from the molds carefully. The two portions of the flask were coated with a separating medium (cold mold seal) to be ready for packing of acrylic resin.

**Proportioning and mixing of acrylic**

Amounts of polymer and monomer for control group along with the percentage of silanized nano fillers used in the study group are presented in table (2).
Table 2: Proportioning and mixing of acrylic resin

<table>
<thead>
<tr>
<th>Conc. of the addition</th>
<th>Proportion 1 : 1 Polymer (g)</th>
<th>Mono-mer (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% (control)</td>
<td>ZrO₂</td>
<td>TiO₂</td>
</tr>
<tr>
<td>2% (study)</td>
<td>0.22g</td>
<td>0.22g</td>
</tr>
</tbody>
</table>

For test group 2% of a mixture of the modified nano fillers (ZrO₂ :TiO₂) was added by weight in equal proportion (1:1) with the aid of an electronic balance of (0.0001g) accuracy, the fillers were well dispersed in the monomer by ultra-sonication using probe sonication apparatus (Soniprep-150, England)(120 W, 60 KHz) for 3 minutes(15). Then it was immediately mixed with acrylic powder to reduce the possibility of particle aggregation and phase separation. The mixing of acrylic resin was carried out and manipulated according to manufacturer’s instructions in a clean and dry mixing container and by a clean wax knife for 30 seconds; then packing of the heat cure acrylic resin was done in the dough stage(16).

After collecting dough mix, it was rolled and packed in the molds that were already painted with a separating medium and allowed to dry, then clamping was done and impart to the water bath.

Curing
The Curing process was carried out according to the manufacturer’s instructions, started by placing the clamped flasks in a digital water bath (Memert, Germany) at room temperature (25°C ±2), then temperature increases gradually until reaching the boiling point (100°C) at which the processing was completed for 30 minutes, the entire cycle took about 2 hours. When the curing cycle is complete, the metal flasks were allowed to cool at room temperature for 30 minutes, then left to cool under tab water for 15 minutes before deflasking (16).

Finishing and polishing
After the specimens were carefully de-flasked, flashes of acrylic were removed with an acrylic bur and stone bur was used followed by (120) grain size sand paper with continuous water cooling. Polishing was accomplished by using bristle brush and ruge wheel with pumice in lathe polishing machine then a gloss surface was obtained by using chamois baffle and polishing swab on dental lathe, both were at low speed (1500rpm) with continuous cooling to avoid over heating which may lead to distortion of the specimens.

Impact strength test
A- Test specimen: Ten specimens for control and ten for study group were constructed for impact strength measurements. Acrylic specimens were conditioned by storing in distilled water at 37°C for 48 hours in an incubator before being tested (16).

B- Testing equipment and procedure
Impact strength test was conducted with charpy impact testing device shown in Figure (3). The specimen was supported horizontally at its both ends ad struck by a free swinging pendulum which released from a fixed height in the middle. A pendulum of 2 joules testing capacity was used. The scale reading gives the impact energy absorbed to fracture the specimen in joules when its stroked by a sudden blow. The charpy impact strength of unnotched specimen was calculated in KJ/m² as given by the following equation:

\[ \text{Impact Strength} = \frac{\xi}{d^2} \times 10^3 \]

Where: \( \xi \): is the impact absorbed energy in Joules, \( d \): is the width in Millimeters of the test specimens, \( d \): is the thickness in Millimeters of the test specimens.

Transverse strength test
A. Test Specimens: Ten specimens for the study group were constructed in addition to ten for the control group which makes total of (20) specimens for the measurement of transverse strength. All the specimens were immersed in distilled water in the incubator at 37°C for (48) hours before being tested (16).

B. Testing equipment and procedure
The transverse strength was measured by three point bending using a universal Instron testing machine (Fig. 5). Each specimen was positioned horizontally on the bending fixture which consists of two parallel supports that are (50) mm apart and the load was applied with a cross head speed of 1mm/min by a rod placed centrally between the supports making deflection until fracture occurs Fig. (6). The transverse bend strength was calculated using the following formula:

\[ \text{Transverse Strength} = \frac{3PL}{2b'd^2} \]
Where: $F$: is the peak load, $L$: is the span length (50mm), $b$: is the sample width, $d$: is the sample thickness (19).

**Thermal conductivity test**

**A. Test specimens:** Twenty specimens were prepared 10 for the control group and 10 for the experimental group to measure the thermal conductivity.

**B. Testing equipment and procedure**

The Lee's disk method was used to measure the thermal conductivity of the specimens using Lee's disk apparatus shown in Figure (7) which consists of three brass discs that are 12.25 mm in thickness and numbered (1,2,3), each one is attached to a thermometer also numbered (1,2,3). An electric heater is fixed between the first (1) and second (2) brass discs and connected to D.C power supply. The specimen-polished from both sides- placed between the second (2) and third (3) brass discs. The electric set up of the apparatus was conducted to power supply after covering the whole assembly to minimize the effects of draughts and providing laboratory condition (25º C± 2º C). Thereafter (6V) voltage and (i=0.25A) current were applied to heat the brass disks (2, 3), temperatures of all disks increases gradually and were recorded every (5 minutes) until reaching to a constant temperature of all thermometers which means that the specimen can no more conduct heat. This process takes about 2 hours for each sample. The losses in heat (e) were calculated from the following equation

\[
i * v = \pi . r^2 . e (T_3 + T_1) + 2 \pi . r . e. \left[ d_1 T_1 + d_2 T_2 + d_3 T_3 \right]
\]

The thermal conductivity (k) was calculated from the following equation

\[
k = \frac{1}{d} \left( T_2 - T_1 \right)
\]

Where: $i$: The flowed current (A), $v$: The voltage (Vol), $r$: The radius (mm), $d$: The thickness of the specimen (mm), $d_1$, $d_2$, $d_3$: Thickness of brass discs (1, 2, and 3) respectively (mm), $T_1$, $T_2$, $T_3$: The temperature of discs (1, 2 and 3) respectively(C), $k$: Thermal conductivity, $e$: The amount of the thermal energy per unit area per second (W/m².°C).
RESULTS AND DISCUSSION

Impact strength

The results of impact strength test in Table (3) showed that addition of 2% nano ZrO₂: TiO₂ in equal proportion to PMMA caused a high significant increase in impact strength and this may be due to the surface modification of the nanofillers with TMSPM coupling agent which provide better dispersion of particles in matrix; avoid agglomeration and in the same time improves interfacial adhesion of the fillers to polymer matrix due to the formation of cross-links or supramolecular bonding covering the nanofillers which in turn prevent the propagation of crack by transferring the stress from matrix to fillers\(^{(10)}\).

On the other hand the different nanoparticle sizes of metallic fillers used in the study (ZrO₂ was 70-80 nm, TiO₂ was <50 nm) provided additional improvement to the mechanical properties by inhibiting the spaces between oxide particles thus they fill the interstitial of polymer particles to give a heterogenous mixture and will not force the displacement of the segments of the polymer chain.\(^{(11)}\)

Additionally the nanoparticles characterized by large specific surface area thus they have the ability to dissipate energy thus may enhance impact strength.

The result of this study agreed with that obtained by Safarabadi et al.\(^{(21)}\).

Transverse strength test

Table (4) showed the Mean values, standard deviation, standard error and independent t test of the transverse strength test results.

Table 4: Descriptive statistics and groups’ difference of the flexural strength (N/mm²)

<table>
<thead>
<tr>
<th>Groups</th>
<th>N</th>
<th>Mean</th>
<th>S.D</th>
<th>S.E.</th>
<th>t-test</th>
<th>p-value</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>10</td>
<td>85.17</td>
<td>3.49</td>
<td>1.10</td>
<td>-10.593</td>
<td>0.000</td>
<td>HS</td>
</tr>
<tr>
<td>Study</td>
<td>10</td>
<td>101.70</td>
<td>3.48</td>
<td>1.10</td>
<td>-10.593</td>
<td>0.000</td>
<td>HS</td>
</tr>
</tbody>
</table>

As presented in Table (4) the result of 2% of ZrO₂-TiO₂ nanoparticles caused highly significant increase in transverse strength of PMMA as compared to control group, this could be attributed to the good distribution of the very fine and different sizes of nanofillers used in the study that enable them to enter between linear macromolecular chains of the polymer and fill spaces between chains, there by restricting the segmental motions of the macromolecular chains and increasing strength and rigidity of the resin, so this improve fracture resistance and lead to improve transverse strength.

In addition the increase in transverse strength could be due to the transformation toughening, when sufficient stress develops and micro crack begins to propagate, a transformation of nanoparticles from the meta stable tetragonal crystal phase to the stable monoclinic phase occurs which depletes the energy of crack propagation, also, in this process expansion of crystals occurs and places the crack under a state...
of compressive stress and crack propagation is arrested\(^{(15)}\).

Additionally both van der waal forces and covalent bonding increases strength and adhesion force.

The result of the present study agrees with those obtained by Safarabadi et al.,\(^{(21)}\) Alhareb and Ahmed\(^{(22)}\) and Acosta-Torres et al.\(^{(23)}\).

**Thermal conductivity test**

The mean values, standard deviation, standard error and independent t test of the thermal conductivity test results are shown in table (5).

There was a non-significant increase in the values of thermal conductivity with the addition of ZrO\(_2/TiO_2\) nanoparticles, this may due to metallic properties of oxides & their ability to conduct heat as compared to the acrylic resin (thermal conductivity of ZrO\(_2\) 1.8- 3.0 W/m.K and that for TiO\(_2\) 1.17 W/m.K) additionally the surface treatment of the nano fillers which increases the cross linking during polymerization of PMMA these cross links help in heat transmission through atoms in covalent bonds as the cross-linking of the double bonds and the other strong groups decrease the spaces and increase the crosslink, thus the heat transfer is more rapid due to the free- volume diminishing.\(^{(24)}\)

### Table 5: Descriptive statistics and groups' difference of the thermal conductivity (W/m.C°)

<table>
<thead>
<tr>
<th>Groups</th>
<th>N</th>
<th>Mean</th>
<th>S.D.</th>
<th>S.E.</th>
<th>t-test</th>
<th>p-value</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cont.</td>
<td>10</td>
<td>0.28</td>
<td>0.03</td>
<td>0.01</td>
<td>-0.597</td>
<td>0.558</td>
<td>NS</td>
</tr>
<tr>
<td>Study</td>
<td>10</td>
<td>0.29</td>
<td>0.03</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**REFERENCES**

الخلاصة

بيان المشكلة: إلزام روابط الأكريليك الحراري المادة الأكثر شيوعا واستخدامها في تحضير قواعد الأظافم المتحركة للاستبان تلك اللافتة موجبة، أهمية ميكانيكيا نظرا لاستغلالها في تحمل الصدمة التي تسبب غالبا في كسر قواعد الأظافم.

الهدف: إلزام روابط الأكريليك الحراري من خلال قوة التوصيل الحراري، والمقاومة الميكانيكية، قوة المضادة للصدمة، ومقاومة الاصطدام.

المواد والطريقة: تم استخدام الجزيئات النانوية الوسط كأوكسيد الزركونيوم وأوكسيد السيليكوني مع المطاط البولي وسط مادة البولي ميثيل ميثاكريلات البولي ميثيل ميثاكريلات. تم تحضير عينات مجموعتين من عينات مجموعتين مع تم تقسيم كل منها إلى ثلاث مجموعات بكميات مختلفة من المونة ومواد مختلفة.

النتائج: تم التحقق من تكوين الطرق التجارية، ومقاومة الاصطدام، ومقاومة الاصطدام الدパイ. تم إجراء ملاحظات على الطرق التجارية ومقاومة الاصطدام، ومقاومة الاصطدام الدパイ. تم إجراء ملاحظات على الطرق التجارية ومقاومة الاصطدام، ومقاومة الاصطدام الدパイ.

الاستنتاج: يمكن أن تستخدم هذه الجزيئات النانوية كأوكسيد الزركونيوم وأوكسيد السيليكوني مع المطاط البولي وسط مادة البولي ميثيل ميثاكريلات البولي ميثيل ميثاكريلات، كمادة الاصطدامية ومقاومة الاصطدام في نطاق ما، ومقاومة الاصطدام الدパイ. يمكن أن تستخدم هذه الجزيئات النانوية كأوكسيد الزركونيوم وأوكسيد السيليكوني مع المطاط البولي وسط مادة البولي ميثيل ميثاكريلات البولي ميثيل ميثاكريلات، كمادة الاصطدامية ومقاومة الاصطدام في نطاق ما، ومقاومة الاصطدام الدパイ. يمكن أن تستخدم هذه الجزيئات النانوية كأوكسيد الزركونيوم وأوكسيد السيليكوني مع المطاط البولي وسط مادة البولي ميثيل ميثاكريلات البولي ميثيل ميثاكريلات، كمادة الاصطدامية ومقاومة الاصطدام في نطاق ما، ومقاومة الاصطدام الدパイ. يمكن أن تستخدم هذه الجزيئات النانوية كأوكسيد الزركونيوم وأوكسيد السيليكوني مع المطاط البولي وسط مادة البولي ميثيل ميثاكريلات البولي ميثيل ميثاكريلات، كمادة الاصطدامية ومقاومة الاصطدام في نطاق ما، ومقاومة الاصطدام الدパイ. يمكن أن تستخدم هذه الجزيئات النانوية كأوكسيد الزركونيوم وأوكسيد السيليكوني مع المطاط البولي وسط مادة البولي ميثيل ميثاكريلات البولي ميثيل ميثاكريلات، كمادة الاصطدامية ومقاومة الاصطدام في نطاق ما، ومقاومة الاصطدام الدパイ.