The Effect of Titanium Oxide (Tio2) Nanoparticles Addition on Polymethyl Methacrylate Denture Base Impact Strength, Tensile Strength, and Hardness

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Abstract
The objective of this study was to evaluate the effect of titanium oxide (TiO2) nanoparticles addition on the impact strength, tensile strength, and hardness of polymethyl methacrylate denture base material. Polymethyl methacrylate bar, sized 60x6x4 mm3 (n=27) for impact strength, 60x12x4 mm3 (n=27) for tensile strength, and 25x10x3 mm3(n=27) for hardness were evaluated. The samples were divided into three concentration groups: the control group, 0.5% of titanium oxide nanoparticles, and 1% of titanium oxide nanoparticles.

The impact strength was tested using izod impact tester, the tensile strength was tested using universal testing machine, and the hardness was tested using Vickers micro hardness tester. Data were analysed using one-way ANOVA and continued with Least Significant Difference (LSD) test (α=0.05).

The results showed that there were significant differences on impact strength, tensile strength, and hardness of PMMA among the tested concentration (P<0.05). The additions of titanium oxide (TiO2) nanoparticles were able to increase the impact strength, tensile strength, and hardness of the PMMA denture base.

Keywords: Hardness, impact strength, PMMA, tensile strength, titanium oxide.

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Introduction
A denture base is a part of a denture that rests on supporting tissue and functions as a place to attach artificial teeth.¹ Denture base received functional loads from occlusion and distributed the functional loads to the oral supporting tissue.² Material used as denture base must fulfil the ideal requirements, which are good biocompatibility, non-toxic, non-irritating, has adequate physical and mechanical properties, aesthetic, easily manipulated, cleaned, repaired, inexpensive and durable.³,⁴

The most used material to manufacture denture bases is PMMA due to its advantages but this material has low strength and hardness.⁵,⁶ The low strength can cause the denture base easily to fracture when falling or during functioning in the oral cavity.⁷ The low hardness of PMMA also can cause the denture base to easily scratched and abraded, this will lead to the micro porous formation on the surface of the denture base which can be an environment that supports microorganisms to grow.⁸,⁹

According to a survey, 63% of dentures had been damaged in three years of use with 71.4% damage was denture base fractures and 80.4% of the cause due to impact failure, followed by 16.1% due to mastication and 3.6% due to accident/trauma.¹⁰ The strength of PMMA can be increased by adding reinforcement materials that are metal, fibre or chemical.¹¹,¹²,¹³ Titanium oxide (TiO₂) is one of the nanoparticle-sized reinforcement choices that can improve the properties of PMMA because of its non-toxic, chemically inert, inexpensive, resistance to corrosion and antibacterial properties.⁷,¹⁴,¹⁵
between titanium oxide nanoparticles with PMMA polymer were the main factor that caused this material to be effective in improving the mechanical properties of PMMA.16,17,18

Ahmed MA et al conducted a study by adding TiO₂ nanoparticles to PMMA with 1% and 5% concentrations, the results showed that the addition of TiO₂ nanoparticles with 1% concentration could significantly increase the impact strength of denture base and 5% concentration could significantly increase the microhardness of PMMA.19 Also, Shirkavand S et al, investigated the effect of TiO₂ nanoparticles addition with 0.5%, 1% and 2% concentration on tensile strength of acrylic resins, the results showed an increase in tensile strength after the addition of 1% TiO₂ but the tensile strength was reduced when adding TiO₂ with 2% concentration.7 In another study, Alwan AS et al, evaluated the effect of the addition of 3% TiO₂ nanofiller on PMMA and the results showed a significant increase in denture base hardness.17

Many studies on the addition of reinforcement materials have been done before, but the right concentration to improve the mechanical properties of denture base have not been found. Therefore, this study was conducted to evaluate the effect of the addition of titanium oxide (TiO₂) nanoparticles on PMMA denture base strength and hardness by using a lower concentration than previous studies which was 0.5% and 1% concentrations, and the size of titanium oxide (TiO₂) nanoparticles were smaller which was 21 nm. The null hypothesis was that the additions of titanium oxide (TiO₂) nanoparticles on the PMMA denture base do not affect the strength and hardness.

Materials and methods

Polymethyl methacrylate bar, sized 60×6×4 mm³ (n=27) for impact strength testing according to ADA specification No.12,19 sized 60×12×4 mm³ (n=27) for tensile strength testing according to ISO 1567,7 and sized 25×10×3 mm³ (n=27) for hardness testing according to ISO 20795-418 were prepared (Fig. 1). The samples were divided into three concentration groups: the control group, 0.5% of titanium oxide nanoparticles, and 1% of titanium oxide nanoparticles.

Custom-made stainless-steel bars; 60.5×6.5×4.5 mm³ for impact strength, 60.5×12.5×4.5 mm³ for tensile strength and 25.5×10.5×3.5 mm³ for hardness were used to create the sample moulds in the flask.

Figure 1. The dimensions of the specimens. A) impact strength, B) tensile strength and C) hardness.

Titanium oxide (TiO₂) nanoparticles (Sigma-Aldrich, Sigma-Aldrich Corp., Singapore) with an average size of 21 nm that have been weighted using a digital balance (Mettler Toledo Al-204, Mettler Toledo, Indonesia) were mixed with PMMA powder (Huge Denture Base Polymer, Huge Dental Material Co., LTD., China) using mortar and pestle until it reached a uniform distribution of nanofiller within PMMA powder, then added to the monomer liquid (Huge Denture Base Polymer, Huge Dental Material Co., LTD., China) and stirred manually using a spatula. The flasking procedure was according to the manufacturer’s instructions. The samples were then mashed with 400, 600, and 1000 grit waterproof sandpaper (Atlas English Abrasives Waterproof Paper, Saint-Gobain Abrasives, France) which was attached to a rotary grinder (Buehler, LTD., USA) with running water at a speed of 500 rpm until an appropriate size was obtained. The final polishing was carried out using pumice with a polishing brush mounted on a polishing motor (M2V, Manfredi, Italy) at a speed of 500 rpm. Then the samples were immersed in the incubator (SSeriker II, Korea) at 37°C for 48 hours before testing.

Izod impact tester (Gotech, Gotech, Inc., Taiwan) at an impact speed of 3.46m/min was used for impact strength testing and universal testing machine (Gotech, Gotech, Inc., Taiwan) at a crosshead speed of 30mm/min was used for
tensile strength testing. Vickers microhardness tester (Future-Tech FM 800, Future-Tech Corp., Japan) was used for hardness testing. Data were analysed using one-way ANOVA and followed by an LSD test (α=.05).

Results

The highest impact strength was observed in the 1% concentration of titanium oxide (TiO₂) nanoparticles (Fig. 2). The highest tensile strength was observed in the 1% concentration of titanium oxide (TiO₂) nanoparticles (Fig. 3). The highest hardness was observed in the 1% concentration of titanium oxide (TiO₂) nanoparticles (Fig. 4). All concentration groups showed statistical differences according to the one-way ANOVA and LSD tests (Table 1, 2, and 3) (P<0.05).

Figure 2. Means and standard deviations of impact strength for all samples (vertical bars show standard deviation; bars with different letter are significantly different).

Figure 3. Means and standard deviations of tensile strength for all samples (vertical bars show standard deviation; bars with different letter are significantly different).

Figure 4. Means and standard deviations of hardness for all samples (vertical bars show standard deviation; bars with different letter are significantly different).

Table 1. Mean values and standard deviations of impact strength (J/m) for all groups with one-way ANOVA.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Numbers</th>
<th>Mean ± Standard deviation</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>9</td>
<td>29.45 ±1.46</td>
<td>0.0001</td>
</tr>
<tr>
<td>PMMA + TiO₂ 0.5%</td>
<td>9</td>
<td>37.07 ±1.65</td>
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</tr>
<tr>
<td>PMMA + TiO₂ 1%</td>
<td>9</td>
<td>43.18 ±3.58</td>
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Table 2. Mean values and standard deviations of tensile strength for all groups with one-way ANOVA.

<table>
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<th>Numbers</th>
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</tr>
</thead>
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<td>PMMA</td>
<td>9</td>
<td>48.14 ±4.75</td>
<td>0.0001</td>
</tr>
<tr>
<td>PMMA + TiO₂ 0.5%</td>
<td>9</td>
<td>62.67 ±5.66</td>
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<td>PMMA + TiO₂ 1%</td>
<td>9</td>
<td>96.58 ±10.68</td>
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Table 3. Mean values and standard deviations of hardness (VHN) for all groups with one-way ANOVA.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Numbers</th>
<th>Mean ± Standard deviation</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>9</td>
<td>15.62 ±0.42</td>
<td>0.0001</td>
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<tr>
<td>PMMA + TiO₂ 0.5%</td>
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<td>16.77 ±0.31</td>
<td></td>
</tr>
<tr>
<td>PMMA + TiO₂ 1%</td>
<td>9</td>
<td>17.62 ±0.32</td>
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</tbody>
</table>

Discussion

This study was conducted to evaluate the effect of the addition of titanium oxide (TiO₂) nanoparticles on PMMA denture base
strength and hardness to increase denture strength and hardness. The null hypothesis was rejected, where the addition of different concentrations of titanium oxide (TiO$_2$) nanoparticles affected both denture base strength and hardness.

The various values of the strength and hardness in each tested group were influenced by several factors including the stirring technique of PMMA polymers and titanium oxide (TiO$_2$) nanoparticles powder which was not carried out simultaneously for all samples. The manually stirring technique could cause air trapping in the PMMA matrix and internal porosity that will affect the strength and hardness of the PMMA denture base. Furthermore, the uncontrolled distribution of the reinforcement material in each sample, which in this study was titanium oxide (TiO$_2$) nanoparticles were less evenly distributed because of the flask pressing process. $^{16, 20}$

The results showed that the addition of titanium oxide (TiO$_2$) nanoparticles could increase denture base mechanical properties. The strength and hardness of the PMMA denture base increased with the increasing concentration of titanium oxide (TiO$_2$) nanoparticles. The results of this study were in line with previous studies regarding polymer reinforcement with titanium oxide (TiO$_2$) nanoparticles by Asar et al. $^{21}$ Ghahremani et al., $^{22}$ Ahmed et al.,$^{19}$ and Aziz et al. $^{23}$ The increasing of denture base impact strength by the addition of titanium oxide nanoparticles can occur due to various factors including good adhesion between the PMMA polymer matrix and titanium oxide nanoparticles. $^{16, 24}$ This adhesion occurred because titanium oxide nanoparticles can be chemically bonded with -COOR group from PMMA polymers. $^{17, 18}$ Titanium oxide nanoparticles will form crosslinking with PMMA polymers where the formation of crosslinking will increase the denture base resistance to fracture. The presence of crosslinking will also cause an increase in the surface shear strength between titanium oxide nanoparticles and the polymer matrix by reducing material cracking possibility. $^{17, 18}$ In addition, the size of titanium oxide nanoparticles which were much smaller than PMMA particle size can fill the space between linear macromolecular chains of PMMA polymer particles thus reducing the porosity of the PMMA by increasing the density of PMMA. $^{25}$

This present study results also showed an increase in denture base tensile strength after the addition of titanium oxide nanoparticles. This study also correlated with previous studies of titanium oxide addition on denture base tensile strength by Ghahremani et al. $^{22}$ and Shirkavand et al. $^7$ The increase in tensile strength can occur because titanium oxide nanoparticles have high structural strength. $^{22}$ The presence of titanium oxide nanoparticles in the PMMA induced most of the loads applied to the PMMA were tolerated by titanium oxide nanoparticles which lead to better load distribution in the samples. $^{7, 16, 22}$ The results of the current study are in agreement with Alrahlah et al$^{5}$ and Alwan et al.$^{17}$ where the hardness of PMMA denture base significantly increase after the addition of titanium oxide nanoparticles in comparison to unmodified PMMA. The increased of denture base hardness could be attributed to the improvement in the stiffness of the PMMA matrix due to the presence of rigid particles within the matrix which lead to the reduction in its free volume and molecular mobility. $^{5, 18}$

The titanium oxide 1% concentration addition group showed higher strength and hardness compared to 0.5% concentration addition. This was due to better distribution of titanium oxide addition at 1% concentration compared to 0.5% concentration based on SEM images. $^{7}$ Moreover, the titanium oxide addition of by 1% concentration will cause more titanium oxide to fill the space between the linear macromolecular chains of PMMA polymer and reduce the porosity of PMMA. The more concentration of titanium oxide in the PMMA matrix also caused more crosslinking to form and the better mechanical properties of denture. $^{16, 18}$

The limitation of this study was a colour change has occurred in all samples after the titanium oxide addition. The change was due to the presence of titanium oxide nanoparticles which has whitish colour in the PMMA matrix. The titanium oxide absorbed more light wave than the PMMA polymer matrix due to the high atomic number which caused the reinforced samples more opaque compared to pure PMMA. $^{18}$ Therefore, Further studies about the effect of TiO$_2$ addition on colour stability and other properties of PMMA are required to attain a denture base with superior properties and acceptable aesthetics.
Conclusions

The addition of titanium oxide (TiO2) nanoparticles can improve the strength and hardness of PMMA denture base which the recommended concentration is 1% titanium oxide (TiO2).

Declaration of Interest

The authors report no conflict of interest.

References
