

# Tribological, microhardness and color stability properties of a heat-cured acrylic resin denture base after reinforcement with different types of nanofiller particles

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## Abstract

**Background.** Polymethyl methacrylate (PMMA) is not an ideal material in all aspects, as it has poor mechanical and antimicrobial properties. The enhancement of the mechanical and physical features of PMMA-based material is highly required.

**Objectives.** The present study aimed to estimate the effect of adding different types of nanoparticle (NP) materials on the mechanical and physical features of heat-cured acrylic resin denture base material.

**Material and methods.** A total of 120 samples were divided into 4 groups: the control group; the 5 wt% ZrO<sub>2</sub> NPs group; the 5 wt% TiO<sub>2</sub> NPs group; and the 5 wt% Ag NPs group. Each one was subdivided into 3 groups according to the test performed: the microhardness test; the abrasive wear test; and the color stability test. Then, the results of these tests were evaluated.

**Results.** The maximum mean value for the microhardness test was observed in the group treated with the addition of 5 wt% Ag NPs, followed by the 5 wt% ZrO<sub>2</sub> NPs group, and finally the 5 wt% TiO<sub>2</sub> NPs group. The lowest mean microhardness value was recorded for the control group. The maximum mean value for the abrasive wear test was attributed to the control group and the lowest mean value was related to the 5 wt% Ag NPs group. The maximum color change was noted in the 5 wt% Ag NPs group, followed by the 5 wt% ZrO<sub>2</sub> NPs and 5 wt% TiO<sub>2</sub> NPs groups. The lowest mean value for the color change was found in the control group.

**Conclusions.** There was an increase in hardness and wear resistance in the group treated by adding 5 wt% Ag NPs, and the control group had the best color stability, followed by the 5 wt% TiO<sub>2</sub> NPs group. However, a detrimental effect on color stability was observed when 5 wt% Ag NPs was added.

**Keywords:** nanoparticles, hardness, wear, ZrO<sub>2</sub>, reinforcement of an acrylic denture base

## Cite as

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## Introduction

Polymethyl methacrylate (PMMA)-based acrylic has been characterized as the most highly favored denture base material.<sup>1</sup> It was introduced in 1937 by W. Wright<sup>2</sup> because of its desirable properties, such as durability, low toxicity, satisfactory esthetics, good stability in oral conditions, low weight, and a low cost.<sup>3</sup> Yet, PMMA is not an ideal material in all aspects, as it has poor surface mechanical properties and limited antimicrobial activity.<sup>4</sup> The enhancement of the physical as well as mechanical qualities of PMMA-based material is highly required.<sup>5</sup> A recently developed procedure can improve the mechanical and physical properties of the polymer by incorporating different nanoparticles (NPs) into PMMA to act as a kind of reinforcing material.<sup>6</sup>

Nanoparticles have often been used in different forms, such as aluminum oxide ( $\text{Al}_2\text{O}_3$ ), zirconium dioxide ( $\text{ZrO}_2$ ), titanium dioxide ( $\text{TiO}_2$ ), silicon dioxide ( $\text{SiO}_2$ ), zinc oxide ( $\text{ZnO}$ ), and silver (Ag).<sup>7</sup> The properties of a polymer nanocomposite are determined by the type, concentration, size, and shape of NPs, as well as their interaction with the polymer matrix.<sup>8</sup>

$\text{ZrO}_2$  NPs are broadly used to improve and reinforce the physical and mechanical properties of PMMA.<sup>9</sup> In addition to its excellent biocompatibility, the PMMA/ $\text{ZrO}_2$  nanocomposite is esthetically acceptable, since  $\text{ZrO}_2$  is white and less likely to alter its color than other metal oxide NPs.<sup>3</sup>  $\text{ZrO}_2$  NPs have good wear and corrosion resistance,<sup>10</sup> thermal stability, high fracture strength, high hardness, and high mechanical resistance.

$\text{TiO}_2$  NPs are increasingly used due to their superior mechanical properties<sup>11</sup> and other features, such as non-toxicity, white color, a low cost, biocompatibility, chemical inactivity, a high refractive index, an antimicrobial effect, corrosion resistance, and high microhardness.<sup>12</sup> According to Alwan and Alameer, adding 3 wt%  $\text{TiO}_2$  NPs resulted in an increase in the surface hardness, impact strength and transverse strength values of a heat-cured acrylic resin.<sup>13</sup> Ahmed et al. studied the effect of  $\text{TiO}_2$  NPs (1 wt% and 5 wt%) on the impact strength, flexural strength and microhardness of 2 heat-polymerized acrylic resins.<sup>14</sup> In their study, the values of flexural strength declined, whereas the values of microhardness increased through adding  $\text{TiO}_2$  NPs.<sup>14</sup> Aziz revealed that impact strength and color stability were improved by the incorporation of 3 wt%  $\text{TiO}_2$  NPs; yet, there was no change recorded for thermal conductivity.<sup>15</sup>

The reason behind considering Ag NPs is that they are characterized by distinctive chemical, biological and physical properties, including chemical stability, non-linear optical behavior, and high electrical and thermal conductivity.<sup>16</sup> Ag NPs show antimicrobial activity against many microorganisms, such as *Streptococcus mutants*, *Candida albicans* and *Staphylococcus aureus*.<sup>17</sup> The reinforcement of PMMA properties, especially the physical

and mechanical ones, e.g., compressive strength and thermal conductivity, is attributed to the addition of Ag NPs.<sup>17,18</sup> Mahross and Ebrahim investigated the effect of adding different concentrations of Ag NPs (1 wt%, 2 wt% and 5 wt%) to a heat-cured acrylic resin.<sup>19</sup> The authors found that the incorporation of Ag NPs into the acrylic denture base material improved its color stability, with the greatest effect observed with the 5 wt% concentration, followed by 2 wt% and 1 wt%.<sup>19</sup> However, different problems may occur with regard to the wear of dentures due to the nature of the material itself and continuous use for a long period in a moist environment. Aging fractures, pigment adhesion and color changes are examples of the problems expected.<sup>20</sup>

Due to the features of NPs, impregnating acrylic resins with them may enhance the physical and mechanical properties of the materials. Therefore, the present in vitro study aimed to evaluate the influence of adding  $\text{ZrO}_2$ ,  $\text{TiO}_2$  and Ag NPs on the microhardness, abrasive wear resistance and color stability of a heat-cured acrylic resin denture base. The null hypothesis was that  $\text{ZrO}_2$ ,  $\text{TiO}_2$ , and Ag NPs would not improve the microhardness, abrasive wear resistance and color stability of the heat-cured acrylic resin.

## Material and methods

### Sample grouping

The materials used in the study and their composition are shown in Table 1. Three types of nanopowders were used at 5 wt%:  $\text{ZrO}_2$ ;  $\text{TiO}_2$ ; and Ag. They were added to the

Table 1. Composition of the materials used for the control and experimental groups

Groups	Composition of the material
Group 1 (control)	heat-cured denture base acrylic resin (methyl methacrylate polymer in a powder form); methyl methacrylate monomer in a liquid form; Cd-free
Group 2	heat-cured denture base acrylic resin (methyl methacrylate polymer in a powder form); methyl methacrylate monomer in a liquid form; Cd-free; 5 wt% $\text{ZrO}_2$
Group 3	heat-cured denture base acrylic resin (methyl methacrylate polymer in a powder form); methyl methacrylate monomer in a liquid form; Cd-free; 5 wt% $\text{TiO}_2$
Group 4	heat-cured denture base acrylic resin (methyl methacrylate polymer in a powder form); methyl methacrylate monomer in a liquid form; Cd-free; 5 wt% Ag

Cd – cadmium;  $\text{ZrO}_2$  – zirconium dioxide;  $\text{TiO}_2$  – titanium dioxide; Ag – silver.

heat-cured acrylic resin (Superacryl™ Plus; SpofaDental, Jicin, Czech Republic) to form 120 samples divided into 4 groups. Group 1 was represented by pure PMMA without any additive (the control group;  $n = 30$ ). The other 3 experimental groups were as follows: group 2 was treated with 5 wt% ZrO<sub>2</sub> (purity: 99.9%, nanopowder particle size: 50 nm, MW (molecular weight) = 123.22 g/mol, CAS number 1314-23-4; US Research Nanomaterials, Inc., Houston, USA;  $n = 30$ ); group 3 was treated with 5 wt% TiO<sub>2</sub> (purity: 99.9%, nanopowder particle size: 50 nm, morphology: near-spherical; US Research Nanomaterials, Inc.;  $n = 30$ ); and group 4 was treated with 5 wt% Ag (purity: 99.99%, nanopowder particle size: 50 nm, morphology: spherical; US Research Nanomaterials, Inc.;  $n = 30$ ). Each group was divided into 3 subgroups according to the test performed: the microhardness test; the abrasive wear test; and finally the color stability test.

## Sample preparation

According to the ISO 20795-1:2008 standard, the samples were made from metal patterns to get the desired shapes and dimensions. For the microhardness test, the dimensions were 25 mm length × 10 mm width × 3 mm thickness ±0.2 mm.<sup>14</sup> For the abrasive wear test, the sample dimensions were 30 mm length × 10 mm diameter, cylindrical in shape; the dimensions were selected with regard to the abrasive wear test machine used in material engineering science (University of Technology, Baghdad, Iraq). As for the color stability test, 35 mm length × 15 mm width × 0.5 mm thickness dimensions were used according to the American Dental Association (ADA) guidelines.<sup>21</sup> To create the molds, the metal patterns were covered with a separating medium (SpofaDental) and left to dry. They were then embedded into two-part flasks (Hanau Engineering Co., Buffalo, USA), with a dental stone type IV (Zhermack, Badia Polesine, Italy) in the lower part of the flask, mixed according to the manufacturer's instructions. Only a half of the thickness of the metal pattern was put in the dental stone. After the stone completely set, another layer of the separating medium was applied and allowed to dry. Then, the upper part of the flask was used and another portion of dental stone was poured until the material extruded from the flask slot. After that, the flask was put aside for dental stone crystallization. Then, the flask was opened carefully and the metal pattern was removed from the mold.

## Addition of nanofillers

The ZrO<sub>2</sub> nanofillers (5 wt%) were added to the resin monomer, and then mixed through the extreme sonication of the fillers. The NPs were suspended in the liquid monomer and well dispersed in the liquid with the use of a sonication probe at 120 V and 60 kHz (Soniprep 150; MSE (UK) Ltd., London, UK), and then separated into

individual nanocrystals for 3 min.<sup>15</sup> To prevent the particle aggregation and segregation as much as possible, the liquid monomer of methyl methacrylate (MMA) with ZrO<sub>2</sub> NPs was blended with the acrylic powder instantly. All the proportions and the manipulations of the acrylic resin were in accordance with the manufacturer's instructions. The recommended mixing ratio was 10 mL of liquid monomer and 22 g of powder polymer, which represented a 3:1 volume ratio. The mixture was left aside until it reached the dough stage. According to the ISO 9001 standard, an electronic balance (the management system certified up to an accuracy of 0.0000 g; Denver Instrument, Göttingen, Germany) was used for measuring the weight of the material. For TiO<sub>2</sub> and Ag NPs, the same procedure was followed, whereas the usual procedure was applied for the control group – according to the manufacturer's instructions, but without any additions.

## Packing and curing

The mold was painted with a separating medium and the mixture in the dough stage was inserted into the mold to be cured. The metal flask in a conventional brass clamp was placed in a water bath (Talleres Mestraitua, MESTRA®, Txorierri Etorbidea, Biscay, Spain) for curing at 74°C for 90 min, and then the temperature was raised to the boiling point for half an hour under the ADA specification.<sup>21</sup> After that, the metal flask was allowed to cool down at room temperature for half an hour. The complete cooling of the metal flask was followed by deflasking, and finally the specimens were removed. Finishing and polishing were performed for all samples to prepare them for testing.

## Testing procedure

### Microhardness test

The Vickers microhardness for both the control and experimental groups was measured according to the ISO 868:2003 standard. The Shore durometer with scale D was used as the preferable measuring device for plastic materials, whether semi-rigid or hard ones.<sup>22</sup> The microhardness testing machine (DIN ISO 7619, DIN EN ISO 868, DIN 53505, ASTM D 2240; Elcometer, Aalen, Germany) allowed the determination of surface microhardness. The test load was adjusted to a load of 25 g for 10 s, as required.<sup>23</sup> All tests were performed at room temperature.

The following formula was used (Equation 1):

$$VHN = \frac{L}{d^2} \quad (1)$$

where:

$VHN$  – Vickers microhardness [kg/m<sup>2</sup>];

$L$  – load [kg]; and

$d$  – length of the diagonals [mm].

### Abrasive wear test

Each sample, before being subjected to the abrasive wear test, was weighed using the electronic balance (Denver Instrument); the measurement was recorded and considered as W1. The abrasive wear test was carried out by repeating sliding contact (900 rpm), with a sliding distance of 6.5 cm for each cycle. It was related to the test machine settings. The wear testing procedure was performed for each specimen under the applied load of 5 N, and the number of cycles that each specimen was subjected to was 2,000.<sup>24</sup> The time each specimen was held stationary in the apparatus with the help of screws was 142 s. Continuous rinsing with demineralized water (73°C) was used during the wear test so that the abraded particles could be removed from the sample surface and the wet environment of the oral cavity could be simulated.<sup>25</sup> After completing the wear test, the specimen was removed from the testing device, cleaned of all debris and left to dry. It was then weighed using the electronic balance to find the difference in weight before and after the 2,000 cycles. The measurement was considered to be W2. Each specimen was then placed again in the testing device for another 5,000 cycles; the same procedure as described for 2,000 cycles was followed, with the time for each sample changed to 322 s. After completing the wear test, the sample was removed, cleaned from all debris and left to dry. It was weighed again with the electronic balance to get the difference in weight before and after the 5,000 cycles. The measurement was regarded as W3. The obtained results were analyzed using the one-way analysis of variance (ANOVA).

### Color stability test

The color stability evaluation was done for the control and experimental groups with the use of a double-beam ultraviolet-visible spectrophotometer (T80+ UV/VIS Spectrometer; PG Instruments Ltd., Alma Park, UK). The color measurement was performed with the use of curves of spectral reflectance to obtain diffuse reflectance data at every 5 nm in the range of 400–700 nm. The integrating sphere attachment was used for the measurement. The attachment was installed in the spectrophotometer according to the manufacturer's instructions; the supplied white calibration standard was used in the reference port for the calibration of zero, 100% reflectance, and to obtain data. A special holder was used to hold the sample in the attachment.<sup>19</sup> The results were recorded using the Computer Color Matching (CCM) system to be tabulated for the statistical analysis.

## Results

According to ANOVA, the microhardness values showed a highly significant difference ( $p < 0.01$ ) for the

specimen groups containing 5 wt% ZrO<sub>2</sub>, TiO<sub>2</sub> and Ag NPs (Table 2, Fig. 1). Among the 4 test groups, the highest mean microhardness value was found in the PMMA group containing 5 wt% Ag NPs (82.05 ± 3.60 kg/m<sup>2</sup>), whereas the control group represented the lowest mean microhardness value (73.65 ± 3.04 kg/m<sup>2</sup>).

With regard to the abrasive wear test with 2,000 cycles, the mean (*M*), standard deviation (*SD*), standard error (*SE*), minimum (*min*), and maximum (*max*) values, as well as *p*-values are summarized in Table 3. There were highly significant differences between all test groups in the mean wear values ( $p < 0.01$ ). The highest mean wear value was related to the control group (0.00150 ± 0.00047 g), while the lowest mean wear value was observed in the group with Ag NPs (0.00051 ± 0.00023 g), as illustrated in the box and whisker plot (Fig. 2).

As presented in Table 4 and Fig. 3, there were highly significant differences in the mean wear values after 5,000 cycles between all test groups ( $p < 0.01$ ). The highest mean wear value was observed in the control group (0.00400 ± 0.00124 g), while the lowest for the Ag NPs group (0.00194 ± 0.00030 g).

According to the descriptive data regarding color stability, the PMMA specimens without the addition of NPs had a lower mean value of color change (1.687 ± 0.144) as compared to the other 3 groups – the TiO<sub>2</sub> NPs group (1.917 ± 0.159), the ZrO<sub>2</sub> NPs group (1.946 ± 0.022) and the Ag NPs group, which showed the highest mean color change (2.344 ± 0.013) (Table 5, Fig. 4).

Table 2. Mean values [kg/m<sup>2</sup>] obtained in the microhardness test for all test groups (*N* = 40)

Groups	<i>n</i>	<i>M</i> ± <i>SD</i>	<i>SE</i>	Range		<i>p</i> -value ANOVA
				min	max	
Control	10	73.65 ± 3.04	0.961	70.0	79.0	0.000**
5 wt% ZrO <sub>2</sub> NPs	10	80.55 ± 3.12	0.987	75.0	84.5	
5 wt% TiO <sub>2</sub> NPs	10	79.55 ± 3.09	0.976	75.0	84.0	
5 wt% Ag NPs	10	82.05 ± 3.60	1.139	77.5	88.0	

*M* – mean; *SD* – standard deviation; *SE* – standard error; *min* – minimum; *max* – maximum; NPs – nanoparticles; \*\* highly statistically significant ( $p < 0.01$ ).

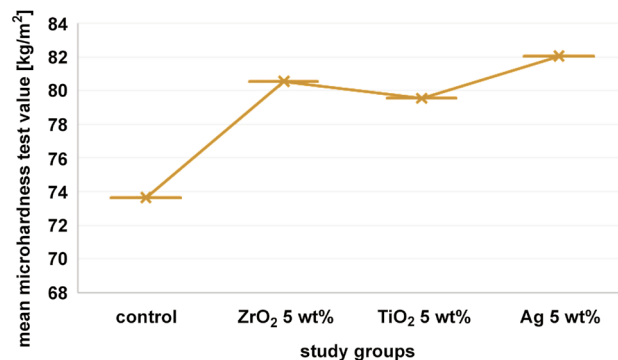
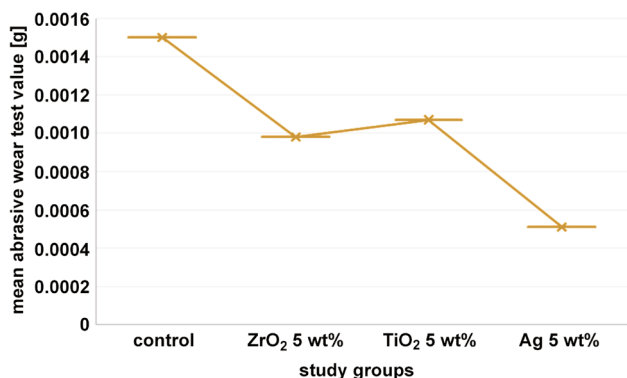


Fig. 1. Distribution of the mean values [kg/m<sup>2</sup>] obtained in the microhardness test for all test groups (*N* = 40)

**Table 3.** Mean values [g] obtained in the abrasive wear test (2,000 cycles – W2) for all test groups (N = 40)

Groups	n	M ±SD	SE	Range		p-value ANOVA
				min	max	
Control	10	0.00150 ±0.00047	0.00015	0.0011	0.0023	0.000**
5 wt% ZrO <sub>2</sub> NPs	10	0.00098 ±0.00049	0.00016	0.0004	0.0019	
5 wt% TiO <sub>2</sub> NPs	10	0.00107 ±0.00043	0.00014	0.0002	0.0019	
5 wt% Ag NPs	10	0.00051 ±0.00023	0.00007	0.0003	0.0009	

\*\* highly statistically significant (p < 0.01).

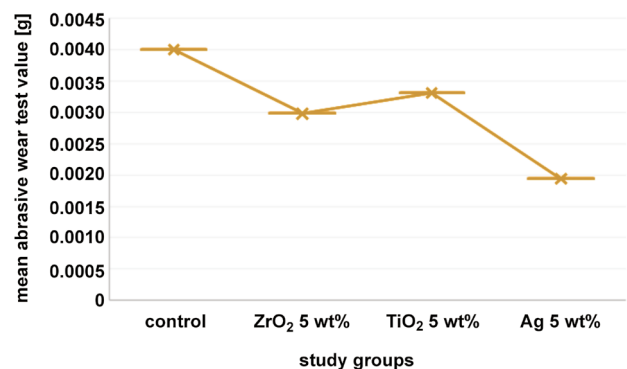


**Fig. 2.** Distribution of the mean values [g] obtained in the abrasive wear test (2,000 cycles – W2) for all test groups (N = 40)

**Table 4.** Mean values [g] obtained in the abrasive wear test (5,000 cycles – W3) for all test groups (N = 40)

Groups	n	M ±SD	SE	Range		p-value ANOVA
				min	max	
Control	10	0.00400 ±0.00124	0.00039	0.0025	0.0063	0.002**
5 wt% ZrO <sub>2</sub> NPs	10	0.00298 ±0.00155	0.00049	0.0016	0.0068	
5 wt% TiO <sub>2</sub> NPs	10	0.00331 ±0.00080	0.00025	0.0026	0.0055	
5 wt% Ag NPs	10	0.00194 ±0.00030	0.00009	0.0015	0.0024	

\*\* highly statistically significant (p < 0.01).

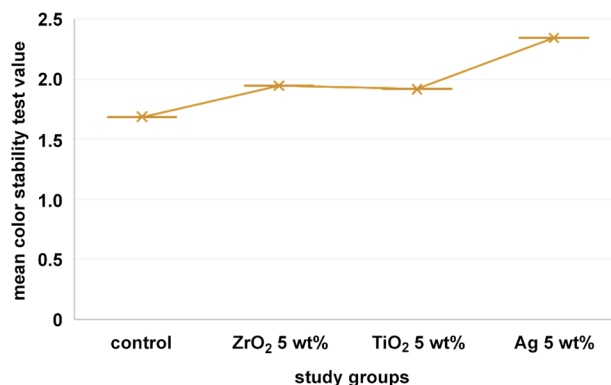


**Fig. 3.** Distribution of the mean values [g] obtained in the abrasive wear test (5,000 cycles – W3) for all test groups (N = 40)

**Table 5.** Mean values obtained in the color stability test for all test groups (N = 40)

Groups	n	M ±SD	SE	Range		p-value ANOVA
				min	max	
Control	10	1.687 ±0.144	0.083	1.590	1.853	0.001**
5 wt% ZrO <sub>2</sub> NPs	10	1.946 ±0.022	0.013	1.923	1.966	
5 wt% TiO <sub>2</sub> NPs	10	1.917 ±0.159	0.092	1.812	2.100	
5 wt% Ag NPs	10	2.344 ±0.013	0.007	2.331	2.356	

\*\* highly statistically significant (p < 0.01).



**Fig. 4.** Distribution of the mean values obtained in the color stability test for all test groups (N = 40)

## Discussion

There is a sort of agreement between the findings of the present study regarding ZrO<sub>2</sub> NPs and those of Ahmed and Ebrahim, who studied the influence of ZrO<sub>2</sub> NPs at various concentrations (1.5 wt%, 3 wt%, 5 wt%, and 7 wt%) on the fracture toughness, hardness and flexural strength of a heat-polymerized acrylic resin.<sup>26</sup> They observed that the values of hardness had risen in all groups in comparison with control.<sup>26</sup> Besides, the present study is in agreement with the observations made by Hu et al., who evaluated the hardness of PMMA enriched with ZrO<sub>2</sub> NPs at various concentrations (0.5 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, and 15 wt%) with the use of different tests, e.g., the pendulum hardness and indentation tests.<sup>27</sup> They found that the ratio of ZrO<sub>2</sub> to PMMA was directly proportional to the hardness values, with the highest records being that for 15 wt%.<sup>27</sup> Also, the current study agrees with that of Hameed and Rahman, who used modified zirconia (Zr) at 3 concentrations (3 wt%, 5 wt% and 7 wt%).<sup>28</sup> They found that the cross-linking density was a dominant factor responsible for the increase in nanocomposite hardness at a low NPs concentration level represented by the addition of 3 wt% ZrO<sub>2</sub>. On the other hand, the increases in the hardness of the nanocomposite at the 5 wt% and 7 wt% concentrations were highly significant, which could be related to the random distribution of ZrO<sub>2</sub> NPs in the acrylic matrix.<sup>28</sup> Moreover, Zidan et al., who evaluated hardness, fracture toughness,

impact strength, and flexural strength of an acrylic resin, also found that surface hardness continuously increased with increases in the Zr content.<sup>29</sup> However, the findings of other studies contradict the results of the present research. Ihab and Moudhaffar found that the increase in the hardness of nano-ZrO<sub>2</sub>/PMMA was non-significant.<sup>30</sup> Ayad et al. revealed that the impact strength, hardness, as well as water solubility of high-impact acrylic resins did not change significantly after reinforcement with the Zr powder for any of the concentrations used (5 wt% and 15 wt%), yet hardness significantly increased in comparison with that of TiO<sub>2</sub>-free PMMA.<sup>10</sup>

There are a lot of studies investigating the impact of the addition of TiO<sub>2</sub> NPs on the qualities of PMMA. For example, it was found that the fracture toughness, hardness and flexural strength of PMMA could be improved by adding TiO<sub>2</sub> NPs; an increase in the amount of TiO<sub>2</sub> NPs added to PMMA was related to increases in the above-mentioned parameters.<sup>31</sup> Owing to the strong adhesion between TiO<sub>2</sub> NPs and PMMA, the polymer chain movements are hindered by the dispersion of TiO<sub>2</sub> NPs within the matrix, and thus a better modulus can be attributed to the TiO<sub>2</sub> NPs/PMMA composite material.<sup>32</sup> In contrast, according to some other studies, there are no signs of improving the flexural strength of PMMA through the addition of TiO<sub>2</sub> NPs. This might be related to the clustering of the particles within the resin, resulting in its weakness.<sup>33</sup> Ahmed et al. studied the influence of 2 concentrations of TiO<sub>2</sub> (1 wt% and 5 wt%) on the impact strength, microhardness and flexural strength of 2 kinds of acrylic resin (a high-impact acrylic resin and a normal heat-cured acrylic resin).<sup>14</sup> The results showed that the microhardness values for the conventional resin material were significantly increased by adding 5 wt% TiO<sub>2</sub>.<sup>14</sup> Therefore, the results of the current study are supported by those of Ahmed et al.,<sup>14</sup> and also Xia et al., who reported that there were 2 factors behind the increases in surface hardness – a silane coupling agent and the proper filler content – which have the capability of increasing the bonding between the resin matrix and the filler.<sup>34</sup> It is in agreement with the research by Hashem et al., who observed increases in the hardness values reaching 20%, 30%, and 34% with 1 wt%, 2 wt% and 3 wt% NPs, respectively, as compared to pure PMMA.<sup>35</sup> This was fully justified by the increased stiffness of the material due to the presence of rigid particles within the matrix, and additionally to a reduction in the matrix mobility.<sup>35</sup> On the other hand, the above results disagree with other findings concerning the addition of TiO<sub>2</sub> to PMMA. Some authors stated that the mechanical features of PMMA and the flexural strength values could be adversely affected by the incorporation of increasing concentrations of TiO<sub>2</sub> NPs.<sup>36</sup>

There have been debatable results reported on how Ag NPs can influence the mechanical features of denture base resins.<sup>37</sup> According to Casemiro et al., the mechanical qualities of denture base resins may be negatively affected

depending on the percentage of added Ag.<sup>38</sup> There has been a lot of argument about the most appropriate concentrations for the addition of a variety of nano-metals to the acrylic resin to get its optimal properties. Zidan et al. explained that the best quantity to improve the distribution of the particles and, at the same time, reduce amalgamation was 5 wt%.<sup>29</sup> In addition, the authors emphasized the fact that tight linking to the resin particles would be promoted by smaller NP sizes, and thus the degradation of NPs could be avoided.<sup>29</sup>

The current study evaluated the effect of 5 wt% TiO<sub>2</sub>, ZrO<sub>2</sub> and Ag NPs on the abrasive wear resistance properties of PMMA. The wear of PMMA after 2,000 cycles was assessed (W2). As shown in Table 3, differences between the groups in the abrasive wear test values were highly significant ( $p < 0.01$ ). Reduced wear was noted with NPs in comparison with NP-free PMMA resins, as illustrated in the results. Polymethyl methacrylate has a lot of positive mechanical properties, such as discontinuity deformation, rigidity, hardness, and easy processing, in addition to its esthetic and biological features. On the contrary, there are a lot of drawbacks regarding PMMA, such as oral mucosa irritation, aging, poor resistance to wear and tear, color instability, staining or discoloration, and volume shrinkage after polymerization.<sup>20</sup> Manufacturers have tried more than once to enhance the quality of acrylic resin artificial teeth by adding different substances to the material to improve wear resistance, which would lead to an increase in the longevity of dental prosthetics.<sup>39</sup> Mohammed and Mudhaffar designed and evaluated the addition of modified ZrO<sub>2</sub> NPs in various percentages (2 wt%, 3 wt% and 5 wt%) to heat-cured acrylic resin PMMA material.<sup>40</sup> There were highly significant increases in abrasive wear resistance, fatigue strength and tensile strength with 3 wt% and 5 wt% of nanofillers as compared to pure PMMA material.<sup>40</sup> A reduction in abrasive wear can be explained mainly by the physical properties of ZrO<sub>2</sub>; they allow the retaining of a highly smooth surface during the entire wear test, thus changing the wear mechanism from severe abrasion to mild sliding wear. To prevent the severe wear of the material caused by abrasive denture cleansers, food or general functional forces, denture base material must have sufficient abrasive wear resistance.<sup>41</sup> Abrasive wear is reduced by a greater hardness of the denture. As for hardness, the results of the above-mentioned research coincide with what was obtained in the current study – high hardness and a reduction in abrasive wear. Similarly, Ahmed et al. revealed that the addition of 5 wt% TiO<sub>2</sub> NPs increased microhardness, and consequently resulted in higher wear resistance.<sup>14</sup> Moreover, the results of the current study are in agreement with Vojdani et al., who also found that a higher wear resistance of resin material results from an increase in microhardness.<sup>42</sup> It is also in line with Zhang, who studied the influence of TiO<sub>2</sub> NPs at 4 concentrations (1 wt%, 3 wt%, 5 wt%, and 7 wt%) on the tribological behavior of PMMA.<sup>43</sup> The results indicated

that adding TiO<sub>2</sub> NPs increased wear resistance. Furthermore, surfaces in the NP-added groups were concluded to be smoother.<sup>43</sup> Improvement in wear resistance can be achieved through the enhanced mechanical properties, i.e., hardness. In the above-mentioned study, all NP groups had greater abrasive wear resistance than the control group, and the statistical analysis based on the least significant difference (LSD) test showed a significant difference when comparing the control group with the ZrO<sub>2</sub> group and a non-significant difference when comparing the control group with the TiO<sub>2</sub> group. The statistical analysis demonstrated that the difference was highly significant when comparing the control and the Ag NPs groups, but a non-significant difference was noticed between the ZrO<sub>2</sub> NPs and TiO<sub>2</sub> NPs groups. On the other hand, a significant difference was observed between the ZrO<sub>2</sub> NPs and Ag NPs groups, and a highly significant difference between the TiO<sub>2</sub> NPs and Ag NPs groups.<sup>43</sup> The results mentioned above can be explained with regard to the microhardness values obtained in the current study. It appears that the hardness of the material is the exponent of the wear resistance of the prosthesis.<sup>14</sup>

It is worth mentioning that ideally, mechanical properties should be improved by consolidating filler materials without having any side effects on esthetics.<sup>15</sup> ZrO<sub>2</sub> NPs are considered to be less likely to alter esthetics in comparison with other metal oxide NPs, as they are white.<sup>3</sup> According to the National Institute of Standards and Technology, the color change ( $\Delta E$ ) can be clinically acceptable when it is less than 2 units, which is very low.<sup>19</sup> So, the results of the present study are in agreement with those of Ihab et al., who studied the effect of the addition of Zr on the color qualities of PMMA.<sup>44</sup> They did not notice any remarkable changes in color. As ZrO<sub>2</sub> is white and biocompatible, it does not adversely affect the esthetic appearance of the denture base.<sup>45</sup> A variety of studies have shown that the best color protection results are achieved with TiO<sub>2</sub> NPs as compared to other studied NPs. The present results confirm the findings of Andreotti et al., who found that TiO<sub>2</sub> NPs helped in maintaining color stability.<sup>23</sup> Aziz also found that TiO<sub>2</sub> NPs improved color stability.<sup>15</sup> Ahmed et al. reported that a change in the color of acrylic occurred when the TiO<sub>2</sub> NPs concentration exceeded 5 wt%.<sup>14</sup> A great deal of attention has been dedicated to the addition of an Ag compound to the acrylic resin as a measure against odor and bacterial proliferation in the oral cavity, but the results were unfortunately fruitless regarding the color change.<sup>46</sup> Hamedi-Rad et al. studied the influence of adding 5 wt% Ag NPs to PMMA on changes in the tensile strength, compressive strength and thermal conductivity values of PMMA.<sup>17</sup> They found a rise in the values of compressive strength and thermal conductivity, but a decline in the tensile strength values. Besides, they demonstrated a brownish discoloration of the prosthesis based on adding 5 wt% Ag NPs.<sup>17</sup> This goes with the results of the present study. Also, it agrees with

the research by Mahroos and Ebrahim, who found that incorporating 5 wt% Ag NPs brought the highest mean color change.<sup>19</sup> In their study, Oei et al. also reported the poor color stability of the Ag NPs/PMMA composite.<sup>47</sup>

## Conclusions

According to the methodology applied in this in vitro study and based on the obtained results, taking into account the study limitations, it was concluded that hardness improved in all NP groups and the Ag NPs group presented the best value in the microhardness test for heat-cured PMMA. Also, abrasive wear resistance increased in all NP groups, with the best value in the abrasive wear test noted for the Ag NPs group. The TiO<sub>2</sub> NPs group had the best color stability, whereas the Ag NPs group had the lowest mean color stability.

## Ethics approval and consent to participate

Not applicable.

## Data availability

The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

## Consent for publication

Not applicable.

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