



RESEARCH ARTICLE

Comparative study for Enhancing Poly (methyl-methacrylate) (PMMA) Performance with Engineered Nanomaterials

Ahmed Abdelwahed Shaaban^{1*}

* ¹Associate professor of prosthodontics faculty of oral and dental medicine ,future university in Egypt ,Cairo

Correspondence: * Associate professor of prosthodontics faculty of oral and dental medicine ,future university in Egypt ,Cairo ,e-mail ahmed.abdelwahed@fue.edu.eg

Phone number:00201006147705

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ABSTRACT

Objectives:The current study was intended to evaluate and compare the effect of addition of Titanium Dioxide Nanoparticles versus Zirconium oxide nanoparticles to denture base materials regarding: impact strength and water sorption

Materials and Methods: Thirty heat-polymerized acrylic resin specimens with the dimensions of (60x8x2 mm) were prepared according to the manufacturer's instructions and divided into three groups each group 10 specimens first group was the control group , the Second group incorporated with 1.5wt% TiO₂NPs (Titanium dioxide nanoparticles) to the heat-polymerized acrylic resin powder. And the third group incorporated with 1.5wt% ZrO₂NPs (zirconium dioxide nanoparticles) to the heat-polymerized acrylic resin powder : impact strength was examined using Universal Testing Machine. A non-contact optical to compare different groups. water sorption were evaluated for all specimens. Data were statistically analyzed.

Results:for heat cured acrylic resin with Zirconium dioxide nanoparticles for flexural strength ,impact strength and water sorption was the highest value compared to Titanium Dioxide Nanoparticles

Conclusions:ZrO₂NPs nanoparticles have increased flexural strength of resins as the concentration increase. For impact strength, water sorption compared to heat cured acrylic resin reinforced with Titanium Dioxide Nanoparticles

Keywords: Polymethylmethacrylate, Nanoparticles,Titanium Dioxide Nanoparticles,Zirconium dioxide Nanoparticles

Introduction

Poly(methyl-methacrylate) (PMMA) is a widely used material due to its ease of processing, cost-effectiveness, aesthetic properties, low weight, biocompatibility, and biostability in the oral cavity. However, two significant challenges persist: the porous surface, which promotes microorganism adhesion, and weak mechanical properties leading to wear and fracture.

To address these concerns, we investigated the impact of incorporating engineered nanomaterials into the PMMA matrix. Specifically, we introduced titanium dioxide nanoparticles (TiO₂NPs) and halloysite clay nanotubes (HNTs) at concentrations

of 1% and 3% w/w. Our evaluation focused on key physical parameters: Young's modulus, surface roughness, and wettability.

Additionally, we explored the potential benefits related to reducing *Candida albicans* (*C. albicans*) colonization—the most common yeast responsible for oral infections. Our experimental results revealed dose-dependent improvements in PMMA performance after adding TiO₂NPs and HNTs. TiO₂NPs notably increased PMMA stiffness, while HNTs significantly reduced *C. albicans* colonization. These findings hold promise for enhancing PMMA's physico-chemical properties, particularly in clinical dentistry applications.

Over the past few decades, extensive research has focused on improving the physico-chemical properties of polymeric materials, including PMMA. Notably, the incorporation of engineered nanomaterials—such as nanoparticles, nanotubes, and nanofibers—into the polymer matrix has demonstrated the ability to modify material behavior¹⁻³.

These modifications depend on factors like nanomaterial type, concentration, size, morphology, and surface charge⁴⁻⁵.

For instance: Zirconium Dioxide Nanoparticles (ZrO₂NPs): These biocompatible and high-strength nanoparticles were introduced into PMMA, resulting in improved mechanical properties in a dose-dependent manner⁶. However, at higher NP concentrations, agglomeration phenomena occurred, leading to material degradation⁷.

Diamond Nanoparticles (DNPs): DNPs, known for their good thermal conductivity and hardness, were also considered for PMMA enhancement. However, challenges related to prosthesis color aesthetics limited their clinical application.

These findings highlight the potential of nanomaterials to enhance PMMA's performance, but careful consideration of concentration and other factors is crucial⁸⁻¹⁰.

Materials and Methods

Fabrication of PMMA Based Samples

Thirty heat-polymerized acrylic resin specimens, each measuring (60x8x2 mm), were prepared following the manufacturer's instructions. These specimens were divided into three groups, with each group containing 10 specimens. The first group served as the control and consisted of plain heat-polymerized acrylic. The second group incorporated 5wt% TiO₂NPs (Titanium dioxide nanoparticles) into the heat-polymerized acrylic resin powder, while the third group incorporated 5wt% ZrO₂NPs (zirconium dioxide nanoparticles). The PMMA-based specimens were obtained by manually mixing the ingredients in a glass container until a semi-liquid consistency was achieved. After a 3-minute rest period to allow the resin to reach a semi-plastic state, the mixture was poured into hard silicone molds. Subsequently, the specimens were transferred to a Pentatlon 205 machine (Effegi Brega, Sarmoto, Italy) for polymerization, which occurred over 30 minutes at a pressure of 5 atm and a temperature of 100 °C.

After curing, the PMMA specimens underwent a series of surface treatments. First, they were roughened, followed by finishing and polishing. Specifically, the surfaces were initially polished using a tungsten carbide multi-blade and then with silicone rubbers of decreasing grain size (ranging from 40 to 100 µm). These rubbers were mounted on

a rotating instrument (SILFRADENT S.R.L, S. Sofia, Italy) operating at 50,000 rpm. Subsequently, a cotton-wool brush, combined with water and pumice powder, was used for further polishing. Finally, a dry cotton-wool brush was employed along with a specialized resin polishing liquid (Dentaurum, Bologna, Italy).

Measurements

Impact strength

The impact strength was evaluated using an impact test machine (Zowek Roell Amsler /RKP 450-Germany) (Fig.1) following the Charpy method. The specimens were positioned horizontally, and the impact strength of unnotched specimens was measured in KJ/m³¹¹.

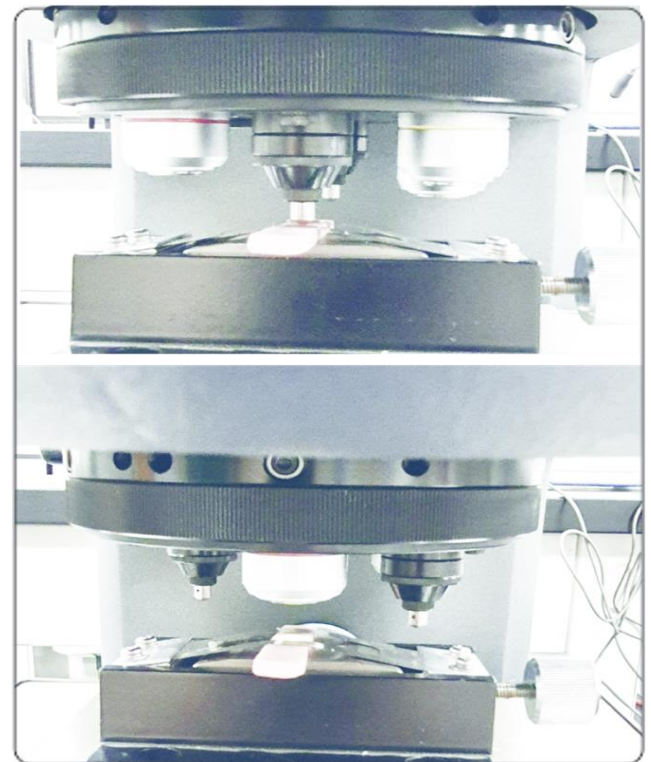


Fig 1 Measuring impact strength using testing machine

Water sorption and solubility

- Initially, the specimens were weighed (referred to as M1) using a four-digit electronic balance.
- All specimens were then immersed in distilled water and stored in Eppendorf tubes for a period of 7 days.
- After the storage period, the specimens were removed from the water, and their weights were measured again using the same electronic balance until a constant weight was achieved (referred to as M2).
- Next, the specimens were dried by placing them on filter paper. Subsequently, they were returned to

the plastic box and kept inside a desiccator containing calcium chloride at room temperature.

□ After removal from the desiccator, the specimens were weighed once more (referred to as M3) using the same electronic balance.

□ The volume (V) of each specimen was calculated.

□ Water sorption (Wsp) values and solubility (Wsl) values in $\mu\text{g}/\text{mm}^3$ were determined for each specimen using the following equations:

Water sorption (Wsp):

$$W_{sp} = VM_2 - M_3$$

Solubility (Wsl):

$$W_{sl} = VM_1 - M_3^{12}$$

RESULTS

Table 1 Regarding impact test, indicated that the highest value 3.83KJ/M3 was for PMMA with ZrO2NPs (zirconium dioxide nanoparticles) and for (1.08KJ/ M3) was for heat cured acrylic resin with TiO2NPs (Titanium dioxide nanoparticles) t test indicated significant difference between ZrO2NPs based pmma and TiO2NPs based PMMA

Regarding water sorption test, indicated the higher value .0013 $\mu\text{g}/\text{mm}^3$ was for ZrO2NPs (zirconium dioxide nanoparticles) based PMMA while for TiO2NPs (Titanium dioxide nanoparticles) based PMMA the value was .0003 $\mu\text{g}/\text{mm}^3$ (Table 1&2)

TABLE (1) Means and Standard deviations (SD) of IMPACT STRENGTH (kJ/m3) of TiO2NPs reinforced PMMA and ZrO2NPs. reinforced PMMA

Material	TiO2NPs	ZrO2NPs	T	P value
PMMA				
0.5 wt%	1.03 ^{3a} ±0.03	3.63 ^{3a} ±0.05	64.84	0.0001
1wt%	1.07 ^{3a} ±0.03	3.80 ^{3a} ±0.1	44.48	0.0001
1.5 wt%	1.08 ^{3a} ±0.028	3.83 ^{3a} ±0.05	74.68	0.0001
LSD	0.1217	0.170		

Means with different letters in one row and column are significantly different (P < 0.05).

TABLE (2) Means and standard deviations (SD) of water sorption ($\mu\text{g}/\text{mm}^3$) of TiO2NPs reinforced PMMA and ZrO2NPs. reinforced PMMA

Material	ZrO2NPs	TiO2NPs	T	P
PMMA				
0.5 wt%	0.0013 ^{3a} ±0.00005	0.0003 ^{3a} ±0.00005	20.5	<0.0001
1 wt%	0.0011 ^{3a} ±0.00005	0.0001 ^{3a} ±0.0001	15.5	<0.0001
1.5 wt%	0.0007 ^{3a} ±0.00005	0.00003 ^{3a} ±0.00005	20.1	<0.0001
LSD	0.0001	0.0002		

Means with different letters in one row and column are significantly different (P < 0.05).

With significant difference regarding ZrO2NPs (zirconium dioxide nanoparticles) based PMMA compared to control group was .011 $\mu\text{g}/\text{mm}^3$ there was significant difference regarding TiO2NPs (Titanium dioxide nanoparticles) based PMMA compared to control group was .011 $\mu\text{g}/\text{mm}^3$ there was significant difference

Discussion

Titanium dioxide nanoparticles (TiO2NPs) exhibit remarkable mechanical properties, with a modulus of elasticity around 230 GPa. These nanoparticles are effectively used to enhance the mechanical characteristics of dental materials. However, one significant drawback is their tendency to agglomerate within the material. Researchers have explored various surface modification processes to mitigate this agglomeration¹³.

In a study investigating the impact of TiO2NPs on the impact strength of heat-curing acrylic resin, it was observed that adding 1.5 wt% TiO2NPs significantly increased impact strength¹⁴. Another study demonstrated that a modified acrylic resin powder combined with 1.5 wt% TiO2NPs exhibited superior impact strength compared to conventional acrylic resin¹⁵.

Interestingly, the impact strength, transverse strength, and surface hardness of heat-cured acrylic resin were enhanced by incorporating 1 wt% TiO2NPs. However, when 1.5 wt% TiO2NPs were added, impact strength decreased due to inadequate distribution of the resin between the filling particles. On the other hand, the microhardness of the material increased, resulting in improved wear resistance and this explain the significant difference in impact strength with PMMA reinforced with ZrO2NPs with the same concentration¹⁶.

In some studies, impact strength was assessed using various testing methods. Notably, an increase in impact strength was observed at ZrO2NP concentrations of 1 wt% and 1.5 wt%. This improvement is attributed to the unique physical and high microhardness properties of ZrO2NPs.

Additionally, the incorporation of ZrO2NPs resulted in decreased water absorption and solubility. Their water-insoluble nature contributed to this effect. Furthermore, the addition of ZrO2NPs led to reduced porosity in the material, resulting in increased density. This inverse relationship between density and porosity aligns with findings from previous research but in comparison with Tio2Nps we will find more water sorption resistance because The incorporation of titanium oxide (TiO₂) nanoparticles can affect the overall water sorption properties of the material. Titanium oxide is known for its high stability and low reactivity, which generally reduces

water absorption. The distribution and concentration of TiO₂ nanoparticles within the OMA matrix can influence water sorption. A well-dispersed and adequately high concentration of nanoparticles might decrease water uptake due to improved barrier properties. TiO₂ nanoparticles can enhance the mechanical strength and potentially reduce the porosity of the composite, leading to low water absorption^{17,18}.

At the 1.5 wt% ZrO₂NP concentration, impact strength reached its maximum value. [19,20].

In a study evaluating the impact of modified nano-zirconium dioxide (ZrO₂) on heat-cured acrylic denture base material.¹⁸

Declaration

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Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. None of the authors have any relevant financial relationship(s) with a commercial interest.

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“Not applicable”

Data Availability

All data generated or analysed during this study are included in this article.

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