

## **EVALUATION OF THE PROPERTIES OF POLY-METHYL METHACRYLATE REINFORCED WITH TITANIUM DIOXIDE FOR DENTURE APPLICATION**

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### **Abstract**

Acrylic resin PMMA (Poly-Methyl Methacrylate) being utilized in the denture bases production, but its mechanical characteristics can be lacking in such role. In present work, the mechanical properties (flexural, impact, compression, and hardness) and the physical properties (thermal conductivity, thermal diffusivity, specific heat, and water absorption) of a cold cured denture base acrylic resin reinforced with various titanium dioxide concentrations have been assessed. The amount of titanium dioxide ( $\text{TiO}_2$ ) incorporated into the poly-methyl methacrylate polymer matrix ranged from (2 wt%) to (6 wt%). The obtained results revealed that all properties enhanced significantly with different concentrations of titanium dioxide compared to control specimens except that the impact property presented the opposite behavior. Furthermore, the results showed that inclusion of ( $\text{TiO}_2$ ) up to (6wt %) in PMMA matrix led to improvement magnitude of compression strength, hardness, flexural modulus, flexural strength, thermal conductivity, thermal diffusivity and specific heat which equal to (90.431 MPa, 80.45, 6.35 GPa, 135 MPa, 0.24 W/m.°C, 0.152 m<sup>2</sup>/s, and 2.084 J/kg.°C) respectively. The collected data have been statistically analysed using SPSS.

Keywords: Denture base, Polymer composites, Poly-methyl methacrylate, Statistical analysis, Titanium dioxide.

## 1. Introduction

Poly-methyl methacrylate (PMMA) resin has a combination of auspicious features, like light weight, stability in the oral environment, the ease of laboratory manipulation, inexpensive fabrication, proper aesthetic and colour-matching capability, and the deficiency of toxicity, so it is the most broadly utilized material for the fabrication of dentures [1, 2]. Nevertheless, it may not be exceptional in each feature and possess many disadvantages required to be considered owing to its destitute mechanical performance. The most popular failure of PMMA denture materials due to the lack of satisfactory resistance to fracture. Structural enhancements of the resin composition, like the filler addition, could improve its mechanical properties [3, 4]. Lately, there has been a rising tendency by mixing the ceramic fillers with the acrylic resins denture base to work as a reinforcing material.

The purpose of this addition is for obtaining a composite resin having highly suitable properties [5, 6]. The ceramic materials are known as the science and the art of creating and utilizing solid substances that possess, as their essential component, inorganic non-metallic materials. Titanium dioxide ( $\text{TiO}_2$ ) material is utilized in a broad variety of the popular and high-tech uses. It is non-toxic, chemically steady, inexpensive, and biocompatible. The particles of titanium dioxide have been employed as filler supplemented to the poly-methyl methacrylate due to their antibacterial properties and their influence upon the acrylic resins mechanical properties. Moreover,  $\text{TiO}_2$  particles are favoured in dentistry because of excellent biocompatibility, durability in addition to their desirable colour [7].

Naji et al. [7] reported the incorporation of titana nanotube to poly-methyl methacrylate to improve the flexural strength, fracture toughness and the hardness of denture base PMMA.

Alrahlah et al. [8] enhanced the nanomechanical, creep-recovery, relaxation and antimicrobial behaviors of a PMMA matrix by adding (1, 2 and 3 wt%) nano titanium dioxide to a polymer matrix. On the other hand, a decrease in the creep strain property was found.

Zidan et al. [9] enhanced significantly flexural modulus, flexural strength, hardness, and fracture toughness of the high impact PMMA resin heat cured denture base by the incorporation of  $\text{ZrO}_2$  nanoparticles at (1.5, 3, 5, 7 and 10 wt%), while the impact strength was found decreased.

Karci et al. [10] ascribed the decreased value of flexural strength at (1, 3 and 5 wt%)  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$  nanoparticles reinforcements having the nonhomogeneous particles distribution that led to the agglomeration.

Choi et al. [11] evaluated the hardness, the modulus of elasticity, and the surface roughness of various light-polymerized glaze materials, including the denture glaze materials, and pumice and high sheen paste for the PMMA denture base materials. It was found from the analysis of the scanning electron microscopy that the surfaces revealed a raised roughness for various treatments. Also, the highest hardness of the surface and the elastic modulus of elasticity obtained at silica-nanoparticle containing surface coatings.

The purpose of the present study is to assess the mechanical and physical properties of the PMMA matrix materials reinforced with different weight percentages of titanium dioxide (2, 4 and 6%) that were originally used for denture applications.

## 2. Materials and Methods

### 2.1. Specimens preparation

The poly-methyl methacrylate resin and titanium dioxide utilized in the current study were supplied from (Spofa Dental) company and (China) respectively. Test samples were prepared by combining the PMMA with  $\text{TiO}_2$  powder with various powder weight fractions (0, 2, 4 and 6 wt%) and grain sizes ( $< 25 \mu\text{m}$ ). This percentage of reinforcement was chosen randomly. The acrylic resin utilized in this study was blended according to the manufacturer's instructions (2.2 g Powder: 1 ml liquid).

The powder of titanium dioxide was combined with the acrylic resin monomer and blended via hand utilizing a stainless steel spatula for making sure that the whole powder being distributed consistently inside the resin monomer. Then, the powder of acrylic resin was supplemented to solution; also the blending was sustained for approximately 20 min until a consistent mixture was obtained.

The obtained mixtures were arranged in a rectangular mold with dimension ( $16 \times 16 \times 0.5 \text{ cm}^3$ ). After cooling, all specimens were de-moulded for separating them from mold and for the cleaning purpose.

All tests were achieved at the room temperature ( $23 \pm 2$ ) beyond the whole processes of finishing and polishing and soaking the samples in the distilled water at a temperature of ( $37 \pm 1^\circ\text{C}$ ) for (48 hour) for removing any remaining monomer, releasing the remaining stress, and ensuring that the denture base materials stay in a semi-oral surrounding. Three specimens were fabricated for each filler ratio.

### 2.2. Characterization of the prepared composites

#### 2.2.1. Flexural test

The flexural modulus and flexural strength of the specimens of composite were assessed according to ASTM D790-03 utilizing a Three-Point Bend Test (width (b)  $\sim 13 \text{ mm}$ , thickness (h)  $\sim 5 \text{ mm}$  and length  $\sim 160 \text{ mm}$ ) in a universal testing machine at a (5 mm/min) across head speed (strain rate), and the applied load was equal to (50 kN) till the occurrence of the specimen breakage.

#### 2.2.2. Impact test

The Izod impact is well-defined as the required kinetic energy for beginning the fracture and continuing the fracture till the specimen breakage. In the impact test, the specimens might be with or without notch. The impact test was performed by using a machine (type XJU-22 Izod impact testing machine) according to (ISO-180). The specimens have dimensions (width (b)  $\sim 10 \text{ mm}$ , thickness (h)  $\sim 5 \text{ mm}$  and length  $\sim 80 \text{ mm}$ ). Unnotched Izod impact is a Single-Point Test for measuring the resistance of material to the impact from a swinging pendulum, in such test, the specimen was first fastened at its one end via fixing it upon the device base, then positioned vertically as a cantilevered beam, and finally it was broken at a (5.5 J) impact energy of pendulum and at the velocity of impact around (3.5 m/s). After that, the pendulum was released for impacting the specimen, and then the energy quantity needed for breaking the specimen was registered. Eventually, three specimens were tested for each ratio, and the average result of these specimens was taken. The impact strength and fracture toughness properties were obtained from this test.

### 2.2.3. Compression test

This test is performed to determine the compressive force or the material resistance of crush and the material capability for retraining beyond a definite compressive force exerted and also kept over a specified time. The extreme stress that the material can withstand over a time beneath a constant load, or a progressive load was obtained. The compressive stress and strain were computed and drawn as a Stress-Strain diagram utilized for determining the compressive strength. This test is achieved according to (ASTM D695-85) with dimensions (width (b) ~5 mm, thickness (h) ~5 mm and length ~10 mm)

### 2.2.4. Hardness test

The hardness test was performed by using hardness (Shore D) according to (ASTM DI-2242) with dimensions (diameter (d) ~40 mm, thickness (h) ~5 mm). For each specimen, the hardness assessments were registered from various areas of each specimen and an average of five readings was calculated.

### 2.2.5. Thermal test

The thermal conduction of composite materials was measured by using a hot disk machine. Additionally, the thermal diffusivity and the specific heat were assessed. Thermal test is highly necessary for denture applications for the purpose of food sensitivity through mastication process. The specimens for thermal test have the same dimensions of hardness test.

### 2.2.6. Water absorption

The water absorption mechanism is clarified as the straight water uptake and flow via the capillary and the transportation along the reinforcement-matrix interface [12]. The percentage of water absorption was computed implementing the base of Archimedes. This test is achieved according to (ASTM D 570-98) with dimensions (diameter (d) ~50.8 mm, thickness (h) ~5 mm).

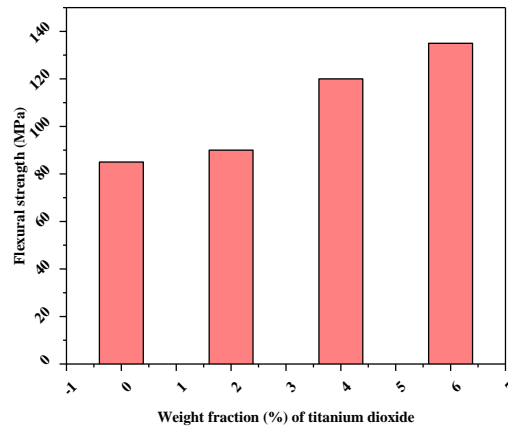
## 3. Statistical Analysis

The data of properties were collected, tabulated, and the investigational data statistical analysis was conducted utilizing (SPSS 22) software. The outputs were compared via the analysis of variance (one-way ANOVA) pursued via Tukey test. These outputs were regarded statistically significant for ( $p < 0.05$ ) [13].

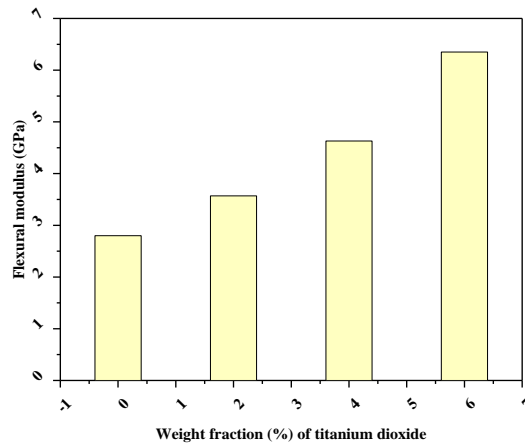
## 4. Results and Discussions

### 4.1. Flexural results

Flexural properties of manufactured composites are presented in Figs. 1 and 2; it was clear that the flexural strength of composite specimens was closely correlated with the content of  $\text{TiO}_2$ . The enhancement of strength can be attributed to the interfacial strength between particles and matrix created by crosslink bonding covering the particles fillers which prevents the crack propagation. The behaviour of the obtained results agrees with [14]. Obviously, higher  $\text{TiO}_2$  content resulted in higher flexural strength when the  $\text{TiO}_2$  content was in the range (0-6%).



**Fig. 1. Flexural strength results with different wt% of titanium dioxide.**



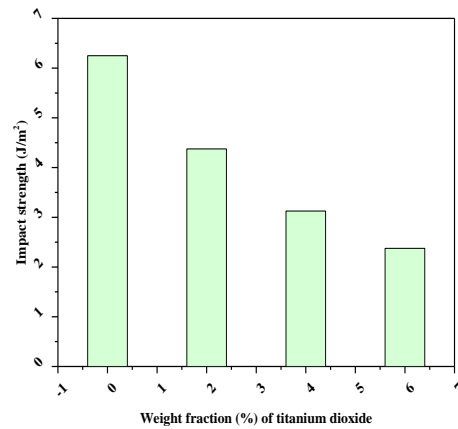
**Fig. 2. Flexural modulus results with different wt% of titanium dioxide.**

The flexural modulus results have a similar behavior as flexural strength. It can be seen that the increase in the amount of  $\text{TiO}_2$  from (0) to (6%) resulted in an increase in the flexural modulus for the composite specimens. The high  $\text{TiO}_2$  elastic modulus and the vigorous bond between fillers and matrix led to an obstruction of the crack initiation and propagation beneath the load of failure; which led to increase the flexural modulus. These results were confirmed with references [6]. The flexural modulus of  $\text{TiO}_2$ /PMMA composites with the  $\text{TiO}_2$  content of 2%, 4% and 6% increased by approximately (27.5%, 65.36% and 96.79%), respectively. The flexural modulus of 6% $\text{TiO}_2$ /PMMA composites was higher than that of the other composite specimens. The flexural strength and the elastic modulus of specimens increased gradually, and the amount of the differences of  $\text{TiO}_2$  groups was statistically significant ( $p < 0.05$ ).

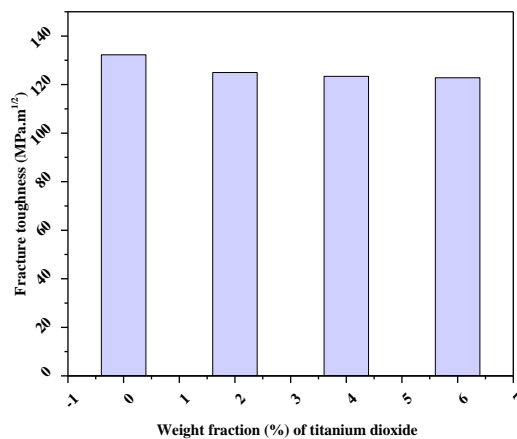
#### 4.2. Impact results

The variation of impact properties of the composite specimens with  $\text{TiO}_2$  content is elucidated in Figs. 3 and 4. It was a remarkable fact that the impact properties of

specimen's reinforcement with  $\text{TiO}_2$  were relatively lower than the neat PMMA. This is attributed to the micrometre particles, possessed large diameter, so, with the large diameter, the specific surface area of particles would decrease, then lead to the weakening of the interaction between the particles and the polymer matrix, and finally would result in the decrease of the impact strength and fracture toughness [15]. Moreover, the values of the impact strength and fracture toughness were statistically different between the groups ( $p < 0.05$ ).



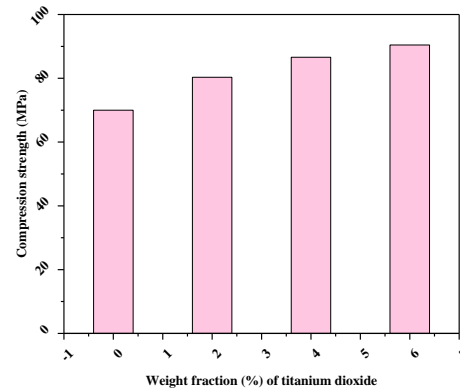
**Fig. 3. Impact strength results with different weight fraction % of titanium dioxide.**



**Fig.4. Fracture toughness results with different weight fraction % of titanium dioxide.**

### 4.3. Compression results

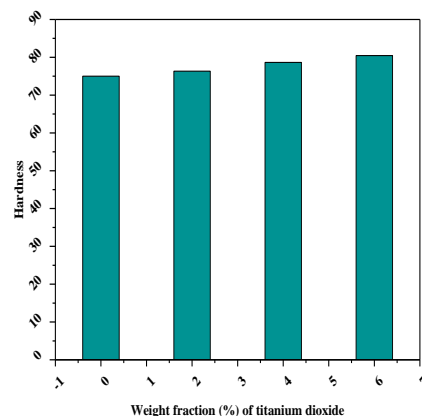
The variation of the compression strength as a function of particles content is manifested in Fig. 5. This figure illustrates that the compressive strength of  $\text{TiO}_2$ /PMMA composites improved compared with the neat PMMA, because the fillers particles work at the beginning on impeding the cracks movement, where that lead to an increase in compression strength value [16, 17]. The value of compression strength was statistically different between the groups ( $p < 0.05$ ).



**Fig. 5. Compression strength results with different weight fraction % of titanium dioxide.**

#### 4.4. Hardness results

Figure 6 displays the hardness value of the neat PMMA and composite specimens. It is obviously apparent that there is a substantial increase in the hardness of PMMA with an increment of the  $\text{TiO}_2$  percentage reinforcement in the PMMA composite correlated to the pure PMMA due to the homogenous distribution of the hard titanium dioxide particles bonded together and the improvement of the resistance to plastic deformation, in addition to the enhanced bonding between the particles and the polymer matrix [18, 19]. Moreover, the value of hardness was statistically different between the groups ( $p < 0.05$ ), as evinced in Fig. 6.

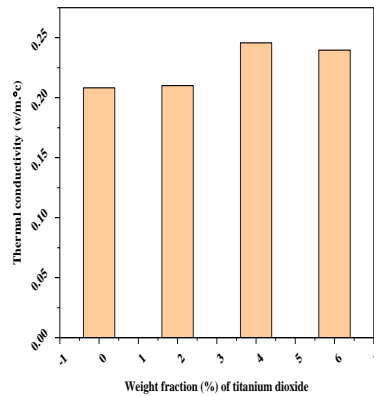


**Fig. 6. Hardness results with different weight fraction % of titanium dioxide.**

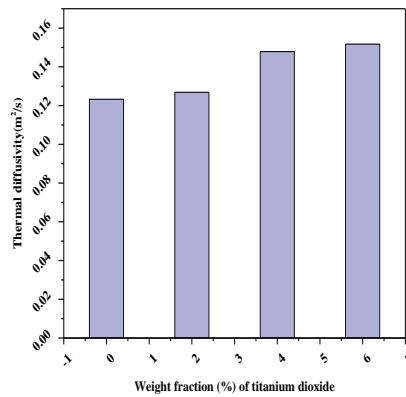
#### 4.5. Thermal results

Figures 7, 8 and 9 demonstrate the thermal conductivity, thermal diffusivity and specific heat curves for composite specimens. It was clearly from these figures by mixing the  $\text{TiO}_2$  particles with the PMMA matrix, the produced composite displayed a marked improvement in specific heat, thermal conductivity, and thermal diffusivity. Thermal properties were found to increase with the increased weight fraction of filler content, this is because the porosity of the pure sample is

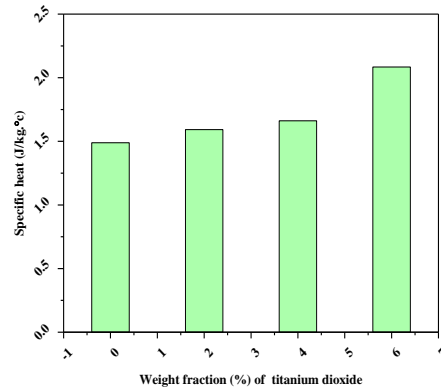
greater than the other samples which are doped with  $\text{TiO}_2$  and also because the thermal properties of filler are larger than PMMA matrix [20]. The thermal properties of specimens were statistically non-significant ( $p > 0.05$ ).



**Fig. 7. Thermal conductivity results with different weight fraction % of titanium dioxide.**



**Fig. 8. Thermal diffusivity results with different weight fraction % of titanium dioxide.**

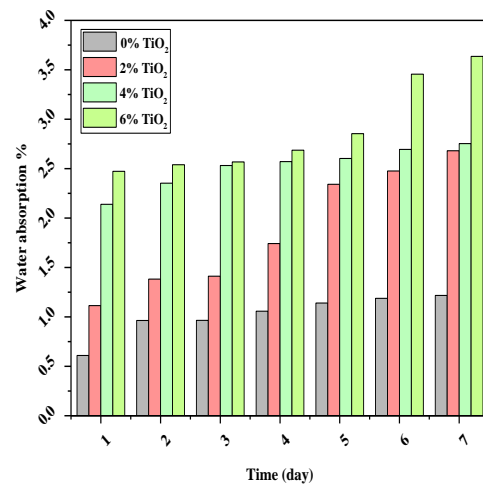


**Fig. 9. Specific heat results with different weight fraction % of titanium dioxide.**



#### 4.6. Water absorption results

The biomaterials are usually exposed to the steam sterilization cycles; so, a high withstanding to moisture being needed. For such consideration, the water absorption kinetics of the resultant composites was discovered, and the outputs are depicted in Fig. 10. An increasing rise of such characteristic at a raising time can be noted for the whole specimens after one week. The addition of  $\text{TiO}_2$  leads to raise the water absorption results. This is attributed to the fact that the  $\text{TiO}_2$  particles being much more hydrophilic than polymer; therefore, the composites hydrophilicity would increase with the increasing loading of particles. Also, the particles dispersion loading degree influences the barrier characteristics, known that the small clusters existence can cause favoured paths for the diffusion of water [21]. Moreover, the water absorption value was statistically different between the groups ( $p < 0.05$ ) for each time of immersion.



**Fig. 10. Water absorption results with different weight fraction % of titanium dioxide.**

#### 5. Conclusions

From the above results, it can be concluding the following:

- $\text{TiO}_2$ -PMMA composites with varying  $\text{TiO}_2\%$  have been successfully fabricated.
- The experimental outputs manifested that the mechanical and physical properties can be tuned via the percentage of  $\text{TiO}_2$ .
- The whole properties were enhanced after adding titanium dioxide except that the impact property has an inverse behavior.
- The greater enhancement has been attributed to the good desparation of  $\text{TiO}_2$  and a good interaction between  $\text{TiO}_2$  and PMMA.
- The 6%  $\text{TiO}_2$ -PMMA demonstrated the superior properties.
- The resultant composites with high mechanical and physical properties are benefit for denture application.

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