



## Effect Of Nanoparticle Addition On Polymethylmethacrylate Resins

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### Abstract

Polymethylmethacrylate (PMMA) is the most commonly used material in the manufacture of prosthetic base materials because it has a combination of convenient properties, such as easy laboratory manipulation, ease of finishing and polishing, light, economical, stable performance, proper aesthetics and color matching ability and non-toxic. However, the polymethylmethacrylate resin denture base material is not ideal in all respects. This article reviews the development of acrylic prosthetic base resin in the last few years. Special attention is paid to the effect of nanoparticles with the properties of polymethylmethacrylate. The review, in addition to scientific reviews, reports, and abstracts, was based on studies on the effect that nanoparticles were PMMAs in 2000 and 2019. The findings of the review may be observable, do not have the ideal prosthetic base material, but with some modifications, the property of PMMA can be improved by the addition of nanoparticle.

**Keywords:** Polymethylmethacrylate; Nanoparticles; Titanium Dioxide Nanoparticles; Zirconium Oxide Nanoparticles; Silver Nanoparticles; Zinc Oxide Nanoparticles; Seashell nanopowder

### Abbreviation

PMMA: Polymethylmethacrylate; TiO<sub>2</sub>NPs: Titanium dioxide nanoparticles; ZrO<sub>2</sub>NPs: Zirconium oxide nanoparticles; AgNPs: Silver nanoparticles; ZnO: Zinc oxide nanoparticles; C.Albicans: Candida Albicans.

### Introduction

Polymethylmethacrylate has been widely used as removable denture base materials, orthodontic appliance, facial prostheses, and temporary tooth restorative materials [1]. PMMA has advantages such as ease manipulation, ease in finishing and polishing, light in weight, economical, stable performance intra-oral tissues, having good aesthetic and color matching ability, and free from toxicity [2-4]. The PMMA is not ideal in all aspect, although it has such good properties. PMMA has a poor surface/mechanical properties and limited antimicrobial properties [5]. Because PMMA has poor impact strength, fractures often occur in prostheses. Therefore, it is important to increase impact strength to prevent prosthetic frac-

tures [6,7]. Various fillers, metal oxides, and carbon graphite fibers are incorporated into the composition to solve these problems and to increase the mechanical properties of the resin [2,8]. One of the most promising approaches recently used to overcome these disadvantages is to incorporate various nanoparticles into the PMMA to act as the reinforcing material [1]. According to the results of the studies, the properties of the polymer nanocomposites have proven to be dependent on the nanoparticle [9-11]. The type of incorporated nanoparticles, shape, size, concentration and interaction of the nanoparticles with the polymer matrix determine the properties of the polymer nanocomposite [12]. The modulus, strength, ductility, antimicrobial properties and aesthetic properties of PMMA have been improved by the addition of nanoparticles [13]. The mechanical properties of polymer nanocomposites depend on the dispersion and adhesion of the fillers between the filler and matrix. Surface treatment with silane coupling agents is applied to the fillers to increase this compatibility between the filler and the matrix [14,15]. The homogeneous distribution and good adhesion

of nanoparticles in the resin matrix increase the flexural properties of the polymer nanocomposites [14]. Although there are various nanoparticles; in the literature nanoparticles such as aluminum oxide ( $Al_2O_3$ ), zirconium oxide ( $ZrO_2$ ), titanium dioxide ( $TiO_2$ ), zinc oxide ( $ZnO$ ), silicon dioxide ( $SiO_2$ ) and silver ( $Ag$ ) has often been used [4,16,17]. Nanoparticles are characterized by their small size, large surface area and intense interface interactions with the polymer matrix. The nanoparticles can thus enhance the physical and optical properties of the polymer matrix. In addition, they can provide resistance to environmental stress, cracking and aging [17].

### Zirconium Oxide Nanoparticles

Zirconium oxide nanoparticles ( $ZrO_2$ NPs) have recently been noted for their excellent biocompatibility. However, they are thought to be less likely to change aesthetics than other metal oxide nanoparticles because they are white in color [2].  $ZrO_2$ NPs are not only biocompatible materials but also have good wear and corrosion resistance. In addition to these features,  $ZrO_2$ NPs have good toughness and mechanical strength properties [18-20].  $ZrO_2$ NPs are often incorporated into polymers to mechanically reinforce. In order to eliminate the possibility of aggregation and increase the compatibility with the polymer matrix, silane coupling agents are applied to the surface of  $ZrO_2$ NPs [14,15]. The stresses resulting from good dispersal of  $ZrO_2$ NPs are transferred from weak PMMA matrix to strong nanoparticles [20].

Increased contact between teeth during chewing causes wear on the prosthetic surfaces. Low wear resistance limits the use of PMMA [21]. Mohammed and Mudaffar investigated the effect of modified zirconium oxide nanoparticles on abrasive wear resistance of polymethylmethacrylate. Abrasive wear was tested using different denture cleaning materials. There was an increase observed in abrasive wear resistance at 3 wt% and 5 wt% nano  $ZrO_2$  concentrations. The reduction in abrasive wear is thought to be due to the physical properties of  $ZrO_2$ NPs. In addition to these results, water absorption and solubility decreased, and this was attributed to the fact that  $ZrO_2$ NPs were water insoluble. As a result of the addition of  $ZrO_2$ NPs, porosity has also decreased. The addition of  $ZrO_2$ NPs to the material increased the density and decreased porosity [22]. This relationship between density and porosity is consistent with the study conducted by Laura, *et al.* [13].

Ahmet and Ebrahim investigated the effect of  $ZrO_2$ NPs (four concentrations 1.5 wt%, 3 wt%, 5 wt%, and 7 wt%) on the flexural strength, fracture toughness and hardness of heat-polymer-

ized acrylic resin. The control groups had the lowest mean flexural strength values. PMMA samples containing 7 wt%  $ZrO_2$ NPs had the highest mean flexural strength values. The test results show significant improvement in tensile strength values of PMMA samples fortified with  $ZrO_2$ NPs. In addition, it was observed that hardness values increased in all groups compared to the control group [3]. In addition to these results, fracture toughness value at the concentration of 3 wt%  $ZrO_2$ NPs reached the maximum. When the 3 wt% concentration was exceeded, there was no significant improvement in the fracture toughness value. This is likely to be due to the full saturation of the polymer matrix with  $ZrO_2$ NPs [3,23].

Gad, *et al.* investigated the effect of  $ZrO_2$ NPs (three concentrations 2.5 wt%, 5 wt%, and 7.5 wt%) on the translucency and tensile strength of the PMMA denture base material. According to the results of the study, mean tensile strength values in all test groups were higher than the control group. Maximum tensile strength was observed in the group containing 7.5 wt%  $ZrO_2$ NPs. Translucency values were lower in the experimental groups than in the control groups. The translucency values of the experimental group containing 2.5 wt%  $ZrO_2$ NPs were higher than the 5 wt% and 7.5 wt%  $ZrO_2$ NPs. In other words, as the concentration of  $ZrO_2$ NPs increased, the translucency values were adversely affected [20].

The rough surface may affect tissues health due to microorganism accumulation. Surface roughness stimulates the adhesion and proliferation of *Candida albicans*, which are important in the pathogenesis of prosthetic stomatitis. The increase in the amount of *Candida albicans* may cause an increase in the incidence of caries, gingival and periodontal diseases and increased stomatitis in the oral tissues adjacent to the material [24]. Gad, *et al.* investigated the effect of  $ZrO_2$ NPs on *C.albicans* adhesion of cold-cured acrylic resin. As a result of the study, it was reported that *C.albicans* adhesion and proliferation were decreased in  $ZrO_2$ NPs added samples [24].

Ihab and Moudhaffar investigated the effect of  $ZrO_2$ NPs on the impact strength, surface roughness, transverse strength, radiopacity of heat cured acrylic denture base material. As a result of this study, it was observed that the impact and transverse strength values increased in the group containing 5 wt%  $ZrO_2$ NPs. However, this increase was not observed in the group containing 7 wt%  $ZrO_2$ NPs. They reported that this was due to the agglomeration of  $ZrO_2$ NPs. In addition, the addition of modified  $ZrO_2$ NPs has been reported to be associated with an increase in radiopacity [25].

### Titanium dioxide nanoparticles

Titanium dioxide nanoparticles (TiO<sub>2</sub>NPs) have superior mechanical properties, the modulus of elasticity is around 230 GPa. The use of TiO<sub>2</sub> to improve the mechanical properties of dental materials is highly effective, but agglomeration within the material is an important disadvantage. Various processes can be applied to the TiO<sub>2</sub> surface in order to eliminate agglomeration [9]. Titanium dioxide nanoparticles have various good properties such as antimicrobial, cheap, biocompatible, white color, chemically stable, free toxicity and corrosion resistant. In the literature, the addition of TiO<sub>2</sub>NPs to the polymeric material has been shown to affect the electrical, optical, chemical and physical properties of the hybrid material [11,26].

TiO<sub>2</sub>NPs have proved to exhibit antimicrobial properties, because of TiO<sub>2</sub>-induced photocatalytic production of cytotoxic oxygen radicals [27]. As a result of doping with metal or metal oxides to TiO<sub>2</sub> nanoparticles, the photocatalytic activity of TiO<sub>2</sub> nanoparticles has been improved and consequently, the disinfection effect has increased [28].

Studies have shown that TiO<sub>2</sub>NPs are effective against various microorganisms such as *Candida albicans*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli*, *Lactobacillus acidophilus*. Due to their antimicrobial properties, TiO<sub>2</sub>NPs have been added to various biomaterials [11,29-31].

In their study, Alrahlah and Fouad reported that antimicrobial behavior of PMMA increased significantly by decreasing bacterial adhesion with increasing TiO<sub>2</sub> ratio. PMMA groups were compared at concentrations of 0, 1 wt% and 3 wt% containing TiO<sub>2</sub>NPs. As the concentration of the nanoparticles increased, the number of adherent *P. aeruginosa* was reported to decrease [32].

Moslehifard and Shirkavand investigated the effect of TiO<sub>2</sub>NPs (three concentrations 0.5 wt%, 1 wt%, 2 wt%) on the tensile strength of heat-curing acrylic resin. The researchers observed that the addition of 1 wt% TiO<sub>2</sub> nanoparticle increased tensile and impact strength but adversely affected its color [33].

Ghahremani, *et al.* showed that color modified acrylic resin powder in combination with 1 wt% TiO<sub>2</sub>NPs had higher tensile and impact strength than the conventional acrylic resin [34].

According to the results of another study, it was observed that the impact strength, transverse strength, and surface hardness values of heat cured acrylic resin were increased by 3 wt% TiO<sub>2</sub>NPs.

This may be due to the increase of the connection between the nanofillers and the matrix as a result of the particle size reduction. In addition, water sorption and solubility are reported to decrease [35].

Sodagar, *et al.* found that 0.5 wt% and 1 wt% of TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles were added to PMMA and the mechanical properties of the material were affected negatively. As the TiO<sub>2</sub> concentration increased, the flexural strength values were decreased. These findings indicate that TiO<sub>2</sub> nanoparticles negatively affect the degree of conversion that occurs in PMMA and leads to an increase in the level of unreacted monomer [11].

Zhang, *et al.* investigated the effect of TiO<sub>2</sub>NPs (four concentrations 1 wt%, 3 wt%, 5wt%, and 7 wt%) on the on tribological behavior of PMMA. The mean tensile strength of the PMMA group without nanoparticle was 98 MPa. TiO<sub>2</sub>NPs added PMMA groups have been reported to increase the mean tensile strength values. The most ideal tensile strength value was found in the addition of 3% TiO<sub>2</sub>NPs. The results also show that the addition of TiO<sub>2</sub>NPs increases the wear resistance. Furthermore, the surface of the nanoparticle added group is reported to be smoother [36].

M. A. Ahmed, *et al.* investigated the effect of TiO<sub>2</sub>NPs (1 wt% and 5 wt%) on the flexural strength, impact strength, and microhardness of two different types of heat-polymerized acrylic resin. As a result of the study, it was reported that the flexural strength values decreased and the microhardness values increased with the addition of TiO<sub>2</sub>NPs. The highest impact strength was observed as a result of the addition of 1 wt% TiO<sub>2</sub>NPs. However, it was observed that the decrease in impact strength values caused by the addition of 5 wt% TiO<sub>2</sub>NPs is due to the fact that the resin cannot be distributed between the filling particles. The addition of 5 wt% TiO<sub>2</sub>NPs resulted in an increase in the microhardness of the material. Increased value of microhardness provides higher wear resistance. It has also been reported that changes in the color of acrylic occur when the TiO<sub>2</sub>NPs concentration exceeds 5 wt% [37].

### Silver nanoparticles

Silver nanoparticles are generally preferred because of their antimicrobial properties. Silver nanoparticles show antimicrobial effects on many microorganisms such as *Streptococcus mutans*, *Staphylococcus aureus*, and *Candida albicans* [38-40].

Li, *et al.* investigated the effect of AgNPs ( 1 wt%, 2 wt%, 3wt%, 5wt%) on the *Candida albicans* adhesion and biofilm formation of heat-polymerized acrylic resin. As a result of the study, it was

reported that *C. Albicans* biofilm formation decreased with an increasing amount of AgNPs. Biofilm formation decreased at a concentration of 5 wt%, but no effect was observed at lower concentrations [41].

Baki., *et al.* investigated the thermal and chemical effects of silver particles on PMMA. According to the results of this study, the use of 0.8 wt% and 1.6 wt.% AgNPs reduced the flexural strength and elastic modulus of microwave-polymerized acrylic resin. In addition, the glass transition temperature has been decreased by the addition of AgNPs into PMMA [42].

In the study conducted by Sodagar., *et al.* it was concluded that the silver nanoparticles had a negative effect on the flexural strength of PMMA [43].

Ghafari., *et al.* investigated the effect of AgNPs concentrations 5 wt% on tensile strength. As a result of the research, it has been reported that the tensile strength decreased in the samples participating in AgNPs [44].

Hamedi Rad., *et al.* investigated the effect of adding 5 wt% AgNPs into PMMA. Studied the changes in thermal conductivity, compressive strength and tensile strength values of PMMA. According to the results of this study, an increase in thermal conductivity and compressive strength values, and a decrease in tensile strength values were reported. In addition, they reported a brownish discoloration of the prosthesis as a result of the addition of 5% AgNPs [38].

Koroglu., *et al.* investigated the effects of adding different concentrations of AgNPs (0.3 wt%, 0.8 wt%, and 1.6 wt %) into conventional heat-polymerized acrylic resin and microwave-polymerized acrylic resin. The transverse strength and elastic modulus of microwave-polymerized acrylic resin containing 0.8% and 1.6 wt.% AgNPs decreased. However, these values have not changed as a result of the addition of AgNPs to the conventional heat-polymerized resin group. The addition of AgNPs had no effect on impact strength. The highest impact strength was observed in the conventional resin group, which was not added to AgNPs. The lowest impact strength was observed in the microwave-resin group with 0.8 wt% AgNPs. The highest flexural strength and elastic modulus values were observed in the microwave polymerized resin group with the addition of 0.3 wt% AgNPs. In both groups, the addition of AgNPs decreased the glass transition temperature [45].

Casemiro., *et al.* investigated the effect of the addition different amount of silver-zinc zeolite on the antimicrobial activity, flexural

and impact strength of heat-polymerized acrylic resin and microwave-polymerized acrylic resin. As a result of the study, it has been reported that the flexural strength and impact strength significantly decreased. In addition, antimicrobial properties have been reported to increase. It is estimated that the decrease in these values will adversely affect the clinical performance of the prostheses and the possibility of fracture in the prostheses [46].

### Zinc oxide nanoparticles

In a study by Salahuddin., *et al.* PMMA was reinforced with ZnONPs and nanotubes. As a result of the study, it was shown that the mechanical and thermal properties of the material were improved. As a result of the addition of ZnO nanotubes, it was observed that the impact strength increased and the flexural strength value increased as a result of the addition of ZnO nanoparticles. It has also been reported that the addition of 0.2-0.4 wt% ZnO increases the flexural strength but when this ratio is 0.8-1 wt%, the flexural strength decreases. It has also been shown that nanocomposites have higher thermal stability than pure PMMA [8].

Cierech., *et al.* investigated the effect of ZnONPs of PMMA. As a result of the study, the color of PMMA was slightly white. However, this bleaching was both clinically and aesthetically acceptable. Furthermore, there was no significant difference in the results of roughness between nanocomposite and pure PMMA [47].

Kamonkhantikul., *et al.* investigated the effect of silanized zinc oxide nanoparticles (1.25 wt%, 2.5 wt%, and 5 wt%) on the antifungal, optical, and mechanical properties of heat-polymerized acrylic resin. The nanoparticle surfaces were modified to prevent the possibility of aggregation. The maximum *C.albicans* reduction was observed in the group containing 5% silanized particles. When the silanized and nonsilanized groups containing the same amount of nanoparticles were compared, it was reported that *C.albicans* formation was reduced in the silanized group. Increased contact between silanized particles and *C.albicans* may increase the antifungal effect. Among the groups of nonsilanized, the antifungal effect was observed only in the group containing 5% nonsilanized particles. Higher flexural strength values were observed in silanized groups. In addition, the addition of ZnONPs has been reported to cause discoloration [48].

### Seashell nanopowder

Seashells with the natural ceramic structure are similar to human bone and tooth structure. Karthick., *et al.* evaluated the hard-

ness and tribological properties of the PMMA reinforced with seashell nanopowder. They concluded that tribological performance was improved considerably at 12 wt% seashell nanopowder content. The maximum microhardness value was observed in the presence of 12 wt% seashell nanopowder [21].

## Conclusion

Nanoparticles have widespread use due to their superior properties and are being investigated extensively in recent years due to their advantages. However, more research and clinical studies are required for the use of nanotechnology for oral health. Long-term antimicrobial, toxic, physical and clinical effects of nanoparticles on PMMA should be investigated in further studies. Future discoveries would probably be that the antimicrobial effects of these nanoparticles would be at the maximum level and their toxicities would be minimal.

## Conflict of Interest

We have no conflict of interest to declare.

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