

Recent Advancement to Improve the Properties of Poly (Methyl Methacrylate) (PMMA) with Addition of Filler, Nanofiller and Fibers: A Review

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ABSTRACT

Background: Poly (methymethacrylate) (PMMA) is still the most predominantly used denture base material because of its many characteristics such ease in processing, stability in oral environment, lightweight, excellent aesthetic properties, low cost, low water sorption and can easily be rechanged and repaired its shape. But, it has certain drawbacks like residual monomer allergy, low modulus of elasticity, low impact strength, low flexural strength, polymerisation shrinkage, porosity, crazing, warpage. This paper reviews reinforcement of poly(methyl methacrylate) (PMMA) acrylic denture base resin. The review is based on scientific reviews, papers, and abstracts, as well as studies concerning the effect of additives, fibers, fillers, and reinforcement materials on PMMA, published between 1974 and 2019. Many studies have reported improvement of PMMA denture base material with the addition of fillers, fibers, nanofiller, and hybrid reinforcement. However, , most of the studies, without bioactivity and clinical implications, were limited to in vitro work. There is no ideal denture base material, but with some modifications, especially with the addition of silanized nanoparticles and a hybrid reinforcement system, the properties of PMMA could be improved.

Keywords: Reinforcement, denture base, PMMA, nano particle, fibers, zirconia.

INTRODUCTION

History of complete dentures back to 700 BC, however complete dentures are constructed from several materials for instances wood, bone, rubber and ivory. The polymers such as cellulose plastics, poly(vinyl chloride) and vinyl acetate became used since 1900's. However, the Poly (methylmethacrylate) (PMMA) material used as denture base, material for the first time in 1937 by Walter Wright and Vernom Brothers in Philadelphia. PMMA became so prevalent in 1940's.^{1,2} PMMA is still the most predominantly used denture base material because of its many characteristics such as ease in processing, stability in oral environment, lightweight, excellent aesthetics properties, low cost, low water sorption

and can easily be rechanged and repaired its shape.^{1,2} But, it has certain drawbacks like residual monomer allergy, low modulus of elasticity, low impact strength, low flexural strength³, poor conductor of heat, high coefficient of thermal expansion, polymerisation shrinkage, porosity, crazing, warpage, poor adhesion to metal and porcelain and requirement of mechanical retention.⁴ Thus, to overcome these drawbacks, there has been much new advancements to improve the properties of PMMA. PMMA have been reinforced using different materials to improve its physical and mechanical properties.

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Many materials such as fibers, fillers and nanofillers are incorporated into PMMA with the goal of enhancing the properties of PMMA. This paper reviews different types of fibers and fillers added to PMMA denture base resin and to evaluate their effect on the physical and mechanical properties.

DISCUSSION

Many materials are suggested to enhance the properties of denture base resin such as fillers, nano fillers and fibers (Table 1).

Table 1: List of filler, nanofillers and fibers used to reinforce poly (methylmethacrylate) (PMMA)

Additives	Modification
Fillers and nanofillers	
Metal oxides	Alumina (Al_2O_3 , Al_2O_3 NPs, Silane treated Al_2O_3) Zirconia (ZrO_2 , ZrO_2 NPs, Silane treated zirconia NPs) Titanium (TiO_2 , TiO_2 NPs)
Noble metals	Silver (Ag) NPs Gold (Au) NPs Platinum (Pt) NPs Palladium (Pd) NPs
Silica based	Glass flake Mica SiO_2 Surface treated silica
Fiber	Glass fiber Silanized glass fiber Aramid Nylon Polyethylene Polypropylene
Hybrid reinforcement	Hybrid fibers Metal oxides and ceramics Fiber and fillers

Fillers and Nano fillers

Several studies have been conducted on the use of fillers (Table 2) to reinforce denture base resin, and their properties have been significantly improved.

Poly (methylmethacrylate) (PMMA) reinforced with metal oxides resulted in the improvement of the physical and mechanical properties of the denture base material. Patient's sensation of hot and cold stimuli was also improved.⁵⁻⁷ Recently, it has been suggested to incorporate nanofillers (Table 2) to improve PMMA properties. The high surface area, fine size, and homogenous nanofillers distribution enhanced the thermal properties of PMMA.⁶⁻⁸ The properties of resin reinforced by nanofillers depend on the size, shape, type, and concentration of the added particles.⁸

Metal oxides

Alumina (Al_2O_3)

Several studies found that, reinforcing PMMA with aluminum increased the flexural strength, impact strength, tensile strength, compressive strength, surface hardness, and thermal conductivity of the resin.^{5-7,9-16} Significant decrease was seen in warpage after addition of aluminium to PMMA. On the other hand, several research, found that adding aluminium decreases PMMA's Impact and tensile strength.^{11,17} Due to stress concentration around the embedded metal and its poor adhesion to the polymer, the resin was weakened.

However, several methods have been suggested to improve the bond between the acrylic resin and metal surface, such as sandblasting, silanization, and metal adhesive resins.⁷ Treating aluminium particles with silane coupling agent [3-(Trimethoxysilyl) propyl methacrylate (TMSPM)] significantly increased the wear resistance and the compressive, flexural, and tensile strength of reinforced denture base resin.^{5,18,19}

Surface roughness and water sorption were not significantly changed with aluminum-reinforced denture resin.^{11,17} However, one study found a significant decrease in water sorption and solubility after addition of Al_2O_3 ⁶ and an increase in water sorption was found by another study.¹¹

The disadvantage of aluminium-reinforced PMMA is discoloration of the resin, which limits its use to areas where it is not visible.²⁰ Although thermal conductivity was significantly increased on addition of Al_2O_3 to PMMA, there was no significant change was seen in flexural strength values of PMMA.¹³

Zirconia (ZrO₂)

Several studies found that, there is significant increase in flexural strength of PMMA on incorporating zirconia (ZrO₂) fillers.^{6-14,17-24} However, there has been a slight decrease in flexural strength; this may result from clustering of the particles within the resin, which weakened the material.²⁵ In addition, incorporating ZrO₂ significantly increased the impact strength, tensile strength, fracture toughness, and hardness of PMMA.^{6,22,26,27} Also, addition of ZrO₂ significantly increased the thermal conductivity of PMMA.¹³ It was found that adding ZrO₂ significantly decreased the water sorption and solubility of PMMA.⁶ It was suggested that adding zirconia NPs improve the mechanical properties of PMMA.^{28,29} PMMA reinforced with zirconia NPs increased its impact strength, flexural strength, compressive strength, fatigue strength, fracture toughness and hardness.^{28,30-33} In addition, it may have an antifungal effect and may play a preventive role in patients susceptible to fungal infections.³⁴ Safi et al,³⁵ studied the effect of adding zirconia NP on the color properties of PMMA and found no noticeable changes in color.

A silane coupling agent was used to improve the bond strength between zirconia NPs and PMMA because poor wettability between fillers and the resin matrix reduced improvement of the physical and mechanical properties of PMMA. It resulted in increased flexural strength and impact strength of acrylic resin, but its tensile strength was not improved. However, silanized zirconia NPs improved the tensile strength, fatigue strength, hardness of PMMA. While, its porosity, water sorption, and solubility decreased.^{27,35-38}

Titanium (TiO₂)

Several studies found that adding TiO₂ particles could improve the flexure strength, impact strength, fracture toughness, hardness and thermal conductivity of PMMA.^{6,13,22,39-41} In addition, a significant decrease in water sorption and solubility were found upon addition of TiO₂ to PMMA.⁶ In comparison, some studies found that TiO₂ did not improve PMMA's flexure strength, which could be due to particle clustering within the resin, resulting in its weakness.^{22,39}

Safi⁸ found that PMMA reinforced with TiO₂ NPs has an effect on its mechanical (decreased E-Modulus) and thermal (decrease in the thermal expansion coefficient and contraction) stability, while a reduction in flexural strength and toughness was reported.⁴¹ A titanium coupling agent could be useful for improving the properties of titanium-reinforced PMMA because adhesion between the resin matrix and filler particles is very important in order to enhance the properties.⁴² PMMA reinforced with silanized TiO₂ NPs improved the transverse strength, impact strength, and surface hardness of the resin and decreased its water sorption and solubility.⁴³

Noble metals

Silver (Ag)

Several studies found that addition of silver NPs (AgNPs) to denture base acrylic resin displayed antifungal properties,⁴⁴⁻⁴⁷ especially at high concentrations,⁴⁸ and acted like a latent antifungal material with low-releasing Ag⁺.⁴⁹ On the contrary, Wady et al⁵⁰ found that incorporating silver NPs in PMMA did not affect the adhesion of *C. albicans* and biofilm accumulation.

Incorporation of silver in PMMA could be beneficial for immune-compromised and geriatric patients because of its antimicrobial effect so it could reduce microbial adhesion and colonization.^{44,45} In addition, PMMA resin reinforced with silver has increased flexural and fatigue strength and improved thermal conductivity.^{12,13} It was suggested that the addition of silver could adversely affect the mechanical properties of the denture base resin, depending on its percentage.⁴⁴ Compressive strength of PMMA was significantly increased upon incorporating silane-treated silver particles. Also, tensile and flexural strength of PMMA were enhanced upon addition of 10wt% and 20wt% silane-treated silver fillers.⁵ The flexural strength values of PMMA were not significantly changed on addition of silver powder to PMMA.¹³

PMMA reinforced with silver NPs resulted in the improvement of its physical and mechanical properties including improvement of thermal conductivity and compressive strength.^{51,52} Therefore, it is recommended to be used in the palatal area of maxillary acrylic resin dentures.⁵¹

Also, it was found that PMMA-silver NPs are not cytotoxic.^{21,46} However, tensile strength did not change significantly after incorporating 0.2% of AgNPs in comparison with unmodified PMMA, but it decreased significantly after incorporation of 2%.⁵³ The disadvantage of silver reinforced PMMA is its poor color stability.^{49,54}

Nano-gold (Au), platinum (Pt), palladium (Pd)

Recently it has been proposed that nano-gold (Au) and platinum (Pt) NPs improve the properties of PMMA denture base. The available studies on the effect of adding nano-gold to PMMA are currently still limited. It has been observed that incorporating gold NPs considerably improved the flexural strength and thermal conductivity to almost double the value of pure PMMA, which could lead to more patient satisfaction.^{55,56} Addition of Pt NPs could improve mechanical properties of PMMA and provide antimicrobial effect.⁵⁷ Platinum was found to significantly increase PMMA's bending deflection, and palladium increased bending strength when compared to silver and gold, which showed the lowest bending strength value. Addition of gold and palladium improved Vickers hardness of PMMA and was decreased with the addition of platinum.⁵⁸

Silica-based filler

Addition of glass flakes to acrylic resin improved its fracture toughness, and silane coupling agent used resulted in further improvement of the acrylic resin properties.²² Micaceous are a group of lamellar silicate minerals and these are characterized by their high aspect ratio. They improved the mechanical, thermal, as well as dimensional properties of PMMA.⁵⁹ Incorporation of mica increased the hardness of acrylic resin, but its flexural strength was reduced because of weak bond of mica with the acrylic resin.⁶⁰ Nanoclay is another material which is used to enhance the properties of acrylic polymers. Thermal conductivity of PMMA is improved upon the addition of Nanoclay particles to PMMA, while flexural strength was decreased.⁶¹ Placing silicon carbide filler powders in the palatal region of dentures can improve PMMA's thermal conductivity without reducing strength or increasing weight.¹³

Carbon family fillers

Carbon fillers are not commonly used to reinforce PMMA because of biological problems, poor denture aesthetics, as well as difficulty in handling and polishing.⁷⁵

Table 2: Classification of fillers and nanofillers

Additives	Filler (μm)	Nano-filler (nm)
Metal oxides	Aluminum oxide (Al ₂ O ₃) Zirconium oxide (ZrO ₂) Titanium oxide (TiO ₂)	Al ₂ O ₃ NPs ZrO ₂ NPs TiO ₂ NPs
Noble metals	Silver (Ag)	AgNPs Gold (Au) Platinum (Pt) Palladium (Pd)
Silica based	Glass flakes Mica	Nanoclay
Abbreviations: NPs-nanoparticles.		

Fibers

Several studies have been conducted on the use of fibers to reinforce denture base resin, and has been reported to improve the flexural and impact strength as well as the fatigue resistance of the resin.⁶² Different types of fibers are used, such as nylon, polyethylene, polyamide fiber, and particularly glass fiber, due to their biocompatibility and superior aesthetics and mechanical properties.^{62,63}

Glass fiber

It has been found that PMMA reinforced with Glass fiber significantly increased its flexural strength, impact strength, toughness, and Vickers hardness.⁶⁴⁻⁶⁸ Also, a significant reduction in deformation of the denture base to less than 1% deformation was found.⁶⁴ Moreover, a recent study found that the position of glass fiber within the denture base

affects its flexural properties. Improvement of flexural strength, toughness, and flexural modulus was obtained from placement of glass fiber close to the surface of the denture base on its tensile stress side. When glass fiber was placed in neutral stress area, only flexural toughness was improved, and when placed in the compressive side, surface flexural modulus was increased.⁶⁹

Preimpregnated and silane treated glass fiber also increased the flexural strength⁷⁰ and impact strength^{71,72} of acrylic resin. Silanized glass fiber was found to be biocompatible when added to heat-cured and light-cured resins.^{64,73} Moreover, fiber-reinforced nanopigmented PMMA showed reduced porosity and *Candida albicans* adherence.⁷³

Polyamide fiber

Polyamide fiber includes both Nylon and Aramid fiber. Denture base resin reinforced with aramid fiber was found biocompatible, and its flexural strength and flexural modulus were increased.⁷⁴ However, the hardness of the resin decreased with increasing fiber concentration. Also, its yellow color is considered a drawback.^{75,76} Nylon increased the fracture resistance of PMMA, as it has high resistance to continual stress. Therefore, incorporating nylon fiber in PMMA increased its structural elasticity.⁷⁷

Polyethylene and polypropylene fibers

Addition of Polyethylene fiber to PMMA significantly increase its impact strength, and a further increase was observed with fiber surface treatment.^{65,78} Woven polyethylene fiber reinforcement can significantly increase the elastic modulus and toughness of PMMA. However, the procedures of woven fiber etching, preparing, and positioning were found impractical.⁷⁸ Addition of Polypropylene fiber to PMMA significantly increase its impact strength, and a further increase was observed with fiber surface treatment.⁷² The highest impact strength was obtained with polypropylene fibers treated with plasma, which can be used to strengthen acrylic resin and reduce fracturing. A study suggested that incorporating silanized polypropylene fiber in PMMA resin significantly improved its transverse, tensile, and impact strengths, but its wear resistance was highly decreased.⁷⁹

Hybrid reinforcement

In 1997, Vallittu first suggested reinforcement of PMMA by more than one type of filler or fiber.⁸⁰ The combination may be between different fibers, fillers (metal oxides) and ceramics,⁸¹⁻⁸⁵ and fibers with metal oxides,^{86,87} or ceramic materials^{32,88-90} (Table 3).

Hybrid fiber reinforcement of PMMA significantly increased its flexural strength and toughness.⁷¹ Similar results were also obtained by incorporating metal oxides and ceramics, in PMMA, particularly NPs.⁹⁰ In addition, improvement in surface roughness,⁸³ tensile strength, flexural modulus,⁸⁸ hardness, thermal conductivity,⁹⁰ and radiopacity⁸⁵ as well as reducing shrinkage. It has antibacterial properties. It is not cytotoxic.⁸²

In addition, a combination of fibers and other fillers increased impact strength, hardness,⁸⁶ surface roughness, and thermal conductivity,⁸⁷ as well as compressive and fatigue strengths.⁴⁹

Table 3: Different hybrid reinforcement materials

Hybrid type	Hybrid materials
Fillers	– Al ₂ O ₃ + ZrO ₂ ^{83,88} – ZrO ₂ -TiO ₂ ⁹⁰
Fibers	Glass fiber + polyethylene fibers ⁶⁵
Fibers + fillers	– Polyester fiber reinforced PMMA + (clay, glass powder, SiO ₂ , or ZrO ₂) ⁸⁶ – Al ₂ O ₃ + plasma-treated polypropylene fiber ⁸⁷ nHA particles, micro-zirconia, glass fiber, and Kevlar fiber (PMMA-nHA and glass fiber), (PMMA-ZrO ₂ and glass fiber), (PMMA-nHA and Kevlar fiber), (PMMA-ZrO ₂ and Kevlar fiber). ³²
Abbreviations: nHA, nano-hydroxyapatite; PMMA, poly(methyl methacrylate).	

CONCLUSION

It can be concluded based on this comprehensive review that:

- ❖ Obvious enhancement in the properties of denture base resin material properties was found with the addition of fillers, nanofillers.
- ❖ Glass fiber reinforcement significantly increases the mechanical properties of PMMA, but further investigations are needed.
- ❖ Silane coupling agents play a central role in improving bonding between fillers, nanofillers and the resin matrix, and they subsequently improved the properties of poly (methylmethacrylate) (PMMA) resin.
- ❖ The hybrid system is the newest reinforcement system. Hybrid fiber, hybrid fillers, or hybrid fiber and filler may significantly enhance the properties of poly (methylmethacrylate) (PMMA).
- ❖ Multiple studies were conducted in vitro, so further studies in vivo are needed, as well as clinical studies.

SUMMARY

To improve quality of life of edentulous patients PMMA acrylic dental prosthesis has been used for years. PMMA is most predominantly used denture base material because of its many characteristics such ease in processing, stability in oral environment, lightweight, excellent aesthetics properties, low cost, low water sorption and can easily be rechanged and repaired its shape. But, it has certain drawbacks like residual monomer allergy, low modulus of elasticity, low impact strength, low flexural strength, poor conductor of heat, high coefficient of thermal expansion, polymerisation shrinkage, porosity, crazing, warpage, poor adhesion to metal and porcelain and requirement of mechanical retention. Thus, to overcome these drawbacks, there has been much new advancements including addition of reinforcing material as, fillers, fibers, fillers-fiber hybrid reinforcement and, recently, NPs to improve the properties of PMMA. PMMA have been reinforced using different materials to improve its physical and mechanical properties. However, the most effective reinforcement is not apparent, and clinicians are confused about designing such reinforcement. Currently, reinforcement has two important purposes on a prosthesis. The first purpose is to improve the strength and prevent fracture, and the

second purpose is to improve the stiffness and prevent residual ridge resorption and overloading to residual teeth or structures. To summarize this review, Undoubtedly, reinforcement of denture base acrylic resins had some efficacy in improving the physical and mechanical properties. The properties of denture base acrylic resin reinforced by fillers, nanofillers, fibers and NPs depend on the size, shape, type, and concentration, surface treatment, and position of the of the added particles for reinforcement.

Clinical significance

Poly (methylmethacrylate) (PMMA) resin with improved properties obtained by addition of fillers, nanofillers, fiber, filler-fiber hybrid reinforcement and NPs can serve in prosthodontic applications.

CONFLICTS OF INTEREST

The authors declare they have no potential conflict of interests regarding this article.

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