

Review Article

Recent Advances and Future Perspectives for Reinforcement of Poly(methyl methacrylate) Denture Base Materials: A Literature Review

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ARTICLE INFO

Article History:

Received: 25 June 2017

Accepted: 8 January 2018

Key words:

Denture base materials

Poly(methyl methacrylate)

Reinforcement

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Abstract

Poly(methyl methacrylate) (PMMA) is the most common material used to fabricate complete and partial dentures. Despite its desirable properties, it cannot fulfill all mechanical requirements of prosthesis. Flexural fatigue due to repeated masticatory and high-impact forces caused by dropping are the main causes of denture fractures. In the past, different reinforcing agents such as rubbers, macro fibers, and fillers have been employed to improve the mechanical properties of denture base resins. Development of Nano dentistry has introduced new approaches for reinforcement of dental materials. Interest in nanostructure materials is driven by their high surface area to volume ratio, which enhances interfacial interaction and specific new biological, physical, and chemical properties. Researchers to reinforce PMMA resins have used Nanoparticles (Nps) which were comprised of silver, Titania (TiO₂), zirconia (ZrO₂), alumina, and ceramic. Although different reports describe the use of nanofiber and nanotubes in dental composites, few studies have evaluated the reinforcement potential of nanofiber and nanotubes in PMMA denture base resins. The current article aims to review the different attempts to enhance the mechanical properties of denture base materials. We also focus on recent advances and potential future developments for reinforcement of the PMMA acrylic resins.

Cite this article as: Abdulrazzaq Naji S, Jafarzadeh Kashi T, Behroozibakhsh M, Hajizamani H, Habibzadeh S. Recent Advances and Future Perspectives for Reinforcement of Poly(methyl methacrylate) Denture Base Materials: A Literature Review. J Dent Biomater, 2018;5(1):490-502.

Introduction

Poly(methyl methacrylate)(PMMA) was introduced in 1937 by Wright [1]. PMMA has been extensively used as a denture base material because of its desirable properties. Satisfying aesthetics, ease of processing, durability, chemical stability, light weight, and acceptable cost are some of the favorable properties. Despite these characteristics, the denture base materials do not have sufficient mechanical properties for every intended purpose. Flexural fatigue due to repeated masticatory forces and high-impact forces caused by dropping the prosthesis are the main intraoral and extraoral causes of denture fractures, respectively [2]. Flexural fatigue occurs consequent to repeated flexing and can be described as growth and propagation of microcracks in the stress concentration areas [3]. Midline fractures, which are a common problem for patients who wear maxillary complete dentures, usually occur due to cyclic deformation consequent to flexural fatigue. A survey by Darbar *et al.* [4] has reported that 29% of failures in dentures occurred at the midline labial frenum. Impact failures usually happen as a result of accidental dropping during cleaning, coughing or sneezing, or sudden strokes to the denture [3]. Therefore, the ability of a denture base material to withstand crack propagation and impact forces is an important factor which affects its performance. Hence, there is a need for enhancement of the mechanical properties of PMMA based materials to achieve stronger and more fracture-resistant dentures [5]. Chemical modification and the addition of some fibers, fillers, and rubberlike substances are different methods introduced to improve the mechanical properties of PMMA-based materials. [3] Here, we provide a general background about different attempts to improve the mechanical properties of denture base materials, and review recent advances and potential future developments for reinforcement of the PMMA acrylic resins.

Discussion

Rubbers, fibers and fillers

In this section, we review different attempts that have been launched during past decades to improve the mechanical properties of denture base resins.

Rubbers, different fibers, and fillers are some additives employed to reinforce dental resins. In addition, we mention the latest advances for each reinforcing agent.

Rubber reinforced poly(methyl methacrylate) (PMMA)

Adequate impact strength and fracture toughness are 2 of the most important requirements for denture based resins. One of the main drawbacks of PMMA denture bases is low fracture toughness; thus, the conventional denture base polymers are susceptible to breakage with high mastication forces and during accidents. Many studies have been performed to evaluate the toughness and mechanisms of toughness improvement in rubber-modified acrylic polymers [6, 7]. In rubber-reinforced polymers, the resin matrix is filled with a rubbery particle which has a modulus of elasticity lower than that of the polymer matrix and a higher Poisson's ratio than the matrix. Therefore the reinforced polymer will have a lower modulus and a higher Poisson's ratio compared to the unmodified polymer. The most significant advantage of this modification is an increase in toughness as well as ultimate elongation in comparison with the relatively brittle resin acrylic material [8]. In this structure, the rate of crack propagation through the PMMA will decelerate at the interface of the rubber and resin since the rubber reinforced resins can absorb greater amounts of energy compared to the unmodified resins. One problem of these reinforced dentures is increased flexibility due to low Young's modulus [3]. Rodford [6, 7] has described the development of high impact strength denture base materials using butadiene-styrene rubber. Butadiene-styrene is a low molecular weight rubber (15-35 000), which has the advantage of up to 30% incorporation in PMMA without excessive increase in viscosity. This polymer contains reactive (acrylate) end groups which facilitate grafting to the PMMA. Alharez *et al.* [9, 10] have suggested that nitrile butadiene rubber (NBR) particles and treated ceramic fillers could improve impact and fracture resistance of heat-polymerized PMMA denture base resins. This research concluded that the optimum addition of the filler in the polymer matrix was 7.5% NBR together with 2.5% Al₂O₃ (Alumina)/2.5% YSZ (Yttria-stabilized zirconia). They proposed

that in cases that need high impact strength and fracture toughness, reinforcement of PMMA denture base by NBR with ceramic fillers could be the best choice for removable prosthodontics.

Fibers

Polymer fiber composites are materials composed of a polymer matrix and a reinforcement fiber, which is the stronger constituent of the composite. In a polymer fiber composite, the fibers are embedded in a polymer matrix. The polymer matrix forms a continuous phase that surrounds the fibers; thus, the applied loads are transferred from the polymer matrix to the fibers. One of the most important factors that affect the strength of the composite is proper adhesion of the fibers to the polymer matrix. This adhesion makes it possible to transfer the stresses from the matrix to the fibers. The stiffness of the fibers is an important characteristic for strengthening of brittle materials like denture base resins. Impregnation of the fibers into the polymer matrix is another important factor which affects the strength of the fiber reinforced composite [11]. In some studies, reinforcement of denture PMMA resin has failed due to the stress concentrations around the embedded fibers. This phenomenon often happens as the result of poor distribution of the reinforced fibers and bad adhesion between resin matrix and fibers. Nylon fibers are one of the fibers used as a reinforcing agent for PMMA due to their resistance to shock and frequent stressing, high resistance to abrasion and creep, elastic memory, and cyclic stress conductivity [12]. Larson *et al.* have reported the use of carbon fibers to improve the strength of denture bases [13]. Carbon fiber is applied in many studies to improve the mechanical properties of the matrix because of its inherent high strength and optimal combination of the carbon fibers and matrix [14]. Mainly, carbon fibers have been used to enhance fatigue and impact strength [15]. Despite good mechanical properties, cytotoxicity of carbon fibers is problematic [15]. Moderate cytotoxicity has been determined by Özen *et al.* [16] for heat-polymerized acrylic resin reinforced with both glass and carbon fiber. The aramid fibers, which have high resistance to impact forces, are another agent for reinforcing denture base materials. They have excellent wettability compared to carbon fibers

and do not need treatment by a coupling agent. Biological evaluations have shown no evidence for any cyto-genotoxic effects of aramid fibers [17]. Disadvantages of these fibers include their yellow hue and poor adhesion to acrylic resin materials. It is also reported that the rough surfaces of materials reinforced with aramid fibers are difficult to polish as the result of exposed fibers at the surface of the material [18]. Recently, a novel botryoidal aramid fiber reinforcement of a PMMA resin was introduced by Xinye *et al.* [19]. In this research, they achieved a homogeneous fiber distribution in the resin matrix by separation of each fiber via grafting of microspheres to aramid fibers. The researchers proposed that this new approach could successfully improve the mechanical properties of fiber reinforced composites along with acceptable safety *in vitro*. However, they suggested that more experimentation would be required to fully evaluate the long-term mechanical performance and biocompatibility of this novel composite *in vivo*. Glass fibers have been considered as reinforcing materials for denture base resins because of their excellent aesthetics, superior strength, and good biocompatibility [20]. Jaikumar *et al.* [21] found that higher flexural strength of the acrylic resin specimens reinforced with glass fibers compared to high impact denture base resins. The same results were reported by Hamouda *et al.* in 2014 [22]. Unalan *et al.* [23] stated that the form of glass fiber could affect the transverse strength of reinforced denture base resins. They obtained the highest transverse strength in samples reinforced with chopped strand mat form. Vallittu *et al.* [24] evaluated the effect of fiber concentration on fracture resistance of acrylic resin and observed better enhancement in fracture resistance of resin-modified materials at higher concentrations of glass fibers. Sang-Hui *et al.* [25] evaluated the effects of glass fiber mesh with different amount of fibers and various structures on the mechanical properties of dentures. They concluded that the content of the glass fiber mesh was more important than the structure, and determined that between 4.35 and 4.73 vol% was the most effective concentration. Nagakura *et al.* [26] reported that the flexural modulus of glass-fiber-reinforced thermoplastics (GFRTPs) use in removable partial dentures (RPDs) increased from 1.75 to 7.42 GPa with increased glass fiber content

from 0 to 50 mass%, such that the flexural strength and modulus of GF RTP with a fiber content of 50 mass% were 3.9 and 4.2 times, respectively, of unreinforced polypropylene. The position of glass fibers in resin matrix could also affect the mechanical properties. It has been reported that placing the fibers normal to the loading force could enhance the mechanical properties [27]. Goguta *et al.* [28] reported that impact strength of PMMA reinforced with stick glass fibers significantly increased when stick fibers were placed parallel to the long axis of the specimen and perpendicularly to the force direction. The mechanical properties of PMMA reinforced with glass fibers also depends on good adhesion between fibers and the resin matrix. In order to achieve better adhesion, glass fibers are treated with silane coupling agent before loading into the resin matrix. Several studies have reported that the reinforced resins with silane-treated fibers have higher transverse strength and fracture resistance than acrylics that have untreated glass fibers [29, 30].

Fillers

Metals in various forms such as wires, plates, and fillers have been incorporated into PMMA to improve thermal conductivity and radiopacity, as well as mechanical properties. One of the disadvantages of PMMA is its low thermal conductivity. The high thermal conductivity of denture bases leads to improved tissue health, a better sense of taste, and reduction of the foreign body feeling of dentures. Various studies have added metal fillers to improve the thermal conductivity of acrylic resins [31, 32]. The reinforcement of polymers used in dentistry with metal strengtheners has been considered by many researchers. [31-33] One of the drawbacks of metal fillers is that they do not chemically bond to resins. Different efforts have been made to enhance the adhesion between the metal to resin matrix such as silanization, sandblasting, and metal adhesive resins [3]. The incorporation of metals as a reinforcement agent into PMMA have limited value because of the negative effects on esthetics, stress concentration, and minor influence of metal wires on flexural fatigue resistance [3]. Ceramic fillers are also incorporated as reinforcing fillers in PMMA denture base resins. Silicon dioxide (SiO_2), commonly used reinforcing filler in dental materials,

has been used as filler in elastomers and composite resins. However, McNally *et al.* [34] reported that the addition of untreated and surface treated silica could not be recommended as a reinforcing agent for denture base resins. Hydroxyapatite (HA), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is another filler employed in different dental materials. Incorporation of HA fillers into PMMA resin has resulted in superior mechanical properties including flexural strength and modulus [35]. However, the mechanical properties of PMMA reinforced with HA could be limited because of the incompatibility between the PMMA and HA. Modification of the composite has been proposed to improve the interfacial interaction between the HA filler and PMMA [36, 37]. Tham *et al.* [37] suggested that the silane coupling agent [3-methacryloxypropyltrimethoxy silane (γ -MPS)] could significantly enhance the mechanical and thermal properties of the PMMA/HA composite due to enhanced adhesion between HA particles and the resin matrix. Reinforcement of denture base resins using mica has also been proposed in some studies [38]. Muscovite mica, a hydrated silicate, is the most common type of mica. It is predominately white. Muscovite mica is commonly employed for reinforcement of polymers. Incorporation of mica into polymeric matrix increases stiffness, strength, scratch resistance, dimensional stability, and lowers the coefficient of linear thermal expansion. [39]. Unalan *et al.* have evaluated the effects of different ratios of silanized mica filler on the surface hardness of a denture tooth material and obtained the best surface hardness value by the addition of 10% mica and 10% glass to the denture teeth material [40].

Nanoscaled reinforcement materials

The concept of nanotechnology was first introduced in 1959 by Feynman. Since then, nanotechnology has been widely used in many applications, including medical sciences, and plays an important role in diagnosis, treatment, and regenerative medicine [41]. A nanomaterial is an object, which at least one of its dimensions is at the nanometer scale (approximately 1 to 100 nm). Nanomaterials are categorized according to dimension – those with all 3 dimensions less than 100 nm [nanoparticles (Nps) and quantum dots]; those that have 2 dimensions less than 100 nm (nanotubes, nanofibers, and

nanowires); and those that have one dimension less than 100 nm (thin films, layers, and coatings) [42]. The development of nanodentistry has led to nearly perfect oral health by the use of nanomaterials and biotechnologies, including nanorobots and tissue engineering. New opportunities in the field of dentistry include local anesthesia, treatment of dentin hypersensitivity, use of nanomaterials in preventive dentistry, and use of different nanofillers and nanofibers in composites to achieve better esthetics and mechanical properties [43]. Here, we focus on new applications of nanomaterials for reinforcement of PMMA dental base materials.

Nanofillers

Recently, researchers have proposed the incorporation of nanofillers for reinforcement of denture base resins. Size, shape, surface area, concentration, and dispersion of nanofillers into resin matrix all affect the mechanical properties of the filler/resin composite. Alumina NPs, zirconia (ZrO_2) NPs, titania (TiO_2) NPs, silver NPs, gold NPs, Pt NPs, HA NPs, SiO_2 NPs, and nanoclay particles are among the fillers that have been introduced to enhance the mechanical properties of denture base acrylics [35]. Here, we focus on some of the most common reinforced nanofillers that have been used for prosthodontics approaches. Silver Nps have been considered due to their distinctive physical, chemical, and biological properties, including high electrical and thermal conductivity, chemical stability, and non-linear optical behavior. It has been reported that silver Nps exhibit broad-spectrum bactericidal and fungicidal activities at very low concentrations [44]. Controversial results have been reported about the influence of silver NPs on the mechanical properties of denture base resins. [45, 46]. More studies should be conducted to evaluate the effects of different concentrations of silver Nps on various types of acrylic resins. The benefit of antibacterial properties of silver Nps has not been wiped out by the adverse effect on the mechanical properties of the denture base material. Modification of polymers with nanoscaled TiO_2 have also been of interest with researchers because of its unique properties. Pleasing color, high biocompatibility, excellent mechanical properties, low cost, high stability, and appropriate antimicrobial effects are among the

desirable properties which make TiO_2 a favorable additive for biomaterials [47]. TiO_2 Nps have been used as an additive to improve both mechanical and antibacterial properties of different dental materials [48]. TiO_2 exhibits great oxidizing power under UV radiation, and can decompose organic materials and bacteria. It has been reported that powdered TiO_2 can kill *Streptococcus mutans*, *Escherichia coli*, and *Candida albicans* [49]. Controversial results have been reported by different researchers about the effect of TiO_2 Nps on mechanical properties of acrylic resins [50, 51]. Good wettability between fillers and the matrix is an important factor in order to improve the composite's properties. It has been shown that incorporation of silanized TiO_2 NPs in PMMA resin matrix increases the impact strength, transverse strength, and surface hardness of the resin [50, 52]. Different attempts have made to add ZrO_2 Nps to PMMA denture base material to improve the mechanical properties. Gad *et al.* [53] reported higher transverse strength in reinforced samples with ZrO_2 Nps compared to unreinforced repaired resin. They suggested that ZrO_2 Nps might be considered as a new approach for denture base repair. Asopa *et al.* [54] reported similar results with significantly higher transverse strength in the reinforced specimens that used ZrO_2 Nps compared to the control group. In their study, incorporation of ZrO_2 Nps into resin matrix adversely affected the impact strength and surface hardness. Ahmed *et al.* [55] also reported enhanced flexural strength, fracture toughness, and hardness in heat-polymerized acrylic modified by the addition of zirconium oxide nanofillers. The improved mechanical properties could be attributed to particle sizes of the ZrO_2 Nps. Also, the phase transformation of ZrO_2 from tetragonal to monoclinic absorbs the energy of crack propagation in a procedure called transformation toughening. Good distribution and surface treatment such as silanization of nano-size particles may affect their reinforcing effect [53]. It has been proposed that Nps have to be distributed evenly within the resin matrix; otherwise, they may adversely affect the mechanical properties of the resin composite at higher concentrations of added fillers due to the agglomeration of ZrO_2 Nps [53, 56].

Nanofibers

Different reports have described the nanofiber-

reinforced effect in dental composites [57, 58]. Based on our findings, few studies have evaluated the reinforcement potential of nanofibers in PMMA denture base resins. Glass nanofibers, HA nanofibers, fibrillar silicate, and polymeric nanofibers have been introduced for reinforcement of dental materials [59]. It has been suggested that extreme reduction in fiber diameter size to the nanometer scale causes improvements in strength, modulus, and toughness. Fibers are the preferred reinforced materials compared to particles since they can provide a larger area for load transfer and promote toughening mechanisms such as fiber bridging and fiber pullout (Figure 1) [60]. One of the limitations for the use of nanofibers as a reinforcing agent is their incomplete wetting by resin, which compromises strength as the result of air inclusion and voids [61]. Another drawback of nanofibers is inadequate dispersion into the resin matrix that leads to the creation of bundles. These bundles may even act as defects and adversely influence the mechanical properties of the resin matrix and resultant composite [62]. Glass nanofibers are among the nanofibers introduced in the field of dentistry. Amorphous SiO_2 (glass) is used in commercially available dental composites because most requirements of dental composites could be obtained by the addition of appropriate amounts of glass. In addition, the refractive index of glass approximates that of dental resins and consequently gives a translucent appearance to the dental composite, which is similar to the structure of human teeth. Conventionally, dental resin composites are modified with glass particles that

range from tens of nanometers to several microns. Despite these properties, the mechanical properties of the glass particle reinforced composites are not adequate for use in large stress-bearing areas. The electrospun glass nanofibers are expected to improve the mechanical properties of dental resins considerably more than micron-scaled glass particles/fibers. The nano-scaled glass fibers have desired properties of small fiber diameter, large aspect ratio, and high mechanical properties. When a micro-crack in the dental resin matrix is formed under an applied stress across the crack planes, the thin and long nano-scaled glass fibers remain intact and support the applied load. Therefore, crack propagation is inhibited by the fibers with simultaneous reinforcement of the matrix. In comparison with micron-sized glass fibers, the glass nanofibers are over 10-times thinner and contain significant surface Si-OH groups that can readily interact with different silane coupling agents. Consequently, the interfacial bonding between the resin matrix and the nanoscaled silanized glass fiber can be extremely powerful [59, 63]. HA is another reinforcing agent used in forms of particles and fibers in numerous dental materials due to its mineral releasing effect, biocompatibility, and strength [64, 65]. Mechanical performances of dental resins could be reinforced using inorganic fibers such as HA nanofibers. Good dispersion of HA nanofibers into a resin matrix at low mass can significantly improve the mechanical properties of the composite, while a higher mass fraction of the nanofibers cannot effectively reinforce the resin due to the formation

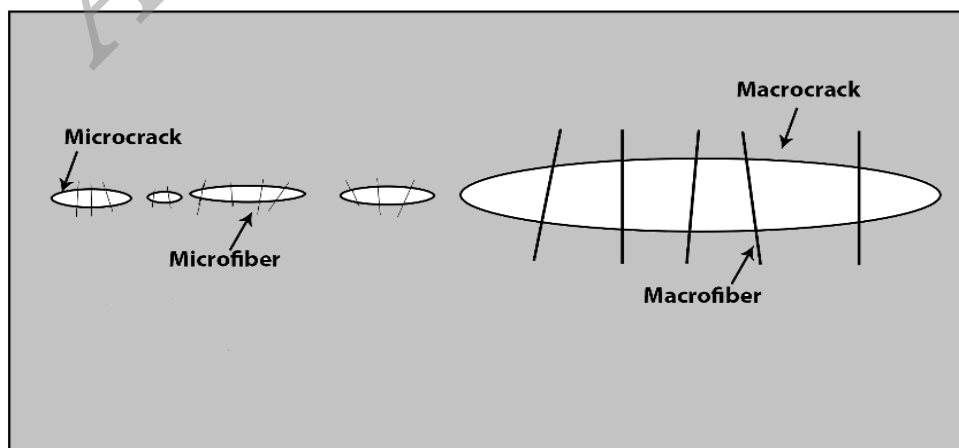


Figure 1: Fiber bridging of micro and macro fibers across micro- and macrocracks

of bundles that may even serve as defects. Chen et al. have reported that good dispersion of HA nanofibers could be obtained by surface treating of nanofibers with glyoxylic acid (GA) [62]. In another attempt, Fong used nylon 6 nanofiber to reinforce dental restorative resin composites and obtained higher mechanical properties in reinforced samples. This study suggested that when a heavy force was imposed on the composite, the existent nanofibers effectively deflected the crack due to the powerful linking force between the nylon 6 nanofibers and resin matrix. When the crack broke away from the nylon 6 nanofibers, a large number of fracture lines were created on the fracture surface that caused tremendous energy consumption during the fracture [66]. A core-shell structure of a polyacrylonitrile (PAN) and PMMA nanofibers is also used as a reinforcing agent for Bisphenol A Glycidyl Methacrylate (BisGMA) dental resins [67]. In this core-shell structure the PMMA is located in the shell and surrounded by a dental resin matrix. After curing, linear PMMA chains become interpenetrated and entangled with the cross-linked resin matrix network and produce a strong nano interface linking force with strong interfacial adhesion between nanofibers and resin matrix, which would consequently enhance the mechanical properties of the resultant composite [59]. It has been reported that incorporation of PAN nanofibers into BisGMA, Triethylene glycol dimethacrylate (TEGDMA) resin blends increased the toughness of the material. This toughening effect depended on the resin monomer solution composition and nanofiber/resin ratio [68].

Nanotubes

The introduction of nano-scale material offers new, promising additives for improvement of

the mechanical properties of dental composites because of their high surface area to volume ratio. This property increases the interfacial interaction between nano materials with the resin matrix and consequently induces the specific biological, physical, and chemical properties in resin composites. In terms of high surface area, nanotubes consist of long cylinders with a hollow cavity at their center. They exhibit increased surface area compared with Nps. The aspect ratio of nanotubes is usually more than 10 and it can reach up to several thousand [69]. It is reported that the open-ended tubular structure of the nanotubes may allow the methyl methacrylate monomer to enter into the tubes by capillary action and undergo polymerization. Thus, the higher degree of cross-linking leads to increased load transfer within the nanotube-resin composite. The acrylic resins modified with nanotubes may exhibit considerably higher mechanical properties than the conventional ones. Crack bridging in the tubular structure of nanotubes by fiber pullout from the matrix has been reported in some studies as the main reason for improvement of the mechanical properties of modified resin acrylics [70]. Carbon nanotubes (CNTs), ZrO_2 nanotubes, TiO_2 nanotubes, and halloysite nanotubes (HNT) are among the nanotubes used for reinforcement of dental materials. CNTs are the most well-known nanotubes that have been introduced to reinforce materials. CNTs are strong, resilient, and lightweight. They have excellent mechanical and electrical properties [71] and are classified into 2 main types according to the structure of the CNTs – single-walled and multi-walled (Figure 2) [72]. Studies have shown superior mechanical properties in CNT modified polymer-based composites compared to unmodified composites. In addition to

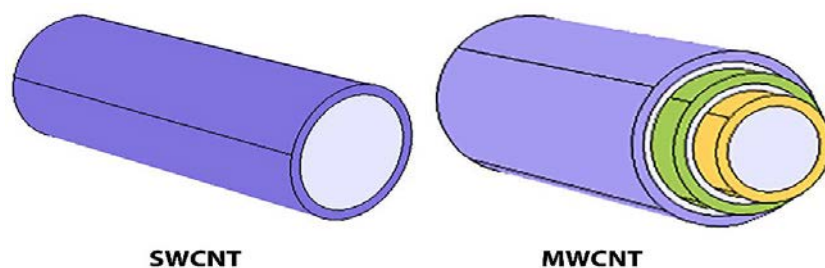


Figure 2: Schematic representation of single-walled and multi-walled carbon nanotubes (CNTs)

the high intrinsic strength and moduli, CNTs can transfer the stress 10 times more than conventional additives [73]. Single-walled CNTs can be used as promising agents to reinforce dental resins due to their ultrahigh specific surface area and exceptional physical performances. The bent single-walled CNTs can recover their original shape on strain release without direct fracture [74]. The reinforcing effect of CNTs may be restricted because of weak interfacial adhesion with the resin matrix as well as the tendency of nanotubes for agglomeration, which causes poor distribution throughout the matrix. The atomically smooth surface of the nanotubes reduces the linking force between the nanotubes and the resin matrix, which limits load transfer from the resin matrix to the nanotube [75]. Hence, good dispersion and enhancement of linking forces between nanotubes and the resin matrix are 2 main factors that affect the reinforcing effect of CNTs. Sonication, chemical modification, surfactant treatment, solution casting, in situ polymerization of monomers, and the combination of these are methods have been introduced to enhance the dispersion of CNTs [76, 77]. Zhang *et al.* [77] modified single-walled carbon nanotubes (SWCNTs) with nano-SiO₂. They observed good levels of dispersion and improved flexural strength in the modified resin composite. Wang *et al.* [72] reinforced PMMA denture base material with 0.5 wt%, 1 wt%, and 2 wt% of multiwalled CNTs and dispersed them with sonication. Their results showed improved flexural strength by the addition of 0.5% and 1% multi-walled carbon nanotubes (MWCNTs) into the PMMA resin, but not for the 2% MWCNTs modified group due to improper dispersion of MWCNTs throughout the matrix. They concluded that MWCNTs adversely affected the fatigue resistance of PMMA resins, particularly with higher concentrations of MWCNTs. HNT has a tubular structure with 2 layers of aluminosilicate (Al₂Si₂O₅(OH)₄•2H₂O) [78]. Abundance, easy purification, safety, biocompatibility, and ease of handling are advantages of halloysite [59, 79]. The chemical characteristic of the outer surface of HNTs is close to SiO₂, whereas the inner surface approximates Al₂O₃. Nano-sized crystals of HNTs have high mechanical properties. Separation of HNTs in halloysites and dispersing them evenly throughout the resin matrix is simple. The HNT can

be completely split in the existence of polar solvents and mechanical agitation. Because of the presence of a rich Si–OH group on the outer layer of the HNTs, a very strong interfacial linking force can be produced between the silanized halloysite and resin matrix [59]. Reham evaluated the mechanical properties of PMMA resin modified with HNT and concluded that incorporation of low percentages of HNTs into PMMA resin significantly increased the hardness values, whereas the flexural strength and Young's modulus did not significantly improve [80]. Recently, ZrO₂ nanotubes have been greatly used in optoelectronic devices, biomedical materials, and industrial catalysts due to their distinctive pore structures and large specific surface area. It is reported that the untreated ZrO₂ nanotubes have a better reinforcing effect compared to those treated with a silane coupling agent. ZrO₂ nanotubes have unique long tubular structures. When the untreated ZrO₂ nanotubes are mixed with PMMA resin matrix, the chains of the polymer form a three-dimensional network with added nanotubes without any bonding effect. Hence, under an applied force, the polymer chain can slip along the nanotube axis and, consequently, bending stress and bending displacement may improve. On the other hand, the silane coupling agent can play a connective role between the polymer chains and the ZrO₂ nanotubes to prevent the polymer from sliding over the surface of the nanotubes. This would reduce the reinforcing effect of the nanotubes [81]. The TiO₂ nanotubes (TNTs) have been considered in medicine due to their high-specific surface area, photocatalytic property, and ion-exchangeability. The tubular form of TiO₂ has a surface area of 250 m²/g that results from the internal and external surfaces, and the surfaces between the layers of the walls, which vary from 2 to 10. The surface area of TNTs is approximately 5 times that of the Nps [69]. Recently, TNTs have been considered for different biological applications such as drug delivery, bio-scaffolds, titanium-based implants, and reinforcement of resin composites. Byrne *et al.* [82] reported improved Young's modulus and strength of modified polystyrene with functionalized TNTs. Porras *et al.* [83] also described improved mechanical properties of polyethylene oxide/chitosan composite reinforced with synthesized TNTs. Improvement of mechanical properties of

resin based cement reinforced with TNTs was also reported by Khaled *et al.* [84] In another attempt, Dafar *et al.* [85] evaluated the mechanical properties of flowable dental resin composites reinforced with TNTs, and reported improved fracture toughness and Young's modulus in the experimental resin composite. Recently, Abdulrazzaq Naji *et al.* incorporated 2.5 wt% and 5 wt% TNTs into the PMMA denture base material and evaluated the fracture toughness, flexural strength, and microhardness of modified denture base resins. They observed significant enhancement in all evaluated mechanical properties. The researchers noted that these improved mechanical properties were a linear function of the concentration of added TNTs [86].

Conclusions

In this review, we provided a general background about the efforts to enhance the mechanical properties of denture base materials and relevant new aspects. Rubbers, different macro fibers, metallic, and ceramic fillers have been used for decades as reinforcing agents for PMMA denture base resins. The concept of nanotechnology presents a new era for reinforcement of materials because of the high surface area to volume ratio and the specific biological, physical, and chemical properties of nanomaterials. Nps that include silver Nps, TiO₂ Nps, ZrO₂ Nps, alumina Nps, and ceramic Nps have been employed to improve the mechanical properties of denture base resins. Recently, nanofibers and nanotubes have been introduced to reinforce dental materials. Nanofibers/tubes with higher surface area to volume ratio than Nps provide higher mechanical properties of reinforced composites compared to Nps. Different mechanisms have been presented for the reinforcing effect of nanofibers/tubes. A larger surface area can provide a larger area for load transfer and facilitate toughening mechanisms such as fiber/tube bridging and fiber/tube pullout. Higher degrees of cross-linking due to the incorporation of monomers into hollow parts of nanotubes have been suggested to reinforce nanotubes. Uniform dispersion and complete wetting of the nanofibers/tubes are 2 important factors that affect the reinforcing effect of nanofibers/tubes.

Further studies have to be conducted on using nanofiber/tubes in PMMA denture base resins in order to evaluate the reinforcing mechanism of these additives. The use of nanofibers/tubes may offer a new approach for reinforcement of PMMA resins and possibly be considered as promising reinforcing agents for denture base resin materials in the future.

Conflict of Interest: None declared

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