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Contemporary hybrid acrylic materials and modern thermoplastics in the manufacture of dental prostheses

Robert Kowalski[A], Małgorzata Kozak[B] ✉, Ewa Sobolewska[C]

Pomeranian Medical University in Szczecin, Department of Dental Prosthetics, Powstańców Wlkp. 72, 70-111 Szczecin, Poland

[A] ORCID: 0000-0001-8811-4800; [B] ORCID: 0000-0002-4314-5600; [C] ORCID: 0000-0001-7932-9631

✉ gosia-ko@o2.pl

ABSTRACT

Introduction: Some modern acrylic denture base resin enhancing materials, investigated by researchers aiming to improve the properties of the resin, were collected and described as part of this review. Poly(methyl methacrylate) (PMMA), is widely used as a prosthodontic base for both partial and complete dentures, but it has many disadvantages such as low strength, insufficient resistance to fatigue, and porosity. Therefore, the topic of modern thermoplastic materials that could replace acrylic dentures will also be discussed.

Materials and methods: In this article, we reviewed literature available on PubMed, Google Scholar, and NIH. The search was conducted in such electronic databases with the following keywords: "acrylic resin", "nanoparticles", "reinforcements of removable dentures", "BioHPP in dentistry", and "acetal resin in dentistry". This study is focused on the effects of adding fibers, fillers, and nanofillers on the properties of PMMA. The paper draws on science-based reviews, original scientific papers, abstracts, and studies published over the past few decades.

Results: The article explores various fillers and fibers that can be added to acrylic resin for dental prostheses. Adding carbon nanotubes, titanium dioxide (TiO_2), silicon dioxide (SiO_2), and zirconium dioxide (ZrO_2) can improve the strength and other properties of the resin. Glass fibers, polyamide, aramid, polyethylene, and polypropylene fibers can increase fracture resistance, impact strength, and modulus. Combining ZrO_2, zirconium nanotubes, and silane-treated ZrO_2 nanoparticles is suggested to be the best solution for reinforcing dental prostheses.

Conclusion: The properties of PMMA denture base material can be enhanced with the addition of fibers, fillers, silanized nanoparticles, and hybrid reinforcements to reduce damage and cracks. Due to the lack of an ideal material for dentures, the properties of PMMA can be improved with these modifications to make it significantly more convenient for patients to use.

Keywords: acrylic resin; reinforcements of removable partial dentures; nanoparticles; modern thermoplastics.

INTRODUCTION

Acrylic resin made of poly(methyl methacrylate) (PMMA) is an organic biological material often used in the production of dental prostheses because of its diverse advantages, such as biocompatibility, durability in oral conditions, satisfying aesthetics, low water sorption and solubility, cheap price, and easy processing and repair. It was introduced in dentistry in 1930. Since then, research has been carried out on this material to improve their hardness, tensile strength, durability, as well as fragility, low thermal conductivity, and high coefficient of thermal expansion [1]. Although light-activated urethane dimethacrylate and polystyrene have also been used in the production of dental prostheses, PMMA still remains the most favored material for both partial and complete dentures [1].

Recent studies on acrylic resins show that the addition of various fillers and fibers, such as nanosilver particles (AgNPs), halloysite nanotubes (HNTs), or carbon fibers may modify the strength and flexural modulus of the resins, and thus, the strength of dental prostheses [2]. The harder the resin is, the more resistant it is to abrasion. Some researchers have proved that polyethylene and sapphire fibers also appear to be enhancing the physical properties of acrylic resin. Furthermore, the incorporation of powdered silver, aluminum, or copper into the resin improves its polymerization shrinkage, thermal conductivity, and water sorption [3, 4, 5]. In this review, we present the possibilities of mixing PMMA with some modern enhancing materials and the results of these combinations, which we have collected and described below.

POLY(METHYL METHACRYLATE) ADDITIVES

Fillers

Nano-carbon fillers

Nanotechnology could not exist without its main branch, i.e., nano-carbon [6]. Incorporating 1% of carbon nanotubes into acrylic resin improves its both flexural and impact strength, simultaneously reducing its hardness [7]. Recent studies focus on adding single- and multiple-wall carbon nanotubes to resin in order to change its mechanical properties. Research results show that filling acrylic resin with 1.5 wt% of single-walled carbon remarkably improves its transverse and impact strength, but reduces the hardness of the outer layer of the resin [8]. High wt% of multiple-wall carbon nanotubes added to PMMA causes its decreased fatigue resistance, but adding 0.5–1.0% of multiple-wall carbon nanotubes increases the flexural strength and elasticity of acrylic resin [9].

Titanium dioxide

Research is also conducted on the introduction of titanium dioxide (TiO_2) particles into acrylic resin. According to some studies, these particles could increase hardness, fracture toughness, and flexural strength of PMMA [10, 11]. The addition of TiO_2 particles also reduces its water solubility and sorption [12], while increasing impact strength [11] and thermal conductivity [13]. However, not all studies prove that TiO_2 particles improve the flexural strength of the resin. This is probably caused by particles clustering in the resin, which weakens its strength [14]. Some papers also show that TiO_2 particles incorporated into PMMA cause decreased E-Modulus and coefficient of thermal expansion and contraction [11]. Alwan and Alameer found out that adding 3 wt% of silanized TiO_2 nanoparticles causes lower smoothness of the outer layer of acrylic resin. They also noticed increased surface hardness, impact strength, transverse strength, and decreased water solubility and sorption after integrating silanized TiO_2 NPs into PMMA [15].

Silicon dioxide

Nanoparticles of silicon dioxide (SiO_2) are also a subject of research because of their ability to improve the thermal and mechanical properties of acrylic resin [16]. Like the above-mentioned particles, SiO_2NPs cause improved impact strength and transverse strength of the resin. Outer layer hardness is increased with a high concentration of SiO_2, but inner hardness and fracture durability are improved with a low concentration of SiO_2. Clusters of concentrated particles cause an increased risk of fracture [17]. According to da Silva et al., the flexural strength of acrylic resin can be improved by adding surface-treated silica, without changing the hardness of PMMA [18]. On the other hand, Cevik and Yildirim-Bicer reported that nanoparticles of silica reduce the flexural strength of acrylic resin [19].

Zirconium dioxide

Some recent studies showed that zirconium dioxide (ZrO_2) increases flexural strength of PMMA [12, 13, 16], but others found that grouped particles of ZrO_2 produce weakened areas, which results in reduced flexural strength [20]. Also, ZrO_2 incorporated into PMMA reduces its solubility and water sorption, while increasing the hardness, fracture resistance, and impact strength of acrylic resin [12]. In addition, another study shows that ZrO_2 improves thermal conductivity when combined with PMMA [13]. Zirconia nanoparticles (ZrO_2NPs) without surface treatment cause improved flexural and impact strength [21, 22], as well as increased fatigue strength and compressive strength. The hardness of PMMA and its fracture endurance are also improved [22]. Some studies have shown that treating nanoparticles with a silane coupling agent causes better connections between ZrO_2NPs and acrylic resin, which leads to even better improvement of the mechanical properties of PMMA. In effect, this combination has increased the impact and flexural strength of PMMA without changing its tensile strength [23]. However, Mohammed and Mudhaffar found that the silanization of nanoparticles also has an influence on tensile strength and fatigue strength, as it increases these properties. Significant improvements in the hardness of acrylic resin, and reduced water sorption and solubility were noticed as well [24].

Yu et al. also studied the influence of combining ZrO_2, zirconium nanotubes, and nanoparticles with PMMA and observed that due to the diversity of ZrO_2 properties such as abrasion resistance, biocompatibility, toughness, and mechanical strength, it improves physical properties of acrylic resin. Zirconium nanotubes were obtained after anodization and then prepared. As a result, mixing acrylic resin powder with ZrO_2 nanotubes caused a better enhancement effect of PMMA than mixing it with ZrO_2NPs. It resulted in improved flexural strength, which was the greatest after adding 2 wt% of untreated zirconia nanotubes [25].

Silver nanoparticles

Nanosilver antimicrobial and healing properties were already described in ancient times by Hippocrates. Ancient Phoenicians stored water, vinegar, and wine in silver vessels. Nowadays, silver ions and their effects are used, for example, in the production of dishwashers, refrigerators, and packaging. Research is being conducted on introducing AgNPs into acrylic resin because due to the roughness and irregular surfaces of dental prostheses, bacteria from the mouth easily accumulate on them, and the antibacterial and antifungal effects of AgNPs [2, 26, 27, 28] could help counteract this. Nanosilver particles are preferred over powdered silver because nanoparticles are easier to work with and create smoother surfaces.

Juan Carlos et al. summarized and described various studies conducted by different authors and came to the conclusion that PMMA infused with AgNPs has its mechanical properties changed depending on the method of AgNPs synthesis, its dispersion, and concentration. Mixing silver nanoparticles with polymethyl methacrylate monomer before the polymerization reaction gives the best results [28]. Hamedi-Rad et al. found that combining PMMA and AgNPs significantly changes properties of this material. They prepared 36 specimens grouped into 3 sections, which were also divided into 2 subgroups of control PMMA (unmodified) and test PMMA (combined with 5 wt% nanosilver). The results of their study showed that the compressive strength and thermal conductivity of PMMA filled with AgNPs increased, while the tensile strength significantly decreased compared to ordinary acrylic resin (control group) [27].

It is not only the antimicrobial and antifungal characteristics of silver nanoparticles but also the better processing and smoother surfaces of acrylic denture base filled with AgNPs that contribute to slowing down the adherence of pathogens, and hence, colonizing patients' mouths.

Fibers

Studies show that reinforcing acrylic resin with glass, polyamide, polyethylene, and polypropylene fibers increases the impact and flexural strength as well as fatigue resistance of the resin [1]. Glass fiber also significantly improves Vickers hardness [29] and toughness of acrylic resin. Furthermore, Agha et al. found in their research that depending on the location of the glass fiber in the resin, its flexural properties vary. Placing fiber near the topmost layer of the denture base, on its tensile stress side, caused improved flexural modulus, toughness, and flexural strength. However, placing glass fiber in an area of neutral stress only resulted in improved flexural toughness of the resin dental base. In addition, flexural modulus increases when it is placed on the compressive side [30]. Combining silanized glass fiber with heat-cured and light-cured resins proved to be biocompatible [31, 32]. Furthermore, PMMA enhanced with glass fiber has decreased porosity, which results in lower adherence of *Candida albicans* [31].

Polyamide fiber, which contains both aramid and nylon fibers, changes the properties of the resin in 2 ways. Nylon was found to increase the fracture resistance of PMMA because of its high resistance to linear stress [33]. The other component, aramid fiber, improves its flexural strength and flexural modulus. On the other hand, when the concentration of the fiber is higher, the resin hardness decreases. Filling the denture base resin with aramid fiber was also found to be biocompatible [34, 35].

The toughness and elastic modulus of PMMA can be significantly increased by weaving polyethylene fiber into the resin. However, all procedures used to prepare polyethylene fiber, such as treating it with acid or positioning, make fiber usage troublesome [36]. Another material, polypropylene fiber, resulted in improved impact strength of the resin. In addition, processing these fibers with plasma, which appears to strengthen acrylic resin, results in obtaining the highest impact strength and reducing susceptibility to cracking [37].

Natural fibers such as oil palm empty fruit bunch and vegetable fiber (ramie fiber) are also the subject of research on enhancing the properties of acrylic resin. The former is found to significantly increase the flexural modulus and flexural strength of PMMA [38], but the latter only increases flexural modulus while decreasing the flexural strength of acrylic resin compared to regular PMMA. The only disadvantage of this fiber is its long form, which needs to be prepared and cut before use [39].

Properties of halloysite nanotubes

Halloysite is a harmless, biocompatible two-layer mineral from the group of aluminosilicates, and has a very similar structure to kaolinite. It is composed of a tetrahedral silicon oxide layer and an octahedral layer of hydrated alumina. There are 2 types of the mineral: dehydrated and hydrated halloysite. The transition from one form to another can even take place at room temperature [40, 41]. It is characterized by high porosity, specific surface area, ion exchange, sorption capacity, and chemical resistance. Halloysite is quite a cheap mineral which is present in large amounts. The layered-tubular structure of halloysite is collected from one of its biggest deposits in Dunino, near Legnica in Poland [42].

Abdallah investigated samples of acrylic resin with the addition of HNTs. Four groups of 10 samples each (in total, 40 specimens) were classified. The first of them was just regular acrylic resin powder, which was the control group. The second, 3 and 4 ones were filled with 0.3 wt%, 0.6 wt%, and 0.9 wt% HNTs, respectively. The values that were measured were flexural strength, microhardness, and Young's modulus. According to that study, mixing a little amount of halloysite powder with acrylic resin powder (0.3 wt% of HNTs) resulted in a higher improvement of microhardness and a lower improvement of flexural strength and Young's modulus. However, the addition of more HNTs (0.6 or 0.9 wt%) resulted in decreased hardness values, but neither flexural strength nor Young's modulus was significantly decreased. These differences are probably caused by halloysite aggregates, which occur when too much halloysite powder is added to PMMA. They seem to be the spots of material weakness where the dentures may break. The research showed that adding only a little amount of halloysite gives the best results as regards enhancing PMMA with HNTs [43].

MODERN THERMOPLASTICS

In addition to strengthening PMMA with various materials, it is worth taking a look at modern thermoplastic materials used in industry and medicine. Below, we present materials such as acetal resins (poly-oxymethylene) and BioHPP (polyetheretherketone – PEEK) enhanced with microceramics.

Acetal resin

Compared to a number of other metals, acetal resins display greater strength, which is why they have been used in industry, among others in the production of drive components (e.g., gears, rollers, and shafts) and construction elements (e.g., handles, and slings). In addition, they are often found, for example, in household appliances, vehicles and electronic office equipment. The biocompatibility of acetal was tested on the DuPont Delrin® material [44, 45]. Due to this feature, acetal has been used in such areas of medicine as cardiosurgery or orthopedics, where it can successfully act as an artificial heart valve or bone, such as the collarbone or hip.

In dentistry, acetal materials are used in surgery, orthodontics (as retainers), and implant prosthetics [46]. Regarding dental prosthetics, they are more and more often used in the production of partial dentures, as frameworks in skeletal dentures, and also as clasps, which, depending on the need to optically shorten or lengthen the clinical crown of the tooth, are made of pink acetal or have the color that resembles the teeth [47, 48, 49, 50]. Without a doubt, this material surpasses metal alloys in terms of aesthetics.

Acetal resin, unlike commonly used acrylic resins, does not contain unpolymerized monomers that can cause allergic reactions and inflammation of the oral mucosa [51, 52, 53]. Moreover, when used in skeletal dentures, it is a good solution for people allergic to metals contained in traditional dental alloys, e.g., chromium, cobalt, and nickel. Additionally, the lack of metal alloys in the oral cavity excludes the formation of a galvanic link between one type of alloy and, e.g., an amalgam filling [54, 55].

Arikan et al. proved in their research that the acetal material has lower solubility and water sorption than PMMA [56]. This is of particular importance when acetal is used in the construction of dentures present in the oral cavity for a long time, as fluid sorption can cause changes on the surface of these dentures. The color of food, its pH, and thus, the saliva's pH, may lead to the discoloration of the material used in the construction. This aspect was studied by Frączak et al. [57]. Using artificial saliva, they observed that acidic pH makes the acetal material brighter, while alkaline pH makes the material darker than the original color.

The susceptibility of prostheses to the accumulation of microorganisms on their surface is also a disadvantage that patients and doctors pay attention to. Due to the increased deposition of bacteria and fungi on removable dentures, oral mucosa is exposed to the occurrence of prosthetic stomatopathy. Microorganisms occurring in the oral cavity, such as *Candida albicans*, *Pseudomonas aerguinosa*, *Staphylococcus aureus*, *Enterococcus hirae*, and *E. coli* bacteria, to the least extent colonize and deposit on acetal as compared to acrylic resin and chromium-cobalt alloy, which has been tested and documented by Sobolewska et al. [58, 59].

Sobolewska et al. conducted studies on the bio-compatibility of acetal material on rats. For this purpose, acetal plates were implanted under the cheek mucosa. After 6 weeks, slight inflammatory reactions were observed at sites in contact with the plates in histopathological analysis [60, 61, 62, 63]. However, more detailed clinical and laboratory tests are still required to provide a specific answer regarding the inertness of acetal resin.

BioHPP

BioHPP is a semi-crystalline and high-grade polymer based on PEEK containing 20% of special ceramic fillers (BioHPP; BredentGmbH, Senden, Germany). Polyetheretherketone was developed by a group of English scientists in 1978, later commercialized for industrial applications in 1981 [64], and in 1998 it was proposed as a material for biomedical applications by Invibio Ltd. (Thornton-Cleveleys, UK). In the same year, Victrex PEEK (London, Great Britain) introduced PEEK-OPTIMA for long-term implantation applications [65, 66].

Polyetheretherketone and polyetherketoneketone belong to a very large family of polyaryletherketones – high-temperature thermoplastics which, thanks to their wide temperature range, are characterized by stiffness, high strength, and resistance to hydrolysis. Due to these properties, they are used in the aviation, automotive, semiconductor technology, and medicine industries.

Polyetheretherketone is an X-ray impermeable, rigid material with excellent thermal stability up to 335.8°C [67]. Water solubility at room temperature is 0.5% by weight [65]. Young's modulus of elasticity (in compression and tension) is 3–4 GPa [68, 69], which is close to, but not identical to, that of human cortical bone of 7–30 GPa [70, 71]. The modulus of elasticity in bending is 140–170 MPa. The thermal conductivity of the material is 0.29 W/mK, and its density is 1.3–1.5 g/cm^3 [68, 72, 73]. Fan et al. found out that the melting point of PEEK is 334°C, the crystallization peak is 343°C, and the glass transition temperature is 145°C. Due to such thermal properties, this material is stable in the human body [74].

Application and biocompatibility of polyetheretherketone

Due to its high strength parameters, PEEK is used in construction, aviation and automotive, as well as in the chemical industry [75]. Various structural elements such as gears, piston rings, pump and valve components are also made of it. Additional characteristics, i.a., biocompatibility with hydroxyapatite and flexibility, enable the use of PEEK in medicine as orthopedic implants in patients suffering from back problems [64].

This material induces a slight immune response in a living organism, which was observed by Williams et al. [76], while the study by Katzer et al. showed that PEEK was neither mutagenic nor cytotoxic [77]. Despite the fact that PEEK is biocompatible, has a modulus of elasticity similar to that of human bone and is chemically stable, it is a biologically inert material with limited osteoconductive properties, which makes it difficult to integrate with bone tissues after implantation [78, 79]. In order to improve the osseointegration of PEEK, a number of possibilities have been proposed, such as coating implants with synthetic hydroxyapatite [80], incorporating nanoparticles of fluorohydroxyapatite into the PEEK structure [81], increasing the surface roughness of PEEK, and chemical modifications with the use of oxygen plasma [82, 83].

Polyetheretherketone as a material for implants

So far, metals such as titanium and its alloys, which have excellent corrosion resistance, high mechanical strength and cytocompatibility, have been very popular orthopedic and dental materials [84]. However, there are some concerns about the release of harmful metal ions, as well as about the fact that the modulus of elasticity of metal alloys differs from that of human bones and can cause resorption [85]. For this reason, metal substitutes are intensively searched for, as this will make it possible to limit negative biological reactions after implantation surgery, such as allergy, osteolysis, loosening and, consequently, even implant rejection, called implantation failure [86]. It is the PEEK material that provides an alternative to metals such as titanium. It is strong, stiff, lightweight, nontoxic, and has a lower modulus of elasticity (3–4 GPa) [68, 69] compared to titanium and other metal alloys, which reduces the stress shielding range that is often seen in titanium-based metal implants [87].

It is well known that one of the main causes of implant failure is microbial infection [88, 89]. The lack of antibacterial action between the implant and the abutment often leads to oral cavity infections, inflammatory reactions, destruction of adjacent tissues, loosening of the implant, and even its loss [90]. Sanpo et al. showed that the enhancement of the antimicrobial properties of PEEK can be successfully achieved by coating the implant surface with hydroxyapatite mixed with silver ions [91]. Unfortunately, excessive secretion of silver nanoparticles limits the growth of osteoblasts [92], causes cytotoxicity and leads to damage to internal organs [93, 94]. The aforementioned incorporation of fluorohydroxyapatite particles into the PEEK structure appears to be a better way to achieve antimicrobial activity in the absence of negative effects on osseointegration. After surface treatment to increase the porosity of the material, the cytocompatible PEEK/nano-FHA biocomposite shows better bioactivity, osseointegration and bone-implant contact compared to the pure PEEK material, as proven by Wang et al. [81].

Polyetheretherketone in dentistry

The use of PEEK is not limited to bone implants; it can also be used in dental prosthetics as a foundation for both permanent prosthetic restorations (crowns and bridges) and removable ones (skeletal dentures). Compared to metals used in dentistry, it is characterized by greater aesthetics, lightness, biocompatibility, and a lower degree of discoloration [95]. It is preferred by patients with high aesthetic requirements; however, due to its gray-brown color, it is not suitable for monolithic aesthetic restorations in the anterior region. The face of the PEEK foundation should be covered with a more aesthetic material, such as a composite, to obtain an aesthetic effect [96]. Costa-Palau et al. also published a clinical report on the use of a PEEK obturator to close the mouth-to-nasal junction [97].

CONCLUSION

New solutions are being developed to improve the mechanical properties and hygiene of dentures. One solution is to reinforce acrylic resin with HNTs or AgNPs to increase patient comfort and oral hygiene. Another promising solution is the use of modern thermoplastic materials, which have better properties than acrylic resin. Additionally, the properties of PMMA denture base material can be enhanced with the addition of fibers, fillers, and silanized nanoparticles to reduce damage and cracks, e.g. in the event of an accidental fall or an inappropriate bite. Unfortunately, most of the reviewed studies were limited to *in vitro* research without clinical consequences. However, due to the lack of an ideal material for dentures, the properties of PMMA can be improved with these modifications to make it significantly more convenient for patients to use.

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