

Acrylate Polymers in Dentistry

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Concerning the composition and method of polymerization initiation, polymers for the production of denture bases are divided into four types: heat-, cold-, light-, and microwave-polymerized. Computer-Aided Design and Manufacturing (CAD/CAM) acrylate dentures are made from factory blocks of dental acrylates and show optimal mechanical and physical properties, undoubtedly better monomer polymerization and thus biocompatibility, and stability of the shape and colour of the base and dentures. Regardless of the number of advantages that these polymers have to offer, they also exhibit certain disadvantages. Technological development enables the enhancement of all acrylate properties to respond better to the demands of the profession. Special attention should be paid to improving the biological characteristics of acrylate polymers, due to reported adverse reactions of patients and dental staff to potentially toxic substances released during their preparation and use.

acrylic polymers

dentistry

biocompatibility

1. Use of Acrylate Polymers in Dentistry

Acrylate polymers represent one of the four most commonly used groups of materials in modern dentistry, primarily in prosthodontics. As building materials, acrylates are used for the production of the base plate of mobile dentures, artificial teeth, temporary crowns and bridges, mobile orthodontic appliances, obturators and maxillofacial prostheses, as well as for the needs of lining and repairing these restorations. As auxiliary materials, acrylates are used for individual tray production, models of prosthetic restorations, bite blocks, and less often for the production of occlusal ridges. Special types of acrylates are an integral part of composite and modified glass ionomer cements ^[1].

2. Types of Acrylate Polymers in Dentistry

According to their consistency and purpose, dental acrylate polymers are divided into hard (brittle), which includes acrylates for the production of denture plate bases, obturator prostheses, epitheses and maxillofacial prostheses, their repair and lining, and soft (flexible), which are used for lining denture bases in special indications: conditioning of oral tissues, cushioning of masticatory pressure on the mucous membrane of the denture support, and treatment of inflammation ^[2].

Regarding the composition and the method of polymerization initiation, polymers for the production of denture bases are divided into four types (ISO 1567: 1999): heat-, cold-, light-, and microwave-polymerized ^[3].

3. Composition of Dental Acrylate Polymers

According to their composition, acrylate materials are esters of poly(acrylic) acid. PMMA (IUPAC name: poly [1-(methoxy carbonyl)-1-methyl ethylene]) is a synthetic polymer prepared by the free radical addition and polymerization of methyl methacrylate ($C_5O_2H_8$) to poly methyl methacrylate ($C_5O_2H_8$)_n [4]. The polymerization reaction is initiated by the creation of free radicals chemically or by heat, microwave or light energy. The propagation phase involves the binding of monomers, followed by the termination phase and the completion of polymer chains by the reaction of monomers and free radicals [5].

The most commonly used heat-polymerized dental acrylates are used to make denture bases. Polymerization occurs by mixing the powder and liquid components in the presence of thermal energy (water bath), which activates the polymerization initiator (dibenzoyl peroxide). Dibenzoyl peroxide dissociates into carbon dioxide creating free radicals at a temperature of 70 to 100 °C. Conventional heat curing cycle involves a longer curing time (~9 h at 74 °C); and today often used rapid-heat-polymerized PMMA requires a significantly shorter (20 min at 100 °C) curing time [6].

The polymerization process can also be started with microwave energy, and the main advantage of this preparation is the time efficiency (three minutes at 500 w) in the microwave, which results in compensations with similar mechanical physical properties as conventional mechanical heating. These materials do not contain benzoyl peroxide as a polymerization initiator [7].

Denture lining is indicated in case of readaptation of the denture after resorption or atrophy of the oral tissues supporting the denture. Materials that are the same or very similar in physical and chemical characteristics to the materials from which denture bases are made are used during this process. Denture lining can be performed directly in the patient's mouth by a standard clinical procedure, using PMMA-based material (hard acrylate) or poly (ethyl methacrylate)-based material (PEMA) soft (resilient) acrylate to act as an oral conditioner to prevent inflammation by reducing mechanical irritation or damping of forces acting on the alveolar ridge [8].

Cold polymerized PMMA (chemically polymerized or auto polymerizing PMMA) contains a polymerization accelerator (N,N dimethyl-p-toluidine, tertiary amines, sulfuric acid) that activates benzyl peroxide, creating free radicals to initiate polymerization [9]. The degree of polymerization of cold polymerized acrylates compared to hot polymerized ones is significantly lower, and the amount of residual monomer affects the biological, physical and mechanical properties of the acrylate material [9].

Regarding soft dental acrylates, the polymer is most often PEMA, but it can also be PMMA, as well as PBUA. Liquids include ester plasticizers (dibutyl phthalate, butyl glycolate) in a percentage of 30% to 60% and ethanol as a solvent, in a proportion of 4–60% of the total mass. Plasticizers provide softness or resilience to this type of material at body temperature. Plasticizers are soluble in oral fluids, and their gradual loss over time leads to hardening of the material in the patient's mouth [10]. Given the proven toxicity of phthalates, the most commonly used plasticizers in dental acrylates, their replacement with citrates would significantly improve the biological value

of dental acrylates. The characteristic of soft acrylates is that they change their composition and consistency over time and harden during their function in the orofacial system, which is in accordance with the indications assigned to them [\[11\]](#).

Unlike classic two-component systems, light-polymerized acrylates are single-component plates or gels, which are easily adapted to the working model and are only then polymerized. According to their composition, they are urethane dimethacrylate (UDMA) with micro silica filler [\[12\]](#). The material has found application in the repair of dentures and the production of individual trays [\[12\]](#).

4. Physico-Mechanical Properties of Dental Acrylate Polymers

All dental building materials become an integral part of the orofacial system and are exposed to the action of high-intensity masticatory forces. Therefore, they must possess optimal mechanical and physical properties.

To meet the expectations, dental acrylate polymers need to have the following: supreme hardness, impact strength (restoration fracture resistance), fatigue strength (resistance to stress in functions of the orofacial system), high tensile strength, abrasion resistance, high modulus of elasticity and good resilience [\[13\]](#). Research done by Kawaguchi et al. has shown that the flexural strength of the specimens with Mw 220,000 and 350,000 PMMA beads was significantly higher than the strength of specimens with beads having other molecular weights [\[14\]](#). The desired physical characteristics of these acrylates have low specific weight so that the dental restoration is as light as possible, as well as thermal and dimensional stability [\[15\]](#).

Differences in these properties among various types of dental acrylates depend on the method of polymerization, as well as the average molecular weight of the polymer. Thus, the presence of residual monomer (MMA) of low molecular weight reduces the hardness, strength, and elasticity modulus of acrylate materials. Even though the hardness, strength, and resistance impact of completely polymerized cross-linked materials are less compared to tooth tissues, acrylates meet the requirements set by the profession. The mechanical properties can be improved by incorporating grains and fibres of glass, zirconium oxide, aluminium oxide, or silicon carbide into a conventional acrylate mass, although there may be a problem with material homogenization [\[16\]](#). Due to low elasticity, acrylates are brittle and prone to fracture. The fracture resistance of acrylate materials can be improved by incorporating elastomers (vinyl copolymers), or polyethylene, polyester, and nylon fibres with a high modulus of elasticity within their matrix [\[17\]](#).

The physico-mechanical properties of heat-polymerized dental acrylates are better in comparison to cold-polymerized ones, which is explained by their more complete polymerization. The majority of research has shown that microwave-polymerized acrylates have mechanical and physical properties similar to heat-polymerized acrylates [\[18\]](#)[\[19\]](#).

On the other hand, single-component light-polymerized acrylates exhibit a more complete bonding, less residual monomer, and therefore better mechanical quality and biocompatibility [20].

The use of Computer-Aided Design and Manufacturing (CAD/CAM) for the production of dentures has been on the constant increase. CAD/CAM acrylate dentures are made from factory blocks of dental acrylates and show optimal mechanical and physical properties, undoubtedly better monomer polymerization and thus biocompatibility, and stability of the shape and colour of the base and dental implants [21].

Higher porosity of cold-polymerized acrylates is a consequence of faster polymerization under poorly controlled conditions [22]. Their internal porosity makes them less resistant to fracture, while the surface porosity enables better adherence of biofilm and food residues [23]. Additional polymerization or post-polymerization could improve these properties, as shown by some studies [24][25][26].

Incomplete polymerization increases liquid absorption and solubility of dental acrylates. Residual monomer acts as a plasticizer in the material, but the decrease in the quality of the material can be attributed to the release of residual monomer into saliva and the compensatory absorption of liquid from the oral environment, which leads to the plasticization of the material and makes it more flexible and resilient [27]. The amount and rate of water absorption depend on network density, potential hydrogen bonds, and polar interactions. Denser polymer networks have a lower possibility of water absorption [28]. According to ISO 1567, the increase in bulk density of dental acrylate polymers per unit volume (water absorption) must not exceed $32 \mu\text{g}/\text{mm}^3$ [3]. Although all dental acrylates show water absorption within the standardized limits, significantly higher values were observed for cold-polymerized ones, which is the consequence of their weaker polymerization [29].

Analogous to water absorption, a more compact dental acrylate material shows lower solubility. The solubility of acrylates in saliva is negligible. According to ISO 1567, the acceptable solubility is $1.6 \mu\text{g}/\text{mm}^3$ for heat- and $8 \mu\text{g}/\text{mm}^3$ for cold-polymerized dental acrylates [3]. However, one should not disregard the fact that acrylate restorations release residual monomer, benzoyl peroxide, plasticizers, and other substances into the oral environment, which dissolve in saliva and act on oral tissues. Soft acrylate plasticizers are soluble in oral fluids and their predicted loss over time leads to the hardening of the material in the patient's mouth [30].

Dental acrylate polymers show lower abrasion resistance compared to teeth. Consequently, dentures erode easily if they are opposed by natural teeth or fixed restorations [17].

Acrylates are dimensionally stable materials, and possible problems can be expected at the points of connection of dentures and orthodontic appliances with other materials, due to internal stress as a result of differences in thermal conductivity [13].

5. Biofilm on the Surface of Dental Acrylate Polymers

The biological activity of dental acrylates can be observed through two aspects: their interaction with tissues and agents from the environment and the release of potentially toxic substances with local and systemic side effects [31][32].

The interaction of acrylate materials with the environment is determined by the surface design of the material, primarily its roughness. The roughness of acrylates depends on the type, i.e., the polymerization procedure, as well as the final treatment or polishing of the dental restoration [33]. The uneven surface of acrylate materials is a preferred place for the accumulation of plaque, pigments, food and drink residues, as well as decayed oral tissue [34].

To compare the adhesive ability of soft and hard dental acrylate polymers, Kostić et al. analysed their structure after a four-week intramuscular implantation by employing SEM analysis (Scanning Electron Microscopy) [35]. The implanted acrylate samples showed a high adhesive potential for the surrounding muscle tissue. After their removal, the tissue remains, with a tendency of growing into the material, could be seen on the surface. Samples obtained by cold polymerization showed a significantly higher degree of adhesion compared to heat-polymerized acrylates.

The obtained results showed that the tissue grows into the porous acrylate material and can decompose in it. Consequently, the polymer becomes the collector of infectious material, enabling recurrent infections. Considering the inhomogeneity of the internal and external structure of dental acrylate polymers, flawless hygiene of dental prostheses is imperative [36].

The most common recurrent infection associated with wearing acrylate dentures is denture stomatitis (*Stomatitis prosthetica*), which occurs in 70% of wearers of acrylate dentures [37]. Fungi of the genus *Candida*, especially *Candida albicans*, are mainly responsible for the occurrence of denture stomatitis. It is a dimorphic fungus that is a commensal colonizer of the oral cavity, gastrointestinal and reproductive systems. In immunodeficient states, *C. albicans* may become virulent and cause candidiasis. Surface roughness, salivary pellicle, hydrophobicity, and electrostatic interactions are the predilection factors that affect adhesion and biofilm formation of *Candida* on acrylate dentures [38].

C. albicans has the ability of a multicellular growth form, and its transition to the mycelium form enables easy adhesion to acrylate material. In the patient's mouth, acrylate polymer is coated with salivary pellicle formed by the precipitation of salivary mucin and glycoproteins [39]. The surface of acrylate polymers is hydrophobic and *Candida* binds to it by hydrophobic interactions and electrostatic forces [40][41]. Surface free energy proportionally increases *Candida* adherence [42][43].

Complex biofilm on the surface of acrylate materials can be the cause of other oral infections, but above all the cause of damage to the periodontal tissue and caries on the remaining teeth [44][45]. Cases of aspiration pneumonia and gastrointestinal infections associated with denture stomatitis [46] have also been reported in the literature. To

prevent various infections triggered by the presence of biofilm on the surface of acrylate dental polymers, it is necessary to work on its removal and reduction, but also on improving the performance of the material itself.

Candida reproduces easily in the porous and moist environment of acrylate material, thus is often more abundant on dentures themselves than on the oral mucosa [47]. The contamination of dentures is irreversible and prevents healing of the oral cavity. Biofilm surrounded by an extracellular matrix is a biological barrier for the penetration of antifungal drugs. Within the biofilm, phenotypic changes occur as a result of limited availability of nutrients and oxygen, which consequently reduces their sensitivity to antimicrobial drugs [48][49].

The incorporation of fluconazole, chlorhexidine, amphotericin B, nystatin, and others improves the antimicrobial properties of acrylate polymers and limits the formation of biofilm on dentures [50][51].

The antimicrobial properties of nanostructured silver, impregnated into acrylate materials for the production of dentures, against *C. albicans* and *Staphylococcus aureus* were also confirmed—in proportion to the concentration used [52][53][54]. Examining the antimicrobial activity of silver incorporation into PMMA, Gligorijević et al. showed the best antimicrobial activity against *C. albicans* (MIC = MMC = 3.13 mg/mL) was identified for samples containing 10% AgCl PMMA, for both cold and heat curing PMMA. Slightly lower activity of these samples was shown against *S. aureus* (MIC/MMC = 3.13/6.25 mg/mL). 10% AgNPs PMMA of both cold- and heat-curing showed lower activity on the tested microorganisms compared to samples with the 10% AgCl PMMA, with MIC = MMC = 12.50 mg/mL [53]. The adhesion of biofilm was significantly reduced by incorporating zirconium dioxide and titanium dioxide into the acrylate structure [55][56].

Improving the surface structure of acrylate polymers, for instance, by modifying and incorporating phosphate or carboxyl groups into the structure of PMMA, can result in less accumulation of microorganisms [57][58]. Copolymers obtained in this way have a negatively charged surface, attract positively charged antimicrobial proteins of saliva, and prevent the adsorption and growth of candida while weakening the mechanical properties of acrylates [59]. Given the complexity of denture stomatitis therapy, as well as frequent resistance and relapses, coating and immersion of acrylate restorations in essential oils and extracts can be an alternative in the treatment of denture stomatitis [60].

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