



Improvement of Acrylic Resins Structure in Removable Prosthesis Base Polymerization

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Abstract: *The materials used in additive techniques are initially in a plastic state so that they can be inserted into various cavities or easily molded after which they pass into a rigid phase. This process is performed by various methods, depending on the nature of the material. The study aims at analyzing the chemical and biological behavior of flexible acrylates compared to classical acrylates, whose structure was optimized through the introduction, at a structural level, of certain polymeric and antiseptic structures in view of obtaining a high degree of biocompatibility, the elements of variability consisting in the difference between the two polymerization regimes, the polymerization under pressure and the classical polymerization. The polymerization of acrylic resins by the technique of thermobaropolymerization with injection compensation leads to the formation of materials with superior impact resistance. The pressure regime is very important, being a factor that influences the polymerization without being initiated. Breaking strength is an essential element in assessing the quality and duration of the prosthesis use.*

Keywords: *Plastic material, polymerization, acrylic resins, adaptability of the base of prostheses*

1. Introduction

Acrylic resins have dominated the technology of dental prostheses for several decades, being the bases of mobile prostheses, artificial teeth, veneers, and even single-tooth prostheses (Jacket crowns, inlays), immobilization rails, etc. Depending on how the materials are presented, there are several systems: one-component systems, two-component systems; three-component systems. Most materials come in a biocomponent form. Three-component systems are rare, and one-component systems have emerged with the possibility of choosing when to initiate light polymerization. The dosage makes sense only in multicomponent systems. The temperature can initiate polymerization reaction in the following ways: high temperature, direct activation of the monomer (used in industry), the average temperature indirectly by the decomposition - placing an initiator (used in the dental laboratory); at low temperatures, the use of a co-initiator greatly favors the decomposition of the initiator. The temperature required for MMA polymerization in the dental laboratory is between 60-100⁰C. The temperature causes the polymerization reaction to accelerate, so in the warmer areas of the material there will be more reaction chains than in cold areas. This can cause variations in the average molecular weight of the polymer and the proportion of residual monomer. Excessive temperature rise can cause the monomer to boil and bubbles are formed in the polymer mass. This happens especially in thick parts of the material where the heat cannot be removed enough and quickly [1-3].

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At a temperature of about 125°C, the polymer is thermoplastic. Between 125 and 200°C the polymer decomposes by depolymerization; at 450°C, 90% of PMMA is depolymerized. It can occur during the finishing and polishing of the material, due to the release of frictional heat produced by the rotary instrument. Increased speed, worn milling cutters, excessive pressure on the instrument, non-stop work or neutralization of a cooling system are the main factors of heat increase. The thermal conductivity of polymers is generally low; the heat cannot dissipate quickly in the mass of the material and thus the increase of the local temperature is high. This way, the degree of polymerization of the polymer is altered and a free monomer can appear, which will remain in the material. This aspect takes place especially in PMMA degradation, when the monomer releases molecule by molecule from the material. All these lead to inferior mechanical, physical and physiognomic properties and a lower biological tolerance. The thermal regime of the thermo-polymerization must be observed [4,5].

The novelty aspects of this study reside in the interrelation aspects brought about by the structural modification of acrylates through the chemical bonding of copolymers, respectively of antiseptic substances with controlled release and the final chemical-biological behavior of the material resulted following the polymerization.

The temperature of the polymerization paste is an additional factor that can influence polymerization. Clinically, a high internal conversion rate results in increased resistance to wear, fatigue, and chemical stability. The pressure regime is a factor that influences polymerization, but without initiating it. In the laboratory, certain phases are performed without the need for a pressure regime, such as: the performance of temporary prosthetic works, individual spoons, occlusion patterns.

The vacuum is used not so much for polymerization as for its precursor. The gaseous inclusions in the material are thus forced to come to the surface due to the pressure gradient. The material will be more homogeneous and, therefore, will result in a protein piece with better characteristics. The use of vacuum in polymerization would make the sub-polymerized layer disappear from the surface due to the lack of inhibitory influence of oxygen in the air, because only a pressure gradient is required.

Pressure polymerization (at the rate of several atmospheres) makes the material better condensed. Another variant of pressure polymerization is the injection of the paste into a mold, representing a thermobaropolymerization by injection [6,7].

2. Materials and methods

A number of 6 test tubes were analyzed in a first stage by means of the SEM technique, under the form of thin rectangular plates of 40 mm in longitudinal dimension and approximately 20 mm in width, with a thickness that varied from 1.8 to 2.5. The mixing ratio between polymer and monomer is specific for each type of product; some acrylates are prepared in the proportion of two parts powder and one part liquid, and others are prepared by mixing three parts powder with one part liquid. Acrylates with a mixing ratio of 3:1 are superior because they have a lower monomer content, are more resistant and have minimal shrinkage. Test tubes were made of flexible acrylate of the Flexite and polyamide type, which were injected according to the technological line destined to this type of material. The Poliapress injecting machine was used. Flexite cartridges were used, which were injected in the mold that contained the specific dimensions of the analyzed test tubes. 10 cm in length, 0.5 cm in thickness and 2 cm in width (Figure 1).



Figure 1.
Poliapress injecting machine. Example of analyzed sample

The test tubes of classical acrylate were made by mixing the acrylate with the monomer, the final material being inserted in the mold and later subjected to the polymerization process.

We created a number of 5 test tubes in which we used various proportions of a type of copolymer elaborated at “P. Poni” Institute of Macromolecular Chemistry from Iasi. AM 88 – maleate copolymer of Na, methyl methacrylate in proportion, to which groups of Eugenol linked.

The biological analysis was carried out by appreciating the degree of adherence of candidiasis yeast, bacteria frequently met at the level of the oral cavity with elder patients. The AFNOR artificial saliva was used, according to the French standards, to which improvements were made, being inoculated with strains of *Candida albicans* yeast isolated from a case of prosthetic stomatitis (10^3 yeasts / mm^2). The test tubes obtained were introduced in 5 containers, incubated at 36, for 72 h. Later, they were introduced in dental plaque revelator, rinsed with pure water, dried, and then recycled. To the basic components of the AFNOR saliva - NaCl 0.70 g/L, KCl 1.20 g/L, Na_2HPO_4 0.26 g/L, NaHCO_3 1.50 g/L, KSCN 0.33 g/L, Urea 1.35 g/L – glucose was added, 5 g/L and casein peptone.

Candida albicans has negative effects on the acrylate it adheres to due to its filament structure, contributing significantly to the degradation of the acrylic material, which is why the individualization of the non-adherence possibilities is extremely important.

The test samples elaborated at the same size were subject to the traction forces on the Hekert test machine within the Polytechnical Institute of Iasi, the Department of Material Resistance.

3.Results and discussions

The SEM analysis reveals structural continuity; at the level of the test tubes whose copolymer proportion was below 1/3 of the powder quantity, there appear aspects of discontinuity with implications at the resistance level in case of test tubes in which a reduction of the monomer was attempted in view of obtaining a higher degree of biocompatibility. Equally, a reduced quantity of Eugenol fails to influence the continuous structure of the acrylate. Polymerization by injection confers a dense structure to the injectable acrylate analyzed, with a net structural superiority compared to the classical acrylate (Figure 2).

The absence of the monomer confers a net biocompatibility to injectable structures, but allows the adherence of candida yeasts.

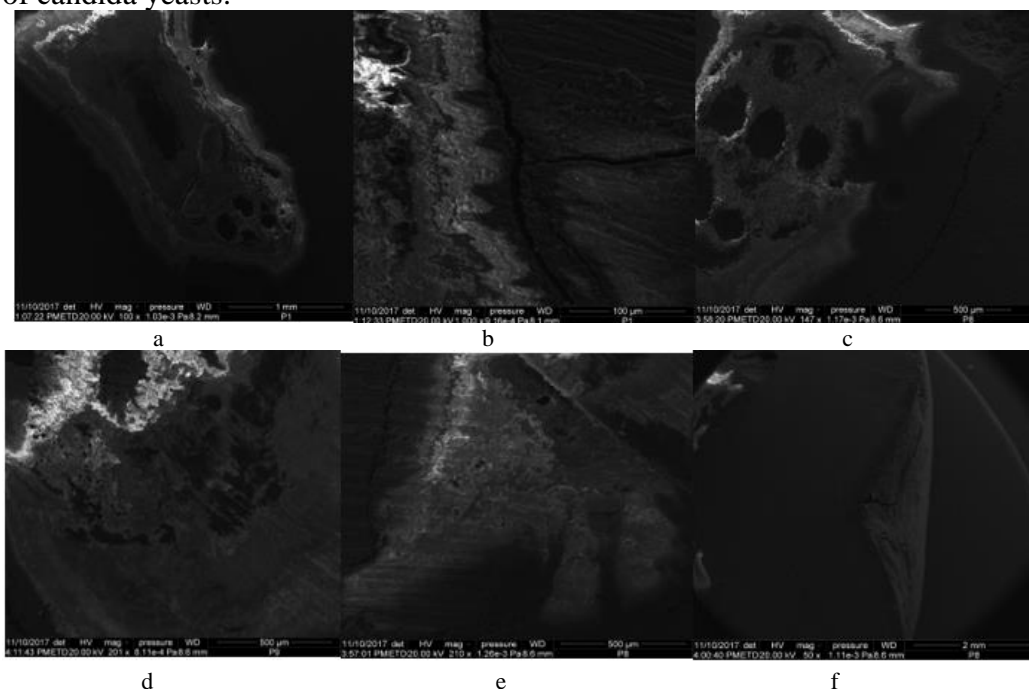


Figure 2. SEM analysis of six sample: a. acrylate +AM88 4g, b. acrylate +2 mg AM88, c. acrylate+5 mg AM 88 + eugenol, d. acrylate and quantitatively diluted liquid, e. classic acrylic sample, f. flexible sample

The techniques for achieving the powder and liquid ratio are weight dosing, weighing of powder and liquid. The monomer must be in the proportion indicated by the package leaflet that accompanies the product. For the homogeneity of the chemical composition and for color uniformity, it is recommended to mix it with a glass rod, after which the container is covered with a glass plate, to prevent vaporization of the monomer.

In the first phase, the mixture forms a friable paste; in the second phase, a sticky, flaky and sticky paste is formed, which flows; in the third phase, the paste is non-sticky, it comes off easily from the walls of the container. In this state of plastic paste, the substance is introduced into the mold.

Upon contact between the monomer and the polymer particles, the outer layers dissolve progressively (the monomer has an active role and the polymer has a passive role): having free valences. The polymerization initiator (benzoyl peroxide) known as the catalyst, produces the release of the double bond of the monomer, followed by activation. As the monomer continues its action of dissolving the polymer particles, the paste becomes more and more viscous, non-sticky, taking on the appearance of dough.

Negative results from the perspective of *Candida* adherence were also noticed in case of test tubes which contained the AM88 copolymer and the eugenol formations introduced at a structural level. These significantly negative results are based on the antibacterial effect of the copolymer, boosted by the eugenol addition (Figure 3). The chemical structure of the AM88 copolymer in the presence of sodium carboxylate, which confers a polyelectrolyte nature, influences the antimicrobial action.



Figure 3. Aspects of the *Candida Albicans* adhesion to the specimens

The duration of these phases is variable, being influenced by the temperature of the environment and of the container; the physicochemical properties of the product (enlargement of the polymer particles) and the presence of plasticizers that facilitate the penetration of the monomer inside the particles.

Following the examination of the tensile strength of the traction test samples one can notice the fragile strength of the classical acrylate at a Force of 1550 N, the breaking of samples which had in their structure a quantity of copolymer AM88 in excess of 4mg, respectively 5mg and eugenol, which gave in at a force of 1400N, respectively 1200 N and the high tensile strength of test samples made of flexible acrylate.

The presence of the AM 88 copolymer, respectively of Eugenol, the substance that binds chemically to the copolymer providing a controlled release, offers the acrylic structure obvious antiseptic qualities; however, the biomechanical resistance is reduced as the quantity of copolymer increases.

If the proportion between monomer and polymer, indicated by the leaflet, is not observed, a series of inconveniences appear: the excess of monomer that determines the increase of the coefficient of contraction of the acrylic mass at the level of ready-polymerized prostheses; the appearance of pores, both in the thickness of the plate and the saddles, as well as on the surface, with negative effects for the mechanical resistance, the maintenance of hygiene and the chromatic appearance; the excess of polymer that determines the reduction of plasticity, the non-uniformity of the chromatic aspect of the prosthesis; low mechanical strength.

In self-curing RAs, the polymer powder contains the initiator and the liquid (monomer) contains the accelerator and inhibitor.

Self-curing acrylic resins have wide applications in the manufacture of gnathoprosthetic devices: making temporary fixed AGPs, making teaching models from RA, modeling with RA. The handling time depends on temperature, mixing intensity and powder/liquid ratio; acrylate fingerprint-model of root canals to make DCRs, making the individual spoon of acrylic resins. The disadvantages are related to the increased percentage of residual monomers, chromatic instability, reduced stiffness. The disadvantages of self-curing resins have led to the use of light curing, thermo-polymerization or other hybrid processes [8,9]. Thermo-polymerization is a polymerization reaction that requires an external caloric intake for initiation. The required temperature depends primarily on the temperature of decomposition of the initiator into free radicals. The heat required for the thermo-polymerization process is obtained by introducing the model-resin-sink assembly in a water bath brought to the desired temperature (maximum 100°C) with the help of a heat source. The lack of water temperature control leads to the obtaining of an acrylate with poor mechanical properties [10,11].

Thermo-polymerization can be used only in indirect techniques, especially for final prosthetic parts and less often for temporary or intermediate stages: obtaining physiognomic components on crowns and mixed bridge bodies, plating a metal skeleton with RA, in the crowns and mixed bridges, making inlays in the DRC by indirect technique; making temporary crowns and bridges; some techniques for making individual ligatures or occlusion patterns; making mobile and movable prostheses, making artificial teeth; making temporary fixed prostheses; repair of fractured prostheses, although, in these cases, self-curing acrylates are preferred, avoiding a new heat treatment-safe source of deformations;

Photopolymerization is the polymerization initiated by the external contribution of electromagnetic radiation, by irradiation with UV or visible radiation.

The photopolymerizable resins for making the bases of the adjunct prostheses are materials based on UDMA and acrylic copolymers, inorganic microfine silica fillers and photo initiation system. They are delivered in the form of foils of a plastic consistency, being foldable. The use of argon laser systems for light curing leads to improved mechanical properties [12,13].

Polymerization of the base of the prosthesis - the base of the prosthesis is made of acrylic resin, by introducing it in the form of a paste in patterns.

Polymerization consists in the formation of a very large molecule, resulting from the gradual addition of identical monomer molecules, resulting in an increase in molecular weight.

According to Skinner, the acrylic resins used for the bases of prostheses must have the following biological and physicochemical properties: be tolerated by the tissues with which they come into contact; be stable in all conditions of use; be insoluble, tasteless and chemically neutral in all foods and enzymes in saliva; not to be distorted, dilated or contracted at the temperature of the oral cavity or under occlusal pressure, be resistant to abrasion and brushing for maintenance; be easy to polish to present surfaces without porosities; be with aesthetic chromatic aspect; be with a stable chromatic appearance; easy to handle; be easy to repair in case of fracture. Acrylic resin comes into liquid and powder form. The liquid is the monomer represented by methyl methacrylate. It has the following physicochemical properties: it is transparent, boils at 100.3°C, is volatile, flammable, insoluble in water, with specific odor, is a strong organic solvent, it can polymerize spontaneously under the influence of light and heat, which requires be preserved in brown vials, in which 1% hydroquinone or pyrogallol are added with an inhibitory role in polymerization. It has a density of 0.945 g cm³ at a temperature of 20°C and a molecular weight of 100. The powder or polymer is the polymerized form of methyl methacrylate. It is composed of specific particles, obtained by dispersing the centrifuged monomer in a neutral liquid (water at high temperature); inert substances (talc) are added to the base substance to prevent physical or chemical bonding of the particles. The well-matched products have various shades of pink, being accompanied by *keys* for choosing the color, in correlation with the color shade of the patient's gingival mucosa. There is also a colorless powder indicated for patients who show intolerance to the dye incorporated in the acrylate. Superacryl acrylic resin (Spofa) is produced in six shades of pink, each marked with a letter: A; B; C; D; E; F. The colorless superacryl is marked with the

number 0 (zero). Each kit is accompanied by instructions for use regarding the proportion of the mixture, the preparation technique, the polymerization rules, etc.

Thermo-polymerization of acrylic resin - polymerization is a physicochemical reaction in which the monomer binds to the polymer and forms the molecular chain from which a solid body results [14,15].

In the oral cavity, the sources of moisture contamination are diverse. The most important is saliva. Another source of contamination is the suction fluid and blood from the marginal periodontium. Moisture is harmful for several reasons. Most monomers and polymers are hydrophobic, so no contaminated areas can appear on contaminated surfaces. Polymerization is a process that takes place over time; it continues slowly due to the chemical mechanism, hardening the material in areas not exposed to light radiation. Self-curing is a polymerization reaction that takes place without the material requiring an external energy input for its initiation. It is sometimes also called chemical polymerization (chemo-polymerization), which is somewhat inappropriate, because obtaining polymers is generally a chemical reaction. The initiation systems in this case consist of two compounds, which leads to the need for biocomponent systems. Factors influencing the polymerization time are temperature-time increases with decreasing ambient temperature; powder particle size; type of polymerization increases with particle size; the volume of acrylic paste subjected to polymerization has no significant influence on time. pH has a value between 4 and 5, being minimal after the second day of polymerization. It grows slowly and reaches the value of 5 only after 2 months. In self-polluting prosthetic RAs, mixing the powder with the liquid is followed by a gradual increase in viscosity, to the saturation stage, similar to what happens in thermo-polymerizable RAs. This increase in viscosity is due to physical and chemical changes in the mixture. The great advantage of thermo-polymerizable RAs over self-polymerizable ones is the stronger diffusion of the monomer and the crosslinking agent in the thickness of PMMA beads. Thermo-polymerizable RAs have a lower residual monomer content, superior hardness, rigidity, and strength. However, the solubility and absorption of water are similar, regardless of the type of polymerization.

The SR Ivocap acrylic resin is much more impact resistant (5845.2N / m) than the others. The technique of thermobaropolymerization with injection compensation leads to the formation of polymers with superior impact resistance. The pressure regime is a factor that influences the polymerization, without an initiation.

The injectable acrylic polymer, which contains polycarbonate nylon, has a higher bending and lower modulus of elasticity [16,17].

These changes increase the impact resistance are accompanied by an increase in transverse deformation. For SR Ivocap, low values of elasticity were obtained.

Regarding the hardness of the obtained materials, it was found that the polymerization technique has an important influence on it and that with the increase of the pressure, materials with higher hardness are obtained.

4. Conclusions

The polymerization regime performed correctly fails to influence the resistance of the biomaterials used, the latter being influenced by the structure of the acrylates, which was optimized through the chemical bonding of the AM88 copolymer, respectively of the eugenol.

The optimum chemical – biological results are due to the addition in the meta-methyl powder of 2 mg of AM 88 copolymer, which modifies the surface state of the material and decisively influences the adherence of candida filaments. With the increase of the copolymer quantity and the addition of antiseptic substance with controlled release, the antiseptic effect increases but the aspects of structural discontinuity revealed by the SEM analysis are correlated with a low tensile strength. The polymerization pressure regime does not increase the bending strength.

The product made by the technique of thermo-polymerization with injection compensation has the highest values of breaking strength. Breaking strength is an essential element in evaluating the quality and duration of use of the prosthesis.



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