Thermoplastic Materials in the Dental Practice: A Review.

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Abstract: Thermoplastic materials (TMs) are composites (co-polymers) that possess the quality of flexibility. They were introduced in dentistry in the 1950s as an alternative to acrylics. TMs have the following characteristics: no residual monomer, no toxic or allergenic additives, high biocompatibility and the ability to keep their shape. At present, the following groups of TMs are used for the fabrication of flexible removable dentures: acetylates, polyamides, thermoplastic acrylic resins, polyolefins and polyesters. These are all non-monomer, high-molecular compounds from different chemical elements with different properties. TMs are made of linear or less branched chains, they can soften during heating and solidify upon cooling.

Keywords: Thermoplastic materials, flexible dentures, polymers

1. Introduction

According to some prognosis, in the year 2025, it is predicted that half of the earth's population will be over the age of 50. Regardless of the dental prophylaxis, the majority of this population will require a full or partial removable dentures. For the purpose of improving the patient's quality of life, it is vital for them to be provided with aesthetic and fully functional dentures.

The acrylic resins are the most used denture base material at the moment. They have several advantages: a simple laboratory protocol, no special equipment is required, satisfactory aesthetics, satisfactory strength and a low price. Disadvantages are also considered: intake of fluids, porous structure, residual monomer, discolouration over time, insufficient mechanical strength, easy aging of the material.

Thermoplastic materials (TMs) are an alternative to acrylics. Nylon polyamides were first synthesized in 1950 as a member of the group of thermoplastic polymers. The first documented case of use of TMs as a denture base material belongs to Arpad and Tibor Nagy. In 1959 they started the Valplast company.

The first thermoplastic fluoropolymer suitable for flexible dentures was introduced in 1962 by the company Rapid Injection System. In the same year, thermoplastic acetate was suggested as a strong denture base material and in 1986 the company Dental D used it for aesthetic clasps, as they are flexible and need no periodical activation.

The TMs used in dentistry are composite materials (copolymers) that possess the quality of flexibility. These materials have the following characteristics: no residual monomer, no toxic or allergenic additives, high biocompatibility and the ability to keep their shape. The high flexibility and accuracy, as well as the variety of shades expand the use of TMs for full and partial dentures, immediate dentures, post resection dentures and temporary dentures after implantation.

At present, the following groups of TMs are used for the fabrication of flexible removable dentures:

- Polyamides
- Acetylates
- Thermoplastic acrylic resins (no residual monomer)
- Polyolefins
- Polyesters

These are all non-monomer, high-molecular compounds from different chemical elements with different properties. The name thermoplastic comes from the ability of the solid resin to transform into liquid when heated. TMs are made of linear or less branched chains, that means they can soften during heating and solidify upon cooling. The long molecule of TMs determines the quality of flexibility and high mechanical stability. The linear molecular type sets the high density of the material, but also a complicated laboratory protocol.

Polyamides

This is the most preferred choice of material within the group of TMs. They have been used since 1938 as toothbrush hairs, but obtained their name "Nylon" in New York in 1939. Polyamides are heterochain polymers with an amide group. These groups are polar and can form long hydrogen bonds with each other (fig. 1).



Figure 1: Chemical structure of a polyamide.

Polyamides are of two types:

- 1) Homopolymers obtained by the polycondensation of diamine and carbonic acid
- 2) Copolymers obtained by the copolymerisation of two or more molecules of diamine and carbonic acid.

There are polyamides 6, 11, 12*, where macromolecules contain only one type of monomer, whilst 66, 69, 610* contain two different types of monomers

* The digits before the polyamide show the number of the carbon atoms included in the monomer.

The macromolecule in a solid state usually has a flat zigzag shape (fig. 2). Due to the amide group the polyamide macromolecules form carbon bonds between each-other, which determines the high melting temperature of the crystal polyamide.



Figure 2: Nylon 6 and Nylon 66 molecular structure models

The polyamides can not be dissolved in solvents such as alcohol, acetone, ketone or other aromatic hydrocarbons and do not uptake liquids. They can withstand mechanical damage and high temperatures. The polyamides also possess sufficient hardness and resistance to hydrolyse at room temperature.

The polyamides used in dentistry are non-toxic and aliphatic. Their molecule has a flat chain configuration made of very long units, containing over 200,000 hydrocarbon atoms. Aliphatic polyamides possess high strength, wear resistance, resistance to decay and bacterial influence. They are used for fabrication of full and partial removable dentures.

Acetal-Polyoxymethylene.

The manufacturing of Polyoxymethylene began in US in 1960, but is used for dental purposes as a non brittle resin in year 1970 (fig. 3).



Figure 3: Polyoxymethylene - chemical formula

The polyoxymethylene has a long chain of alternating oxygen bonded methylene groups. It has a crystalline structure with no residual monomer. This polymer can be synthesized in two forms: homopolymer or heteropolymer. The latter possesses better mechanical properties and stability. In the solid state this compound has a white colour and molecular mass from 10,000 to 30,000. Polyoxymethylene does not have high thermal and chemical stability, but it has high hardness and wear resistance, and

also a high working temperature. It is a hydrophobic molecule, insoluble in chemical solvents and can be processed through high pressure casting. This is a non-toxic polymer with high dynamic hardness, stability and strength at 100° C, high wear resistance to friction. Due to its dense structure and smooth surface, no plaque, stains or smell are retained. Over 90% of polyoxymethylene is used to replace coloured metals and alloys in different industries. The economical benefits come from the fact that the polymers do not require complicated processing unlike the metals.

The acrylic resins used in dentistry are non-modified to avoid toxic and allergenic reactions. Their mechanical stability is approximately 20 times lower than the stability of other dental materials suitable for dentures, whilst the stability of polyoxymethylene dentures is comparable with the stability of the removable cast metal dentures. Due to their high precision and minimal discrepancy polyoxymethylene polymers successfully replace metal alloys in fabrication of removable dentures with precision attachments.

Thermoplastic acrylic resins.

The main difference between the thermoplastic acrylic resins and the classical acrylic resins is the absence of residual monomer. Polymethylmethacrylate $(C_5O_2H_8)_n$ is an amorphous, transparent thermoplastic material, where the molecular mass can reach up to several millions. It is soluble in its own monomer and aromatic compounds such as ketones and formic acid. The material is non-toxic and it is stable in water, alcohol, simple aromatic hydrocarbons, saliva and stomach acids. It has high wear resistance, mechanical strength, aesthetics and variation of shades [Fig.4].



Figure 4: Ppoly(methyl methacrylate) molecular model.

Through heating over 120° C, the polymethylmethacrylate starts melting and goes into high elastic state and can be easily moulded. After 200° C starts evident depolymerisation, which accelerates above 300° C. In dentistry, methylmethacrylate resin is used mainly for full and partial removable dentures.

Polyolefins

This group includes thermoplastic materials such as polybutene, polyethylene, polypropylene. These are flavorless, inodorous, amorphous, non-toxic polymers. Their mechanical stability depends on their molecular weight. Due to their good mechanical and aesthetic qualities they are popularly utilized in dentistry. The most used member of this group is polypropylene - a semi-crystalline transparent polymer with stable colour, that does not absorb liquid.

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Polypropylene has a molecular weight between 75,000 and 200,000 and has high wear resistance. It is indicated for partial removable dentures, temporary dentures and implant supported dentures.

Polyesters

A group of polymers containing ester functional group in their main chain. Polyesters include naturally occurring chemicals, such as in the cutin, as well as synthetics such as polycarbonate. They possess good mechanical properties - high impact strength, high resistence to environmental impact, stability in temperature range from -40° C up to $+120^{\circ}$ C. The polyesters are also elastic (elastic modulus - 1490 MPa) and biocompatible. They are transparent and easy to polish. These qualities make Polyesters suitable for temporary fixed dentures and recently for removable dentures. The working temperature is between 230° C and 290° C.

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