

МИНИСТЕРСТВО ЗДРАВООХРАНЕНИЯ РЕСПУБЛИКИ БЕЛАРУСЬ
БЕЛОРУССКИЙ ГОСУДАРСТВЕННЫЙ МЕДИЦИНСКИЙ УНИВЕРСИТЕТ
КАФЕДРА ОБЩЕЙ СТОМАТОЛОГИИ

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**ПОЛИМЕРНЫЕ МАТЕРИАЛЫ В СТОМАТОЛОГИИ
И ТЕХНОЛОГИЧЕСКИЕ ПРОЦЕССЫ,
ИСПОЛЬЗУЕМЫЕ ПРИ ИЗГОТОВЛЕНИИ
ПОЛИМЕРНЫХ ЗУБНЫХ ПРОТЕЗОВ**

**POLYMER MATERIALS IN DENTISTRY
AND TECHNOLOGICAL PROCESSES USED
IN THE FABRICATION OF POLYMER
DENTAL PROSTHESES**

Учебно-методическое пособие



Минск БГМУ 2018

УДК 616.314-089.23:615.4(075.8)-054.6

ББК 56.6я73

П52

Рекомендовано Научно-методическим советом университета в качестве учебно-методического пособия 21.02.2018 г., протокол № 6

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П52 Полимерные материалы в стоматологии и технологические процессы, используемые при изготовлении полимерных зубных протезов = Polymer materials in dentistry and technological processes used in the fabrication of polymer dental prostheses : учебно-методическое пособие / Н. М. Полонейчик, Д. В. Гарабурда, И. А. Шипитиевская. – Минск : БГМУ, 2018. – 42 с.

ISBN 978-985-567-986-9.

Содержит необходимые студенту сведения о полимерных материалах в стоматологии, а также изложены основные данные о технологических процессах, используемых при изготовлении зубных протезов из полимерных материалов.

Предназначено для иностранных студентов 1–2-го курсов, обучающихся на английском языке.

УДК 616.314-089.23:615.4(075.8)-054.6

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ISBN 978-985-567-986-9

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POLYMER MATERIALS IN DENTISTRY

Polymers are the substances, which molecules consist of many elements of same chemical composition and structure, and these molecules are called macromolecules.

Macromolecules can be built of monomers of same chemical structure (such polymers can be also called homopolymers) or different ones (copolymers). During synthesis main molecular chain which consists of same monomers, can graft parts of other monomers, and thus *grafted polymers* are received.

By **chemical composition** polymers are classified into organic, elementoorganic and inorganic.

Organic polymers composition includes carbon atoms, and besides — hydrogen, oxygen, nitrogen, sulfur, halogens atoms as well; and oxygen, nitrogen or sulfur belong to the main chain composition.

Elementoorganic polymers — are the substances, in which main chain consists of carbon, and side groups contain geteroatoms (except nitrogen, sulfur, oxygen and halogens), which are connected directly to carbon atoms of main chain. The main chain may contain different atoms of silica, aluminum, titanium, nickel and other elements. The most spread examples of this group are *silicone* ones.

Inorganic polymers do not contain carbon atoms (silicate glasses, asbestos, isinglass stone etc). The widest group is represented by organic polymers which are divided on base of main chain composition into *homochain and heterochain* ones.

Homochain polymers' main chains consist of same atoms, for example carbon, sulfur, phosphor etc. If the main molecular chain is made only of carbon atoms, such polymers are called carbochain: their carbon atoms are connected with hydrogen atoms or organic radicals, or functional groups such as hydroxyls, amino groups etc.

Heterochain polymers have main chain made of various atoms, which come into composition of organic substances. Atoms of various elements, except carbon, which are present in main chain, change significantly the properties of polymers. Therefore, oxygen atoms induce plasticity of the chain, playing a join role, which provides growth of polymer elasticity; atoms of phosphor and chlorine increase fire resistance; fluoride atoms add to the polymer high chemical stability etc.

According to the **shape of macromolecules** polymers are classified into linear, branched, striped, or ladder, spatial or reticulate.

Linear macromolecules of the polymer are represented by long zigzag or spiral chains. Flexible macromolecules with high toughness along the chain and weak intermolecular connections provide elasticity of the material, its property to get soft at heating and get solid at cooling down. Typical linear polymers are polyethylene, polytetrafluoroethylene, polyvinylchloride.

Branched macromolecules of the polymer have side branches which block approaching of macromolecules and their tight packing. Such polymers (for

example polyisobutylene) have decreased intermolecular interaction, decreased toughness, increased density and solubility. Graft copolymers which have different composition of main chain and its branches, also belong to the branched group.

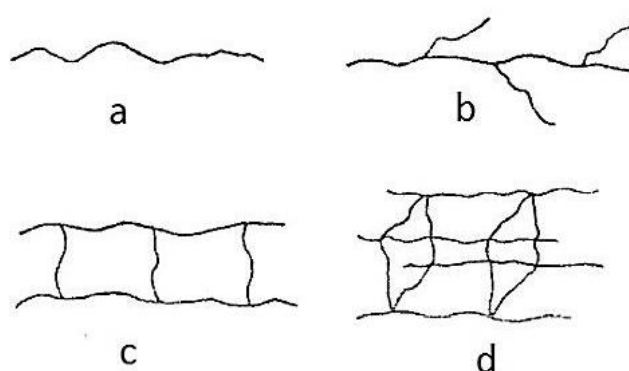


Figure 1. Shapes of polymer macromolecules (Y. K. Mashkov, 2002):
a — linear; *b* — branched; *c* — ladder; *d* — reticulate

Ladder macromolecules consist of two chains, connected between each other by transversal chemical links or chains. Polymers with ladder macromolecules have stiff main chain, and increased fire resistance. Ladder structure is present in several silicone polymers.

Spatial or reticulate polymers are created during connection (stapling) of macromolecules in transversal direction with strong chemical links. In result a reticulate structure appears with different density of the net. Spatial reticulate polymers of high density make a base of constructive polymer materials.

On base of ***physical-mechanical properties*** (20 °C temperature) plastic masses are divided into rigid, semi-rigid and plastic polymer materials.

Rigid polymer materials are hard elastic materials (polymethylmethacrylates, aminoplasts, polystyrene etc.) with mostly amorphous structure, high elasticity modulus and low lengthening on extension. Under outer loads, which are below destroying border, they maintain their shape for long time at normal and higher (until definite border) temperatures.

Semi-rigid polymer materials — are hard elastic materials (polyethylene, polypropylene, polyamides), which mostly have crystalline structure, middle values of elasticity modul and residual lengthening on extension. Residual lengthening of these polymers is reversible and usually disappears on heating.

Plastic polymer materials — are soft and elastic materials (polyvinylchloride plasticate, polyurethane foam etc.) with mostly amorphous structure and low elasticity modulus. They are characterized with relatively high general extension, but low residual extension. Development and disappearing of reversible part of their deformation at normal temperature occurs with slower speed. This is their main difference from elastic plastics, also soft and elastic materials, but with reversible deformation which develops and disappears with big speed (in a moment).

According to ***thermal properties*** plastic masses are divided into thermoplastic and thermoset. It is a very important and convenient classification,

referring mostly synthetic polymers, underlines principal difference in properties of polymers and their reaction in technological processes of manufacturing and running of the samples.

Thermoplastic polymers (thermoplastics) is a name of such polymers, which get plastified and easily formed into samples at heating, and get solid at cooling (after molding). Their properties change reversibly. Only during long-term thermal influences irreversible changes are possible.

Thermoplastics include: polymethylmethacrylates, polyethylene, polyvinylchloride, polystyrene, polyamides (nylon, caprone), and some other polymer materials.

Thermoset polymers (thermosets) are the polymer materials, which are softened only at the moment of molding the sample (during heating and pressure) and lose this property in result of chemical reactions which occur with thermal influence. Stapling of polymer chains occur, and material transits irreversibly into insoluble and unmolding phase. Thermosets include plastic on base of phenol aldehyde, aminoaldehyde, polyester and some other resins.

Classification of dental polymers according to their aim of use:

- main (constructive) polymer materials for producing of dentures, splints and devices;
- auxiliary polymer materials (impression, model, modelling, for individual impression trays etc.);
- clinical polymer materials, used chairside in dental clinic (impression, modelling, specific types of filling materials, adhesives, sealants etc.).

Classification of dental polymers according to the initiation mechanism of polymerization reaction:

- heat activated;
- self cured (chemical initiation, cold polymerization);
- light cured (photo polymerization);
- dual curing (chemical and light polymerization).

BASE MATERIALS

Base — is one of main elements of removable dentures, laying on the tissues of denture bearing area bed and accurately replicating relief of the mucosa.

In the denture base artificial teeth and retention elements are fixed (Fig. 2).

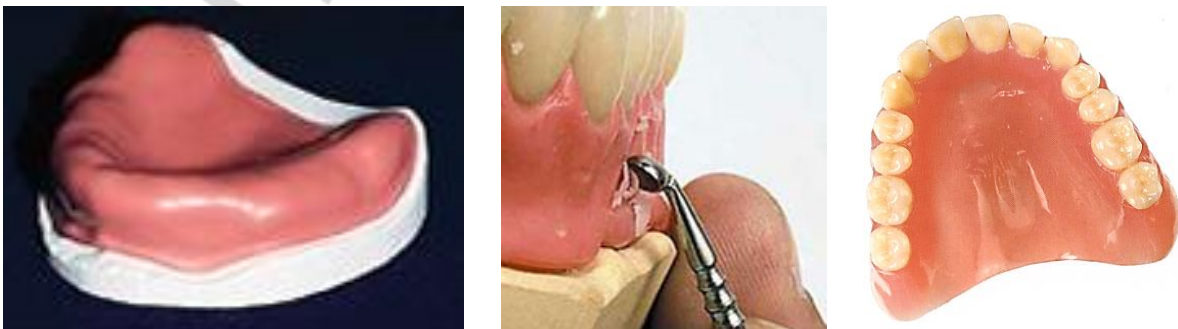


Figure 2. Base of removable partial dentures

Requirements for the base materials (R. Noort, 2002):

- biocompatibility;
- high toughness, hardness, impact viscosity;
- low density;
- processability;
- linear stability;
- natural look (correspondence to the color of oral mucosa);
- detailed replication of surface;
- good heat conductivity;
- good hygiene properties (no odors, stability towards absorption of oral liquid, stability towards bacterial growth, cleaning should be easily performed);
- ability to show strong connection with polymers, ceramic and metals;
- durability;
- low cost;
- ability to be easily repaired.

Classification of polymer materials used for fabrication of bases of removable dentures according to GOST RF 51889-2002, is shown in Table 1.

Table 1

Classification of polymer materials for bases of removable dentures

Acrylic polymer-monomer materials			Thermoplastics (type 3)			
Initiating of polymerization with outer energy			Initiating of polymerization with chemical reaction		For injection molding	For molding of sheet patterns
Heat cured (type 1)	Microwave cured (type 5)	Light cured (type 4)	Self cured (type 2)			
			For molding	For casting		

BASE ACRYLIC PLASTICS OF HEAT POLYMERIZATION

Classic technology of receiving polymethylmethacrylate supposes the synthesis of polymers (in solution or emulsion). After synthesis and picking out of the environment a polymerizate is received in powder or granules. In heat cured plastics size of granules (balls) makes 50–150 mkm. Afterwards functional and technological additives are introduced into polymer.

Composition of acrylic heat-cured polymers is shown on Fig. 3:

Initiator — benzoyl peroxide easily dissolves into free radicals under temperature action due to breakage of weak chemical links.

Pigments/colorants (oxides of metals etc.) add to polymer materials colours and shades, which mimic dental tissues or oral mucosa.

Opacifiers eliminate transparency of polymer materials.

Plastificators decrease stiffness and brittleness of polymers.

Fillers change properties of plastics, increase mechanical strength and hardness, decrease shrinkage value during forming of the sample. Mechanical properties, specifically impact resistance increase very well on introducing into plastic of fibrous fillers which play a role of reinforcing elements and reducing brittleness of unfilled plastics.



a

Powder (polymer)

granules of polymethylmethacrylate
 initiator — benzoyl peroxide
 pigments/colorants
 opacifiers — titanium/zinc oxides
 plastificator — dibutyl phthalate
 synthetic fibres — nylon/acryl



b

Liquid (monomer)

methyl ether of methacrylic acid
 inhibitor — hydroquinone
 stapling agent — dimethacrylic ether
 of ethylenglycole

Figure 3. Composition of heat cured acrylic polymers

Methyl ether of methacrylic acid is a flying, transparent liquid without colour (density 0.95, boiling temperature 100.3 °C).

Inhibitors block irreversible change of plastic properties under action of heat, oxygen of the air, light, moist and other factors. Hydroquinone prolongs shelf life of monomer, by instant entering reaction with free radicals which can spontaneously appear in the liquid and form stable free radical combinations which are not able to initiate polymerization process.

Stapling agent, such as dimethacrylate of ethylenglycole, is included into material composition for improvement of mechanical properties. It is connected in several sites with polymer chain of polymethylmethacrylate and forms transversal staple between itself and neighbouring chain of the polymer with the help of two ending double links.

The process of addition (free radical) polymerization of methylmethacrylate (PMMA) occurs as 4 steps:

- activation;
- initiation;
- propagation;
- termination.

On the Fig. 4 a scheme of addition (free radical) polymerization of methylmethacrylate is shown.

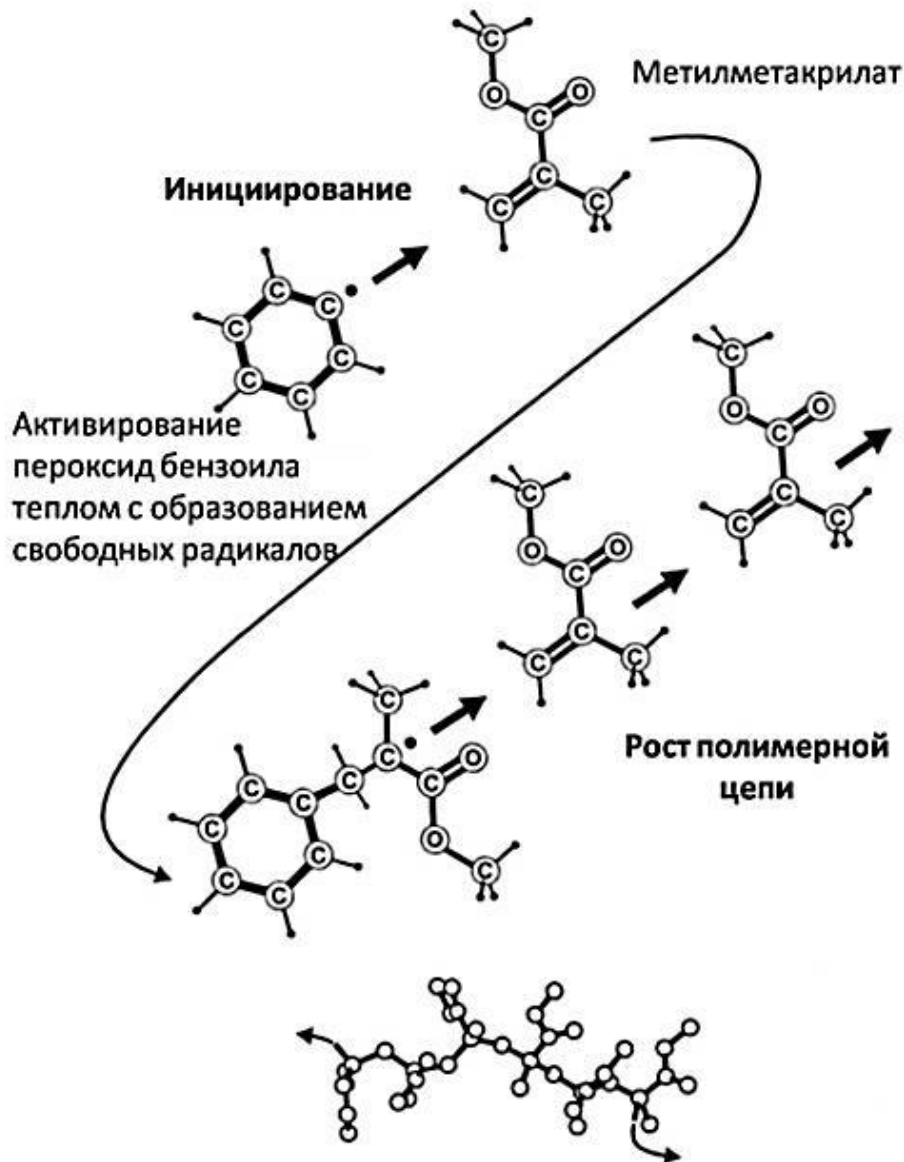


Figure 4. Scheme of methylmethacrylate polymerization reaction (N. Ray, 1998)

Activation is achieved by dissolving of initiator (benzoyl peroxide) under heat action. At heating more than 65 °C dissolving of benzoyl peroxide occurs with formation of free radicals (•).

Free radicals enter reaction with monomer (methylmethacrylate) after which a monomer becomes free radical and in its turn enters reaction with another monomer.

Repeating of this process again and again leads to growth of polymer chain (propagation). This process will go on until growing chains will collide into each other or until all free radicals join chemical reaction.

On the Fig. 5 some types of heat cured acrylic polymers which are used for fabrication of dentures, are shown.



Figure 5. Heat cured acrylic plastic, used for manufacturing of denture bases:
a — acrylic plastic (“Ethacryl-02” is characterized with high technological properties, increased strength (STOMA, Ukraine); *b* — plastic on base of fluoride-containing acrylic copolymers “Ftoraks”. Bases are highly strong and elastic (STOMA, Ukraine); *c* — colorless plastic, used when colorants of base are contraindicated. Highly strong and transparent (STOMA, Ukraine); *d* — acrylic plastic “ProBASE Hot” (Ivoclar, Lichtenstein)

SELF-CURED ACRYLIC BASE PLASTIC (CHEMICAL INITIATION, COLD POLYMERIZATION)

In self-cured plastics powder component, as well as in heat cured plastics, contains benzoyl peroxide, and liquid contains tertiary amine (n.n-dimethyl-p-toluidine or derivatives of sulfuric acid). Activation of benzoyl peroxide (dissolving into free radicals) occurs under influence of tertiary amine without temperature influence (at room temperature).

This cure method is less effective than heat cure and creates a polymer of lower molecular mass. Produced polymer chains are shorter than at heat polymerization. Such state makes a negative influence onto strength properties of the material and also increases rate of residual monomer in it. At the end of polymerization self cure plastic contains till 5 % of monomer, which didn't join polymerization reaction, which is $\times 10$ more than in heat cured plastics. Self cure plastics have worse colour stability than heat cured plastics. Besides, during polymerization of self cure plastics big amount of heat is exhaled, which promotes big number of pores and voids. Polymerization of self cure plastics under pressure of 1.5–2 atm in moist environment reduces number of pores and increases their elasticity.

Meanwhile, self cure acrylic plastics are widely used during repair of removable denture bases (fixing of cracks and fractures), and during detailing of denture base relief, by contacting with denture bearing area (rebasing of the denture).

On the Fig. 6 there are shown several types of self cure acrylic plastics which are used in dentistry for fabrication of denture bases by casting (“CASTDON”), cold polymerization in autoclave under pressure of 2 atm. (“ProBASE Cold”), for repairing and rebasing of dentures (“Protacryl-M”, “Redont-03”).



Figure 6. Acrylic plastics of cold polymerization (self cured):
a — “ProBASECold”, for fabrication of denture bases (Ivoclar, Lichtenstein); *b* — “Protacryl-M”, for repairing of denture bases (STOMA, Ukraine); *c* — “CASTDON”, for fabrication of denture bases by casting (Dreve, Germany); *d* — “Redont-03”, for repairing of denture bases (STOMA, Ukraine)

Light cure base plastics (photo polymerization). There are base materials which are polymerized under influence of light with wave length of 400–500 nm (read composite polymer materials). Chemical composition consists of urethane dimethacrylate matrix, which contains a small quantity of colloidal silica oxide to give necessary consistency to the material, and filler — acrylic spheres, which become a part of interpenetrative structure of the polymer net during setting. Activator of polymerization reaction is light with wave length of 400–500 nm. Polymer material “TRIAD” (Dentsply, USA) is one of materials of this group and is used for rebasing of dentures and manufacturing of orthodontic appliances (Fig. 7).



Figure 7. Photo polymerized material “TRIAD” (Dentsply, USA)

Microwave cure base plastics. Microwave radiation is used for contactless, inner heating of acrylic material in a short period of time, increasing speed of polymerization process. For microwave induced polymerization of plastic a source of microwave radiation is needed as well as special plastic flasks, reinforced with fiberglass and capable of letting microwave radiation through itself.

Such plastics as “Microbase” (Dentsply, USA), “Acron MC” (GC, Japan), “Basis MC” (Yamahachi Dental, Japan), “AKP-MB” (Russia) etc. On the Fig. 8 equipment and base plastic for microwave polymerization are shown.



Figure 8. Microwave cure plastic “Microbase” (Dentsply, USA)

Thermoplastic base materials, used for injection molding. Thermoplastics form a separate group from all plastics used in dentistry for fabrication of removable dentures (Fig. 9). This is comparatively new direction, which receives more and more followers, because comparing to acrylic plastics, thermoplastics are more homogenous and elastic.

Thermoplastics which are used in dentistry for fabrication of “flexible” denture bases, are represented with such materials as polyamides (nylon), polyoxymethylen, polycarbonates, polypropylene, thermo molding acrylates (monomerless acrylic plastics), ethylenvinylacetate etc.



Figure 9. “Flexible” base of removable denture, made of thermoplastic with injection molding

Thermoplastics used in dentistry are compound of substances (copolymers) with thermoplastic properties, and fillers which provide color stability of materials.

For these materials absence of residual monomer is typical, they don't contain toxic or allergenic additives, are highly biocompatible and have shape memory. High degree of plasticity, accuracy during manufacturing process, wide shade scale allow to extend possibilities of removable dentures and improve their esthetic properties.

The widest use in dentistry belongs to trademarks of thermoplastics, which are shown in the Table 2.

Table 2

Thermoplastics, used in dentistry

Base	Trademarks
Polyoxymethylen	”Biocetal” (Poland), ”Dental D” (Italy), ”T.S.M. AcetalDental” (San Marino), ”Aceplast” (Israel) etc.
Polyamide (nylon)	”Arkon”, ”Dentiflex” (Poland), ”Valplast”, ”Flexite” (USA), ”Flexy-Nylon” (Israel), ”Flexiplast”, ”Bre.Flex” (Germany), ”Flexi-J” (San Marino), ”Dental D Nylon” (Italy), ”Deflex” (Argentina), ”Vertex Termosens” (Netherlands) etc.
Polymethylmethacrylate	”Polyan” (Germany), ”Fusicryl”, ”Fusicril” (Italy), ”Acry-free” (Israel), ”Thermo Free” (San-Marino), ”Flexite M.P.” (USA) etc.
Polypropylene	”LIPOL” (Ukraine) etc.
Ethylenvinylacetate	”Flexidy 80”, ”Flexidy 65”, ”Flexidy 50” (Italy), ”Corflex Orthodontic” (San-Marino) etc.
Polycarbonate	”Evihard” (Russia) etc.
Polyetheretherketone	”Bio XS®”, ”Bio HPP” (Germany)

Polyoxymethylen (polyformaldehyde, polyacetale) — is a product of formaldehyde polymerization.

Polyoxymethylen doesn't possess high thermal and chemical stability, but due to its hardness, high melting temperature and stability towards organic dissolvants is widely used in injection molding. Ready polyoxymethylen samples

outstand with high rigidity, fatigue strength, low shrinkage during processing, low creep, stability towards wear and moist, alkaline dissolvants.

Polyamides (nylon, caprone) — are heteropolymers, containing in the main chain macromolecules — amide groups. In 1935 a group of scientists in Du Pont company, leaded by Wallace Carothers, created a material consisting of hydrogen, nitrogen, oxygen and carbon. Scientists were trying to discover material, similar to silk by its qualitative characteristic. The discovery was made accidentally. After heating mixture of coal resin, water and ethanol, scientists found out that something similar to silk was received, transparent and very strong. Its commercial use started in October 1938, and the name of this polymer appeared in 1939 on World fair in New York — “Nylon” — first letters of New-York city. In medicine, and particularly in dentistry only untoxic polyamides are used. Macromolecules of polyamides in solid phase usually have configuration of flat zigzag. Due to amide groups macromolecules of polyamide are connected to each other with hydrogen links, which provide relatively high melting temperatures of crystalline polyamide. Polyamides are processed with molding, injection molding, extrusion and compression. Polyamide samples can be welded (heat welding or high frequency currents) or glued with solutions of same polymer in polyhydric phenols or with formic acid. Polyamide — is the first synthetic polymer, which physical properties overpass properties of some metals. It has inevitable combination of properties — high strength, middle toughness and stability towards high temperature, inflammables and lubricants and most of chemicals.

Acrylates — are ethers or salts of acrylic acid. In dentistry polymethylmethacrylate — amorphous transparent thermoplastic is used for injection molding. At heating over 120 °C PMMA plastifies, transits into highly elastic phase and is molded easily.

Polypropylene — is a thermoplastic polymer of propylene (propene). Polypropylene is received with the help of polymerization of propylene in presence of metallocomplex catalysts. Its main characteristics are similar to nylon but some of its physic-chemical parameters are poorer. Nowadays polypropylene is used for fabrication of prosthodontics constructions as a cheap alternative to nylon.

Ethylenvinylacetate — is a substance, referring to polyolefins. It's received in result of copolymerization of ethylene and monomer of vinyl acetate.

Polycarbonates — is a group of thermoplastics, complex polyesters of carbon acid and dialcohols.

Polyether etherketone (PEEK) — is a semycrystalline polymer, a material with high mechanical and thermal properties (higher than 240 °C). Its characteristics are stable against load and wear. Has low friction coefficient.

Physical properties of thermoplastics are shown in the Table 3.

Industrial manufacturing of thermoplastics for injection molding of dentures bases is performed in granules, which are packaged into aluminum containers. Melting of thermoplastic (depending on the composition base, melting temperature varies from 165 till 400 °C) and casting under pressure of 4.5–5.5 bar is provided with the help of special thermoinjection presses.

Physical properties of thermoplastic materials (by I. D. Tregubov, 2007)

Materials	Properties									
	Density at 20 °C (g/cm ³)	Melting temperature °C	Strength (MPa) on			Elasticity modul (MPa) on		Impact viscosity (kJ/m ²)	Relative extension (%)	Imbibition within 24 hours (%)
			extrusion	compression	bend	extrusion	bend			
Polyamides	1.1	185–280	50–82.7	46–110	90–100	1.2–2.9	2.1–3.5	50–80	15–90	0.2–2.6
Polyoxy-methylene	1.43	173–180	68–71	110–130	100–120	2.9	3.5	90–120	15–45	0.2
Polypropylene	0.9	172–260	25–40	35–70	80–90	1.1–2.7	1.5–2.9	40–60	20–100	0.5
Polymethyl-methacrylate	1.19	180–240	55	105–112	110–140	2.5–3.8	2.8–3.1	15	2	0.45–0.6
Ethylenvinyl-acetate	1.38	90–160	10.5–23	1–2	300–400	0.4–0.5	0.7–0.8	170	500–600	0.4–0.6
Polyetheretherketone	1.3	343–355	91–112		160–170	3600	4100		12.4–25	0.1–0.5

POLYURETHANE BASE MATERIALS

Polyurethanes — is a class of polymers, in which general feature is the presence of more or less regular urethane groups in the main chain. In 2004 scientists of Research institute of resin and latex fabrics together with MSMSU developed a material for bases of removable dentures — “Dentalur”.

Composition is made of two components — isocyanate and polyol. Polyol component contains in small quantities additives — colorant, catalyst. Componentes of the material are prepackaged into cartridges and mixed in dispenser (Fig. 10).



Figure 10. Material on base of polyurethane for bases of removable dentures

Flowable material is used in methodic of silicone forms molding (free molding) with following temperature influence onto the material within 120 °C.

Parameters of specific impact strength, relative extension on tear, tests for static bend of polyurethane dentures exceed parameters of classic acrylic polymer-monomer compositions (Y. M. Alter, M. Y. Ogorodnikov, 2007).

BASE ELASTIC LINING MATERIALS

Elastic lining materials are used during manufacturing of removable dentures with 2-layered base. Developing of soft elastic lining materials for the denture base is connected with necessity of reducing pressure of rigid base onto prosthetic tissues. When there are osseous protuberances, sharp ridges on the denture bearing area, when alveolar ridge mucosa is thin and in other clinical situations elastic plastics play a role of amortization lining between mucosa and rigid base.

Elastic materials, used for producing amortization linings under removable denture bases, should correspond to the following requirements: 1) should be harmless for the organism; 2) should have strong connection with denture base; 3) should maintain elastic properties and volume stability; 4) should be well wetted (A. I. Doynikov, V. D. Sinitsyn, 1986).

Chemical origin of elastic plastics can belongs to various groups of chemical substances. Elastic properties of their majority is provided with process of plastification, which occurs during polymerization. For lining materials 5 types of elastic plastics are used which are divided by their chemistry: acrylic, polyvinyl chloride, silicone, polyurethane and FPM (fluoride caoutchouc).

On the Fig. 11 some types of elastic lining materials used in fabrication of 2-layered bases are shown.



Figure 11. Elastic lining materials:
a — “Elastacryl-P” (Raduga P, Russia); *b* — “UfiGel P” (VOCO, Germany); *c* — “PM-S” (STOMA, Ukraine)

Acrylic elastic plastics are technological and strongly connected with hard base layer. Usually they include powder of polymer or copolymer, liquid with monomer of methacrylate and plastificator (usually phthalate). Acrylic elastic plastics are most similar material to the oral mucosa of denture bearing area by elasticity. A significant disadvantage of acrylic plastic is their fast wear, which is followed with loose of elasticity. Examples of acrylic plastics are Vertex soft (heat cured, Dentimex Zeist, Netherlands), Coe soft (self cured, Coe Laboratories, USA), Visco-gel (self cured, Dentsply, Germany) и “Elastacryl P” (heat cured, Raduga-P, Russia).

Silicone materials for lining of removable denture bases were offered in 1958. High and stable elasticity and compatability are advantages of this material. Disadvantage of silicone materials is insufficient strength of connection with

PMMA base. But usage of modern adhesives allows to increase primary strength of connection with acryl base, as well as adhesion strength after various liquids influence. Examples of silicone elastic materials are Orthosil, Orthosil-M, PM-S (STOMA, Ukraine), Ufi Gel (Voco, Germany), Molloplast-B and Mollosil plus (Detax, Germany). Hospital prosthodontics department of MSMSU and specialists of “Med-Sil” society develop heat cured silicone material GosSil.

Elastic plastics on base of FPM are well connected with acrylates, possess good amortization properties, exceeding silicone and elastic acrylates. Their disadvantage is complexity and imperfection of manufacture technology. Manufacturing of this group of materials is expensive and ecologically dangerous. The plastic Novus (Hygenic Corp, USA) is a representative of this group.

Polyvinyl chloride materials withstand abrasion better than acrylic and silicone ones, they have stronger connection to rigid base than silicones. But, presence of outer plastificator provides migration of plastificator, and aging of the base. The representatives of polyvinyl chloride materials are Eladent-100 and PM-01 (Russia).

Plastics on base of polyurethane are characterized with higher elasticity than acrylates, high wear-resistance and biological inactivity. Due to condensational mechanism of polymerization, polyurethane nearly doesn't contain residual monomer. In Russia at the department of faculty prosthodontics in MSMSU together with research institute of resin and latex products such materials as Dentalur and Dentalur-P were created.

POLYMER MATERIALS USED FOR MAKING OF FIXED DENTURES

Heat cured acrylic polymer materials. “SINMA-M” is a plastic for fixed prosthodontics, making of crowns, facings of fixed dentures (stamped and casted ones). It is acrylic plastic of heat curement represented as powder/liquid. Powder is a suspended grafted copolymer containing fluoride; liquid is a mixture of acrylic monomers and oligomers.

“SINMA-M+V” is a fluoride containing plastic for fixed prosthodontics (Fig. 12).



Figure 12. Heat cured acrylic plastics used for making fixed dentures

Powders “SINMA-M” are manufactured in shades, corresponding to universal scale of dental shades. Polymerization mechanism of heat cured acrylic materials occurs as addition (free-radical) polymerization of methylmethacrylate, which was described before (watch heat cured base PMMA materials).

Self cured acrylic polymer materials. Self cured acrylic polymer materials (Fig. 13) are widely used for manufacturing of temporary (provisional) dentures.



Figure 13. Self cured acrylic plastics (cold polymerization), used for making of temporary (provisional) dentures:
a — “Acryloxide” (STOMA, Ukraine); *b* — “Acrodent” (STOMA, Ukraine); *c* — “Unifast Trad” (GC, Japan)

One of self cured acrylic polymer representatives is “Acryloxide”. It is industrially manufactured as powder with liquid. Powder is a suspended copolymerization of methyl- and butylmethacrylate (30–35 %) with mineral fillers (fused quartz, 10–13 %) and other ingredients. The base of liquid is methylmethacrylate (75–78 %) and epoxymethacrylate (15–20 %) — a product of addition reaction. Powders have 3 color shades, similar to colour of tooth tissues, on base of the shades scale. Polymerization mechanism of self cured acrylic polymers is a free radical polymerization of methylmethacrylate, described before (watch self cured base PMMA materials).

COMPOSITE POLYMER MATERIALS (by R. Noort, 2002)

Composite material (composite, CM) is a synthetically manufactured heterogenous material, consisting of two or more components and possessing a number of properties, differing from the properties of its each component.

Polymer composite material (PCM) is a material, in which at least one of sustained phases is an organic polymer (polymer matrix, copolymer link).

In most of PCM components are divided into matrix and reinforcing elements which are incremented into it. In constructive composites reinforcing elements provide necessary mechanical characteristics of the material (strength, toughness etc.) and the matrix (or binding element) provides cooperative work of reinforcing elements and their protection from mechanical lesions and aggressive chemical environment.

Restorative composite materials on polymer base (shortly — composites), which are used in dentistry, contain three main components, such as:

- organic polymer matrix;
- inorganic filler;
- binding agent.

Polymer builds a matrix of composite material, connecting separate particles of the filler with the matrix by coupling agent and therefore forming a united structure.

Polymer matrix. Polymer is a chemically active component of composite. Originally it is a liquid monomer, which transits into rigid polymer in result of polymerization reaction of radical type.

Monomer Bis-GMA (bisphenol-glycidylmethacrylate) is most commonly used. It is received in result of interaction of bisphenol-A and glycidylmethacrylate. This monomer is usually named after its discoverer Bowen. Its molecular mass is much more than molecular mass of methylmethacrylate, which allows to decrease polymerization shrinkage. Value of industrial shrinkage of methylmethacrylate is 22 vol.%, and the shrinkage of Bis-GMA — 7.5 vol.%.

A number of composites use urethane-dimethacrylate (UDMA) instead of Bis-GMA.

Bis-GMA and urethane-dimethacrylate monomers are very viscous liquids because of their high molecular weights. After adding even small quantity of filler too dense composite paste is received, which doesn't allow usage of such material in clinic. For elimination of this disadvantage, monomers with low viscosity are introduced into composition. These are so-called dissolving monomers, such as methylmethacrylate (MMA), ethyleneglycole-dimethacrylate (EDMA) and triethylen glycol-dimethacrylate (TEGDMA). The last substance is most extensively used.

For providing necessary shelf life of the composite, its premature polymerization should be warned. Hydroquinon is applied as an inhibitor (moderator of the polymerization process) in a rate of 0.1 % or less.

Polymer matrix contains as well activator/initiator systems to provide the setting process. Using of concrete components in this system depends on the type of setting reaction, supposed in the material, which can be chemical reaction or light activated reaction.

For enhancement of composite properties various **fillers** were added into their composition. In the end of 50's quartz was used as a filler in the composition

of filling material on base of methylmethacrylate. Introduction of fillers gives five main advantages, such as:

1. Polymerization of methylmethacrylate leads to high polymerization shrinkage (21 vol.%) even when using polymer-monomer system of powder with liquid (7 vol.%). Introduction of big amount of glass fillers significantly decreases shrinkage, because the quantity of used monomer binder decreases, and filler doesn't take part in the polymerization process. Nevertheless, shrinkage can't be fully eliminated, its value will depend on the origin of used monomer and amount of introduced filler.

2. Methacrylate polymers have big thermal expansion coefficient (nearly $80 \times 10^{-6} \text{ }^\circ\text{C}$). This coefficient lowers on adding of inorganic filler, which has TEC similar to the one of tooth tissues ($8\text{--}10 \times 10^{-6} \text{ }^\circ\text{C}$).

3. Filler can improve such mechanical properties as hardness and compression strength.

4. Using of such heavy metals as barium and strontium, impregnated into glass, brings radio-opacity to the material.

5. Filler is a perfect mean for achieving esthetic parameters — colour, transparency and translucency. Developing of filler introduction technology is the main direction of improving materials, which led to creation of modern composites.

Binding agents. For good mechanical properties of the composite it's extremely important to make strong connection between filler and polymer matrix. If this connection breaks, tensions during load spread not equally along all material volume; phase interface acts like primary destruction source, leading to destroying of the whole composite.

Secure connection is reached thanks to introduction into polymer of binding agent. Lately silica organic substances (silanes) are used. Only of most widely used glass-filled polymer composites is γ -metacryloxypropyltrimethosilan (γ -MPTS).

The connection between polymer and filler particles should be strong and durable. If there is no such connection the tension won't pass from polymer to the glass filler and therefore the bigger load will fall directly onto polymer matrix.

Polymers are hydrophobic, and quartz glasses hydrophilic due to superficial layer of hydroxyl groups, connected with glass. That's the reason of major problem: polymer doesn't have natural affinity with the surface of silica glass, which is principal for their connection.

A suitable binding agent can solve this problem Silica organic coupling agent can be used for this, because it has ending hydroxyl groups, which are attracted with hydroxyl groups of glass surface. On the other end of coupling agent molecule there is a methacrylate group, which can bond to monomers of the coupling agent due to opening of double carbon link.

Condensation reaction on the border between glass and silica organic coupling agent provides covalent link of silane with glass surface. Improving of connection quality between polymer and glass filler provided successful developing of wear-resistant composites.

Mechanisms of polymerization. Process, which leads to transition of composite paste into solid phase, is a process of polymerization of monomer matrix.

In primary generations of composites this process was provided with fabrication of the material in a form of two pastes, mixing of which created necessary ingredients for polymerization. In one of pastes activator was contained, such as tertiary amine, in another past — initiator, usually benzoyl peroxide.

In the beginning of 70's light-cured composites, which were activated with ultraviolet light, appeared. In this materials UV was used for making free radicals, necessary to start process of polymerization. UV light energy was enough for breaking of central link of benzoin methyl ether and creating two primary radicals. Therefore, it was enough to have only one paste, which doesn't set until it is affected with UV light. But several serious disadvantages were found out during using of UV light cured systems. UV could cause burns of soft tissues and harm eyesight. That's why protection and careful manipulation of UV apparatus were needed. The source of UV light was an expensive mercury discharge lamp, with its ageing the output of light energy lowers, and the deepness of material solidification is limited because of high degree of light absorption within the composite layer.

Nevertheless, an idea of a single paste which can be set whenever it is necessary, was well accepted with dentists and opened the way for developing of composites cured with visible light. A source of free radicals was camphorquinon. Its excitation energy was lower than benzoin methyl ether, that's why light in blue part of spectrum with the wave length 460–480 nm turned out to be very effective. Application of this light for setting has an advantage of using much cheaper source of light as a quartz halogen lamp, which is not same harmful as UV radiation. Visible light penetrates through composite better, providing bigger depth of solidification. In apparatus special filters for distinguishing UV and infrared parts of spectrum on the outcome, which allows to avoid burn of soft tissues and excessive temperature rise on the lightened surface.

Restoring of teeth with direct method using composite materials is combined with a number of complications. First of all, inserting of composite into the cavity is a rather hardwork. Beside, an accurate reproducing of corresponding contacts with antagonist teeth is required. Composites have polymerization shrinkage and besides there is a risk of unfull solidification of the filling because of insufficient depth of polymerization. One of ways to fight these complications is using of indirect composite restorations — inlays, onlays and veneers.

Inlays, on lays, overlays, veneers, artificial composite crowns are produced in dental laboratory by dental technician on stone model. Advantage of this type of restoration is that the biggest work on reproducing anatomical shape and interdental contacts is done by technician in laboratory.

Another advantage is a full solidification of the material along all the depth, because polymerization process is performed in laboratory conditions, and not in the oral cavity. Laboratory process of solidification for composite inlays is more sufficient.

For indirect restorations several composite light-cured systems are known, such as Targis/Vectris (Ivoclar), Bellglass (Kerr), Cristobol (Dentsply), Sculpture/FiberKor (Pentron), Sinfony (Espe), Estenia (Kuraray), ArtGlass (Jelenko), Gradia (GC), Tescera ATL (Bisco) and other (Fig. 14).



Figure 14. Composite light cured systems for fixed dentures production and facing of metalloplastic dentures with indirect method:
a — Sinfony (Espe); *b* — Tescera ATL (Bisco)

Light cured composite materials (Fig. 15) are widely used for making of provisional (temporary) crowns in clinic (direct method).



Figure 15. Light cured composite materials, used for manufacturing of provisional (temporary) crowns:
a — “REVOLTEK LC” (GC, Japan); *b* — light cured preformed provisional crown “Protemp Crown”, 3M ESPE (USA, Germany)

On the Fig. 16 a composition of light cured preformed provisional crowns “Protemp Crown”, 3M ESPE (USA, Germany) is performed.

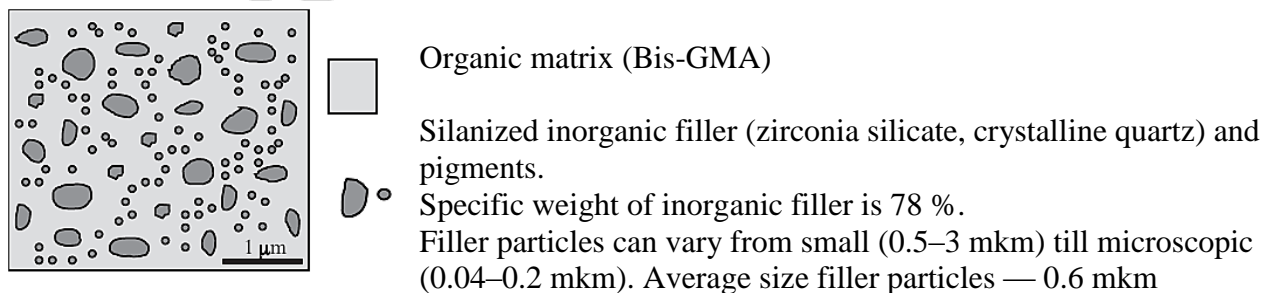


Figure 16. Composition of preformed provisional (temporary) crowns “Protemp Crown”, 3M ESPE (USA, Germany)

POLYMER MATERIALS USED FOR MANUFACTURING OF MAXILLA-FACIAL PROSTHESES

In dentistry for making biological ekzoprotheses of ear, nose etc. (“ekzo” — outer) copolymer plastified elastic material “Orthoplast” is used. It is a copolymer of chloride vinyl and butyl acrylate plastified with dibutyl phthalate and is manufactured in 6 shades. The material is heat cured. Manipulation of work with this plastic is similar to technic of work with acrylic plastics.

“Orthoplast” ekzoprotheses are not meant for big loads, that’s why they are not very strong, but highly elastic and imitating well skin colour on the face.

POLYMER MATERIALS FOR INDIVIDUAL IMPRESSION TRAYS

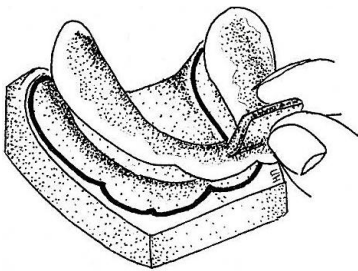


Figure 17. Individual tray (watch polymer materials for splints fabrication).

Individual tray (custom or tailor made tray) — a device, used for making impressions (Fig. 17). It is produced in dental laboratory individually for the patient (comparing to standard impression trays, fabricated industrially).

For making individual trays self cured acrylic polymers are used, standard light cured patterns of composite materials and thermoplastic sheet materials

Acrylic plastics for making individual trays have similar composition with self cured acrylic plastics, used for repair and rebasing of dentures (“Protacryl-M”, “Redont-03” etc.). One specific detail in composition of self cured acrylic plastics for individual trays is 50 % filler (chalk) containing in it. Introduction of chalk into polymer-monomer composition reduces price of the material and simplifies mechanical processing of the tray after plastic polymerization.

On the Fig. 18 several types of self-cured acrylic plastics for making individual trays are shown.

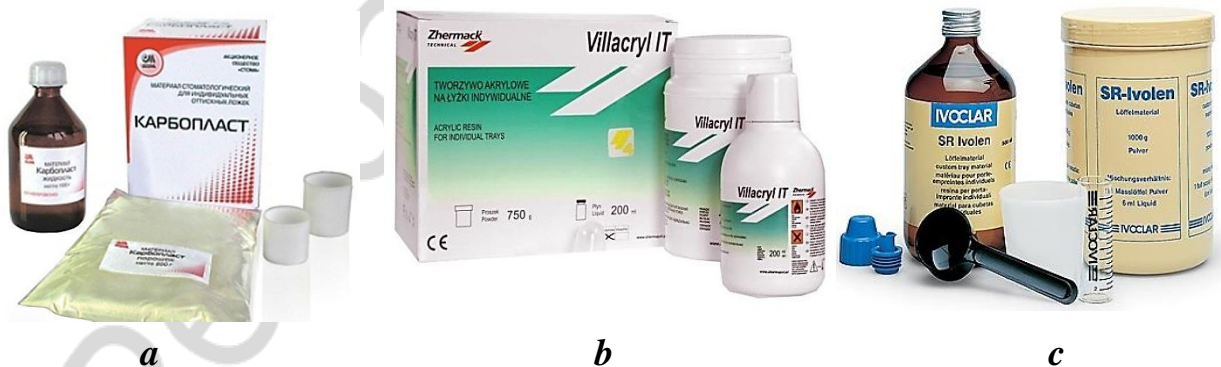


Figure 18. Self cured acrylic plastics, used for making individual trays: a — “Carboplast” (Stoma, Ukraine); b — “Villacryl IT” (Zhermack, Italy-Poland); c — “SR IvoIen” (Ivoclar, Lichtenstein)

Light cured materials for making individual impression trays (Fig. 19) are industrially produced as preformed chablones. Patterns in a form of plates with

2.2 mm thickness are prepackaged into boxes, protecting material from light influence. Due to universal shape plates are pressed against stone model, excesses are removed, to be used as a holder. After shaping on the model material is polymerized in photobox for 5 minutes. High quality of the material provides insignificant shrinkage and perfect shape stability.



Figure 19. Light cured materials, used for making individual trays:
a — “Individuo Lux” (VOCO, Germany); *b* — “Megatray” (Megadenta, Germany)

POLYMER MATERIALS FOR MAKING SPLINTS

Dental splints are special removable coverings for the teeth, which are used in some cases of dental treatment (whitening of teeth, applications of therapeutic substances, correcting of malocclusion by aligners, protection of teeth in the case of bruxism, relaxation of masticatory muscles) and also as protection from trauma during doing sports (sport splints).

Splints (Fig. 20) are manufactured of thermoplastic plates (polypropylene, polychlorvinyl, polycarbonate and polyethylentherephthalate).



Figure 20. Dental splints

These plates have thickness of a wide range — from 0.5 mm till 3 mm. They can be transparent, semitransparent, milky shade or any color possible.

When thermoplastic materials are heated, they receive “flowable” phase and under vacuum or pressure action they accept corresponding shape by tight pressing against the model.

On cooling down material is crystallized and “remembers” the shape, which it received from the model, accurately reproducing all its configuration (watch lecture “Technological processes, used for making plastic dentures”).

Besides thermoplastics named above, elastic polymer “Boxil” is used for making sport splints (boxing splints). The material is on base of silicone caoutchouk of cold polymerization. Also there are polymethylsiloxane (77 %), modified aerosil (19 %), zinc oxide (4 %) in the composition. Liquid — catalyst — methyltriacetoxylan. They are used for making boxing splints by compression in flasks without heating. Plastic is hygienic, highly elastic and strong.

PLASTIC ARTIFICIAL TEETH

For filling the defects of dental arches with the help of removable dentures, a wide use in dentistry belongs to plastic artificial teeth (Fig. 21).



Figure 21. Set of plastic artificial posterior teeth

Artificial teeth are manufacture industrially in special press-forms by hot compression of acrylic plastics. Artificial teeth are stable against water, saliva, foods, provide strong chemical connection with acrylic base materials, correspond to the anatomical shape and color of natural teeth, are wear-resistant and have similar TEC with base materials. Artificial teeth are fabricated in sets of a wide size range and color spectrum.

TECHNOLOGICAL PROCESSES USED IN THE FABRICATION OF POLYMER DENTAL PROSTHESES

Processing of plastics into products of dental purpose is produced as one of the following methods: molding, milling and thermopressing.

Selection of the technology is determined by construction of the denture, type of plastic (thermoset or thermoplastic), its viscosity or flowability characteristics and other factors.

Molding of products from plastic is a very complicated process, which provides through a short period of time changing of physical state of the material, and in some cases its chemical structure and composition as well.

In prosthodontic dentistry the main techniques of molding products from plastics are: compression molding, injection molding, casting and free molding (Fig. 22).

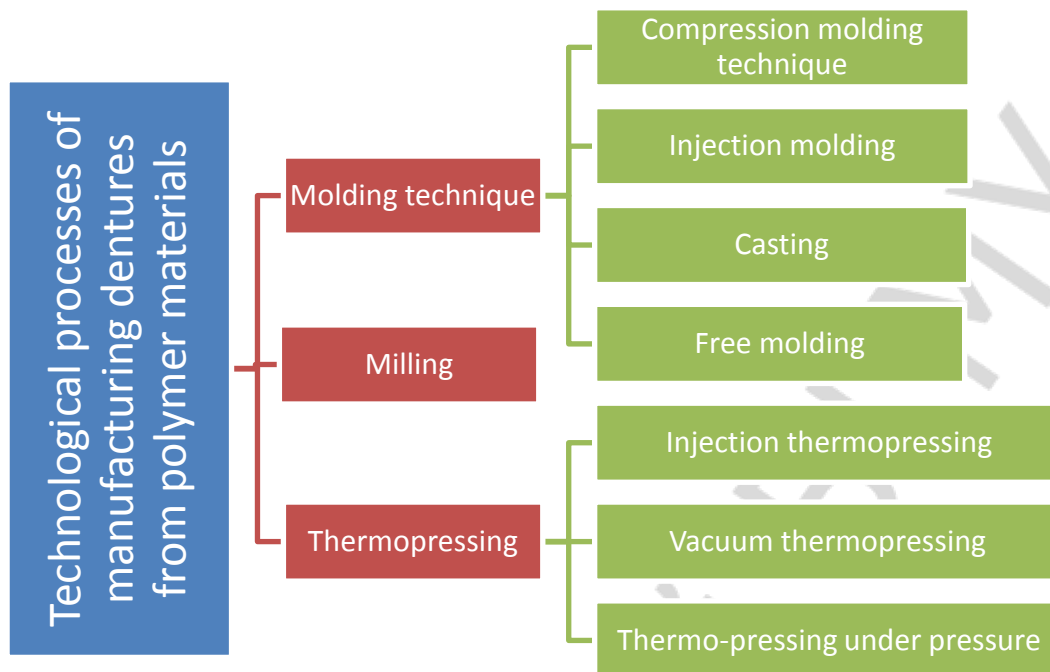


Figure 22. Technological processes of manufacturing dentures from polymer materials

COMPRESSION MOLDING TECHNIQUE OF PLASTIC DENTURES FABRICATION

Fabrication of plastic dentures by compression molding is carried out on gypsum models in gypsum compression forms, received after burning out of wax reproductions of dentures, and consists of the following steps:

1. Manufacturing of compression-form:
 - wax dentures on the model are placed in the flask;
 - gypsum investment (with isolation);
 - wax elimination.
2. Preparing of acrylic resin (mixing polymer + monomer).
3. Packing of acrylic dough into the compression-form (pressing by pressure clamp).
4. Curing (polymerization in water bath, temperature regime).

In the dental lab conditions manufacturing of plastic dentures bases with the use of heat-cured acrylic plastics by compression molding is carried out according to the steps, shown on the Fig. 23.

1. Wax denture is made on gypsum model.
2. Model with the wax denture is placed into bottom part of flask and invested by gypsum. Since the gypsum gets solid it is cut at the level of flask edge. Soaking of the cast in cold water.
3. Upper ring of the flask is attached and second portion of gypsum fills the flask by portions, lid covers the flask. Crystallization of gypsum.
4. Wax elimination in hot water.

5. The flask is opened, upper part detached from the base, remains of wax are removed by stream of hot water. The free space, created by eliminated wax, is to be filled by polymer-monomer dough.

6. Gypsum is covered by separating medium. Teeth are degreased by monomer. Polymer-monomer mixture (**at dough stage**) is packed into the space in flask (the part with artificial teeth) and covered by wet cellophane film. The flask is covered by lid and pressed in clamp.

7. Polymerization of resin dough.

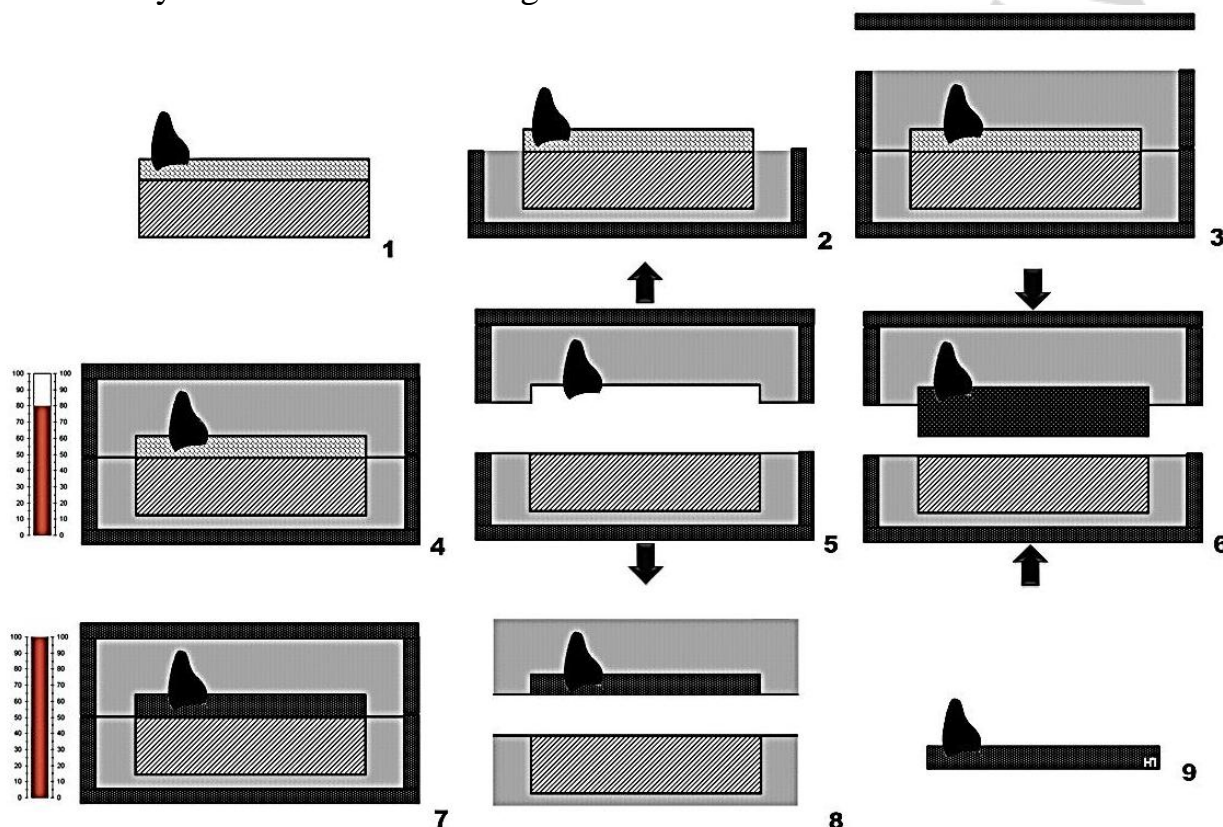


Figure 23. Steps of replacing wax composition into plastic by compression molding

Temperature regime:

1) during 60–70 minutes flask is slowly heated, from room temperature till 80°C;

2) temperature is quickly risen from 80 °C till 100 °C;

3) during 60 minutes flask is kept in boiling water;

4) flask cools down in same water.

8. When polymerization is over and flask cools down, it is unclamped, both lids are opened, and the denture base is recovered.

9. Sprues are cut off, finishing and polishing of the denture.

Replacing of wax reproduction with plastic is made with the help of polymer-monomer composition (plastic dough). To prepare it polymer and monomer are mixed together in mass rate recommended by manufacturer (Fig. 24). Measured amount of monomer (Fig. 24, a) is poured into capacity, and the necessary amount of powder is added gradually afterwards (Fig. 24, b). During introduction of

monomer, and within 1 minute more the mixture is thoroughly mixed (Fig. 24, *c*), then mixture is covered by cap, to exclude evaporating of liquid part of the mixture, and let alone for soaking (Fig. 24, *d*). During soaking the mass is mixed 1–2 times carefully for equal dissolution of the powder in liquid. Soaking lasts 20–30 minutes. There are 4 periods (stages) distinguished in the process of acrylic plastic soaking:

1) *sandy stage*, when monomer penetrates free into polymer grains, and the mass is like sand soaked in water;

2) *stringy stage*, when the mass becomes sticky, and during its mixing there appear fibres, looking like capron threads and stretching after the spatula;

3) *dough-like stage*, with homogenous, dough-like and soft consistency, plastic dough doesn't stick to instrument, is easily moulded and *suitable for filling compression mould* of the denture;

4) *rubber stage* with specific springy properties. After elasticity decrease hardening of the material follows.

Prepared plastic dough in its 3 stage (dough-like) is used for filling previous prepared compression moulds (Fig. 24, *e*).

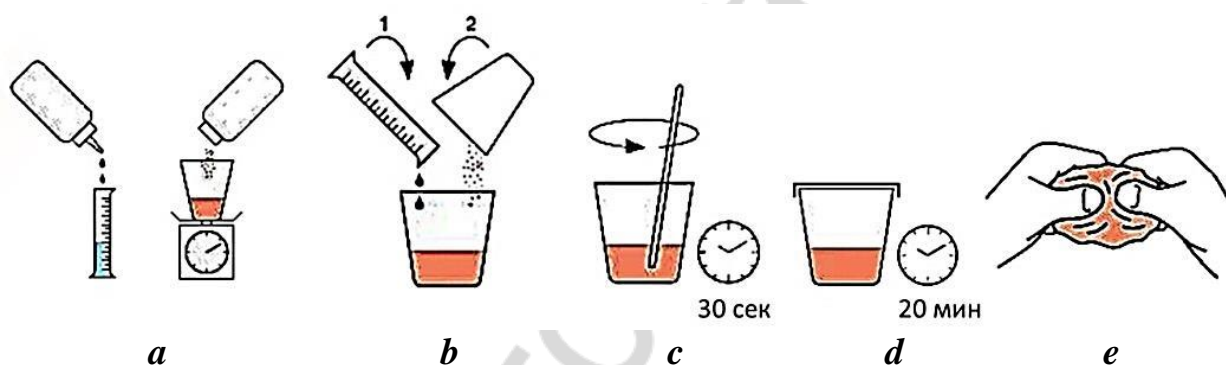


Figure 24. Preparing of plastic dough (polymer-monomer composition)

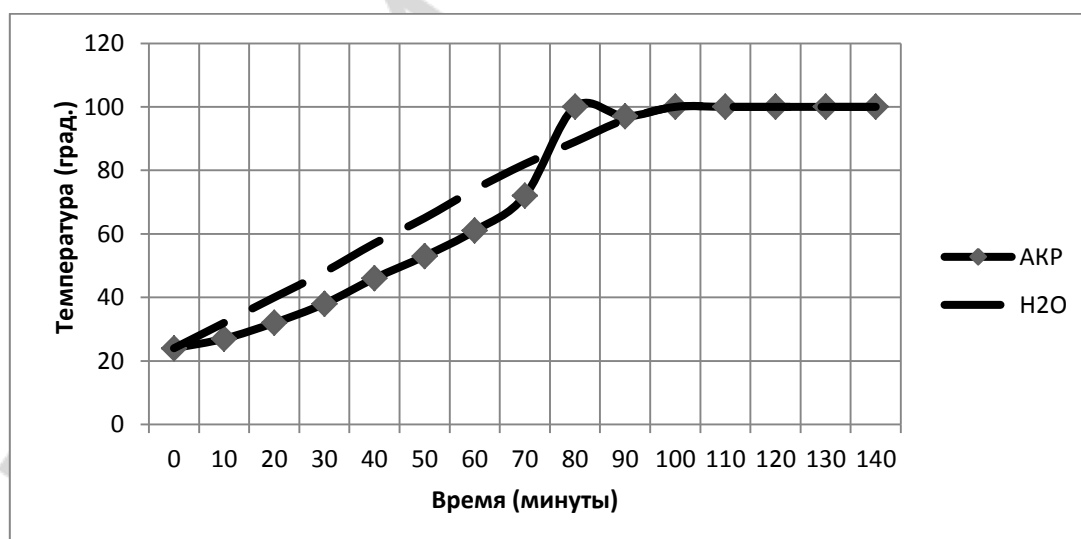


Figure 25. Graphic of acrylate (AKP) temperature changing according to the temperature of water (H₂O) and time of polymerization (in minutes 0–140) (R. Phillips, 1991)

To receive a denture with high strength properties, polymerization of polymer/monomer mixture should be carried out in the conditions which provide maximal density of polymer. Which means: 1) optimal rate of the components of mixture; 2) full maturation of plastic dough before moulding; 3) strict following the temperature regime of polymerization; 4) maintaining of the necessary pressure in the mould.

INJECTION MOLDING TECHNIQUE OF PLASTIC DENTURES FABRICATION

Principle of injection molding is based on methodic of introduction of the plastic into flask under pressure. Injection (casting) of flowable polymer-monomer acrylate composition is provided with using of special apparatus. Their majority is performed as press-injector or special flask. Press-injector is detachable, of various sizes. Mechanical screw presses (Fig. 26, *a*), electromechanical or pneumatic presses (Fig. 26, *b*) are used to squeeze out the plastic dough. In the flask there is a hole for installation of injector and introduction of plastic mass. Inside of the press-mould there are created casting channels for delivery of plastic to the mould of denture. Investing plastic composition is prepared as usually, and in *stringy stage* is packed into injector which is secured on the cap of the flask. After securing of the flask in the flask-press, injector's piston slowly pushes out the plastic into the flask. Nearly 10 minutes after filling of the mould the pressure is increased, piston is secured in the compressed state and polymerization of plastic under heat begins (watch temperature regime of polymerization).

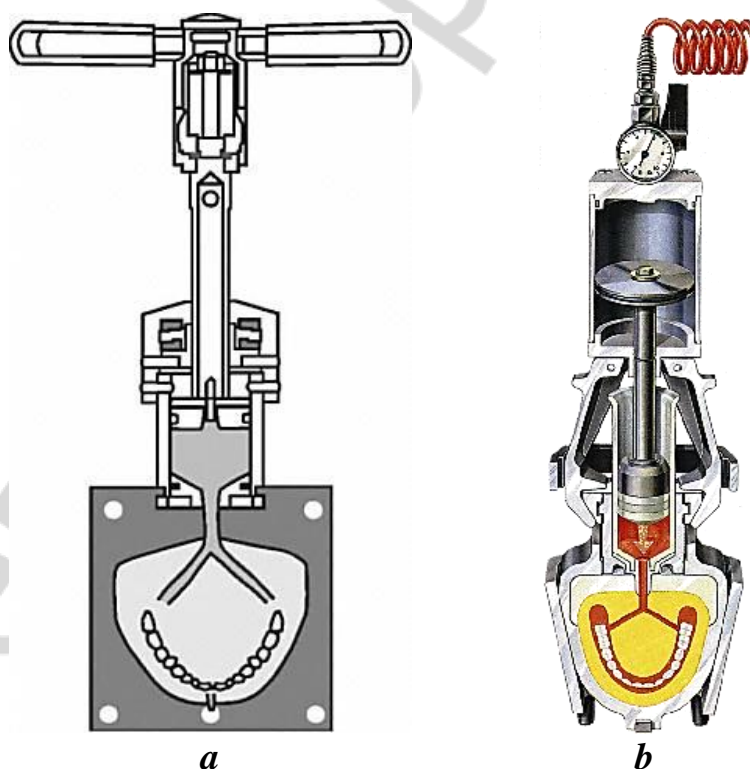


Figure 26. Mechanical screw press (*a*) and pneumatic press (*b*)

On the Fig. 27 the steps of injection molding of plastic are shown.

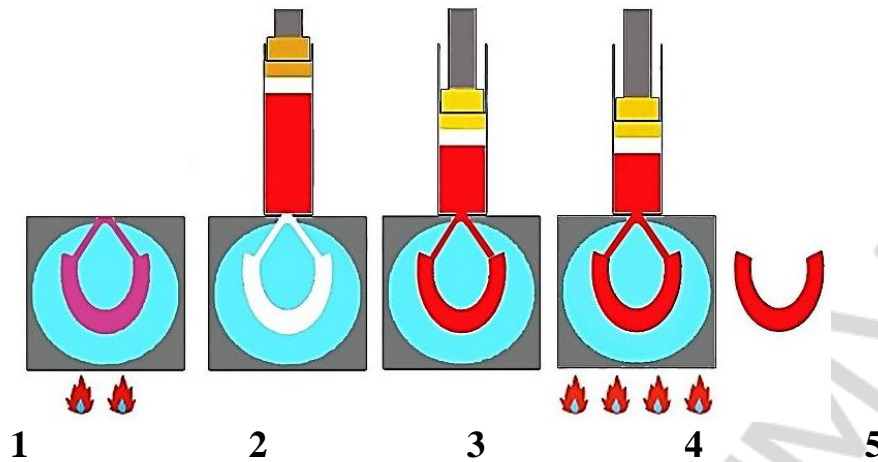


Figure 27. Steps of injection molding of plastic:

1 — removing of wax composition from split gypsum model with heating; 2 — installing of press- injector with flowable polymer/monomer acrylate composition onto the flask slot; 3 — packing of polymer/monomer plastic composition into flask under press action; 4 — polymerization of plastic under heat; 5 — recovery of plastic denture out of gypsum mould and its processing

Injection molding method allows increase quality of produced plastic bases and has the following advantages:

- delivery of acrylate into the flask under permanent pressure allows homogenous filling of the mould and the space appearing in result of shrinkage;
- the risk of incomplete connecting of flask parts is excluded, which prevents extra thickening of the base and supra-occlusion;
- high coefficient of polymerization excludes free monomer in the base;
- good physical properties of the base material are provided;
- easy to use.

FLUID RESIN TECHNIQUE

Polymers of cold polymerization (self-hardening) are rather liquid while mixing and therefore can be simply filled in a form from silicone or agar-agar hydrocolloid. They reproduce superficial details well though other their properties concede to acrylic polymers of hot polymerization.

Sequence of a form production for technology of plastic bases casting is presented in Fig. 28. The wax pattern of the denture with false teeth (Fig. 28, 1) is flowed to the gypsum model on borders of basis by means of the modeling wax (Fig. 28, 2). The model with wax is located into water of a room temperature for 10 minutes. Then the model is established on the bottom of a flask for duplication (Fig. 28, 3) and is closed by a cover (Fig. 28, 4). The flask is filled with agar-agar hydrocolloid or vinyl polysiloxane material for duplication (Fig. 28, 5). After hardening of the form gypsum model together with the wax pattern are extracted from the investment material. False teeth and wax basis are separated from the model and gypsum model is processed by the boiling water (100 °C). False teeth are placed into the holder with cells and with the use of the steam-ejecting device the wax remains are removed from their surface. Gypsum model is covered

by an isolating varnish. 3 channels (1 channel for filling of a form and 2 channels for an air outlet) are made in the form (Fig. 28, 6). False teeth are established in the teeth prints in the form. The model from gypsum is established into the investment material. The flask is closed by a cover and established in a vertical position.

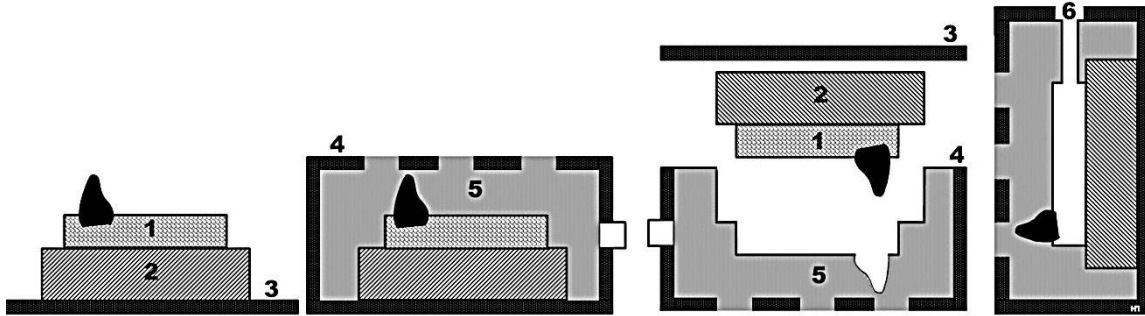


Figure 28. Sequence of a form production for the denture plastic bases casting

In Fig. 29 sequence of the resin preparation, casting and resin polymerization is presented. Resin is prepared according to the instruction of a producer (Fig. 29, 1–29, 3). The flask is established vertically and through the central opening liquid resin (Fig. 29, 4) is filled in the form. The flask, filled with the resin, is maintained at room temperature within 5–6 minutes. Then the flask is established in the polymerization reactor filled with water (water temperature 45–55 °C). Polymerizer is closed with the cover and pressure from 1.5 to 5 atmospheres is established (Fig. 29, 6). The flask is kept in the polymerizer under pressure within 30 minutes. Polymerization of self-cured resins under pressure in the damp environment narrows amount of pores. Then the flask is opened and the denture is taken from the form. Cutting of sprues, finishing and polishing of the denture finishes a technical stage.

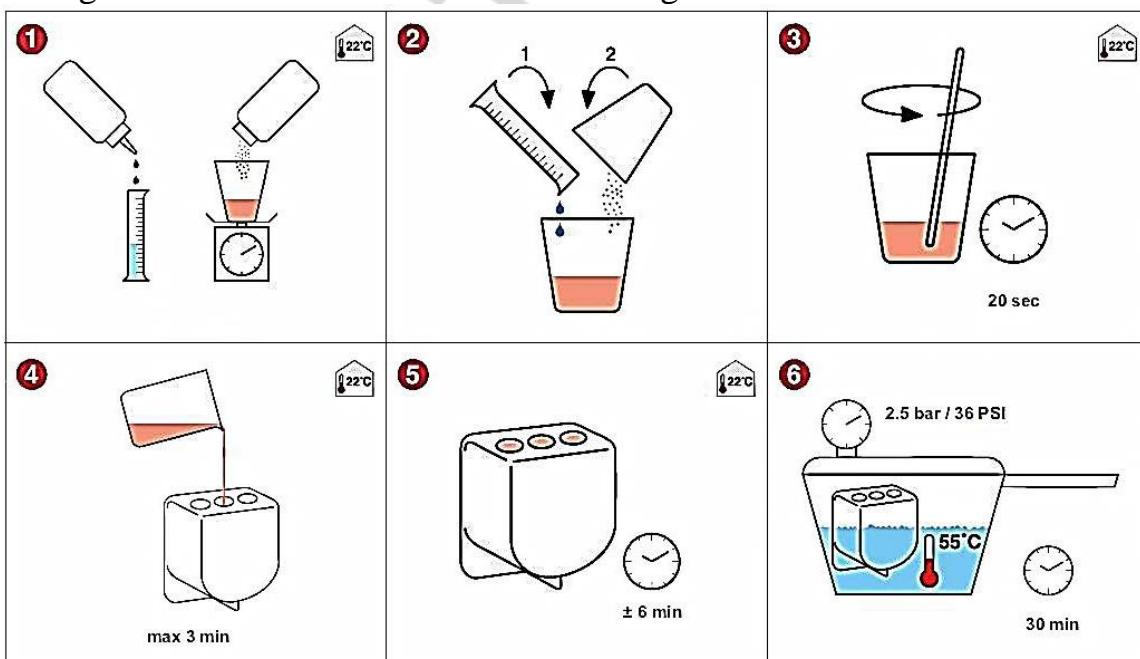


Figure 29. Sequence of resin preparation, casting and resin polymerization

FREE MOLDING OF RESINS

The method of free molding with the use of self-cured resins is used at production of individual trays in dental laboratory and at production of provisional (temporary) dentures in clinic.

Sequence of the individual tray production by free molding with the use of self-cured resin is presented in Fig. 30. Originally the individual tray borders are marked on the gypsum model received on a preliminary impression. After drawing of the individual tray borders isolation of the model by a separating material is carried out (Fig. 30, *a*). It is easier to make powder and liquid dosage with the use of special dosimeters (Fig. 30, *b*). After components dosage self-cured polymer/monomer composition is mixed in capacity, covered and maintained before dough-like stage, periodically mixing. Dough-like plastic can get necessary thickness within 3–4 mm after its rolling with the use of a roller between polyethylene films (Fig. 30, *c*) or using fatty isolation of a roller and a surface on which plastic dough is rolled. Plastic dough is imposed on the gypsum model and free molding on the model contours is carried out. Excess of plastic is cut off on the tray borders (Fig. 30, *d*). In a frontal site of the tray a handle is formed from excess of plastic (Fig. 30, *e*). After the end of polymerization plastic tray is exempted from the model and processed (Fig. 30, *f*).

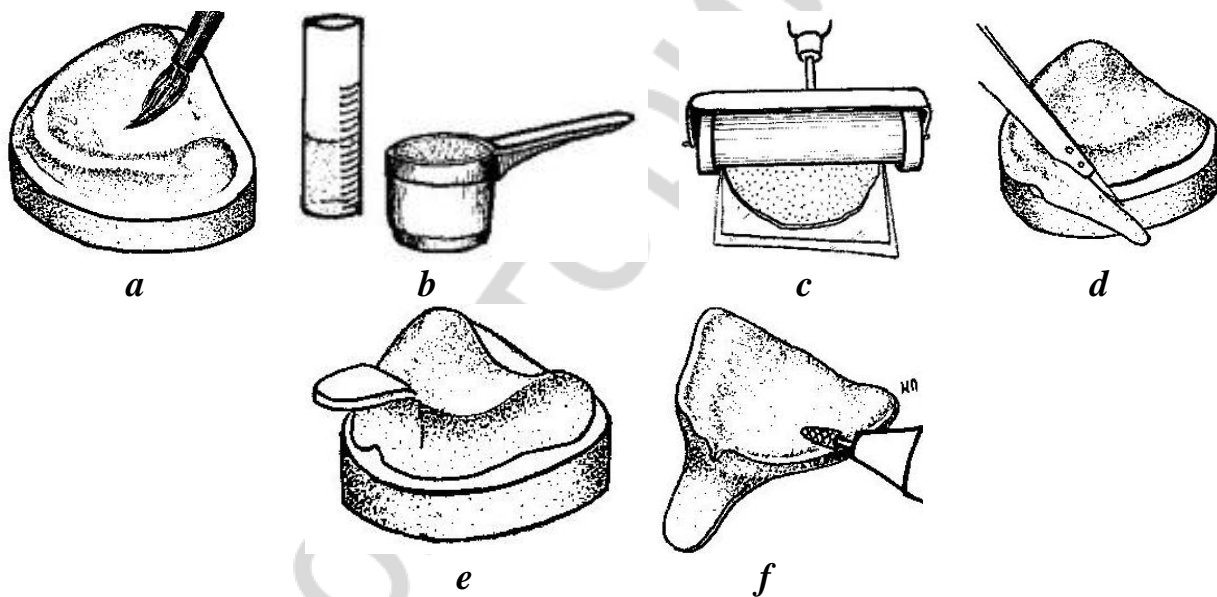


Figure 30. Sequence of the individual tray production by free molding using self-cured resins

One of free molding types is the bulk method. Sequence of orthodontic appliances plastic bases (plates) production with the use of a bulk method is presented in Fig. 31. Here polymer (powder) is evenly poured on the previously isolated gypsum model surface (Fig. 31, *a*). Through a thin needle nozzle powder is moistened (impregnated) with the monomer till saturation (Fig. 31, *b*). Manipulations are repeated layer-by-layer till the whole surface is formed and the product is given a necessary thickness (Fig. 31, *c*–*31, d*).

Self-cured resins used for the bulk technique are resistant to draining and have the prolonged time mode of polymerization. Bulk technique can be used also for individual trays production (I. Yu. Lebedenko and co-authors., 2005).

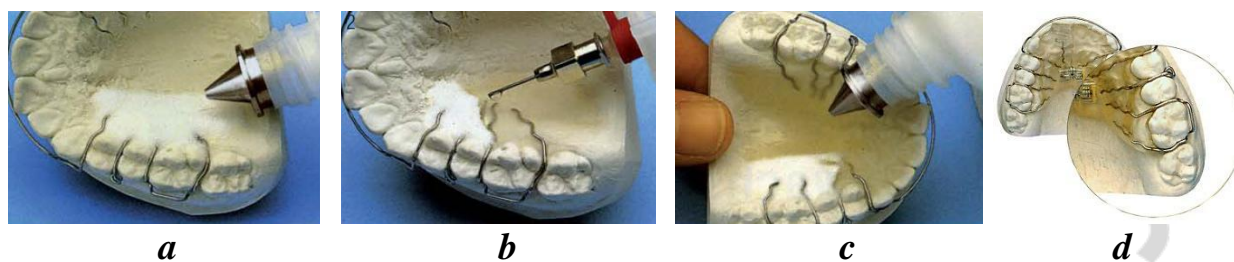


Figure 31. Sequence of the orthodontic appliance plastic basis production by bulk technique with the use of self-cured resins

Production of the individual tray from self-cured acrylic resin on the model has indisputable advantage in time. However a material toxicity at long contact with it and its shrinkage don't allow to make this method priority.

In some clinical situations at the individual trays production it is required to create sufficient place for the impression material. In Fig. 32 sequence of the individual tray production by free molding with the use of photopolymeric resin with creation of the place for impression material is presented. After drawing of the individual tray borders (Fig. 32, *a*) the plaster model is covered by the softened plate of basic wax (1.5–2 mm thickness) (Fig. 32, *b*), excess of wax is cut off on the individual tray borders. The plate of photopolymeric material is pressed out on the model (Fig. 32, *c*). The cut-off excess of photopolymeric material can be used for production of the handle (Fig. 32, *d*). Polymerization of resin is carried out in special stationary photoboxing (Fig. 32, *e*). The individual tray made of photopolymeric material needs the minimum processing (Fig. 32, *f*).

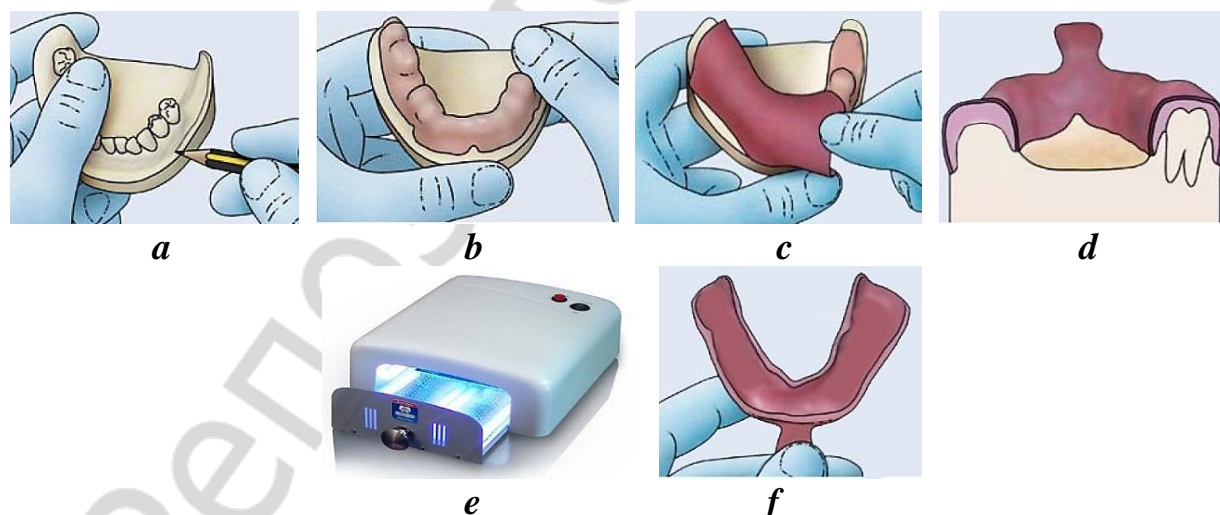


Figure 32. Sequence of the individual tray production by free molding with the use of photopolymeric resins

For individual trays production standard photopolymeric (light-cured) plates (Fig. 33) are used. Photopolymeric materials — single-component compositions of resins (bisphenol glycidyl methacrylate, urethane dimethacrylate and monomer-

thinner triethylene glycol dimethacrylate) which aren't containing methylmethacrylate. They are produced in the form of soft standard plates 2.5–3 mm thick for upper and lower jaws.



Figure 33. Standard plates from photopolymeric (self-cured) materials for individual trays production

For individual trays production by free molding shellac thermoplastic materials are used (Fig. 34). Shellac — resin, polymer of a natural origin. It is produced by insects (lac bugs) parasitizing on some tropical and subtropical trees in India and the countries of Southeast Asia.

Shellac contains aleurethanic acid, dihydroxy phycocerollic acid, shellolic acid, shellac wax (to 5 %), water and water-soluble dye. A mineral filler is added into the composition of shellac plates. Thickness of standard plates is 2.5–3 mm. Melting temperature is 60–80 °C.

High material plasticity allows pressing it out easily on the model without damages. Excess of the material can be easily cut off by a scalpel. A material plasticity guarantees uniformity of its thickness in all sites. Hardening of the material happens within 10 min.



Figure 34. Shellac plates for individual trays production by free molding

After a thermal softening shellac plates are well adapted on the plaster model, it is simple to work with them, they keep a form after hardening, have optimum mechanical strength and don't stick to the plaster.

As an example of provisional (temporary) crowns free molding it is possible to present sequence of crowns production with the use of preformed preparations from light-cured composite material Protemp™ Crown (Fig. 35).

After the tooth preparation a standard size of the provisional crown, using a template for mesiodistal sizes measurement and an attached to a set table, is

defined. The preparation corresponding to a group accessory of the tooth and earlier determined size is taken from the individual hermetically closed box (Fig. 35, 1) and is separated from a film (Fig. 35, 2). It is easy to correct the crown height, cutting off excess of the material taking into account borders of preparation (Fig. 35, 3). After primary correction the crown is established on the prepared tooth and is adapted to abutment, proximal contacts and an occlusal surface due to its initial plastic state (Fig. 35, 4–35, 6). Photopolymerization of crowns is carried out in two steps. The first photopolymerization (in “a tacking mode”) is carried out in the oral cavity within 2–3 seconds (Fig. 35, 7). Final crown polymerization is carried out outside the oral cavity within 60 seconds (Fig. 35, 8). After occlusal contacts assessment the denture is polished and fixed in the oral cavity with the use of temporary cement.

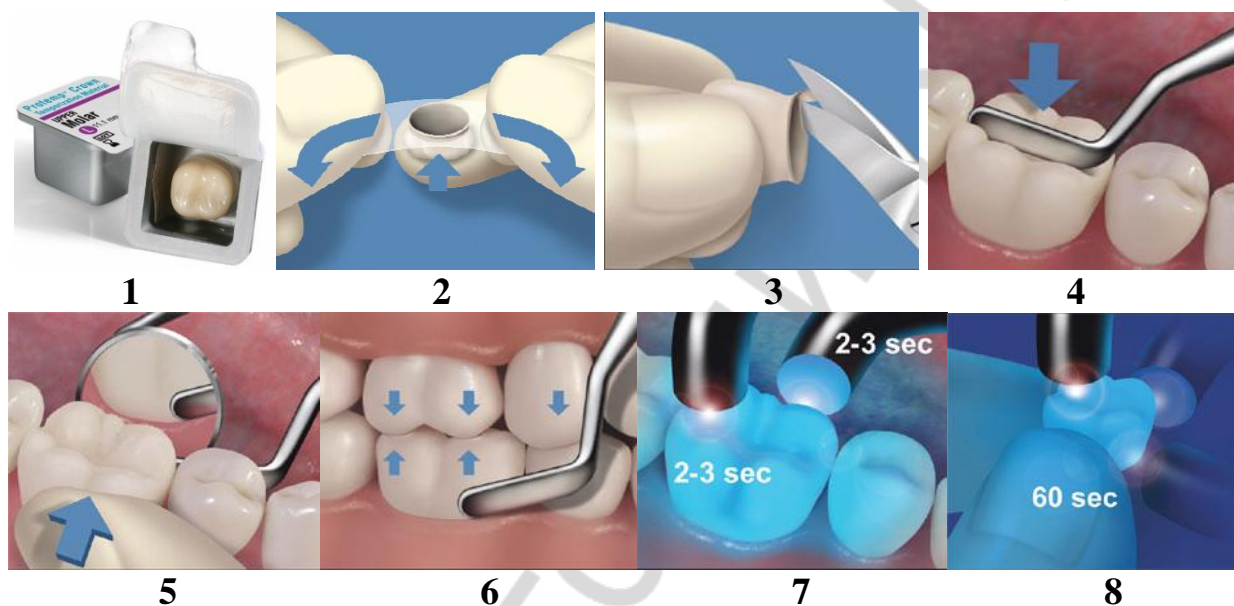


Figure 35. Sequence of provisional (temporary) crowns production by free molding with the use of preformed preparation from photopolymeric composite material

Provisional crowns from self-cured PMMA (“Акрилоксид”, Ukraine, “Villacril STC”, Italy, “Tempron”, Japan, “Unifast Trad”, Japan, etc.) and light-cured composite materials (“Revotek LC”, Japan, etc.) are made by *free molding*.

MILLING OF RESINS

Milling (milling processing) — processing of materials by cutting with the help of a mill. During milling two objects — a rotating mill and a preparation (future detail) — participate.

For milling of polymer materials CAD/CAM technologies, stated in the lecture “Technological Processes Used at Production of Dentures from metals alloys”, are applied.

In Fig. 36 the examples of some polymers used for milling are presented.

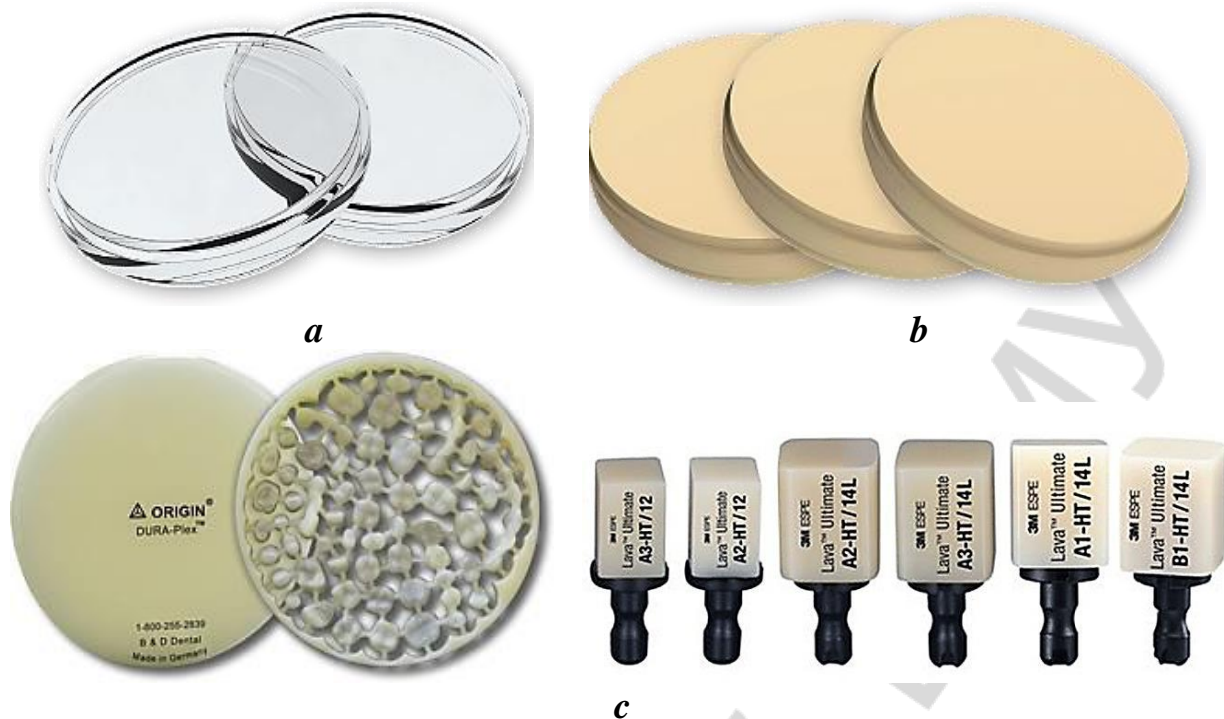


Figure 36. The polymers used for production of dentures by the milling method: *a* — ashless PMMA for milling of the frameworks that will be replaced into a constructional metal alloy by casting; *b* — PMMA for milling of provisional (temporary) dentures; *c* — nanocomposite resins (resin-nanoceramics) for milling of fixed dentures, consisting of 80 % $\text{SiO}_2 + \text{ZrO}_2$ and 20 % of dimethacrylate

THERMOPLASTIC INJECTION MOLDING

Thermoplastics — polymers, capable to pass reversibly when heating into a highly elastic or plastic state, are applied for thermoplastic injection molding method in dentistry.

At a usual temperature thermoplastics are in a firm state. As temperature increases they pass into a highly elastic and further into a plastic state that provides possibility of molding by various methods.

Melting temperatures of thermoplastic polymers applied in dentistry are presented in Table 4.

Table 4

Melting points of thermoplastic materials applied in dentistry

Materials	Melting temperature, °C	Materials	Melting temperature, °C
Polyamides	185–280	Polymethyl methacrylate (PMMA)	180–240
Polyoxymethylene	173–180	Ethylene-vinyl acetate (EVA)	90–160
Polypropylene	172–260	Polyether ether ketone (PEEK)	343–355

Nylon is a generic name for a type of thermoplastic polymers belonging to the class of polyamides.

Principle of thermoplastic injection molding. Thermoplastic is introduced in the granulated or powdery state into the injection cylinder of the molding machine (Fig. 37, 1) where it is warmed up by means of the thermoelement mounted around the cylinder (Fig. 37, 2). Plastification of the polymer is followed by transition of the material to a plastic state. The melted thermoplastic is forced in the form through a nozzle under 4–10 bar (Fig. 37, 3) where it hardens after cooling (Fig. 37, 4). After hardening the mold is opened and the products are taken. Sprue system is cut off and the denture is processed.

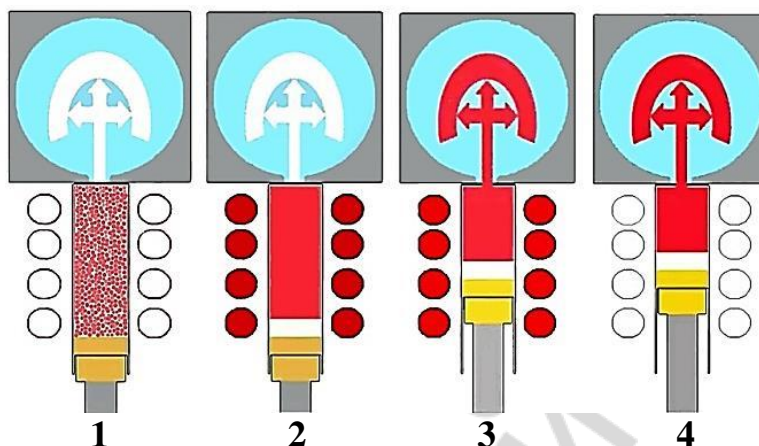
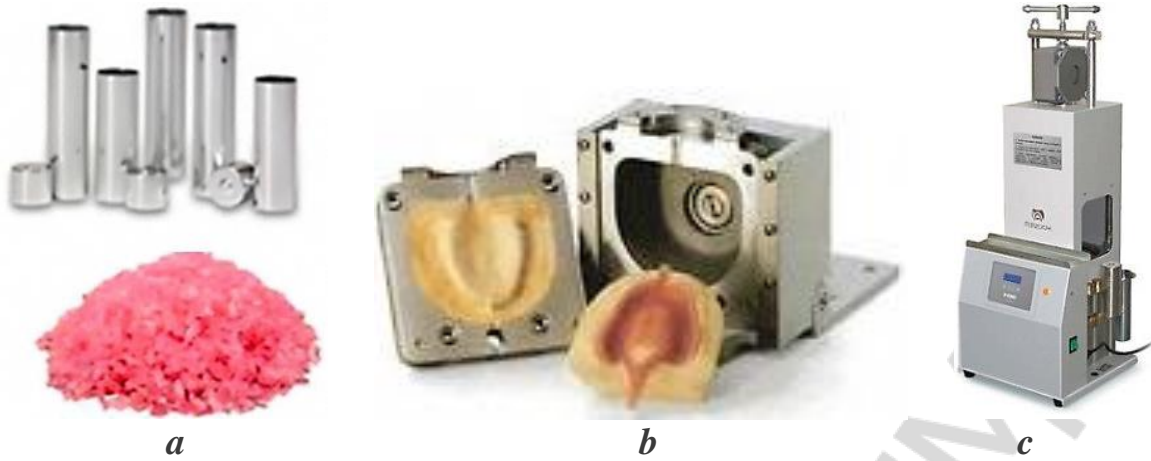


Figure 37. Scheme of thermoplastic injection molding

Steps of thermoplastic injection molding:

1. Investing of wax pattern in a special flask (e.g. valplast flask) and spruing.
2. Wax elimination by boiling.
3. Undercuts (diatorics) are made (prepared) in the centre of each tooth so that the melted fluid polyamide will flow into the undercuts for mechanical retention.
4. After preparation, each tooth is cemented back into its place in the top half of the flask with valcement (cement provided with the valplast system).
5. Thermoplastic nylon is melted at temperatures from 274 to 302 °C for 11 min before injection.
6. The opened flask is placed directly in a pre-heated oven maintained at 65–80 °C. Furnace timer was set for 17 minutes.
7. The flasks halves are assembled with brackets and together with the cartridge containing melted nylon; they are placed on to the injection unit. The injection molding pressure is maintained at 5 bars for 1 min.
8. The dental flask is bench-cooled before deflasking.

Production of dentures by thermoplastic injection molding is carried out by means of thermopresses of various designs. All the thermopresses consist of the heating block, the pressing block (pneumatic or electromechanical) and placement block of the flask. In Fig. 38 thermoplastic polymer in granules, aluminum cartridges (used for loading of different in structure resins while working on one device), flask for thermoplastic injection molding, placement block of the flask and a general view of the thermopress are presented.



a

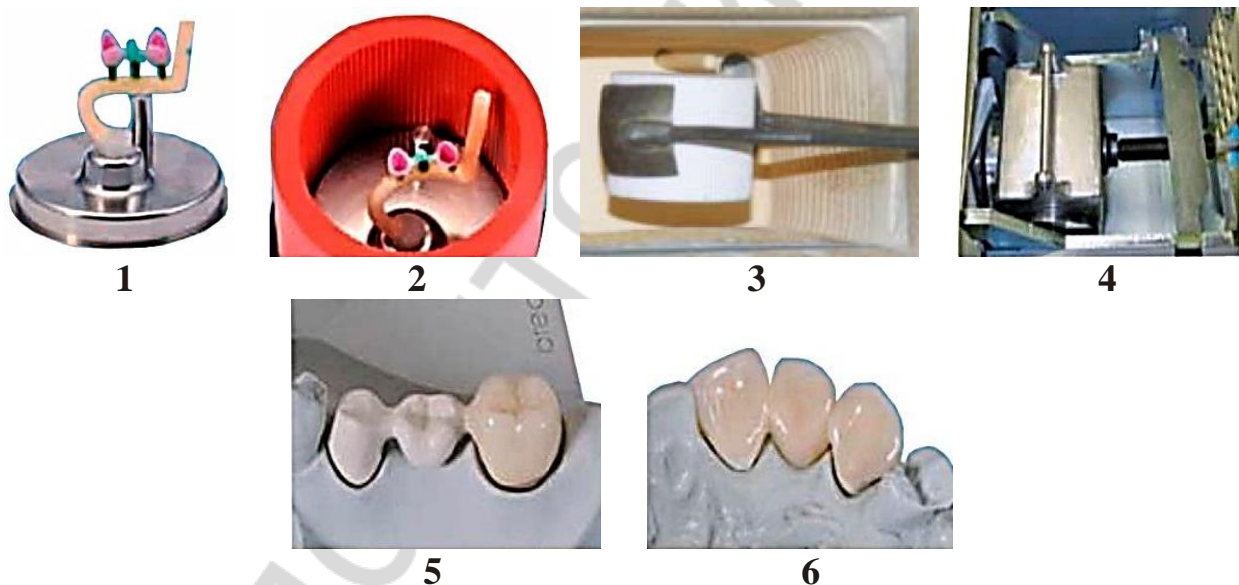
b

c

Figure 38. Device elements for thermoplastic injection molding:

a — thermo-plastic polymer in granules, aluminum cartridges; *b* — a flask for thermoplastic injection molding, placement block of the flask; *c* — general view of a thermopress

Fixed dentures (such as crowns and small bridges with only one artificial tooth) also can be manufactured with the help of thermoplastic injection molding. For this purpose there is used special thermoset material “Bio XS” (Bredent, Germany) which belongs to the group of PEEK. High hardness and rigidity of the material allows making frameworks of crowns and bridges of a small extent (one false tooth) with the subsequent facing by composite materials (Fig. 39).



1

2

3

4

5

6

Figure 39. Steps of injection thermoforming of fixed dentures:

1 — wax pattern of denture is settled on a sprue; 2, 3 — wax elimination (30 min in heating furnace at the temperature 900 °C); 4 — thermopress for injecting thermoplastic material; 5, 6 — carcasses of dentures, covered by composite materials

Uses of thermoplastic resins:

1. Flexible RPD.
2. Tooth colored clasps.
3. Preformed RPD clasps.
4. Flexite-metal combination.

5. Obturators.
6. Impression tray.
7. Provisional crowns and bridges.
8. Orthodontic braces.
9. TMJ's, bruxism & anti-snoring devices.
10. Sports mouth guards.

VACUUM FORMING AND THERMOFORMING UNDER PRESSURE (PNEUMATIC FORMING)

Vacuum and pneumatic forming is used for manufacturing of splints, individual impression trays from thermoplastic plates which are plastified under high temperature. Plates of thermoplastics (polypropylene, polychlorvinyl, polycarbonate, polyethylentherephtalate) with thickness from 0.5 till 3 mm are used. They can be high/low translucent, with milky colour and other colours.

When thermoplastic materials are heated, they get a condition of “fluidity”, and then under the influence of vacuum or the forcing pressure they are taken the corresponding form by dense fitting of the model. Elastic environment (atmospheric pressure or compressed air) plays role of a punch or a matrix.

Vacuum forming of thermoplastic plates is widely spread thanks to simple equipment and process (Fig. 40, *a*). Thermoplastic plate is fixed on the frame and heated by infrared radiator or electric heating arch till soft condition (Fig. 40, *b*). When plastified, frame with thermoplastic is placed onto the model and vacuum pump is switched on (Fig. 40, *c*). Due to negative pressure between model and material plate (vacuum) thermoplastic is formed into product.

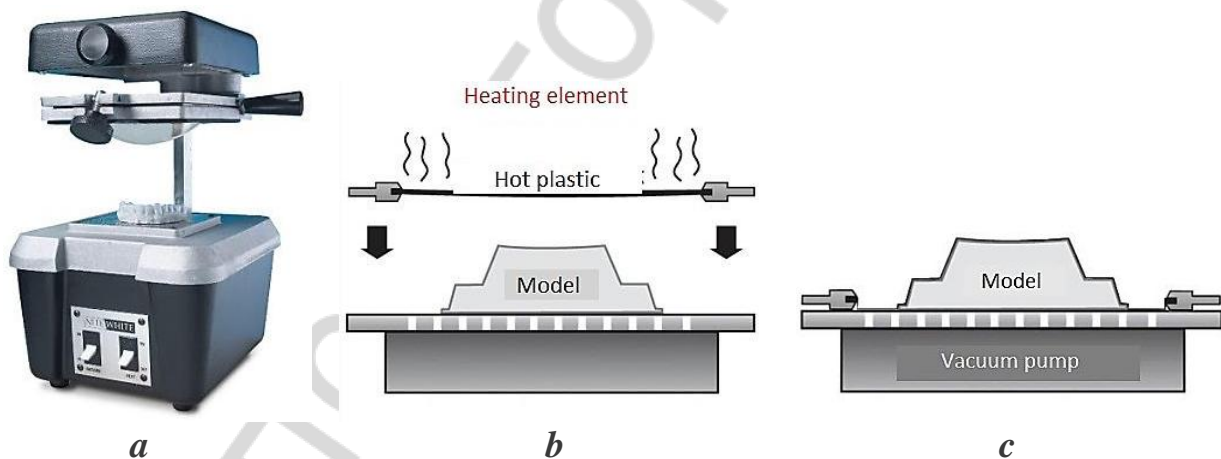


Figure 40. Unit for vacuum forming of thermoplastic (*a*) and scheme of its work (*b, c*)

The method of vacuum forming can be used for production of individual trays with the use of special preparations-plates from 3 to 5 mm thick (Fig. 41). Under the influence of negative pressure the plate densely presses out the model. After cooling the formed plastic is separated from the gypsum model and cut off on borders. This method allows quick making of qualitative individual trays from highly rigid thermoplastic.



Figure 41. Vacuum forming of an individual impression tray

Pneumatic forming with the use of high pressure (till 5 atm.) provides more detailed manufacturing than vacuum forming. Unit for pneumatic forming of thermoplastic consists of the model and the camera for the air that presses on the thermoplastics. Gypsum model is set into the forming cylinder of the device, a standard thermoplastic plate is fixed in clamping rings or frame. Thermoelements heat thermoplastic till the melting point. Then high pressure is created in the molding cylinder and plastic adapts to the model (Fig. 42).

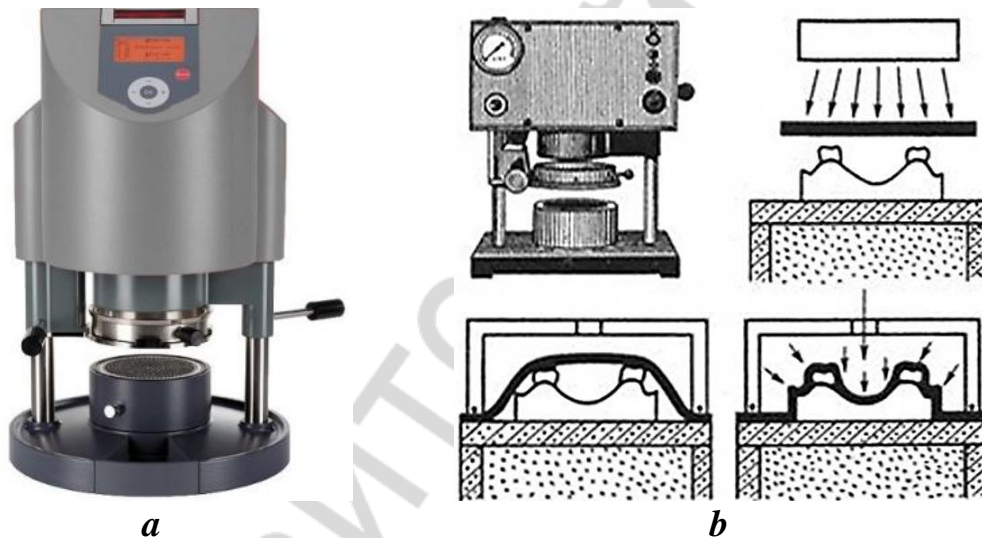


Figure 42. Device for thermoforming of polymeric materials under pressure (a) and scheme of its work (b)

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РЕПОЗИТОРИЙ БГМУ

Учебное издание

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**ПОЛИМЕРНЫЕ МАТЕРИАЛЫ В СТОМАТОЛОГИИ
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Ответственный за выпуск Н. М. Полонейчик
Переводчики Д. В. Гарабурда, И. А. Шипитиевская
Компьютерная верстка Н. М. Федорцовой

Подписано в печать 14.03.18. Формат 60×84/16. Бумага писчая «Снегурочка».

Ризография. Гарнитура «Times».

Усл. печ. л. 2,56. Уч.-изд. л. 2,45. Тираж 90 экз. Заказ 144.

Издатель и полиграфическое исполнение: учреждение образования
«Белорусский государственный медицинский университет».
Свидетельство о государственной регистрации издателя, изготовителя,
распространителя печатных изданий № 1/187 от 18.02.2014.
Ул. Ленинградская, 6, 220006, Минск.