POLYMERS

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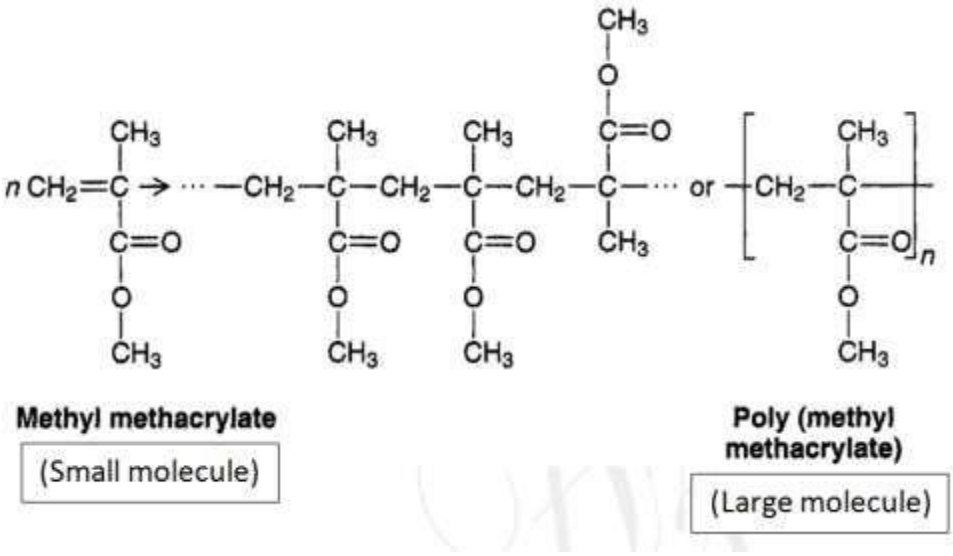
polymer is a chemical compound consisting of giant molecule formed by the union of many (poly) smaller repeatingn parts (mers).

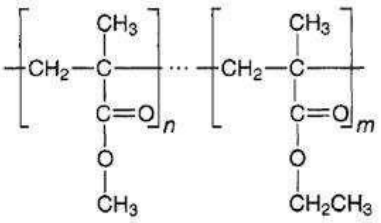
Monomer (one part): It is a molecule that forms the basic unit for polymers, and can combine with others of the same kind to form a polymer (homopolymer).



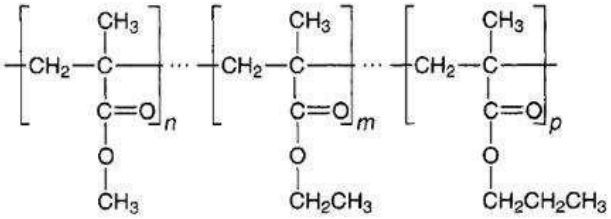
Copolymer: It is a polymer made by reaction of two different monomers. Have better physical property.

Terpolymer: It is a polymer synthesized from three different monomers.

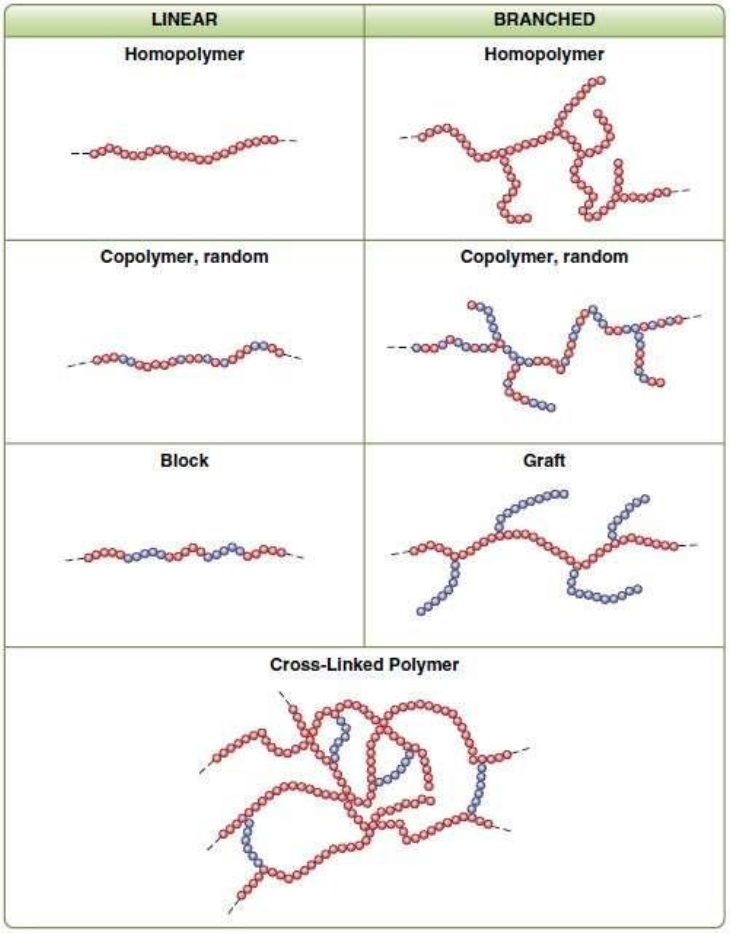
- Mers connected in a linear sequence => linear polymers
- Mers arranged in a branched fashion => branched polymer
- Mers chains that are cross connected by permanant links between them => cross linked polymer (network polymer). This restricting the motion of the chains and improve the rigidity of polymer, icrease thermal and wear resistances and decrease water sorption and solubility.



Methyl methacrylate–ethyl methacrylate copolymer



Methyl-, ethyl-, propyl methacrylate terpolymers



MOLECULAR WEIGHT

The molecular weight of the polymer molecule equals the molecular weight of the various mers multiplied by the number of the mers. The higher the molecular weight of the polymer, the higher the degree of polymerization.

The term POLYMERIZATION is the chemical process by which the monomers convert into polymers, but the DEGREE OF POLYMERIZATION is defined as the total number of mers in a polymer molecule. The higher the degree of polymerization, the better will be the physical properties and increasing the strength of the resin and its resistance to solubility.

POLYMERIZATION types:

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1. ADDITION POLYMERIZATION (Free-Radical Polymerization)

Most dental resins are polymerized by addition polymerization which simply involves the joining together of monomer molecules to form polymers chain with no change in composition of the monomers. In this type of reaction, no byproduct is obtained.

The reaction takes place in three CHEMICAL STAGES:

1- Activation and initiation stage

The addition polymerization process is start when free radicals are present. (Free radicals are very reactive chemical species that have an unpaired electron).

The free radicals are produced by reactive agents called initiators. Initiators are molecules which contain one weak bond which is able to undergo decomposition to form two reactive species (free radical), the decomposition of bond of initiator need source of energy (activator) such as heat, chemical compound, light, electromagnetic radiation.

Initiator is used extensively in dental polymers is (Benzoyl peroxide).

Addition polymerization reaction is initiated when the free radical reacts with monomer molecules producing another active free radical species which is capable of further reaction.

$$R\text{-}O - - - O\text{-}R \longrightarrow RO^{\bullet}\cdots\cdots + RO^{\bullet}\cdots\cdots$$

(initiator) *(free radicals)*

$$RO^{\bullet} + M \longrightarrow RO\text{-}M^{\bullet}$$

(Free radical + monomer ⟶ reactive free radical species)

2- Propagation stage

The initiation stage is followed by the rapid addition of other monomer molecules to the free radical and the shifting of the free electron to the end of the growing chain.

$$RO\text{-}M^{\bullet} + M \longrightarrow RO\text{-}M\text{-}M^{\bullet}$$

$$RO\text{-}M\text{-}M^{\bullet} + M \longrightarrow RO\text{-}M\text{-}M\text{-}M^{\bullet}$$

$$RO\text{-}M\text{-}M\text{-}M^{\bullet} + M \longrightarrow RO\text{-}M\text{-}M\text{-}M\text{-}M^{\bullet} \ \ldots\ldots \text{etc.}$$

3- Termination stage

This propagation reaction continues until the growing free radical is terminated either by: a- Reaction of two growing chains to form one dead chain b- Reaction of growing chains with inhibitors as (hydroquinone, eugenol, impurities, or large amounts of oxygen).

2. CONDENSATION POLYMERIZATION

A condensation reaction involves two different molecules reacting together to form a third, large molecule with production of byproduct such as water, halogen, acid, and ammonia. Condensation reaction progresses by the same mechanism of chemical reaction between two or more simple molecules.

Factors control the structure and the properties of polymers:

1- The molecular structure of repeating units including the use of copolymer.
2- Molecular weight or chain length.
3- The degree of chain branching (Linear, network, 3D).
4- The presence of cross-linking agent.
5- Presence of plasticizers or fillers.

Uses of polymers in dentistry:

Polymers are either natural or synthetic.

1- Denture base, special tray, record base.
2- Artificial teeth.
3- Obturators for cleft palate.
4- Composite tooth restoration.
5- Orthodontic space maintainer and brackets.
6- Crown and bridge.
7- rubber dams.
8- Impressions.
9- Maxillofacial prosthesis.
10- Dies.
11- Endodontic filling material.
12- Splints and stents. 13- Athletic mouth protectors. 14- Cements.

15- bonding agents.

16- relining materials and tissue conditioners.

Denture base materials

1- Metallic denture base
   a. Cobalt chromium
   b. Gold alloys
   c. Aluminium
   d. Stainless steel
2- Non-metallic denture base
   a. Cellulose products
   b. Phenol formaldehyde
   c. Vinyl resin
   d. Vulcanite rubber
   e. Acrylic resin (poly methyl methacrylate PMMA)
      This is the material of choice nowadays as denture base material due to its good esthetic qualities, easy manipulation and processing and cheap prices.

DENTURE BASE RESINS

The following list indicates the requirements for a clinically acceptable denture base material:

1- High strength, stiffness, hardness, toughness, and durability.
2- Good thermal conductivity.
3- Processing accuracy and dimensional stability. 4- Chemical stability (unprocessed as well as processed material).
5- Insolubility in and low sorption of oral fluids.

6- Absence of taste and odor.
7- Biocompatible.
8- Natural appearance.
9- Color stability.
10- Adhesion to plastics, metals, and porcelain.
11- Ease of fabrication and repair.
12- Moderate cost.
13- Accurate reproduction of surface detail.
14- Resistance to bacterial growth.
15- Radiopaque.
16- Easy to clean.
17- light in weight.
18- good shelf life.

Types:

1- Heat cured resin.
2- Cold cured resin.
3- Visible light cured resin.
4- Microwave activated resin.

HEAT CURED ACRYLIC & COLD CURED ACRYLIC)

COMPOSITION:

POWDER

1- Poly methyl methacrylate granules. With only chemical cured acrylic the granules are smaller in size and have a lower molecular weight.
2- Initiator as benzoyl peroxide to initiate the polymerization of the monomer
3- Pigments as cadmium sulfate is used to obtain the various tissue-like shades.
4- Titanium oxides are used as opacifiers.
5- Nylon or acrylic fibers are usually added to simulate the minute blood vessels of oral mucosa=> natural appearance.

LIQUID

1- Methyl methacrylate monomer: it is clear, colorless, low viscosity liquid, boiling point is 100.3°C, and distinct odor exaggerated by a high vapor pressure at room temperature. Care should be taken to avoid breathing the monomer vapor. Animal studies have shown that the monomer can affect respiration, cardiac function, and blood pressure.

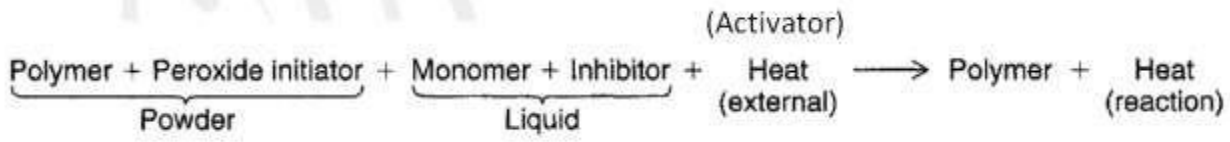
2- Hydroquinone inhibitors are added to give the liquid an adequate shelf life. The inhibitor is a chemical material added to prevent polymerization during storage and in order to provide enough working time.

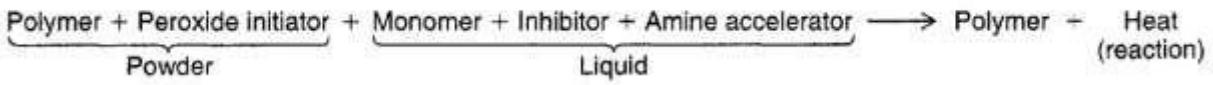
3- Plasticizers are sometimes added to produce a softer, more resilient polymer. They are relatively low-molecular weight esters, such as dibutyl phthalate.

4- If a cross-linked polymer is desired, organic compounds such as Ethylene glycol dimethacrylate (EGDMA) are added to the monomer, using cross-linking agents (chemical bonds between different chains) provides greater resistance to minute surface

cracking, termed crazing, and may decrease solubility and water sorption.

5- With only chemical cured acrylic an accelerator is included in the liquid. These accelerators are tertiary amines (N,N-dimethylpara-toluidine). These acrylics also called self-curing, cold-curing, or autopolymerizing resins.





POLYMER/MONOMER INTERACTION

The liquid placed in clean, dry mixing jar followed by slow addition of powder, allowing each powder particle to become wetted by monomer. After mixing the powder with liquid the mixture is left until it reaches a consistency suitable for packing. During this period, a lid should be placed on the mixing jar to prevent evaporation of monomer. The type of reaction is addition polymerization reaction.

The resultant mixture will pass into 5 STAGES:

(1) Sandy stage.

The polymer gradually settles into the monomer forming a fluid, incoherent mass.

(2) Stringy or sticky stage.

The monomer attacks the polymer by penetrating into the polymer. The mass is sticky and stringy (cobweb like) when touched or pulled apart.

(3) Dough stage.

As the monomer diffuses further into the polymer, it becomes smooth and dough like. It does not adhere to the wall of the jar. It consists of undissolved polymer particles suspended in a plastic matrix of monomer and dissolved polymer. The mass is plastic and homogenous and can be packed into the mold at this stage.

(4) Rubbery stage.

The monomer disappears by further penetration into the polymer and/or evaporation. The mass is rubber like, non-plastic, and cannot be molded.

(5) Stiff stage. on standing for a period, the mixture becomes stiff and very dry.

Working time: the time that a denture base material remains in dough like stage to remain moldable for at least 5 minutes.

FOLLOWING ARE THE RECOMMENDED CURING CYCLES:

- LONG CYCLE: heat the flask in water at 60-70 °C for 9 hours.
- SHORT CYCLE: heat the flask in water at 74 °C for 90 minutes

In comparison to heat cured acrylic; The cold cured acrylic has:

1. Lower molecular weight
2. Processed denture has more residual monomer => allergy and toxicity
3. Shorter working time
4. Lower dimensional change (lower shrinkage)
5. Lower hardness, impact strength, compression strength and tensile strength
6. Lower modulus of elasticity (lower stiffness)
7. Lower color stability

LIGHT CURED DENTURE PLASTICS

It consists of:
1- Urethane dimethacrylate matrix.
2- Acrylic copolymer.
3- Microfine silica filler.
4- Camphoroquinone-amine photo initiator system.

5- inhibitors
It is supplied in premixed sheets (single component) having clay like consistency. It is provided in opaque light-tight packages to avoid premature polymerization. The denture base material is adapted to the cast while it is in a plastic state. It is polymerized in a light chamber (curing unit) with blue light of 400-500 nm from high intensity quartz-halogen bulbs. The denture is rotated continuously in the chamber to provide uniform exposure to the light source.

Microwave polymerized polymer

Using specially formed acrylic resin processed in microwave by using non-metallic flask. The advantages of this process are cleaner and faster , shorter processing time and better accuracy and properties tha that of heat cured material

Flexible dentures (thermoplastic polymer)

Is a plastic becomes moldable above a specific temparature and returns to a solid state upon cooling.

Types:

1. Thermoplastic acetal
2. Thermoplastic acrylic
3. Thermoplastic polycarbonate
4. Thermoplastic nylon : because of its flexibility it is indicated in every case has an undercut, tilted teeth, patient has allergy to acrylic monomer and/on nickel, reduced mouth opening and when high esthetic is in demand.

Properties of flexible dentures:

1. High strength
2. Excellant flexibility and ductility
3. Semi translucent and provides excellent esthetic since no metal clasps appearrance on the tooth surface
4. Biocompatible because of free of monomer and metal that cause allergic reaction
5. High fracture resistance and impact properties, unbreakable even if thrown from height
6. Lower water sorption than PMMA resin
7. Good resistance to most chemicals but affected by strong acids and alcohols
8. Light weight
9. Apply minimal stress on abutments and underlying bone
10. Difficult to adjust, polish and repair
11. Aprone to creep
12. Minimal bonding strength to artificial teeth and to relining materials
13. Tendency to deteriorate, stain and develop a rough surface after short period of time

Processing errors

1. Porosity

   Presence of bubbles in/on the surface of resin lead to: a. Unsightly appearance of the denture base

b. Improper cleaning of the denture => denture and oral hygiene are suffered

c. Weaken the denture base Types:

Internal porosity	External porosity
voids or bubbles within the mass of polymerized acrylic confined to the thick portion of denture base.	White color voids localized on surface and subsurface
Due to vaporization of monomer when the temp.of resin increases above the boiling point of monomer (100.8C) in thick portion	Due to: 1. Lack of homogenity, this result from inadequate mixing of powder and liquid components lead to not homogeous dough at time of polymerization=> more shrinkage 2. Lack of adequate pressure during polymerization or inadequate amount of dough in mold during final closure=> irregular bubbles

Avoided by using long low temp.curing cycle for thick dentures	Avoided by: 1. using proper powder/liquid ratio and mixing it well to be more homogenousin dough stage 2. Using the required amount of dough in flask and check for exess during closure.

2.Crazing

Is formation of surface cracks on the denture base. These lead to:

Reduce esthetic quality and Weaken the denture and can cause fracture .
Causes:

a.Mechanical stresses

b.Attack by solvent (alcohol)

c.Incorporation of water during processing

3.Denture warpage

Is the deformation of denture or change in shapethat affect the fit of the denture.

Causes:

A.Release of stresses in denture during processing are curing shrinkage, rapid cooling, packing of acrylic in rubber stage or improper deflasking

b.Rise in temp.during polishing

c.Recuring of denture after addition of relining material

d.Repeated wetting and drying of denture

care of acrylic denture

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stored in water when not used

brushed carefully with soft brush

no hot water used

no abrasive toothpaste or houshold cleansers used