# Polymerization Reactions

- ***Types of polymerization reactions:***

**1-** ***Condensation polymerization*** :

The reaction produces by-products not like addition polymerization such as water hydrogen or alcohol (condensation reaction progress by the same mechanism as chemical reaction between two or more simple molecules). Usually more than one type of monomer is used.

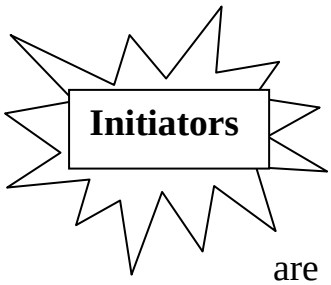
**2-** ***Addition polymerization***:

Most dental resins are polymerized by addition polymerization which simply involves the joining together of monomer molecules to form polymer chain in this type of reaction no by- product is obtained**.**

- ***The reaction take place in three stages:***

***1- Initiation stage***

To start an addition polymerization process, free radicals must be present which are produced by reaction agents called initiators.



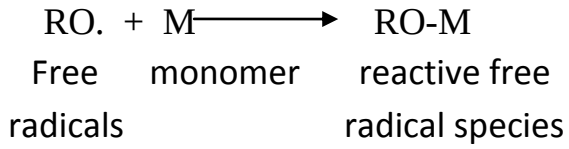

are molecules which contain one relatively weak bond which is able to undergo decomposition to form tow reactive species (free radical), each carrying an unpaired electron, the decomposition of initiators need source of energy like heat light or chemical activator.

R-O--O-R = 2Ro

Initiator free radicals

R= represent any organic molecular grouping. The free radicals react with a monomer and initiate the polymerization process.

Initiator, which is used extensively in dental polymers, is benzoyl peroxide (need to be activated by ether heat or chemical) decomposed and free radicals are produced.




Initiation reaction is an addition reaction producing another active free radical species which capable of further reaction (addition of free radical on the double bond of monomer).

## ***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 growing chin.

RO-M+M=RO-M-M

RO-M-M+M=RO-M-M-M

RO-M-M+M=RO-M-M-M

RO-M-M+M=RO-M-M-M

## ***3- Termination stage***:

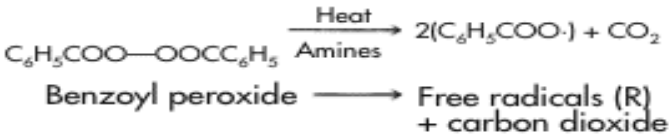
(the growing chin is stopped ) termination occurs when monomer units are used up or free radical can be terminated either by reactions of tow growing chain to form one dead chain or by reaction of growing chains with molecules of initiator dead polymer impunity or solvent if present.

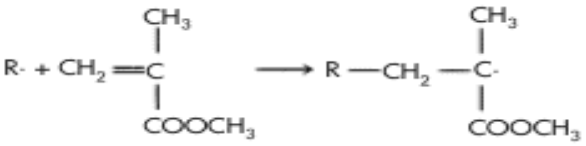
****Inhibitor:*** it is chemical material like ***hydroquinone*** added to prevent or delay polymerization during storage and in order to provide enough working time and decrease sensitivity to ambient light.

Impurity in monomer often inhibits polymerization, presence of oxygen also cause retardation of polymerization because oxygen react with free radicals.

***Plasticizers:*** substances added to resins to increase the solubility of the polymer in the monomer and decrease the brittleness of the polymer. However it also decreases strength, hardness and softening point; it is used to prepare flexible polymer.

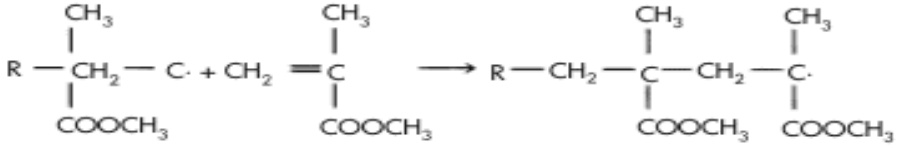
**1. Initiation**



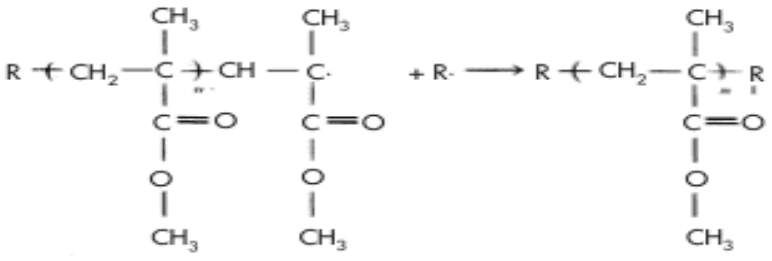
Free radical + Monomer ⟶ Free radical (activated monomer)

**2. Propagation**



Polymer free radical + Monomer ⟶ Growing chain

**3. Termination**



Free radical polymer + Free radical ⟶ Polymer chain

# ***Denture base material***

## ***Ideal requirements for denture base materials:***

1- Adequate strength and durability.
2- Satisfactory thermal properties.
3- Processing accuracy and dimensional stability.
4- Good chemical stability.
5- Insolubility in and low sorption of oral fluid.
6- Absence of taste and odor.
7- Biocompatible.
8- Natural appearance.
9- Color stability and Radio-opaque.
10- Adhesion to plastic , metal and porcelain.
11- Easy to fabricate and repair.
12- Moderate coast.

***** Old materials were used to construct dentures:**

| No. | Materials | Disadvantages |
|---|---|---|
| 1 | Cellulose products | Warpage, bad taste, blister staining & loss of color |
| 2 | Phenol formaldehyde | Loss of color & difficult to process |
| 3 | Vinyl resins | Low fracture resistance |
| 4 | vulcanite | Inferior esthetics |

**Nowadays the material of choice as a denture base material is acrylic resin (polymethyl methacrylate) which is supplied as (powder & liquid), its advantages are good esthetics, cheap and easy to process and use.**

## ***Types of poly methyl methacrylate resins***

**1-** Heat cured set by heat.
**2-** Cold cure it doesn't need heat only chemical amine cause them to become hard.
**3-** Light cured harden as subjected to light at certain wavelength.
**4-** High impact strength resins.
**5-** Pour cure resins very fluid and poured into the model.

## ***Heat cured resin***

It's the most popular acrylic resin used in fabrication the denture base. External heat is needed to activation.

## ***Composition of heat cured acrylic:***

### ❖ ***Powder***

- Beads or granules of PMMA (poly methyl methacrylate ).
- Initiator benzoyl peroxide 0.5% (produce free radical ).
- Pigments.
- Opacifiers : titanium / zinc oxide to make it radio – opaque.
- Plasticizer : Dibutyl phthalate make the material softer added flexibility (not present in all types ).
- Synthetic fibers: - nylon or acrylic to look likes blood vessels to give the gingival a natural appearance.

### ❖ ***Liquid***

- Methyl methacrylate monomer.
- Cross linking: ethylene glycol dimethacrylate, this component improves mechanical properties (add strength).
- Hydroquinone (0.006%): inhibitor – prevent fast setting.

## ***Methyl methacrylate monomer:-***

It is clear, transparent, volatile, liquid at room temperature it has characteristic sweetish odor, the physical properties of monomer:

*Boiling point 100.3C°.

*Density 0.945 gm/ml at 20 C°.

*Volume shrinkage during polymerization 21%

*Polymer / monomer ratio:

- 3:1 by volume.
- 2.5:1 by weight.

***Manipulation:*** The liquid placed in clean dry mixing jar fallowed by slow addition of powder, allowing each powder particle to become wetted by monomer; after mixing the powder with the liquid the mixture is left until it reaches a consistency suitable for packing. During this period mixing jar should be covered to prevent evaporation of monomer. The resultant mixing will pass into 5 stages:

**1- Sandy stage: -** this when monomer wets the outside of polymers particle.

**2- Sticky stage: -** the monomer attaches the surface of polymer beads. Some polymer chains are dispersed in the liquid monomer, the viscosity of the mix was increased and this stage is characterized by stickiness when the material is touched.

**3- Dough like stage: -** when the monomer diffuses further into the polymer particles and the mass becomes saturated, the mass dose not adheres to the walls of mixing jar. Clinically the mass behaves as pliable dough.

**4- Rubber stage: -** in this stage monomer is dissipated by evaporation and by further penetration into remaining polymer beads. The mass is no longer plastic, it is rubber like

**5- Stiff stage:** - on standing for a period, the mixture becomes stiff; this may be attributed to the evaporation of free monomer. Clinically the mixture appears very dry.

**Dough – forming time :-** the time form beginning of mixing the polymer with monomer until reach a dough like consistency in less than 10 minutes.

**Working time: -** the time that a denture base material remains dough like stage.

*****ADA specification NO.12 requires the dough to remain moldable for at last 5 minutes.**

The working time of acrylic denture base can be extended via refrigeration, the resin stored in refrigerator in air tight container to a void moisture contamination. In heat activated acrylic the transitions from sandy to sticky to dough and eventually rubber and hard stages are due to physical changes occur within the mixture. NO substantial polymerization occurs until the denture flask is heated to above 70C°. The average time need to reach packing consistency (dough stage) is only 5 minutes for chemically accelerate type compared with 15 minutes for heat polymerization acrylic.

## ***Heat activated denture base resin are shaped via***

1- Compression mold techniques.
2- Injection molding techniques.

### ***Compression mold technique***

- Flasking.
- Dewaxing.
- Application of separating medium.
- Placing acrylic dough.
- Packing, closing the flask together and removing excess.
- Heat curing under pressure, the denture flask under pressure is placed in heated polymerization bath.

**Polymerization cycle: -** the heating process used to control polymerization is termed polymerization cycle or curing cycle. This process should be well controlled to avoid the effect of uncontrolled temperature rise such as boiling of monomer and denture base porosity.

- ***We have two recommended curing cycles:-***

**1- Long cycle**: a satisfactory processing procedure is to cure the plastic in a constant temperature water path at 74C° for 8 hours or longer (10hs).

**2- Short cycle:** 74 C° for 2 hours and then increase temperature to 100C° or 1 hours.

The denture flask should be cooled slowly to room temperature, rapid cooling may result in warpage of denture base because of different in thermal contraction of resin and investing stone.

In addition to water bath curing methods, curing may be done in microwave where the flask used should be non metallic. Advantage of this technique is the speed with which polymerization may be accomplished.

## ***Properties of heat processed acrylic***

- Taste and odor: completely polymerized acrylic resin is tastelees & odorless.
- Esthetics: it is a clear transparent resin which be colored easily to duplicate the oral tissue.
- Density: polymer has a density of 1.19 gm/cm².
- Strength: two strengths: Compressive strength 75 Mpa.
  Tensile strength 52 Mpa.

Self cured resins generally have lower strength value.

- Impact strength: addition of plasticizers increases the impact strength.

Self cured resins have lower impact strength.

- Hardness: acrylic has a low hardness, can be easily scratched and abraded.

Heat cure acrylic 18-20KHN.
Self cure acrylic 16-18 KHN.

- Modulus of elasticity: sufficient stiffness for use in complete and partial denture but less than metal.
- Dimensional stability: a well proceed acrylic resin dentures has good dimensional stability, the processing shrinkage is balanced by the expansion due to water sorption.
- Shrinkage: acrylic resin shrinks during processing due to:

1- Thermal shrinkage on cooling.
2- Polymerization shrinkage:
*Volume shrinkage 8%.
*Linear shrinkage 0.53% for heat cure.
self cure type has a lower shrinkage (linear shrinkage 0.25).

- Water sorption: acrylic resin absorb water (0.6mg/cm2) and expand, this partially compensate for its processing shrinkage. This shrinkage is reversible.
- Solubility: acrylic is insoluble in water and oral fluid, it is soluble in ketones and esters.
- Thermal conductivity:poor conductor.

Coefficient of thermal expansion is light ($81*10^{-6}/C°$), addition of fillers reduce the coefficient of expansion.

- Color stability: heat cared acrylic have good color stability, cold cured is slightly lower.
- Biocompatibility: completely polymerized acrylic is biocompatible.
- Adhesion : the adhesion of acrylic to metal and porcelain is poor and mechanical retention is required, adhesion to plastic denture teeth is good (chemical adhesion).
- Instances of toxicity or allergic reaction have been related to excessive residual monomer that results from improper processing.

## ***Chemically activated resins***

Identical in composition to heat cure resin. Except liquid contain tertiary aromatic amine 1% which activate benzyl peroxide to produce free radicals and polymerization is initiated in manner similar to that describe for heat activated systems, also the particle size of polymethyl methacrylate powder is fine.

### ➢ ***Compared to heat activated resin :-***

**1-** Lower molecular weight (degree of polymerization is not as complete as that achieved using heat activated).
**2-** Higher amount of free monomer 3.5wt% while heat activated up to 1%.
**3-** Less colour stability due to oxidation of aromatic amine accelerators.
**4-** Working time is shorter.
**5-** Less shrinkage than heat activated because less complete polymerization.
**6-** Lower strength.
**7-** Lower hardness.

## ❖ ***Light activated resin***

Composition: (usually one component).
**1-** Dimethacrylate resin.
**2-** Light initiating system (camphorquinone – amine ).
**3-** Inhibitors.
**4-** Filler particle (silica filler)it supply in premixed sheets having a clay like consistency. It polymerized in a light chamber (curing unit) with blue light of 400-500 nm.

## ▪ ***Other polymeric materials***

**1.** Maxillofacial materials.
**2.** Endodontic materials: Gutta percha .
**3.** Orthodontics elastics: Natural rubber & Synthetic rubber.

# ***Processing errors***

❖ ***Porosity:*** when porosity is present on the surface it:

**a.** Makes the appearance of denture base unsightly.

**b.** Proper cleaning of denture is not possible causing bad oral hygiene.

**c.** It weakens the denture base.

***Types of porosity***:

**1-** Internal porosity.

**2-** External porosity.

## ➢ ***Internal porosity:***

They are voids or bubbles within the mass of polymerized acrylic (not present on the surface of the denture), this type of porosity develop in thicker portion of denture base. Internal porosity is due to the vaporization of monomer when the temperature of resin increases above the boiling point of monomer (100.3C°).

✓ Avoided by: denture with excessive thickness should be cured using long low temperature curing cycle.

## ➢ ***External porosity:***

It can occur due to two reasons:

**1-** Lack of homogeneity: if the dough is not homogenous at the time of polymerization, the portions containing more monomer will shrink more than the adjacent area, this localized shrinkage results in voids; the resin appears white.

✓ Avoided by : using proper powder – liquid ratio and mixing it well, the mix is more homogenous in the dough stage so packing should be done in the dough stage

**2-** Lack of adequate pressure :lack of pressure during polymerization or inadequate amount of dough in the mould during final closure causes bubbles which are not spherical; the resin is lighter in color

✓ Avoided by: using the required amount of dough, check for excess or flash during trail closure (flash indicates adequate material).

❖ ***Crazing:*** formation of surface cracks on the denture base resin. Crazing has a weaking effect on the resin and reduces the esthetic qualities, the cracks formed can cause fracture.

➢ ***Crazing is due to***

**1-** Mechanical stresses (tensile stresses ).

**2-** Attack by solvent.

**3-** Incorporation of water.

❖ ***Denture warpage:*** is the deformity or change of shape of the denture which can affect the fit of the denture, warpage can occur during processing as well as at other times.