NON-METALLIC DENTURE BASE MATERIAL

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INTRODUCTION

All through the history of the making of dentures, we find a constant struggle of the dentist to find a suitable denture base material.

DEFINITION

According to GPT - VI, Denture Base is defined as the part of Denture that rests on the foundation tissue and to which teeth are attached. Denture Base Material is any substance of which denture base may be made.
HISTORY

- Skillfully designed dentures were made as early as 700 BC.
- Talmud a collection of books of hebrews in 352-407 AD mentioned that teeth were made of gold, silver, and wood.
- Egypt was the medical center of ancient world, the first dental prosthesis is believed to have been constructed in Egypt about 2500 BC.

Hesi-Re Egyptian dentist of about 3000 BC
Front and back views of mandibular fixed bridge, four natural incisor teeth and two carved ivory teeth Bound With gold wire found in Sidon-ancient Phoenicia about fifth and fourth century BC.
• During medieval times dentures were seldom considered, when installed they were hand carved and tied in place with silk threads.

• Those wearing full denture had to remove them before eating.

• Upper and lower teeth fit poorly and were held together by steel springs.

• Earlier pictures of dental prosthesis are delivered to us by ABUL-CASIM an Arab born in Cordova Spain.
WOOD

- For years, dentures were fashioned from wood.

- Wood was chosen
  - readily available
  - relatively inexpensive
  - can be carved to desired shape

- Disadvantages
  - warped and cracked in moisture
  - esthetic and hygienic challenges
  - degradation in oral environment
Wooden denture believed to be carved out of box wood in 1538 by Nakoka Tei a Buddhist priestess

Wooden dentures
Bone was chosen due to its availability, reasonable cost and carvability.

It is reported that Fauchard fabricated dentures by measuring individual arches with a compass and cutting bone to fit the arches.

It had better dimensional stability than wood, esthetic and hygienic concerns remained.
IVORY

• Denture bases and prosthetic teeth were fashioned by carving this material to desired shape
• Ivory was not available readily and was relatively expensive.
• Denture bases fashioned from ivory were relatively stable in the oral environment
• They offered esthetic and hygienic advantage in comparison with denture bases carved from wood or bone.
• Since ancient times the most common material for false teeth were animal bone or ivory, especially from elephants or hippopotomus.

Carved ivory upper denture retained in the mouth by springs with natural human teeth cut off at the Neck and riveted at the base.
• Human teeth were also used, pulled from the deceased or sold by poor people from their own mouths
Waterloo dentures

1788 A.D. Improvement and development of porcelain dentures by DeChemant.

G. Fonzi an Italian dentist in Paris invented the Porcelain teeth that revolutionized the construction of dentures. Picture shows partial denture of about 1830, porcelain teeth of Fonzi’s design have been soldered to a gold backing.
CERAMICS

- Porcelain denture bases were relatively expensive
- During subsequent years secrets of porcelain denture became known and it became common and inexpensive.
- ADVANTAGES over wood, bone, ivory were
  - Could be shaped using additive technique rather than subtractive (carving).
  - Additive technique facilitated correction of denture base surface.
  - This permitted more intimate contact with underlying soft tissues.
  - Could be tinted to simulate the colors of teeth and oral soft tissues.
  - Stable in oral environment.
  - Minimal water sorption, porosity, and solubility.
  - Smooth surface provided hygienic properties.
- Among the drawbacks BRITTLENESS was most significant, fractures were common, often irreparable.
One piece porcelain upper denture crafted by Dr John Scarborough, Lambertville, New Jersey 1868.
In 1794 John Greenwood began to swage gold bases for dentures. Made George Washington's dentures.

George Washington’s last dental prosthesis. The palate was swaged from a sheet of gold and ivory teeth riveted to it. The lower denture consists of a single carved block of ivory. The two dentures were held together by steel springs.
• In 1839 an important development took place CHARLES GOODYEAR discovered VULCANIZATION of natural rubber with sulphur (30%) and was patented by Hancock in England in 1843.

• NELSON GOODYEAR (brother of Charles Goodyear) got the patent for vulcanite dentures in 1864.

• They proceeded to license dentists who used their material, and charged a royalty for all dentures made. Dentists who would not comply were sued.

• The Goodyear patents expired in 1881, and the company did not again seek to license dentists or dental products.

• Vulcanite dentures were very popular until the 1940s, when acrylic denture bases replaced them.
A set of vulcanite dentures worn by Gen. John J. (Blackjack) Pershing, commander of the American Expeditionary Forces in France during the First World War.

Set of complete dentures having palate of swaged Gold and porcelain teeth set in vulcanite.
• In 1868 John Hyatt, a US printer, discovered the first plastic molding compound, called celluloid. He made it by dissolving nitrocellulose under pressure.

• In 1909, another promising organic compound was found. This was phenol formaldehyde resin discovered by Dr. Leo Backeland.

Celluloid upper denture 1880, celluloid as a substitute for vulcanite was unsuccessful as it absorbs stains and odors in the mouth. Gradually turns black and was flammable.
• In 1937 Dr. **Walter Wright** gave dentistry its very useful resin.

• *It was polymethyl methacrylate which proved to be much satisfactory material tested until now.*

*Dentures made of polymethyl methacrylate*
Disadvantages of different denture base

**Vulcanite**

In 1839 Vulcanized rubber was discovered and introduced as a Vulcanite and Ebonite.

For the next 75 years Vulcanite rubber was the principal Denture base Material. But failed because of following reasons:

**Disadvantages**

- It absorbs Saliva and becomes unhygienic due to bacterial proliferation.
- Esthetics were poor.
- Dimensionally unstable.
- Objectionable taste and odor
Celluloid

Although it was having tissue like color but having principal disadvantages like

Disadvantages

- Lack of stability
- Unpleasant taste
- Unpleasant odor
- Stainability
- Flammable
Bakelite

It was formed by heating and compressing a mixture of phenol and formaldehyde.

Disadvantages

• Lack of uniform quality
• Variable strength
• Variable color
• Dimensional unstability.
POLYMERS

Chronology of events

• Charles Goodyear discovery of vulcanized rubber in 1839.
• John Hyatt discovered celluloid in 1868
• Dr Leo Bakeland discovered phenol-formaldehyde resin (Bakelite).

• In the 1930's **Dr Walter Wright and the Vernon brothers** working at the Rohn and Haas company in Philadelphia developed **Polymethylmethacrylate (PMMA)**, a hard plastic.

• Although other materials were used for dental prosthesis, none could come close to PMMA and by the 1940's 95% of all dentures were made from this acrylic polymer.
Natural polymers include:

- Proteins (polyamides or polypeptides) containing the chemical group (-CO-NH-); this is known as an amide or peptide link.

- Polyesoprenes such as rubber and gutta percha.

- Polysaccharides, such as starch, cellulose, agar and alginates.

- Polynucleic acids, such as deoxyribonuclei acids (DNA) and ribonucleic acids (RNA).

Synthetic polymers are produced industrially or in the laboratory, by chemical reaction.

It is defined as a non metallic compound synthetically produced (usually from organic compounds) which can be molded into various useful forms and then hardened for use.
**DEFINITION:** A polymer is a long chain organic molecule. It is produced by the reaction of many smaller molecules called monomers, or mers.

- If reaction occurs between two different but compatible monomers the polymeric product is called a **COPOLYMER**.

- **Resin**: A broad term used to describe natural or synthetic substances that form plastic materials after polymerization (GPT-7th edition).

**USES IN DENTISTRY**

- Denture bases and artificial teeth.
- Denture liners and tissue conditioners.
- Composite restorative and pit and fissure sealent.
- Impression materials
- Custom trays for impression
- Temporary restoratives.
- Mouthguards.
- Maxillofacial prosthesis.
- Space maintainers.
- Veneers.
- Cements and adhesives.
CHEMISTRY OF POLYMERIZATION

- Monomers react to form polymer by a chemical reaction called polymerization.
- The most common polymerization reaction for polymers used in dentistry is **addition polymerization**.

**ADDITION POLYMERIZATION**

- **INDUCTION**
- **PROPOGATION**
- **CHAIN TRANSFER**
- **TERMINATION**

**INDUCTION**

1) **ACTIVATION**
2) **INITIATION**
**ACTIVATION**

Free radicals can be generated by activation of radical producing molecule using:

- Second chemical
- Heat
- Visible light
- Ultraviolet light
- Energy transfer from another compound that acts as a free radical.

\[
\text{R—R + external energy \rightarrow 2 R•}
\]

![Diagram of the reaction]
• Commonly employed initiator is Benzoyl peroxide which is activated rapidly between 50 degree and 100 degree C to release two free radicals per benzoyl peroxide molecule.

• Second type is chemically activated, consists of two reactants when mixed undergo reaction eg tertiary amine (the activator) and benzoyl peroxide (the initiator). Amine forms a complex with benzoyl peroxide which reduces the thermal energy (and thus the temperature) needed to split it into free radicals.

• Third type is light activated. The visible light light cured dental restoratives, camphorquinone and an organic amine (dimethylaminoethylmethacrylate) generate free radicals when irradiated by light in the blue to violet region.

• Light with a wavelength of about 470nm is needed to trigger this reaction.
INITIATION

A

B

C

D
The resulting free radical monomer complex acts as a new free radical center which is approached by another monomer to form a dimer, which also becomes a free radical.
CHAIN TRANSFER

- The active free radical of a growing chain is transferred to another molecule (e.g., monomer or inactivated polymer chain) and a new free radical for further growth is created, terminating one chain in the solution.
TERMINATION

- Can occur from chain transfer.
- Addition polymerization reaction is terminated by
  - Direct coupling of two free radical chains ends
  - Exchange of hydrogen atom from one growing chain to another.
INHIBITION OF ADDITION REACTION

- Addition of small amount of Hydroquinone to the monomer inhibits spontaneous polymerization if no initiator is present and retards the polymerization in the presence of an initiator.

- Amount added is 0.006% or less

- Methyl ether of hydroquinone is generally present.

COPOLYMERIZATION

- When two or more chemically different monomers each with desirable properties can be combined to yield specific physical property of a polymer. eg small amount of ethyl acrylate may be co-polymerized with methyl methacrylate to alter the flexibility and fracture resistance of a denture.
METHYL METHACRYLATE

- The acrylic resins are derivative of ethylene and contains a vinyl group (-c=c-)
- Polyacids tends to imbibe water, due to polarity related to carboxyl group.
- Water tends to separate the chain and cause softening and loss of strength.
- Methyl methacrylate is a transparent liquid at room temp.
- Physical properties
  - Molecular wt=100
  - Melting point=-48 C
  - Boiling point=100 C
  - Density=0.945g/ml at 20 C
  - Heat of polymerization=12.9 Kcal/mol
POLYMETHYL METHACRYLATE

- Transparent resin, transmits light in uv range to a wavelength of 250 nm. it has got remarkable clarity.
- Hard resin, knoop hardness no of 18 to 20.
- Tensile strength is 60 MPa
- Density is 1.19 g/cm cube.
- Modulus of elasticity 2.4 GPa (2400 MPa)
- It is chemically stable and softens at $125^0C$
- It can be molded as a thermoplastic material between 125 and 200 C
- Depolarization takes place at approx 450 C.
- Absorbs water by imbibition
- Non crystalline structure possess high internal energy.
- Polar carboxyl group can form hydrogen bridge to a limited extent with water.
CURING CYLES EMPLOYED IN THE STUDY

A. Recommended curing cycles

   overnight water-bath cures:

1) 7hr at 70°C
2) 14hr at 70°C
3) **7hr at 70°C + 1hr at 100°C**
4) 14hr at 70°C + 1hr at 100°C

Short and reverse cures:

5) Boil water, insert flask, remove heat for 20 min, return to boil for 10 min.
6) Boil water, insert flask, return to boil, boil for 10 min.

Dry heat cure:

7) temp in excess of 100°C using dry heat system

B. Short curing cycles

8) 7hr at 60°C
9) 7hr at 60°C + 1 hr at 90°C
10) Boil water, insert flask, remove heat for 20 min, return to 90°C, hold at 90°C for 5 min
11) Boil water, insert flask, return to 90°C, hold at 90°C for 5 min.
CONCLUSION

1. A curing cycle of 7hr at 70°C followed by a terminal boil at 1hr at 100°C is the optimum curing cycle resulting in max monomer conversion.

2. Short cut curing cycles are undesirable and result in significantly raised levels of residual monomer.

3. The residual monomer levels of 23 available denture base polymers cured using the optimum cycle ranged from 0.54 to 1.08%.
PHYSICAL PROPERTIES

• Should possess adequate strength and resiliency and resistance to biting and chewing forces, impact forces, and excessive wear in oral cavity.

• Should be dimensionally stable under all conditions of service including thermal changes and variations in loading.

Specific gravity: It should have low value of specific gravity in order that dentures should be as light as possible.

Thermal conductivity: It is defined as the number of calories per second flowing through an area of 1cm\(^2\) in which the temperature drop along the length of the specimen is 1°C/cm.

• It should have high value of thermal conductivity

Radiopacity: It is the inhibition of passage of radiant energy.

• It should be ideally radiopaque
**Glass transition temperature:**

- It is the temperature at which molecular motions become such that whole chains are able to move. It is close to softening temperature. At this temperature sudden change in elastic modulus occurs.
- Amorphous polymer below Tg behave as rigid solids while above Tg they behave as viscous liquids, flexible solids or rubbers.
- Increased chain branching $\rightarrow$ Decreased Tg.
  
  $\text{Increased number of cross links } \rightarrow \text{Increased Tg}$

**Effect of molecular weight on properties**

In many polymers the chains are held together by secondary, or Vander Waals forces and molecular entanglement. Materials of high molecular weight have a greater degree of molecular entanglement, and have greater rigidity and strength and higher values of Tg and melting temperature than low molecular weight polymers.
**Effect of plasticizers**

- Plasticizers penetrate between the randomly oriented chains of polymer as a result of which molecules are further apart and forces between them are less. They soften the material and make it more flexible by lowering its Tg. They lubricate the movements of polymer chains and are sometimes added to help molding characteristics. This principle is used in producing acrylic soft lining materials.

- **Effect of fillers**
  - Modulus of elasticity and strength are generally increased.
  - A degree of anisotrophy exist, that is the strength depends on the orientation of fibres in the polymers.

- **Viscoelasticity**: Polymers show viscoelastic behaviour. Elastic behaviour is caused by uncoiling of polymer molecules. Plastic behaviour is caused by breaking of intermolecular Vander Waals forces
(III) MANIPULATION

• Should not produce toxic fumes or dust
• Easy to mix, insert, shape and cure and short setting time
• Oxygen inhibition, saliva and blood contamination should have little or no effect.
• Final product should be easy to polish and easy to repair in case of breakage.

(IV) AESTHETIC PROPERTIES

• Should be translucent to match oral tissues
• Capable of pigmentation
• No change in color after fabrication.

(v) ECONOMIC CONSIDERATION

• Cost should be low
• Processing should not require complex and expensive instruments.
(VI) CHEMICAL STABILITY

- Conditions in mouth are demanding and only the most chemically stable and inert materials can withstand such conditions without deterioration.

“No resin has yet met all of these ideal criteria”. Methacrylate polymers fulfill the aforementioned requirement reasonably well.
TYPES OF DENTURE BASE POLYMERS

CONVENTIONAL HEAT CURED POLYMETHYL METHACRYLATE

• Supplied as powder and liquid

POWDER

• Polymer of PMMA in the form of spheres or beads.

• Benzoyl peroxide is attached to it (initiator) 0.5%

• Plasticizer is incorporated (methacrylate or acrylate monomer).

• Coloring pigments cadmium/ organic dyes/ iron are added for esthetics.
POLYMER POWDER OF ACRYLIC DENTURE BASE MATERIAL
LIQUID

- Methyl methacrylate monomer
- Cross linking agent Ethylene glycol dimethacrylate (5-15%). They are added to avoid crack or craze produced by stresses during drying.
- Inhibitor Hydroquinone (trace) to avoid premature polymerization and enhance shelf life.
- When MMA polymerizes it shrinks 21% by volume.
- Using a 3:1 powder liquid ratio it could be minimized to 6%.
- A correctly heat processed denture base could have as little as 0.3% to 2% residual monomer.
• As a rule, heat activated denture base are shaped via compression molding technique.

**Polymer monomer interaction**
When polymer and monomer are mixed it passes through following stages
• Sandy
• Stringy
• Dough like
• Rubbery or elastic
• Stiff

**Dough forming time**
• According to ANSI/ADA specification no 12 for denture base resins requires that this consistency be reached in less than 40 min from start of mixing time.
• In clinical use it is achieved in less than 10 min.

**Working time**
• Time that a denture base remains in a dough like stage. ANSI/ADA specification no 12 requires the dough to remain moldable for 5 min.
AUTOPOLYMERIZING/COLD CURE POLYMETHYL METHACRYLATE (POUR RESIN)

• Composition same as the heat cure version with following differences
  1) The powder contains beads of polymer that have a lower molecular wt. and benzoyl peroxide (initiator)
  2) The liquid contains a chemical activator, tertiary amine such as dimethyl-para-toluidine.

• Upon mixing tertiary amine causes decomposition of benzoyl peroxide.
• Dentures processed have more residual monomer (1-4%), but lower dimensional change.
• Decreased transverse strength (residual monomer act as plastisizer).
• Compromised biocompatibility (residual monomer)
• Color stability inferior (tertiary amine susceptible to oxidation), stabilizing agents should be added
• Fluid resin and compression molding technique can be employed for the fabrication of denture.
• Also used as repair material
HIGH IMPACT RESISTANT ACRYLIC

- Similar to heat cured material but less likely to be broken if dropped.
- Produced by substituting the PMMA in the powder with a copolymer.
- Copolymer of butadiene with styrene or methyl methacrylate are incorporated into the beads.
- **Phase inversion** resulting in dispersion throughout the beads of tiny islands of rubber containing small inclusions of rubber/PMMA graft polymer.

Electron micrograph of high impact denture Base showing size and shape of polystyrene-butadiene Rubber inversion phase.
**Injection molded polymers**

- These are made of Nylon or Polycarbonate.
- The material is supplied as a gel in the form of a putty.
- It has to be heated and injected into a mold.
- Equipment is expensive.
- Craze resistance is low.

The SR-Ivocap system uses specialized flasks and clamping presses to keep the molds under a constant pressure of 3000 lbs.
MICROWAVE POLYMERIZED POLYMERS

- Resins are the same as used with conventional material and are processed in a microwave.
- Denture base cures well in Special polycarbonate flask (instead of metal).
- The properties and the accuracy of these materials have been shown to be as good or better than those of the conventional heat cured material.
- Processing time is much shorter (4-5 min).

Microwave resin and non metallic microwave flask
RAPID HEAT POLYMERIZED POLYMER

• Same as conventional material except that they contain altered initiation system.

• These initiator allow them to be processed in boiling water for 20 min.

• A problem with these is that areas of the base thicker than approx. 6mm have a high level of porosity.

• Short duration of heating also leaves a higher level of residual monomer, 3-7 times greater than conventional heat cured denture base.
**Light activated denture base resins**

- This material is a composite having a matrix of urethane dimethacrylate, microfine silica and high molecular wt acrylic resin monomers.
- Acrylic resin beads are included as organic fillers.
- Visible light is the activator, whereas camphorquinone serves as the initiator for polymerization.
- Can be used as repair material and as custom tray material.
- Single component denture base is supplied as sheet and rope form in light proof pouches.
FIBER –REINFORCED POLYMER

• Glass, carbon/graphite, aramid and ultrahigh molecular wt polyethylene have been used as fiber reinforcing agents.

• Metal wires like graphite has minimal esthetic qualities.

• Fibers are stronger than matrix polymer thus their inclusion strengthens the composite structure.

• The reinforcing agent can be in the form of unidirectional, straight fiber or multidirectional weaves.
**VALPLAST**

Valplast is a flexible denture base resin that is ideal for partial dentures and unilateral restorations.

- The resin is a biocompatible nylon thermoplastic, it eliminates the concern about acrylic allergies.
THANK YOU