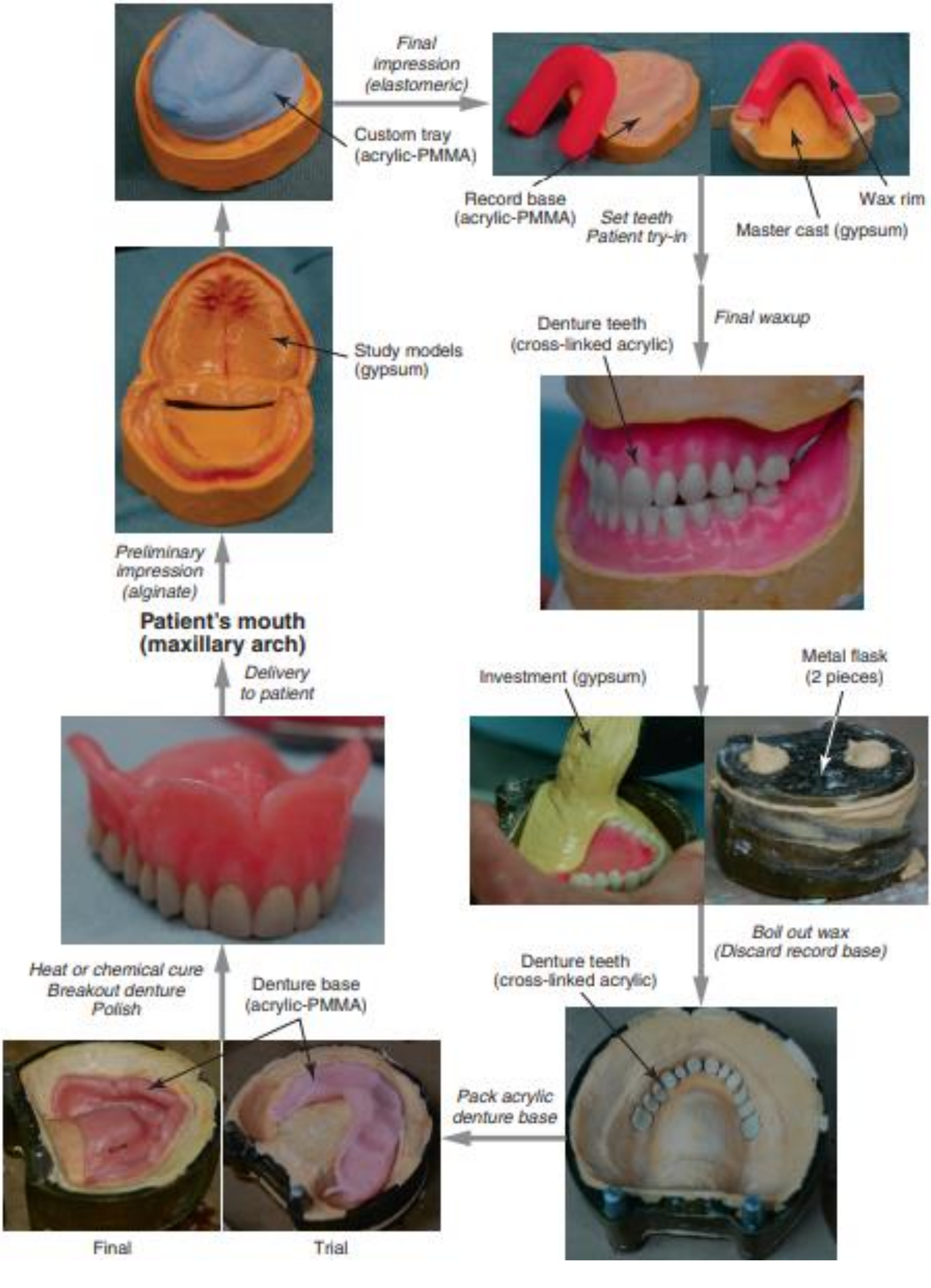
Polymerization: The process by which monomers unite to form a polymer

Types of Polymerization:

1) Addition polymerization:
    - No by-product is formed.
    - The addition polymers contain the same atoms as the monomer in their repeating units.
    - Materials that set by addition polymerization include PMMA, used in the construction of dentures, and bisphenol A glycidyl methacrylate (bis-GMA), a common component of the matrix of resin composites.
2) Condensation polymerization:
    - A low-molecular-weight byproduct such as water or alcohol is formed.
    - Condensation polymers contain fewer atoms because of the formation of by-products during the process.
    - Materials that set by the condensation mechanism include polysulfide rubber and some silicone rubber impression materials.

General Technique of Denture Base Fabrication

- Several processing techniques are available for the fabrication of denture bases.
- Each technique requires a suitable impression of the associated dental arch, followed by the fabrication of an accurate gypsum cast.
- In turn, a resin record base is fabricated on the cast.
- Wax is added to the record base, and prosthetic teeth are positioned in the wax. The prosthetic teeth are related to the opposing dentition and evaluated in the patient's mouth before proceeding.
- In the laboratory, a bronze denture flask is used, and the completed tooth arrangement is encased in a suitable investing medium (usually gypsum).
- A plastic denture flask is mandatory if microwave energy is used.
- Subsequently, the denture flask is opened, and the wax denture base is eliminated in a hot-water bath, leaving the prosthetic teeth in place.
- After a thorough cleansing of the mold, an appropriate separator is applied to the gypsum surface. In turn, a resin denture base material is introduced into the mold cavity and polymerized under pressure.
- Following polymerization, the denture is recovered and prepared for clinical placement. Not all denture base processing requires flasks. When light-activated resin or computer-aided design/computer-aided manufacturing (CAD-CAM) processing is used, no flask is needed.


Final impression (elastomeric)
Custom tray (acrylic-PMMA)
Record base (acrylic-PMMA)
Set teeth Patient try-in
Wax rim
Master cast (gypsum)
Study models (gypsum)
Final waxup
Denture teeth (cross-linked acrylic)
Preliminary impression (alginate)
Patient's mouth (maxillary arch)
Delivery to patient
Investment (gypsum)
Metal flask (2 pieces)
Boil out wax (Discard record base)
Denture teeth (cross-linked acrylic)
Heat or chemical cure
Breakout denture
Polish
Denture base (acrylic-PMMA)
Pack acrylic denture base
Final
Trial

Denture Base Materials:

Heat-Activated Denture Base Resins:

Composition: Heat-cured acrylic is supplied as powder and liquid.

- Powder:
  1. Poly methyl methacrylate beads or granules (PMMA).
  2. A small amount of benzoyl peroxide (initiator) to produce free radicals.
  3. Dibutylphthalate as a plasticizer to assist dough formation.
  4. Pigments.

- Liquid:
  1. methyl methacrylate monomer
  2. small amounts of hydroquinone (inhibitor) to prevent untimely polymerization of the liquid during storage. Inhibitors also retard the curing process and thereby increase working time.
  3. Crosslinking agents (glycol dimethacrylate) to reduce the denture base's solubility to organic solvents and to reduce the tendency of the denture base to crazing (forming precracks) under stress. However, excessive levels of cross-linking agent in the monomer result in denture bases that are brittle.

Light-activated materials:

- This material consists of a urethane dimethacrylate matrix, microfine silica, and high-molecular-weight acrylic resin monomers. Acrylic resin beads are included as organic fillers.
- It is supplied in premixed sheet or rope form and packed in lightproof pouches to prevent inadvertent polymerization
- A baseplate is made by adapting the material to a cast and polymerizing in a light chamber at 400 to 500 nm (blue light is the activator). Teeth are then added to the base with additional material followed by a second period of light exposure.
- The system eliminates the need for flasks, wax, boil-out tanks, packing presses, and heat-processing units required for the construction of conventional dentures.
- It has the advantage of significant time savings in both the dental office and the laboratory.

Steps in denture fabrication (light-activated denture base resins). **A,** Representative light-activated denture base resin. Sheet and rope forms are supplied in light-proof pouches to prevent inadvertent polymerization. **B,** Teeth are arranged, and the denture base is sculpted using light-activated resin. **C,** The denture base is placed into a light chamber and polymerized according to the manufacturer's recommendations.

Chemical-Activated Denture Base Resins

- The same initiator used in heat-activated denture base resin can also be activated by a tertiary amine, such as dimethyl-para-toluidine.
- The tertiary amine may be added to the liquid monomer.
- Upon mixing liquid and powder components, the tertiary amine causes decomposition of the benzoyl peroxide contained in the powder. As a result, free radicals are produced, and polymerization progresses in a manner similar to that described for heat-activated systems.
- Chemical activation does not require the application of thermal energy and can be completed at room temperature. For this reason, chemical-activated resins often are referred to as coldcuring, self-curing, or autopolymerizing resins.
- The working time for chemical-activated resins is shorter than that for heat-activated materials. Therefore special attention must be paid to the consistency of the material and rate of polymerization.
- The polymerization of chemical-activated resins is never as complete as the polymerization of heat-activated materials.
- Resins polymerized via chemical activation generally display 3% to 5% free monomer, whereas heat-activated resins exhibit 0.2% to 0.5% free monomer. Therefore it is important that the polymerization of chemical-activated resins be as complete as possible. Failure to achieve a high degree of polymerization will predispose the denture base to dimensional instability and can lead to tissue irritation.
- The activator is present only in those products which are described as self-curing or autopolymerizing materials and not in heat curing denture

Heat-Activated Versus Chemical-Activated Denture Base

1. The residual monomer in chemical-activated denture base materials creates two difficulties.
   First, the residual monomer acts as a plasticizer, resulting in decreased transverse strength of the denture resin.
   Second, the residual monomer serves as a potential tissue irritant, thereby compromising the biocompatibility of the denture base.

2. From a physical standpoint, chemical-activated resins display slightly less shrinkage than their heat-activated counterparts. This imparts greater dimensional accuracy to chemical-activated resins.
3. The color stability of chemical-activated resins generally is inferior to the color stability of heat-activated resins. This property is related to the presence of tertiary amines within the chemical-activated resins. Such amines are susceptible to oxidation and accompanying color changes that affect the appearance of the resin. Discoloration of these resins can be minimized via the addition of stabilizing agents that prevent such oxidation.

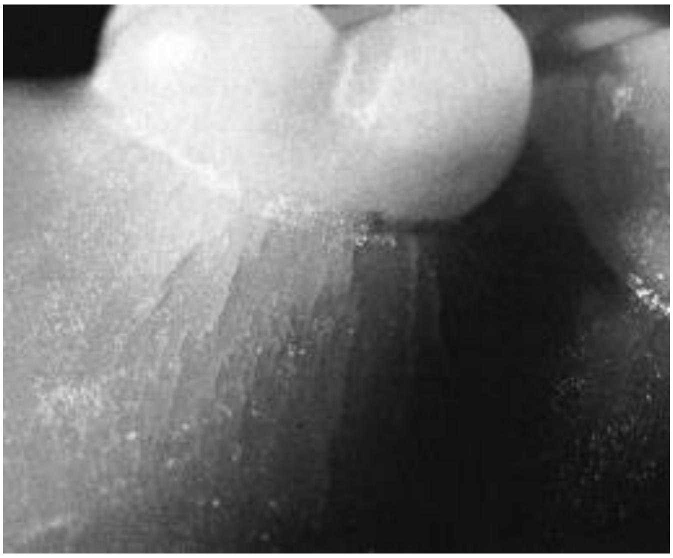
Physical Properties of Denture Base Resins:

1. Adequate colour matching.
2. The value of Tg may vary from one product to another depending on the average molecular weight and the level of residual monomer. Tg values for cold curing resins are generally lower than those for

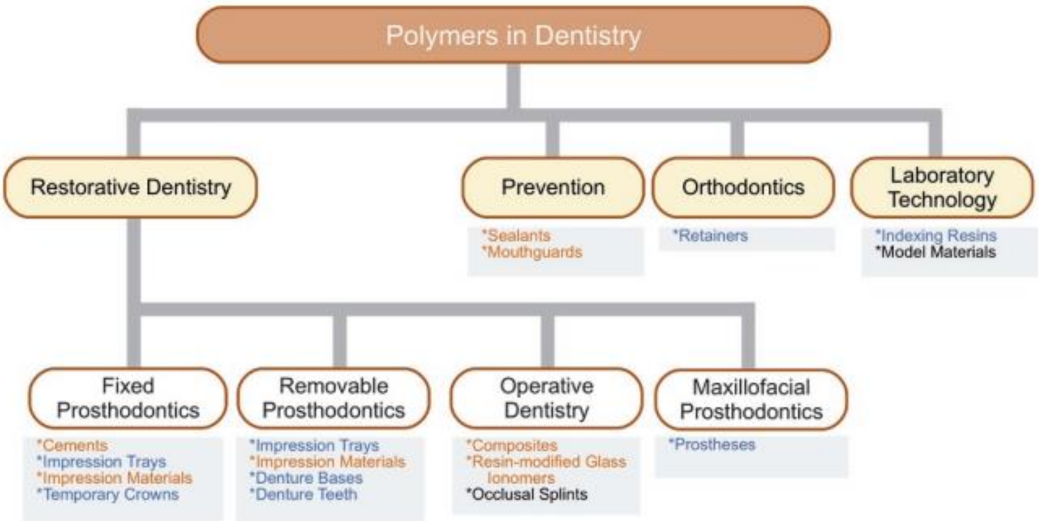
heat curing products. The light-activated materials tend to have higher values of Tg than conventional acrylic products.

3. Acrylic resins have relatively low values of specific gravity (approximately 1.2 g cm^{-3}) because they are composed of groups of ‘light’ atoms, for example, carbon, oxygen and hydrogen. The ‘lightness’ of the resulting denture is beneficial, since the gravitational forces causing displacement of an upper denture are minimized.
4. Dentures constructed from acrylic resin are radiolucent. This is a serious disadvantage of these materials. If a patient swallows or inhales a denture or fragment of a denture it is diffi cult to detect using simple radiological techniques.
5. Acrylic resin may be considered a good thermal insulator. This is a disadvantage for a denture base because the oral soft tissues are denied normal thermal stimuli which help to maintain the mucosa in a healthy condition. In addition, the patient may partially lose the protective reflex responses to hot and cold stimuli. This may result in some painful experiences when taking hot drinks.
6. The transverse strength of acrylic sufficient to resist fracture caused by the application of a high masticatory load.
7. Acrylic resin has a relatively poor resistance to fatigue fracture.
8. Acrylic resin also has a relatively poor impact strength and if a denture is dropped onto a hard surface there is a high probability of fracture occurring. Impact strength is essentially a measure of the toughness of the material as it measures the energy required to initiate and propagate a crack through a specimen of known dimensions.
9. Crazing may sometimes appear on the surface of an acrylic denture. This is a series of surface cracks which may have a weakening effect on the base. The cracks may arise by one of three mechanisms. *If the patient develops the habit of frequently removing his denture and allowing it to dry out, the constant cycle of water absorption followed by drying may develop sufficient tensile stresses at the surface to cause crazing. Thus, patients are instructed to keep their dentures moist at all times. *The use of porcelain teeth may cause crazing of the base in the region around the tooth neck due to differences in the coefficient of thermal expansion between porcelain and acrylic resin. *Thirdly, crazing may arise during denture repair when MMA monomer contacts the cured acrylic resin of the fragments being repaired. One function of the cross-linking agent is to reduce the degree of crazing by binding polymer chains together.

   Crazing in a transparent resin imparts a “hazy” or “foggy” appearance. In a tinted resin, crazing imparts a whitish appearance



10. Acrylic denture base is subjected to wear, caused by abrasive foodstuffs and particularly abrasive dentifrice cleansers.
11. Creep: Acrylic denture resins display viscoelastic behavior. When a denture base resin is subjected to a sustained load, the material may exhibit deformation with both elastic (recoverable) and plastic (irrecoverable) components. If this load is not removed, additional plastic deformation can occur over time. This additional deformation is termed creep.
    Creep rates for chemical-activated resins increase more rapidly when compared with heat activated resins as stresses are raised.
12. Porosity is noted in thicker portions of a denture base. Such porosity results from the vaporization of unreacted monomers when the temperature of a resin reaches or exceeds the boiling points of these species.
    Porosity also may result from inadequate mixing of powder and liquid components.
    A third type of porosity can be caused by inadequate pressure or insufficient material in the mold during polymerization. Voids resulting from these inadequacies are not spherical; they assume irregular shapes. These voids may be so abundant that the resultant resin appears significantly lighter and more opaque than the intended color.
    A final type of porosity most often associated with fluid resins is air entrapment during mixing and pouring procedures.



The role of polymers in dentistry continues to expand. Polymers are used for diverse applications including fixed, removable, and maxillofacial prosthodontics; orthodontics; preventive dentistry; operative dentistry; and laboratory technology.