# DENTAL MATERIAL

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# COMPOSITE RESINE (FILLED resins)

# Composition of composite resins

# A–Any composition should contain three main phases:

The organic matrix phase (dispersion medium)
The inorganic phase (dispersed phase)
The coupling agent

## B- In addition to these three main phrases there are:

**initiator activator systems, inhibitor, and pigments**

# I. Organic matrix (dispersion medium)

**1) Bowen began in the early1960s, experiments to reinforce epoxy resins with filler particles**

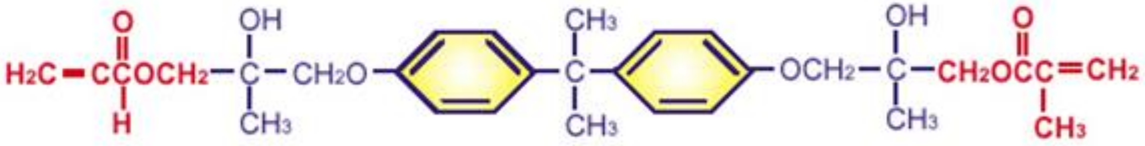
2) **Deficiencies in the epoxy resin system**, **such as a slow curing rate and a tendency to discolor**, **stimulated him to work on combining the advantage of epoxies and acrylates.**

**This work culminated in the development of bis-GMA molecule which results from reaction of bisphenol A & Glysidyl Methacrylate.**

# :BIS-GMA

BIS phenol A +Clycidl methacrylate = BIS-GMA

Bis-GMA

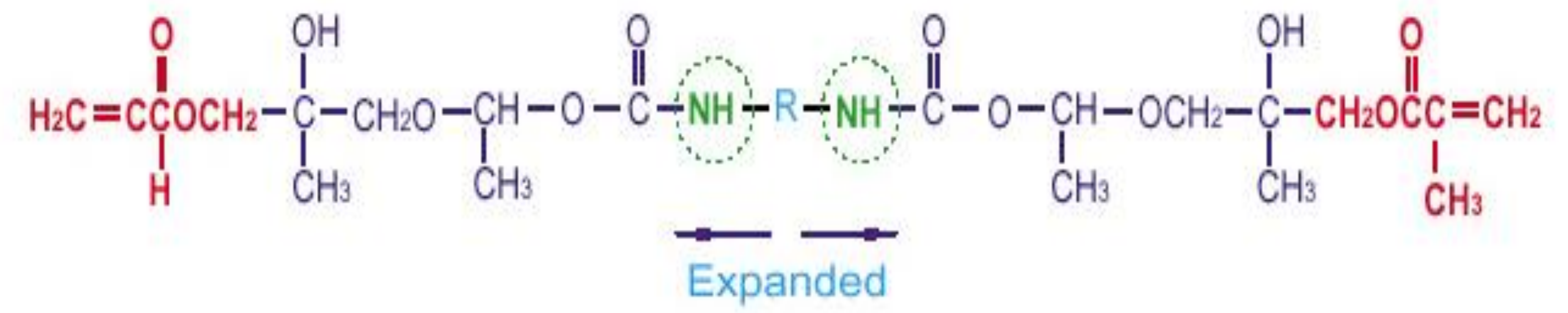


**It satisfied many of the requirements for the resin matrix of a dental composite. It is the organic matrix of a dental composite. It is the organic matrix of early composites**

**3) More recently, urethane dimethacrylate (UDMA) monomers are the organic matrix for current composites.**

## UDMA

## Urethane di Metha Crylate



$$H_2C{=}C\overset{O}{\underset{H}{C}}OCH_2{-}\overset{OH}{\underset{CH_3}{C}}{-}CH_2O{-}\underset{CH_3}{CH}{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{CH_3}{CH}{-}OCH_2{-}\overset{OH}{\underset{CH_3}{C}}{-}CH_2O\overset{O}{\overset{\|}{C}}\underset{CH_3}{C}{=}CH_2$$

**4) Recently silorane (reaction of siloxane + oxirane) is used instead of Bis–GMA or UDMA. It undergoes polymerization through ring opening, therefore it overcome polymerization shrinkage.**

# Functions of the organic phase

1) Surrounds, cements and protects the dispersed filler of the composite so as to retain their shape and strength.

**2) Distributes the load between matrix and filler.**

**3) Responsible for composite hardening through polymerization.**

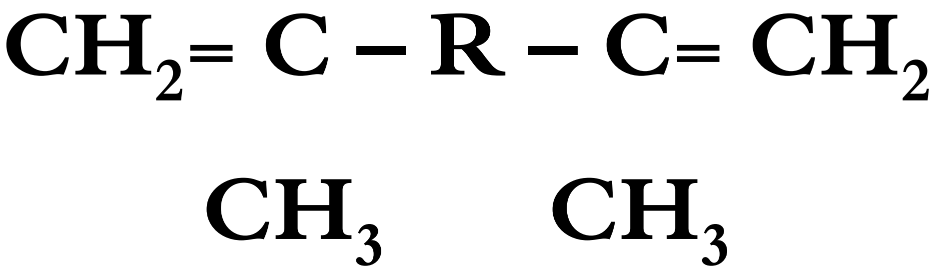
# Ingredients of the organic phase:

## A–High molecular weight monomer (oligomer):

1) This the principle constituent of the organic matrix.

2) They are either (BIS– GMA) that is called Bowen's resin Or (UDMA). Some products contains mixtures of the above.

3) These oligomers have the general chemical formula:



$$CH_2=\underset{\displaystyle CH_3}{C}-R-\underset{\displaystyle CH_3}{C}=CH_2$$

**They have two unsaturated bonds, hence can undergo free radical addition polymerization to give a rigid cross–linked polymer.**

**Oligomer viscosity is high and of viscosity will further increase after incorporation of inorganic filler.**

**In order to reduce their viscosity to a useful clinical level, diluents are added.**

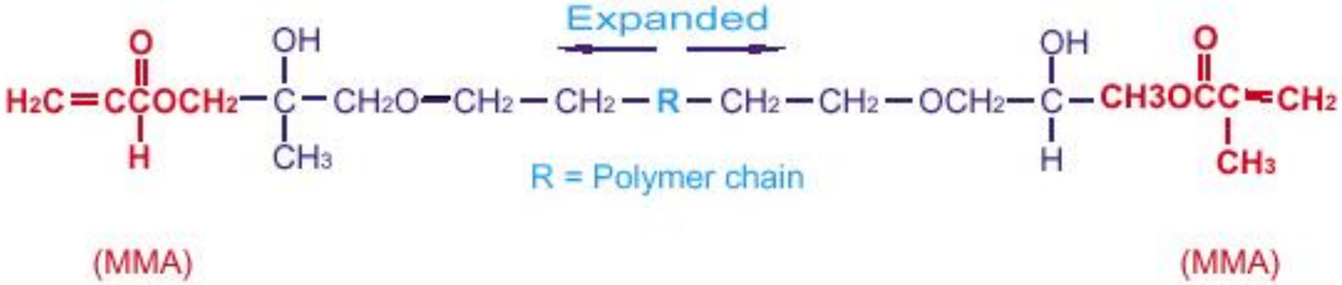
## B. Diluents (low molecular weight monomers):

1) They form about 25% of the matrix.

2) They reduced the viscosity of the matrix to enable incorporation of the inorganic filler without undue thickening.

3) Monomers used are either diethylene glycol dimethacrylate (DEGAMA) or treithylene glycol dimethacrylate (TEGAMA).

# TEGDMA



$$H_2C{=}\underset{H}{C}\overset{O}{\overset{\|}{C}}OCH_2-\overset{OH}{\underset{CH_3}{C}}-CH_2O-CH_2-CH_2-R-CH_2-CH_2-OCH_2-\overset{OH}{\underset{H}{C}}-CH3O\overset{O}{\overset{\|}{C}}\underset{CH_3}{C}{=}CH_2$$

**4) Drawbacks of adding diluents:↑ polymerization shrinkage + water sorpation.**

# II. The inorganic phase (dispersed phase or filler)

## A. Materials used as filler

**1) Qurartz: was used with traditional composite and was extremely hard resulting in polishing difficulty.**

**2) Glasses containing heavy metal Ba, Zr and Sr: used with current composites (their refractive indices are similar to tooth structure and provide radio-opacity).**

## B– Production of filler particles of composites:

they are produced:

either mechanically by grinding quartz to obtain particles of size 0.1–100 um

or chemically by pyrolytic process to obtain colloidal silica particles of size 0.04 um.

## C- Role of filler in composite properties

1) Improvement of the mechanical properties, optical properties, and radio-opacity of composite.

2) Reduction of the coefficient of thermal expansion of the resin matrix to become nearer to that of tooth structure.

3) **Reduction of water sorption**.

4) **Minimizing polymerization shrinkage**.

# Classification of dental composite

## Methods of classifying dental composite are

**A. According to the particles size of the inorganic filler into:**

| Size | Type |
|---|---|
| > µm 100 | Megafill |
| 10 to <100µm | Macrofill |
| 1 to <10 µm | Midifill |
| 0.1 to < 1µm | Minifill |
| 0.01 to <0.1 µm | Microfill |
| 0.005 to <0.0 1µm | Nanofill |
| Mixed ranges | Hybird |

## B. According to curing method:

1) **Chemically activated composite resin.**

2) **Photo–activated composite resin.**

## C. According to handling characteristics (viscosity):

1) **Flowable composite.**

2) **Packable composites.**

## D. According to clinical performance:

1) **Anterior composite.**
2) **2) Posterior composite.**

# Megafill composite

- For a posterior composite restorations
- it is possible to place one or two large glass inserts (0.5 –2 mm particles) into composites at points of glass are referred of occlusal contact or high wear.
- These pieces of glass are referred to as inserts.

# Macrofill composite

1. Its filler are prepared mechanically and size 10–100um.

2. They have perfect mechanical properties due to the higher content of the inorganic filler.

**3. They have terrible surface properties making difficulty in their finishing and polishing. The matrix is easily abraded, but the fillers are harder, therefore they will protrude out**

# Microfill composite (polishable)

1) Fillers are prepared chemically. Fillers size (0.01 to 0.1 um); thus are 200–300 times smaller than the average particle in macrofilled composites.

**2) This permits microfilled composites to be finished to a much smoother surface than macrofilled composites, hence called polishable composites.**

# Nanofill

New ultra small fillers (e.g. nanosilicate) from 0.005 to 0.01 µm in diameter in diameter which is below the wavelength range for visible light (0.02–2µm).

## Properties:

1) They are more translucent because their particles do not interact with visible light, they dint produce scattering or significant absorption.

2) Nanosilicate fillers do not tend to agglomerate in chains like typical silica–based fillers. Therefore, they remain so small that fit between several polymer chains.

These high filler loading levels in composites while still maintaining workable consistencies.

# Hybird (blended) composites

a) After it was realized that highly filled microfills were difficult to use, composites were formulated with mixtures of particles) The largest particle range is used to define the hybrid type (e.g., minifill hybrid) because microfillers are normally the second part of the mixture.

**B)**

**microfiller range and 2–5 µm range. These bimodal distribution allowed higher filler levels and still permitted good finishing. All types of mixtures are known collectively as hybrid composites.**

**c) Currently, the principle particle size for newer hybirds in the range of 0.1–1μm. this composite is called as mini–hybird.**

**d) Due to their surface smoothness and reasonably good strength, these composites are widely used for anterior restorations.**

# III. Coupling agent

## Functions of the coupling agent

1) It provides a chemical bond of the filler particles to the resin matrix. This allows the more flexible polymer matrix to transfer stresses to the stiffer particles, thus liming crack propagation.

**2) A properly applied coupling agent can impart improved physical and mechanical properties and provide hydrolytic stability by preventing water from penetrating along the filler–resin interface.**

## Materials used as coupling agents:

1) Titanates and zirconates can be used as coupling agents.

2) Triethoxy vinyle silane (now has been replaced by the more reactive organosilance).

# Mechanism of action of the coupling agent ：

**Each hydrolyzed silane coupling agent has two functional groups**：

1) **The inorganic group (silanol group) can bond with silanol on the filler surface by formation of a siloxane bond (Si–O–Si).**

**2) The organic group (methactylate group) forms covalent bonds with the resin when it is polymerized, thus completing the coupling process.**

# IV. Activator–initiator systems

They are responsible for hardening of the organic matrix of composite.

**Composite resin polymerizes by the addition polymerization mechanism initiated by free radicals.**

**Free radicals can be generated by:– Chemical activation or external energy activation (heat or light).**

## Chemical activation

1) **The initiator is benzoil perxido.**

2) **The activators are:**

**a. tertiary amine (dihydroxyethyl–*p*– toluidine is now widely used than dimethyl–*p*– toluidine because of its better color stability).**

**b. sulphinic acid.**

**3) Chemically activated composite are two paste systems, therefore, one paste contains the initiator and the other past contains the activator.**

They are mixed just before insertion into the cavity, where the activator leads to splitting of the initiator to produce the free radicals. The free radical, in turn, attacks the unsaturated carbon carbon double bonds, leading to polymerization.

# Light activation (light–curing)

## Types of light activation

### A– Ultra violet activation:

The first LA systems used UV light to initiate free radicals. Today, UV light composites have been replaced visible light– activating systems because of:

–limited depth of polymerization

– potential harmful effects on skin cancer and eye.

## B– Visible light activation composites

1) Much more widely used than are chemically activated materials.

2) They are supplies as a single paste contained in a light protected syringe.

**The free radical initiating system, consisting of the photo–initiator molecule and an amine activator, is contained in this paste**

3) **When these two component are left unexposed to light, they do not interact.**

**Exposure to light of the correct wave length (470nm) produces an excited state of the photo-initiator and an interaction with the amine to form free radicals that initiate addition polymerization.**

**4) A commonly used photo initiator is a–diketone such as camphoroquinone, which has an absorption range between 400 and 500 nm that is in the blue region of the visible light spectrum.**

5) There are a number of amine accelerators that are suitable for interaction with camphoroquinone.

Camphoroquinone most common photoinitiator absorbs blue 400– 500 nm range. It reacts initiating addition polymerization.

## C) Argon laser curing:

emits a blue light at about 480 nm. Absorbed by camphoroquinone to initiate polymerization

## Advantages of it are:

1. Radiation is absorbed in a narrow wavelength distribution which increases efficiency.
2. Can emit a collimated beam so it can travel long distances without dispersion.

3. **Heat production is minimized.**

4. **Shrinkage takes place all over restoration, so no leakage.**

# Disadvantages:

1. More expensive.
2. Rapid curing prevent stress relaxation.

Solved by using pulsed not continuous laser

## D) Light emitting diode:

**produce blue light over a narrow wavelength band.**

## Advantages:

1. Uses a low current so portable re–chargeable designs is possible.
2. No heat production.
3. Consistent output.
4. Quiet, there are no cooling fans.

**Disadvantage** for laser LED is that some initiators in composite maybe insensitive to them to their specific wavelength output.

## Precautions for light curing

1. Inadequate light output: monthly check on light source, to examine output (using radiometers), any scratches on light probes or darkening due to disinfection.
2. Premature set of composite.
3. Eye protection
4. Heat generation

**The difference between the three types of activation namely:**

**cold cue, laser cure, and light cure is in the direction of shrinkage..**

.In cold cure the shrinkage is toward the center of the restoration and away from cavity walls. This leads to either leakage if restoration is not sensitivity if there strong bond.

In light cure shrinkage takes place toward light source.

In laser the shrinkage takes place in different direction, leading to no bad effects such as the other types of curing.

## Advantages of light cured composites over chemical cure:

1) Command cure (complete control of working time).

2) Supplied as single component pastes that need no mixing, therefore less void incorporation and no internal porosity within the mix.

3) Contoured before curing, thus need less finishing and polishing.

4) More color stability and more wear resistance.

# Factors affecting depth of cure:

1) **Composite shade**:

darker shade → shallower light penetration.

## 2) **The distance between light source and restoration**:

Light intensity is inversely proportional to the square of the distance, i.e the closer the closer the curing tip the deeper the light will penetrate

**3**) **Exposure time**:

Longer time exposure → deeper light penetration

**4) The initiator system absorption characteristics:**

The development of light sources of improved intensity dictate that each increment of filling 1.5-2 mm thick should be cured, in 20 sec, individually before putting successive layer.

## Polymerization inhibitors:

They minimize or prevent spontaneous polymerization, of composite monomers, during storage.

## Mode of action:

1) These inhibitors have a storage reactivity potential with free radicals.
2) Therefore, if a free radical has been formed, such as by brief exposure to light when the material was dispensed, the inhibitor reacts with the free material was dispensed, the inhibitor reacts with the free radical and inhibits chain propagation by terminating the ability of the free radical to initiate the polymerization process

2) **When all the inhibitors are consumed**, **chain propagation occurs**.

**Materials used as inhibitors**:

1) Hydroquinone had been widely used, but discontinued because it caused discoloration of the restoration.

2) Currently, the monomethyl ether of hydroquinone is used.

## Pigments:

**Metal oxides added to composite to provide shading and opacity, Examples are Ti oxides**

# Properties of composite resins

# A. Physical properties:

## Polymerization shrinkage

1) Shrinkage is due to change of their monomers (oligomers) into polymers.
2) It depends upon resin type and amount in the unpolymerized form

## **Effects of polymerization shrinkage**:

It creates shrinkage stresses, depending upon C-factor [configuration factor] between restoration and tooth cavity walls, leading to:

1) Gap formation; As polymerization stresses exceed composite bond strength to cavity walls, gap is formed marginal leaking of saliva.

2) Pulpal sensitivity following placement of composite: if bond strength of the composite exceeds the polymerization stresses, the shrinkage will cause tooth cusps to be pulled inwards.

## Minimizing polymerization shrinkage and its effects:–

1) Incremental addition of light cure material and polymerization of each increment independently. This method eliminates gap formation, but does not reduce polymerization stresses. Each increment should touch minimal cavity walls.

2) Achieving strong bond of the composite to the cavity wall.

3) Indirect composite restorations (inlays).

4) Soft start polymerization.

# Water sorption

It is mainly by the organic matrix. It depends upon the amount of resin matrix and the quality of the resin-filler bond.

**Consequences of water sorption by the composites**:

Excessive water sorption has a detrimental effect on:

1. The color: The absorbed water and other fluids form the oral cavity results in the discoloration.
2. The wear resistance: The absorbed water leads to hydrolytic breakdown of filler-matrix bond resulting in a high wear rate.

## Thermal properties

### A. Coefficient of thermal expansion :

1) **a** of composite needs to be as close as possible to that of tooth tissue to minimize the possibility of thermal stresses development.

2) The glass filler have a low **a**, while the resin has high **a**. therefore the higher inorganic filler loading of the composite, the lower the **a** and the closer to that of tooth tissues will be.

**B**. **Thermal conductivity**: Composite have much lower thermal conductivity than metallic restorations

## Radio– opacity

1) Posterior composite should at least be as radio-opaque as enamel to help in detection of secondary caries.

2) For a composite to be radio-opaque, it must contain an element with a high atomic number, such as Bs, Zr, Zn< or Sr because the atomic number of C,H,O or Si is not high to attenuate x-rays

## Color match:

**A. Earliest composites suffered discoloration in one of three forms:**

1) **Marginal discoloration**: due to presence of a marginal gap. Acid-etch technique of bonding to enamel will overcome this problem.

2) **General surface roughness**: due large filler particles that are difficult to polish.

3) **Bulk or deep discoloration**: Occurs with chemically-cured composites .

**B. The new, composites with fine or microfilled particle composite have much color stability.**

# B. Mechanical properties

## Compressive and tensile strength

Composites with higher filer loading have higher compressive and tensile strengths than those with lower filler loading, e.g. that of fine particle composites > the microfiller composites.

Generally composites are brittle materials, i.e. they fail tension rather than in compression

# Elastic modulus

1) The stiffness depends upon the amount of filler, i.e the lower the filler content of the resin, the lower its stiffness.
2) Stiffness is important in application where high biting forces are involved and wear resistance is essential

## Hardness and penetration resistance

Hardness of composites depends greatly upon filler content and to a less extent upon the hardness of the filler, i.e. the higher the filler content, the higher resistance to non-recoverable penetration (knop hardness test).

## Wear

It is the process by which material is displaced or removed by the interfacial forces which are generated as two surfaces rub together.

**Types of composites wear are**:

* **Abrasive wear** (**attrition**): When two or three surfaces rub together rub, the harder of the two materials will indent other surface(s).

* **Corrosive wear**: Chemical attack on the resin or the resin- filler interface,

* **Fatigue wear**: The repeated loading of teeth produces cyclic stresses that can in time lead to the growth of fatigue cracks. These cracks often form below the surface.

# Biocompatibility of composition

**Philosophy:**

1. **Dental materials do not naturally belong in the mouth!**
2. **All synthetic materials evoke a host response.**
3. **Synthetic material not as good as health tooth substance.**
4. **Best treatment is the least treatment.**
5. **Best treatment is the most durable treatment.**

## Composite resin mareials can affect the pulp tissues adversely by:

**1**) **Chemical irritation**: Residual oligomers diffuse from improperly cured composite and reach the pulp causing its irritation. Properly cured composites are relatively biocompatible.

2) **Bacterial and/or bacterial toxins irritation**:

Shrinkage of the composite during polysequences merization and the subsequent marginal leakage might cause bacterial or toxin ingress, with subsequent caries recurrence pulp reaction or both.

## Composites for posterior restorations

With the increasing demand for aesthetic dentistry and the concern about the potential toxicity mercury, there has been an increased interest in the use of composites for Class I and II restoration.

## Shortcomings of posterior composites as compared with amalgam:

1) **Technique sensitivity**: the highly plastic monomeric pastes dictate that the matrix band be carefully contoured and wedged to obtain an acceptable proximal content.

**2) Gingival margins gap formation: if cavity margin is located in dentin and resin is firmly anchored to the etched enamel at the margins, the material tend to shrink away from the gingival margins during polymerization forming gap and subsequent leakage**

## 3) Low occlusal wear resistance.

## Methods of overcoming posterior composites shortcoming

1) The use of minimal shrinkage silorane composite

**2**) **Conservative cavity preparation**: Since large restorations tend to wear more than do smaller ones, as do restorations that are subjected is preferred so that the tooth rather than the composite absorbs more of the stress. For the same reason, composite is contraindicated for a patient with bruxism.

**3**) **Minimizing polymerization shrinkage by**:

a) Using **composite inlay** system that re polymerized outside of the mouth.

b) **The use of Argon laser curing**.

c) **The use of soft polymwriazation**.

**D**)**The use of ceramic inserts**

# 4) The use of *packable* (condensable) composites.

# Rheology of Resin Composites

1) **Thixotropy is a reversible structural breakdown of material that occurs when the material is stressed. This means that when the material is being syringed, the high stress from syringing breaks down some of the structure (e.g. hydrogen bonding), so the material flows.**

2) But when the material is placed into the cavity, it will not flow ('non-drip') because the hydrogen bonding structure quickly recovers.

3) **Flowable composites** were designed to be **thixotropic**.

**Self healing composite**

The end