

Dental materials

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Dental Materials

Restorative

- metals and metal alloys
- ceramics
- cements
- plastics

Auxiliary

- impression materials
- model materials
- casting investments
- acrylic resins
- dental waxes
- finishing and polishing
abrasives

Metals, alloys and amalgams in dentistry

Metals are only exceptionally used in pure form. Most often alloys are used that have better properties.

Using

Crowns, bridges, partial dentures, implants.....

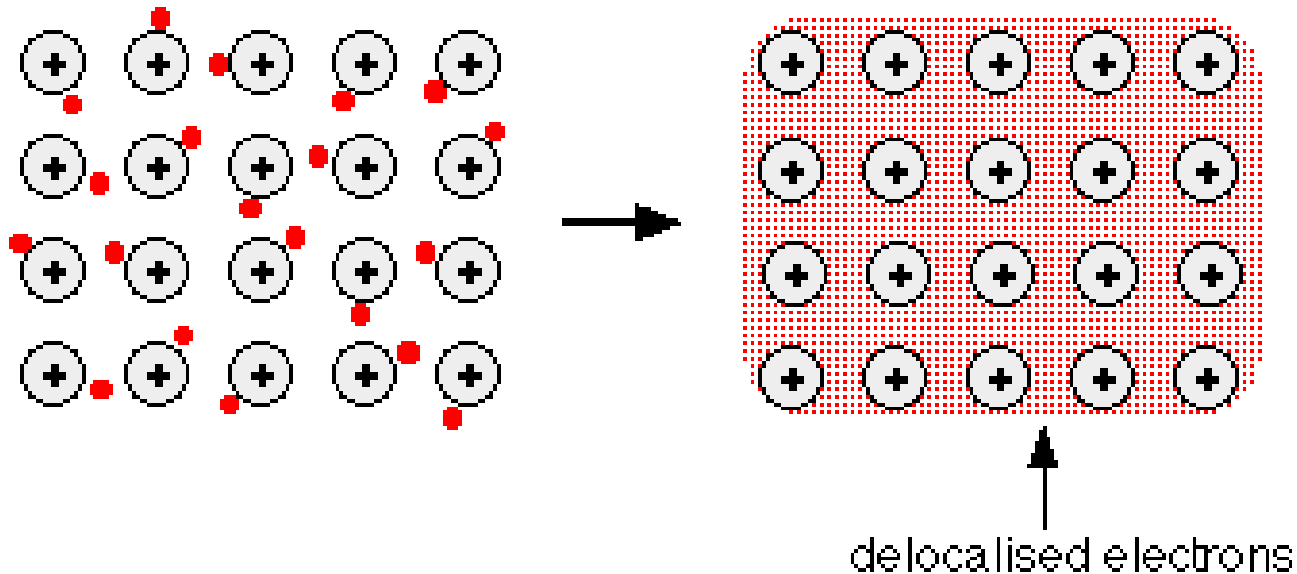
Requirements

Chemical stability, malleability

Metals

Metallic bond

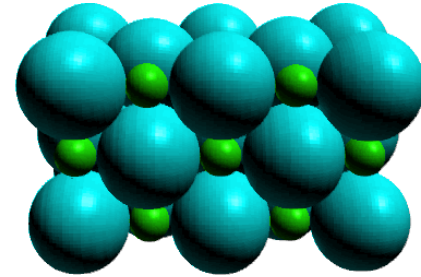
- Metal atoms have large numbers of electrons in their valence shell. These become delocalized and form a "sea" of electrons surrounding a giant lattice of positive ions.



Metallic bond

- Metallic bonds are something like covalent bonds except that large numbers of electrons are shared by massive numbers of atoms.
- This trading back and fourth of electrons is what holds metallic crystals together
- Each metal forms a specific type of crystalline structure based upon the internal atomic properties for that metal.
- Electrons acts as conductors for both thermal energy and electricity

Metals



Typical properties

luster

opacity

toughness (an ability to absorb energy and
inhibit crack propagation)

compactness

stiffness

thermal and electric conductivity

ductility

Corrosion and tarnish of metals

Tarnish

- surface discoloration on a metal
- slight loss or alteration of the surface or luster

Often occurs from the formation of hard or soft deposits (calculus, plaques, films)

Corrosion –deterioration of metal due to chemical reaction with environment

Caused by action of moisture, atmosphere, acid or alkaline solutions, certain chemicals, tarnish

Types of metal corrosion

- Chemical corrosion

Processes of oxidation, halogenation, sulfurization etc.

Less common in dental materials

- Electrochemical corrosion

Metals behave as electrodes of galvanic cell in the presence of saliva.

Electrochemical corrosion of metals

- The corrosion is the dissolution of metals in the mouth
- The corrosion tendencies of metals are related with their position in the electromotive series (standard potentials).
- Depends on the composition of saliva
- Some metals have tendency to be easily oxidized and their ions go into solution (anode)
- The other metals have little tendency to go into the solution, but ions of the electrolyte try to accumulate on the surface of the metal (cathode)
- Cathodic and anodic reactions can take place simultaneously on the surface of the metal

Standard reduction potentials of selected metals

A_{OX}/A_{RED}	E° (V)
Li ⁺ /Li	-3,00
K ⁺ /K	-2,92
Ca ²⁺ /Ca	-2,87
Na ⁺ /Na	-2,71
Mg ²⁺ /Mg	-2,37
Al ³⁺ /Al	-1,66
Zn ²⁺ /Zn	-0,76
Fe ²⁺ /Fe	-0,44
Sn ²⁺ /Sn	-0,14
Pb ²⁺ /Pb	-0,13
2H⁺/H₂	0,00
Sn ⁴⁺ /Sn ²⁺	0,15
Cu ²⁺ /Cu	0,34
Ag ⁺ /Ag	0,80
Hg ²⁺ /Hg	0,85
Pd²⁺/Pd	0,99
Pt³⁺/Pt	1,2
Au³⁺/Au	1,5

Metals placed in an electrolyte have various tendency to go into solution.

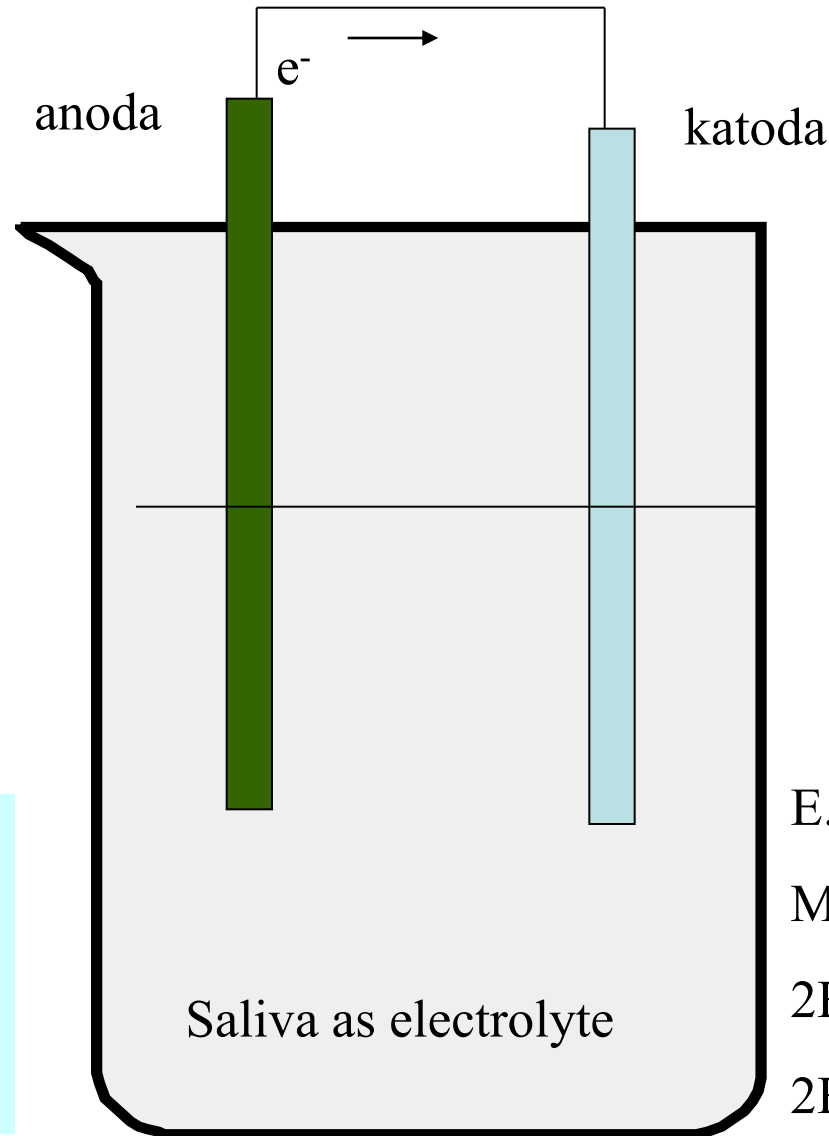
E.g.aluminium alloy has a strong tendency to go into solution.

Gold has little tendency to go into solution

Noble metals

Resistant against corrosion

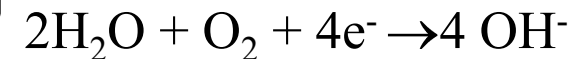
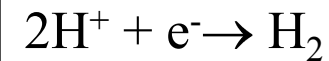
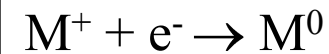
Elektrochemical corrosion



Ions of a metal are released into the solution, the electrode become positively charged (=anode)

Gold alloy
Reduction reaction.

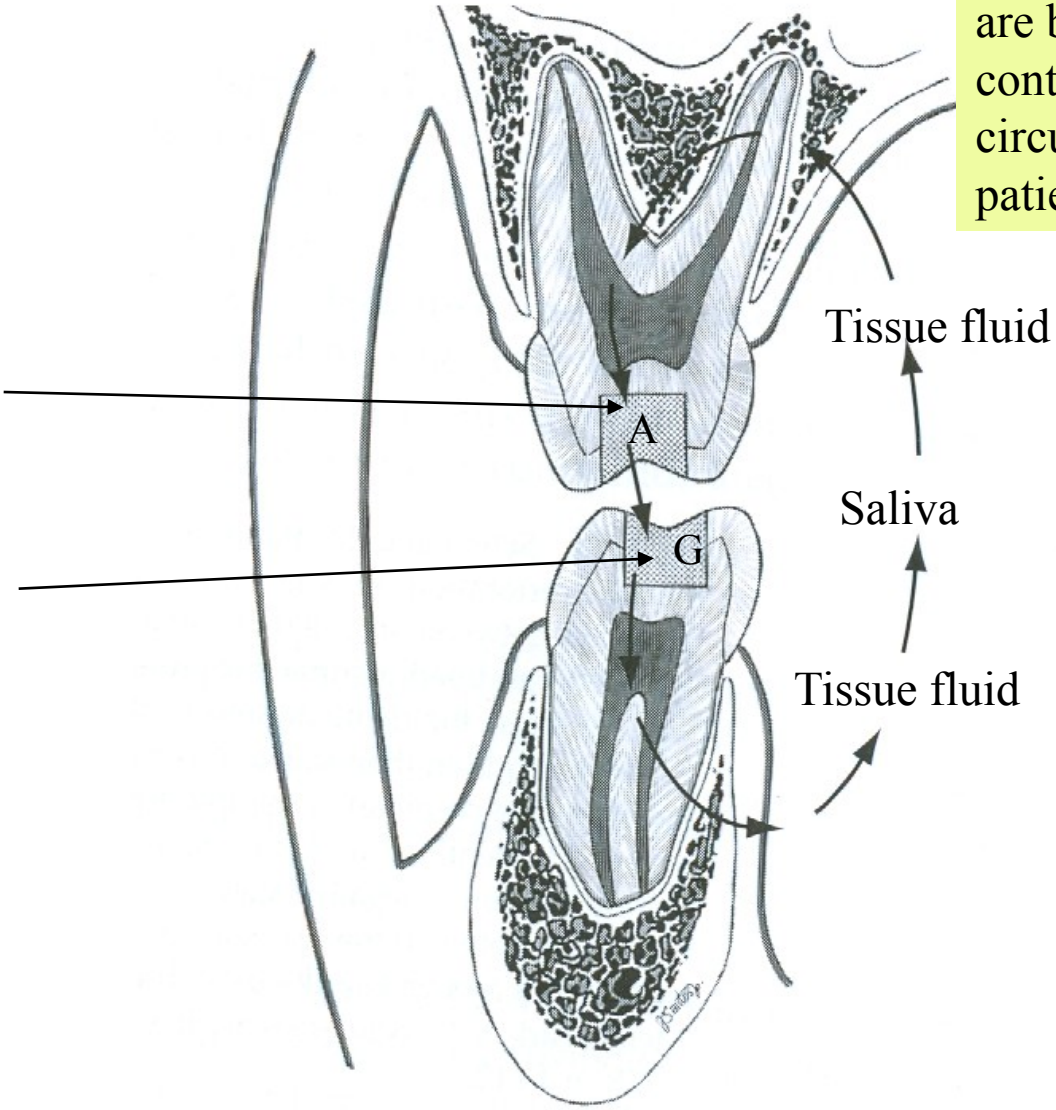
E.g.:



Galvanic shock

When the two restorations are brought into direct contact, sudden short-circuit occurs and the patient experiences pain

Two different restorations
e.g. gold and amalgam

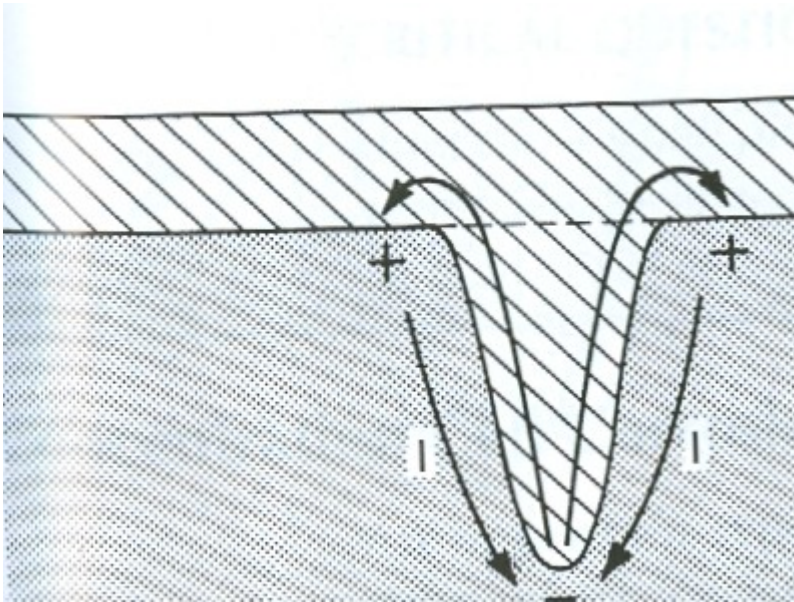


Possible path of galvanic current in the mouth

The same effect can be experienced if a piece of aluminium foil becomes wedged between two teeth and contacts gold restoration

Concentration cell corrosion

A pit on a dental alloy as corrosion cell



The region of a pit is an anode, and surface around the rim of the pit is cathode

The ionic current flows through the electrolyte and the electronic current flows through the metal

It is a consequence of accumulation of food debris in the pit. The debris produces an electrolyte in that area that is different from the electrolyte that is produced by normal saliva.

Noble (precious) metals

Periodic Table of Elements

1	Au Gold (Aurum) 79 Mass: 196.966569 Oxidation states: +1,+3 Electron configuration: -32-18-1																18	
H	2											13	14	15	16	17	He	
Li	Be											B	C	N	O	F	Ne	
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg								
		*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	D
		**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	T

Characters : cubic cryst., yellow ductile metal
 Discoverer : known since ancient times
 Name Origin : from 'geolo' (Anglo-Saxon)
 Atomic Radius, A : 1.74 Ionization Potential, kJ/mol : 890 Density, g/cm³ : 19.3
 Electronegativity : 2.54 Electron Affinity, kJ/mol : 222.8 Melting Point, K : 1338
 Boiling Point, K : 3080

General NMR Mass Coloration

Noble (precious) metals

- corrosion resistance
- tarnish resistance
- expensive

Au aurum

Pt platinum

Pd palladium

Os osmium

Ir iridium

Ru ruthenium

Most common noble metals in dental casting alloys – Au, Pt

Characteristic properties of noble metals

Element	Atomic number	Density (g/cm ³)	Melting point(K)	Boiling point (K)
Ru	44	12,2	2583	4173
Pd	46	12	1825	3413
Ir	77	22,5	2683	4403
Pt	78	21,4	2045	4100
Au	79	19,3	1338	3080

Gold (Au)

- Tarnish and corrosion resistance
- Highest ductility and malleability of all metals (29g/100 km)
- Relatively soft
- Can be used for direct filling in pure state
- Pieces of gold are placed in the prepared cavity
- Welding by pressure at the mouth temperature (compaction)
- In alloys with Cu, Ag, Pt, Pd, Ni, Zn

Platinum (Pt)

- Chemical and thermal resistance
- Using in fixed protetics.
- Pt in alloys with gold has whitening effect.

Paladium (Pd)

- Using only in alloys, increases the corrosion resistance
- Contributes to strength. Whitening effect.
- Similar to Pt, more effective and less expensive therefore has replaced Pt in most alloys

Iridium (Ir)

- Is combined with Pt for preparation of tough and hard alloys

Base metals

- used in alloys,
increase strength, elasticity
- lower cost

Ti titanium

Ni nickel

Cu copper

Ag silver

Zn zinc

Characteristic properties of base metals

Element	Atomic number	Density (g/cm ³)	Melting point(K)	Boiling point (K)
Ti	22	4,51	1993	3560
Ni	28	8,9	1726	3008
Cu	29	8,96	1357	2840
Ag	47	10,5	1235	2485
Zn	30	7,14	693	1180

Titanium (Ti)

- Mechanic properties are close to bone. Nearly completely biocompatible, corrosion resistant. Suitable for dental implants.
- Can be used in pure state.

Copper (Cu)

- increase the strength
- in pure state used for impression materials
- principle hardener in gold alloys.
- imparts reddish color

Silver (Ag)

- Using mostly in alloys
- Increases ductility and hardness of alloys
- Antimicrobial effect
- Controls color (neutralizes the red color imparted by Cu).
- Promotes ductility

- the best heat and electricity conductor
- formation of AgS with sulfur from food
- soluble in HNO₃, conc. H₂SO₄, HCl

Mercury

Element	Atomic number	Density (g/cm ³)	Melting point(K)	Boiling point (K)
Hg	80	13,6	234,3	630
			-39°C	357°C

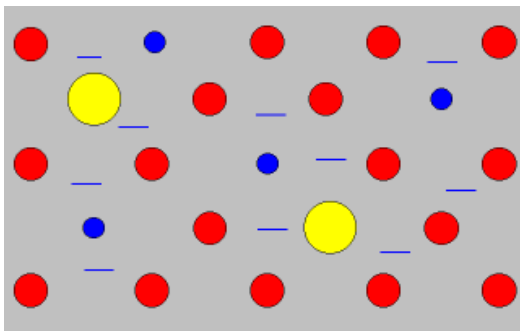
- Dense metal that is liquid at room temperature
- II.B group = Hg⁺, Hg²⁺
- High vapour pressure
- Monoatomic in vapour

Alloys

- formed, when two or more molten metals are mixed together and allowed to cool to a solid crystalline state

Physical properties

- Characteristic properties of metals – metallic luster, thermal and electric conductivity, given arrangement in crystalline lattice
- Properties depend on the nature of its internal microscopic crystalline structure
- affected by factors such as the speed of the cooling



Alloys

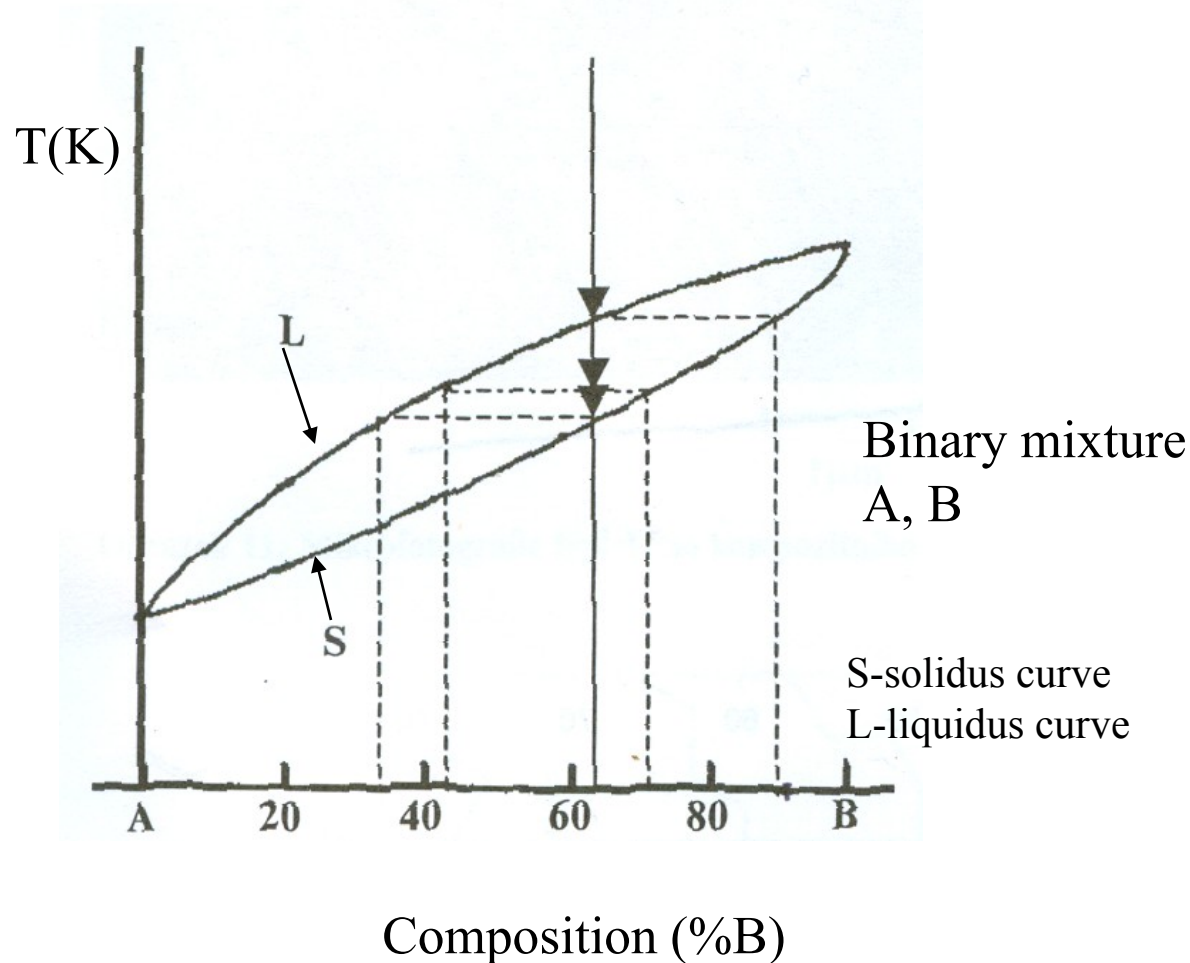
Binary alloy – an alloy containing two chemical components

Tertiary, quaternary.....

Phase diagram – a graphs of the phase field

they express dependence of phase state and composition on the temperature during cooling

Phase diagram = solidus line (solid phase is below) and liquidus line (above is only melt), follows the equilibrium composition of melt and co-existing solid phase at various temperatures during cooling



Dental alloys

- Hardness, toughness x plasticity
- Corrosion and abrasivity resistance
- Color
- Biological compatibility x toxicity

Gold alloys

Two types:

- high noble alloys (the content of of gold and platinum metals min.75%)
- noble alloys (25-75% of gold and noble metals)

Other metals contained in gold alloys: Cu, Ag, Pt, Pd, Ni, Zn.

Most often (Au,Cu), (Au,Cu,Pt,Zn) (Au,Pd,Cu)

Cu increases hardness but decreases the corrosion resistance

Very expensive

The amount of gold in an alloy is expressed in carats

Pure gold is defined as 24 carat (24K). An alloy with 50% gold is 12K, an alloy with 75% gold is 18K

Examples of gold alloys

Examples of alloys containing minimally 75% of gold and platinum metals

	Au a kovy Pt skupiny (hmotn. %)	Au (hmotn. %)	Pt (hmotn. %)	Pd (hmotn. %)	Ag (hmotn. %)	Cu (hmotn. %)
1 (Pt)	95 - 97	80 - 85	5 - 11	3,4 - 4,4	3 - 5	0
2 (Pt)	95	70	7,5	15	5	0
3 (Pt)	98 - 99	82,6 - 86,0	9,7 - 10,4	0 - 2,2	0	0
4 (Pt)	82,9 - 97,4	73,8 - 84,4	8,0 - 9,0	5,0 - 8,9	1,2 - 9,2	0
1	88,6	87,5	0,3 - 14	1,0	11,5	0
2	80,5 - 81,2	75,7 - 79,3	0 - 2,4	1,6 - 3,3	12,3 - 20,5	4,1 - 6,5
3	78,0 - 78,5	74,0 - 74,4	4,4 - 12,9	2,0 - 3,5	9,0 - 13,5	7,0 - 11,5
4	75,5 - 80,0	65,5 - 71,0	5,0 - 11,0	0 - 2,0	10,0 - 14,0	8,2 - 10,0

Examples of alloys containing 25-75% of gold and platinum metals

Komponenta	Au (hmotn. %)	Ag (hmotn. %)	Pd (hmotn. %)	Pt (hmotn. %)	Cu (hmotn. %)	Zn (hmotn. %)
Aurix L	65,1	20,0	3,0	1,3	9,6	1,0
Aurosa	20,0	44,8	20,0	-	14,4	-
Palargen L	-	57,4	40,0	-	-	2,1
Argenpal IVA	5,0	59,9	22,5	-	10,0	2,0

Predominantly base metal alloys (> 75% base metals)

a) Co based alloys

Examples of composition:

- Co, Cr, Mo, Si, Mn
- Co, Cr, Mo, W, Si (addition of Cr and Mo increases hardness)
- Co, Cr, Mo, Ti

b) Ni based alloys

Examples of composition:

- Ni, Cr, Mo, Si (Cr – min. 20%, Mo – min. 4%)

Total content of Ni + Cr + Mo – min 85%

Biocompatibility of alloys

It is related to ability of their corrosion

If alloys corrodes more, it releases more of its elements into the mouth and increases the risk for unwanted reactions in the oral tissues (unpleasant tastes, irritation, allergy...)

Alloys are tested – e.g. in a solution of lactic acid for 7 days – the changes on the alloy surface and in the solution are analyzed.

Amalgam

still the most commonly used filling material

Amalgam fillings

Alloys containing mercury

mixture of mercury (from 43% to 54%) and powdered alloy made mostly of silver, tin, zinc and copper (amalgam alloy).

History

1826 – Auguste Taveau developed his own dental amalgam from silver coins and mercury



This amalgam contained a very small amount of mercury and had to be heated in order for the silver to dissolve at an appreciable rate.

When the French Crawcour brothers emigrated to the United States in 1833, they introduced Taveau's amalgam. Because of the amalgam's poor quality, many dentists refused to use it. Numerous experiments were carried out from the 1860s through the 1890s to develop improved amalgam filling materials. Chicago, Illinois, dentist G. V. Black (1836-1915) finally standardized both cavity preparation and amalgam manufacture in 1895.

Modern dental amalgams

approximately equal parts

50% of liquid mercury + 50% of an alloy powder

Typical components of dental amalgam alloy: Ag, Sn, Cu

Low copper alloys: Cu max. 6%

High copper alloys: Cu > 6%

Alloy powder composition:

- > 40% silver (Ag)
- < 32% tin (Sn)
- < 30% copper (Cu)
- < 2% zinc (Zn)
- < 3% mercury (Hg)

Reaction of silver alloy with mercury

Amalgamation

Setting reaction of amalgam alloy with mercury

- When high-copper alloy particles contact the mercury, they begin to dissolve in the mercury
- However, once some of the alloy particles has dissolved, new solid products begin to crystallize as the chemical reaction occurs
- As the crystallization of new products continues, the amalgam becomes stiffer and eventually hardens completely

Hardening of the amalgam

The hardening of the amalgam occurs before all the original alloy particles can dissolve

The set amalgam contains much of the original silver alloy particles surrounded by the new products

The amalgamation reaction:

Silver alloy (γ) + mercury \rightarrow silver alloy (γ , unreacted) + silver-mercury (γ_1) + copper-tin(η)

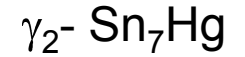
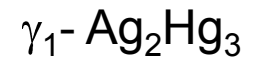
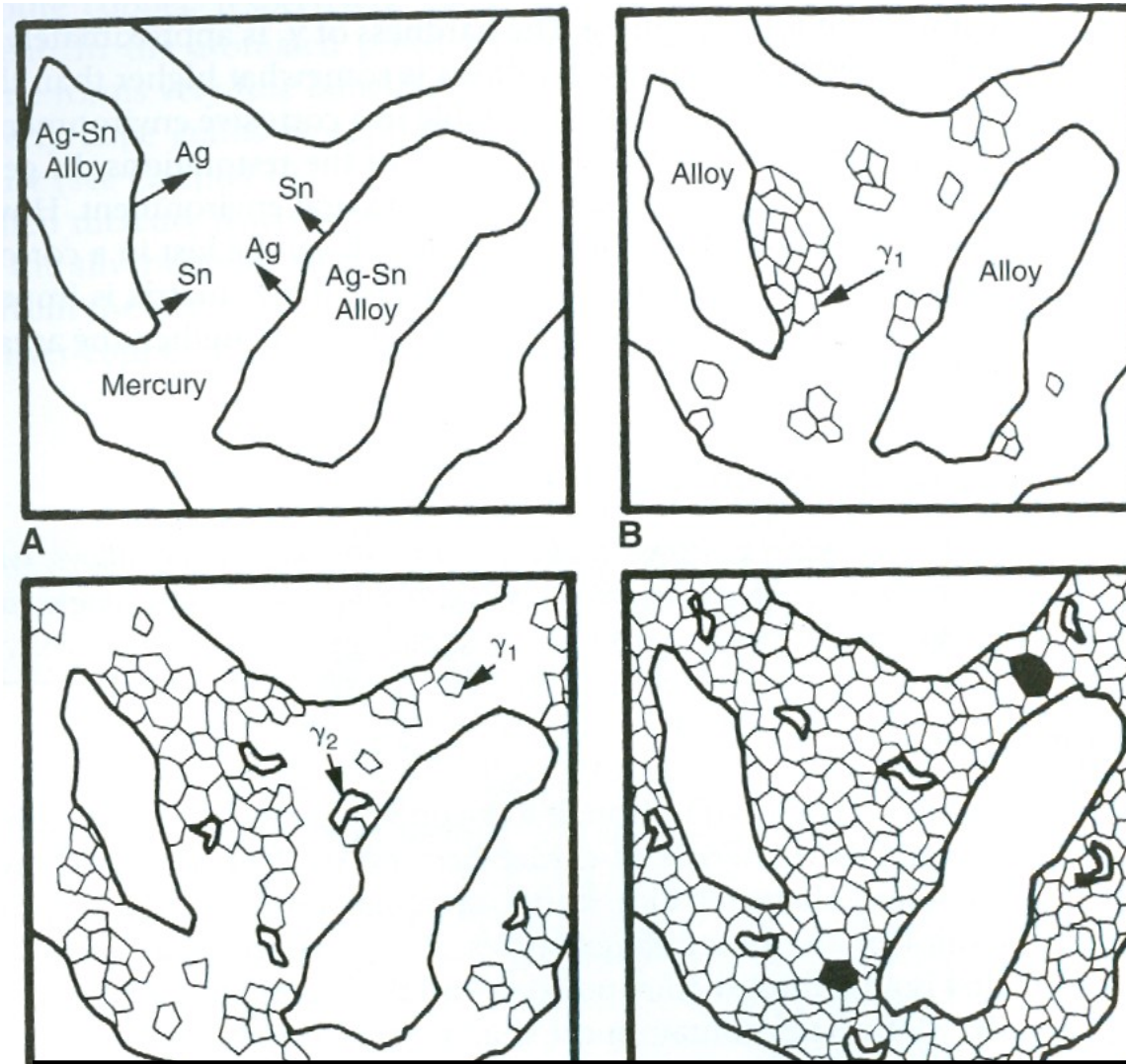
γ - silver alloy Ag_3Sn

γ_1 - silver-mercury Ag_2Hg_3

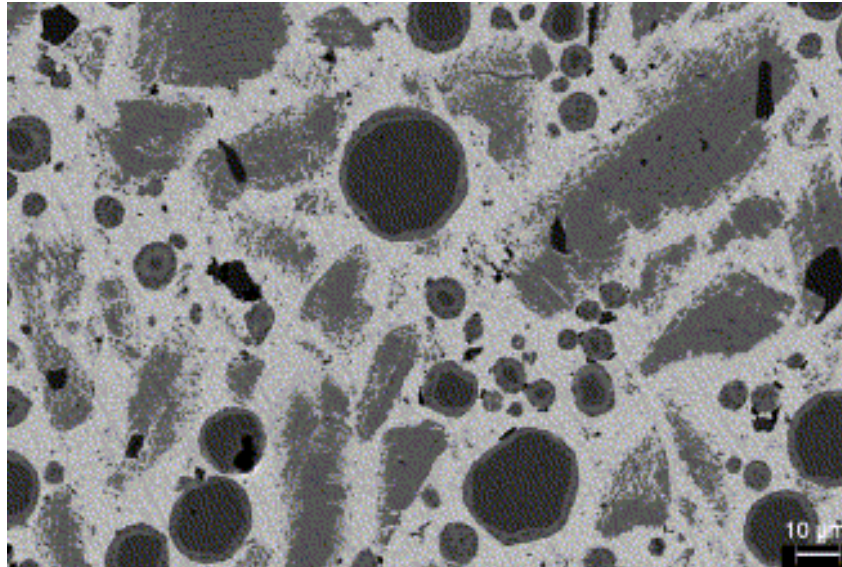
η' - copper tin Cu_6Sn_5

γ_2 phase Sn_7Hg – only in low-copper amalgams

Hardening of the amalgam



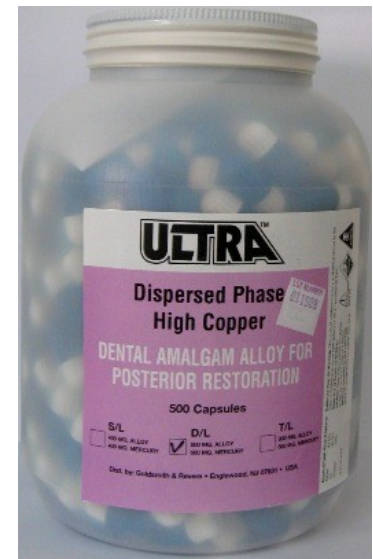
Amalgam is a complex metallurgical structure, containing up to six phases



Dental amalgam alloys

- Powder is produced by milling or the lathe cutting a part of ingot (particles are irregularly shaped)
- Atomizing of liquid alloy (particles are spherical)
- Mixed- lath-cut + spherical particles

Powder can be supplied in the form of pellets



Amalgamation (trituration)

Setting reaction of amalgam alloy with mercury

- Amalgam alloy is mixed with mercury in ratio 1:1, mixing (cca 10 s) – amalgamators
- Plastic phase – (5-10 min) - condensation under the firm pressure in the cavity of prepared teeth
- Hardening – increase in strength and hardness – 1-2 h → 24 h
- Amalgam become sufficiently strong within first hour

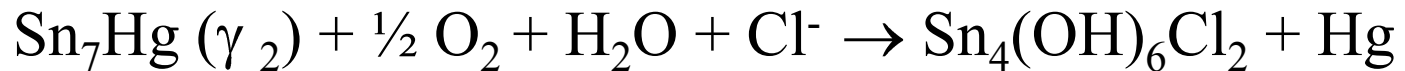


Properties of amalgam

- Strength
- Dimensional change
- Creep
- Tarnish
- Corrosion

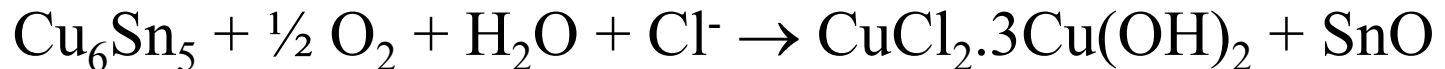
Amalgam corrosion

γ_2 phase is attacked by chlorides



Half-life cca 6 years

High copper amalgam



Half-life cca 20 years

Toxicity of amalgams

There is some controversy about the use of amalgams

Although mercury by itself is classified as a toxic material, the mercury in amalgam is chemically bound to other metals to make it stable.

Once the amalgam reaction is complete, little or no mercury remains unreacted

In practice, minute amounts of mercury vapor (appr. 1-2 $\mu\text{g}/\text{day}$) are released from dental amalgams as a result of chewing

Higher release may occur during the setting reaction, during removal of old amalgams or if the amalgam is heated above 80°.

Mercury hygiene

Process of handling mercury to minimize health risks:

- Never touche mercury even with gloved hands
- Mask should be worn to decrease exposure to particulate amalgam
- Using precapsulated amalgam
- Using high-volume evacuation during placement and removal amalgam restorations
- Amalgam scrap should be stored in containers and capped tightly and kept cool

Dental ceramics

Structure:

Usually amorphous glass with crystalline phase –both components are bonded by covalent or ionic bonds.

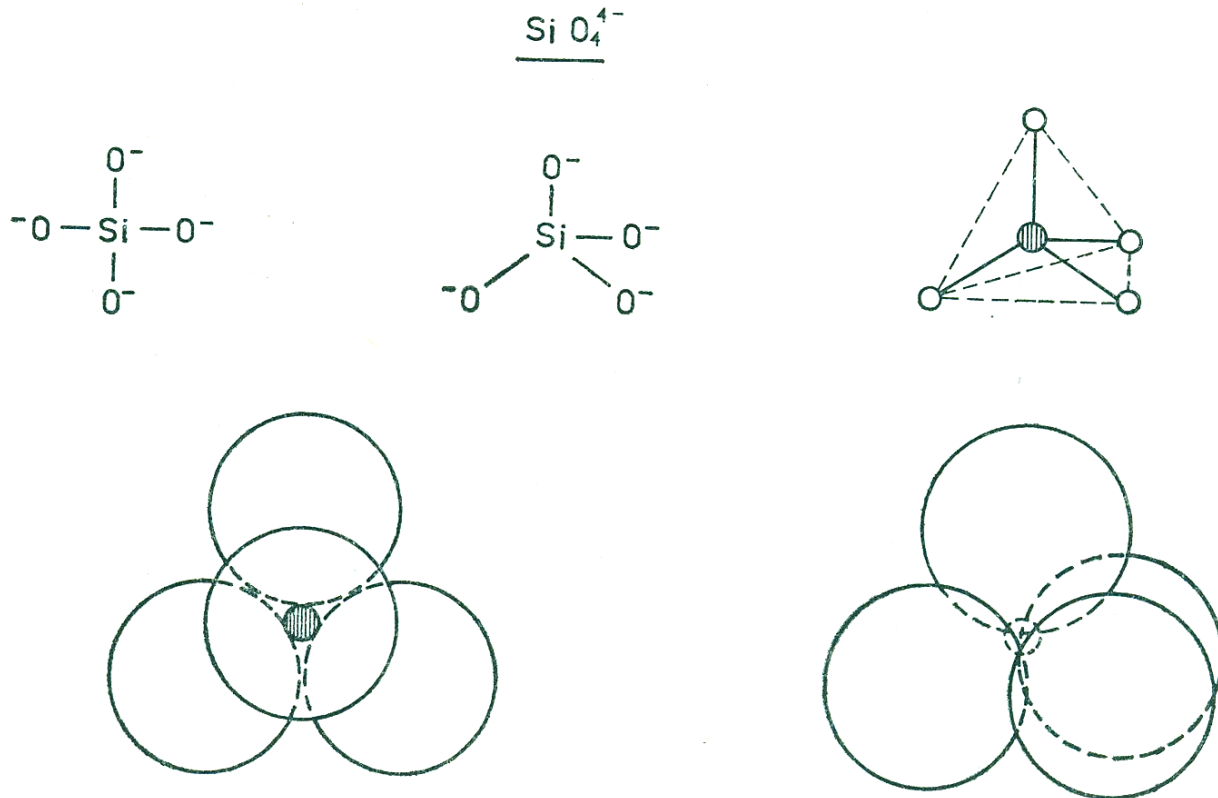
Diferent properties in comparision with other materials (metals, cements, resins)

- do not conduct electricity and heat
- long time resistant to corrosion and chemical effects, hard
- flexure strenght and fracture toughness
- color stability
- biocompatibility
- brittle

Crystalline structure of silicates

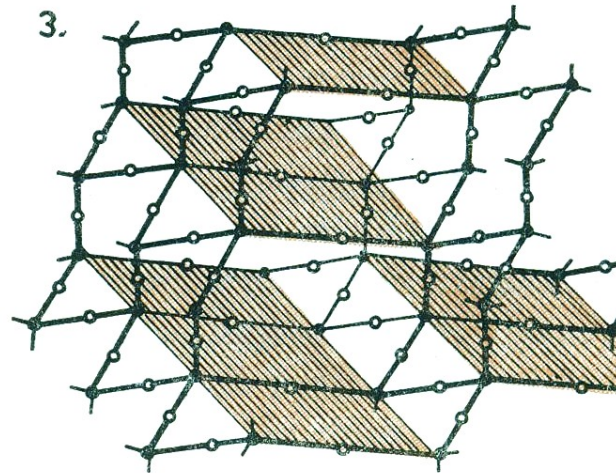
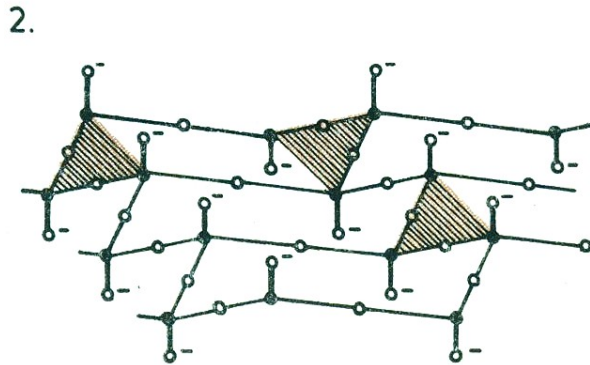
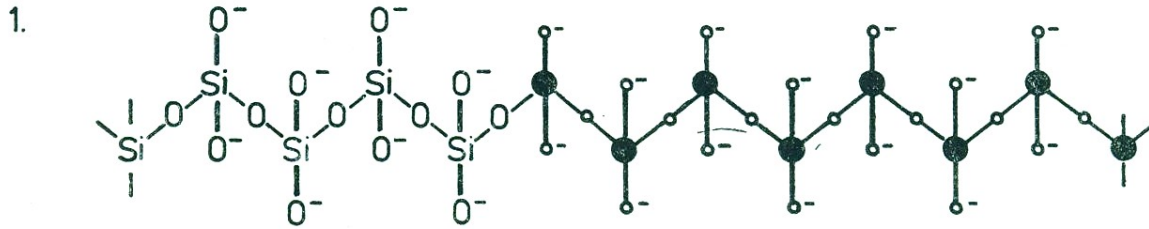
The main unit is tetrahedron with composition SiO_4^{4-} .

SiO_4^{4-} reacts with cations or other SiO_4^{4-} .



Formation of linear and branched networks.

Struktura silikátů



Dental ceramics comprise a crystalline and amorphous phase on the basis of silicate structure

Structure of quartz

Depending on temperature different minerals are formed. By heating of quartz structure of tridymite is formed, after it cristobalite and at the temperature higher than 1700°C amorphous melt is formed.

Composition of dental ceramics

Base component

Mostly oxides

Conventional dental porcelain: **feldspar** (aluminosilicates) and silica (SiO_2)

In modern ceramics alumina (Al_2O_3) spinell ($\text{MgO} \cdot \text{Al}_2\text{O}_3$), leucit (KAlSi_2O_6) or zirkonium oxide (ZrO_2).

Fluxes

The fluxes cause the other raw ingredients to form a glass that is not crystalline and melts at a relatively low temperature .

Borax, Na_2CO_3 or K_2CO_3

Pigments

e.g. NiO_2 (brown), CuO (green), CoO_2 (blue)

Processing of dental ceramics

These crystalline ingredients are heated together with fluxes such Na_2CO_3 or K_2CO_3

The fluxes cause the other raw ingredients to form a glass that is not crystalline and melts at a relatively low temperature

Dental porcelain is then refired with metal oxides to add color and fluorescence. After the porcelain is cool, it is ground to a fine powder.

Processing: powder is mixed with water, pressed into the mold, heat treated (sintering), overglazing, shading.

Zirconia ceramics

ZrO₂ is important modern material for production of ceramics

ZrO₂ is brittle (during sintering tetragonal phase changes to monoclonal)

Change of the phase can be suppressed by addition of other oxides (např. MgO, Y₂O₃, CaO, CeO)

Y-ZTP –yttrium stabilized tetragonal zirconia polycrystals

Dental cements

Temporary filling materials, thermal insulation, mechanical support to teeth restored with other materials, protection to the pulp from irritants, special using in endodontics and orthodontics

Most dental cements are supplied as two component – powder and liquid (or two pastes)

The liquid partially dissolves the powder particles and forms a matrix. Reaction occurs on the surface of unreacted particles of powder that become covered by the layer of reaction product. During setting it becomes hard enough to act as a "glue" and is used to cement crowns and posts.

Types of dental cements

- Zinc-phosphate
- Silicate
- Polyalkenoate
- Calcium-hydroxide
- Zinc oxide - eugenol
- Resine

Aqueous cements: zincphosphate, silicate, polyalkenoate

Non-aqueous cements: calcium-hydroxide, zincoxide-eugenol, resine

Classification according to process of setting

Setting by acid-base reaction (formation of a salt)

- Zinc phosphate
- Silicate
- Polyalkenoate
- Calcium-hydroxide
- Zinkoxide- eugenol

Setting by radical polymeration

- Hybrid glass-ionomer
- Resine

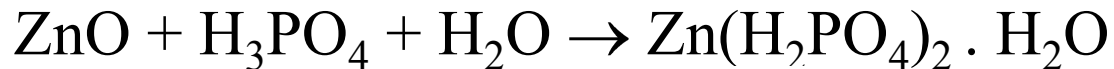
Examples of Cements

Zinc phosphate cement

powder: ZnO (+ MgO + traces SiO_2)

liquid: H_3PO_4 (+ buffered by aluminium phosphate, zinc phosphate and magnesium phosphate)

Chemical reaction of setting:

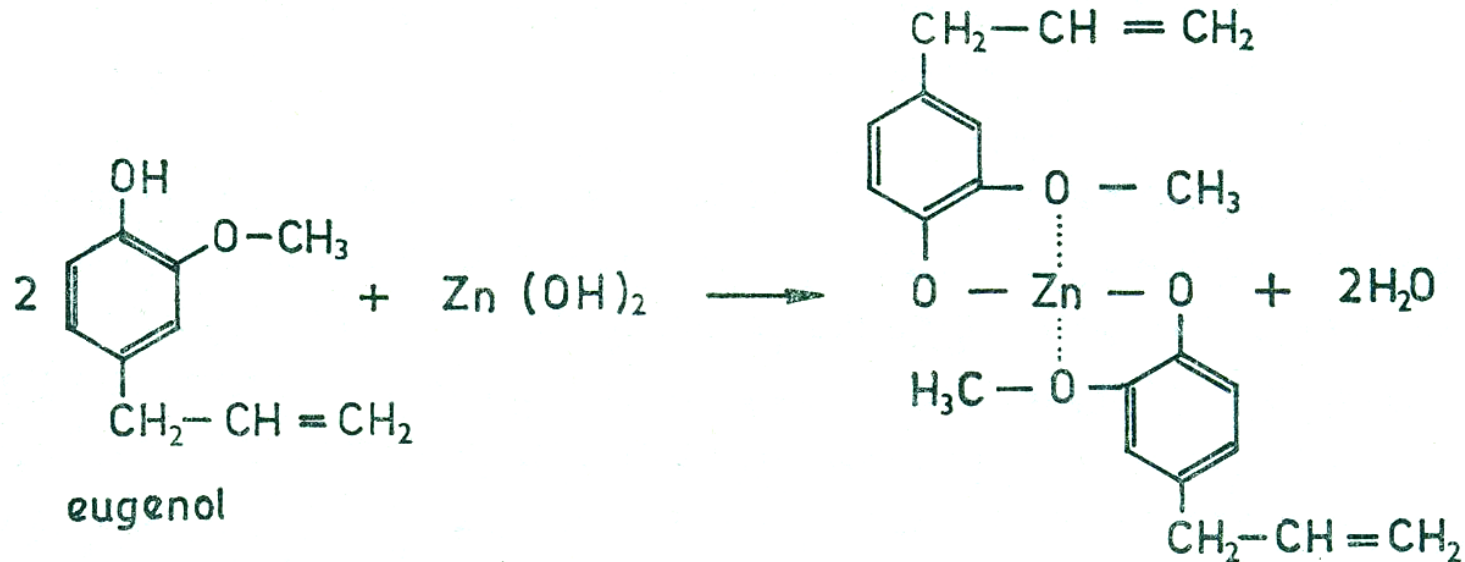


The set cement is a cored structure consisting primarily of unreacted zinc oxide particles embedded in a cohesive amorphous matrix zinc-aluminium phosphate

Zinc oxide eugenol cement

Powder: ZnO,

Liquid: eugenol



Eugenol –oil from rose-apple

Zinc-eugenolate (chelate)

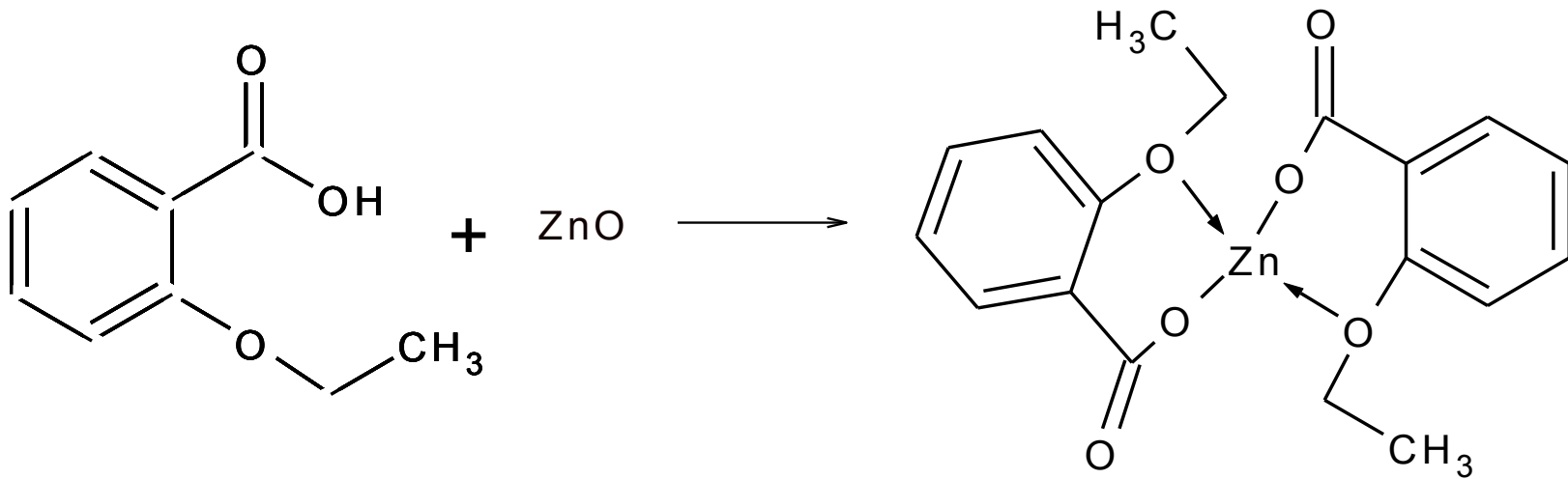
Has sedative effect on the pulp

Useful for cementation on prepared teeth

Moderate strength and low acidic quality

Modification of zinc-oxide-eugenol cements

Addition of ethoxybenzoate



Mixture of 62,5% ethoxybenzoate, 37.5% eugenol, powder max. 30% Al₂O₃

Silicate cements

powder: aluminium silicate glass prepared by fusing of SiO_2 , Al_2O_3 , CaO , NaF and sodium fluorosilicate at 1400°C

liquid: cca 50% H_3PO_4 (+ buffering salts aluminium phosphate, zinc phosphate and magnesium phosphate)

Structure after setting is formed by amorphous AlPO_4 and particles of glass covered by the layer of SiO_2

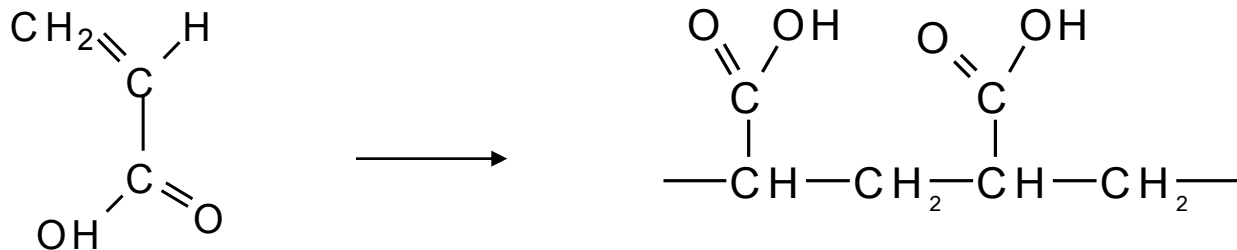
Zinc polycarboxylate cements

Water based-cements used as final cements for retention of crowns and bridges

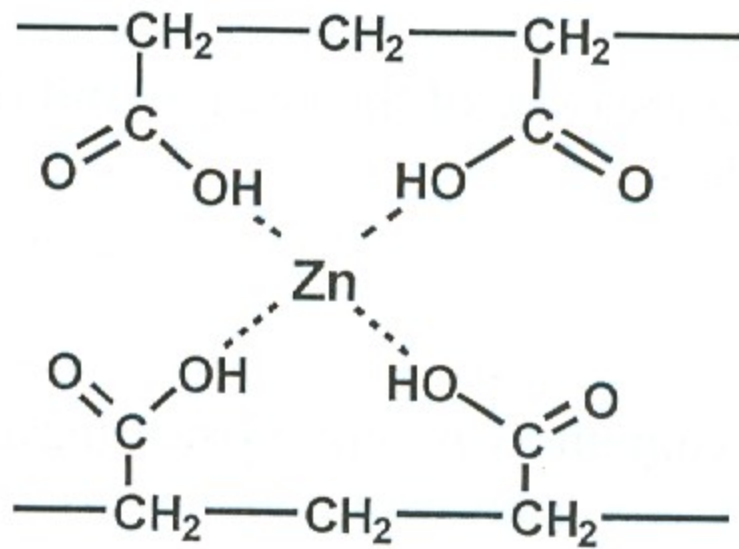
Powder: Zinc oxide + Al_2O_3 , SnF_2

Liquid: 40-50% polyacrylic acid in water

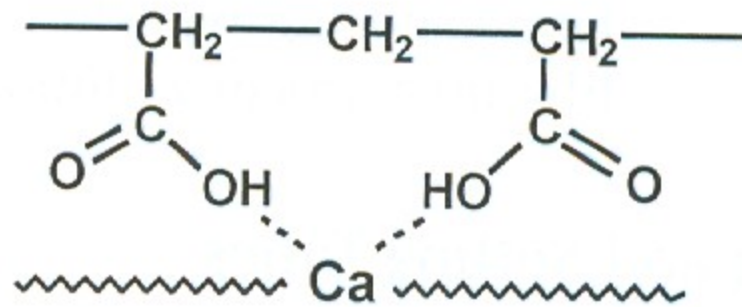
They react to form zinc polyacrylate that surrounds the partially reacted zinc oxide powder particles



Properties: moderate viscosity, moderate strength, ability to bond enamel, mild acidity.



A



B

Glass Ionomers Cements (GIC)

mixture of aluminosilicate glass and aqueous solution of polymers and copolymers of organic acids (acrylic acid, maleinic, itaconic)

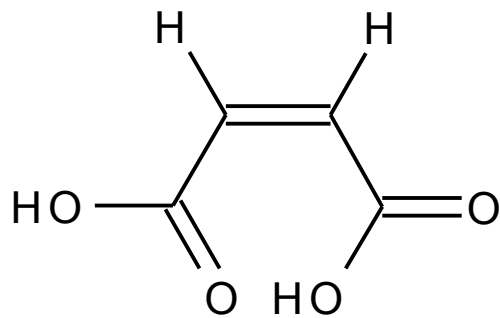
Composition:

Powder: particles of 10-20 μ m alkaline fluorosilicate glass with the high content of Ca,Al,P,F-

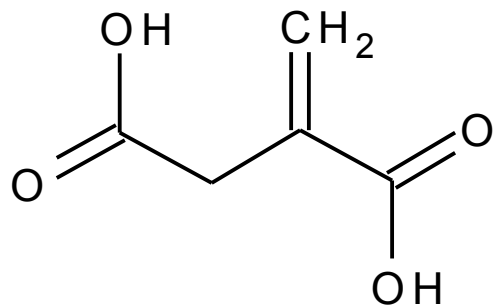
(prepared from SiO_2 , Al_2O_3 , CaF_2 , AlPO_4 , $\text{Na}_3[\text{AlF}_6]$, AlF_3 , addition of polyacid)

Liquid: polymer soluble in water e.g. polyacrylic, polymaleinic acid, addition of tartaric acid

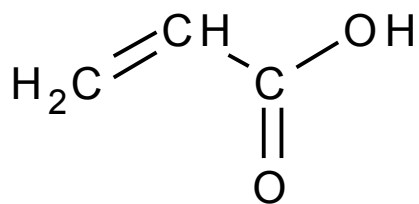
water as a reaction medium



Maleinic acid



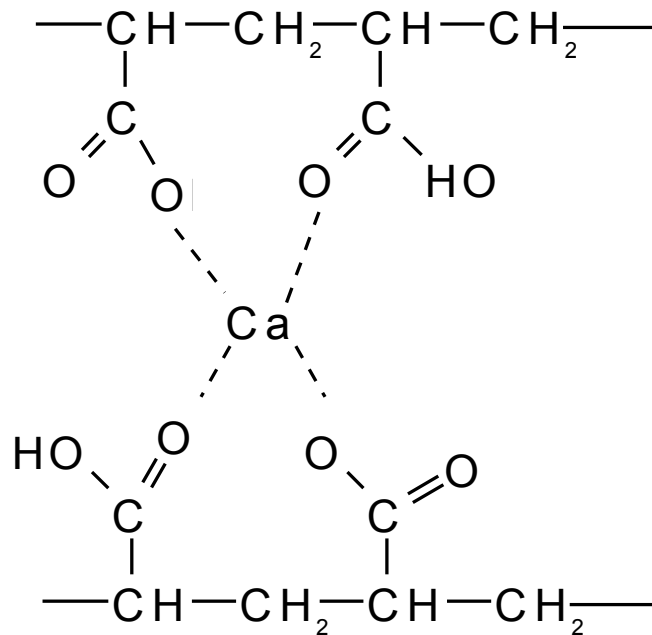
Itaconic acid



Acrylic acid

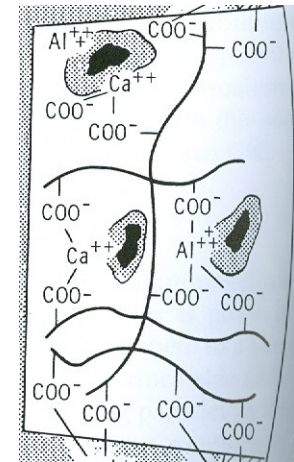
Reaction principle:

The material sets as a result of the metallic salt bridges between the Al^{3+} and Ca^{2+} ions and the acidic groups on the polymers

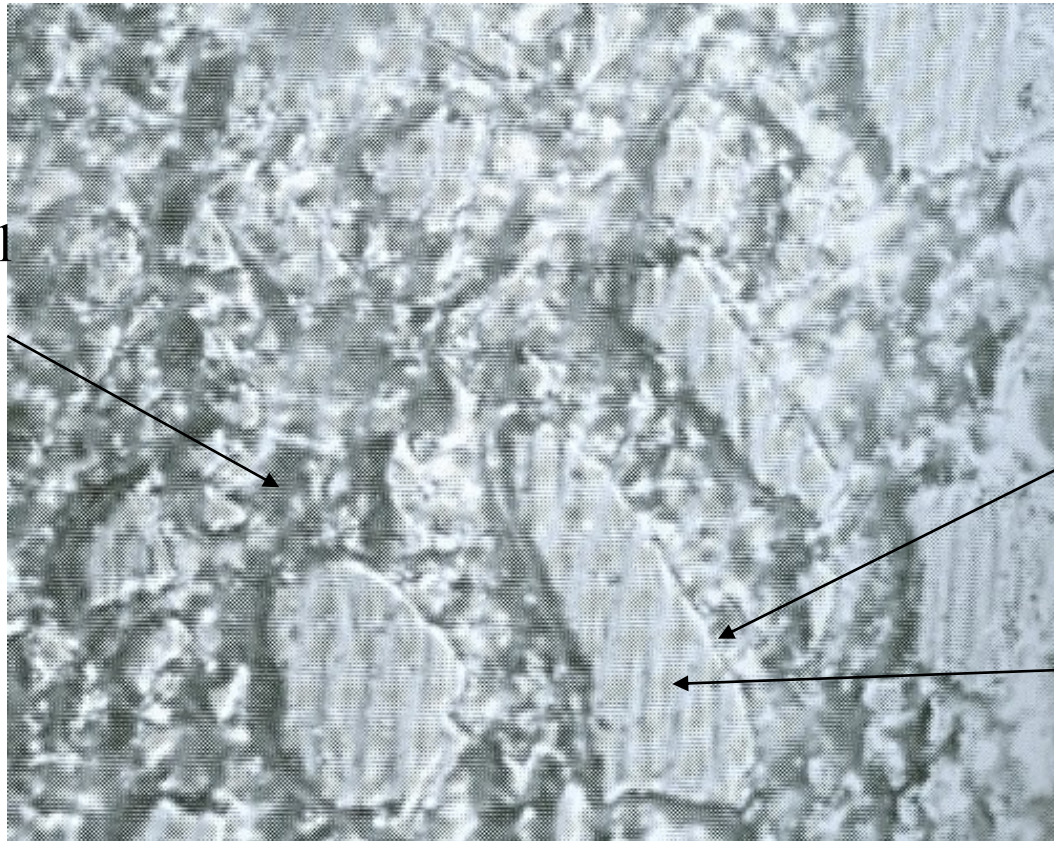


a small amount of tartaric acid is added to the water to provide a sharper, better defined setting reaction

Structure of GIC after setting

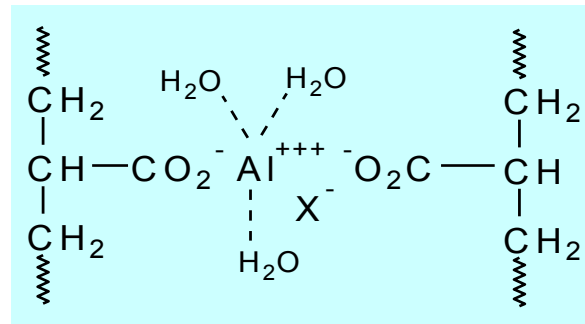
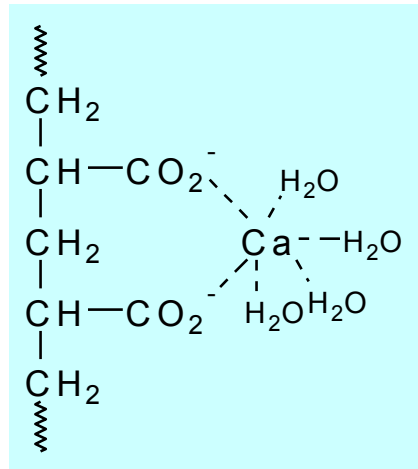
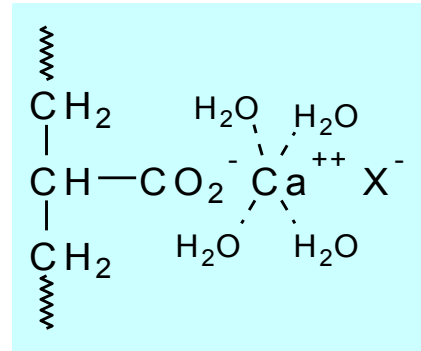
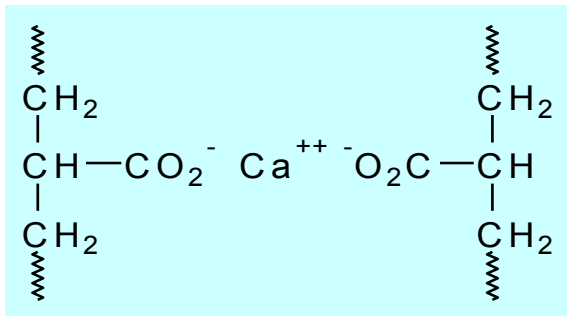


Matrix of Ca,Al
polyalkenoates



Gel of
 SiO_2

Glass particles



Possible inter- and intramolecular interactions in glassionmer cements ($X = \text{OH}^-$, F^-)

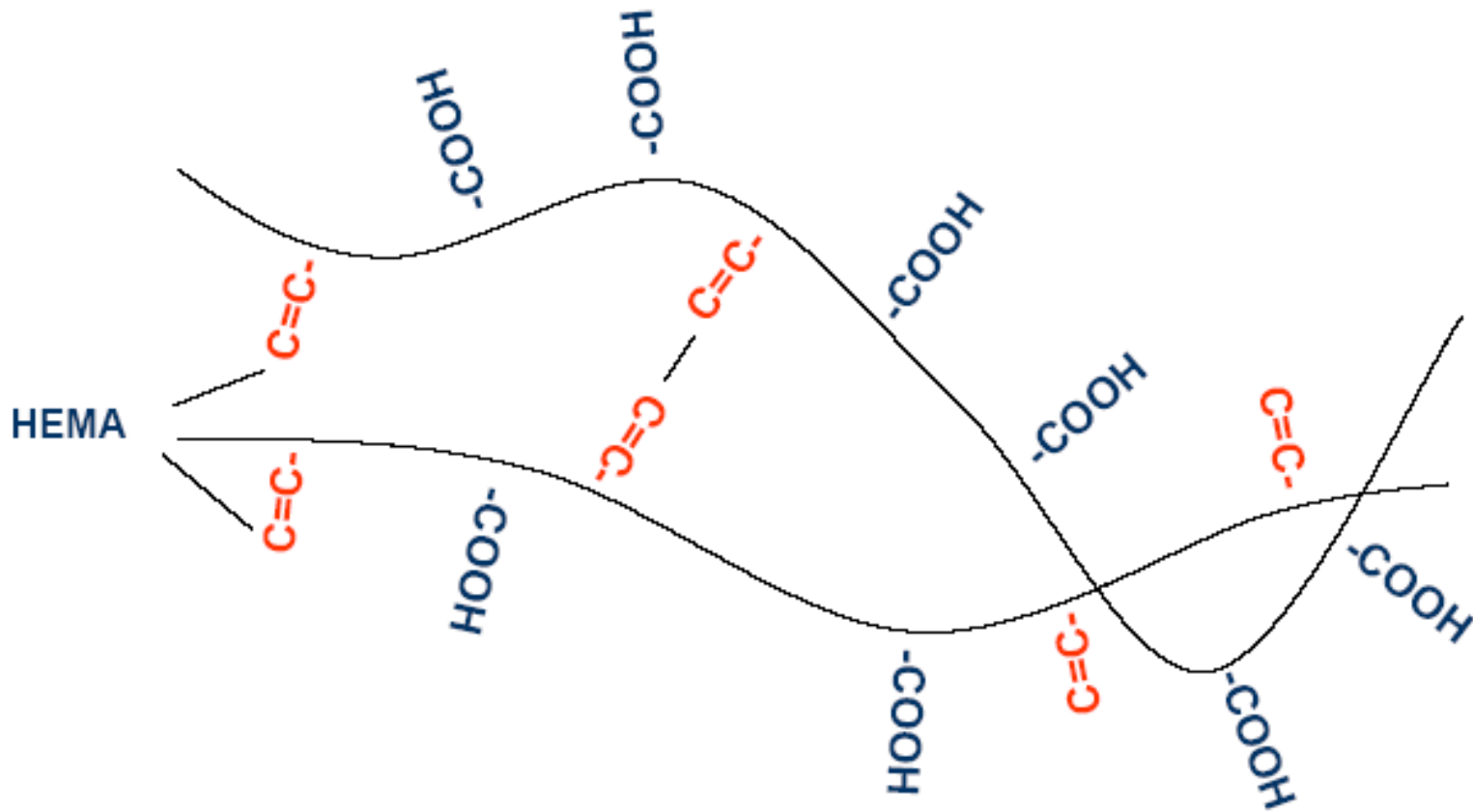
Hybrid Ionomer Cements or Resin-modified Glass Ionomers

The powder is similar to that of glass ionomers

The liquid contains monomers (HEMA – hydroxymetacrylate), polyacids and water

Hybrid ionomers set by acid-base and resin polymerization reaction (light-cured or self-cured)

Acid-base reactions are supplemented by a second resin polymerization



Resin cements

Used for bonding of ceramic and indirect composite crowns, inlays and onlays

Temporary resin cements are used for temporary cementation of část crowns and restorations

Composed of dimethacrylate resin and glass filler (see the composite fillings)

Metal-reinforced glass ionomer cements

GIC can be reinforced by physically incorporating silver alloy powder with glass powder (**silver alloy admix**) or by fusing glass powder to silver particles through sintering (**cermet**)

Gypsum in dentistry

production: from mineral gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ by removal of crystalline water (calcining).

Dental plaster = calcium sulfate hemihydrate $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$

Plaster setting: reverse reaction with H_2O to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – setting is caused by different solubility of hydrate and hemihydrate in water.

Volume changes during plaster setting: after mixing of water volume contraction, during setting volume expansion. Dental plaster: expansion $< 0,25\%$. Addition of borax or K_2SO_4

Plaster setting



Solubility 0,9 g/100g water

solubility 0,2 g/100g water

Setting accelerators: K_2SO_4 , NaCl

Setting retarders: $\text{Na}_2\text{B}_4\text{O}_7$, sodium citrate, CH_3COOH ,
gelatin

Macromolecular compounds and plastics in dentistry



Polymers

Polymers are macromolecules composed of regulary repeated units. The building unit is **monomer** .

The molecular weight of monomers is about 100, the molecular weight of polymer ~10 000

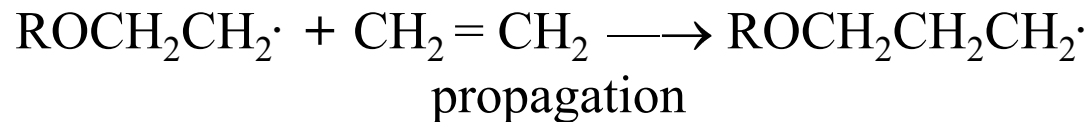
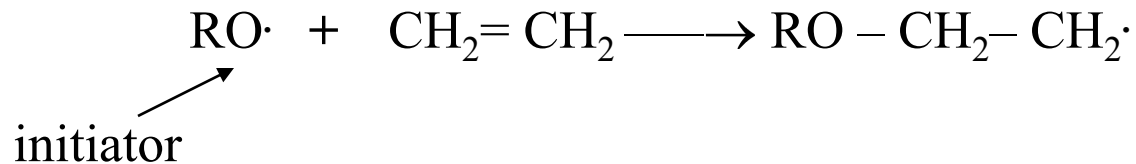
Carbon atom with the tendency to form chains has in macromolecular chemistry dominant role.

Types of polymerization reactions

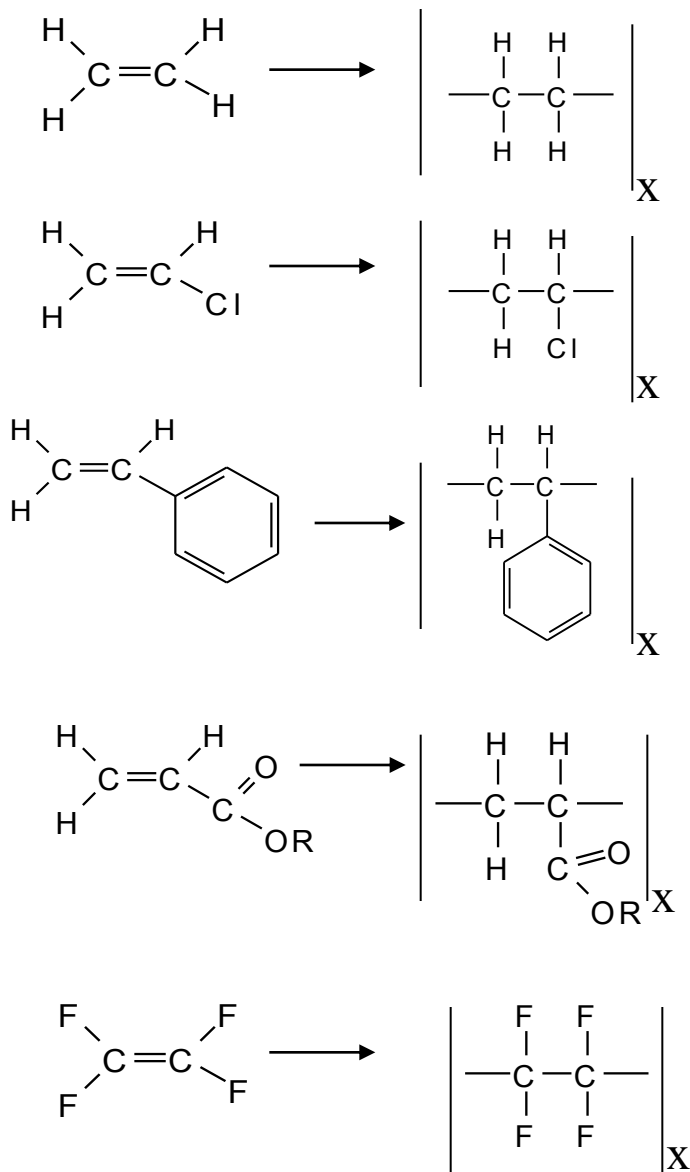
- **radical polymeration**
- **ionic polymeration**
- **polyadition**
- **polycondensation**

Radical polymerization

- From unsaturated hydrocarbons (monomers) macromolecules (polymers) are formed



Monomers and products of polymerization - examples



polyethylene PE

polyvinylchloride PVC

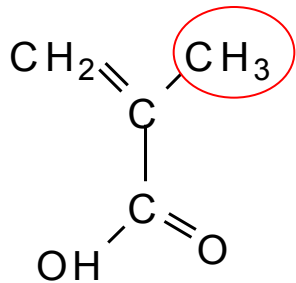
polystyrene PS

polymethyl-acrylate

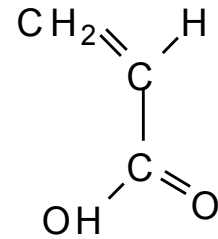
teflon

Acrylate polymers

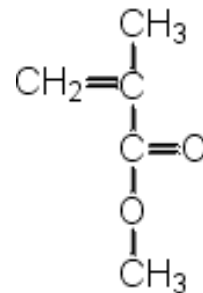
most common plastics in stomatology (95%)



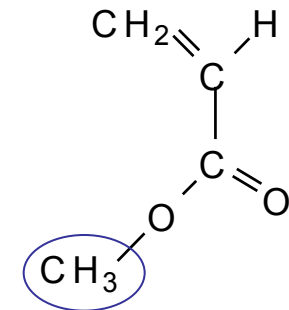
Metacrylic acid



Acrylic acid



methyl-**met**acrylate

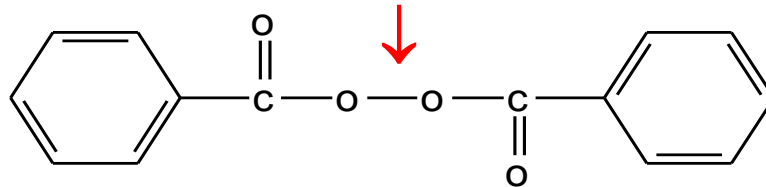


methyl-acrylate

Initiator: organic peroxide

dibenzoylperoxide

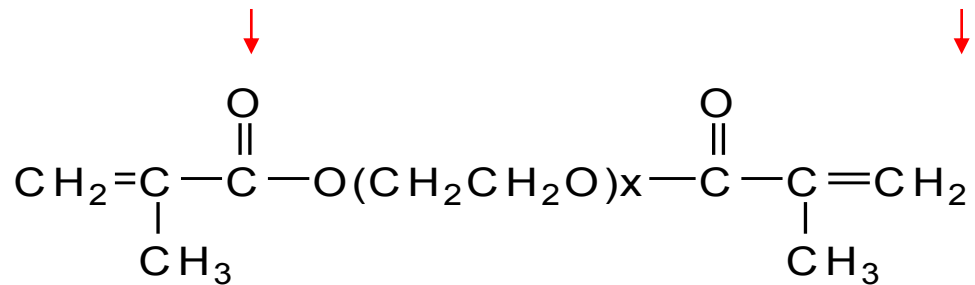
it is activated by the heat or
organic accelerator



Cross-linked polymers

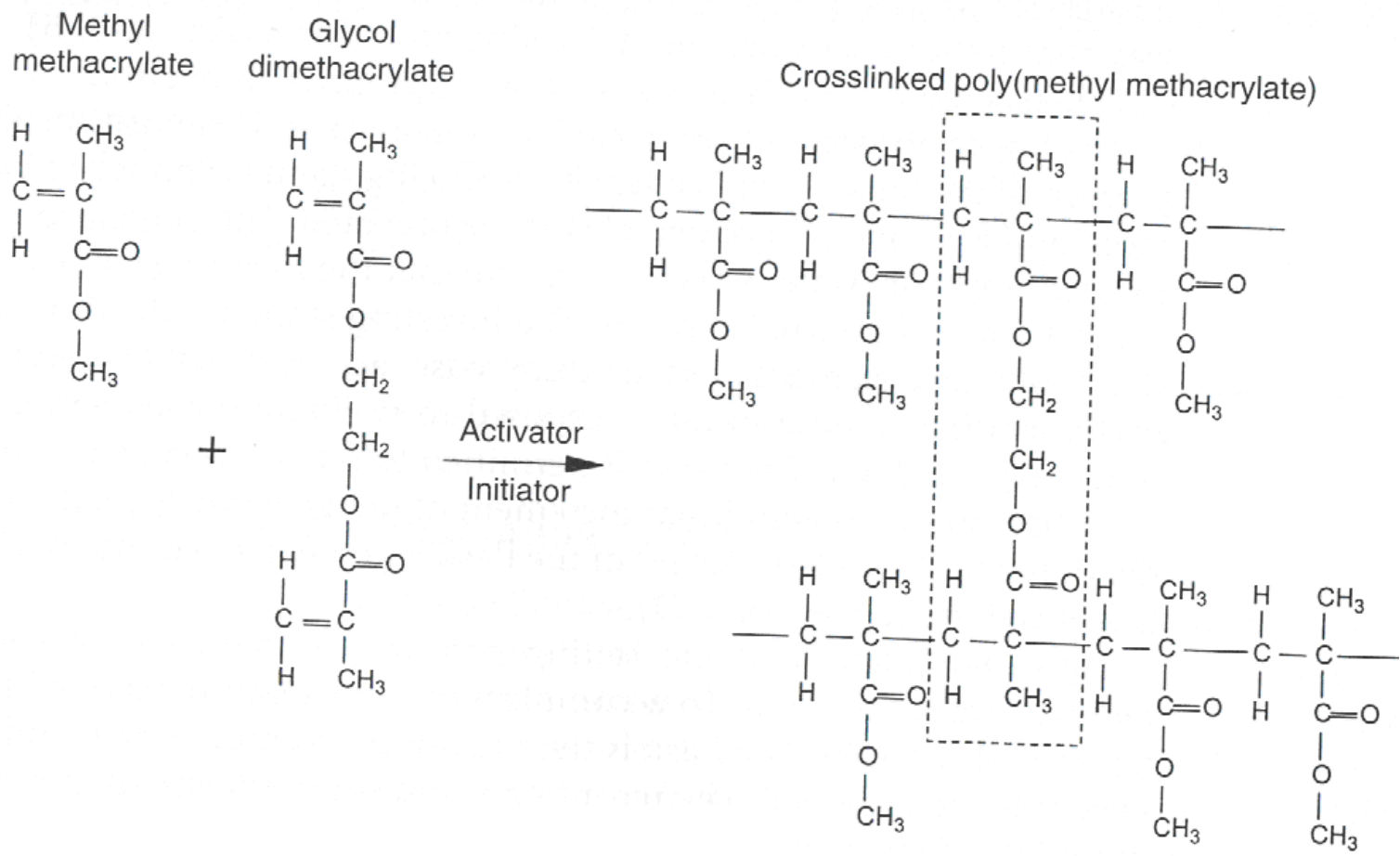
Produced in the presence of small amounts of different monomer units with reactive double bonds on each end of the molecule

Eg.. glycoldimetacrylate



Advantage: higher resistance against surface cracking or crazing in the mouth.

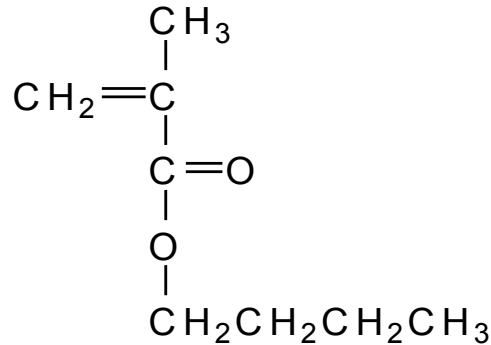
Crosslinking using glycoldimethacrylate



Copolymers – two or more different monomers

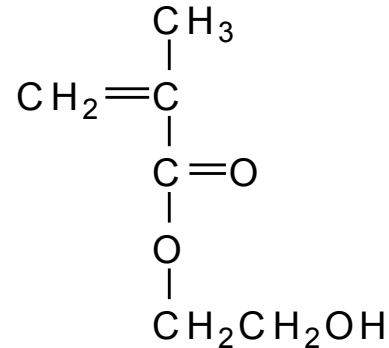
both units are spaced randomly along the chain

Examples of monomers added to methylmetacrylate



butyl metacrylate

more resistant to fractures



Hydroxyethyl metacrylate

Oktyl metacrylate - increases softness and flexibility

Modified polymers

Modification by the addition of compounds that do not enter into the polymerization

Oily organic esters, rubbers, inorganic fillers

E.g.: addition of dibutyl phthalate plasticize the polymer

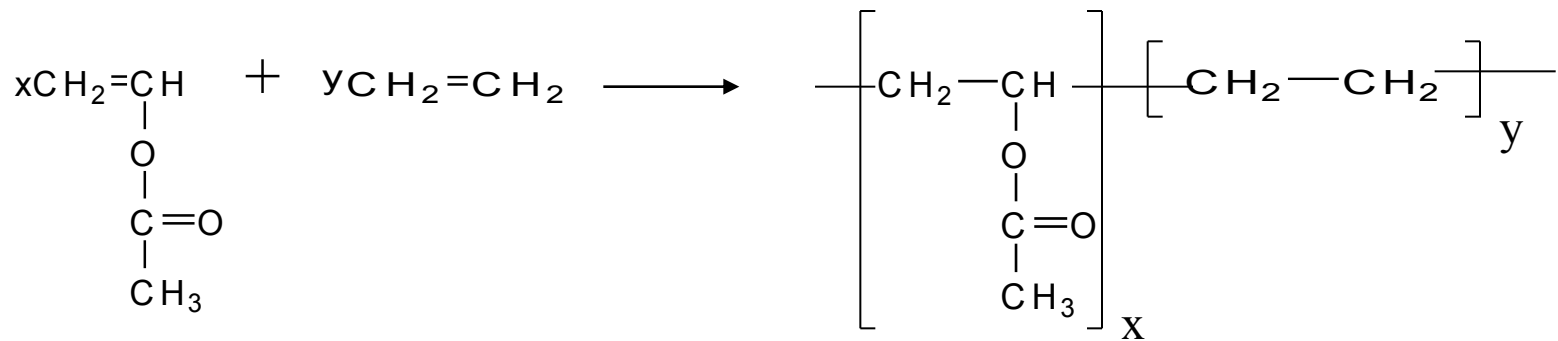
Components of the powder and liquid of an acrylic denture base

Powder	Liquid
Polymer (polymethylmetacrylate)	Monomer (methylmetacrylate)
Organic peroxide	Hydrochinon (inhibitor) 0,1%*
TiO ₂ (translucence)	Cross-linking monomer
Anorganické pigmenty	Organic accelerator (amine)**
Dyed synthetic fibers for esthetics	

*prevention of polymeration during storage

Vinyl plastics

Copolymers of vinylacetate and ethylene



vinylacetate-ethylene copolymer

Using in preventive dentistry as mouth protectors

Resin-Based Fillings

Consist of three phases:

- Resin matrix
- Dispersed inorganic filler particles
- Silane coupling agent

Natural composite materials

Enamel

95% anorganic component
(mainly hydroxyapatite)

1% organic component
(enamelin)

4% water

Dentin

75% anorganic component
(hydroxyapatite)

20% organic component

5% water

The differences in properties are given by matrix/filler ratio

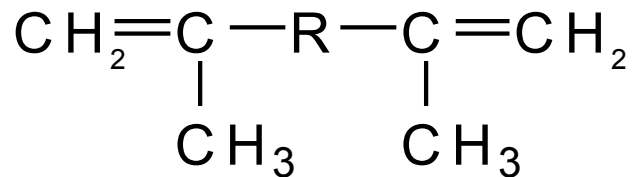
Resin matrix

The most common resins

Oligomers based on:

bis(phenyl-glycerol-metacrylate)-propane (bis-GMA)

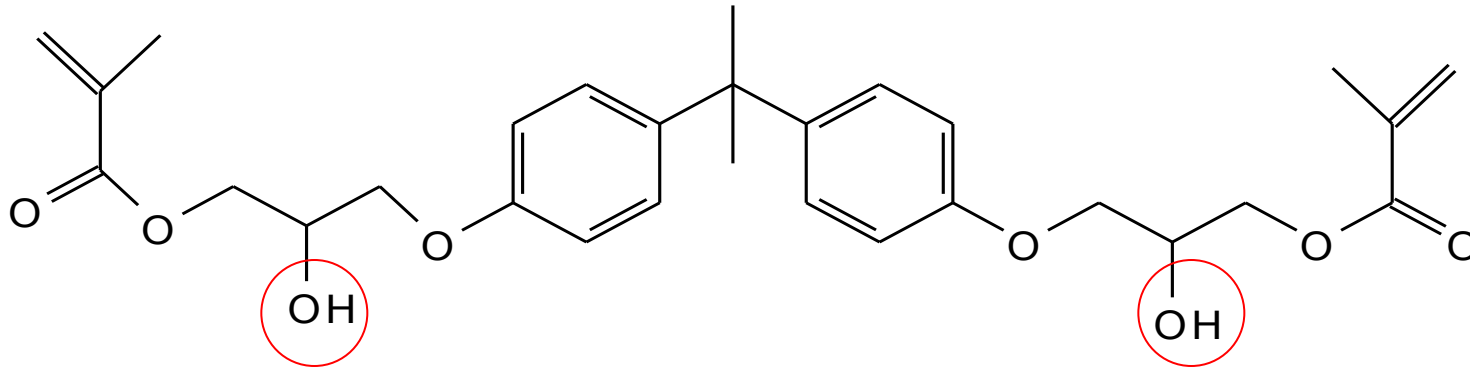
urethane dimethacrylate (UDMA)



R-large organic group
(phenyl, carboxyl, amide ...)

The reactive double bonds undergo polymerization after appropriate initiation.

bis-GMA

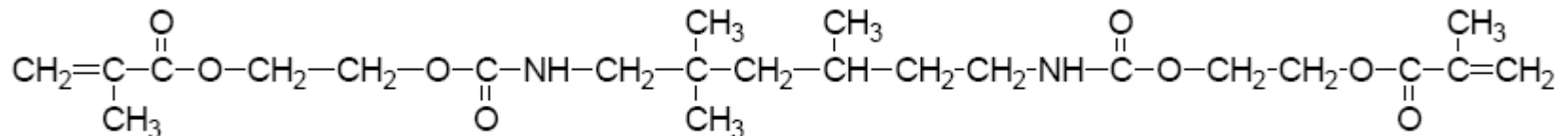


bis(fenyl-glycerol-metacrylate)-propane

2,2-bis-[4-(2-hydroxy-3-methacryloxy-propyloxy)phenyl]-propane

(1-methylethylidene)bis[4,1-phenyleneoxy(2-hydroxy-3,1-propanediyl)] bismethacrylate

Bisphenol A-glycidyl methacrylate

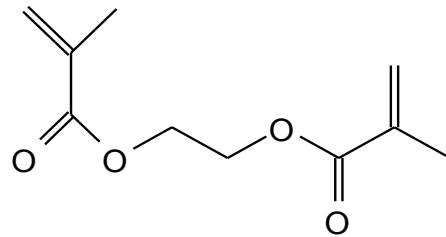


UDMA

urethamethacrylate

Resin matrix

Bis-GMA and UDMA oligomers are viscous liquids to which low molecular weight monomers (dimethacrylates) are added to control the consistency of the composite paste



EDMA

Filler composition

Conventional fillers – silica or glass
(aluminium/borosilicates) (diameter 1-50 μm)

Fine fillers (diameter 0,2-3 μm)

Quartz

lithium aluminium silicate

Barium, strontium, zinc or ytterbium glasses

Microfine fillers (diameter 0,04 μm)

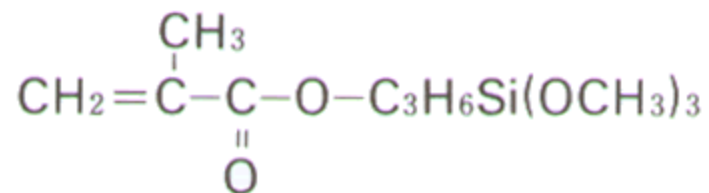
Colloidal silica particles

Hybrid fillers – mixture of macroparticles grind
glass > 1 μm and SiO_2 0,01-0,1 μm

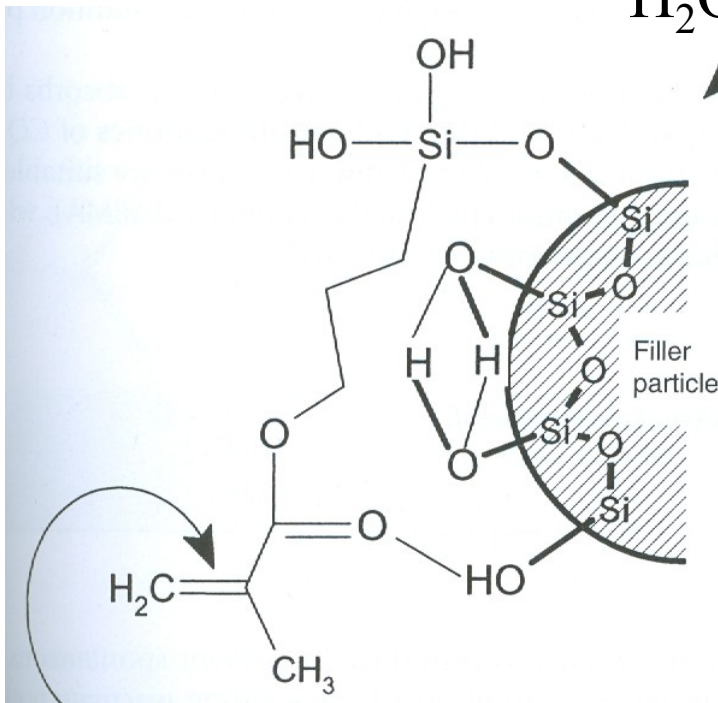
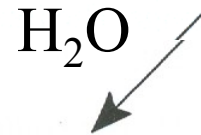
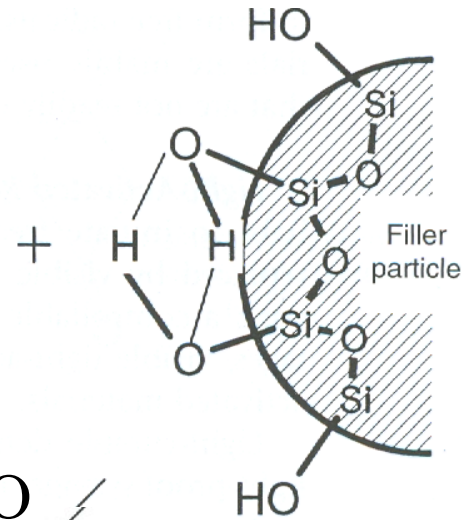
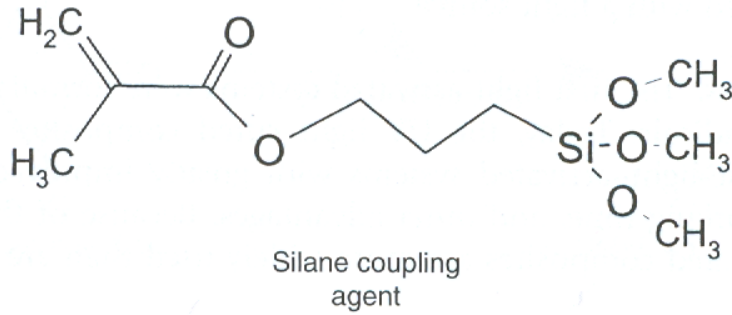
Silane coupling agents

- class of organosilane compounds having at least two reactive groups of different types bonded to the silicon atom in a molecule.
- One of the reactive groups of different types (ex. methoxy, ethoxy and silanolic hydroxy groups) is reactive with various inorganic materials such as glass, metals, silica sand and the like to form a chemical bond with the surface of the inorganic material
- the other of the reactive groups (vinyl, epoxy, methacryl, amino and mercapto groups) is reactive with various kinds of organic materials or synthetic resins to form a chemical bond.

Examples of silane coupling agents



Effect of coupling agent



Polymerization of composite

Polymerization is based on radical reaction.

Two types of initiation:

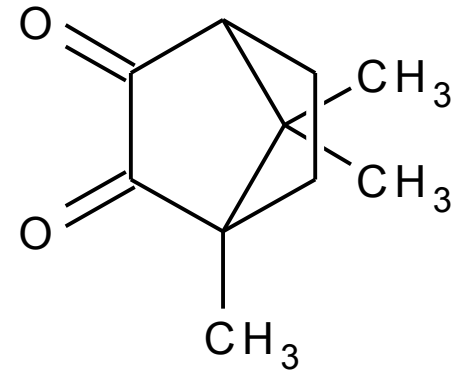
Light curing systems – polymerization is initiated by the blue light

Self-cure systems – polymerization is initiated by chemical way.

Light curing systems

For inciation is used camphorquinone

It is excited by blue light (468 nm) and interacts with tertiary amine to form free radicals that initiate polymerization



Self-curing systems

Two pastes. One of which contains the dibenzoylperoxide (initiator) and the other an aromatic tertiary amine (N,N-dimethyltoluidine) (activator)

When the two pastes are mixed together, the amine reacts with dibenzoylperoxide to form free radicals

Dual-cure resins

Combination of both principles