Dental cements

Chemistry, composition, properties

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2009

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What are cements?

<u>In the Oxford dictionary:</u>

A material which „glue" various things together e.g. **embedded particles in minerals are glued** in a compact body (sand, particles of rocks are „glued" using Portland cement in a concrete)

<u>In dentistry</u>

Materials used for:

- **Luting, fixation, cementation** - i.e. luting inlays crowns, bridges, veneers on the prepared tooth
- **Liners and bases** - to **protect pulp** from heat („thermal insulation") and from chemical irritation

  - to **stimulate secondary dentin** formation
- **Fillings** (temporary at stress bearing areas)

Cements are formed by:

1. Reaction of acid and alkaline (base) components – setting via **acid-base reaction** (neutralization in case of water based cements)
2. **Free radical polymerization** (the same as that of acrylics and also composites)
3. Via **combination** of free-radical polymerization and the acid-base reaction

Types of dental cements:

Usually two-component – powder and liquid or paste-paste systems

- Zinc phosphate
- Silicate (silico phosphate, **not used anymore**)
- Polyalkenoate:
  - Zinc oxide polycarboxylate (**polycarboxylate**)
  - Glass ionomer
- MTA Mineral-Trioxide-Aggregates
- Zinc oxide-eugenol
- Calcium hydroxide

- Resin cements

Types according to setting reaction:

<u>Setting reaction is acid-base:</u>

- Zinc phosphate
- Silicate
- Polyalkenoate:
  - Polycarboxylate
  - Glass ionomer

} **Water-based**

- MTA
- Zinc oxide-eugenol
- Calcium hydroxide

} **Non-aqueous**

<u>Setting reaction via free radical polymerization</u>

- Hybrid glass ionomer } **Water-based**
- Resin cement **Non-aqueous**

Terms and definitions:

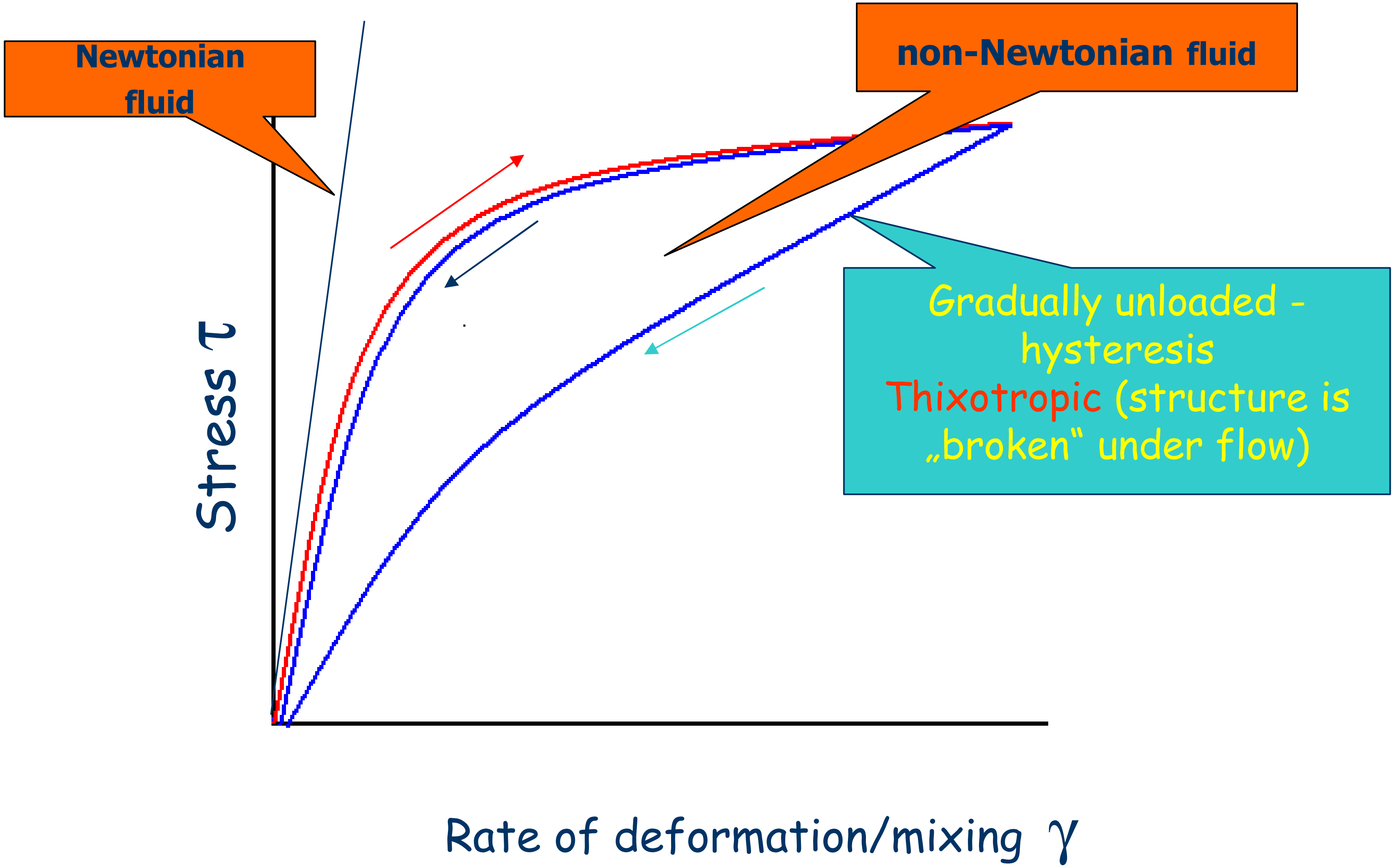
- Working time (WT) – time period from the beginning of mixing to the maximum time at which it is possible to manipulate with the material without an adverse effect on its properties

- Setting time (ST) – time interval measured from the end of mixing untill cement reaches such resistance that external force under specific conditions* **will not make its** permanent deformation

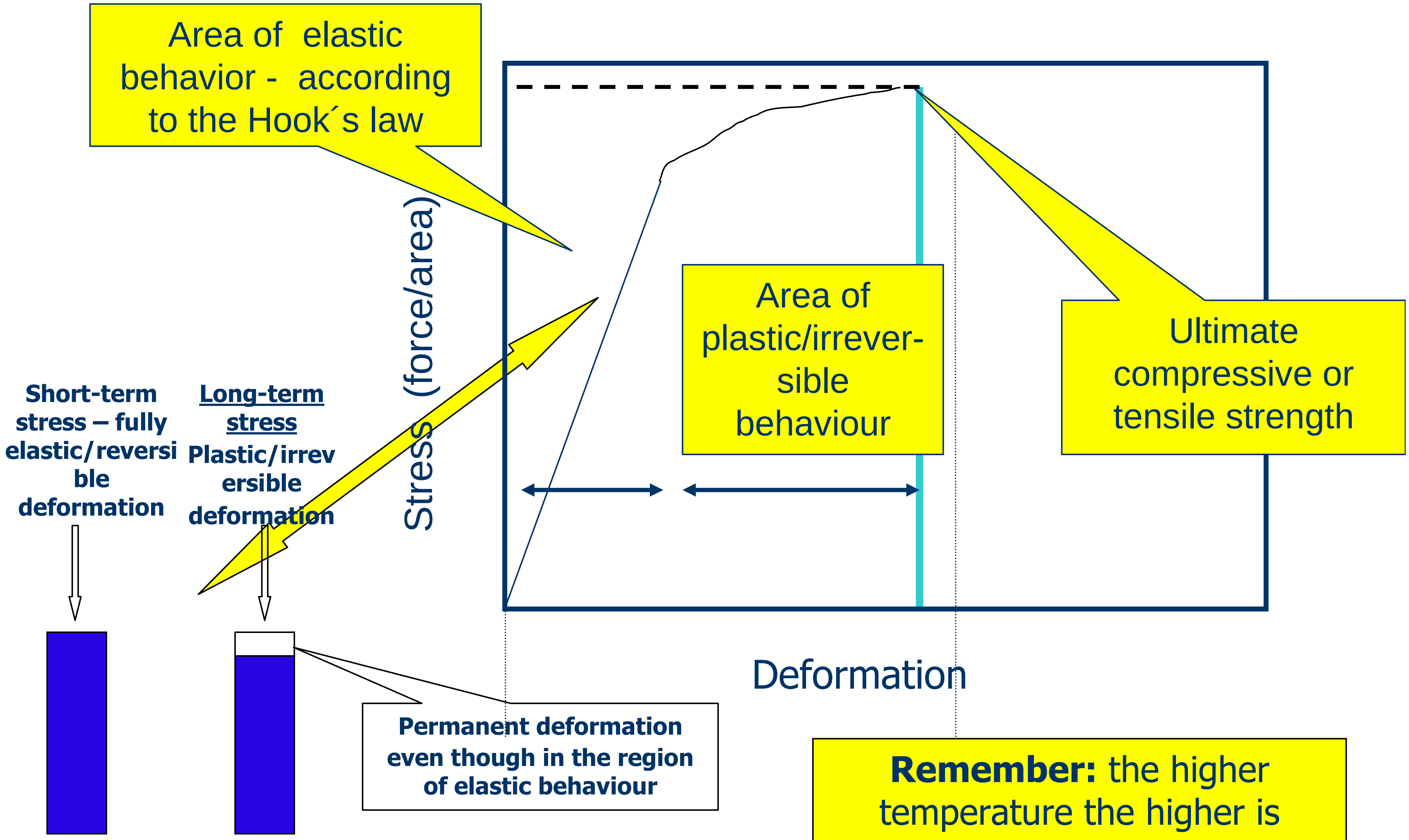
* EN ISO 9917-1 Water-based cements – Part 1: Powder/liquid acid-base cements (indentor of a flat end, diameter 1.0 mm, weight 400 g)

Properties of fluids

Pseudoplasticity/thixotropy



Properties of solids
Strength and creep



Remember: the higher temperature the higher is polymer creep

Water-based cements

Setting reaction - neutralization

$$\text{base} + \text{acid} \xrightarrow{\textit{water}} \textbf{salt} + \text{water}$$

powder **liquid** **matrix**

Why is water needed?

- dissolves acids
- enables dissociation of acidic groups
- hydrates particles of cements and releases alkaline ions from their surface

Zinc phosphate cements (temporary fillings, lining and luting material)

In dentistry used since 19th. century.

Main components:

- Powder: ZnO (90%) + MgO (10%)
  - Deactivated – sintering at 1100 – 1200°C (reduction of specific surface area and densifies ZnO)
  - Grinding to 10 – 20 μm
  - Dying with pigments

- Liquid: 33 – 40 % aqueous phosphoric acid H_3PO_4:

  Partly neutralized (buffered) by **$Al(OH)_3$** (app. 3 %) and **ZnO** (0-10 %) to slow setting reaction during mixing

Setting reaction:

1. Reaction of pure ZnO and the phosphoric acid:

$3ZnO + 2H_3PO_4 + H_2O \xrightarrow{\text{Strongly exothermic}} Zn_3(PO_4)_2.4\ H_2O$

crystaline material resembles mineral **Hopeit**

Fast setting reaction, fast crystalization unsuitable properties

When H_3PO_4 partially is neutralized with Al ions, different setting mechanism

2. At Al presence:

much slower formation and crystalization of $Zn_3(PO_4)_2.4\ H_2O$
→ slower setting reaction

Precipitation of amorphous Zn, Al phosphates on the surface of ZnO particles, which inhibits penetration of phosphoric acid to particle core and lower crystalization of hopeit

surface is covered with aluminophosphate (hydrated amorphous) gel

Slower reaction, suitable manipulation properties – prolonged working time

Structure of set cements:

1. Particles of incompletely dissolved ZnO covered with Al phosphate in matrix of britle amorphous/crystaline Zn phosphate

2. High porosity (diameter app. 0.5 μm) arising from excess unbound water which can be removed by diffusion – porosity decreases strength of cement and makes it permeable to water

How can be setting affected:

1. Finer particles – increase in particle surface accesible to an acid attack (faster setting)
2. Dilution of liquid – lower Al concentration (faster setting)

In the cabinet:

1. Higher powder/liquid ratio – (lower fraction of Al to ZnO surface) – faster setting
2. Higher temperature (37°C) – a decrease in setting time app. 5 times (cooled mixing glass slab) – cement is dispensed in the crown not on a prepared tooth
3. Fast mixing – prolongation of setting breaking the formed cement structure into fragments

Improper manipulation:

Water lost or liquid dilution – faster setting

Hygroscopic/alkaline powder CO_2- absorption – cement deterioration

Advantages:

- Easy to prepare
- Long working time
- Not sticky consistency
- Rapid setting to a hard material
- Low creep – suitable for bridge fixation
- RTG opacity

Disadvantages:

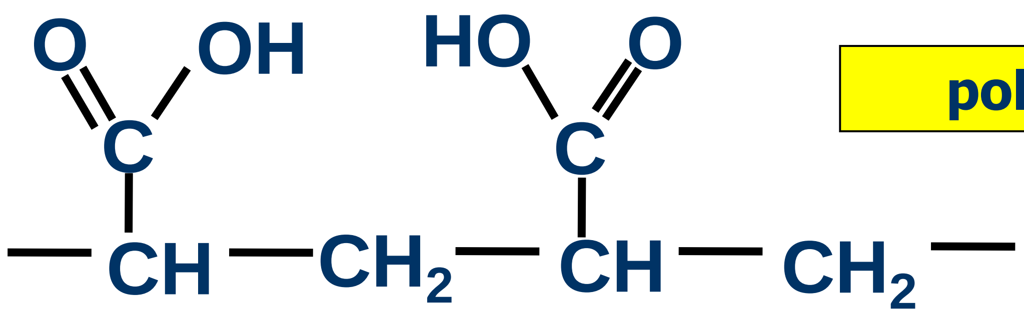
- Low adhesion to tooth structures
- Decreased biocompatibility in deep cavities due to lower pH even after application
- Erosion in aqueous environment
- Highly opaque

Zinc polycarboxylate (polycarboxylate) cements (lining and luting material)

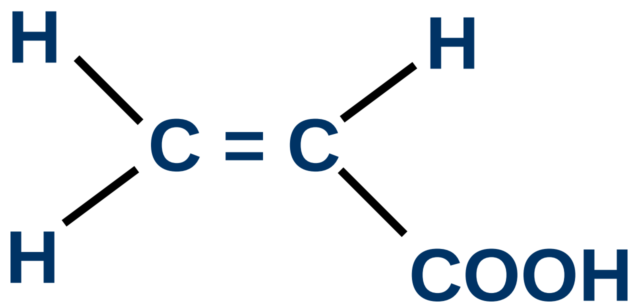
Invented by Smith in 1968

Main components:

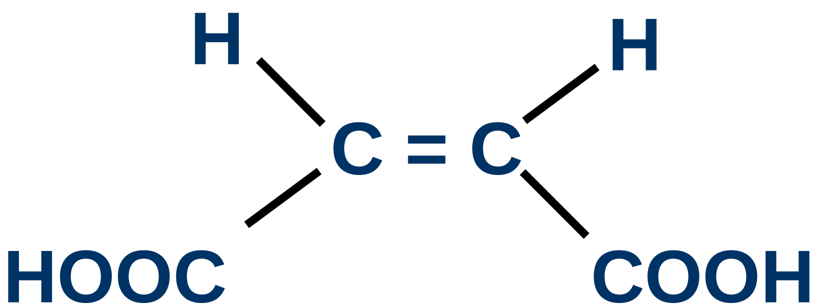
- Powder – similar to that used for zinc phosphate cement, but Al_2O_3 and SnF_2 are also added in new formulations to improve strength, release F^- and improve its manipulation
- Liquid: 40 – 50 % aqueous solution of polyacrylic acid or copolymers of acrylic acid with itaconic or maleic acids (molecular weight app. 20 000-50 000 - viscous)



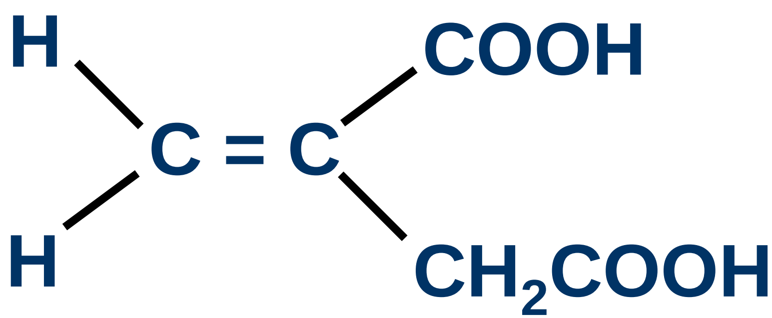
polyacrylic acid



Acrylic acid



Maleic acid

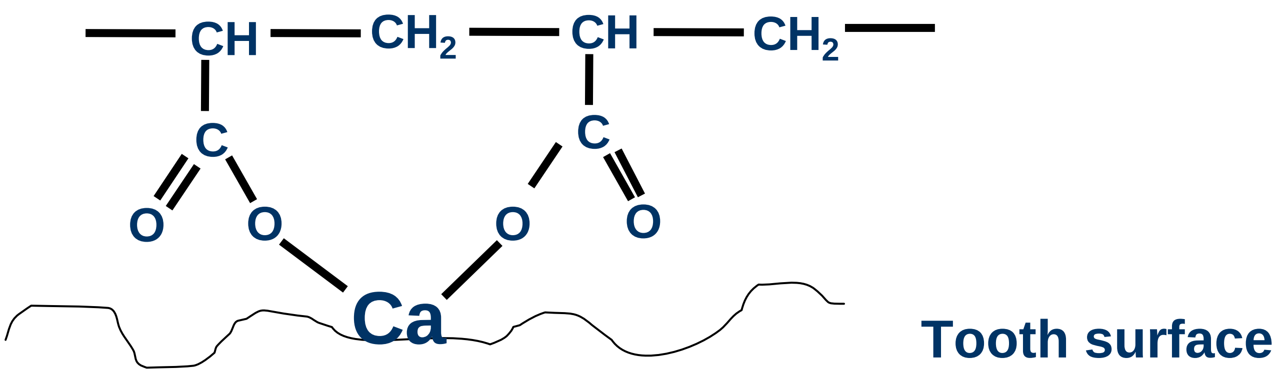


Itaconic acid

Comparison with zinc phosphate cements

Advantages:

- Very good biological properties
- Adhesion to the tooth tissues
- Higher pH than for Zn phosphate cement
- Lower disintegration in the mouth environment



Disadvantages:

- Shorter working time, worse manipulation properties – too high viscosity of the liquid
- Lower resistance to the mechanical load
- High creep

Silicate cements (silico phosphate cements)

The very first translucent „aesthetic" anterior restorative material (1900-1950)

- **Powder:** particles of acid-soluble calcium fluoroalumino-silicate glass (oxide composition SiO_2-Al_2O_3-CaO/CaF_2)
- **Liquid:** solution of app. 50 % phosphoric acid H_3PO_4, partially neutralized with Al a Zn

Too acidic, **irritating pulp**, brittle and highly soluble, but **releasing F^- ions**.

Even-though not used anymore it **opened a way** how to prepare aesthetic cements with anticariegenic potential

Glass ionomer cements (filling, lining and luting)

(**GIC** – **G**lass-**I**onomer **C**ements)

First prepared by Wilson, Kent and McLean, 1971

Types:

- Chemically curing, classical, autocuring

  - setting via neutralization reaction

- Hybrid, fortified, reinforced, resin-modified glass ionomer cement, dual-cured

  - setting reaction is free-radical polymerization and neutralization

Chemically curing glass ionomer cements

Main components:

- **Powder:** particles app. (10 – 20 μm) of acid-soluble calcium fluoroaluminosilicate glass, with high content of Ca (**Sr, La-RTG**), Al, P, F^- and, in some types, freeze-dried polyacid to improve manipulation properties, pigments

  Reactivity of glass particles must be decreased by special (thermal or acidic treatment – depletion of surface ions)

  if Ag particles are added – metal-reinforced glass ionomer cement (cermets)

- **Liquid**: solution (viscous) 25 – 40 % of poly(itaconic, acrylic, maleic acid or their copolymers)

  - tartaric acid app. 5 % (to prolonge WT)

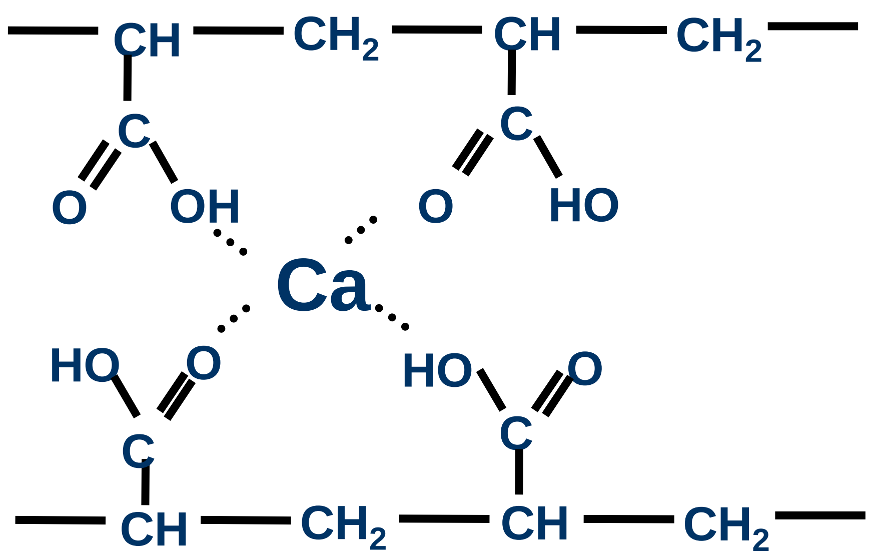
Setting reaction:

1. Particle surface dissolution by polyacid attact – cations release

2. Reaction of Ca and Al cations with COOH groups and formation of amorphous, cross-linked polyacrylates

$$\text{base} + \text{acid} \xrightarrow{\textbf{water}} \text{polysalt} + \text{water}$$

$$(Ca^{+2} + -COO^{-} \longrightarrow -COOCa + H_2O)$$



Hybrid glass ionomer cements

fortified, reinforced, resin-modified glass ionomer cement, dual-cured, LC light-cured

- **Powder:** similar to that of chemically curing GIC Ca (Sr, La), Al, P, Si, F glass (5–20 μm)
  - decreased reactivity by thermal, acid treatment (depletion of surface cations)
  - surface modified by silanes (coupling agents, see polymeric materials for details)
  - freeze-dried polyacid with pendant (methacrylate /acrylic) groups

initiators: camphorquinone/amine, dibenzoyl peroxide/amine

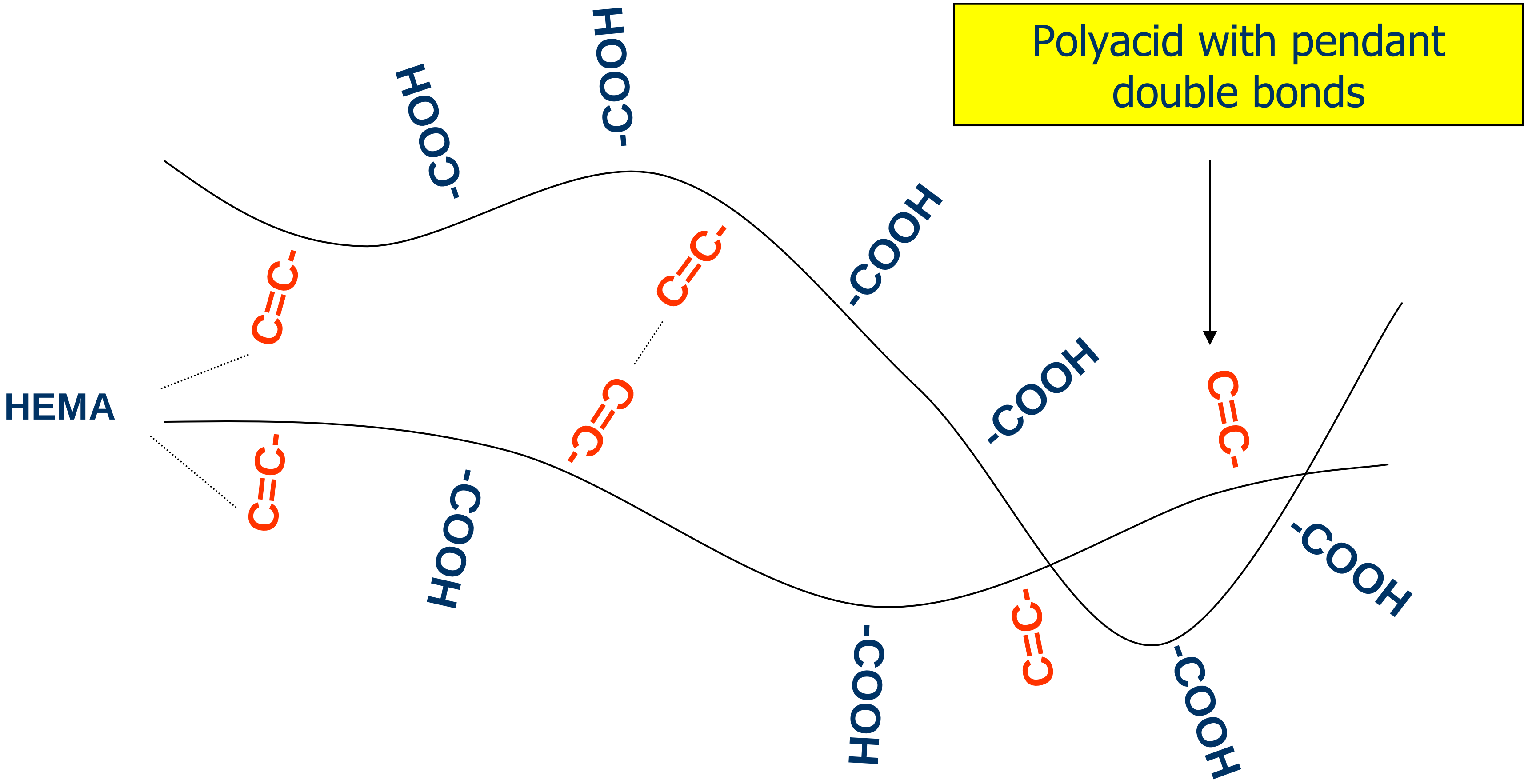
- **Liquid**: an aqueous solution of poly(acrylic, itaconic, maleic acids or their copolymers) with pendant methacrylic /acrylic groups
  - HEMA (2-hydroxyethylmethacrylate)
  - components of an initiating system (camphorquinone)

Setting reaction:

1. Free-radical polymerization of monomeric HEMA and pendant double (methacrylate/acrylate) bonds on a polyacid backbone

$$-C - C^{\cdot} + M \xrightarrow{\textit{CQ, peroxide}} -C - C - M^{\cdot}$$

(compression strength: 50 – 70 MPa/10 min.)



2. Neutralization (acid-base) reaction (compression strength 150 – 180 MPa/24 h)

Advantages:

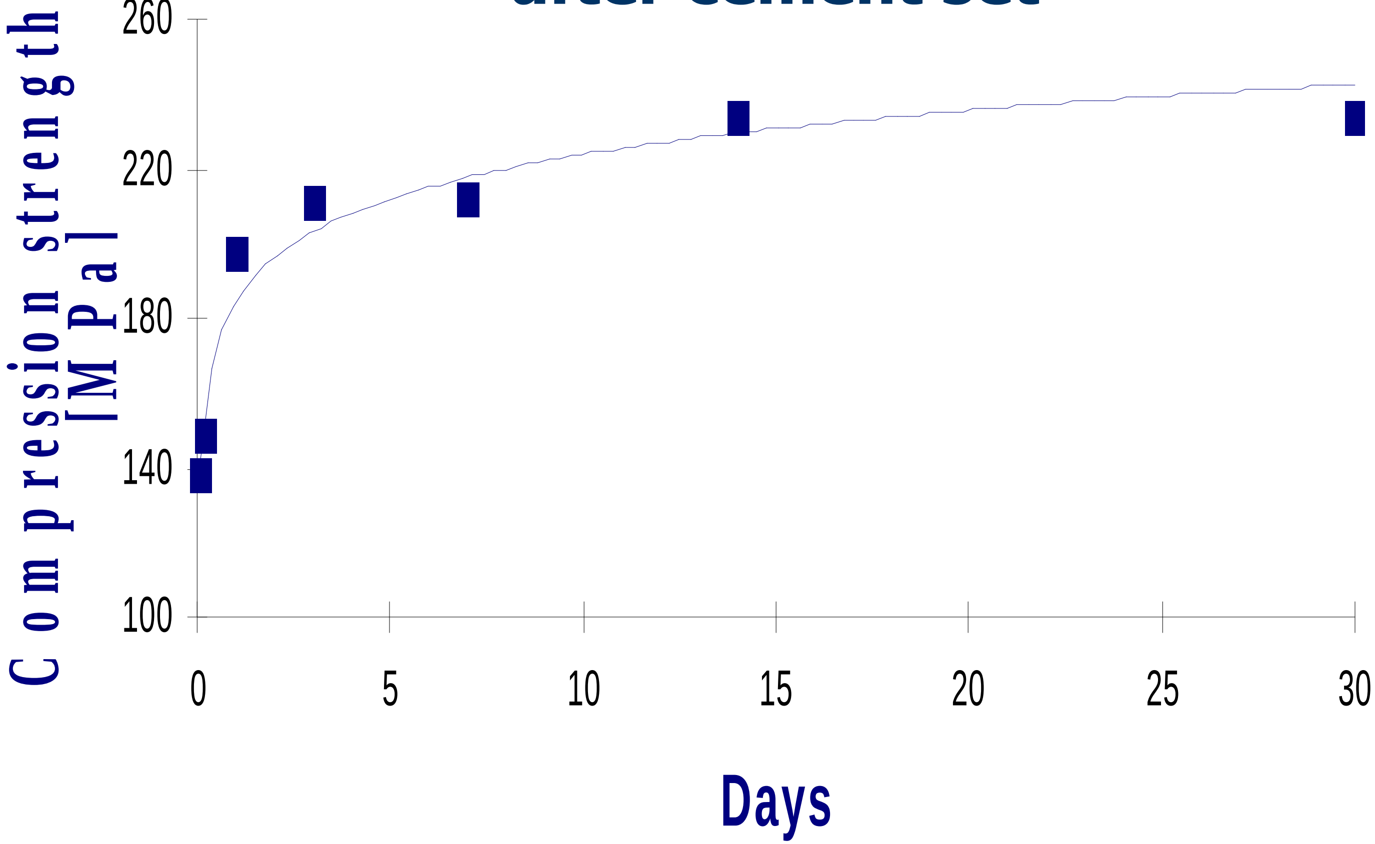
- F^- ions release (support of remineralization processes, increased resistance of enamel and dentine)
- Adhesion to the tooth tissues (Ca^{+2} of enamel and dentin apatite)
- Tolerant to moisture contamination of cavity
- Fast treatment
- Tooth coloured - acceptable aesthetic properties
- Good biological properties (mainly chemically curing types)
- Thermal and mechanical properties similar to human dentin

Disadvantages:

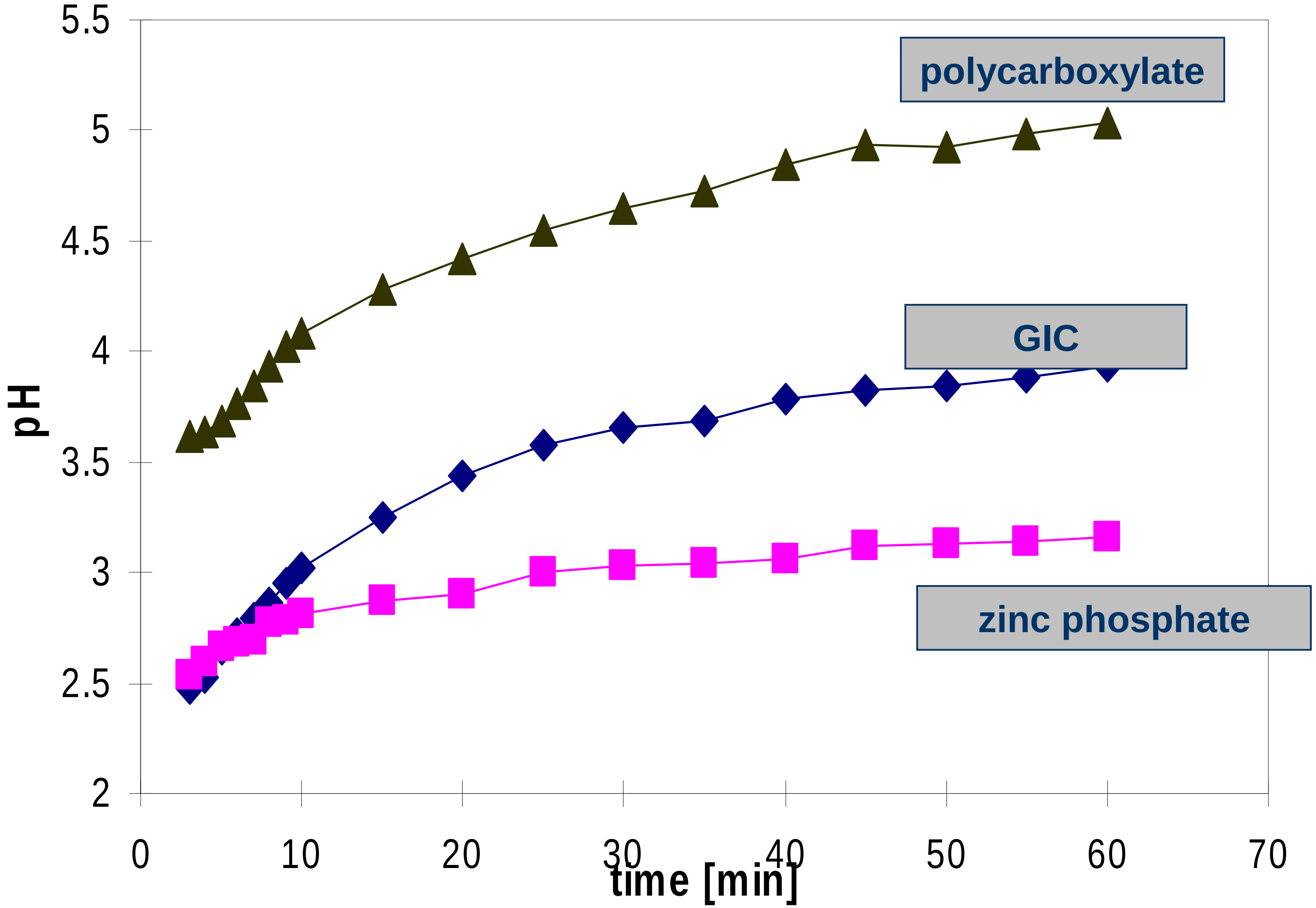
- **Lower resistance to the mechanical load, creep and abrasion (plastification with water)**
- Sensitive to water in app. 24 hours after setting
- Decreased radiopacity
- Long maturation

Few typical properties of GIC

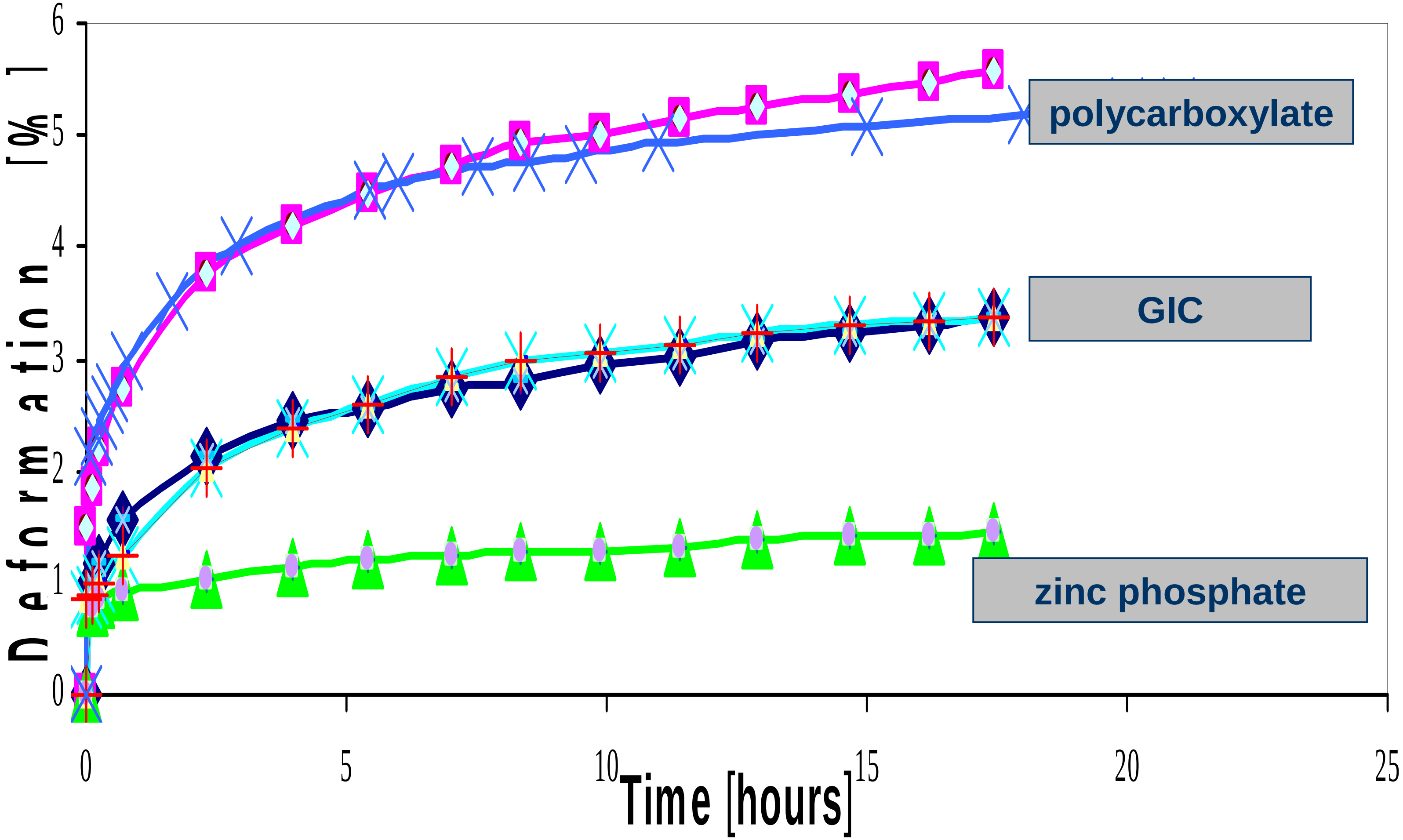
Maturation – strength increase in the first month after cement set



pH increase after cement set



Creep



Deformation [%]
0
1
2
3
4
5
6
0
5
10
15
20
25
Time [hours]
polycarboxylate
GIC
zinc phosphate

Mineral Trioxide Aggregates (MTA cements)

Root-end filling, root perforation repair, pulp capping

(Composed of Portland Cement with radio-opaque fillers e.g. Bi_2O_3)

Main components:

oxide	Mass %
Calcium oxide, CaO	61-67
Silicon oxide, SiO_2	19-23
Aluminum oxide, Al_2O_3	2.5-6
Ferric oxide, Fe_2O_3	0-6
Sulfate Ca (controls setting time)	1.5-4.5

After hydration:

Tricalcium silicate - $3CaO.SiO_2$, dicalcium silicate - $2CaO.SiO_2$ and tricalcium aluminate $3CaO.Al_2O_3$:

Properties of the cement:

Alkaline - similarly to calcium hydroxide (salycilate) cements or to $Ca(OH)_2$ suspensions

Non-aqueous cements

Zinc oxide-eugenol (ZOE, „phenolate") cements

Delivered as powder/liquid – liners, bases, temporary fillings, root canal sealers, paste/paste – temporary cementation

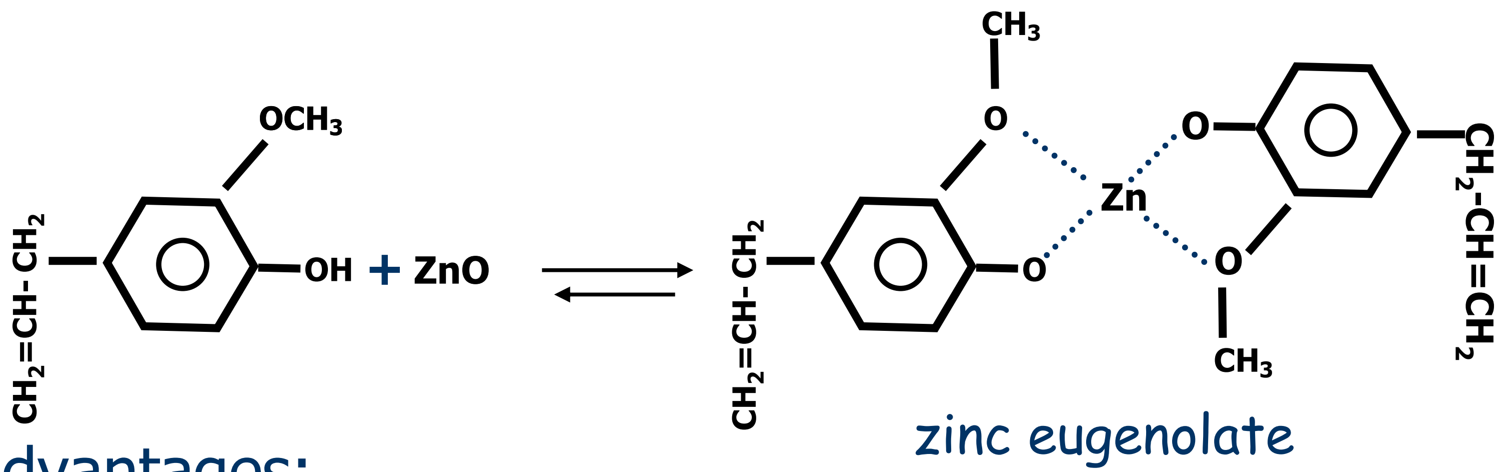
Setting reaction:

water (as an accelerator)

base + acid ⟶ chelate + water

Donor of electrons **Electron acceptor**

- **Powder:** ZnO, covered with Zn stearate, Zn acetate – accelerators, Al_2O_3 – to improve strength
- **Liquid:** eugenol, oil, rosin, acetic acid - accelerator, poly(methylmethacrylate) to improve strength



Advantages:

- Good biological properties (pH 7 after setting)
- Antibacterial properties
- Sedative effect
- Fast setting in the mouth environment (presence of water)
- Ease to dislodge

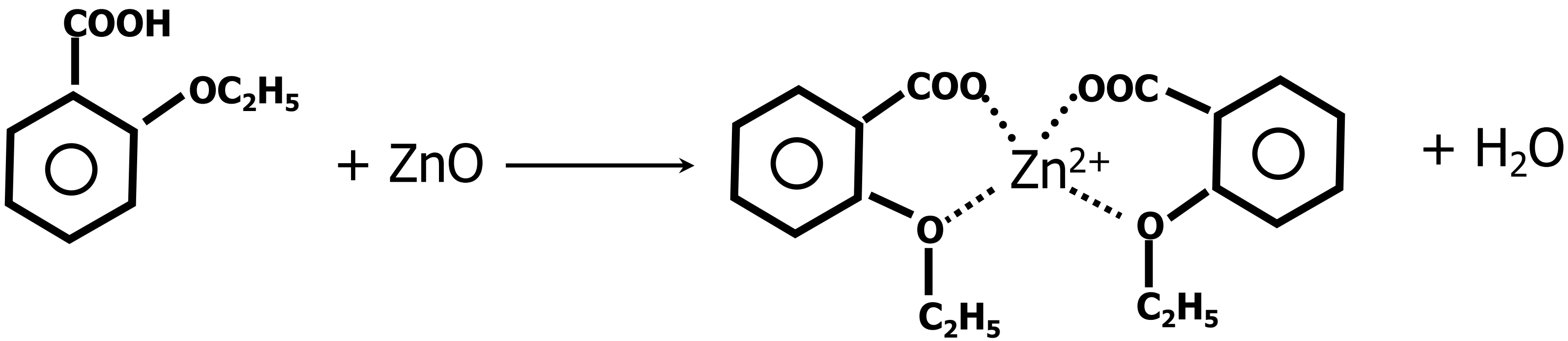
Disadvantages:

- Low strength, not adhesive
- High solubility in water

!! Inhibits free radical polymerization!!

Modified zinc oxide-eugenol /ethoxybenzoic acid (EBA) cements

Incorporation of ethoxybenzoic acid **(EBA)** increases strength of ZOE cements



Mixtures 62.5 % EBA and 37.5 % eugenol, powder contains up to 30 % of Al_2O_3 – to increase strength

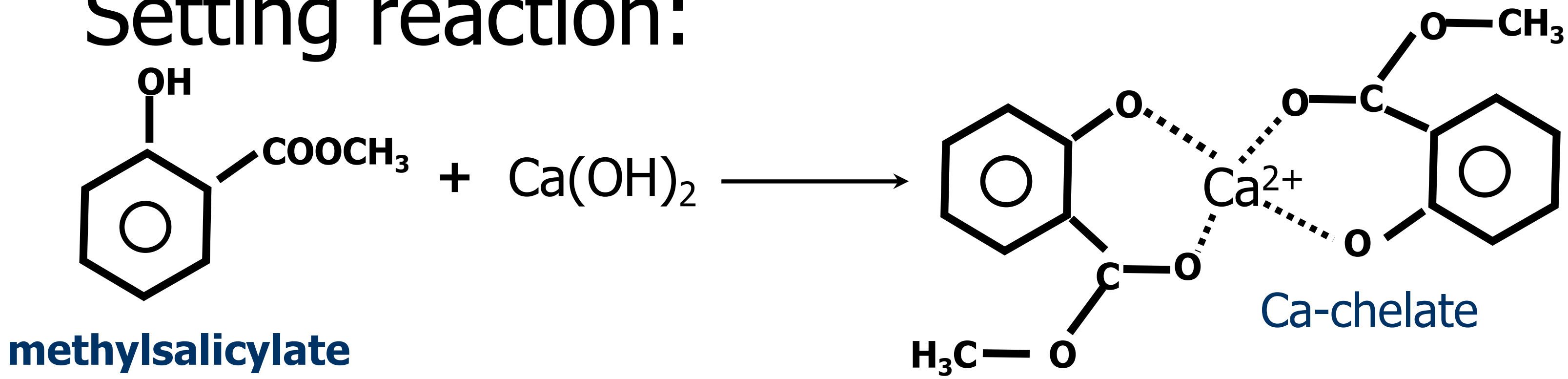
Non-eugenol cements for temporary cementation are frequently based only on **EBA type structures – to avoid eugenol inhibiting effect**

Calcium hydroxide (salicylate, chelate) cements

paste/paste, used as liners, bases, indirect or direct pulp capping

- **Paste A:** $Ca(OH)_2$, plasticizer (N-ethyl toluensulphonamide)
- **Paste B:** salicylates, disalicylates, fillers - $BaSO_4$ (RTG), TiO_2, $CaSO_4$

Setting reaction:



Low strength, alkaline after hydrolysis, antibacterial effect, induce formation of secondary dentine

Some properties of dental cements and composites

Cement	ST [min]	FT [µm]	CS [MPa]	Solubility %	Pulp irritation	Adhesion [MPa]	Elution **F-** **[µg/cm²]**
Zinc phosphate	5-6	20[1]	90-120	0.06	moderate	0	0
Polycarboxylate	5-6	20-30	40-60	0.06	mild	1-3	0
Glass ionomer	4-6	20-25	170-200	1.3	mild-moderate	7-10*	150-600
Zinc oxide-eugenol (luting type)	4-10	25	20-50 (100 EBA)	0.04	mild	0	0
Calcium hydroxide	3-4	-	5-20		mild	0	0
Composite	Chem. Cured 2-4	5-10	200-400	0-0.01	moderate	10-20**	0-5
Dentin			250-300				
Enamel			350-400				

ST- setting time, FT- film thickness , CS - compression strength after 24 hours, *using primers and **adhesive systems, [1]max 25 µm (ČSN EN ISO 9917-1

Phillips´s Science of Dental Materials, KJ Anusavice, Sounders 2003