

# Dental cements

## Chemistry, composition, properties

Pavel Bradna

[pavel.bradna@lf1.cuni.cz](mailto:pavel.bradna@lf1.cuni.cz)

Institute of Dental Medicine

First Faculty of Medicine, Charles University  
Prague 2022

# What are cements?

## In the Oxford dictionary:

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

## In dentistry

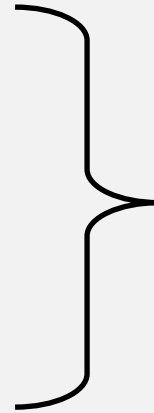
- **Luting, fixation, cementation** - i.e. luting inlays crowns, bridges, veneers on the prepared tooth,
- To **protect pulp** from heat („thermal insulation“) and from chemical irritation, bacterial attack,
- Temporary filling material.

# Classification of dental cements:

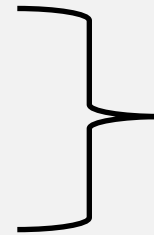
- Zinc phosphate,
- **Silicate** (silicophosphate cements),
- Polyalkenoate:
  - Zinc polycarboxylate („polycarboxylate“),
  - Glass-ionomer,
- Calcium silicate („Mineral Trioxide Aggregates“, MTA),
- Zinc oxide-eugenol („phenolate“),
- Calcium hydroxide („salicylate“),
- Resin cements.

# Types according to the solvent:

- Zinc phosphate,
- Silicate,
- Polyalkenoate:
  - Polycarboxylate,
  - Glass ionomer,
- Calcium silicate (MTA),
- Zinc oxide-eugenol,
- Calcium hydroxide,
- Resin cement.



**Water-based**



**Non-aqueous**

# Classification according to the setting reaction:

1. **Setting via acid-base reaction** (neutralization with aqueous systems) between basic (alkaline) powder and acidic liquid

- Zinc phosphate,
- Silicate,
- Polyalkenoate:
  - Polycarboxylate,
  - Glass ionomer,
- Calcium silicate
- Zinc oxid-eugenol
- Calcium hydroxide

## 2. **Setting via radical polymerization** – similarly to polymerization of methacrylic monomers

- Resin cements

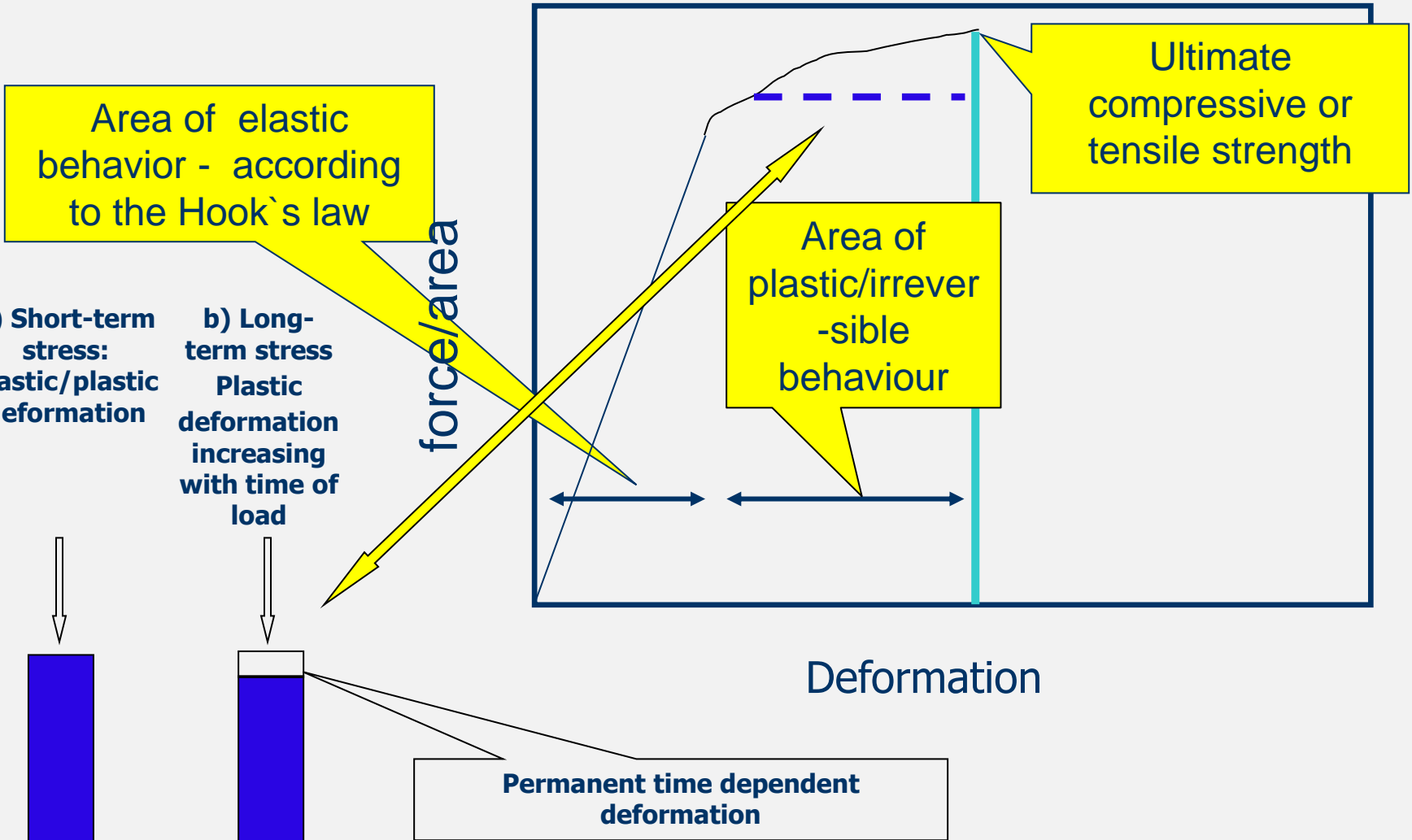
## 3. **Setting via combination of both mechanisms**

- Hybrid glass-ionomer cements

# 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 until cement reaches such resistance that **external force** under specific conditions **will not make its** permanent deformation.

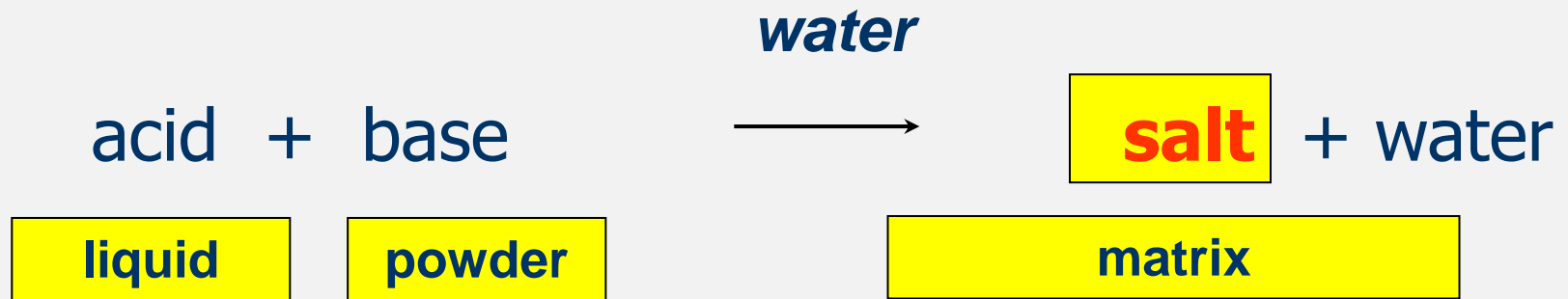
- Strength and creep





# Water-based cements

## Setting reaction - neutralization



### Why water is needed?

- enables dissociation of acidic groups,
- hydrates particles of cements and releases alkaline ions from their surface,
- acts as a reaction environment.

# Zinc phosphate cements

In dentistry used since 19th. century.

Temporary filling, lining and luting material

Main components:

- Powder: ZnO (90%) + MgO (10%)
  - Deactivation – sintering at 1100 – 1200°C (reduction of specific surface area and densification of ZnO)
  - Grinding to 10 – 20 μm
  - Dying with pigments
- Liquid: 33 – 40 % aqueous phosphoric acid H<sub>3</sub>PO<sub>4</sub>:
  - Partly neutralized (buffered) by Al(OH)<sub>3</sub> (app. 3 %) and ZnO (0-10 %) to slow setting reaction during mixing

# Setting reaction:

## 1. Reaction of pure ZnO and the phosphoric acid:



**Fast setting reaction, fast crystallization  
unsuitable properties**

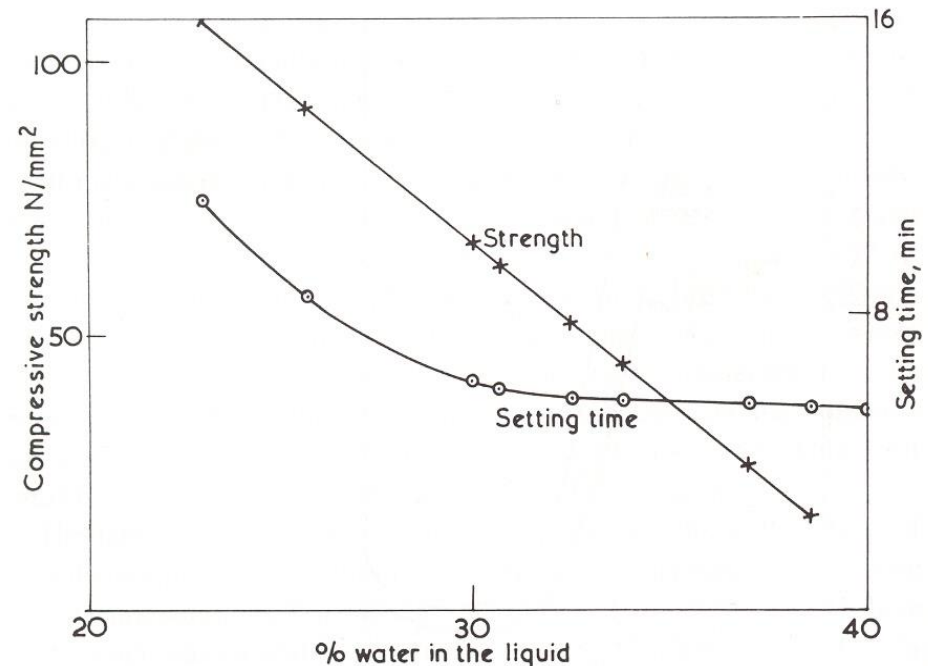
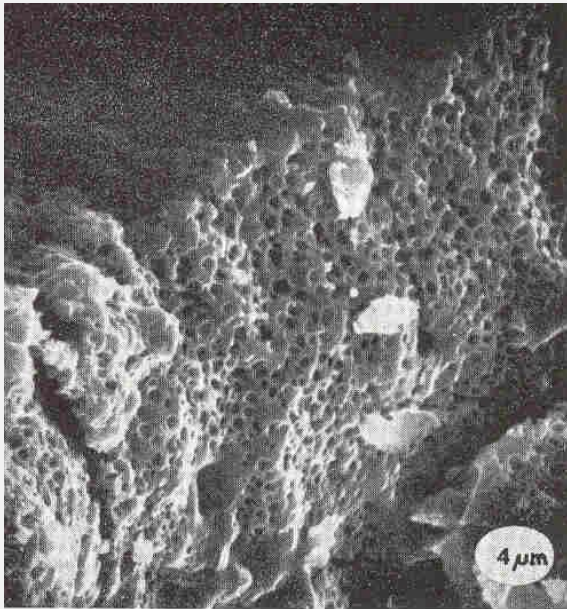
When  $\text{H}_3\text{PO}_4$  is partially neutralized with **Zn** and **Al ions** different setting mechanism

## 2. At $\text{Al}^{+3}$ presence:

Precipitation of amorphous  $\text{Al}^{+3}$  phosphates on the surface of ZnO particles, which inhibits penetration of phosphoric acid to particle core and lowers the rate of hopeit crystallization

# Structure of set cement:

1. Particles of incompletely dissolved ZnO (present in a great excess) covered with Al phosphate in matrix of **brittle amorphous/crystalline Zn phosphate**.
2. High porosity (diameter app.  $0.5 \mu\text{m}$ ) arising from excess unbound water - **decreases strength of cement and makes it permeable and more soluble in water.**



**higher amount of water in the acid decreases cement properties (effect of higher porosity)**

# Zinc polycarboxylate (polycarboxylate) cements

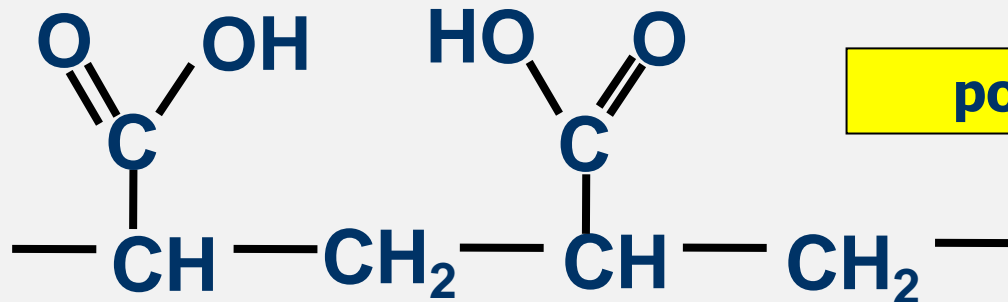
(lining and luting material)

Invented by Smith in 1968

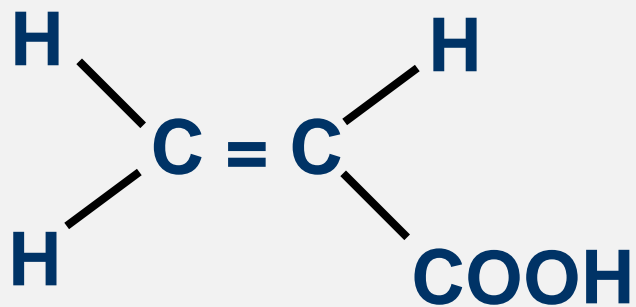
## Main components:

- Powder: similar to that used for zinc phosphate cement,  $\text{Al}_2\text{O}_3$ ,  $\text{SnF}_2$  are also added to improve its strength, to release  $\text{F}^-$  and improve its manipulation,
- Liquid: 40 – 50 % aqueous solution of polyacrylic acid or copolymers of acrylic acid with itaconic or maleic acids.

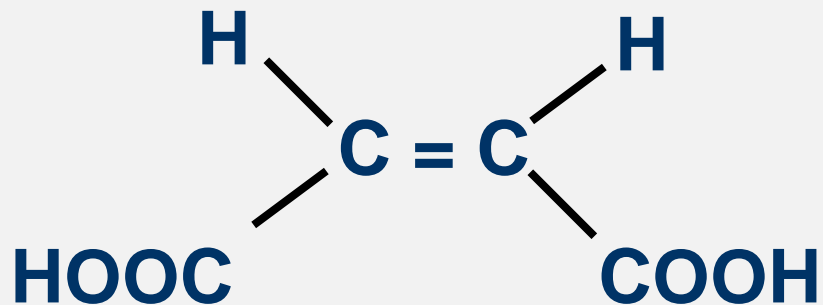
(molecular weight app. 20 000-50 000 - **VISCOUS**)



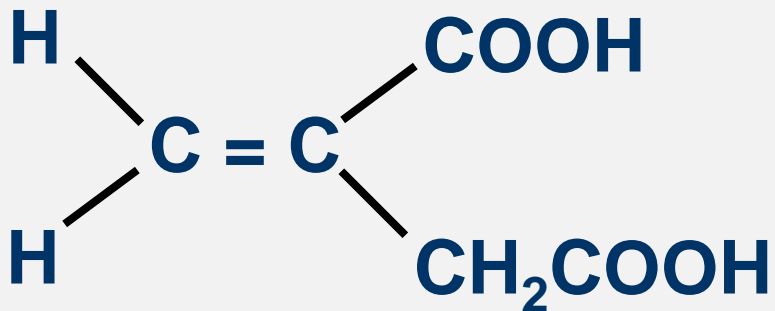
polyacrylic acid



**Acrylic acid**



**Maleic acid**

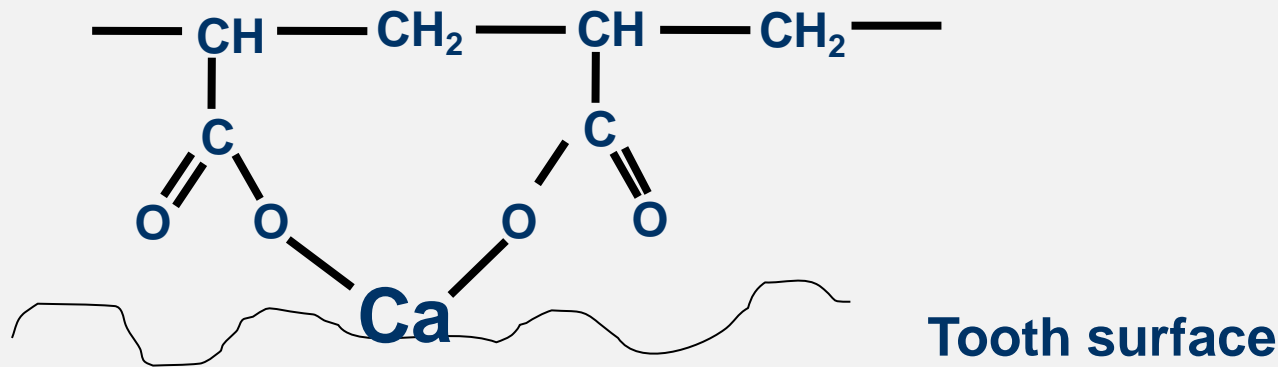


**Itaconic acid**

# Comparison with zinc phosphate cements

## Advantages:

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



## Disadvantages:

- Shorter working time, worse manipulation – because of 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 fluoroaluminosilicate glass (oxide composition  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO/CaF}_2$ ),
- **Liquid:** solution of app. 50 % phosphoric acid  $\text{H}_3\text{PO}_4$ , partially neutralized with Al a Zn.

Too acidic, irritating pulp, brittle and highly soluble, but releasing  $\text{F}^-$  ions.

Not used **anymore** but 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 dual-cured, light cured (LC)
  - setting reaction via combination of free-radical polymerization and neutralization

# Chemically curing glass-ionomer cements

## Main components:

- **Powder:** particles app. (10 – 20  $\mu\text{m}$ ) of acid-soluble calcium fluoroaluminosilicate glass, with high content of Ca (Sr, La-RTG), Al, P, F<sup>-</sup> and pigments

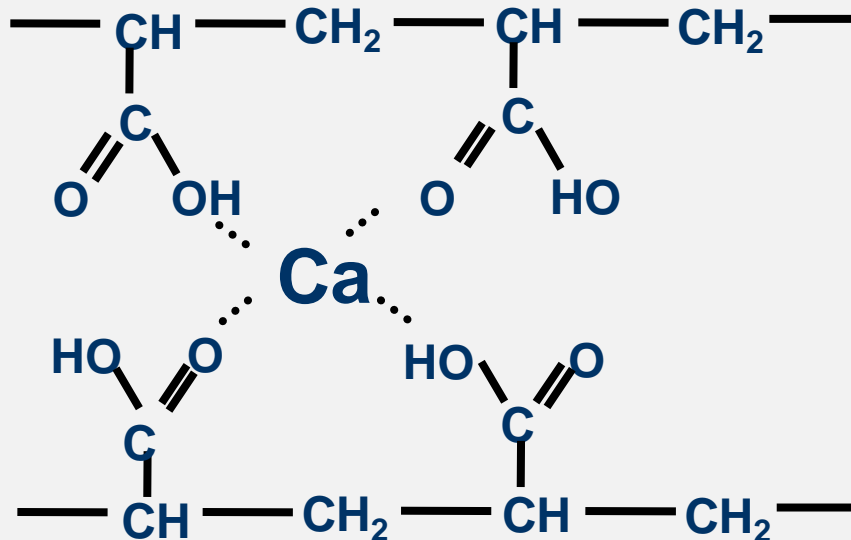
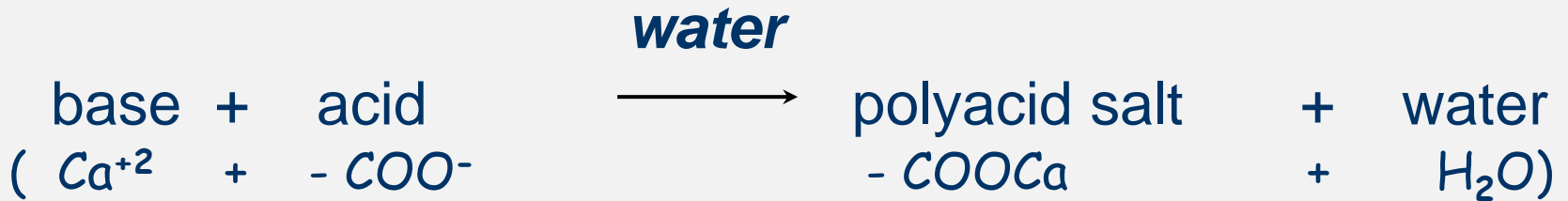
Reactivity of glass particles must be decreased by special (thermal or acidic treatment – depletion of surface ions)

(cermets) - Ag particles are added (metal-reinforced glass-ionomer cement) to improve the strength of GIC

- **Liquid:** solution (viscous) 25 – 40 % of poly(itaconic, acrylic, maleic acid or their copolymers)
  - tartaric acid app. 5 % (to prolonge WT)

# Setting reaction:

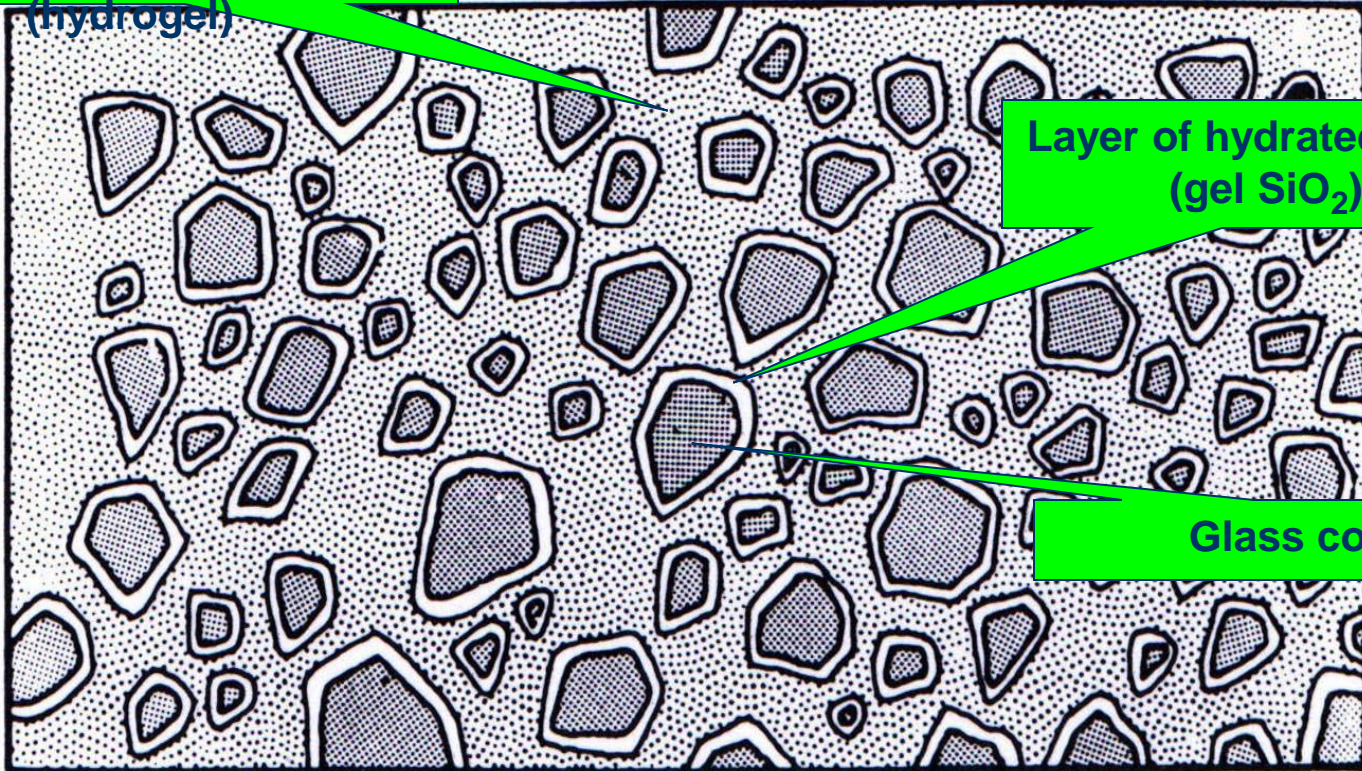
1. Particle surface dissolution by the polyacid attack – Ca and Al cations released,
2. Reaction of Ca and Al cations with COOH groups and formation of amorphous, cross-linked polyacrylates.



# Scheme of GIC structure after being fully set

Matrix of amorphous Ca, Al  
polyacrylates

(hydrogel)



Layer of hydrated glass  
(gel SiO<sub>2</sub>)

Glass core

# Why tartaric acid retarder is needed ?

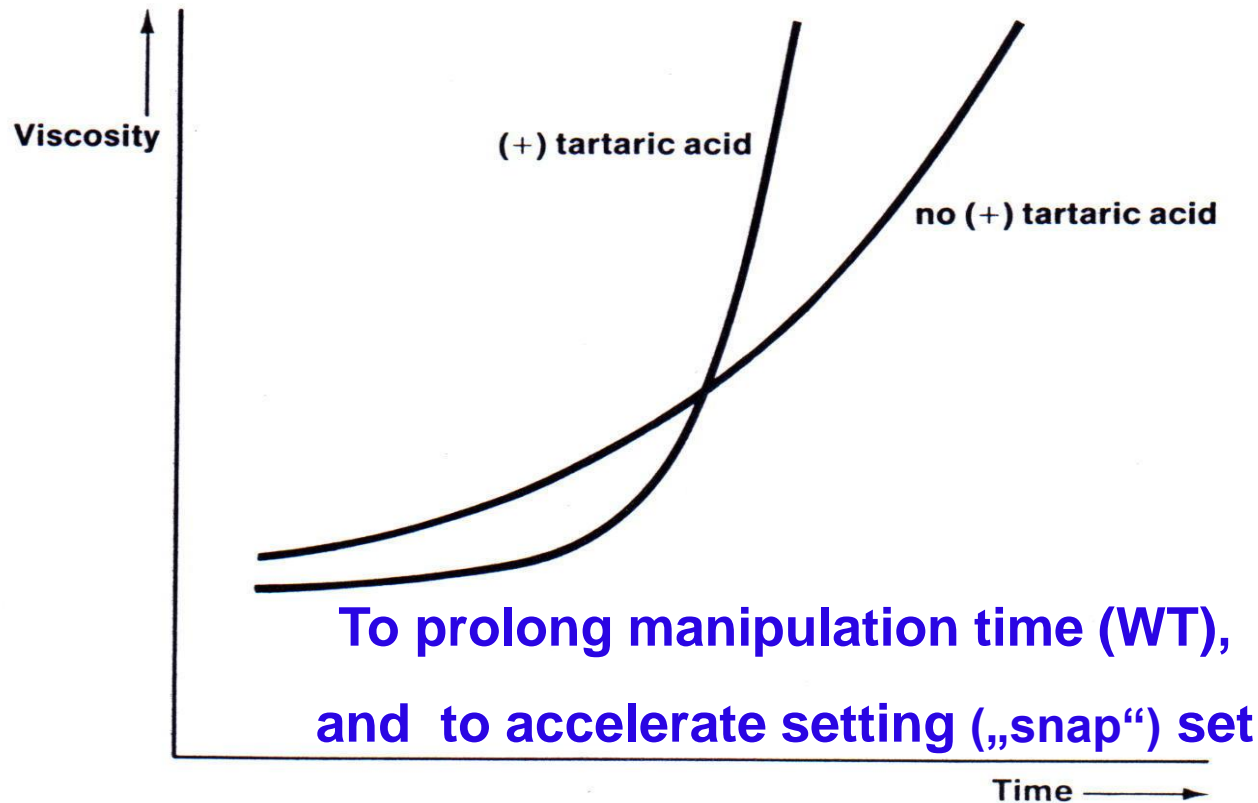


Figure 5.13 Effect of tartaric acid on viscosity development (Hill & Wilson, 1988b).

## Hybrid glass-ionomer cements

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

- **Powder:** similar to that of classical GIC with Ca (Sr, La), Al, P, Si, F glass (5–20  $\mu\text{m}$ )
  - surface modified by coupling agents, see polymeric materials and composites for details)
  - freeze-dried polyacid with pendant methacrylate /acrylic groups.

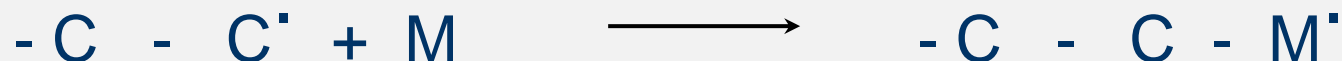
In some cements initiators: camphorquinone, dibenzoylperoxide, p-toluenesulfinate sodium salt

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

## Setting reaction:

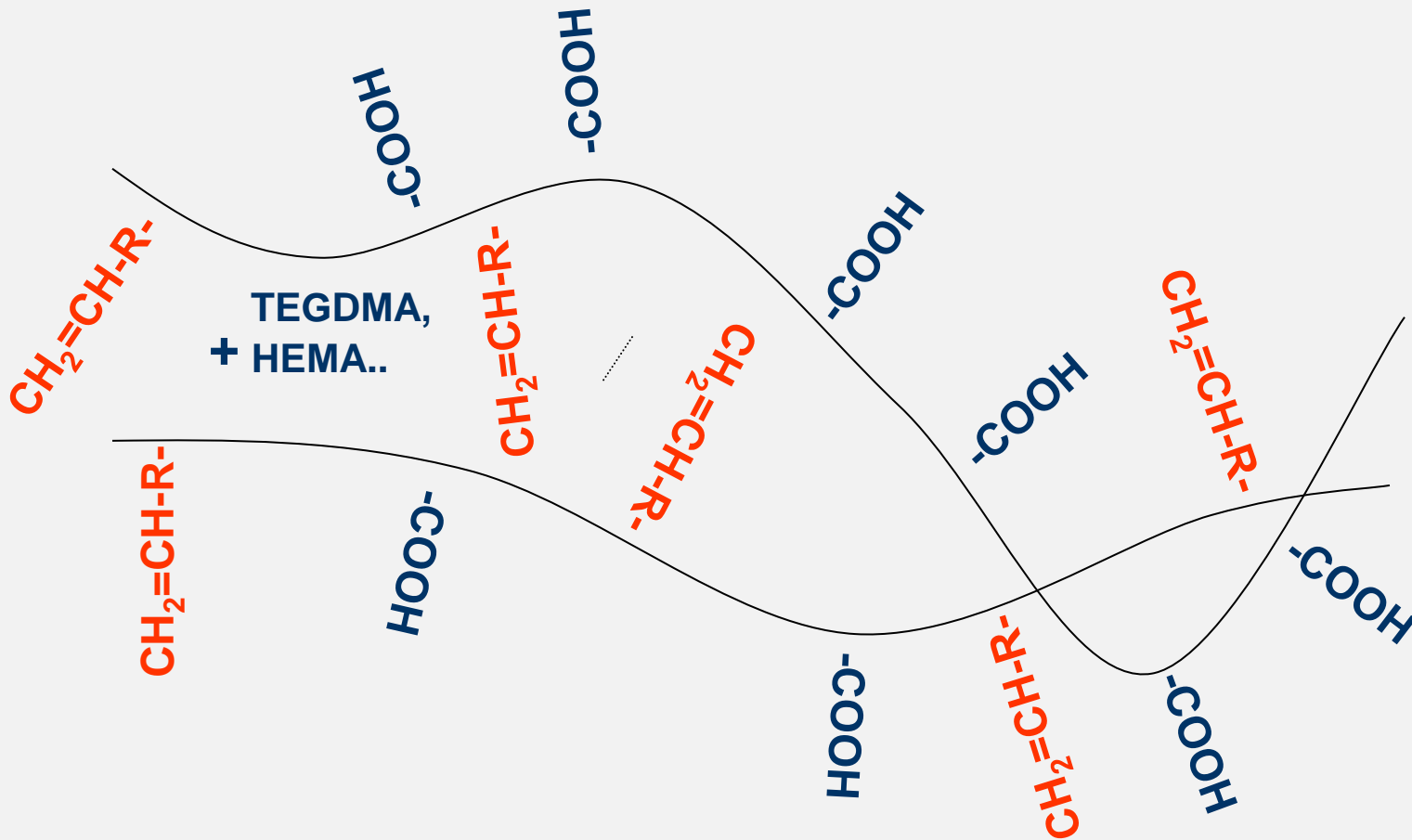
1. Free-radical polymerization of monomeric HEMA, TEGDMA... with pendant double bonds (methacrylate/acrylate) on a polyacid backbone

***CQ, peroxide/amine..***





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



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



## Advantages:

- F<sup>-</sup> ions release
- Adhesion to the tooth tissues (Ca of enamel and dentin apatite)
- Good biological properties (mainly chemically curing types)
- Fast treatment, tolerant to moisture
- Acceptable aesthetic properties
- Thermal and mechanical properties similar to human dentine

## Disadvantages:

- **Lower resistance to the mechanical load, creep and abrasion (plastification with water)**
- Sensitive to the loss and water sorption
- Long maturation

# Calcium silicate cements

(Mineral Trioxide Aggeregates, MTA cements)

Invented app. 1990, root-end filling, pulp capping

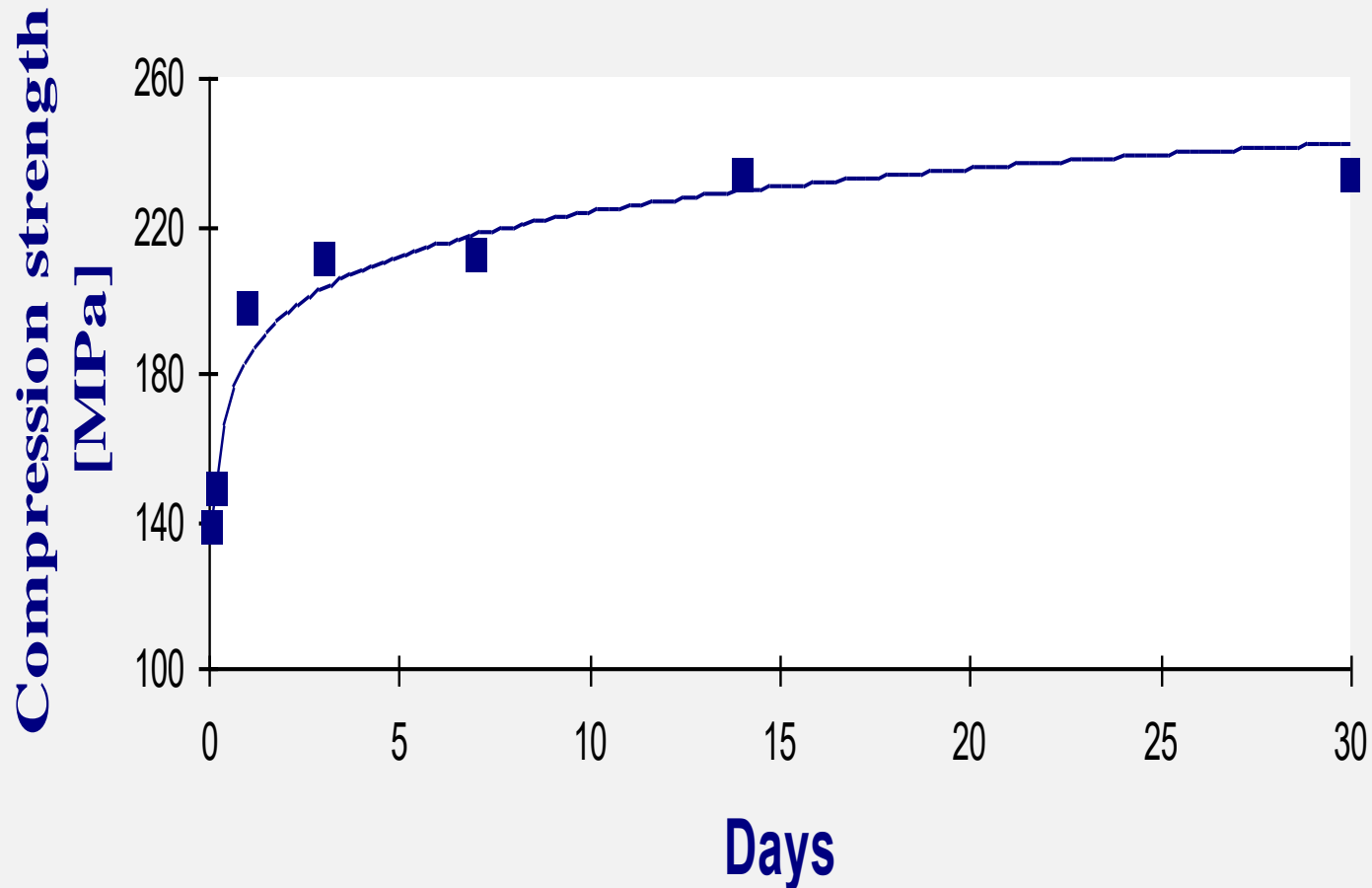
(Similar composition as Portland cement with radio-opaque fillers e.g.  $\text{Bi}_2\text{O}_3$ )

- **Powder:** tricalcium silicate -  $3\text{CaO}\cdot\text{SiO}_2$ ,  
dicalcium silicate -  $2\text{CaO}\cdot\text{SiO}_2$   
tricalcium aluminate -  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$   
bismuth oxide -  $\text{Bi}_2\text{O}_3$  (to increase radiopacity)  
calcium sulphate – a setting retarder
- **Liquid:** aqueous phosphate buffer solution

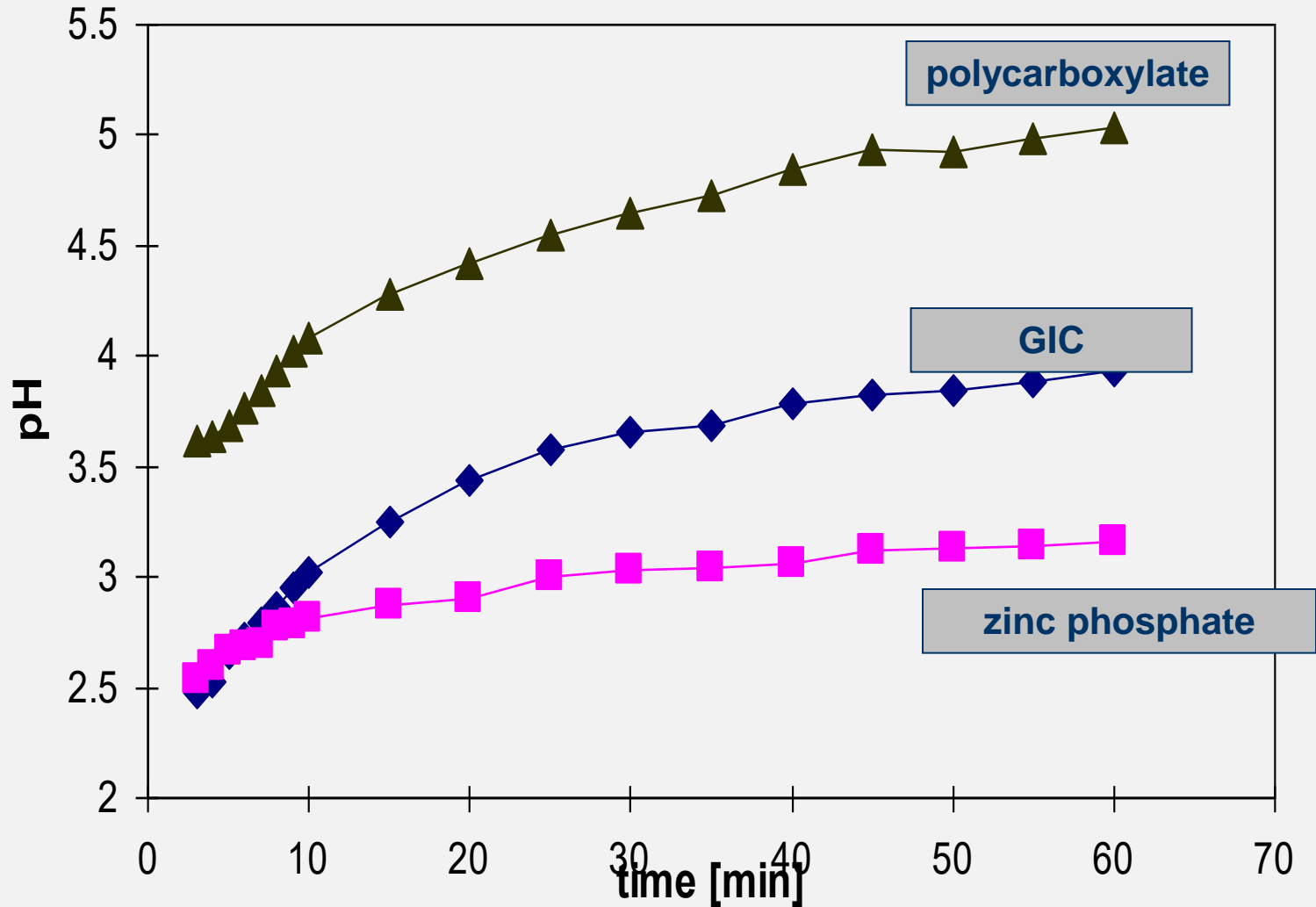
Alkaline - similar to calcium hydroxide cements but non resorbable

# Few typical properties of GIC

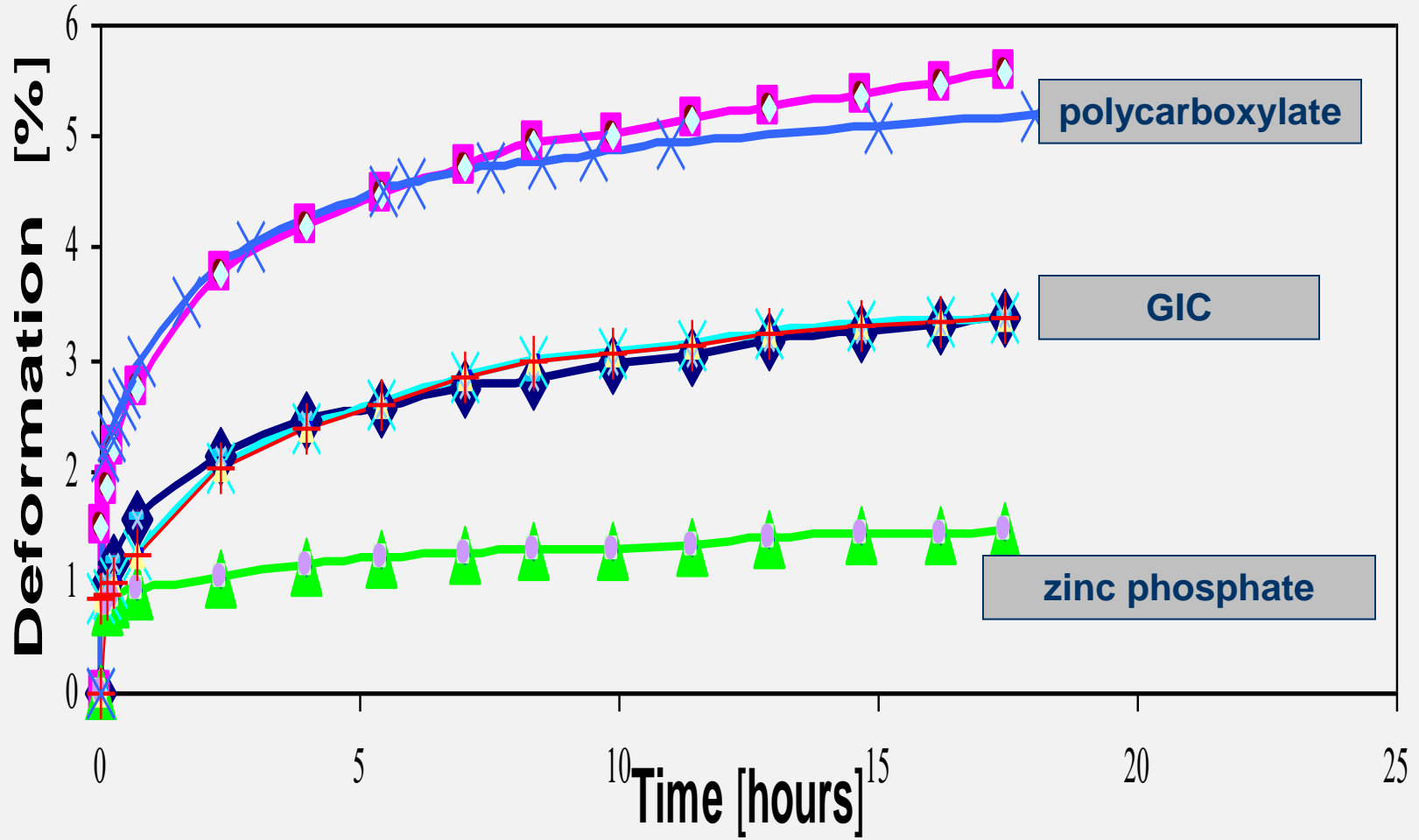
## Maturation – strength increase in the first month



# Fast pH increase after cement set



# Creep

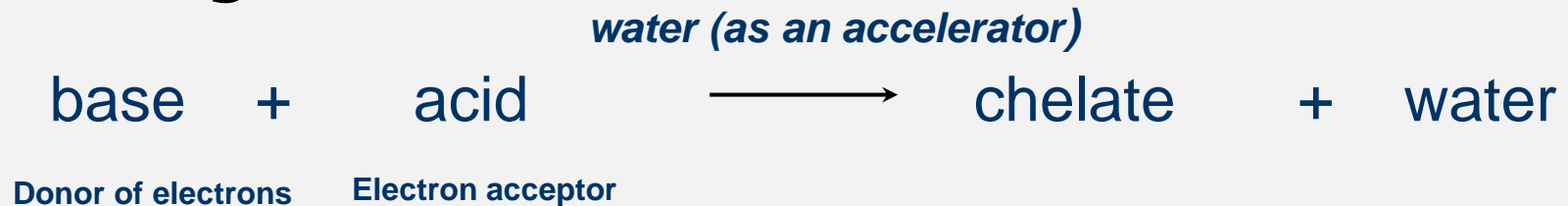


# Non-aqueous cements

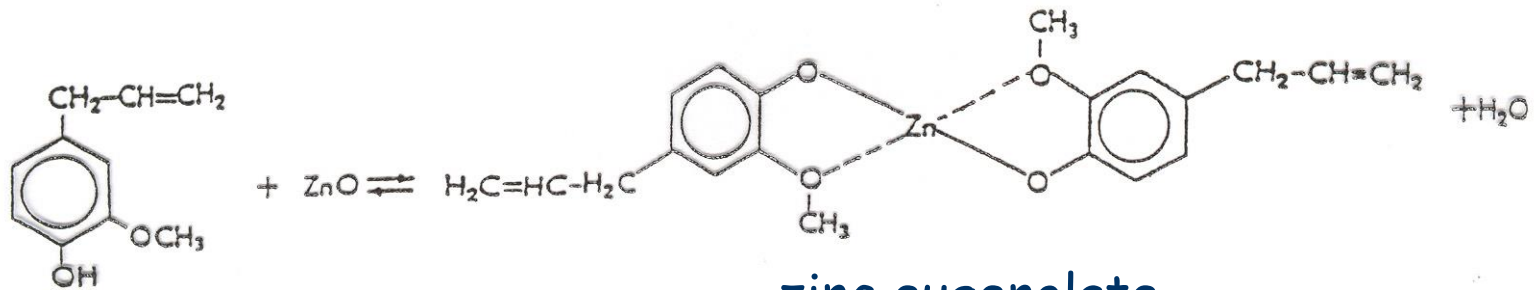
# Zinc oxide-eugenol (ZOE, „phenolate“) cements (first introduced at the end of 19th. century)

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

## Setting reaction:



- **Powder:** ZnO, covered with Zn stearate, Zn acetate – accelerators, Al<sub>2</sub>O<sub>3</sub> – to improve strength
- **Liquid:** oil of cloves or eugenol, mineral oil, rosin, acetic acid - accelerator, poly(methylmethacrylate) to improve strength



eugenol (4-allyl-2-methoxyphenol)

zinc eugenolate

## 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:

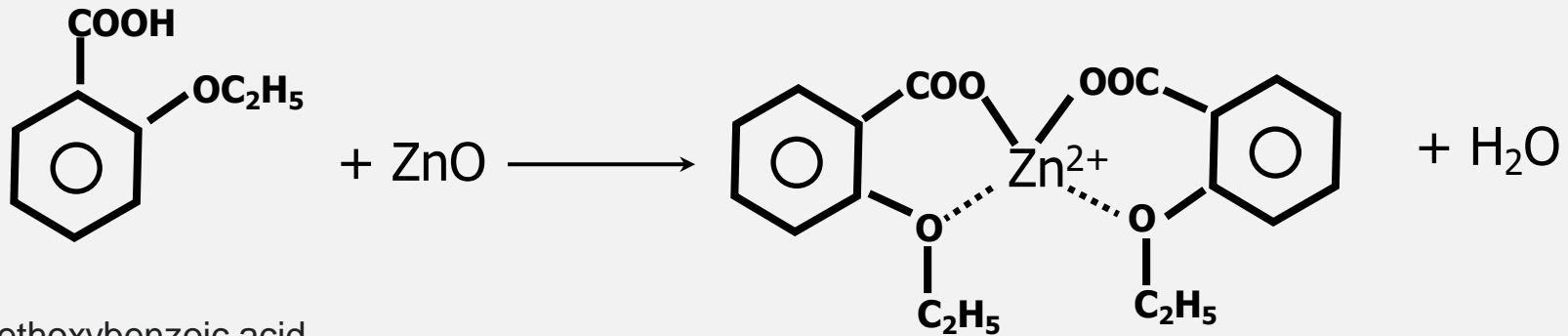
- Low strength, not adhesive
- High solubility in water

**!! Phenol - inhibits free radical polymerization!!**



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

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



**The so called „non-eugenol (NE)“ cements for temporary cementation are frequently based only on EBA type structures – to avoid eugenol inhibition effect**

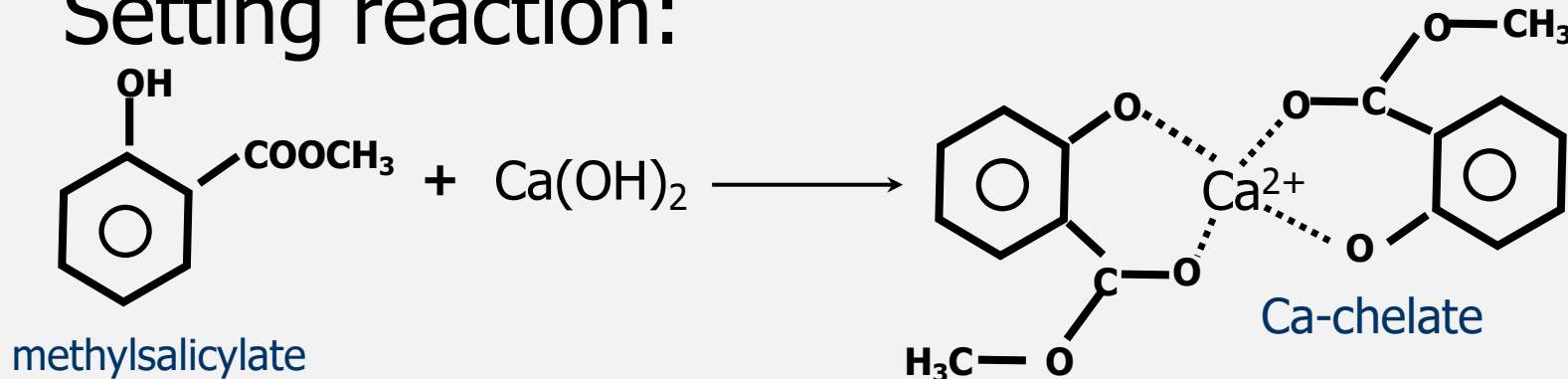
# Calcium hydroxide (salicylate) cements

introduced app. 1960

paste/paste - used as liners, indirect pulp capping

- **Paste A:**  $\text{Ca}(\text{OH})_2$ , plasticizer (N-ethyl toluensulphonamide)
- **Paste B:** salicylates, disalicylates, fillers -  $\text{BaSO}_4$  (RTG),  $\text{TiO}_2$ ,  $\text{CaSO}_4$

Setting reaction:



**Low strength, alkaline after hydrolysis, antibacterial effect, induce formation of secondary dentine but prone to resorption – dissolution**

# Resin cements

They are composites or *compomers* (usually two-component LC and CC):

with decreased amount of filler particles – to reduce cement viscosity – flowable material

with small particles to reach film thickness below 20  $\mu\text{m}$

Other properties:

- ✓ High mechanical resistance
- ✓ Excellent aesthetic properties
- ✓ Low solubility in oral environment

# COMPOMERS

A hybrid materials „combining“ COMPOsite and glass-ionoMER  
(Polyacid modified composite resins)

## Synergetic combination of composites and glass ionomer cements

### a) From composites

- ✓ Mechanical resistance
- ✓ Excelent aesthetic properties
- ✓ One-component

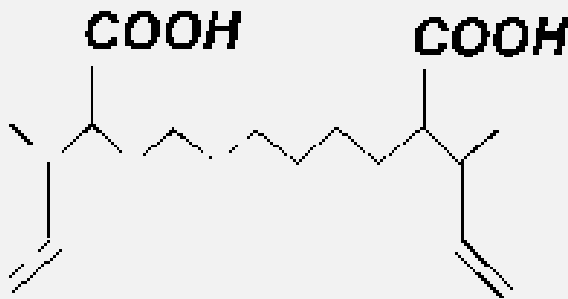
### b) From glass ionomers

- ✓ F<sup>-</sup> release
- ✓ Adhesion to the tooth tissues

# Main components:

## 1. Matrix:

Monomers with **COOH groups** (app. 5 %),  
BIS-GMA, TEGDMA, UDMA etc.



e.g. aduct of alkyldiacarboxylic acid and HEMA

## 2. Fillers:

Ca, Sr reactive glass similar to that of GIC, Ba  
glass (RTG), YbF<sub>3</sub>

Properties similar to composite materials but lower  
resistance to mechanical forces, abrasion etc.

# Setting reaction

- Prevails free-radical polymerization
- Neutralization between COOH groups of monomers and basic cations only in a small extent after water sorption (long-term effect)

Properties similar to composites but lower mechanical resistance

# Some properties of dental cements and composites

Cement	ST [min]	FT [ $\mu\text{m}$ ]	CS [MPa]	Adhesion [MPa]	Elution F- [ $\mu\text{g}/\text{cm}^2$ ]
Zinc phosphate	5-6	20 <sup>1</sup>	90-120	0	0
Polycarboxylate	5-6	20-30	40-60	1-3	0
Glass-ionomer	4-6	20-25	170-200	7-10*	150-600
Zinc oxide-eugenol (luting type)	4-10	25	20-50	0	0
Calcium hydroxide	3-4	-	5-20	0	0
Composite	Chem. Cured 2-4	5-10	200-400	10-30**	0-5

ST- setting time, FT- film thickness , CS - compression strength after 24 hours, \*using primers, \*\*with adhesive systems (shear bond strength measurement), <sup>1</sup>max 25  $\mu\text{m}$  ČSN EN ISO 9917-1

Phillips' s Science of Dental Materials, KJ Anusavice, Saunders 2003

# Literature:

- Craig RG., Powers JM., WatahaJC:  
Dental Materials, Properties and Manipulation  
8th. Edition, Mosby
- Powers JM., Sakagushi RL: Craig's Restorative Dental  
Materials, 12th. Edition, Mosby
- Gladwin M., Bagby M.: Clinical Aspects of Dental  
Materials, Theory, Practice and Cases, 2nd. Edition,  
Lippincott Williams/Williams
- Anusavice KJ.“ Phillips' Science of Dental Materials,  
11th Edition, Saunders



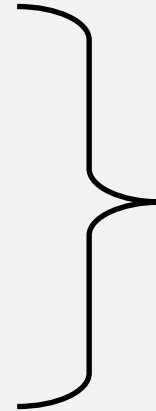
# Dental cements are formed by:

1. Reaction of acids with bases – 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 the acid-base reaction and free-radical polymerization.

# Types according to setting reaction:

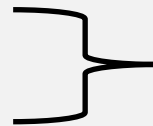
## Setting reaction via acid-base reaction:

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



**Water-based**

- Zinc oxide-eugenol,
- Calcium hydroxide,



**Non-aqueous**

## Setting reaction via free radical polymerization

- Hybrid glass ionomer,
- Resin cement.

**Water-based**

**Non-aqueous**