Impression materials

Chemistry and properties

Pavel Bradna
pavel.bradna@lf1.cuni.cz

Institute of Dental Medicine

1st. Faculty of Medicine, Charles University, Prague, Czech Republic

Prague, 2019
Purpose:

To prepare accurate and true replicas of oral structures (teeth, mucosa)

The replica is prepared in 2 steps:

Step 1. Making a negative (impression)

Step 2. Prepare a replica - an accurate positive model of teeth and adjacent oral tissues
General requirements

Before set:

1. Good handling properties - easy to prepare/mix, flowable-plastic before set, but viscous enough not to flow out of a tray, adequate working and setting times

2. Capable to fast transformation from plastic to rigid body (setting time up to 5-7 min)

3. Acceptable to a patient
   - not toxic, not irritant, tasteless
After being set:

1. **Accuracy** and good **detail reproduction** (25-50 µm),

2. Dimensional stable,

3. **Elastic, tear resistant, low creep,**

4. Resistant to disinfection solutions,

5. **Compatible with model (gypsum) materials,**

6. **Cost effective.**
Important properties and terms

- Hydrophilic/hydrophobic,
- Pseudoplastic/thixotropic,
- Elastic, plastic (permanent, irreversible) deformations,
- Strength,
- Working time,
- Setting time.
Important properties of impression materials before setting

Hydrophobic/hydrophilic

Hydrophobic material ($\alpha > 90^\circ$) unable to wet humid surfaces

Hydrophilic material ($\alpha < 90^\circ$) able to wet humid surfaces

Contact angle $\alpha$

Important properties of impression materials before setting

Hydrophobic/hydrophilic
Pseudoplasticity/thixotropy (shear thinning)

A decrease in viscosity with shear rate e.g. - mixing, vibrations, flow with the aim to decrease stress inducing the flow of fluids

- Newtonian liquid viscosity is constant

- Non-Newtonian liquid

  Viscosity decreases with flow rate and its time - PSEUDOPLASTIC and THIXOTROPIC behavior
Impression tray

Prepared tooth

Seating pressure

Broad "channel" high flow at low seating pressure

Narrow "channel" seating pressure rapidly increases

Impression material
Flow in narrow channels

Poiseuille’s law:

\[ \Delta P = 8.\eta.L \cdot Q/\pi r^4 \]

Poiseuille’s law states that the flow rate \( Q \) is also dependant upon fluid viscosity \( \eta \), pipe length \( L \) and the pressure difference between the ends \( \Delta P \).

Where:
\( \Delta P \) is the pressure drop
\( L \) is the length of pipe
\( \mu \) is the viscosity
\( Q \) is the volumetric flow rate
\( r \) is the radius or a width of a tube/gap
Important properties of impression materials after their setting

1. Elastic behavior
   A spring – ideally elastic behavior (Hook’s law)
2. Plastic behavior

A dashpot - ideally plastic behavior

Plastic = permanent/irreversible deformation

When unloaded! No recovery!
Viscoelastic behavior of real impression materials - a combination of a spring and a dashpot

- Loaded for a short time
- Loaded for a long time

Recovery from deformation

Plastic/permanent deformation

Pouring after material relaxation

2019
Effect of recovery from deformation on the accuracy of a model
Setting time - a period from the start of mixing till the impression becomes elastic enough to resist deformations during its withdrawal from the mouth.

Viscosity changes during setting.

Apparent setting.

Working time - a period from the start of mixing to the final time at which the impression material can be seated in the mouth without its distortion.
## Classification of impression materials

<table>
<thead>
<tr>
<th></th>
<th>Irreversible</th>
<th>Reversible*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inelastic/rigid</td>
<td>Impression plaster</td>
<td>Impression compounds</td>
</tr>
<tr>
<td></td>
<td>ZnO-eugenol (ZOE)</td>
<td></td>
</tr>
<tr>
<td>Elastic</td>
<td>Alginate</td>
<td>Agar hydrocolloid</td>
</tr>
<tr>
<td></td>
<td>Elastomeric:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polysulfide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polyether</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Silicone</td>
<td></td>
</tr>
</tbody>
</table>

*On heating

2019
Inelastic/rigid impression materials

A. Irreversible
1. Impression plaster

**Main indication:** impression of edentulous ridges

**Setting reaction:**

\[
\text{CaSO}_4.0.5\text{H}_2\text{O} + 1.5\text{H}_2\text{O} \rightarrow \text{CaSO}_4.2\text{H}_2\text{O} + \text{heat} + \text{expansion}
\]

**Composition:**

\[
\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} \beta\text{-hemihydrate}
\]

- Potassium sulfate - to accelerate setting and to reduce expansion
- Borax - a retarder to prolonge setting time
- Diatomiceous earth, quartz, lime - to make the plaster more brittle

app. 0.1 lin %
Advantages:

1. Cheap and long shelf life, easy to prepare
2. Very good surface detail reproduction
3. Excellent dimensional stability
4. Non toxic

Disadvantages:

1. Very rigid - often need to be fractured when
2. May dry soft tissues - unpleasant to patients

Old fashioned - not frequently used
2. Zinc-oxide eugenol impression pastes (ZOE)

Main indications: impression of edentulous ridges, surgical dressing

Setting reaction:
A two-paste system composed of:

**Paste A** - ZnO/mineral or vegetable oil as a plasticizer

**Paste B** - oil of claves with app. 85% of eugenol or pure eugenol, rosins and fillers, accelerators

H$_2$O, acetic acid, Zn acetate
Advantages:

1. Low viscosity - no compression of soft tissue
2. Low viscosity - no compression of soft tissues
3. Dimensional stability (shrinkage less than 0.1 %)
4. Good surface detail reproduction
5. Low price

Disadvantages:

1. Cannot be used in deep undercuts
2. Eugenol allergy in some patients (o-ethoxy benzoic acid [EBA] to replace eugenol)
B. Reversible rigid materials

3. Impression compounds
   (Kerr's, Stent's impression compounds)

Thermoplastic material (softens when heated 50°C and hardens on cooling) for tooth impressions in a copper band

Composition:
1. Resins (wax, shellac, gutta-percha)
2. Filler (talc)
3. Lubricants (stearic acid, stearin)
Advantages:

1. Can be reused, easy to use
2. Non irritant and non toxic

Disadvantages:

1. Poor dimensional stability
2. Easy to distort when withdrawn from the mouth

Old fashioned - not frequently used
Elastic impression materials

A. Hydrocolloidal impression materials

B. Elastomeric impression materials

Hydrocolloid

Reversible
Irreversible

Polysulfide
Silicone - condensation and addition types
Polyethers

Elastomeric (nonaqueous) (irreversible)

2019
A. Hydrocolloid impression materials

Hydrocolloid - a colloidal system (particle size up to app. 0.5 μm) with water as a dispersion medium so called HYDROCOLLOID SOL which can be transformed to a solid GEL by physical or chemical reactions:

Setting reaction

reversible/agar sol \[\xrightarrow{\text{Cooling}}\] gel

Via intermolecular interactions: H-bond or Van der Waals interactions

irreversible/alginate sol \[\xrightarrow{\text{Coagulation}}\] gel

Via chemical-ionic bonds
1.1. Reversible hydrocolloid

**Agar impression materials**
(Reversible hydrocolloid impression material)

Based on thermoreversible gelation of natural polysaccharide – agar (isolated from red algae/seaweeds)

- **Agarose**, is a strongly gelling, non-ionic polysaccharide

- **Agaropectin**, is more complex polysaccharide having sulfate groups

1,3- linked β-D-galactopyranose and 1,4-linked 3,6-anhydro-α-L-galattopyranose units
Gelation:
Agar sols form gels upon cooling of a hot solution to (30 - 40)°C

Agar gels melt to sols upon heating to (90 - 95)°C
Composition:

1. Agar
2. Borax to increase the gel strength
3. Potassium sulfate as a gypsum hardener
4. Water - dispersion medium

2019 Tray material

Filled tray
Material in syringes

Compartments for liquefying: 100°C, storage: 65°C and tempering the material in a tray at 45°C

**Advantages:**

1. Very good biological properties
2. Excellent surface detail reproduction

**Disadvantages:**

1. Need special equipment (water bath) and special technique
2. Dimensional instable - evaporation or imbibition
3. Low strength and poor tear resistance
4. Slow setting time
1.2. Irreversible hydrocolloid

**Alginate impression materials**
(Irreversible hydrocolloid impression material, preliminary, orthodontic impressions etc.)

Based on natural polysaccharide - Na\(^+\), K\(^+\), triethanol amine alginate salts (isolated from brown seaweeds)

**Constituent units**

Alginate chains $\bar{M} = 30 - 150\ 000$

Creating viscous sols and gel in the presence of Ca\(^{+2}\) ions
Setting/gelation reaction:

\[ \text{Na}_n\text{Alg} + \text{CaSO}_4 \xrightarrow{\text{H}_2\text{O}} \text{nNa}_2\text{SO}_4 + \text{Ca}_n\text{Alg}_2 \]

powder → gel

Cross-linked structure of alginate gels
1. Na/K alginate
2. Calcium sulfate (CaSO$_4$.2H$_2$O, CaSO$_4$.1/2 H$_2$O)
3. Diatomaceous earth (amorphous SiO$_2$)
4. A retarder – to prolong working time
5. A setting accelerator - K$_2$TiF$_6$ (makes also stone surface hard)
6. Additives – glycol, parafine oils – to agglomerate particles and make material „dustless"

**Composition:**
Mixing ratio powder/water app. 10 g/20 mL

2019

*Mixing ratio powder/water app. 10 g/20 mL*
Alginates - the most frequently used impression material

Properties:

1. Set after mixing with water

2. Shrink due to lose of water by **Syneresis** – expression of water from the surface of impression (if contains Na$_2$SO$_4$ - decreased quality of stone surface) by **Evaporation** - of water from the surface

3. **Imbibition** - sorption of water causing a dimensional change

4. Chromatic phase indicator may be incorporated to signal the impression setting
Dimensional changes of a cast prepared from alginate impression stored in various environments

Store in a closed container with a towel saturated with water
Advantages:

1. Very good biological tolerance
2. Ease of use and mix
3. Fast setting
4. Low price

Disadvantages:

1. Poor dimensional stability
2. Setting dependent on water temperature and water hardness
3. Although 100 h pouring time is also recommended they should be poured as soon as possible
4. Sometimes problems with a model stone compatibility
Other applications of hydrocolloid materials

Reversible hydrocolloid impression materials are used as a duplicating materials to prepare dental cast models (gypsum or from investment materials)
B. Elastomeric (nonaqueous) impression materials

Synthetic polymers with rubber properties after setting

Elastomeric (nonaqueous) (irreversible)

- Polysulfide
- Silicone - condensation types - addition types
- Polyethers

Main indications
- impressions for partial prostheses (removable)
- impressions for crowns and bridges (fixed)
- impressions for implantology

2019
Compensated for using a combination:

1. Highly filled-viscous material „Putty“ for preliminary impression (low polymer content - low shrinkage)

2. Low filled-low viscosity „wash“/„light“ impression material (high polymer content - higher elasticity but higher shrinkage)

Generally a two-component system: base and catalyst
1. Polysulfide impression materials

(Thiokol rubbers, mercaptan rubbers)
The very first elastomeric impression material

Based on reaction between polymer with free mercaptan (-SH) groups and oxidizing agent PbO$_2$ which cross-links chains via reaction of terminal and pendant -SH groups
Setting reaction:

polysulfide polymer

Catalyst strong oxidizing agent

PbO$_2$ → PbO + O

Cross-linked polymer

Water released increases shrinkage

2019
Composition:

Supplied as a two-paste system

Base paste:

polysulfide polymer, filler, plasticizer (e.g. dibutyl phtalate)

Catalyst paste:

lead dioxide, Cu-hydroxide based catalyst in lead free materials, small quantity of sulfur, plasticizer (e.g. dibutyl phtalate)

Volume mixing ratio 1:1
**Advantages:**

1. Low price
2. Long working time

**Disadvantages:**

1. Should be poured within 0.5 - 1 hour
2. Lead oxide may cause toxic effects
3. Unpleasant mercaptane smell
4. Long setting time app. to 10 min
5. Poor elastic recovery - prone to plastic deformation

Old fashioned - not frequently used
2. Silicone impression materials

2. 1. C-silicone impression materials  
(condensation silicones)

Based on cross-linking polycondensation reaction of hydroxy terminated polysiloxane prepolymer with tetraalcoxy silanes catalysed by dibutyltin dilaurate (DBTD)
Polycondensation cross-linking

Tetraethoxy/methoxy silane + dibutyltin dilaurate as a catalyst

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{O-Si-O-Si-OH} & \quad \text{HO-Si-O-} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[+ \text{Si(OCH}_2\text{CH}_3)_4\]

4\text{CH}_3\text{CH}_2\text{OH}

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{O-Si-O} & \quad \text{O-Si-O} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

Hydroxyterminated polydimethylsiloxane prepolymers

Linear polymer - plastic properties

Cross-linked polymer - elastic properties

Alcohols released contributes to the contraction/shrinkage of the impression

2019
Composition:

Supplied as a two-component system

**Base paste:**

1. Hydroxyterminated polysiloxane polymer
2. Filler (cristobalite, talc, starch, calcium carbonate)

**Catalyst:**

**Liquid catalyst:**

- Crosslinking agent (e.g., tetraethoxy silane, TEOS) + activator (dibutyl-tin dilaurate, DBTD)

**Paste catalyst:**

- Cross-linking agent, activator, inert oil
- Filler
**Advantages:**

1. Accurate impressions when poured soon
2. Good elastic recovery
3. Lower price

**Disadvantages:**

1. Hydrophobic
2. Shrinking of impression over time, pouring time till 4 h
3. Catalyst may cause allergic reaction
4. Difficult to dispense proper volumes of both components
5. Usually only hand-mix versions
2. 2. A-silicone impression materials
(addition silicones, vinyl siloxane, poly(vinyl siloxane))

Impression material, duplicating material,
relining material, bite registration material,
root canal sealer

Setting reaction - based on cross-linking reaction
(polyaddition) of vinyl terminated polysiloxane polymer
with methylhydrogen silicone cross-linking agent in the
presence of platinium catalyst
In the presence of Pt catalyst H₂ may be released from water or -OH groups from the reaction mixture causing bubbles on a gypsum model.
**Composition:**

Supplied as a two-component 1:1 system

**Base paste:**
1. Vinyl terminated polysiloxane polymer
2. Pt catalyst
3. Filler (cristobalite, talc)
4. Surfactant (hydrophilic agent)

**Catalyst:**
1. Vinyl terminated polysiloxane polymer
2. Cross-linking agent
3. Filler, silicone oil (to adjust viscosity)
Advantages:
1. Accurate impressions, very low shrinkage
2. Very good surface detail
3. Highly elastic
4. Perfect elastic recovery
5. Dimensionally stable
6. Non toxic and non irritant

Disadvantages:
1. Hydrophilic - due to surfactants addition
2. Setting inhibited by latex gloves or some adstringents (sulfur, heavy metals)
3. Hydrogen release - surface bubbles - pouring time 1 h after removal from the mouth
4. High price
3. Polyether impression materials

Based on cross-linking of polyether chains via cationic polymerization of aziridine rings using an aromatic sulfonate ester as an initiator

**Initiation reaction**

\[ \text{SO}_3\text{R} + \text{R}^+ \rightarrow \text{SO}_3^- \]

*Active cation*
Propagation

Linear prepolymer

Ethylene oxide units - hydrophilic part of a polymer molecule

CH₃-CH-CO-O-[CHR-(CH₂)ₙ-O]ₘ-O-CO-CH-CH₃

aziridine rings

Ring opening

Cross-linked structure

2019
Composition:

Supplied as a two-paste system

Base paste:
1. Polyether
2. Filler, plasticizer

Catalyst paste:
1. Sulphonic acid ester
2. Inert oil
3. Filler
Advantages:

1. „Naturally“ hydrophillic
2. Accurate and high dimensional stability
3. Good elastic recovery
4. Low setting contraction
5. Excellent surface detail reproduction

Disadvantages:

1. Rather stiff when set (difficult to remove from mouth)
2. Very expensive
3. May cause allergic reaction due to the sulphonic acid ester
### Typical properties of elastic impression materials

<table>
<thead>
<tr>
<th>Property</th>
<th>Algin ate</th>
<th>Agar</th>
<th>Polysulfide</th>
<th>Polyether</th>
<th>C-silicone</th>
<th>A-silicone</th>
</tr>
</thead>
<tbody>
<tr>
<td>No of components</td>
<td>1</td>
<td>1</td>
<td>2 pastes</td>
<td>2 pastes</td>
<td>2 pastes or paste/liquid</td>
<td>2 pastes</td>
</tr>
<tr>
<td>Working time [min]</td>
<td>1.5</td>
<td>-</td>
<td>4-7</td>
<td>2-3</td>
<td>2-4</td>
<td>2-4</td>
</tr>
<tr>
<td>Setting time [min]</td>
<td>3-4</td>
<td>3-5</td>
<td>7-10</td>
<td>5-6</td>
<td>5-8</td>
<td>4-7</td>
</tr>
<tr>
<td>Contraction [lin %] after 24 h</td>
<td>0.5</td>
<td>0.01</td>
<td>0.4-0.5</td>
<td>0.2-0.3</td>
<td>0.2-1.0</td>
<td>0.01-0.2</td>
</tr>
<tr>
<td>Recovery from deformation [%]</td>
<td>96</td>
<td>98.8</td>
<td>94.5-96.9</td>
<td>98.3-99.0</td>
<td>97.2-99.6</td>
<td>99.0-99.9</td>
</tr>
<tr>
<td>Detail reproduction [μm]</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Hydrogen release</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>Contact angle [°]</td>
<td>Very low</td>
<td>Very low</td>
<td>82</td>
<td>50-60</td>
<td>98</td>
<td>30*-80</td>
</tr>
<tr>
<td>Relative cost</td>
<td>Very low</td>
<td>high</td>
<td>low</td>
<td>Very high</td>
<td>lower</td>
<td>high</td>
</tr>
</tbody>
</table>

*Hydrophilic types*