Impression materials

Chemistry and properties

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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 replicate - cast/die
- an accurate positive model of teeth and adjacent oral structures
General requirements

Before set:

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

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

3. Acceptable to a patient - not toxic, not irritant, tasteless
General requirements

After being set:

1. **Accuracy** and good detail reproduction (25-50µm)
2. Dimensional stable
3. Elastic, tear resistant, low creep
4. Compatible with model materials
5. Resistant to disinfection solutions
6. Cost effective
Important properties and terms

• Hydrophilic/hydrophobic
• Pseudoplastic/thixotropic
• Elastic, plastic (permanent, irreversible) deformations
• Strength
• Working time
• Setting time
Hydrophobic/hydrophilic

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

doesn’t copy wet surface

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

copy wet surfaces
Important properties of impression materials before setting

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

Seating pressure

Impression material

Prepared tooth

Seating pressure

Broad „channel“ high flow at low seating pressure

Narrow „channel“ seating pressure rapidly increases
Flow in narrow channels

Poiseuille’s law:

\[ \Delta P = 8 \eta L \frac{Q}{\pi r^4} \]

Poiseulle'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 ther setting

1. Elastic behavior

A spring - ideally elastic behavior (Hook's law)

When unloaded !fully recovers!
2. Plastic behavior

A dashpot – ideally plastic behavior

Plastic = permanent/irreversible deformation

When unloaded! No recovery!

Deformation

Permanent deformation

$\text{loaded}$ $\text{t}_1$ $\text{t}_2$ $\text{unloaded}$
3. Elastic/plastic deformations of real bodies

Describes behaviour of material under load

Region of elastic deformations Hook’s law

Region of plastic deformations

Slope - Young's modulus, modulus of elasticity

Deformation

Proportional limit

Maximum load at fracture - ultimate strength
Viscoelastic behavior of real impression materials – a combination of a spring and a dashpot

Plastic/permanent deformation

Pouring after material relaxation

Recovery from deformation

Loaded for a short time

Loaded for a long time

Recovery from deformation

\( t_1 \) < \( t_2 \)

Time
Effect of recovery from deformation on the accuracy of a model

% Recovery from deformation

Plastic deformation

99% 95%
Setting time - a period from the start of mixing till the impression becomes elastic enough to resist deformations during its withdrawal from the mouth.

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.

Changes of viscosity during setting.

Apparent setting.
# Classification of impression materials

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<th>Material Type</th>
<th>Irreversible</th>
<th>Reversible*</th>
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<td>Inelastic/rigid</td>
<td>ZnO-eugenol (ZOE)</td>
<td>Impression compounds</td>
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<td>Impression plaster</td>
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<tr>
<td>Elastic</td>
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<td>Elastomeric:</td>
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<td>Polysulfide</td>
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<td>Polyether</td>
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<td>Silicone</td>
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*On heating (thermoplastic)
Inelastic/rigid impression materials

A. Irreversible
1. Impression plaster

**Main indication:** impression of edentulous ridges

**Setting reaction:**

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

**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:**

![Chemical structure](attachment:image.png)

- Initial state: \(\text{CH}_2=\text{CH}-\text{CH}_2\text{OH} + \text{ZnO}\)
- Final state: Chelate structure

2012 20
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

\[ \text{H}_2\text{O}, \text{acetic acid, Zn acetate} \]
Viscosity changes during setting of ZOE cements and silicone impression materials

Silicone impression materials (too high viscosity - deformation of soft tissues)

Low viscosity of ZOE impression pastes enables mucostatic impressions

Edentulous ridges - low viscosity is favourable to avoid displacement of soft tissues
Advantages:

1. Low viscosity - no compression of soft tissues
2. Dimensional stability (shrinkage less than 0.1 %)
3. Good surface detail reproduction
4. 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 making impressions of edentulous ridge, tooth impressions in a copper band

Composition:
1. Resins (wax, shellac, guttapercha)
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. Hydrocolloid impression materials

B. Elastomeric impression materials

Hydrocolloid

Elastomeric (nonaqueous) (irreversible)

Irreversible
Reversible
Polysulfide
Silicone – condensation and addition types
Polyethers
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 state

Setting reaction

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

irreversible/alginate sol  \[\xrightarrow{\text{Coagulation}}\]  gel
1.1. 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)

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

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

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

powder \hspace{2cm} \text{gel}

Egg-box structure

Cross-linked structure of alginate gels
Composition:

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. Retarder - phosphates prolonge working time
   \[3CaSO_4 + 2Na_3PO_4 \rightarrow 3Na_2SO_4 + Ca_3(PO_4)_2\]
5. Setting accelerator - K$_2$TiF$_6$ (makes also stone surface hard)
6. Additives - glycol, parafine oils - to agglomerate particles and make material „dustless“

Mixing ratio powder/water app. 10 g/20 mL
Alginates - 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
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
1.2. 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

1,3-linked β-D-galactopyranose and 1,4-linked 3,6-anhydro-α-L-galattopyranose units

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

- Sol: random coils
- Gelation I: Double helices
- Gelation II: aggregation of helices
Composition:

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

Compartment 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 unstable - evaporation or imbibition
3. Low strength and poor tear resistance
4. Slow setting time
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
Shrinkage during setting is 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
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 pendat -SH groups
Setting reaction:

Linear polysulfide polymer

Catalyst

PbO₂ → PbO + O

Water released increases contraction

Cross-linked polymer

Water released increases contraction

Setting reaction:
Composition:

Supplied in a two-paste system

Base paste:

polysulfide polymer, filler, plasticizer

Catalyst paste:

lead dioxide, small quantity of sulfur, inert oil (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)
Setting reaction - polycondensation

Releases from the reaction mixture and contributes to the contraction/shrinkage of the impression
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))

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

Impression material, duplicating material,
relining material, bite registration material,
root canal sealer
Setting reaction - polyaddition

Pt may release H₂ 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 (adjust viscosity of duplicating materials)
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. Hydrophobic - necessary to add a surfactant
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:

$$
\begin{array}{c}
\text{SO}_3\text{R} \\
\text{SO}_3^-
\end{array} \rightarrow
\begin{array}{c}
\text{SO}_3^- \\
+ \text{R}^+
\end{array}
\text{Active cation}
$$
Propagation

Linear prepolymer

Ethylene oxide units - hydrophilic part of a polymer molecule

Ring opening

Cross-linked structure
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</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>
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<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*
Examples of typical packages of impression materials

Putty

Light

Light