New Ideas. New Materials.

UNIVERSITÄT DES SAARLANDES

INM

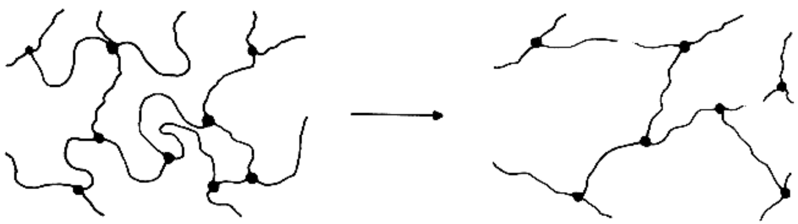
TECHNOLOGIE POLYMERE & KOMPOSITE

MC07, UdS WS 2019/2020

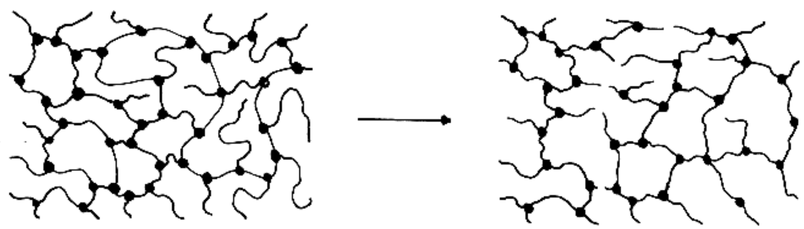
Chapter 2: Elastomers and Thermosets

Deformations on the molecular level during tensile load

elastomer

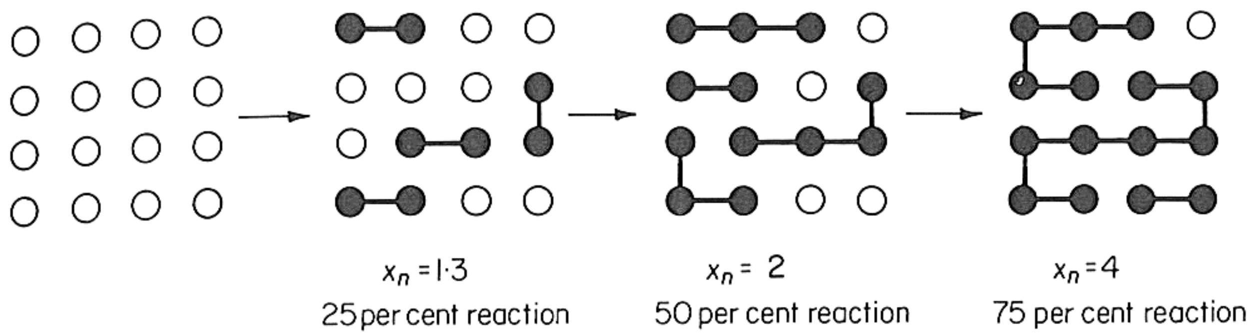


thermoset resin

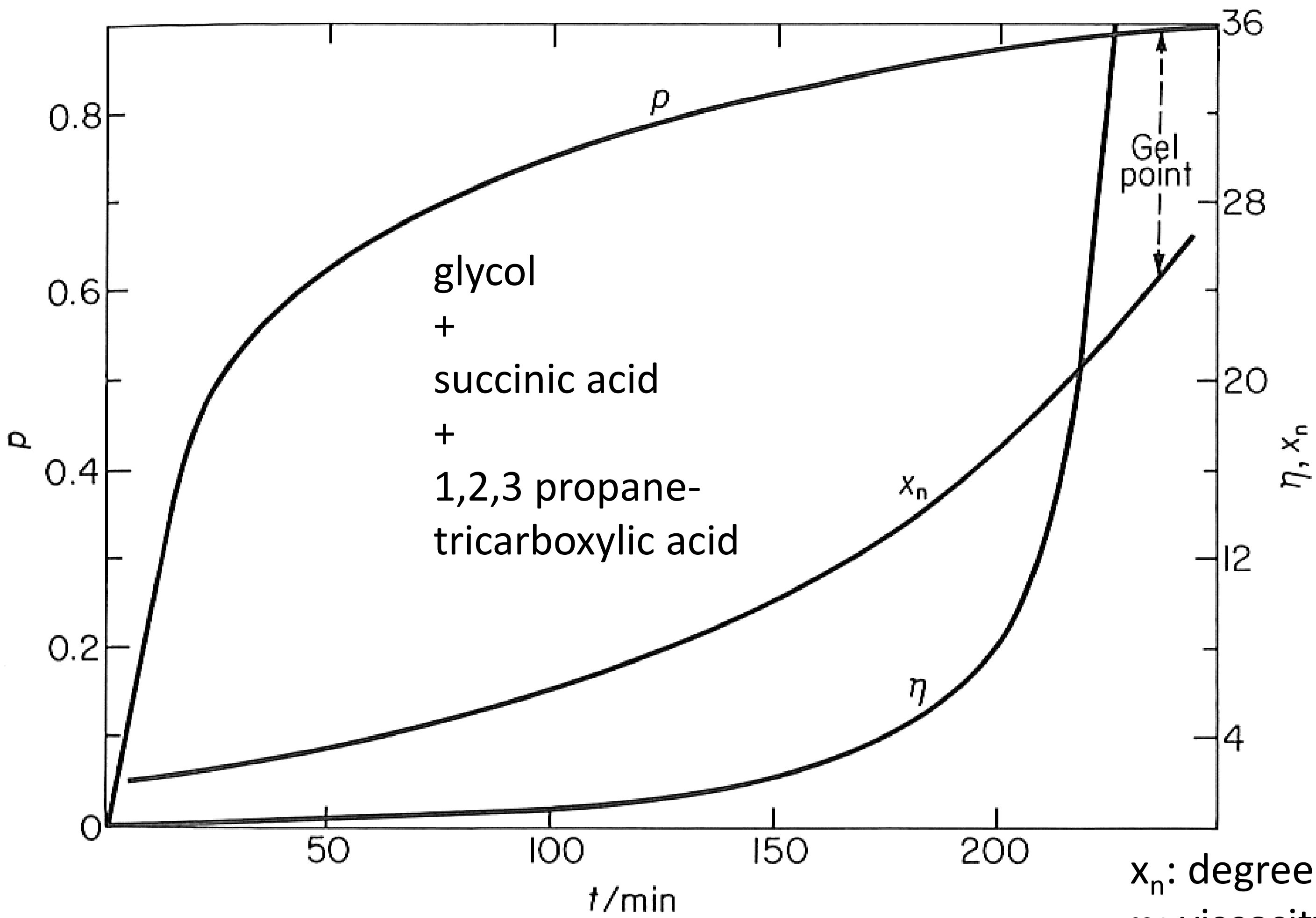


H.G. Elias

Structure formation in step growth reaction



Kinetics of the step growth reaction

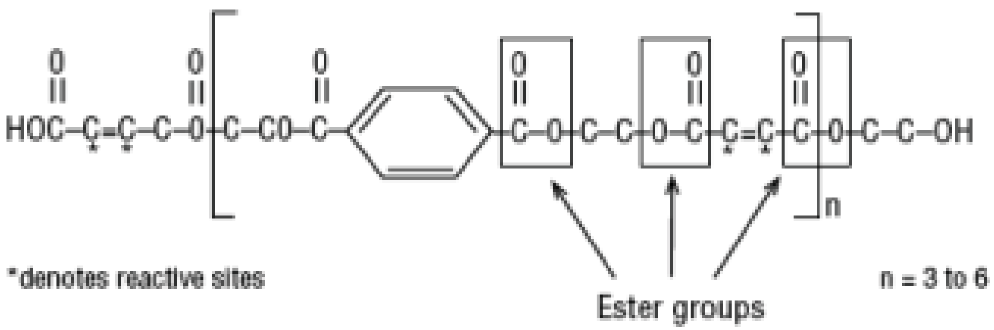


x_n: degree of polymerisation
η: viscosity
p: amount of polymer

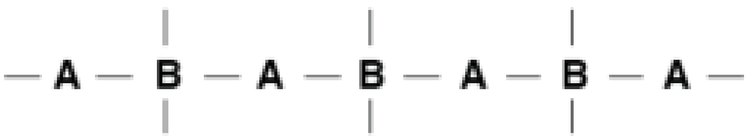
Flory

Typical thermosets: Polyester Resins

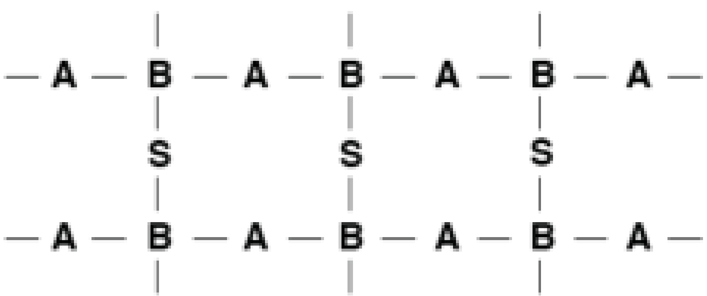
Isophthalic polyester



uncured polyester



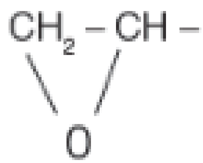
cured polyester + styrene network



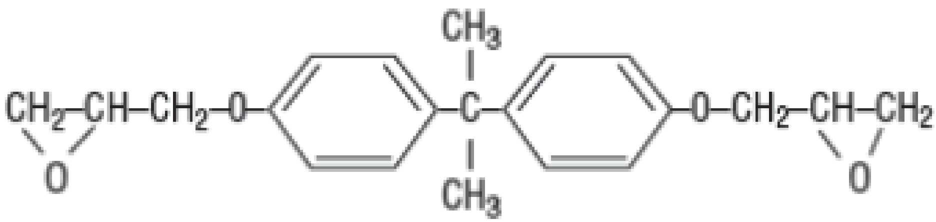
Polyesters have a limited storage life as they will polymerise on their own

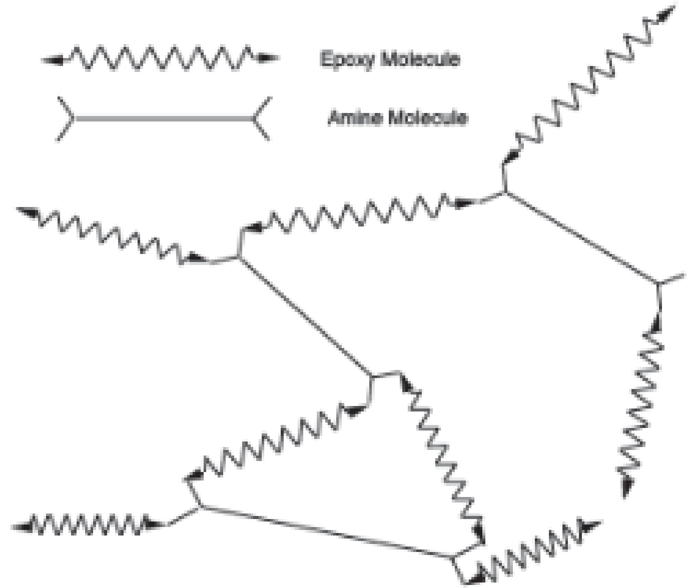
Typical thermosets: Epoxy Resins

Ethylene Oxide

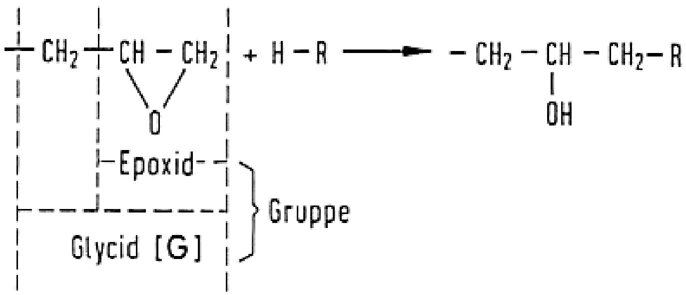


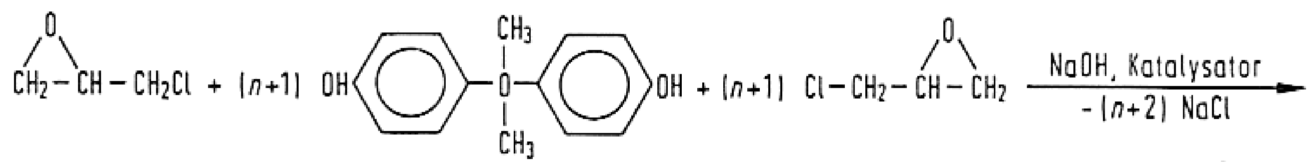
Diglycidyl Ether of Bisphenol-A



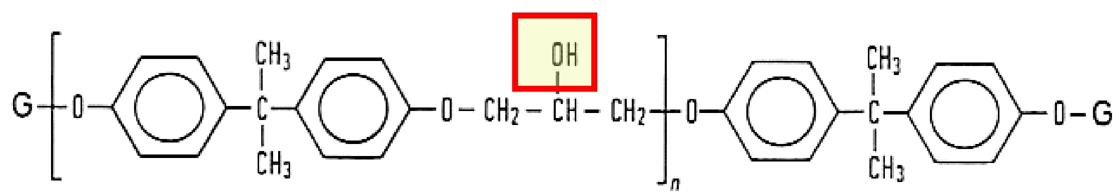


Typical thermosets: Epoxy resins





Epichlorhydrin Bisphenol A Epichlorhydrin

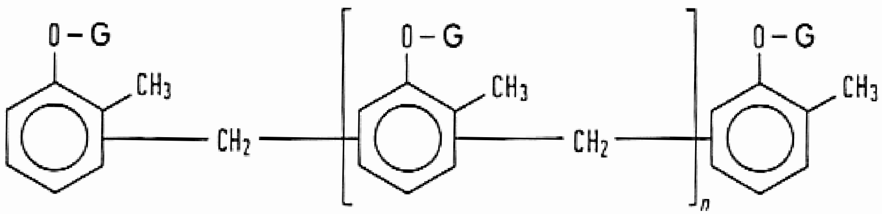


„Dian"-Harz:

n = 0: Bisphenol A-Diglycidether (BADGE), $0 < n < 10$: flüssige oder feste Harze

Typical thermosets: Epoxy resins

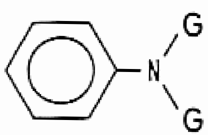
(2) Epoxid-(Kresol)-Novolak-Typ



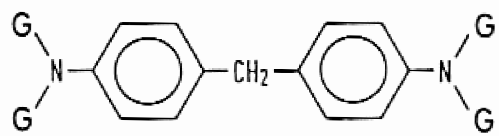
(3) Aliphatische Diglycidether-Typen

$G-O-(CH_2)_n-O-G$ flexible Harze mit z. B. $n = 4$

(4) Diglycidamin-Derivate



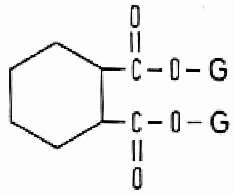
Diglycidanilin
(bifunktioneller Verdünner)



Multifunktionell
für HT-Beschichtungsharze

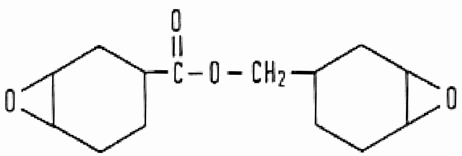
Typical thermosets: Epoxy resins

Cycloaliphatische Diglycidester-Typen

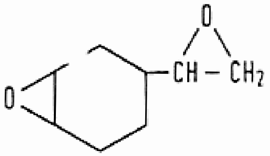


Hexahydrophthalsäure-Diglycidester
für lichtbogen- und kriechstromfeste HT-Harze

Cycloaliphatische Typen mit direkt gebundenen EP-Gruppen



3,4-Epoxycyclohexylmethyl-
3,4-Epoxycyclohexancarboxylat

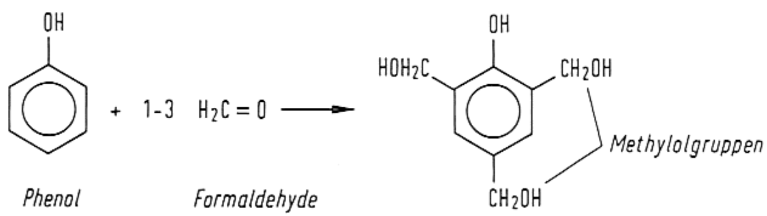


Vinylcyclohexendioxid

Grundstoffe für elektrotechnische Verkapselungs- und Vergußharze

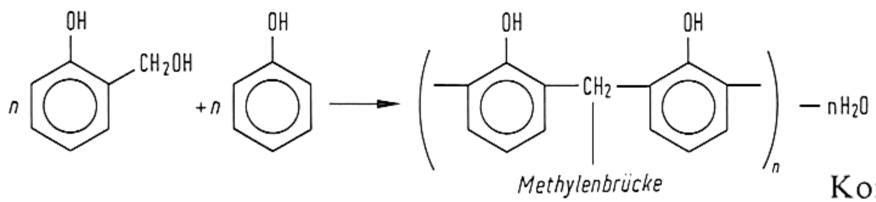
Typical thermosets: Phenolic resins

Anlagerung zu Phenolalkoholen:



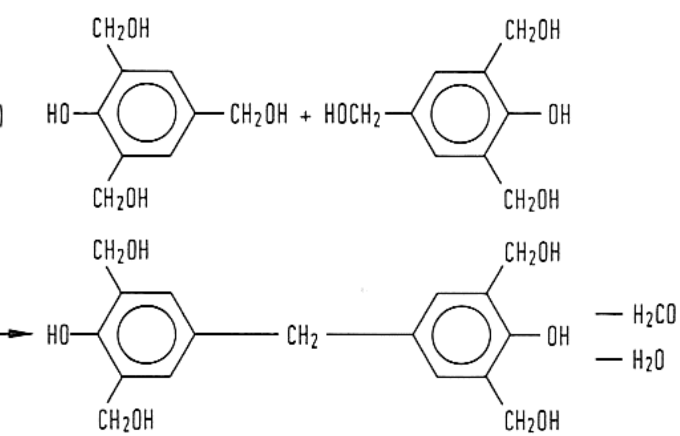
Kondensation unter Wasserabspaltung:

(1a)

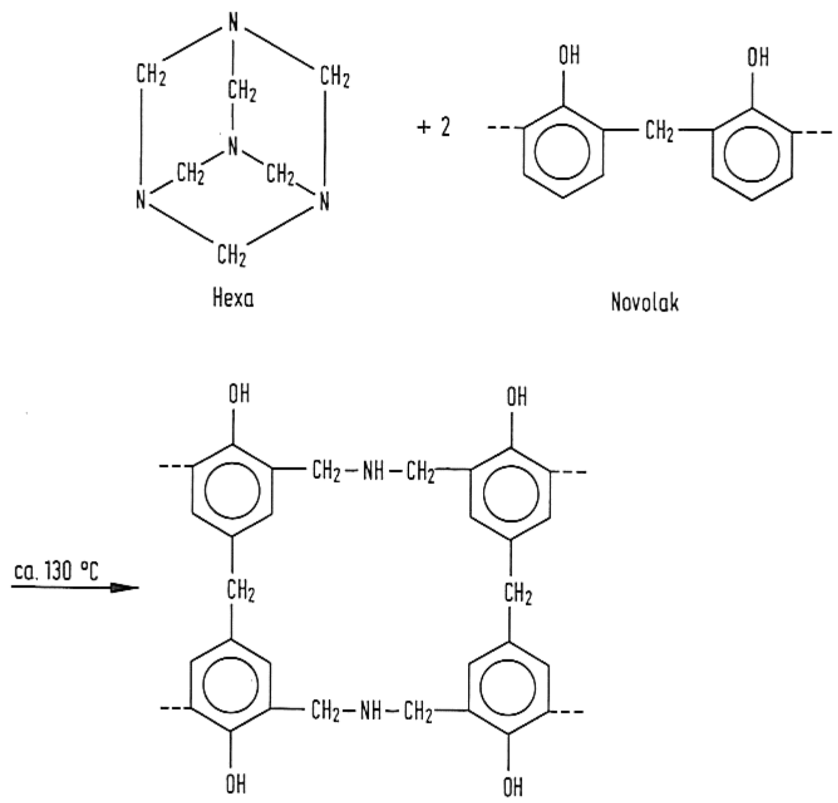


Kondensation unter Wasser- und Formaldehydabspaltung:

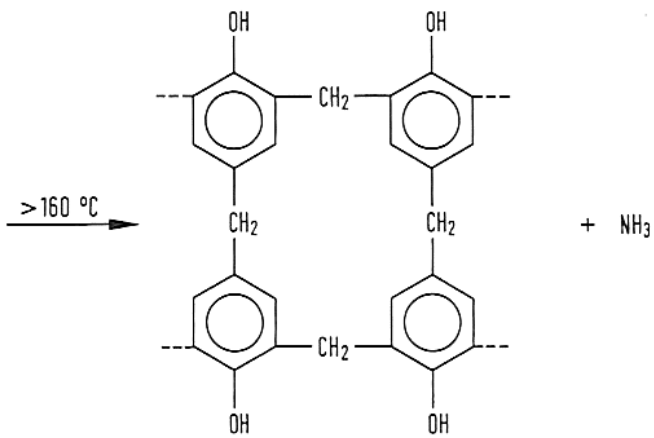
(1b)



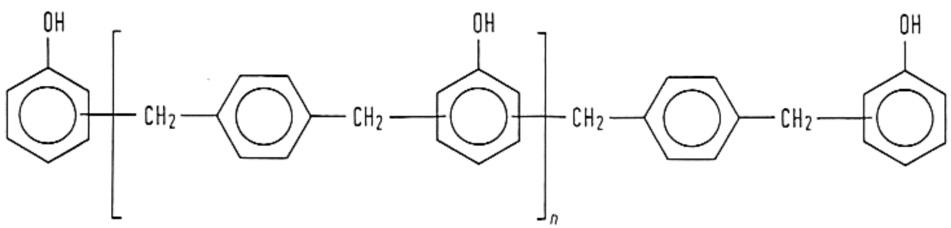
Typical thermosets: Phenolic resins



Typical thermosets: Phenolic resins



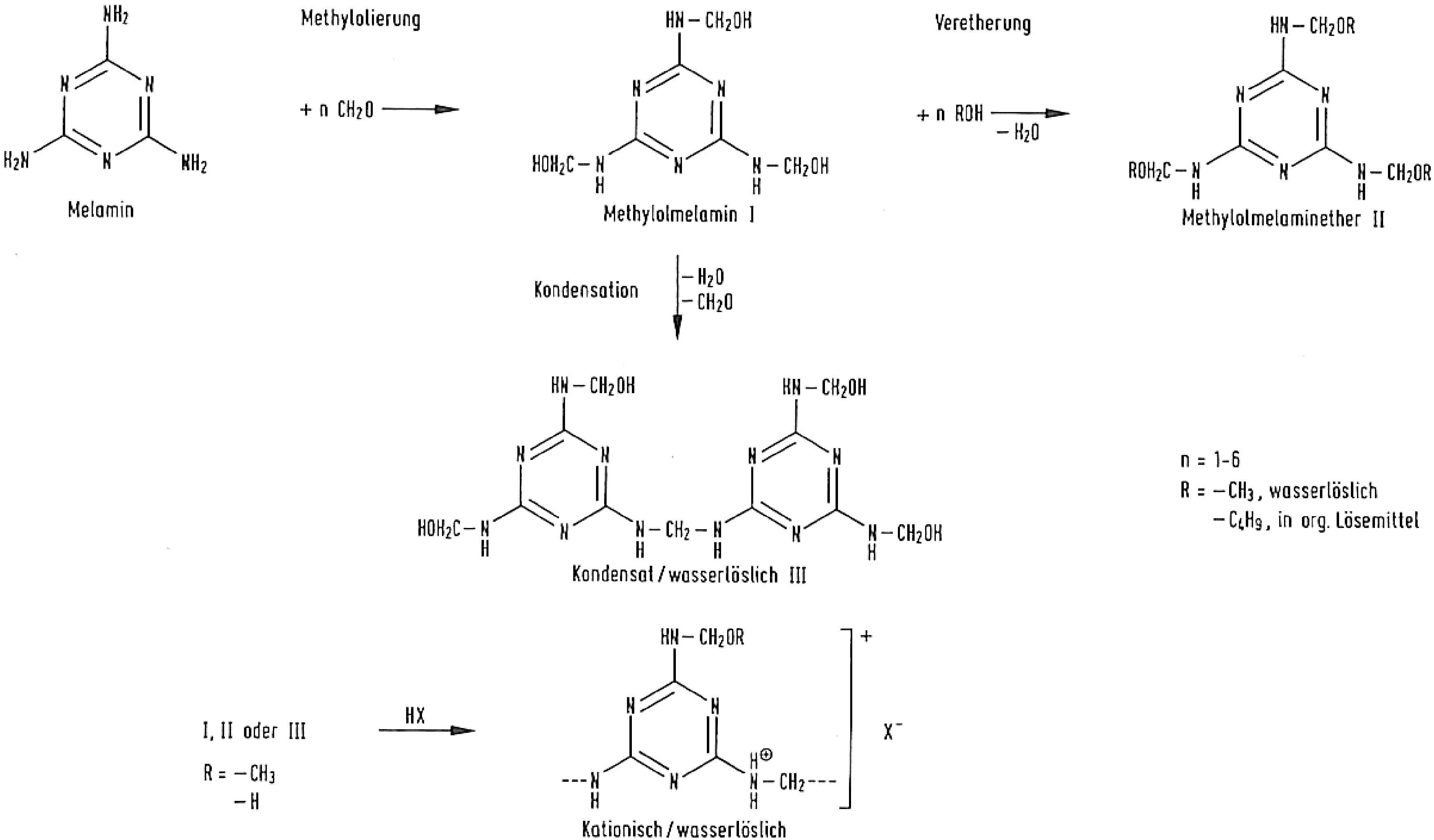
Auch *Phenol-aralkylharze* auf Basis von Pre-Kondensaten wie



Anwendungsgebiete:

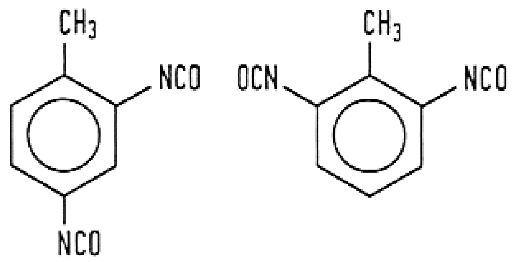
- Holzwerkstoffe
- Formmassen
- Dämmstoffe
- Lacke
- Gießereibindemittel
- Reibbeläge

Melamine based phenolic resins



Polyurethanes

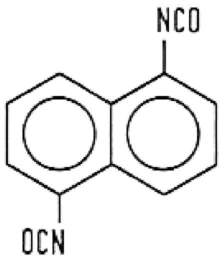
1. TDI



Toluylen-2,4-diisocyanat + Toluylen-2,6-diiso-
cyanat

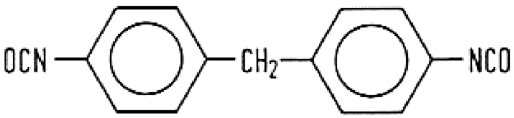
80% + 20% = TDI 80/20
65% + 35% = TDI 65/35

3. NDI

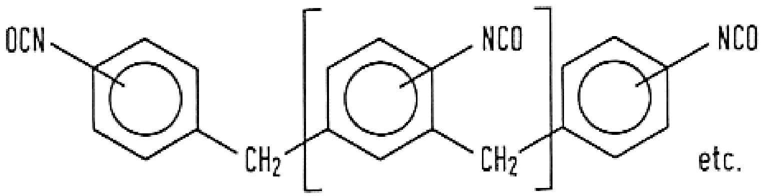


Naphtylen-
1,5-diisocyanat

2. MDI



MDI rein monomer

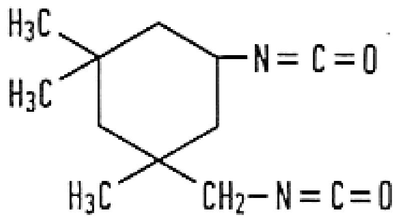


MDI roh polymer

Diphenylmethan-4,4′-diisocyanate

Polyurethanes

4. IPDI



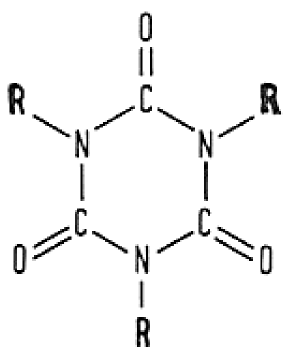
Isophorondiisocyanat

5. HDJ

$$O=C=N-(CH_2)_6-N=C=O$$

Hexan-1,6-diisocyanat

6.



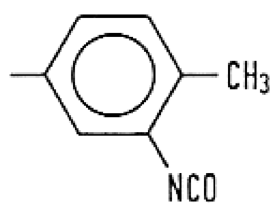
Isocyanurat-Triisocyanat

7.

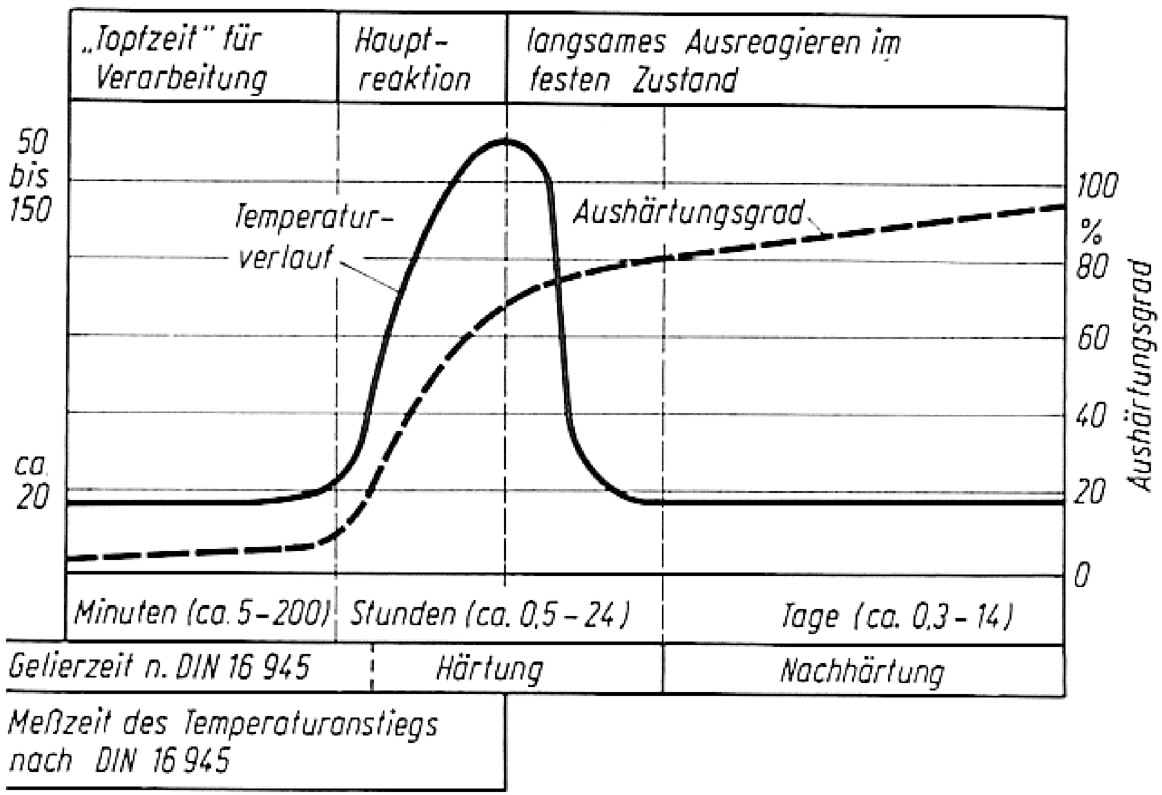
$$\mathbf{R}-N=C=N-\mathbf{R}$$

Carbodiimid-Diisocyanat

R in 6 und 7



Cold curing of reactive resins



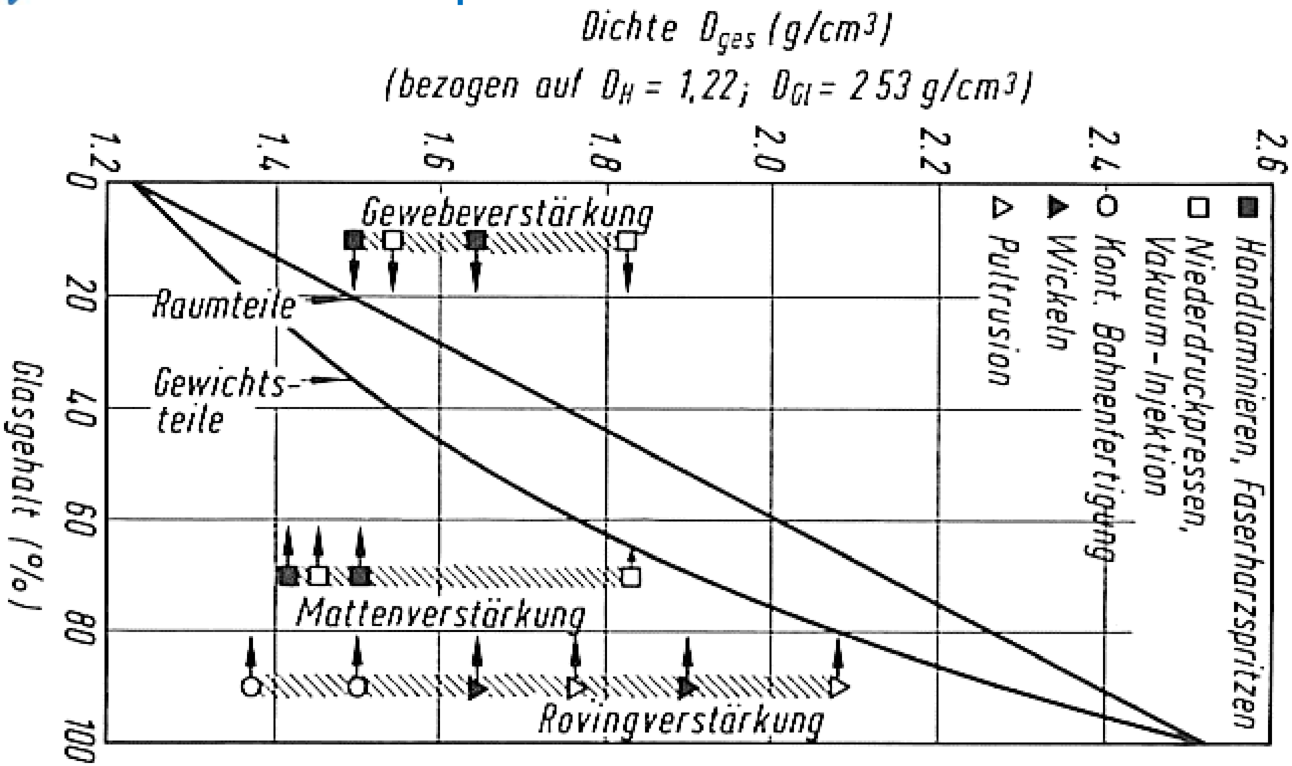
Formation of composites: polymer + concrete

Eigenschaft	Einheiten	Polymer-Beton	Zement-Beton
Bindemittel-Gehalt			
in Volumenanteilen	kg/m^3	150–270	350
in Gewichts-Prozent	%	6–12	14–15
Dichte	g/cm^3	2,4–2,2	2,5–2,1
Bei 20 °C			
Druckfestigkeit			
nach 1 Tag	N/mm^2	70–100	2–5
nach 28 Tagen	N/mm^2	95–150	40–50
Biegefestigkeit			
nach 1 Tag	N/mm^2	23–30	0,5–3
nach 28 Tagen	N/mm^2	30–40	6–8
Elastizitäts-Modul..................	kN/mm^2	15–30	30–60
Therm. Längenausdehnungskoeff......	$10^{-5}/K$	1,5–2,0	1,0–1,4
Beständigkeit gegen			
Säuren.............................		hoch	gering
Öle, Treibstoff....................		hoch	gering
Frost		hoch	mäßig

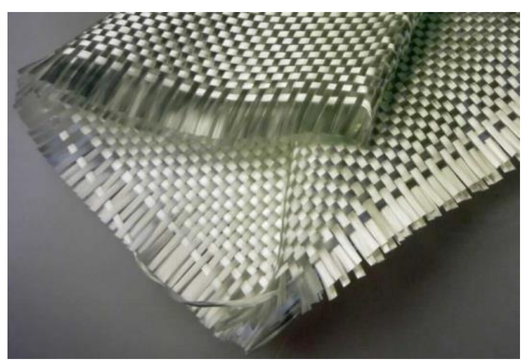
*) je nach Polymer-Art.

MMA
UP
EP

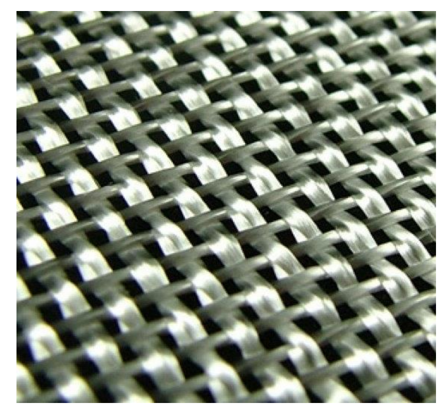
Glass fibre composites



multi-filament-yarn



roving

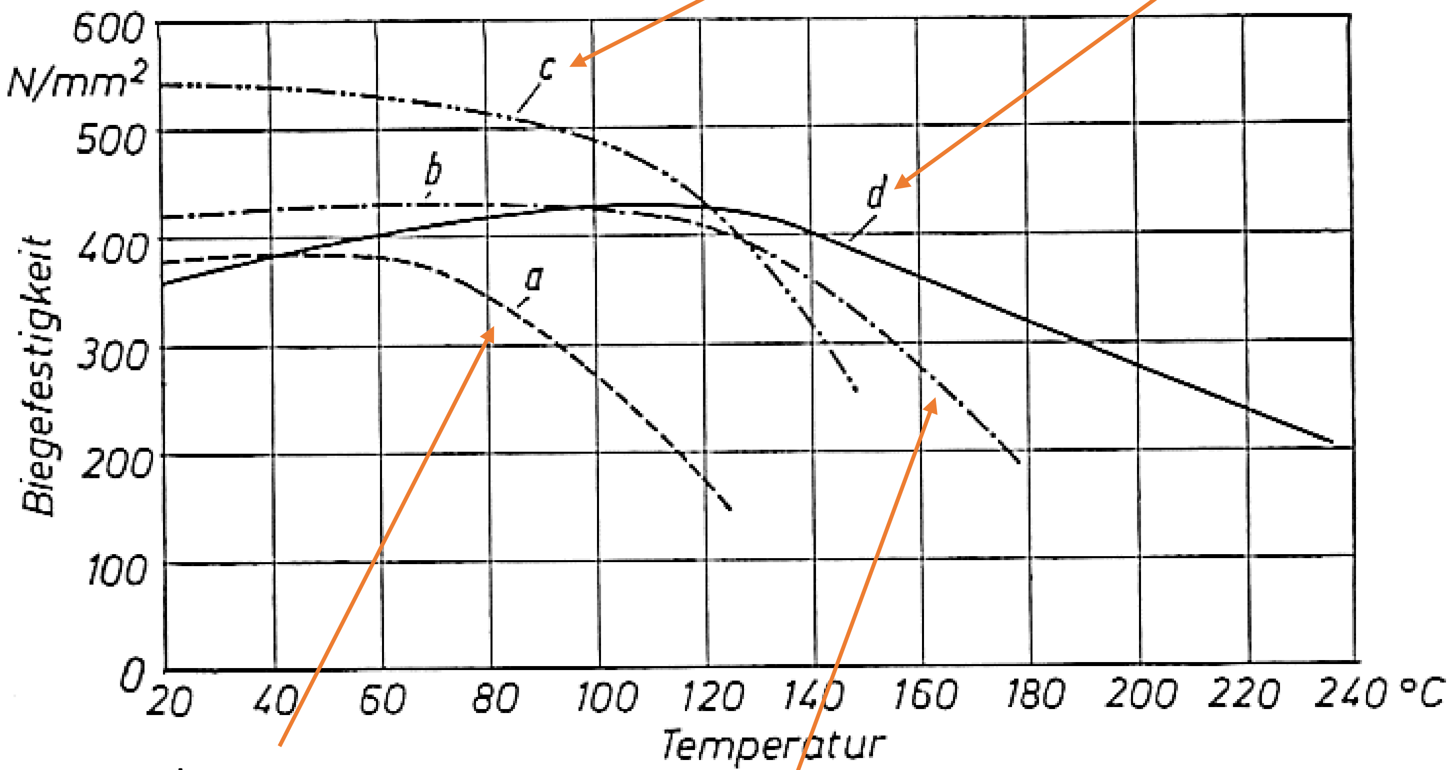


Heat resistance

temperature dependence of glass rowing containing resins

epoxy resin

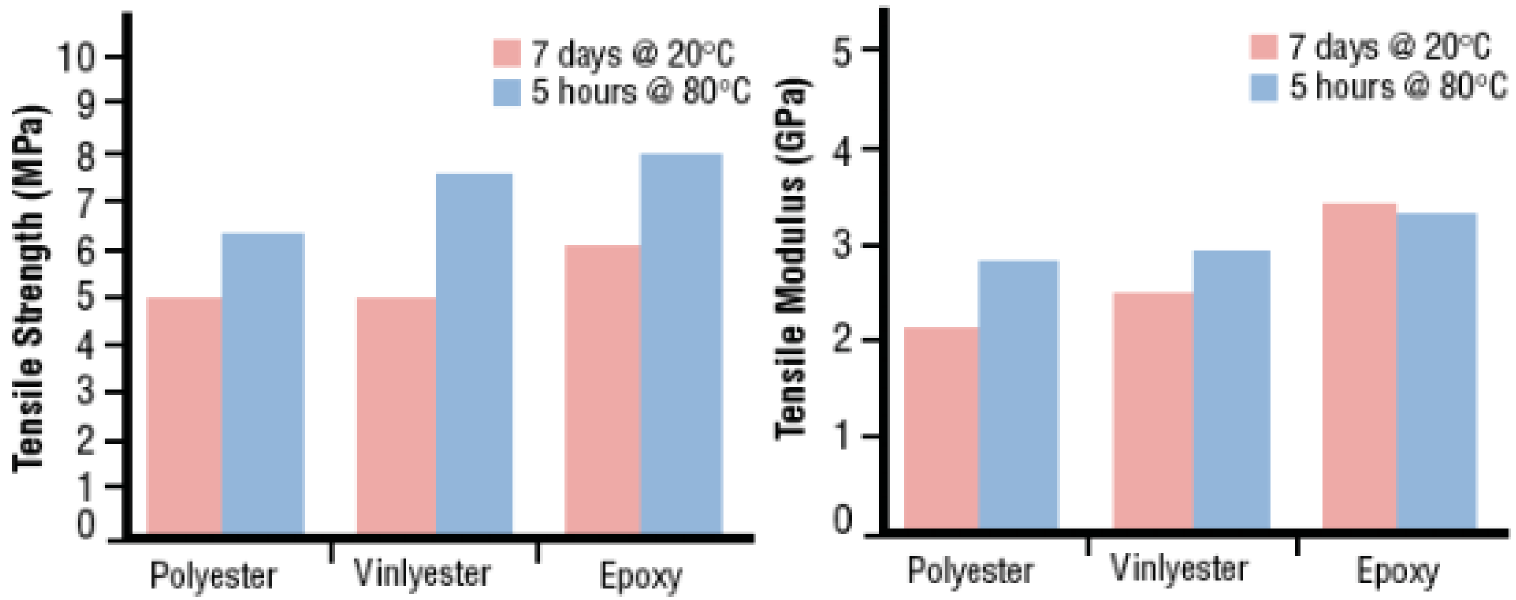
phenolic resin



polyester
(standard resin)

polyester
(temperature resistant resin)

Comparison of mechanical properties



thermal post-curing reaction

Selection of suitable matrix

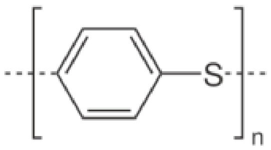
	Advantages	Disadvantages
Polyesters	**Advantages** Easy to use Lowest cost of resins available (2-3€/kg)	**Disadvantages** Only moderate mechanical properties High styrene emissions in open moulds High cure shrinkage Limited range of working times
Vinylesters	**Advantages** Very high chemical/environmental resistance Higher mechanical properties than polyesters	**Disadvantages** Postcure generally required for high properties High styrene content Higher cost than polyesters (3-5€/kg) High cure shrinkage
Epoxies	**Advantages** High mechanical and thermal properties High water resistance Long working times available Temperature resistance can be up to 140°C wet / 220°C dry Low cure shrinkage	**Disadvantages** More expensive than vinylesters (4-18€/kg) Critical mixing Corrosive handling

Selection of suitable matrix

- Phenolic resins
  - primarily used when high fire resistance is required
- Bismaleinimides (BMI)
  - primarily used in aircraft composites when operation at higher temperature (230 °C wet / 250 °C dry) is required
  - e.g. engine-inlets, highspeed aircraft flight surfaces
  - very expensive (> 70 €/kg)
- Polyimides
  - further increased temperature stability (up to 250 °C wet / 300 °C dry)
  - missile and aero engine components
  - extremely expensive (> 90 €/kg)
  - toxic raw materials in ist manufacture

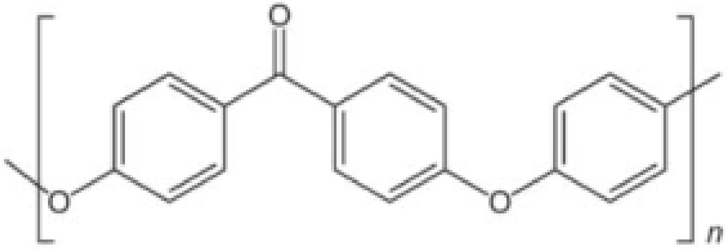
Selection of suitable matrix

- PPS (Polyphenylene Sulfide)
  - semicrystalline thermoplastic
  - good chemical resistance
  - good mechanical properties
    - elastic modulus 3.6 GPa
    - tensile strength 90 MPa
    - T_g =90 °C
    - T_m = 280 °C

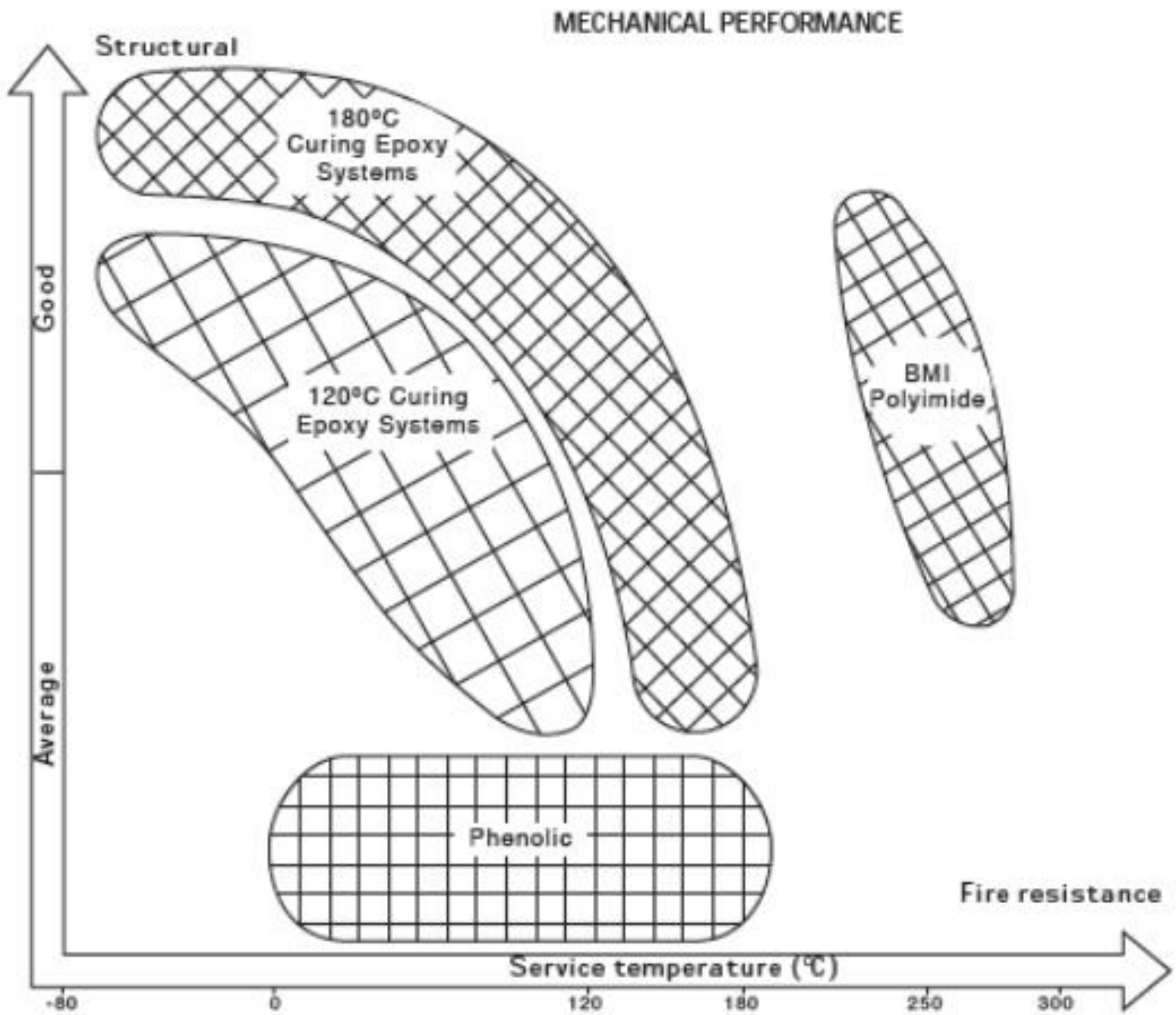


Selection of suitable matrix

- PEEK (Polyether-ether-ketone)
  - semicrystalline thermoplastic
  - excellent chemical resistance
  - hydrolytic stability
  - excellent mechanical properties
    - elastic modulus 3.6 GPa
    - tensile strength 100 MPa
  - highly resistant to thermal degradation
    - T_g 140 °C
    - T_m = 340 °C

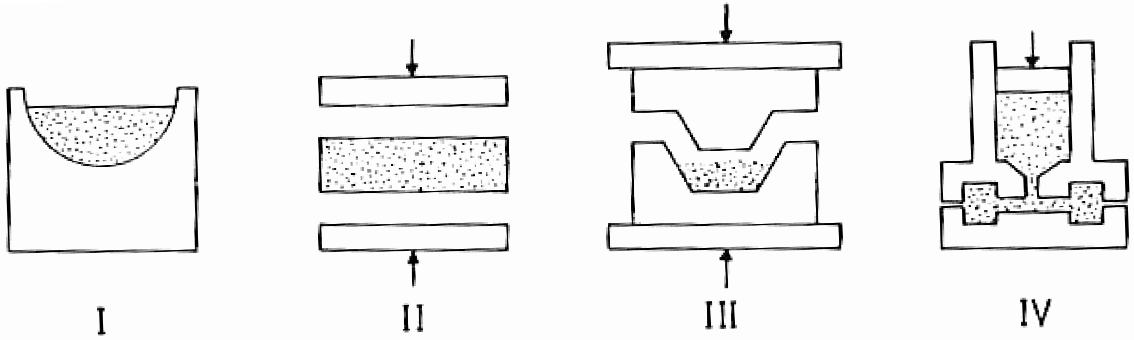


Selection of suitable matrix

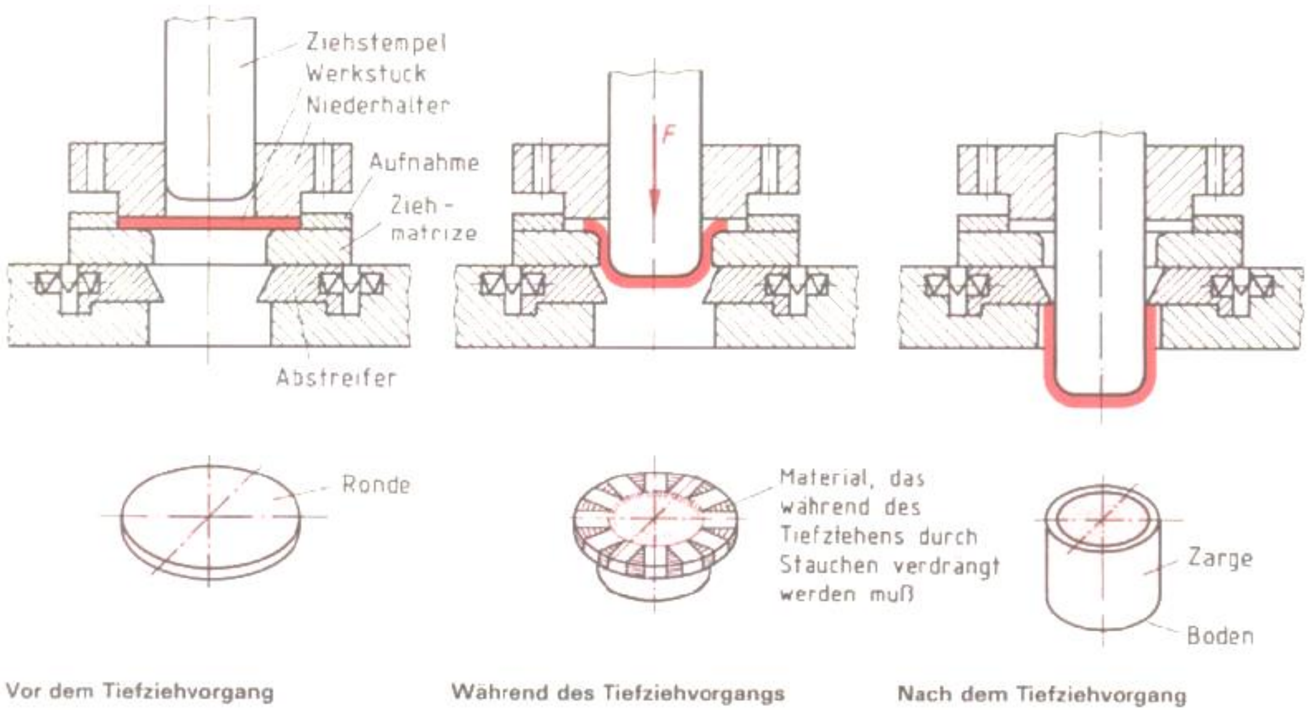


Different preparation techniques

casting	sheet pressing	mould pressing	inject pressing



Deep drawing process



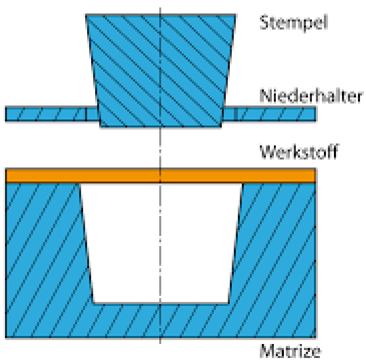
Processing via elastoplastic state

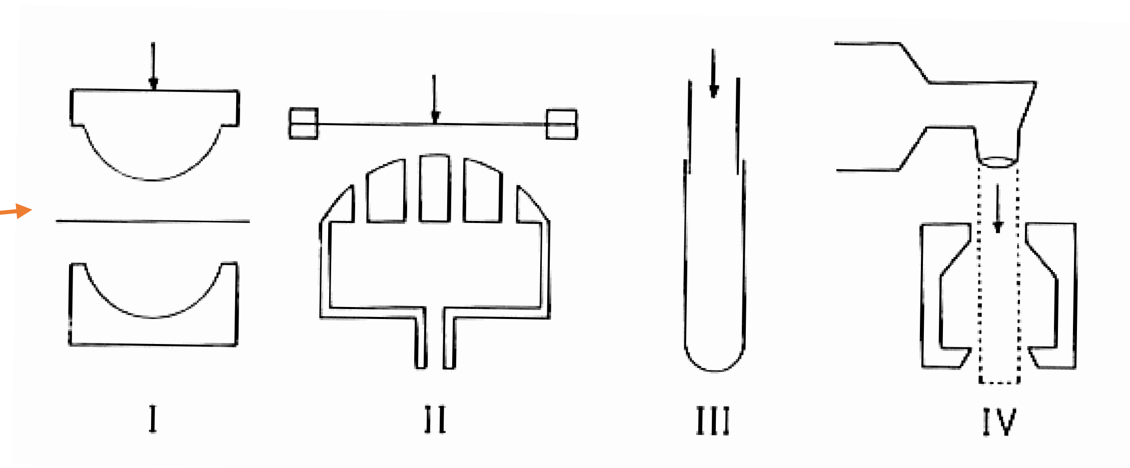
deep drawing

deep drawing with vacuum

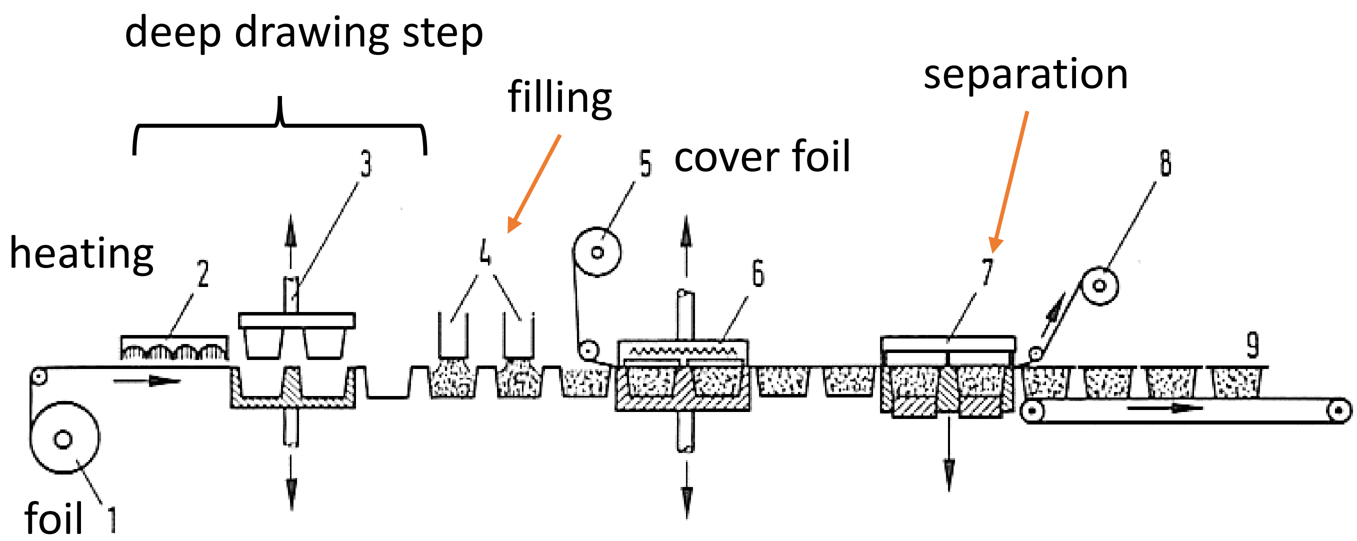
blow moulding

extrusion blow moulding





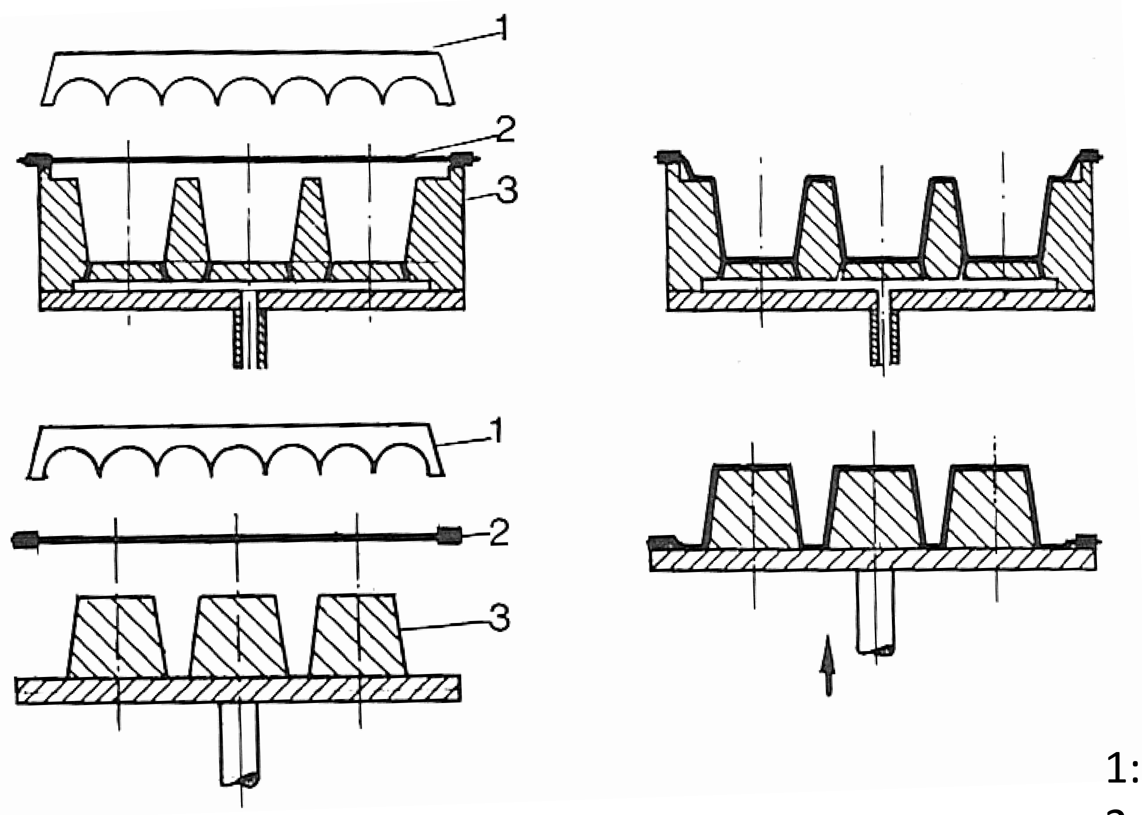
Thermoplastic beaker fabrication



Hot forming

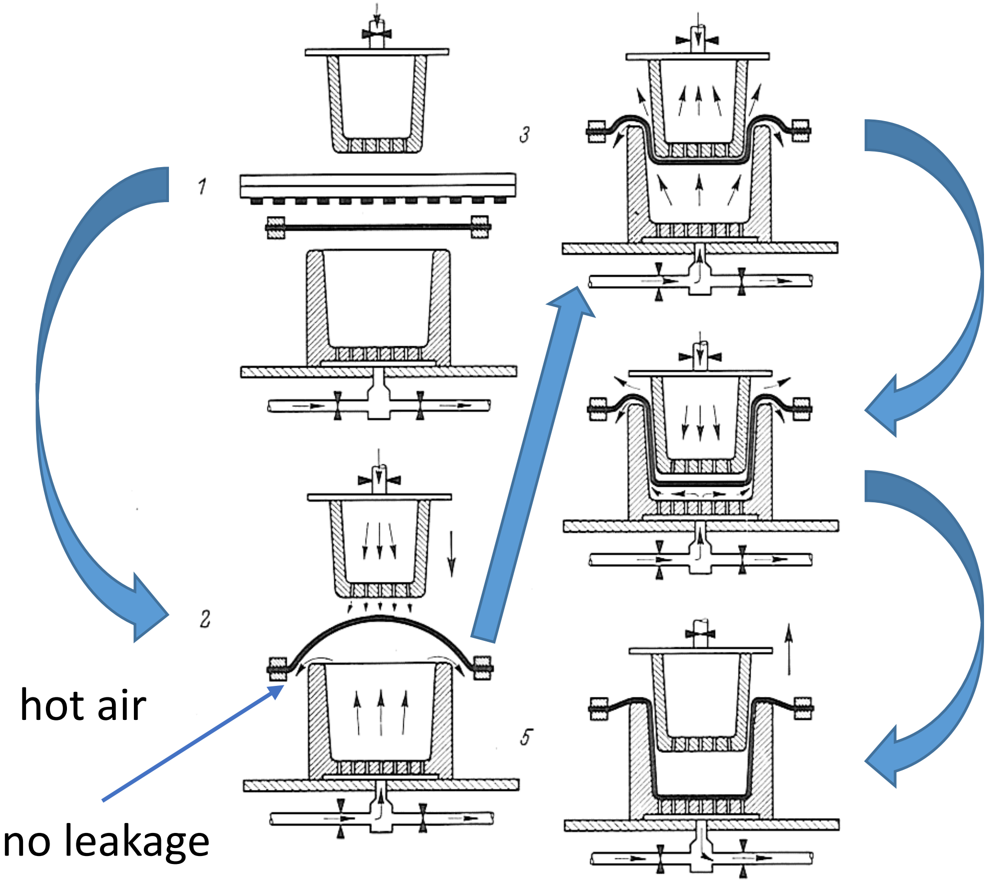
negative mould + vacuum

positive mould



1: heating element
2: foil
3: tool (Al)

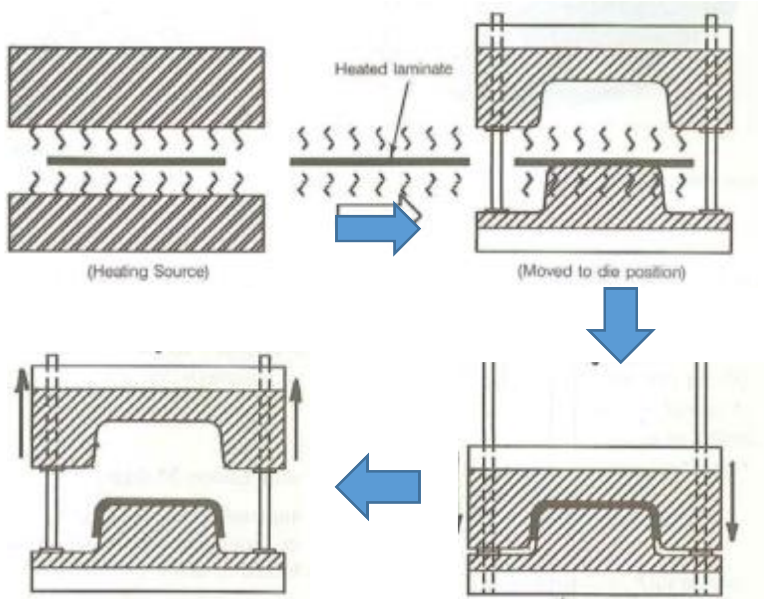
Combinations of heat forming process

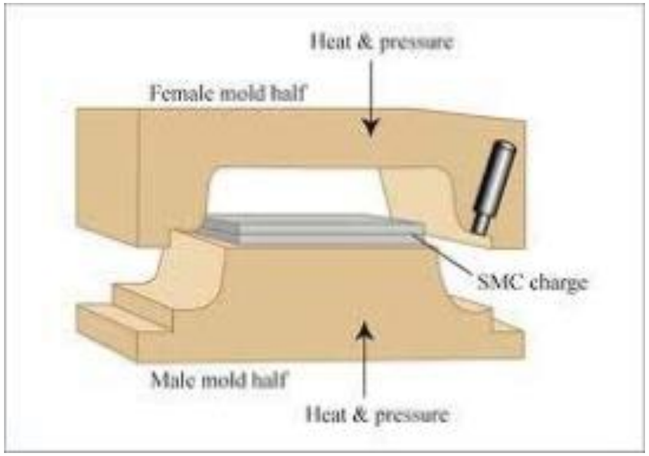


pre-forming
air-slip process

final forming process
vacuum from backside

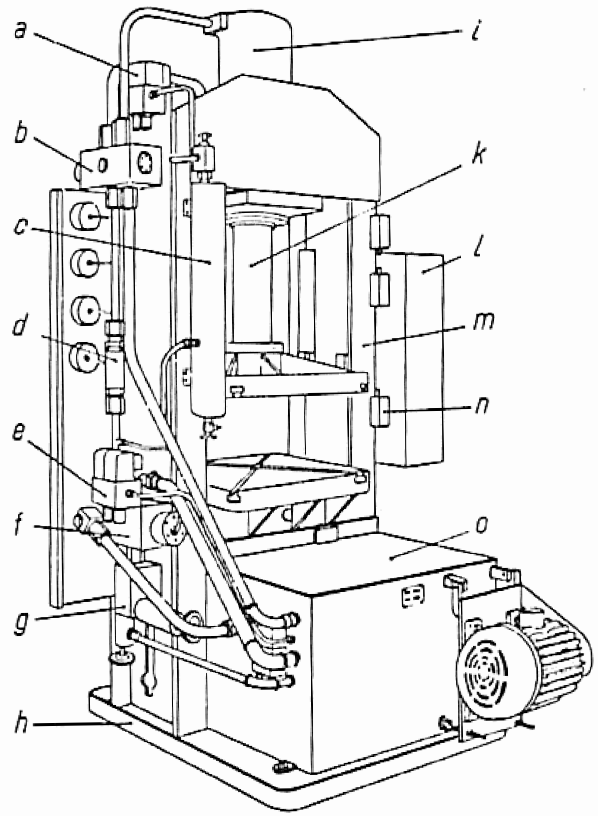
Compression Moulding





SMC: sheet moulding compound

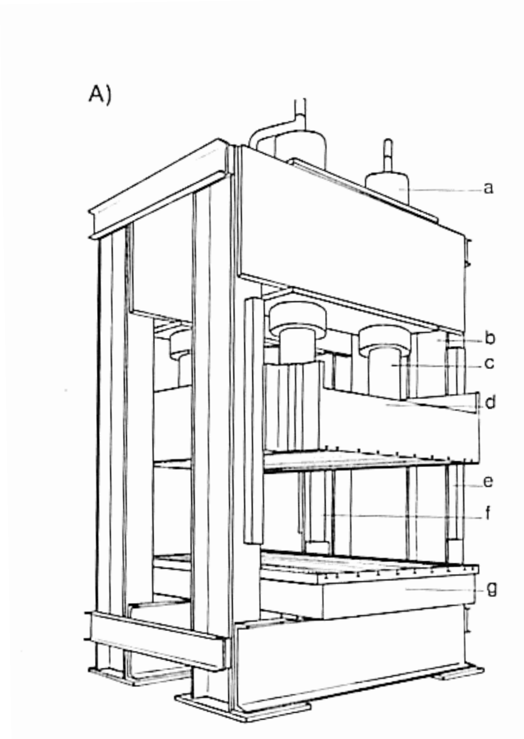
Hydraulic press for GFK

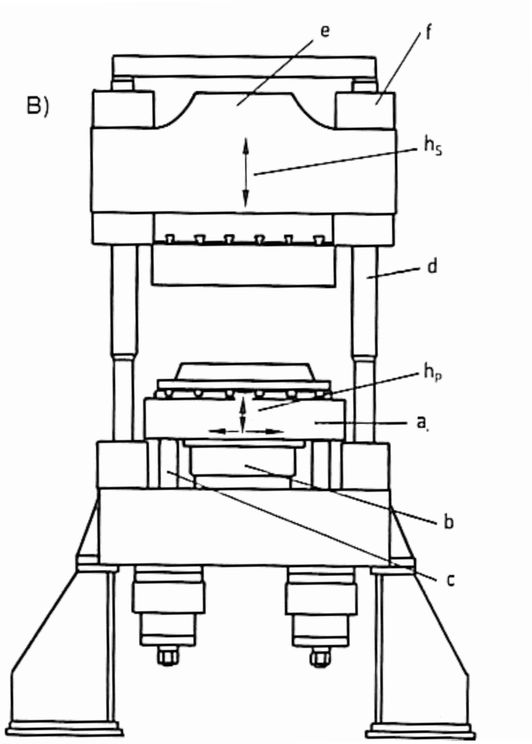


Hydraulic press for GFK

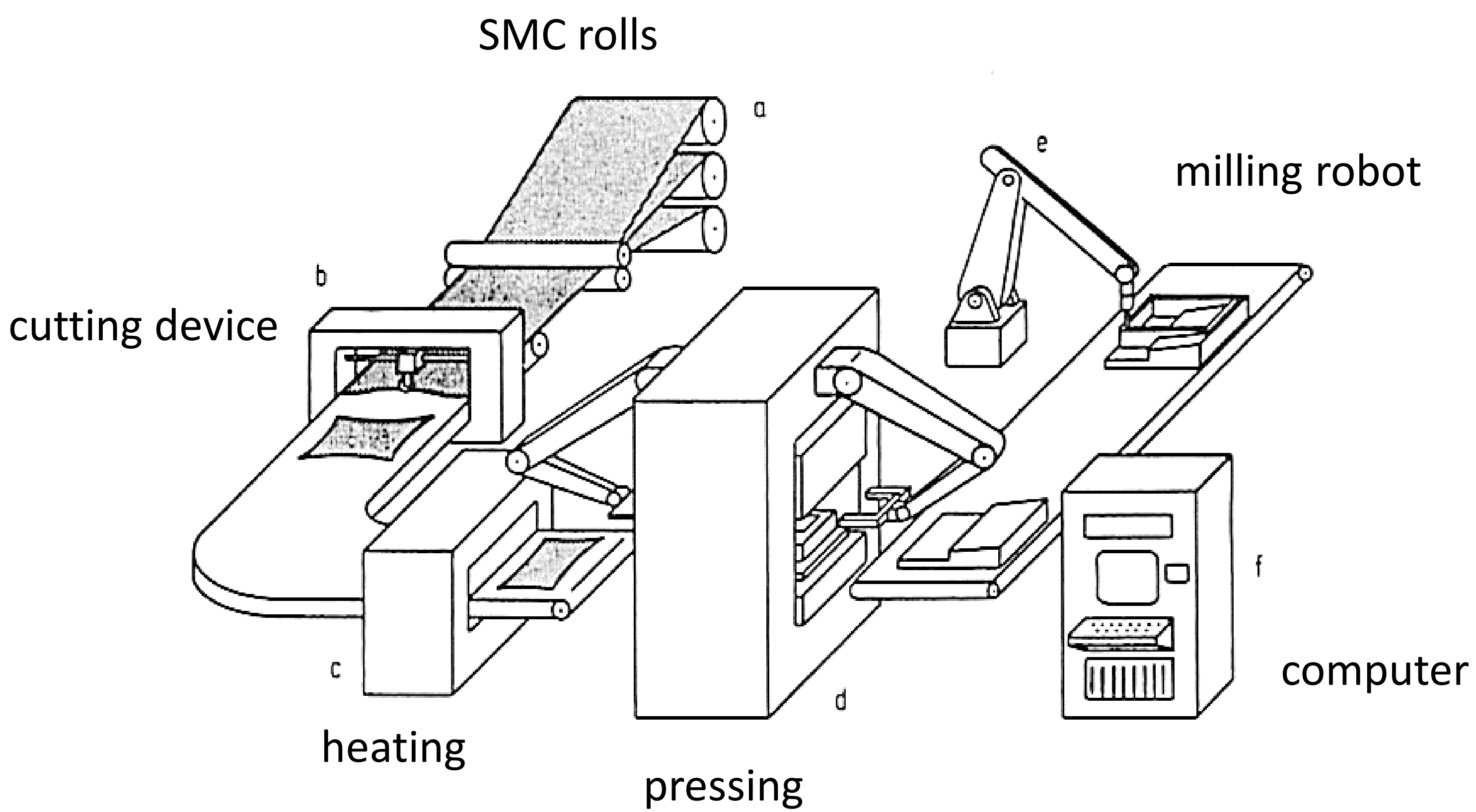
frame press

SMC press



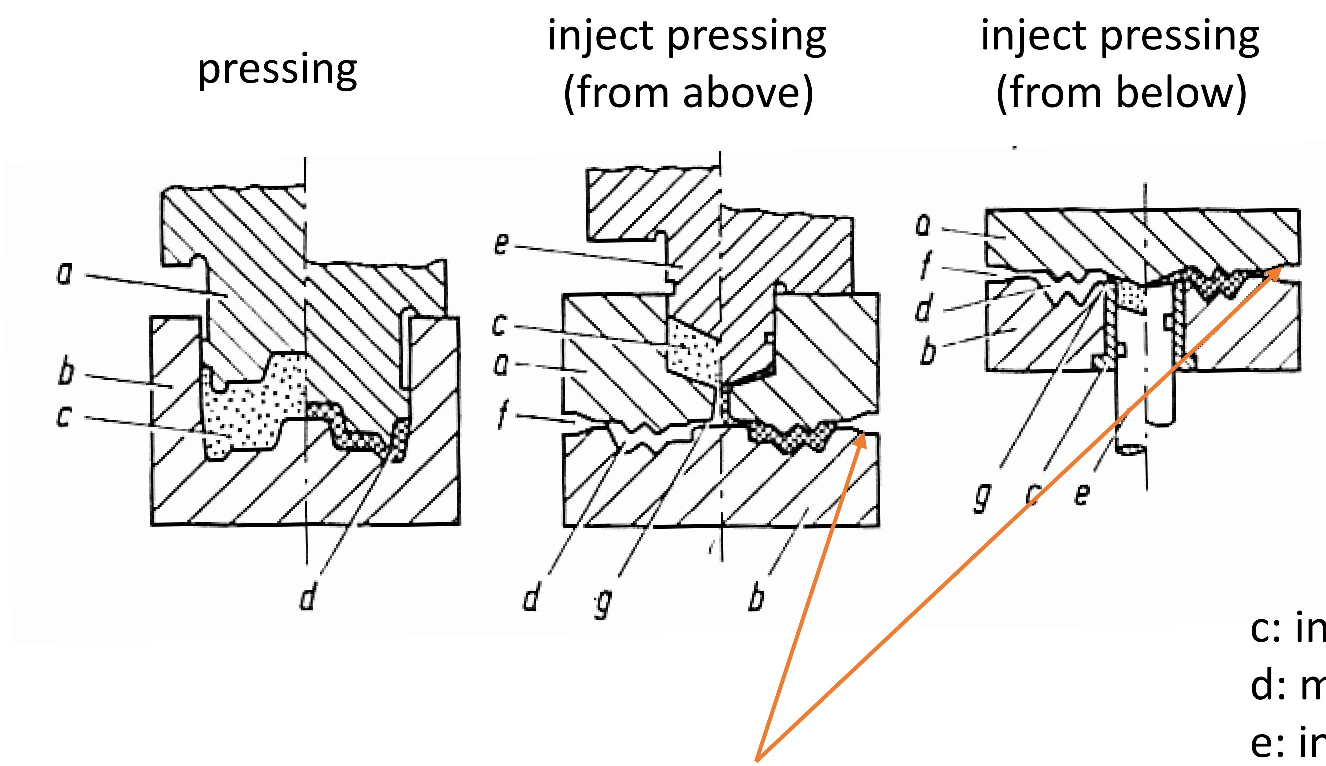


Automated SMC processing



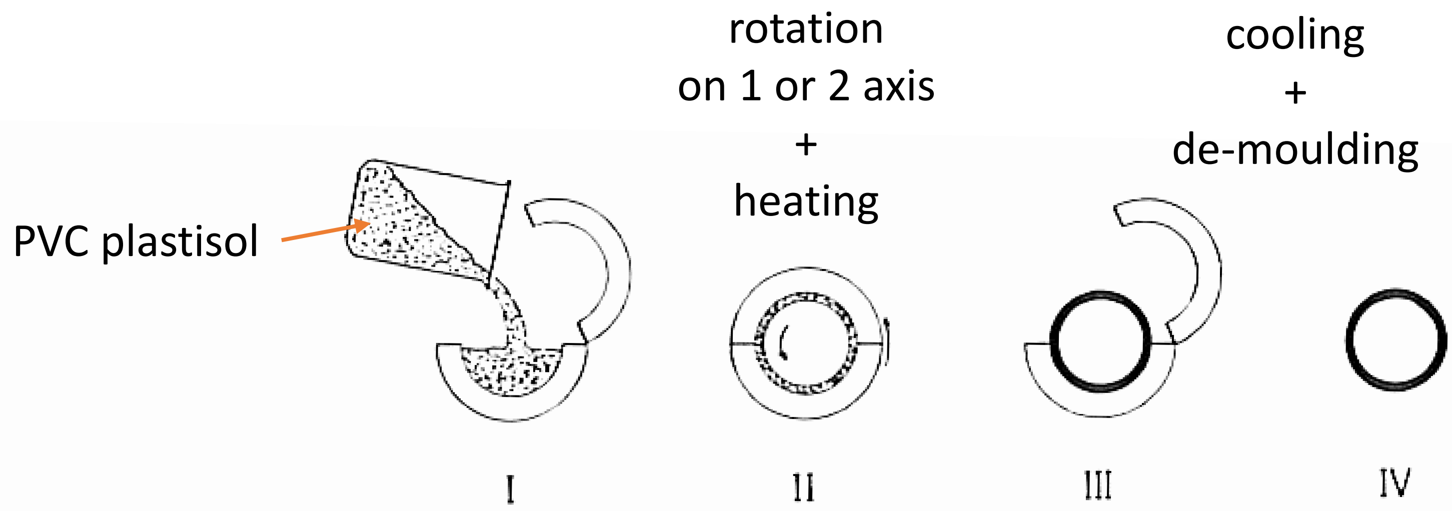
Different pressing configurations

- for loose plasticised material

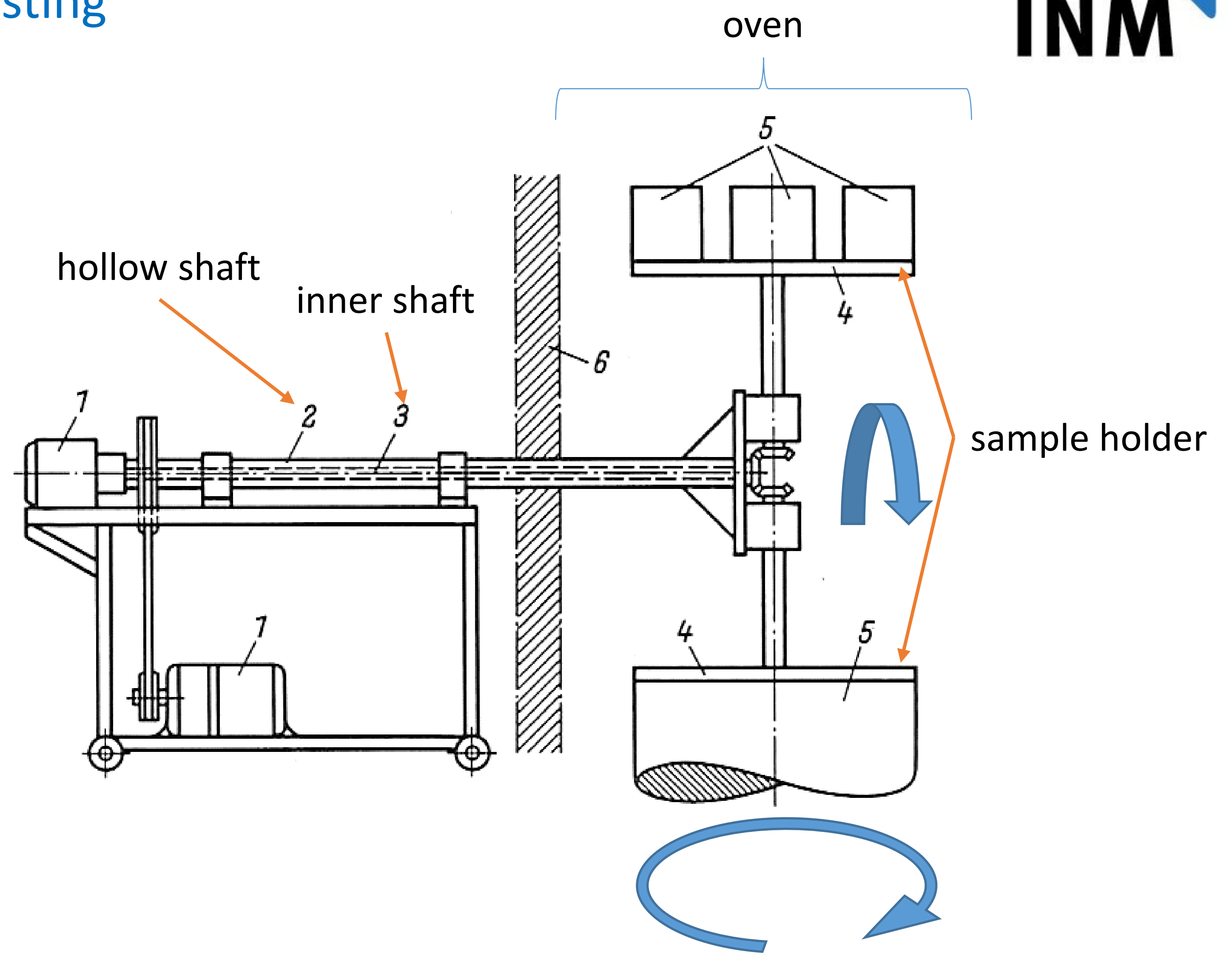


c: inject cylinder
d: mould
e: inject piston
f: exhaust

Rotational casting

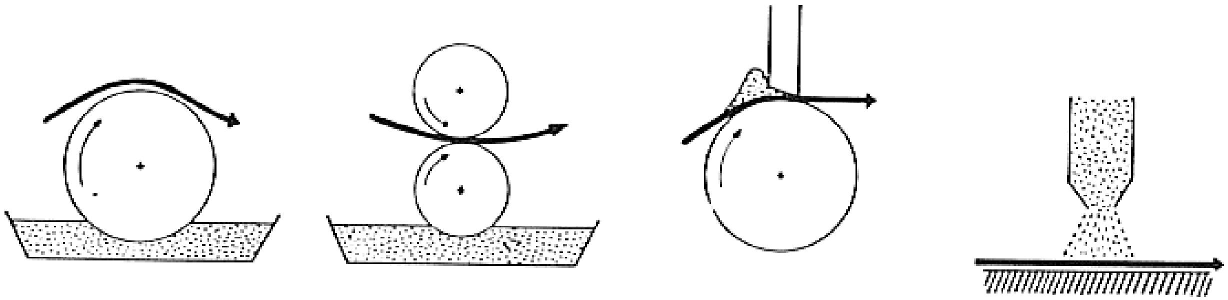


Rotational casting



Coating

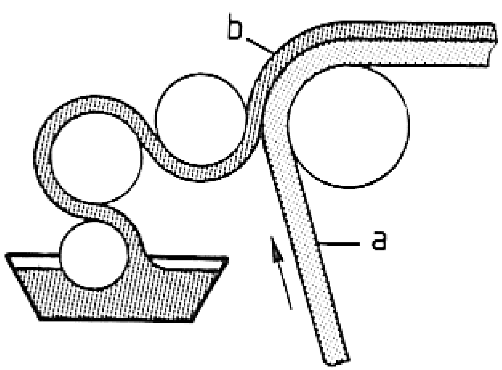
roller coating | gravure coating | raking | spraying



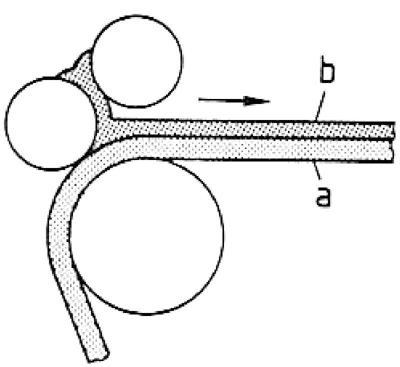
a | b | c | d

Coating techniques

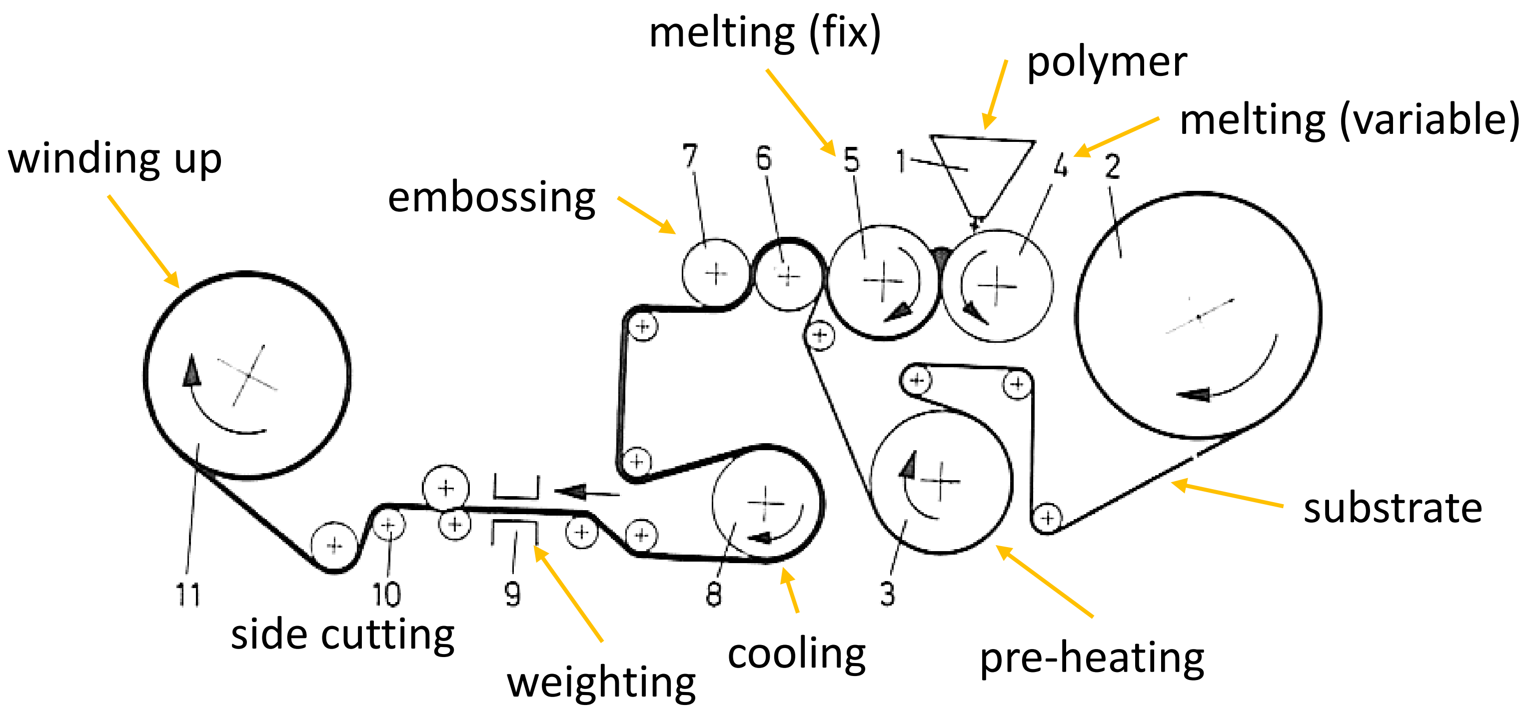
4-roll direct coater



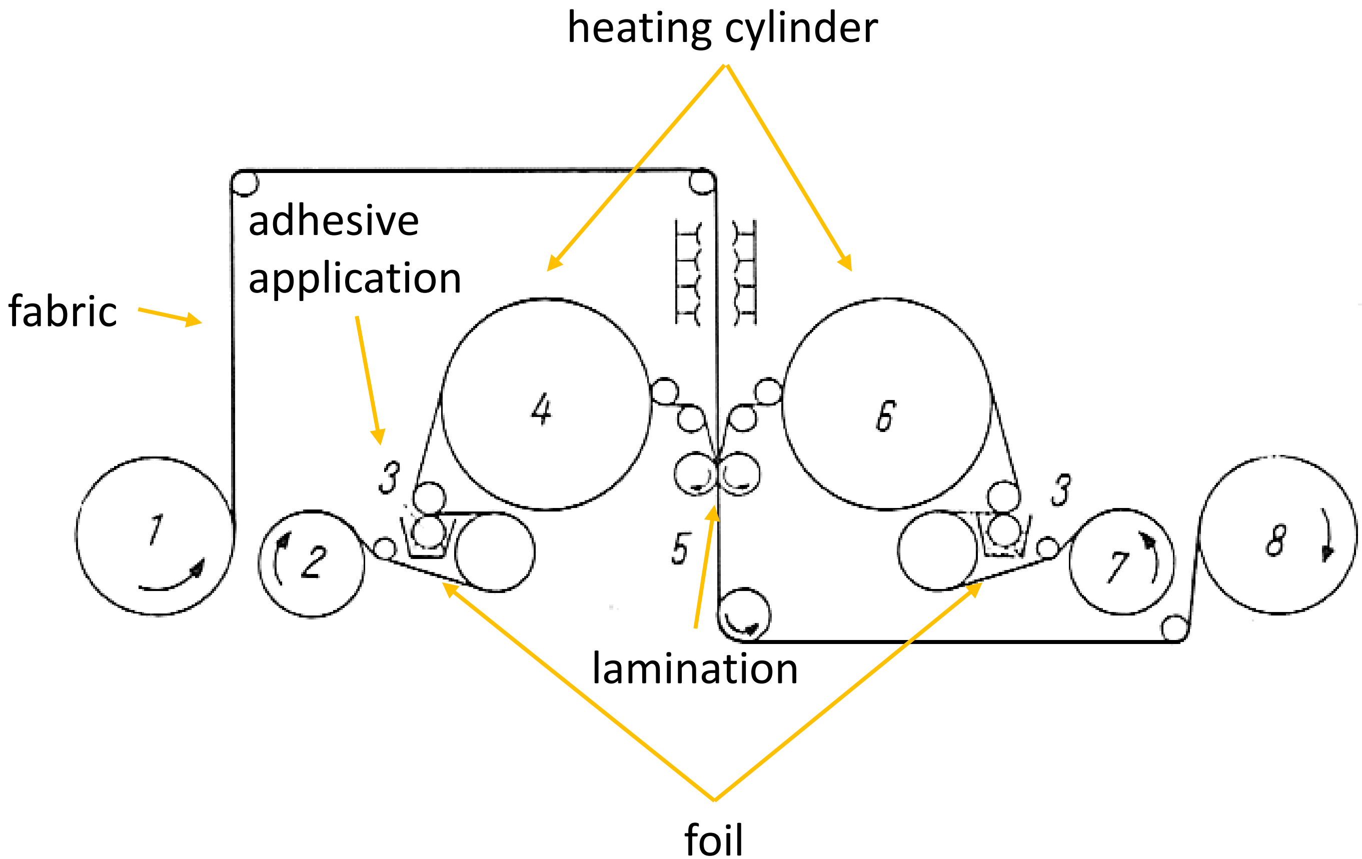
reverse roll coater



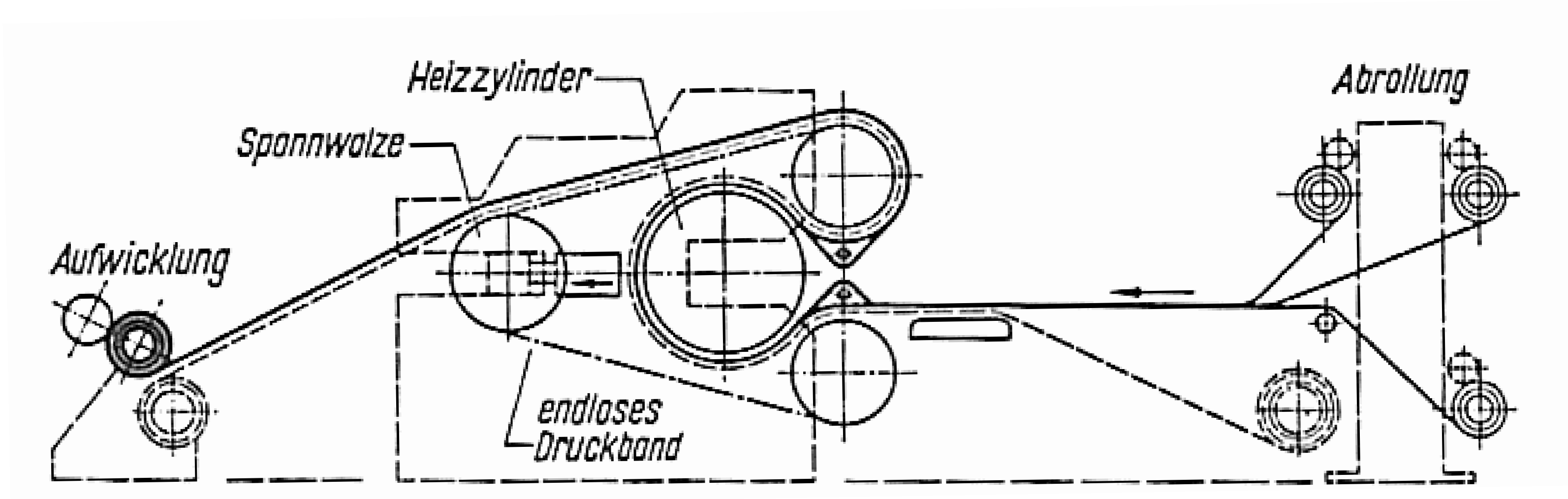
Melt coating process



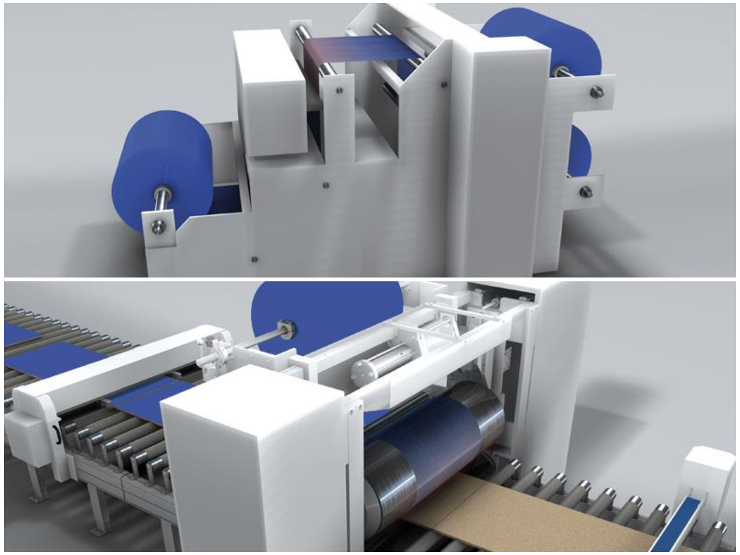
Laminating process

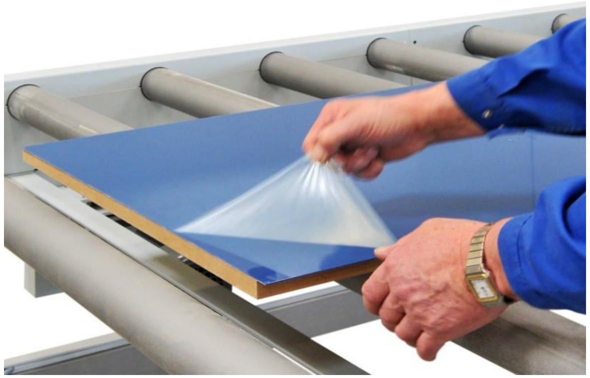


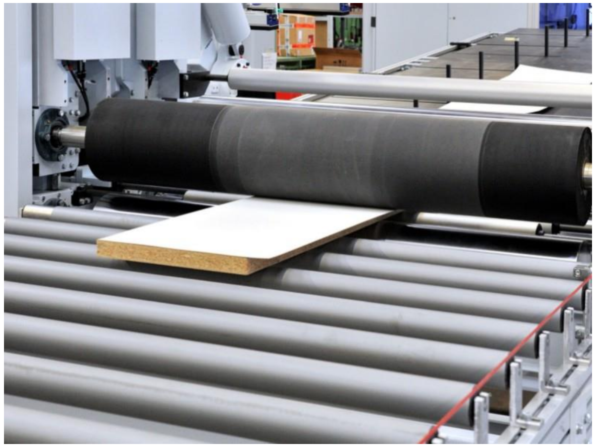
Doublieren und Kaschieren



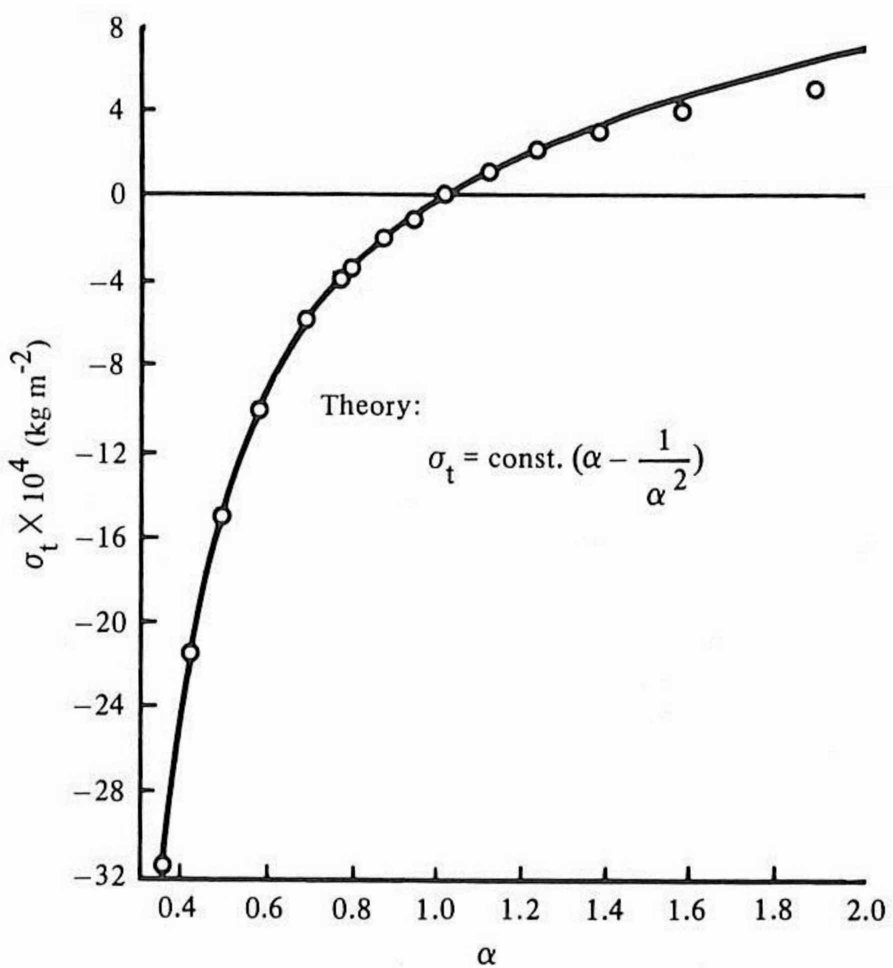
Kaschieren







example:
cross-linked
natural rubber

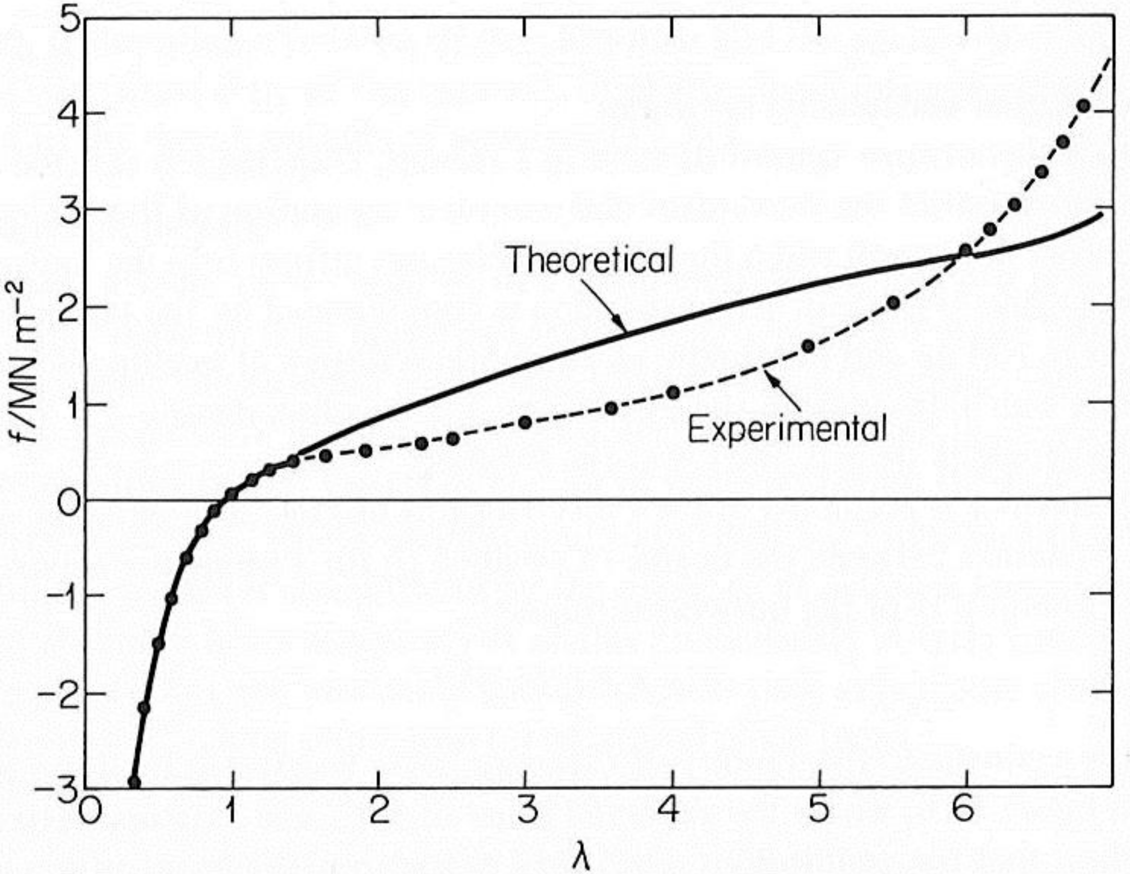


comparison
experiment and
theory

L.R.G. Treloar, Trans. Faraday Soc 40:59 (1944)

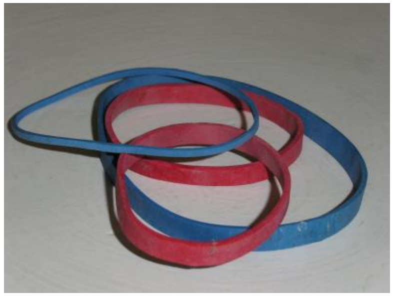
Entropy elasticity (ideal elastomer)

extension or compression ratio λ as a function of tensile or compressive force f



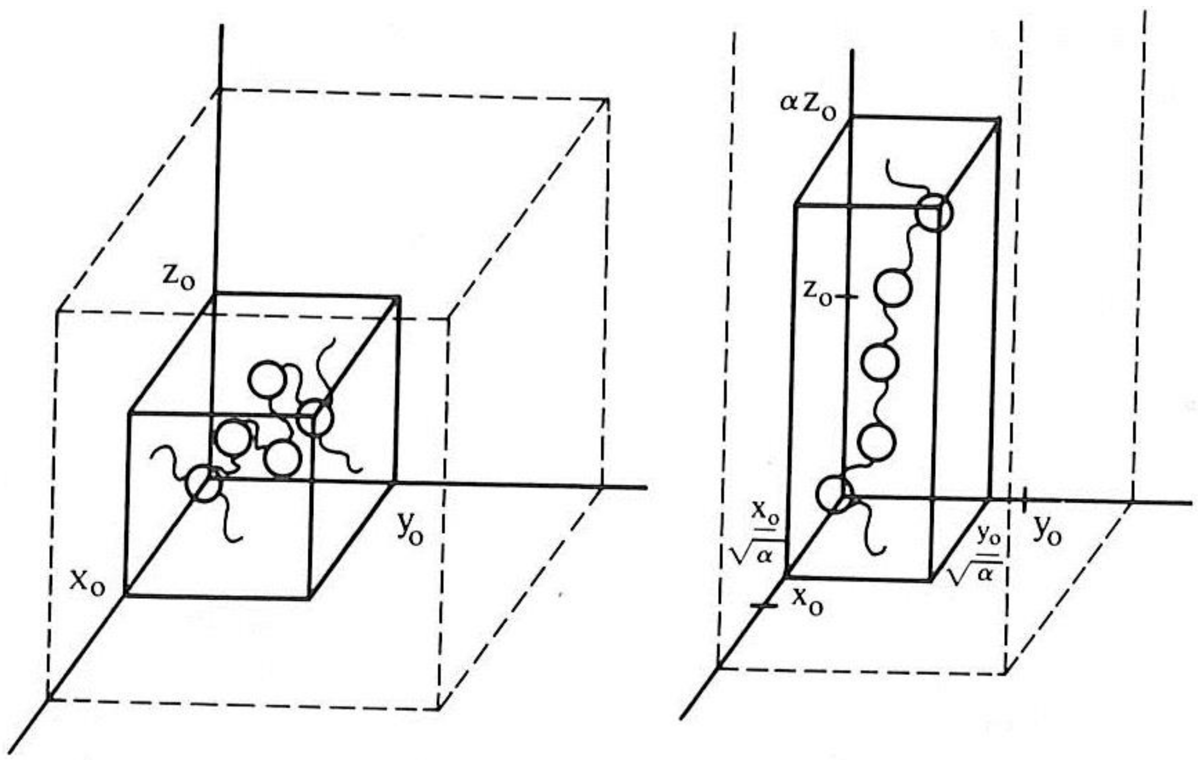
rubber vulcanisate

G = 0.392 MNm^{-2}



L.R.G. Treloar, Trans. Faraday Soc 40:59 (1944)

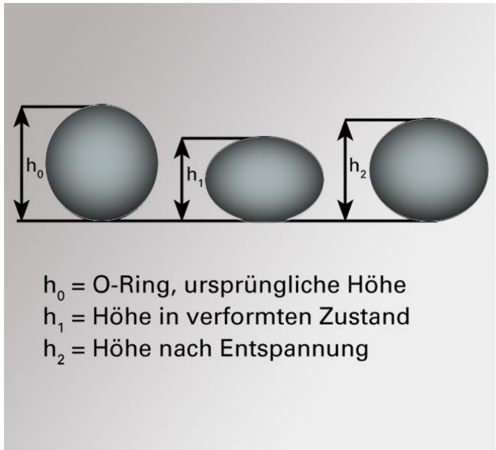
Affine deformation of polymer subchain



extension in z-direction

Real elastomers have network defects

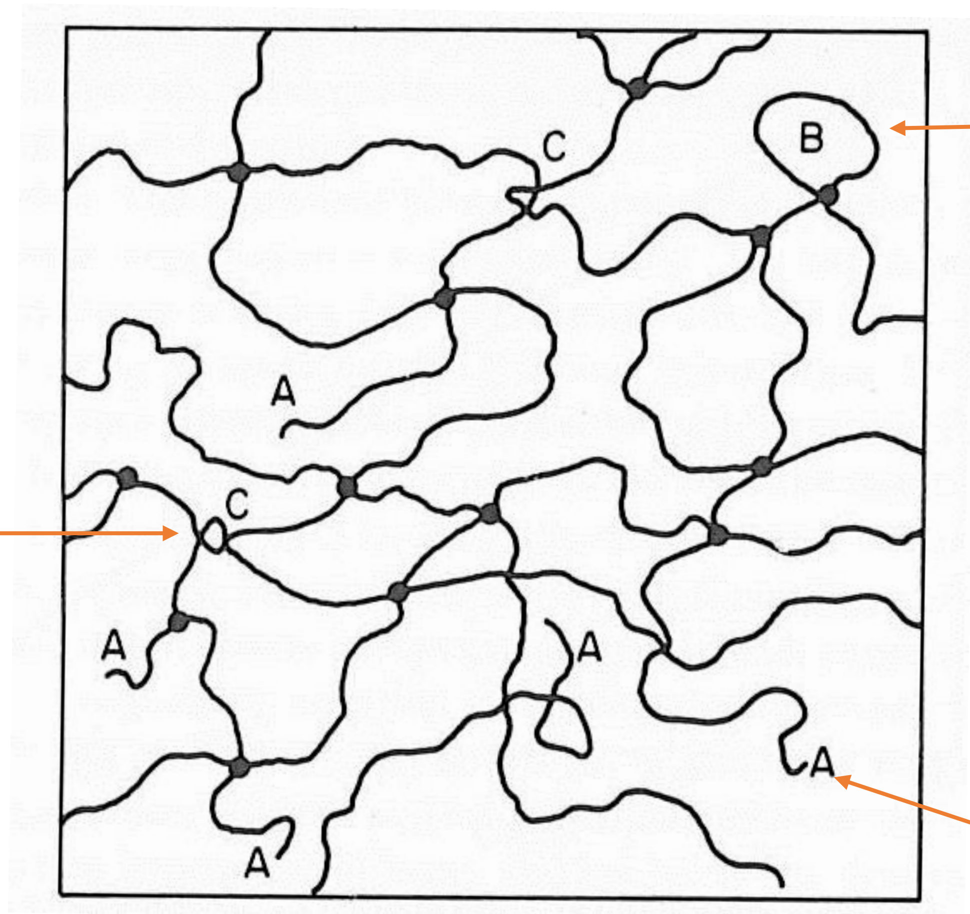
o-ring cross section



Defects in an elastomeric network

intramolecular
chain loops

entangled
chain loops



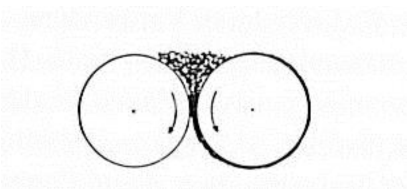
loose chain ends

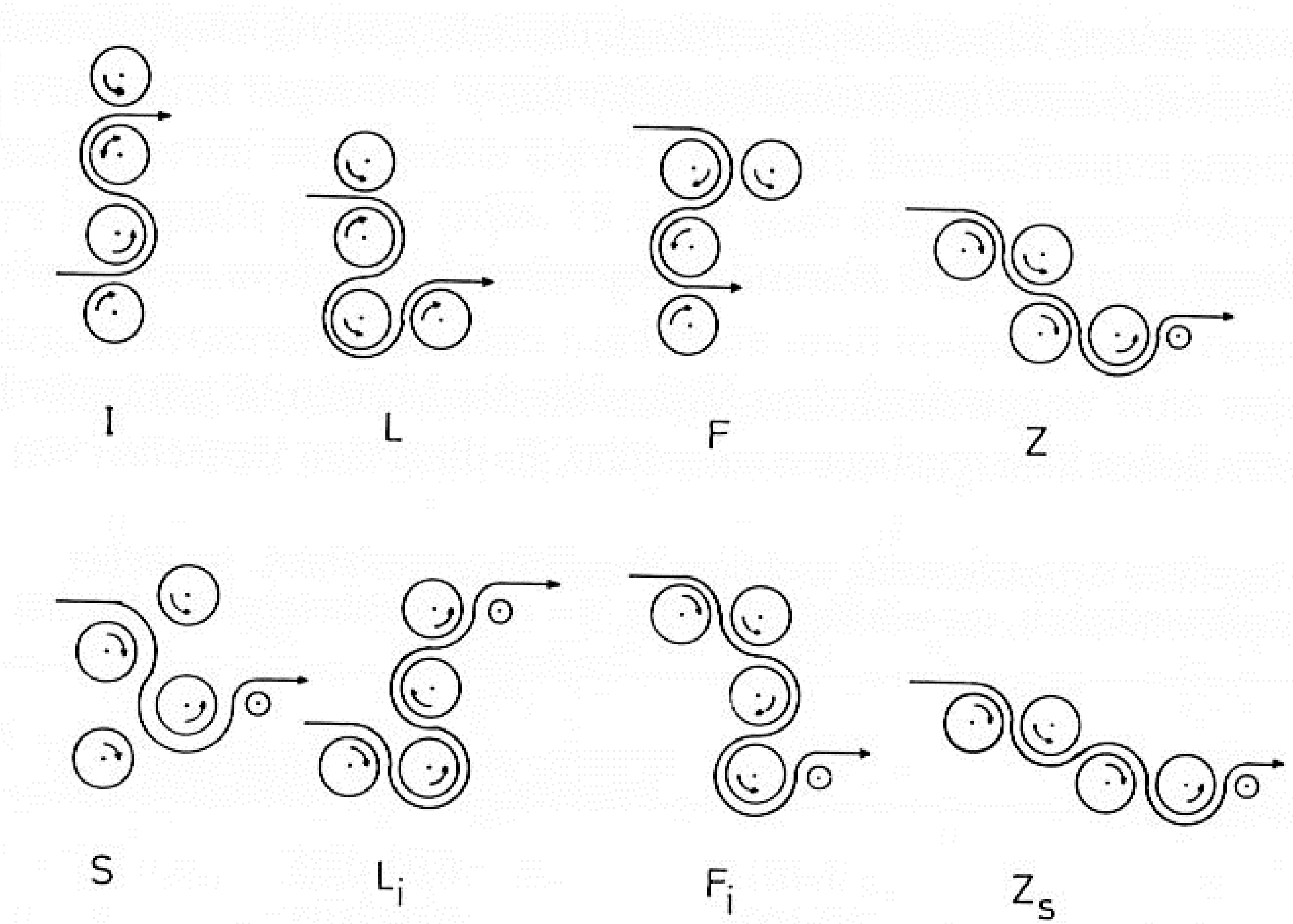
Rubber

?


Ruß
Naturkautschuk
Synthesekautschuk
Rapsöl
Silicia
Aktivator
Stearinsäure
Alterungsschutzmittel
Lichtschutzwachs
Mineralöl
Schwefel
Zinkoxid

Some 4-roll calanders



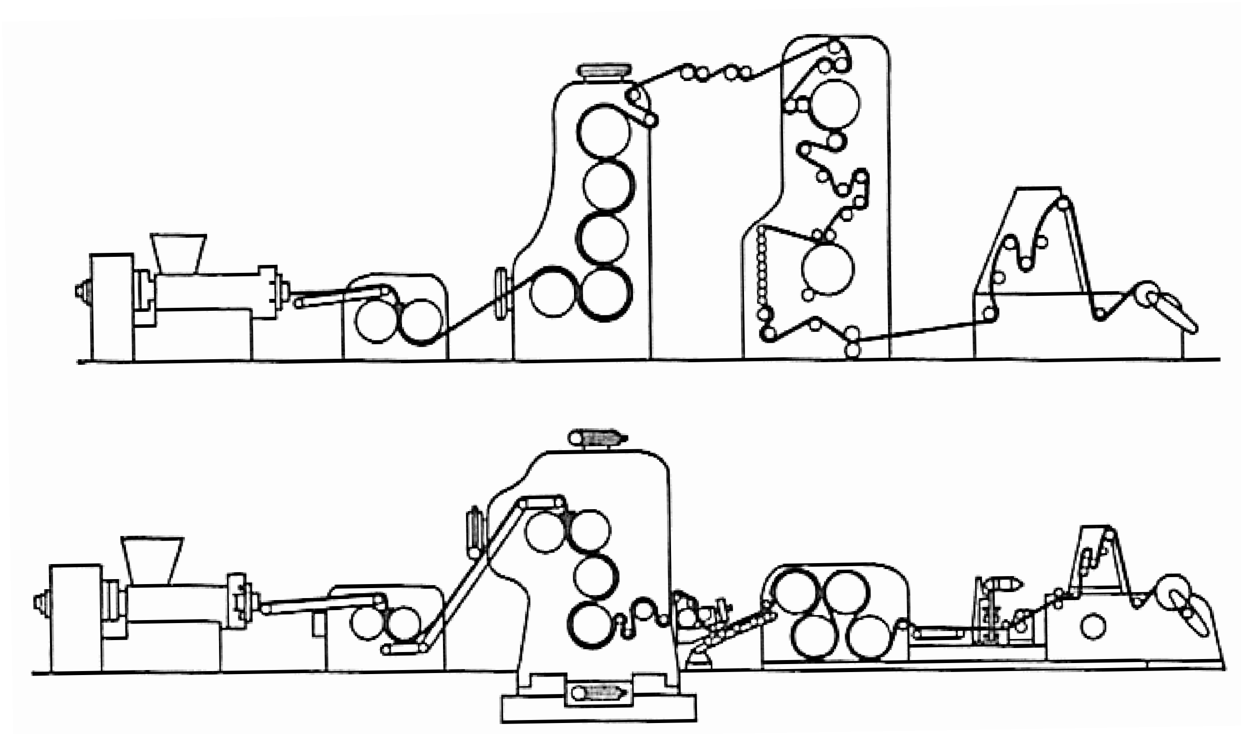


i = inverted
s = stretched

Calander roll

Calanders for elastomer preparation

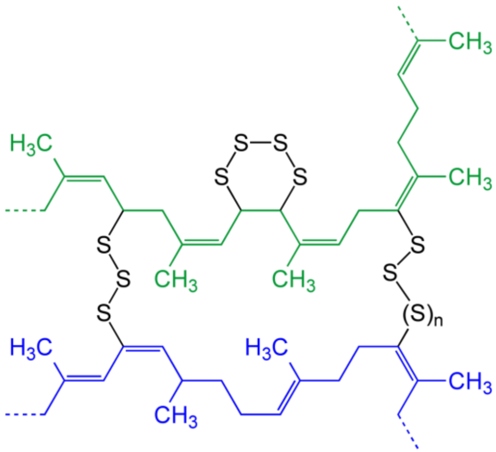
Examples for calanders



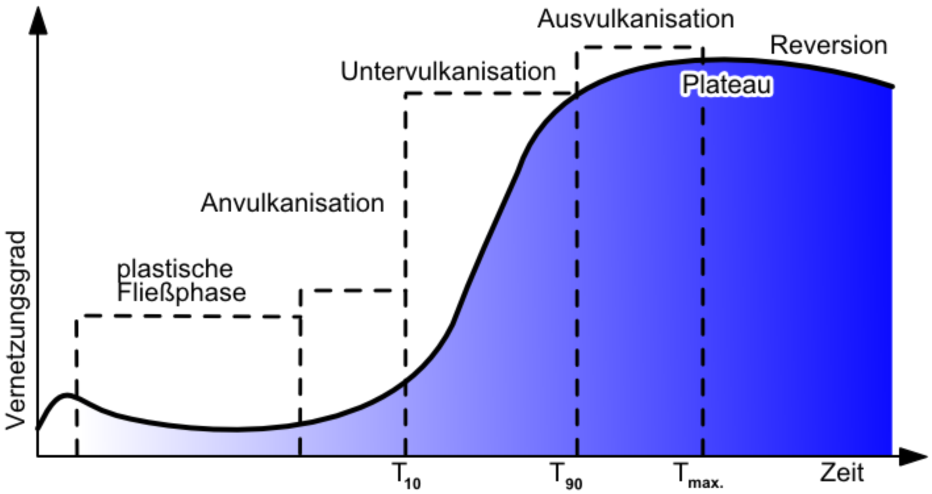
5-roll calander
Luvitherm process
PVC foils

4-roll calander
PVC-P foils
(soft)

The cross-linking: vulcanisation



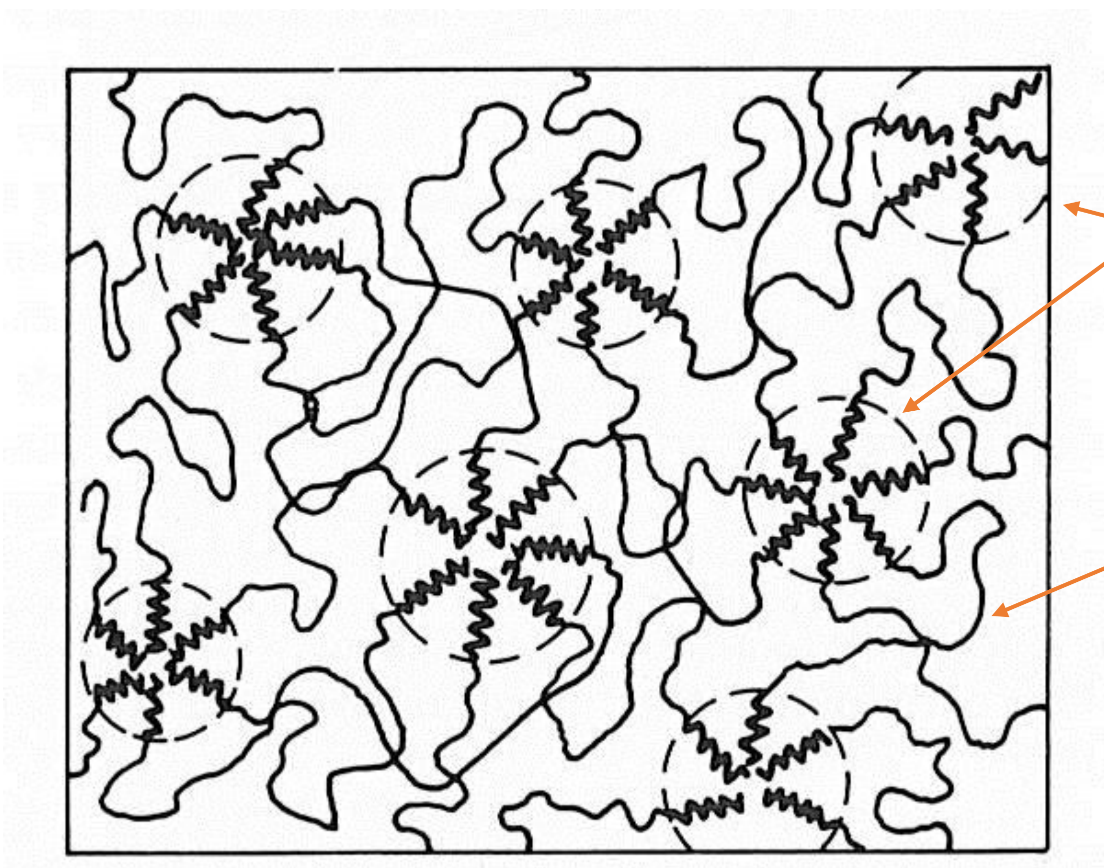
process



product

Thermoplastic elastomers

elastoplastic sandwich block copolymers



glassy blocks

amorphous
rubber like chains