MŰEGYETEM 1782

BUDAPEST UNIVERSITY
OF TECHNOLOGY AND ECONOMICS
FACULTY OF MECHANICAL ENGINEERING

Rubber technologies

Polymer Processing, BMEGEPTAGE3

Bélas ZINK, PhD, assitant professor

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DEPARTMENT OF
POLYMER
ENGINEERING

Definition

Elastomer: Polymers that are capable of min. 100% reversible elongation. Low load (a few MPa) results in large deformation, which goes off immediately upon unloading.

Rubber (uncured) – raw rubber material - uncured

Rubber mix – uncured raw rubber + additives, curatives, fillers, reinf.

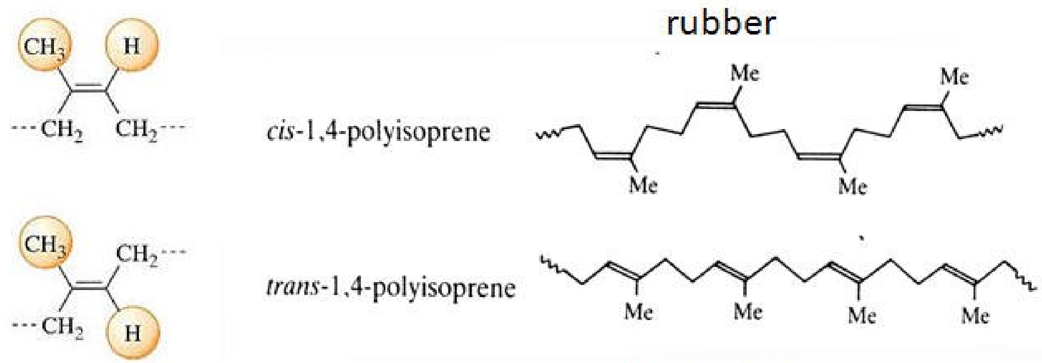
Rubber (cured) – cross-linked rubber mix

Elastomer can be **cross-linked** (cured rubber) or **thermoplastic** (TPE)

TPE: physical cross-links, incompatiblesoft (low Tg)+hard (high Tg) segments

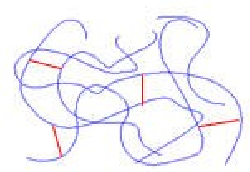
Natural rubber production: https://youtu.be/lUg7r7fu_eo

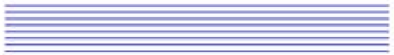
rubber



Gutta-Percha

Rubber forms an amorphous structure





Gutta-percha forms crystalline arrays

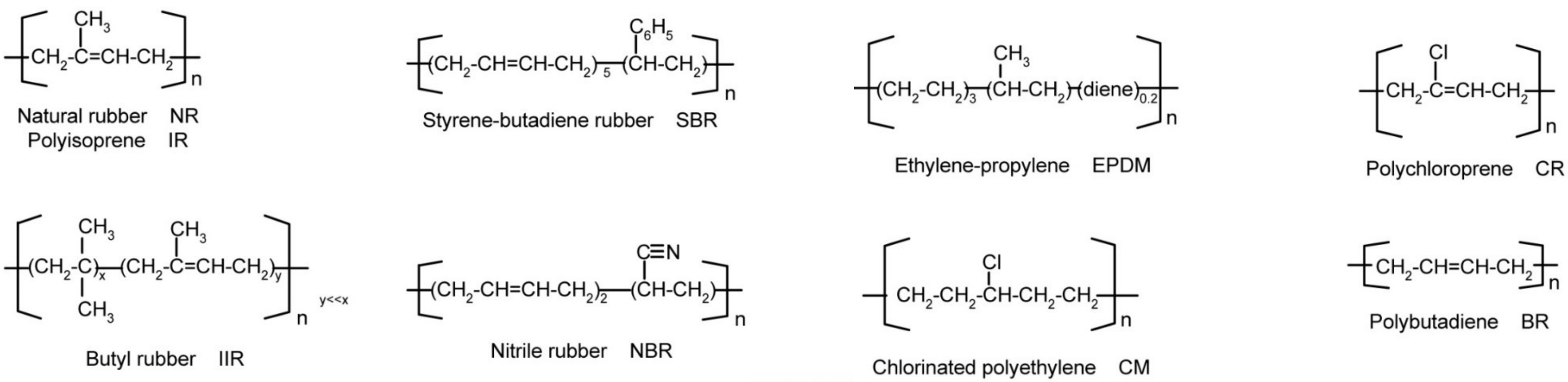
Definition

Natural rubber (NR): cis-1,4-polyisoprene disperged in water -> latex
water is coagulated, smoke is used to preserve -> smoked rubber

Natural rubber compared to synthetic rubber:

- Lower hysterisys
- Higher heat dissipation
- Higher mechanical properties

Synthetic rubber (SR): polymerization process is used to produce
butadiene-rubber, styrene-butadiene-rubber etc



Rubber recipe

What does a rubber recipe contain?

- Uncured rubber
- Curatives
- Additives (antioxidant, flame retardant, colouring)
- Fillers/Reinforcement (carbon black, silica, sand, etc.)
- Plasticizers (processing aids, plasticizers, extenders): mineral oil, natural oil, synthetic plasticizers

Curatives:

- Sulphur (S)
- Peroxide
- Resin
- Activator (e.g. Zinc-oxide + stearic acid)
- Accelerators (e.g. Sulfenamides)
- Retarders

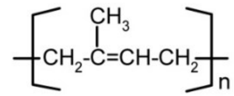
Raw materials

Raw material of rubbers: uncured rubbers:

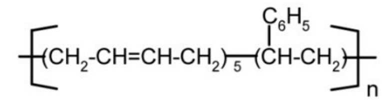
- Natural rubber (NR)
- Synthetic rubbers (e.g. BR, IR, SBR, EPDM…)

Uncured rubber:

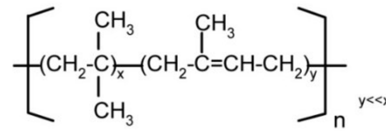
- Linear thermoplastic polymer
- Amorphous or semi-crystalline
- T_g below RT
- Low modulus, high deformability
- Use of uncured rubber is limited (latex, impact additives)
- Main applications after curing (crosslinking) as (cured) rubber



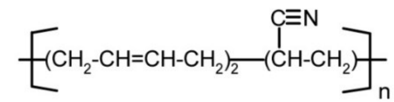
Natural rubber NR
Polyisoprene IR



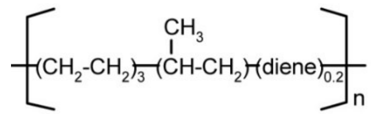
Styrene-butadiene rubber SBR



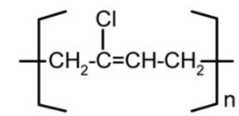
Butyl rubber IIR



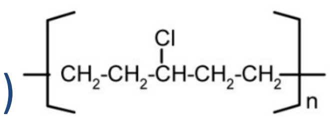
Nitrile rubber NBR



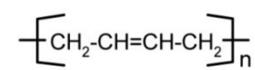
Ethylene-propylene EPDM



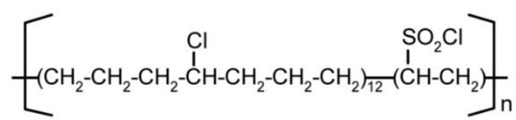
Polychloroprene CR



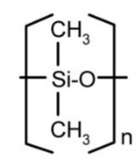
Chlorinated polyethylene CM



Polybutadiene BR



Chlorosulfonated polyethylene CSM

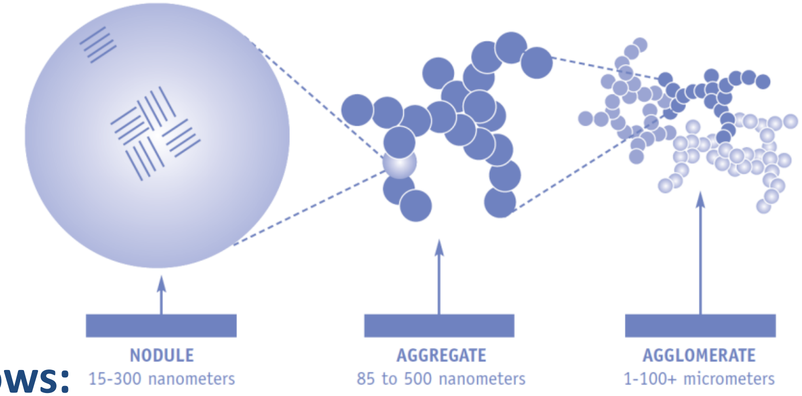


Silicone MQ

Raw materials

Fillers/reinforcement

- Carbon black (most important): increases tensile and tear strength, and wear resistance significantly. Active CB: small size (10-15 nm to few μm), so it has large specific surface (up to 2 000 m^2/g).
- Kaolin clays
- Calcium carbonate
- Silica



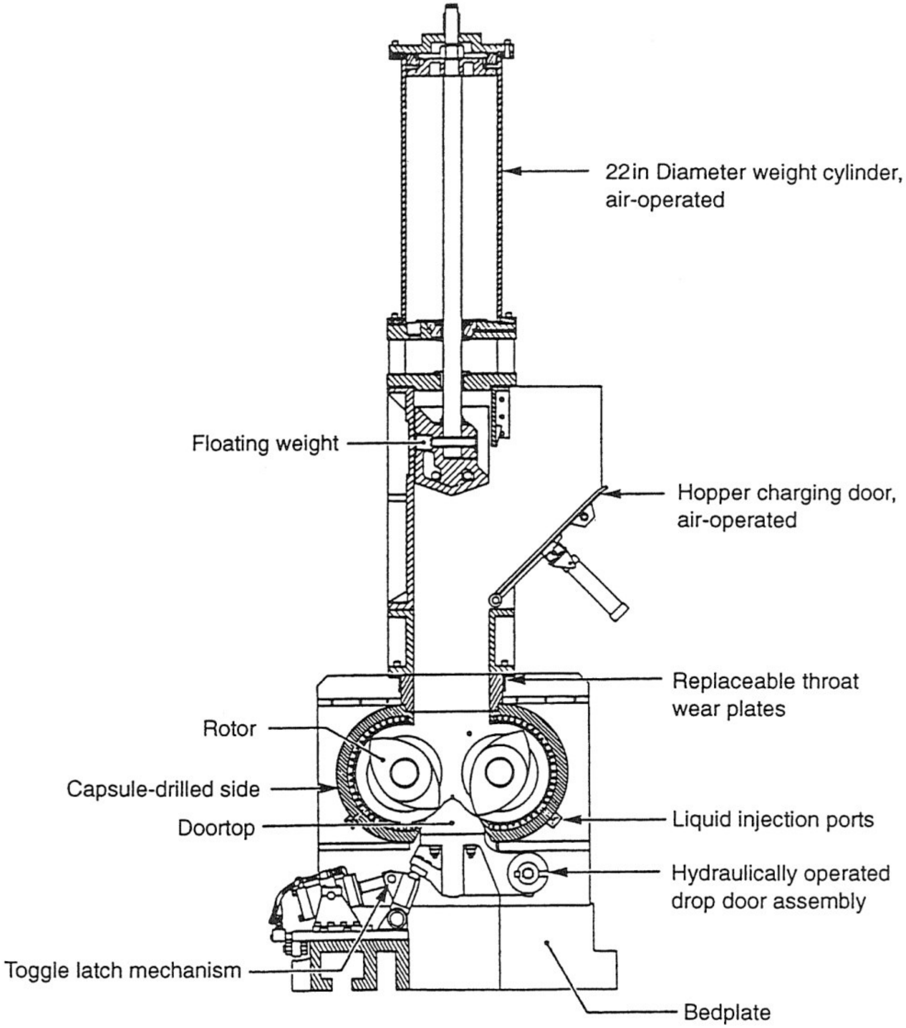
Fillers' properties affect the properties as follows:

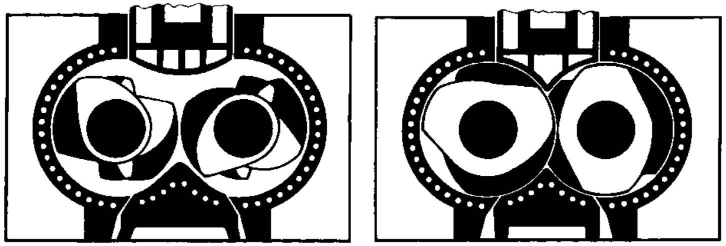
- With increasing specific surface, viscosity, tensile and tear strength, and wear resistance, hysteresis increase.
- With increasing surface activity, wear resistance, modulus and hysteresis increases.

A rubber recipe usually contains 10-15 components (proper design is necessary) which have to be distributed/dispersed homogenously in rubber matrix.

Rubber mixing

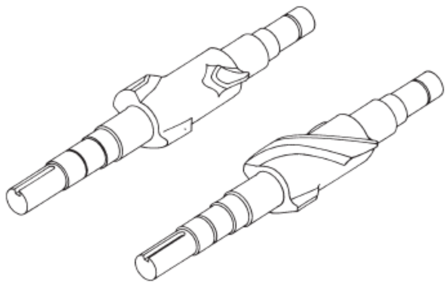
Internal mixers - Banbury-type mixers



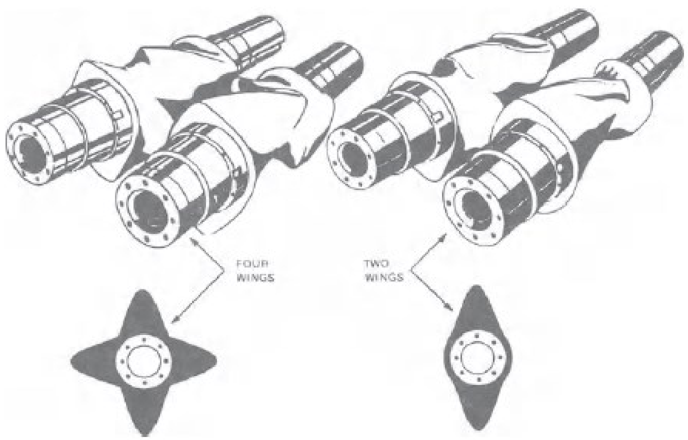


a) b)

Fricition between the rotors



Francis Shaw Intermix rotors

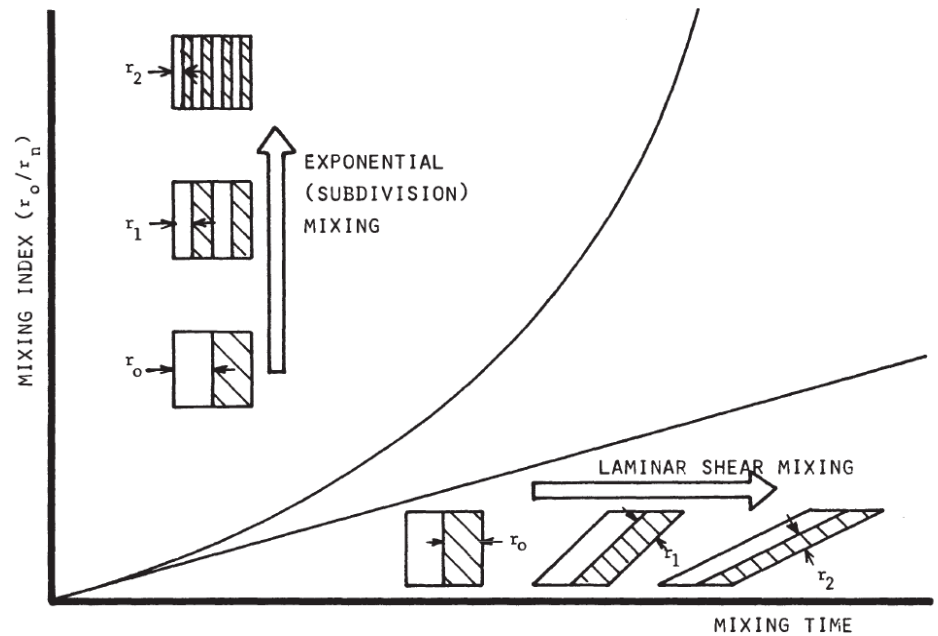


Farrel Bridge Banbury rotor

Rubber mixing

Mixing stages:

1. viscosity reduction
2. incorporation
3. distributive mixing
4. dispersive mixing



1. Temperature rise, chain extension, mastification (chain scission)

2. Low viscosity material flows around additives

3. Simultaneously with incorporation the volume of additives decreases

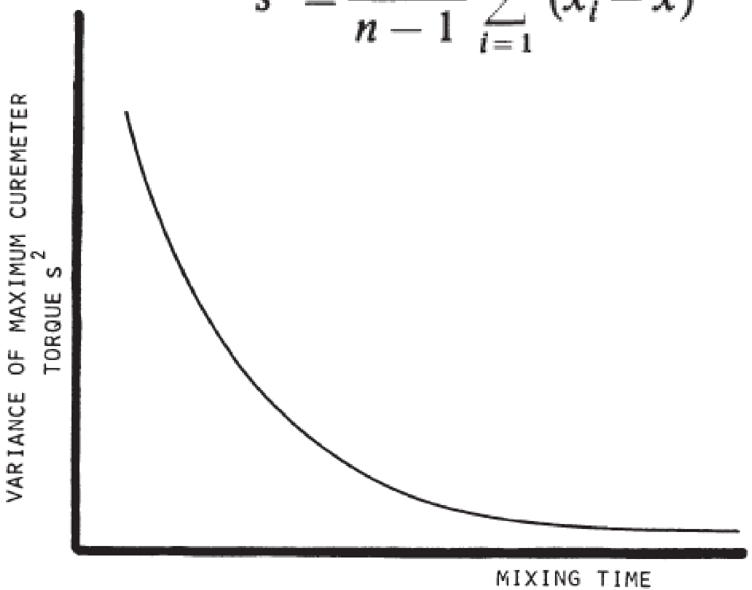
Folding flow+separation and recombination -> exponential mixing

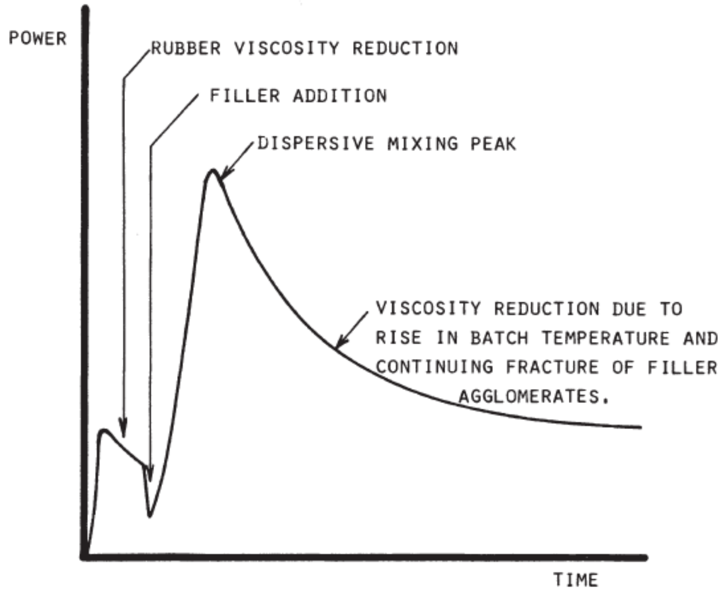
4. Slow viscosity increase causes dispersive mixing

Rubber mixing

s^2 the variance of the maximum curemeter torque, n is the number of samples taken from a batch mixed to a specified value of the dump criterion, X_i is the value of the i-th sample, and $\bar{x}$ is the average value of n samples, for a number of batches mixed to different dump-criterion values

$$s^2 = \frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2$$





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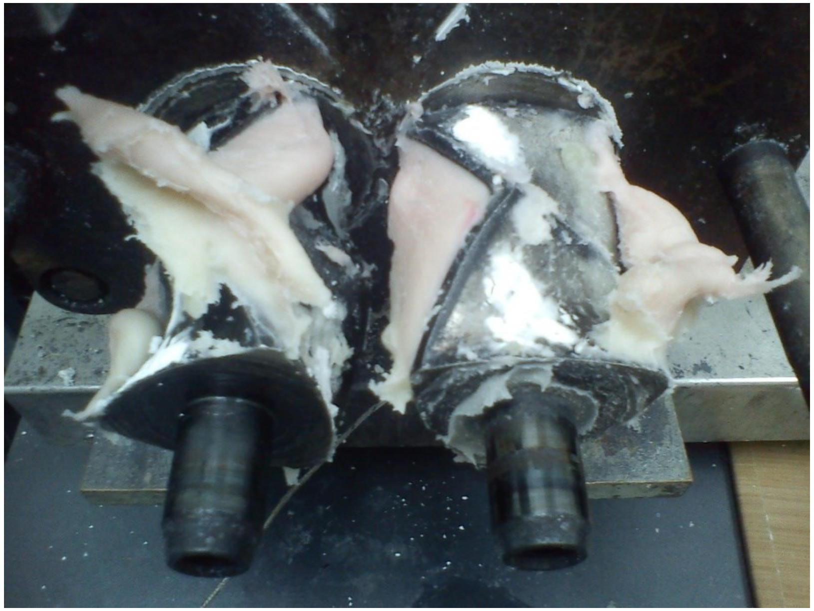
Rubber mixing

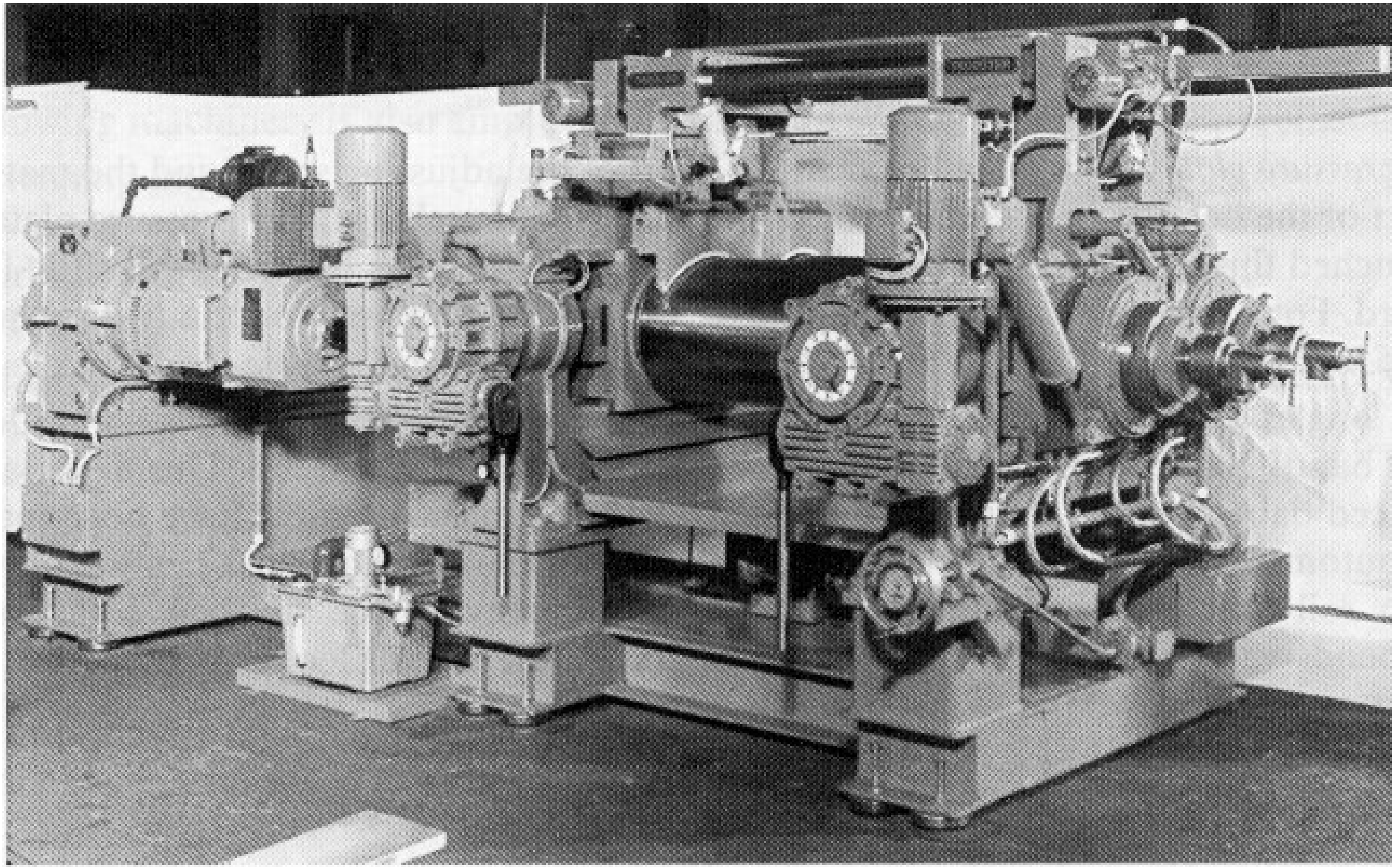
Internal mixers – laboratory scale



Rubber mixing

Rubber mixing: Roll mill/open mill

https://youtu.be/7Ju7J9zJ1Ow



Rubber mixing

Roll mill – laboratory scale

Rubber mixing

Roll mill

Shaping

Solution

Petrol was used before to dissolve caoutchouc

Nowadays watersolution is prefered -> latex

Before dissolving roll-mill is used to produce 3 mm thick plates

Impregnation

Textile is impregnated with low viscosity solution

Max 15 m% rubber is applied on the textile -> calendering or lubrication

Lubrication

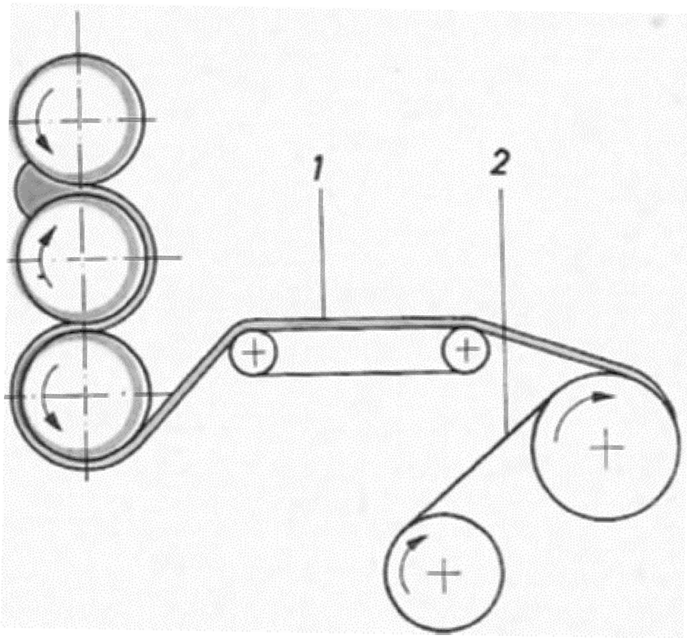
It is only used for thin, impregnated textiles

Higher m% of rubber can be achived than in the case of calendering

Lubrication knife is used disperse the rubber solution, dissolvent is evaporated

Shaping

Calendering for sheeting, coating

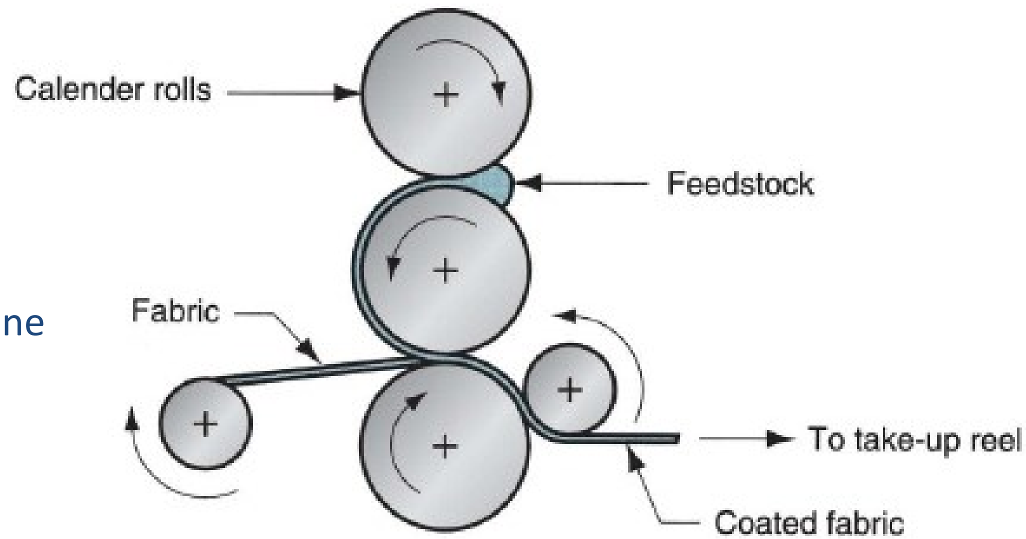


Lower temperatures compared to thermoplastic materials -> higher forces acting on the rolls

Feeding can be done by 2-3 internal mixers or extruder

Sheets: 3-4 calenders in a row

- textile or PE foil is just for windig
- 0.1-2 mm thick sheets in one layer
- above 2 mm thickness two layers are pressed together

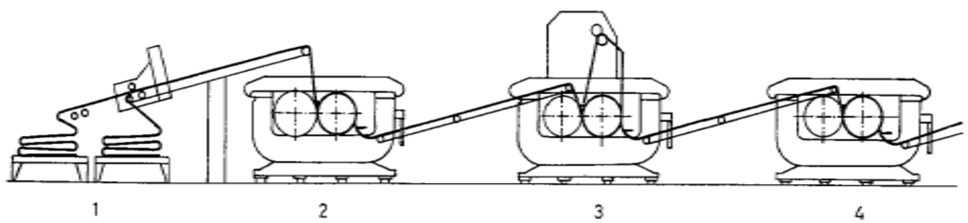


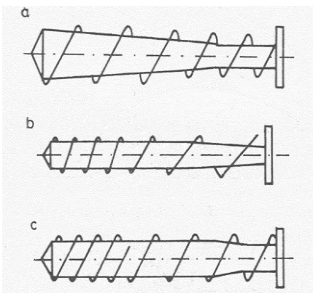
Coating: one or two sided

- two sided coating can only be done in one step with a 4 roll calender
- steel and fabric is used mostly

Shaping

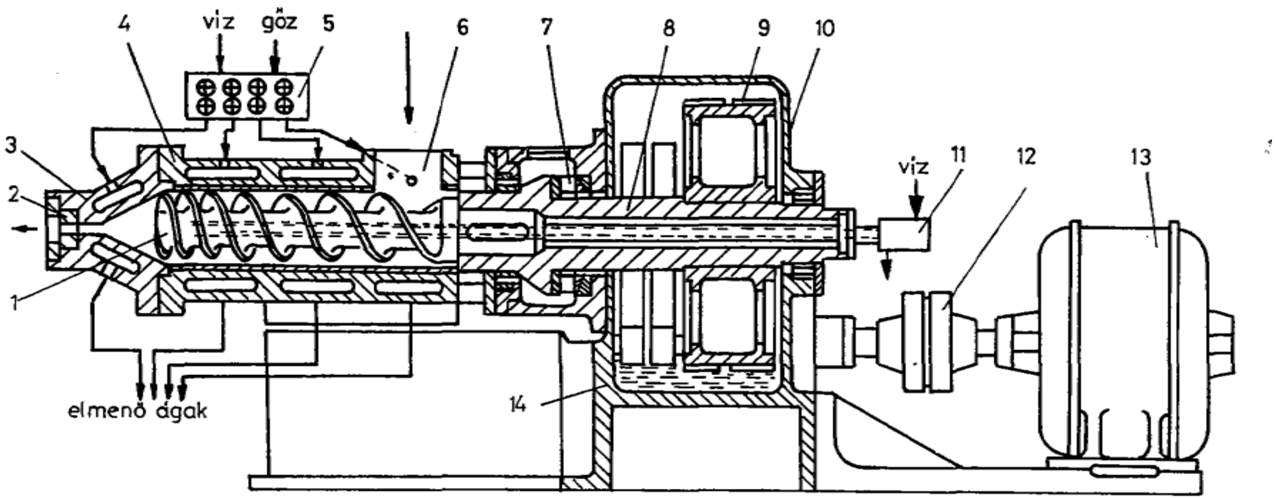
Extrusion - warm feed extruders





- Relies on the roll-mill for temperature control
- Used when short runs and versatility needed
- 3-5D screw length
- Conveying and pressurizing

Simple screw design, two or single start



- Dump/batch extruder
- Specil hot feed extruder
- Designed to accept discharged mix from internal mixer
- Large diameter screw plus pneumatic pusher
- Slab or sheet

Shaping

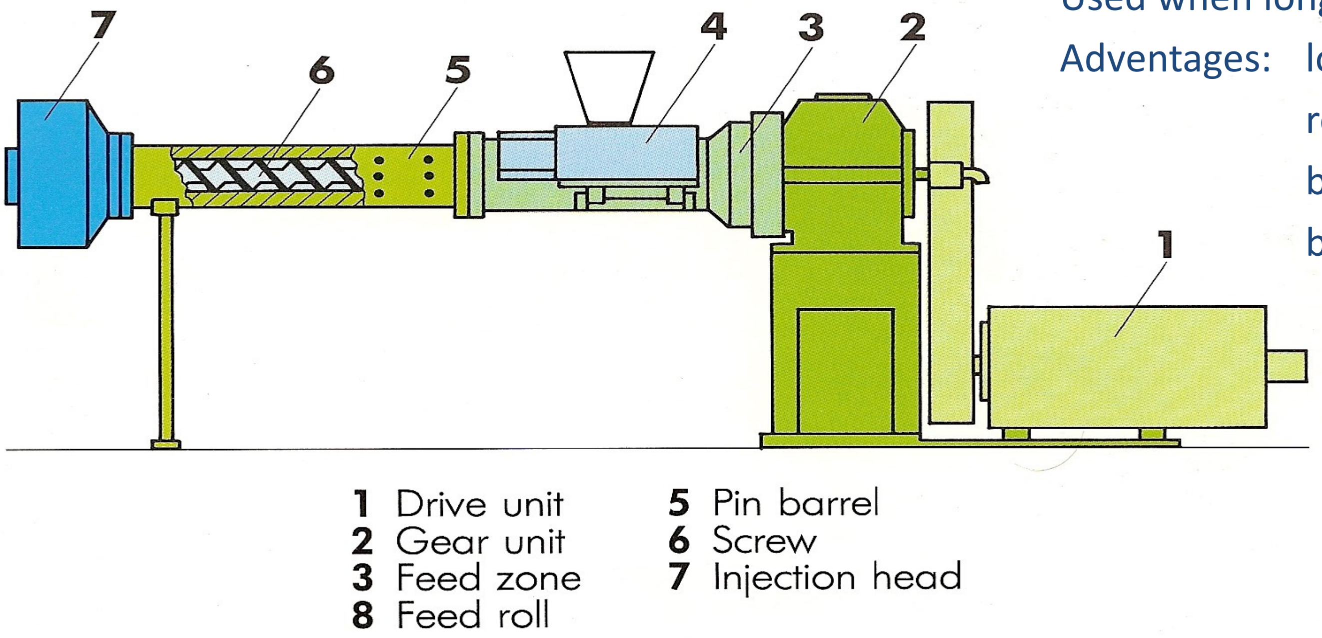
Extrusion - cold feed extruders

New screw design
longer screw, decreased pitch, decreased flight depth -> longer residence time, better mixing, better heat transfer
Mixing screws and sections ->limited range of rubbers can be used efficiently

No roll-mill needed

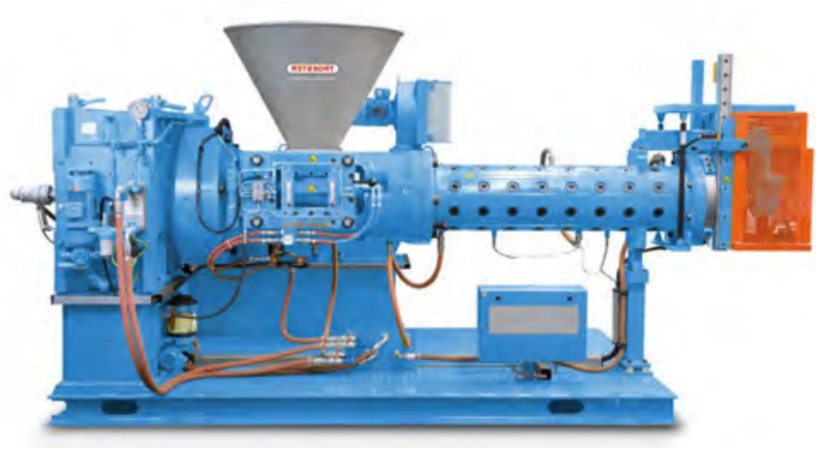
Used when long runs and limited mixes

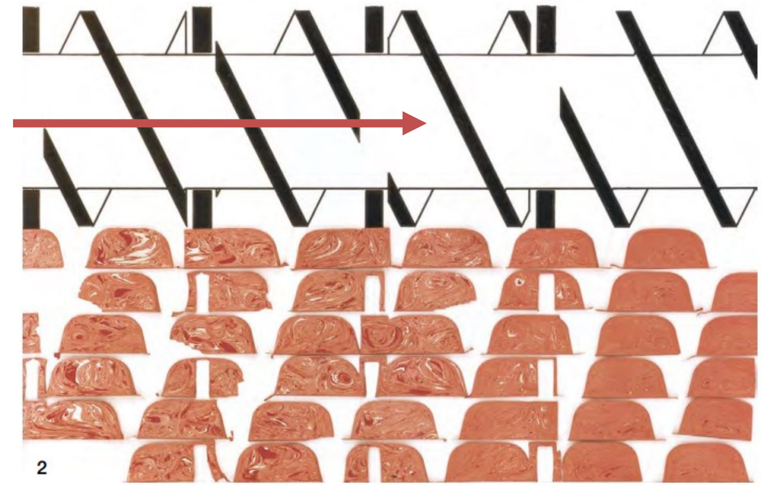
Adventages: lower capital cost
reduced labor cost
better temperature control
better dimensinal control



Shaping

Extrusion – Pin/QSM extruder



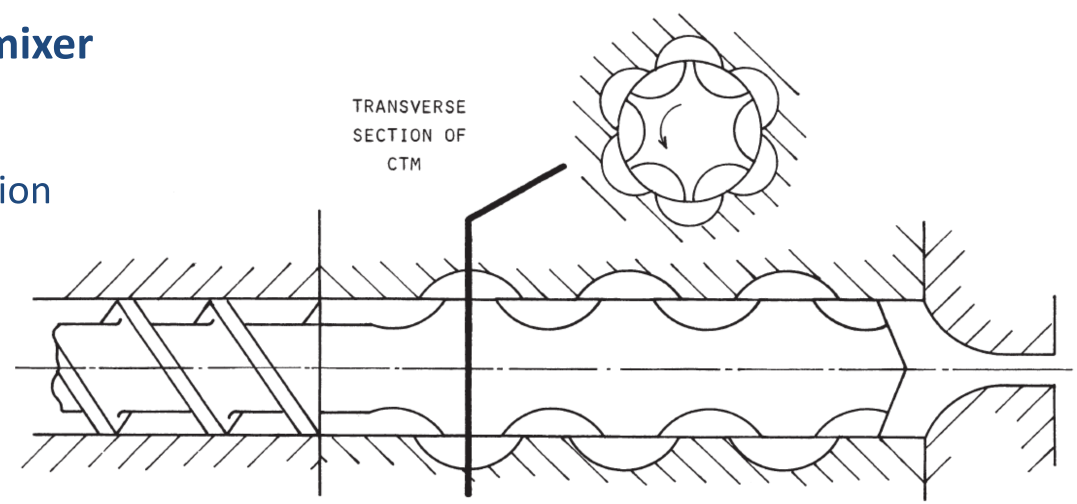


Extrusion – Cavity transfer mixer

Hemispherical cavities

Flow stream division+reorientation

Exponential distributive mixing

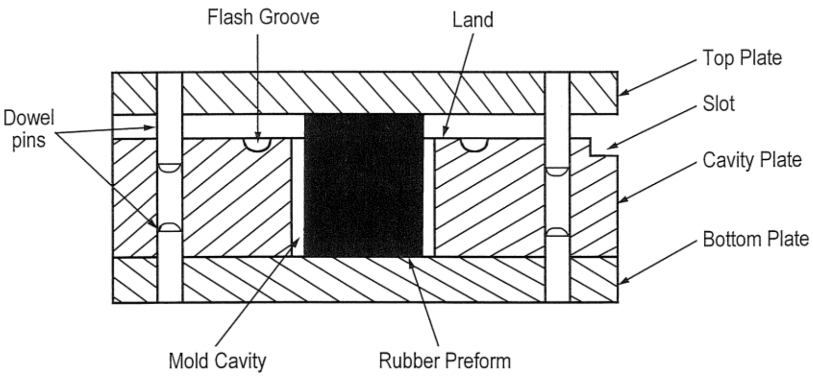


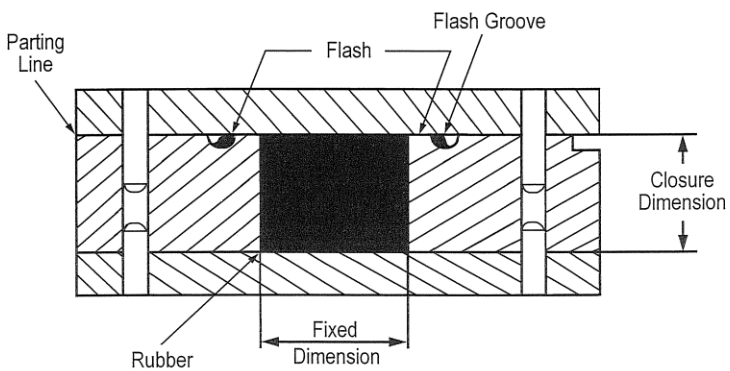
Shaping

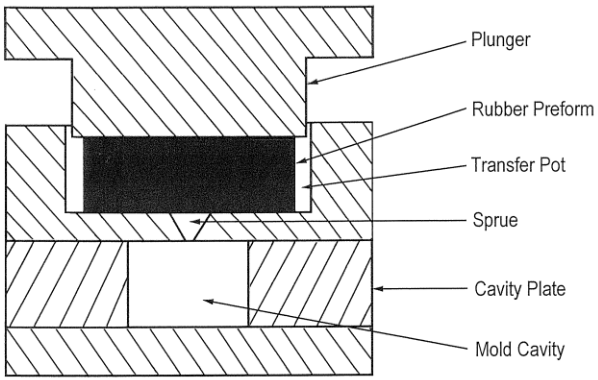
Shaping

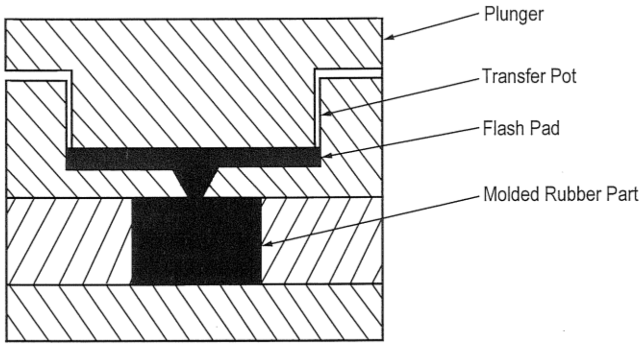
Compression, transfer moulding

Rubber needs to be preheated -> microvawe heater









Improved dimensional accuracy.

New and clean surfaces are generated on the rubber, which is extremely important for achieving a strong and consistent rubber-metal bond.

Transfer presses, lower unit manufacturing costs are possible.

Shaping

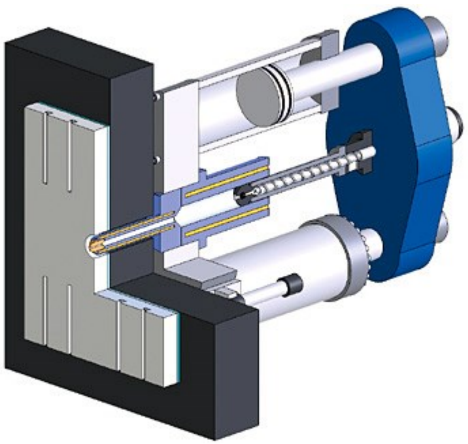
Injection moulding – typically with FiFo system

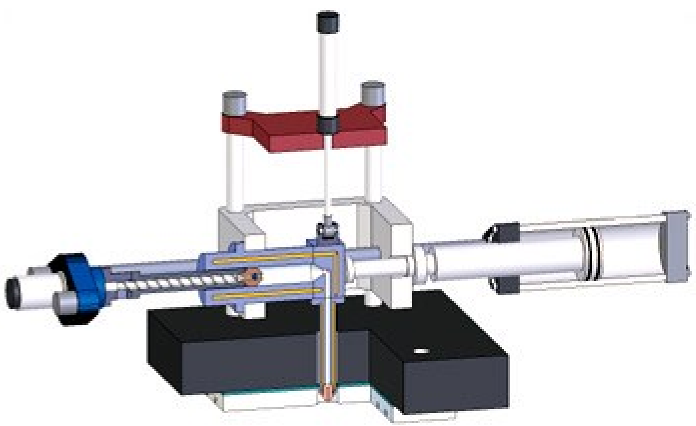
Compared to compression molding:

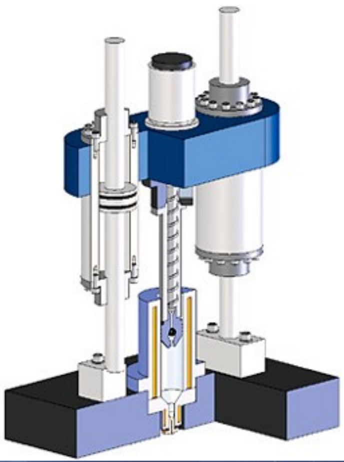
Better heat control

Higher temperature and flow rate -> reduced injection time and curing

Smaller runner system -> less waste

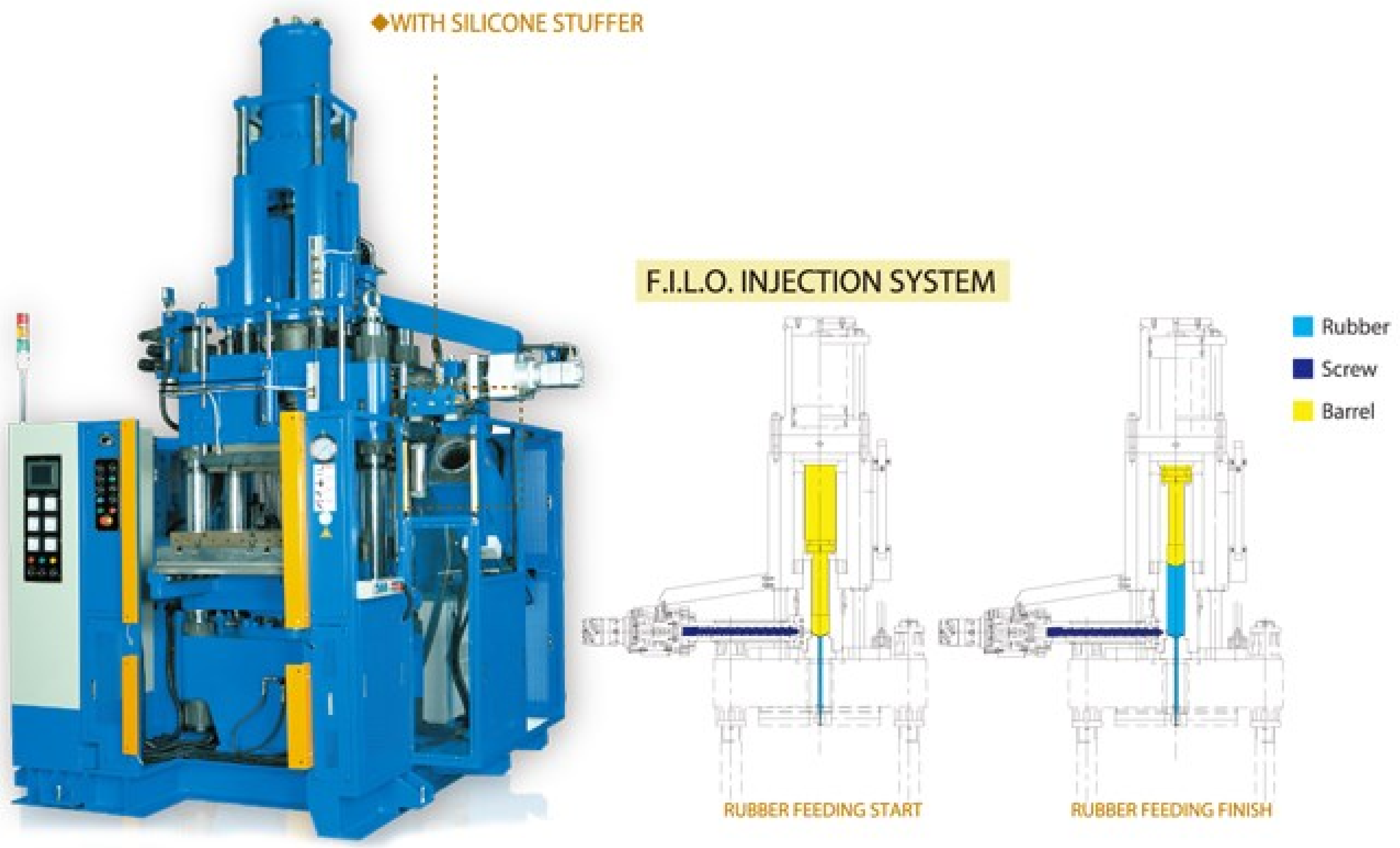






Shaping

Injection moulding –FiLo system



Shaping

Injection moulded products

https://youtu.be/_i44jbTlM1M

Shaping

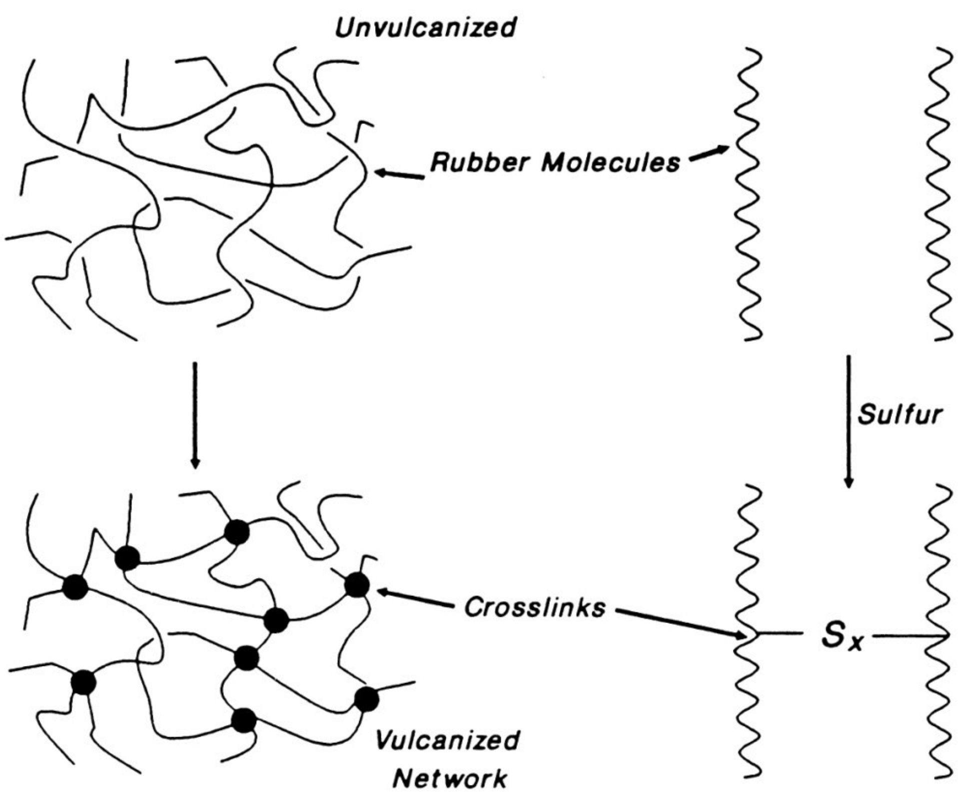
Injection moulded products

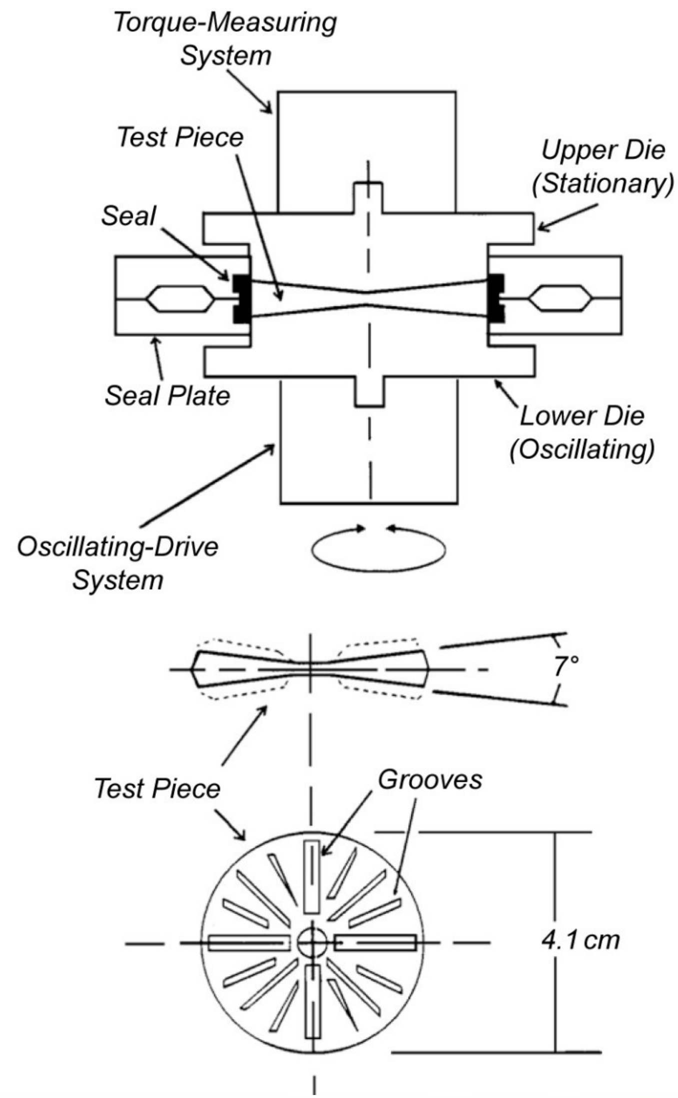
Curing

Curing: crosslinking process of rubber mixes

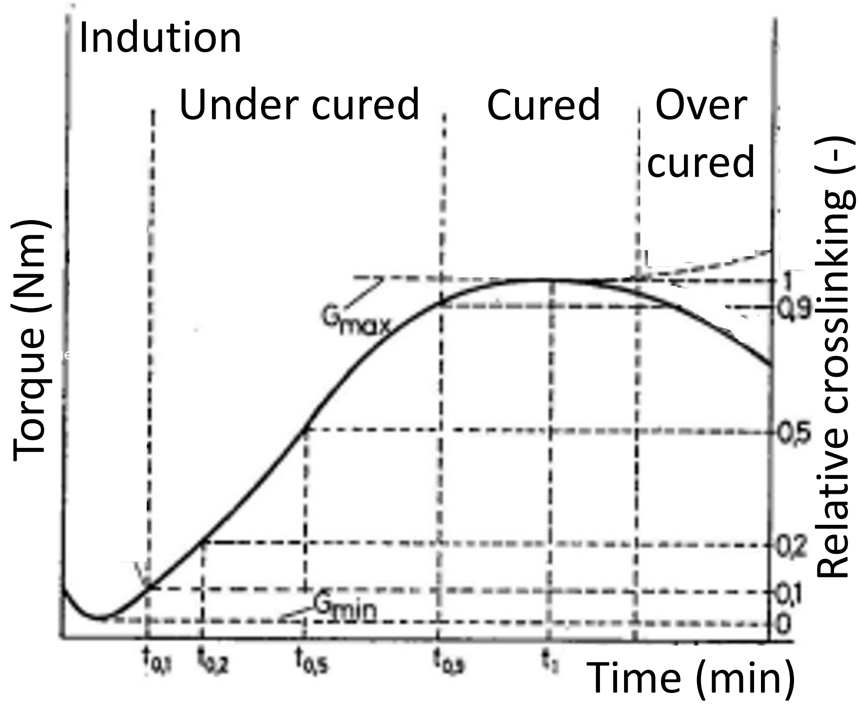
Sulfur for materials with double bonds

Peroxide for all others





Curing curve



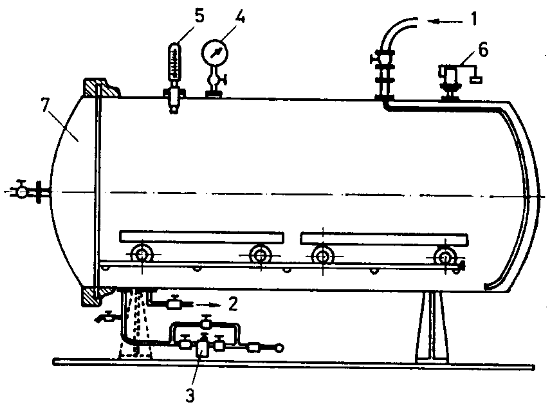
Vulcameter

$t_{0,1}$: scorch time, material starts curing, can't be formed anymore
$t_{0,9}$: optimal curing time
Post curing: reversion – decomposition of macro molecules rubber get softer
post curing- rubber gets harder
Curing is influanced by: chemical factors – accelerators, activators, retargents etc.
physical factors – pressure, time, temperature, moisture

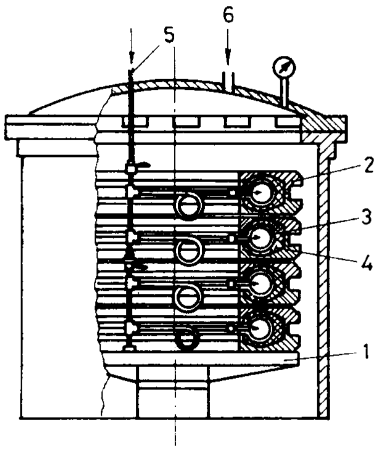
Curing processes

Discontinuous/batch

Autoclave: pressurized/vacuum cabin wich is heated by gases/steam/hot air

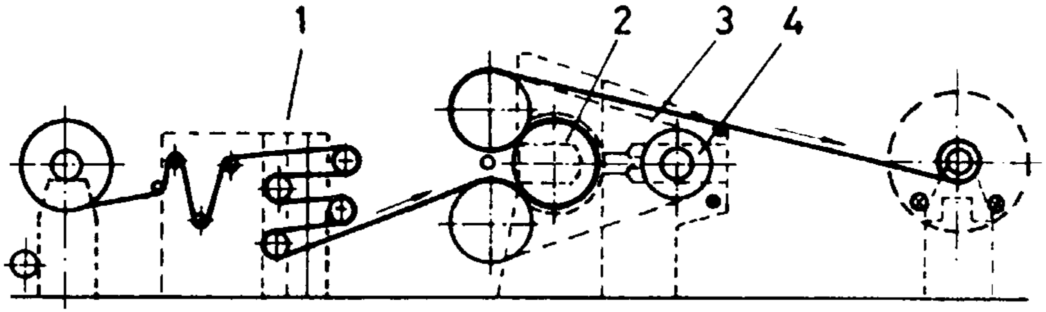


Pressure furnace
Used for tyres
The mold is in the furnace, compression molding is done under pressurized steam



Continuous

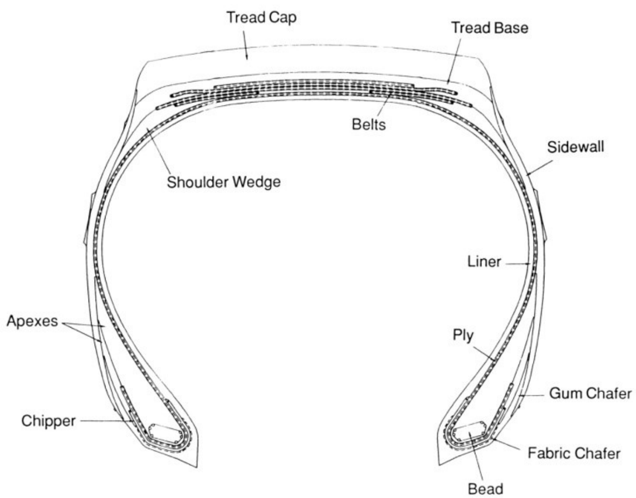
Mostly for extruded parts: tubes, sheets, cables etc.
Can be done under pressure or without pressure

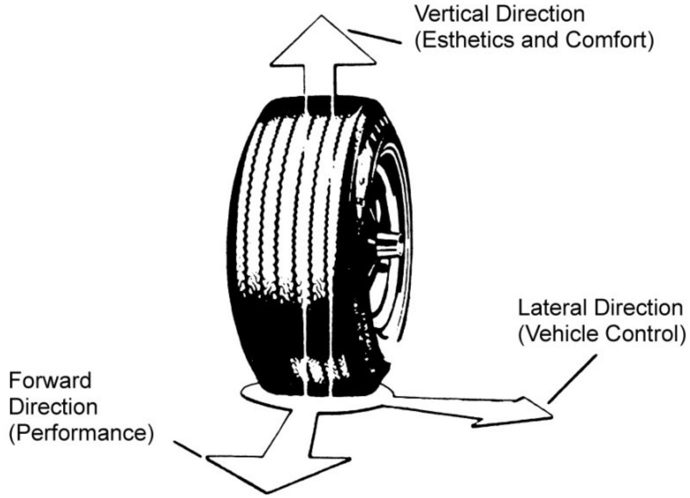


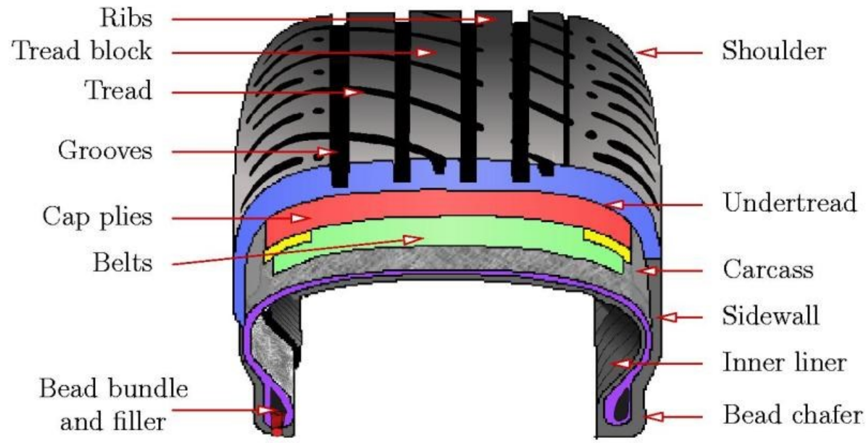
Tyre manufacturing

Tyre: complex rubber-based system

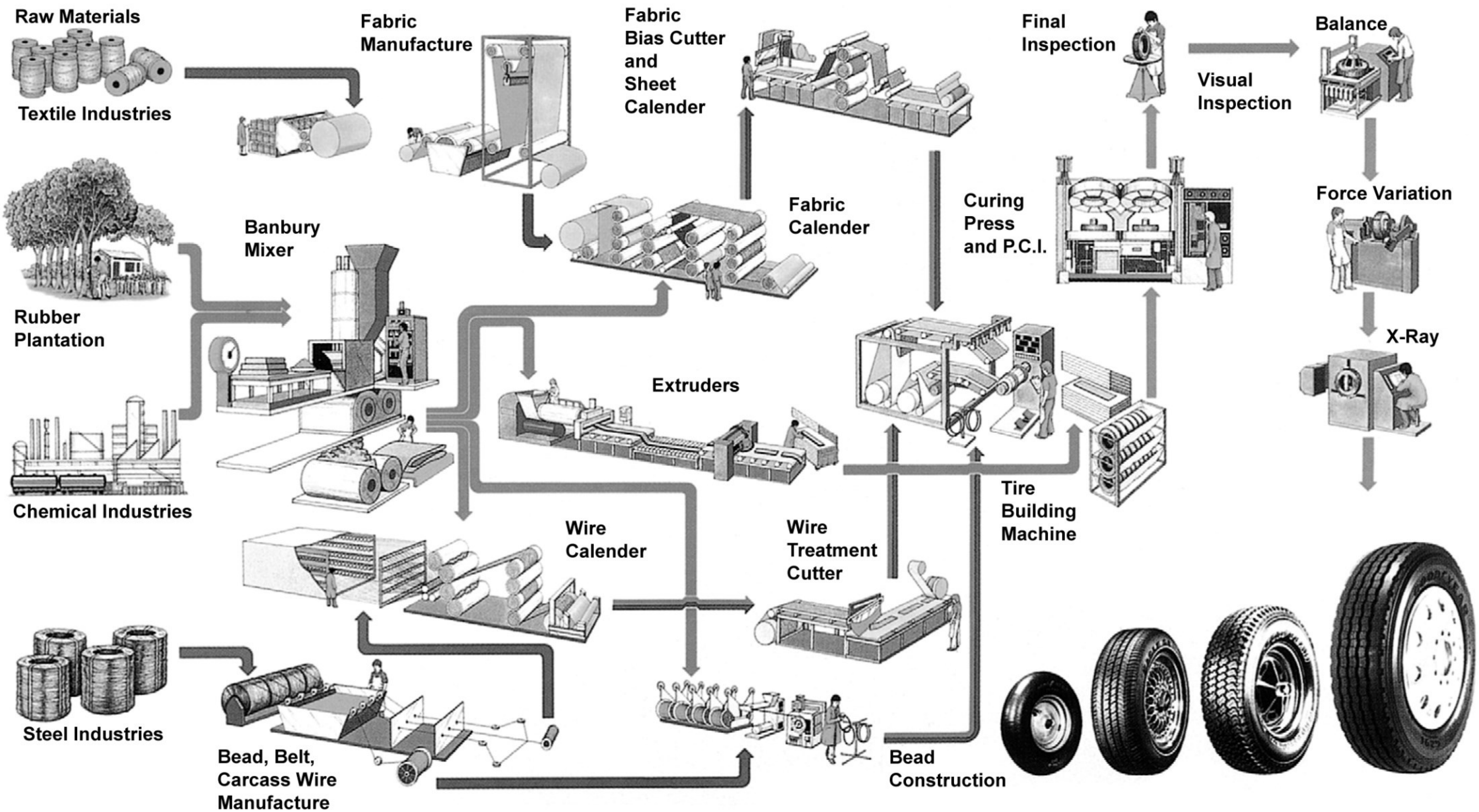
https://youtu.be/Li-MKobBg5w







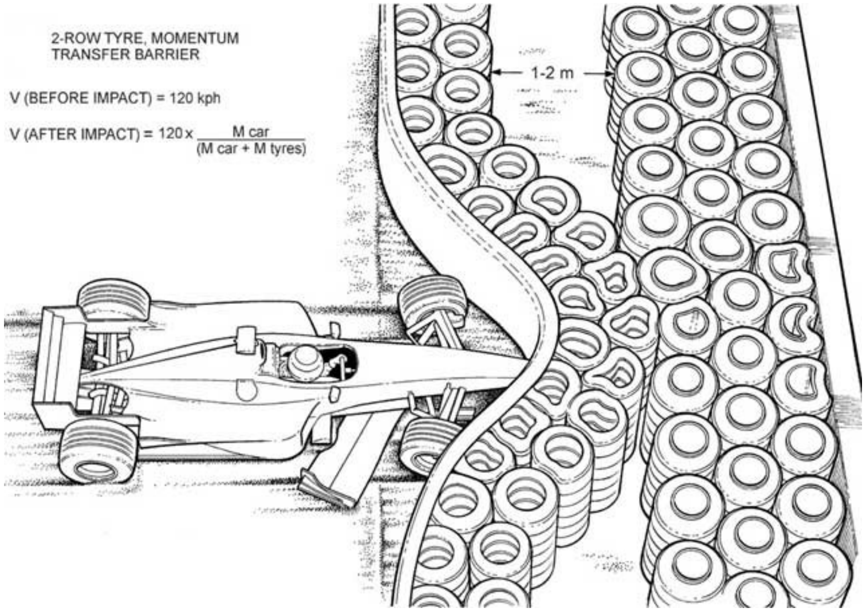
Tyre manufacturing



Recycling

Recycling possibilities of rubbers:

- **Devulcanization/regeneration**
- **Grinding of the rubbers (tyres, conveyor belts) and incorporating into:**
  - Thermoplastic polymers
  - Rubber mixes
  - Asphalts
- **Energy recovery**
- **Etc.**



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- Internet

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