SPECTACULAIRE BANDENRECYCLING

VERKENNEN VAN PYROLYSE- EN DEVULKANISATIETECHNIEKEN

(BANDEN)RUBBER:

BRON VAN HOOGWAARDIG UITGANGSMATERIAAL

VOOR DE RUBBERVERWERKER

WILMA DIERKES

ROUNAK GHOSH, HANS VAN HOEK, SITI SAIWARI

UNIVERSITY OF TWENTE.

Elastomer Technology and Engineering

Universiteit Twente

14 Februari 2024

Introduction

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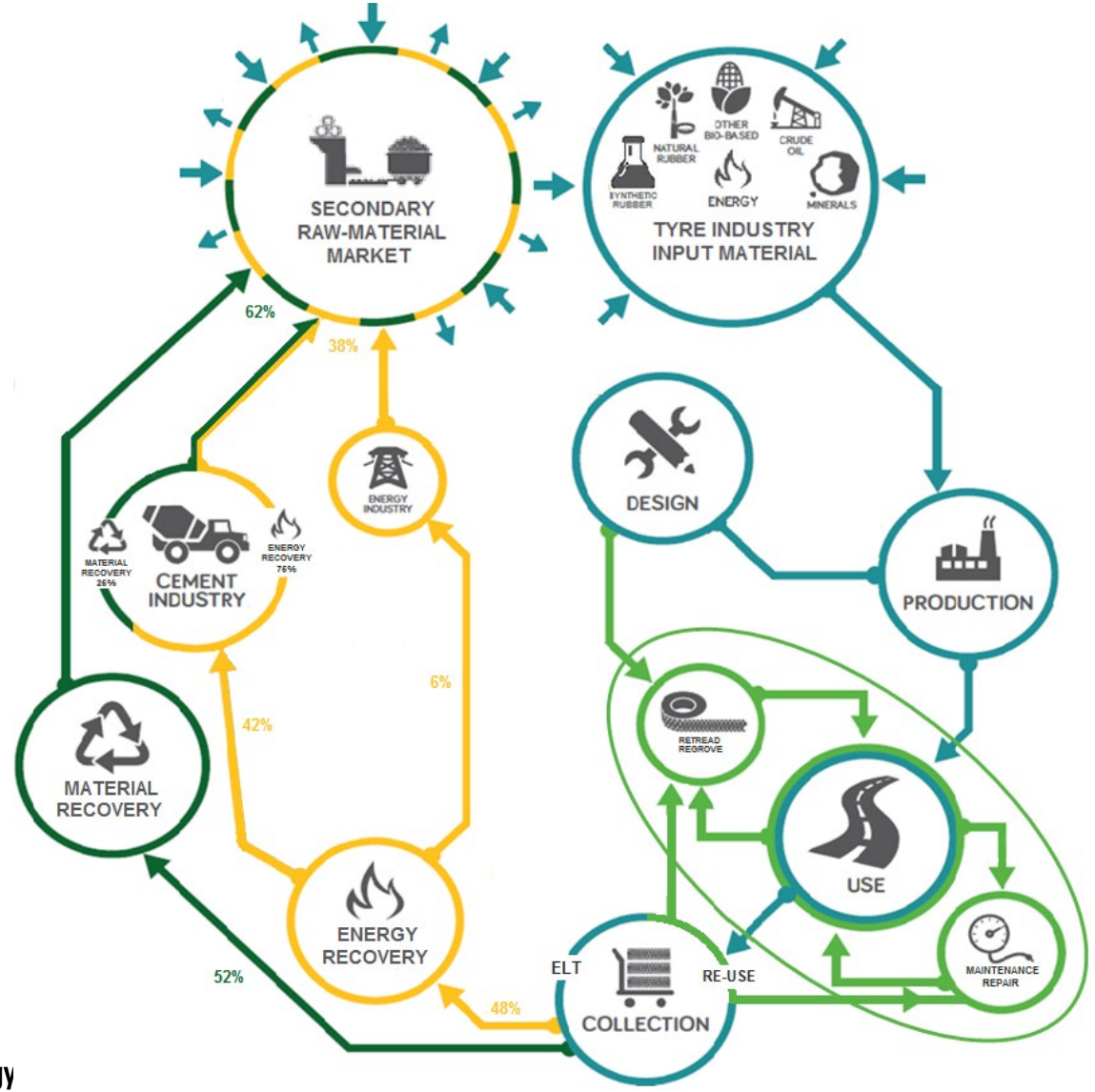
How can *tires* be recycled?



https://www.etrma.org/wp-content/uploads/2019/10/Circular-Graphic-2017-data-v5a.png

Elastomer Technology and Engineering

ETRMA: European Tyre & Rubber Manufacturers Association

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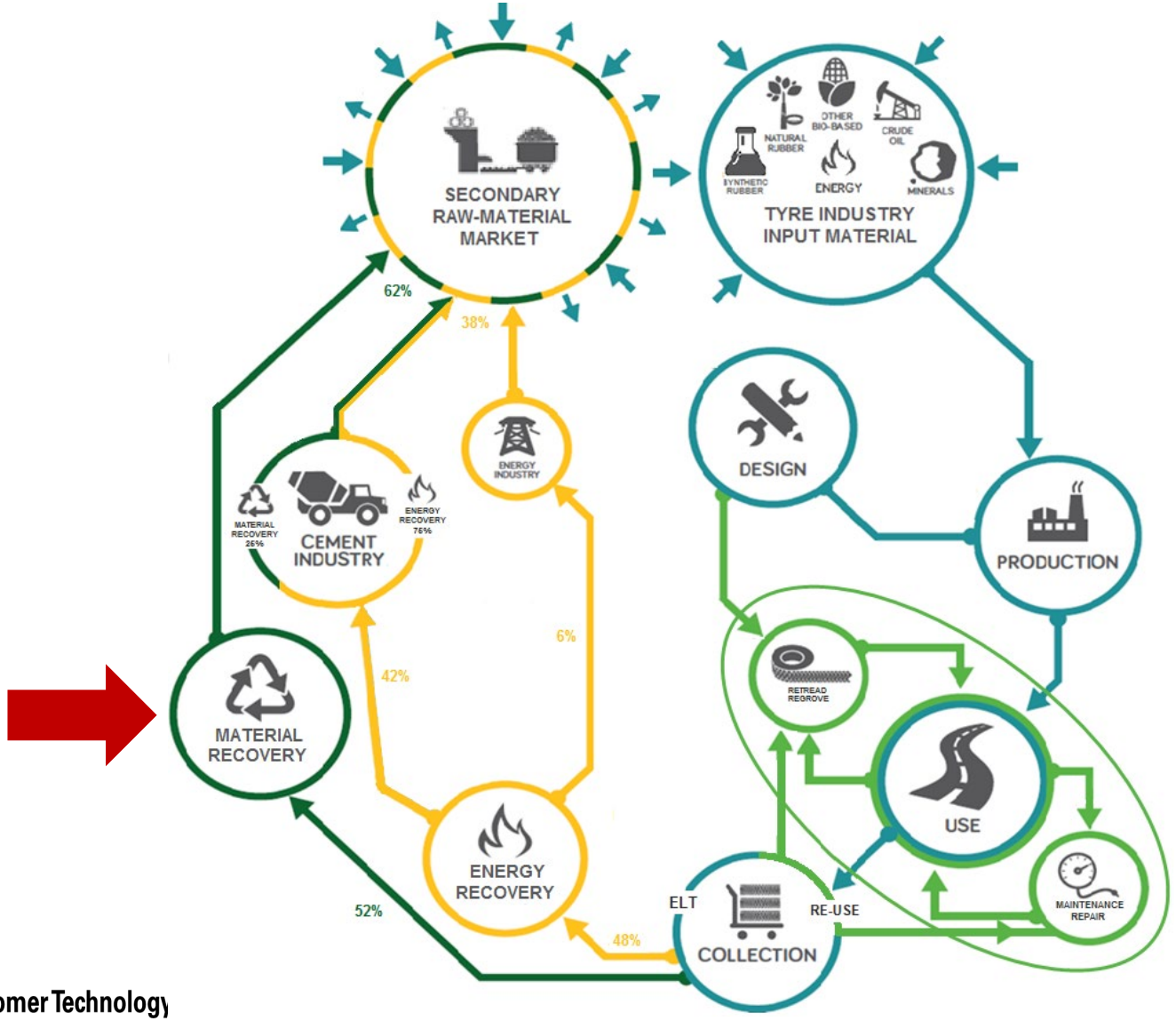

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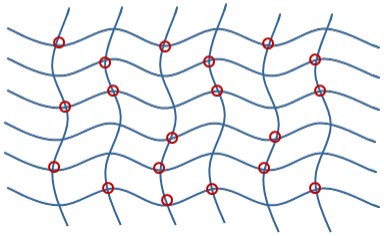
What's the benefit of material recovery and reuse of rubber?

https://www.recycledrubberfacts.org/wp-content/uploads/2016/03/Infographic_Environmental_Benefits_of_Recycled_Rubber-144x300.jpg

Introduction

How can *materials* be recycled?

Devulcanisate



- **Technology Readiness Levels (TRL):**
  - **Passenger car tire rubber: TRL5-6 (technology demonstration)**
  - **Truck tire rubber: TRL 6-8 (system/subsystem development)**
- **Concentration of devulcanizate in tire compounds: a multitude of current concentrations (depending on the compound type)**

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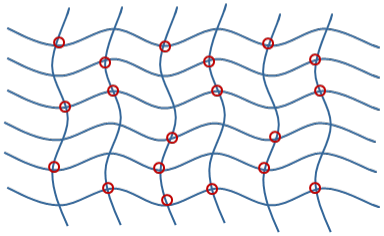

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Pyrolysis

- Technology Readiness Levels (TRL):
  - Conventional technologies (batch, long residence time, high temperatures): no significant development possible
  - New technologies: flash pyrolysis (TRL 5: development-demonstration)
- Large-scale application in tires only possible with significant quality improvements

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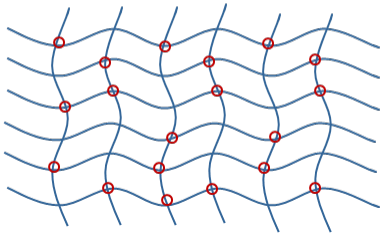

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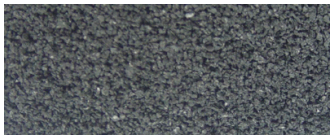
Grinding



- Technology available, also for very fine powder
- No further quality improvements possible
- Limited application in virgin compounds
- Main application in floor mats etc.

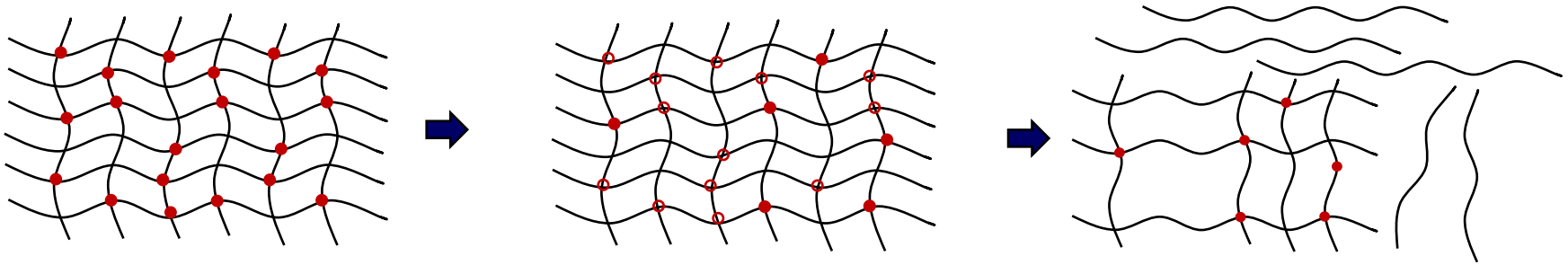
The processes on molecular scale

… a bit of chemistry…

Devulcanization

What happens in the devulcanization process?

DEVULCANIZATION:

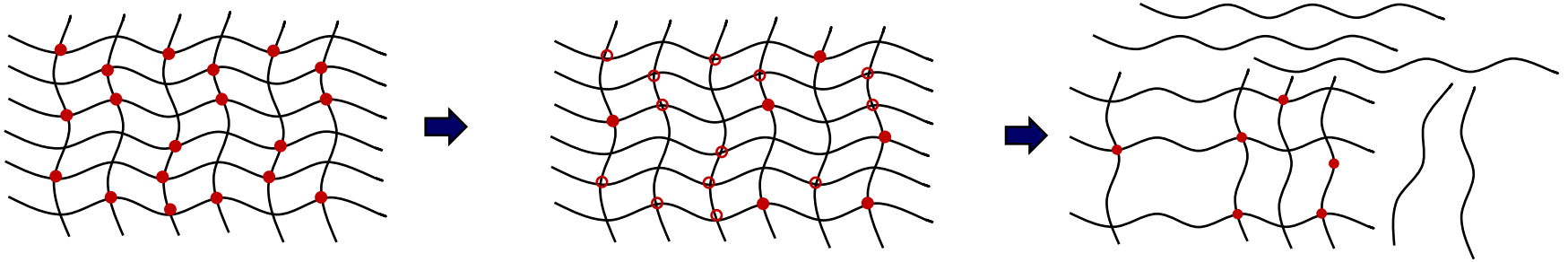


Crosslink scission ⇨ properties of devulcanisate similar to properties of original material

Devulcanization versus reclaiming

What's the difference?

DEVULCANIZATION:



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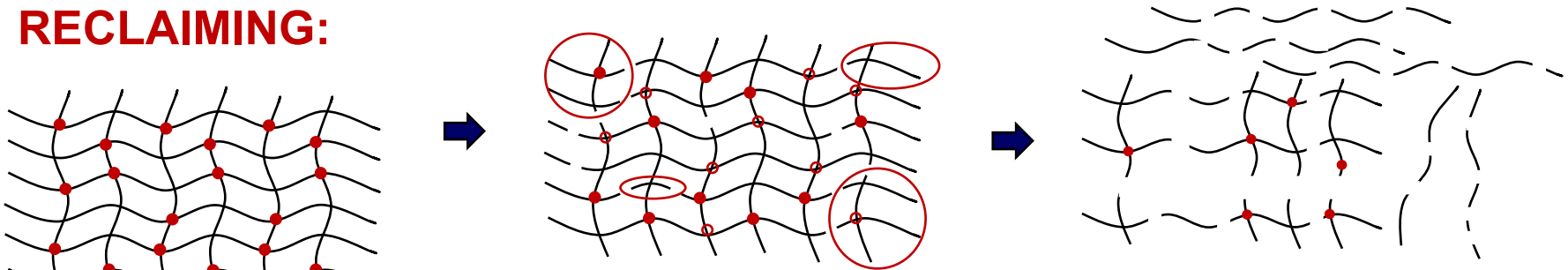
RECLAIMING:



Polymer scission
⇨ shorter polymer chains and small network fragments
⇨ poor properties

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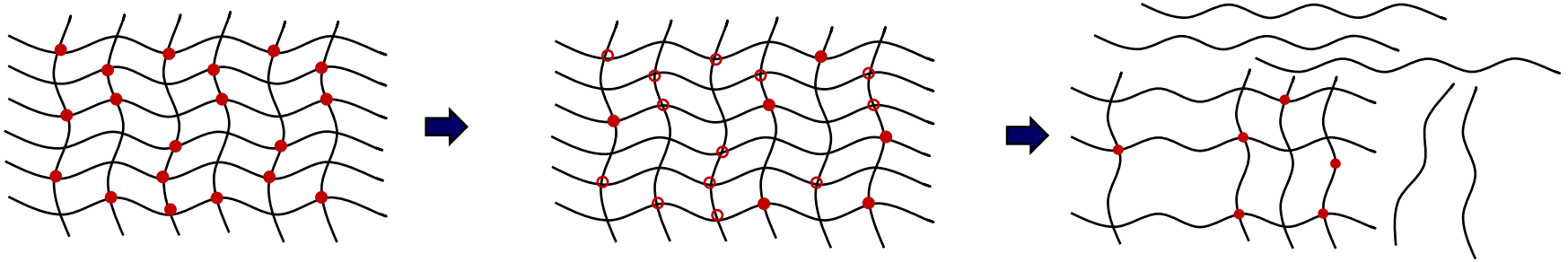

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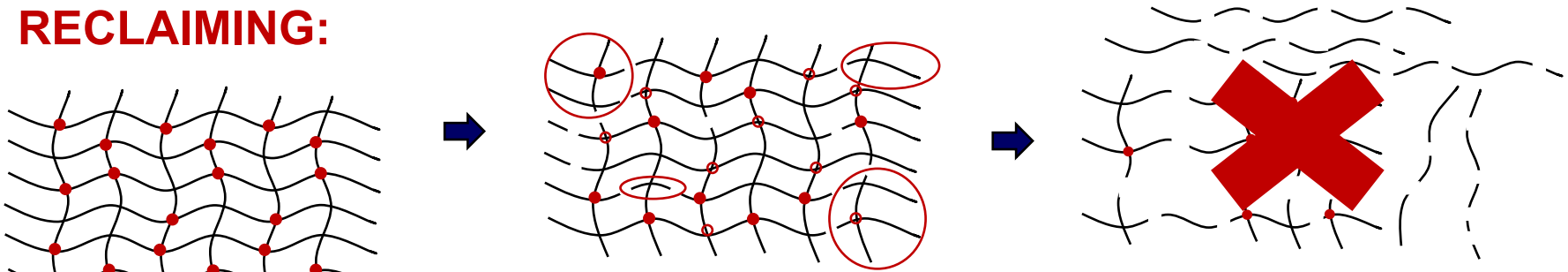


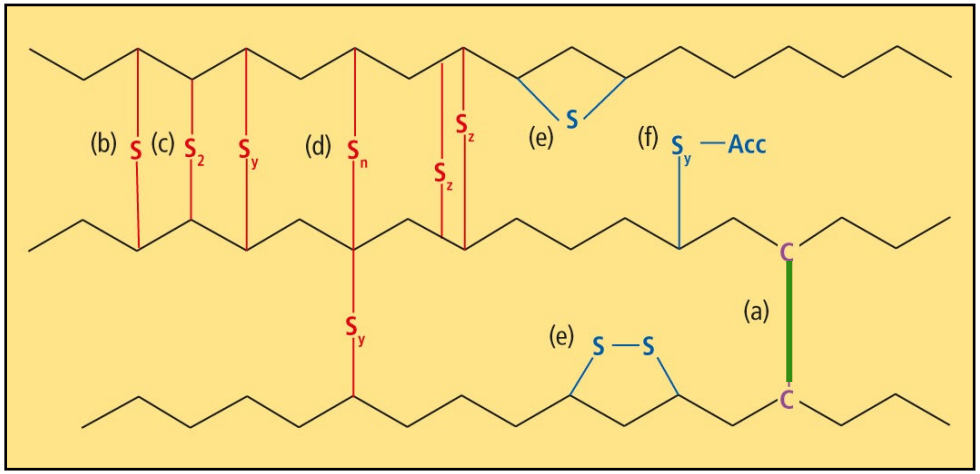
Polymer scission
⇨ shorter polymer chains and small network fragments
⇨ poor properties

Vulcanized rubber

What are the components of the network?

The polymer-polymer network

Chemical bonds



https://static.gupta-verlag.com/news/image/Scheme_of_network_structure.jpg

a: C-C bonds

b: monosulfidic bonds

c: disulfidic bonds

d: polysulfidic bonds

e: cyclic structures

f: dangling chains

Chemical sulfur bonds between polymer chains have to be broken

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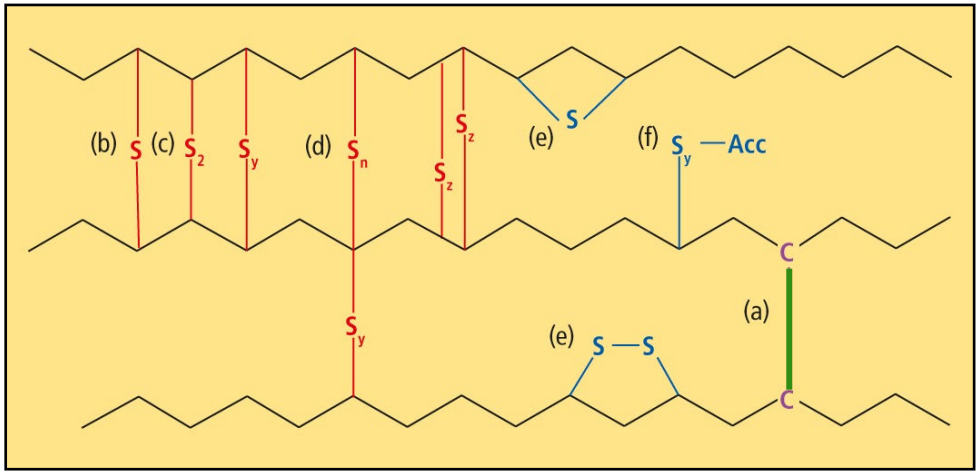

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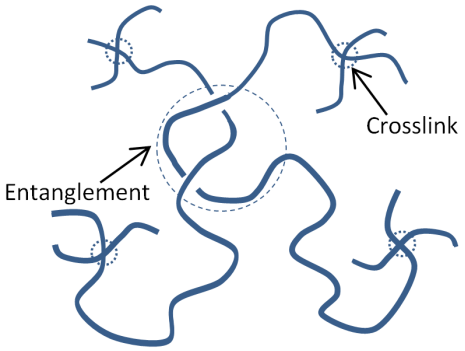
Physical bonds



http://polymerdatabase.com/polymer%20physics/images/rubber%20network.png

a: C-C bonds

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Chemical sulfur bonds between polymer chains have to be broken

Physical bonds are not much of a worry

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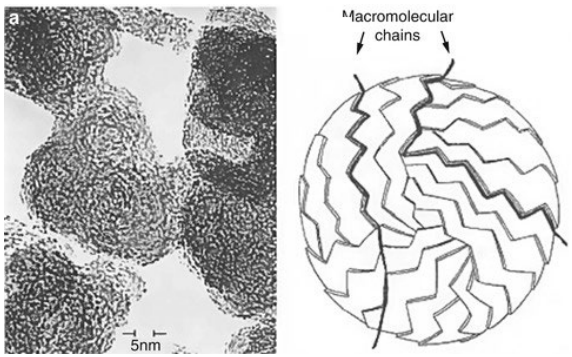
Vulcanized rubber

What are the components of the network?

The filler-polymer network

Physical bonds



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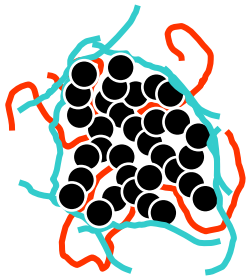

Bound rubber

Occluded rubber

Physical bonds are not much of a worry

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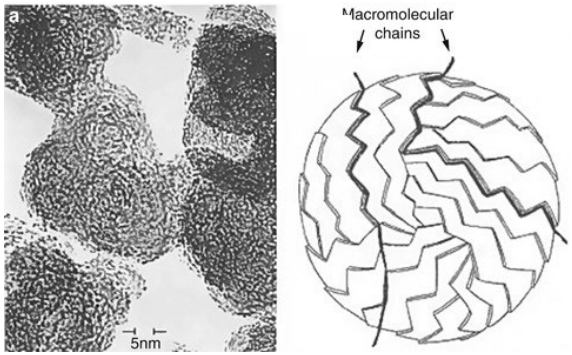
Vulcanized rubber

What are the components of the network?

The filler-polymer network

Physical bonds



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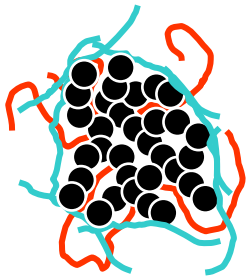
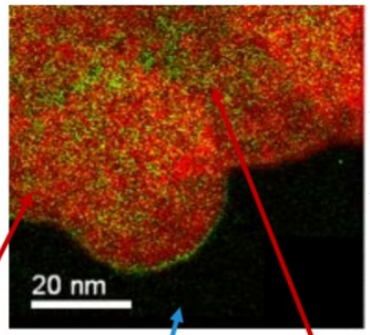


Bound rubber

Occluded rubber

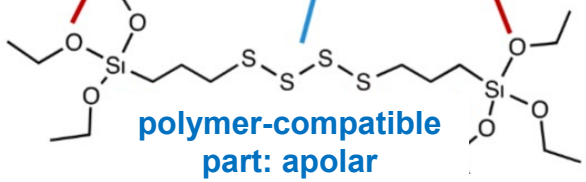
Chemical bonds

silane layer (thickness of ≈ 1 nm)
on silica surface in polymer matrix



Thesis A. Anjum, University of Twente, 2022

silica-compatible part: polar



polymer-compatible part: apolar

- Physical bonds are not much of a worry
- Chemical polymer-filler bands have to be broken

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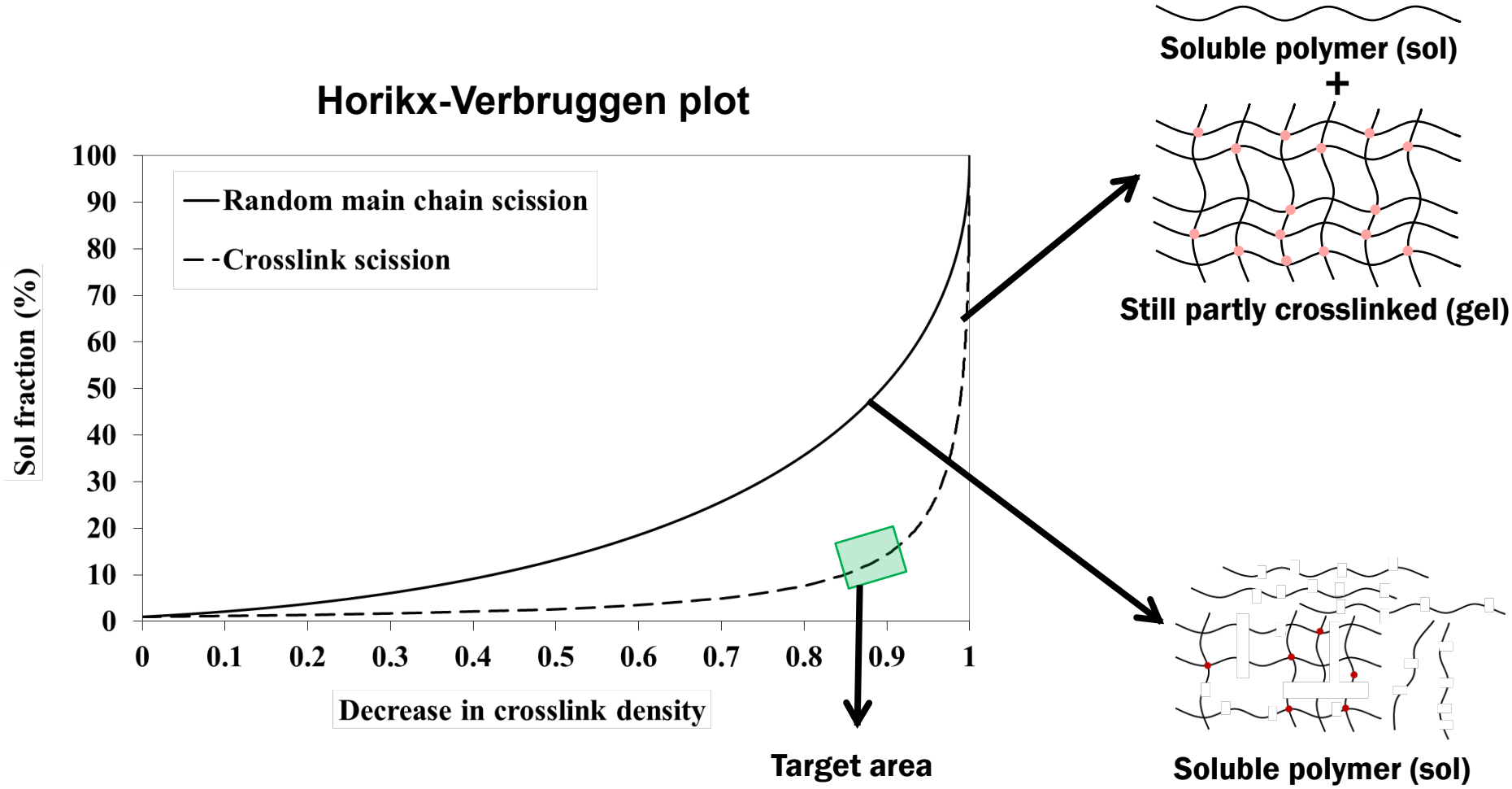
Devulcanized rubber

How do we know what we do?



The devulcanization process: Feedstock

What are the challenges…

… in terms of feedstock?

Feedstock

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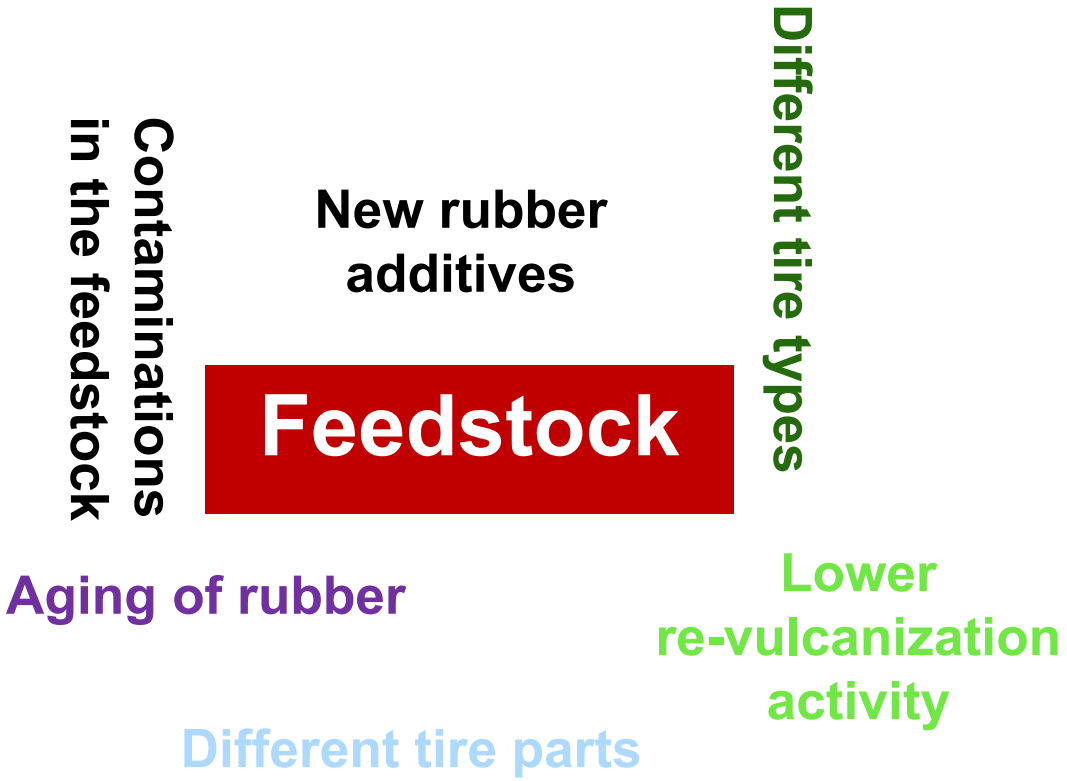

What are solutions…

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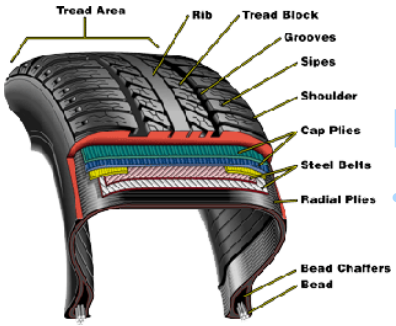

https://www.hogantire.com/portals/43/Skins/master/img/tcTireConstruction.gif

Different tire parts:

- Separation of tire parts

Different tire types:

Separation of

- Passenger car, truck tires
- Winter, summer
- Silica, CB
- …

https://www.hankooktire.com/mea/en/help-support/tire-guide/sizes-specs.htm

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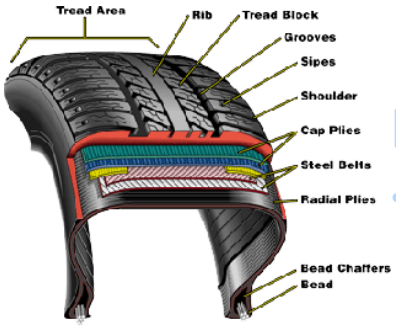

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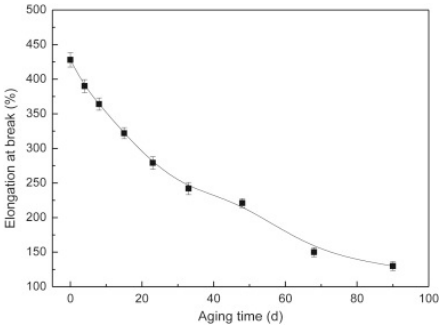


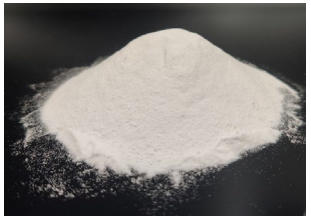
https://ars.els-cdn.com/content/image/1-s2.0-S0142941816302860-gr5.jpg

Aging of rubber:

- Has its advantages
  → less aging in the new tire

Lower strength:

- Addition or reactivation of fillers



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https://pixel.zeppelin-systems.com/images/slider/gummi-_und_reifenindustrie.jpg

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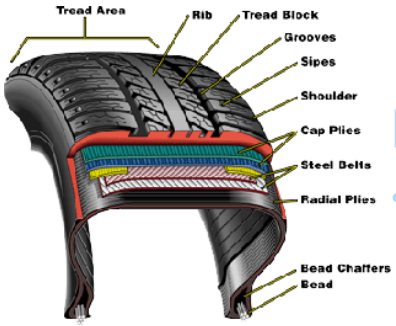

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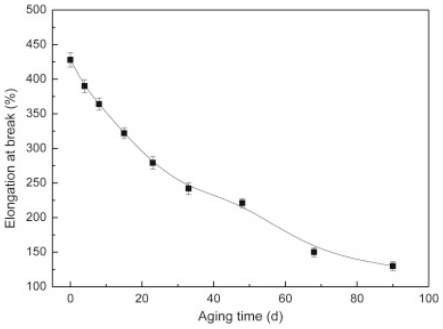

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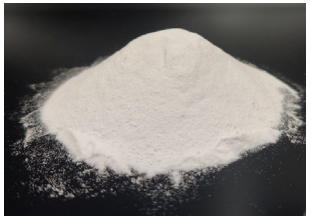

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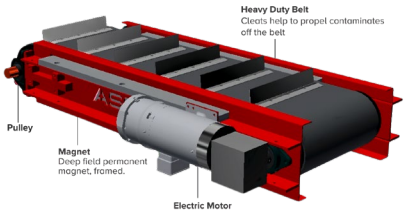
https://pixel.zeppelin-systems.com/images/slider/gummi-_und_reifenindustrie.jpg

Contaminations in the feedstock:

- Metals: magnets, eddy current detectors
- Stones, glass, …: wind sieving



https://www.asgco.com/wp-content/uploads/2019/07/ASGCO-Magnetic-Separator-2.png

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The devulcanization process

Devulcanization process

What type of equipment is used for rubber processing?

Internal mixer

https://4.imimg.com/data4/BT/SV/MY-15067125/banbury-rubber-mixer-machine-500x500.jpgar

Extruder

https://www.bplittleford.com/assets/components/phpthumbof/cache/MP-48-Screws2-guide.e59ff5841c8910071a2b2ef4f54fa3b9.jpg

Mill

https://upload.wikimedia.org/wikipedia/commons/thumb/5/5e/Calender_machine.jpg/407px-Calender_machine.jpg

Devulcanization process

What are the main process parameters?

Process parameters

Devulcanization process

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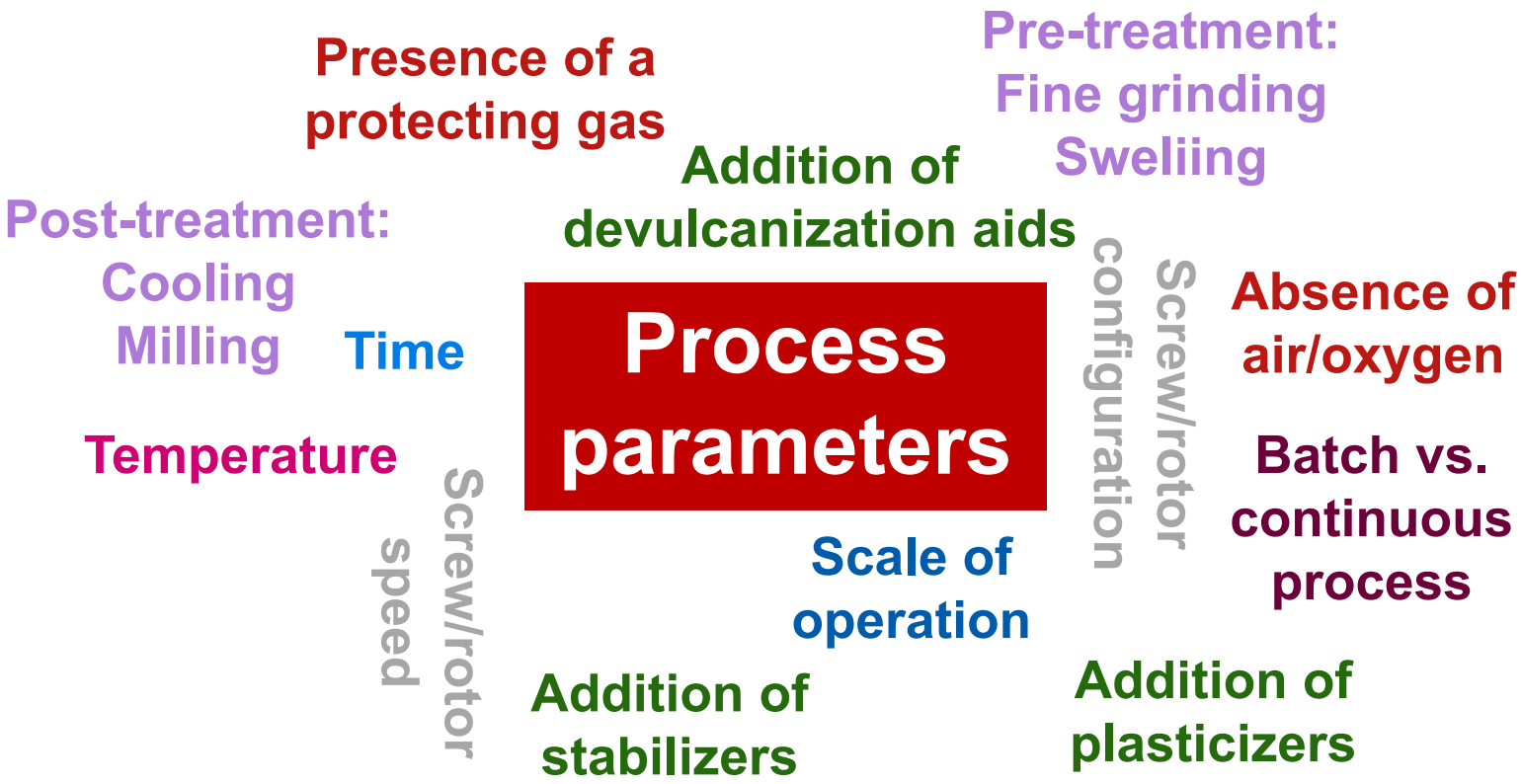
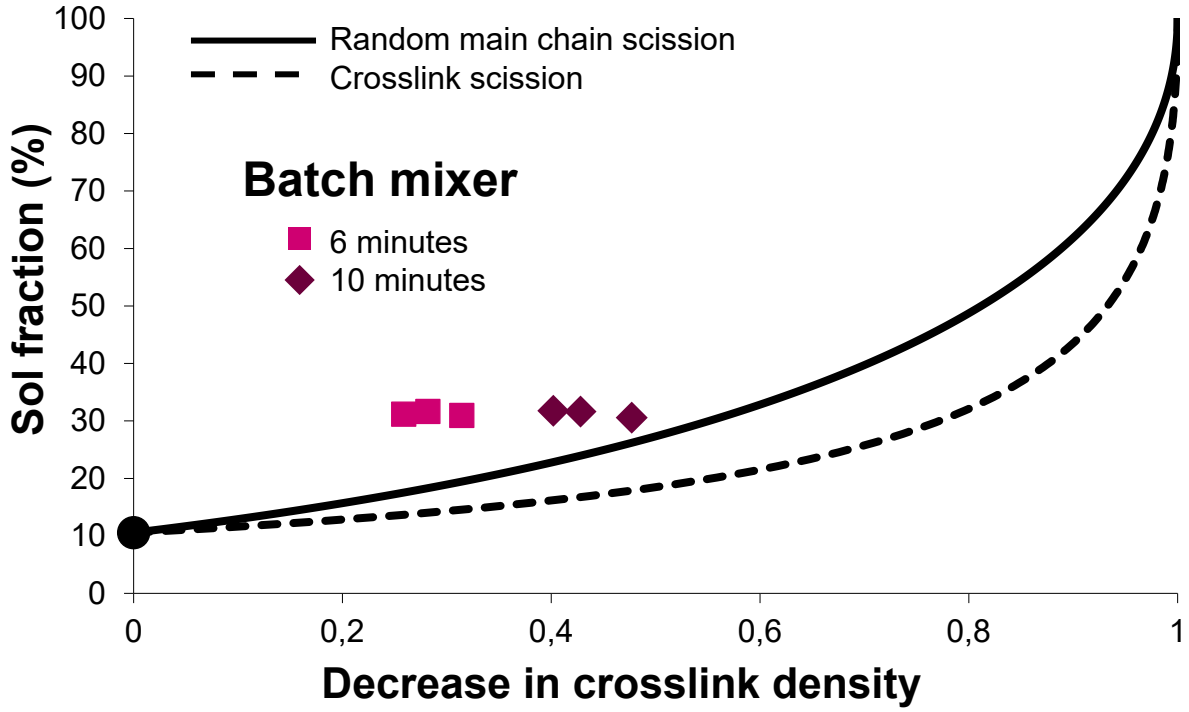


Devulcanization process

What is the equipment of choice?

Internal mixer



Process conditions:
Swelling: 65ºC, 30 min
TDAE: 5%
N2 purging

Batch mixer:
Fill factor: 0,7
Rotor speed: 50 rpm
Mixer TCU: 220ºC
Screw speed: 50 rpm
Residence time: 5 min

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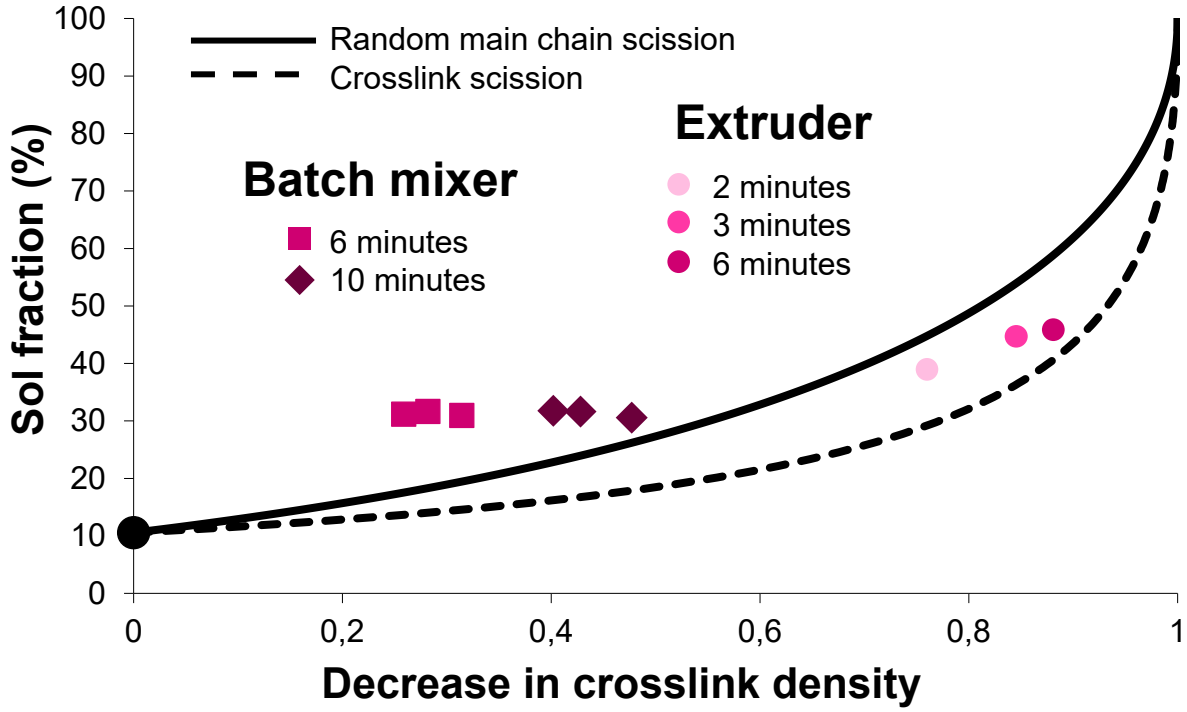
Devulcanization process

What is the equipment of choice?

Internal mixer vs. extruder



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Extruder process:
Screw speed varied to match residence time: 10, 20, 30 rpm

Continuous devulcanization (extruder) → higher degree of devulcanization

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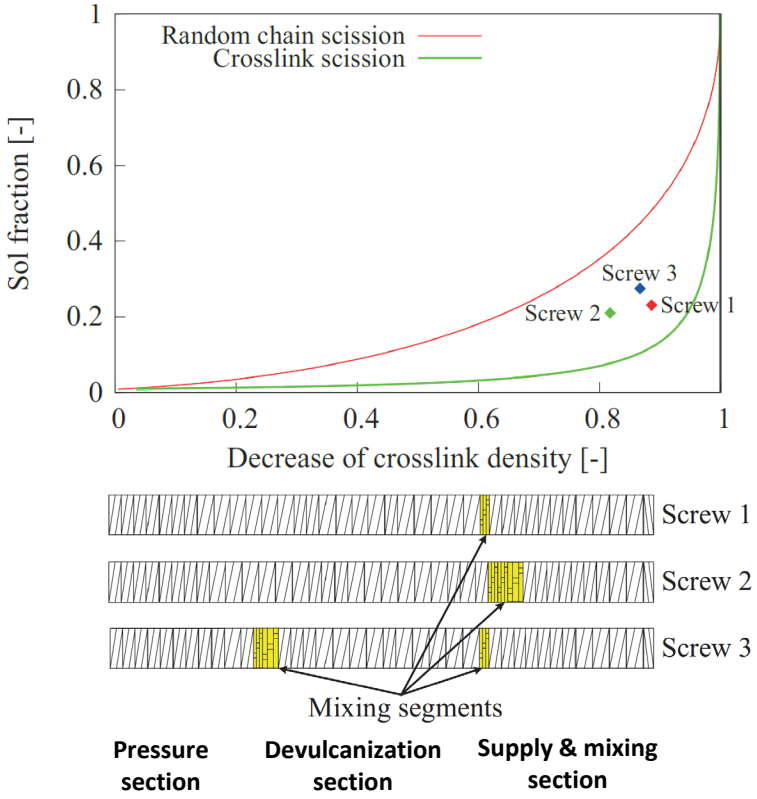
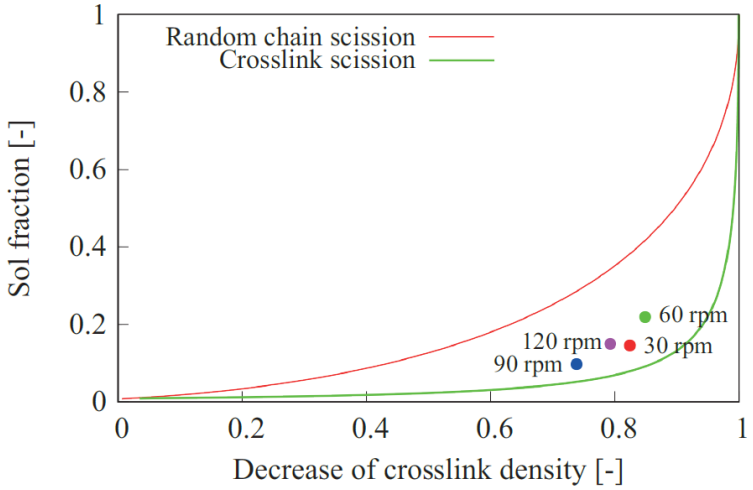
Devulcanization process

What are the extruder parameters?





Continuous devulcanization
(KrausMaffei ZE 25 UTX co-rotating)
TCU extruder: 220°C
Screw speed: 10 rpm or varied
Whole passenger car tire rubber
DA: DPDS, 18 mmol/100g
TDAE: 6.2 wt%
Anti-ox: 1 wt%

Reduce polymer chain scission & recombination:
Balanced shear by number of mixing sections & screw speed

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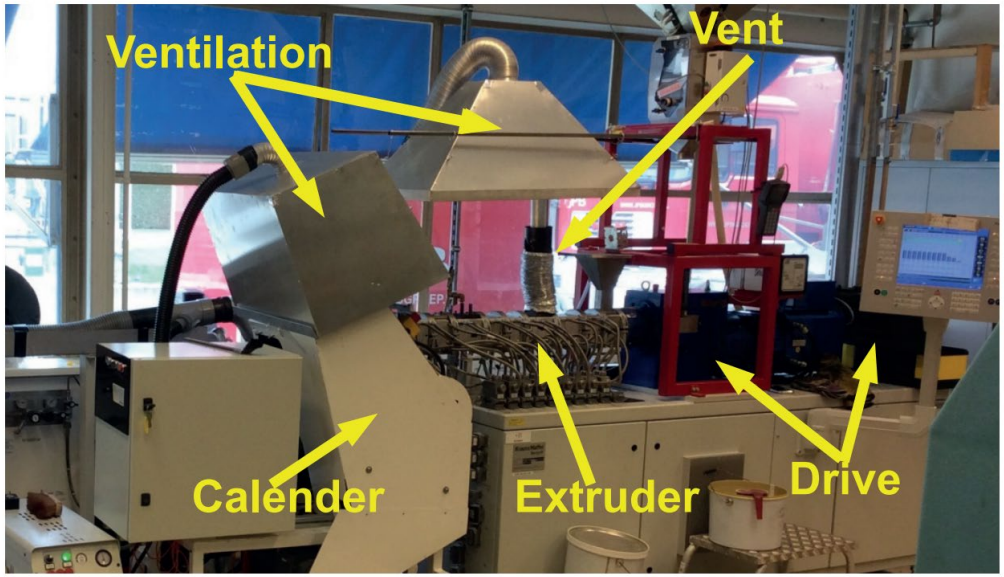
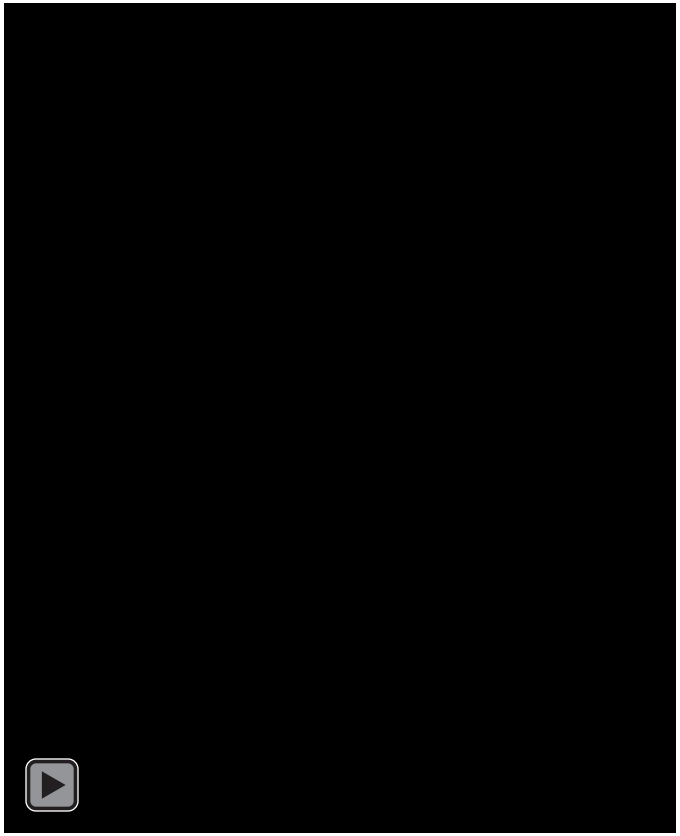
Devulcanization process

What does it look like?





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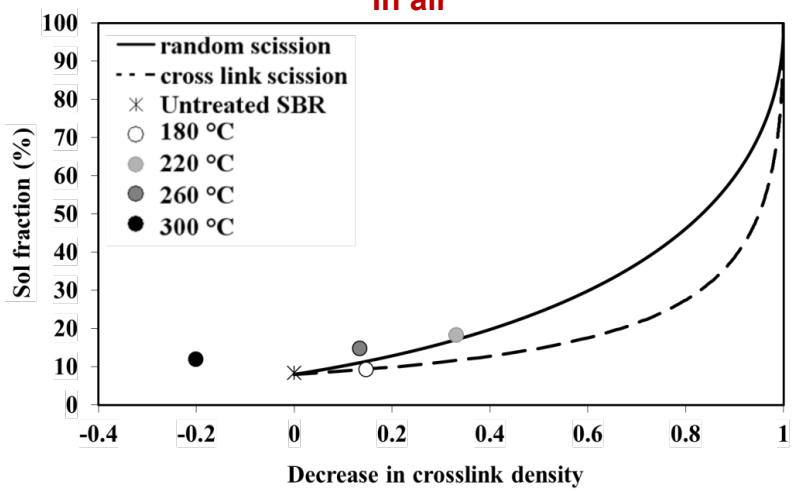
Devulcanization process

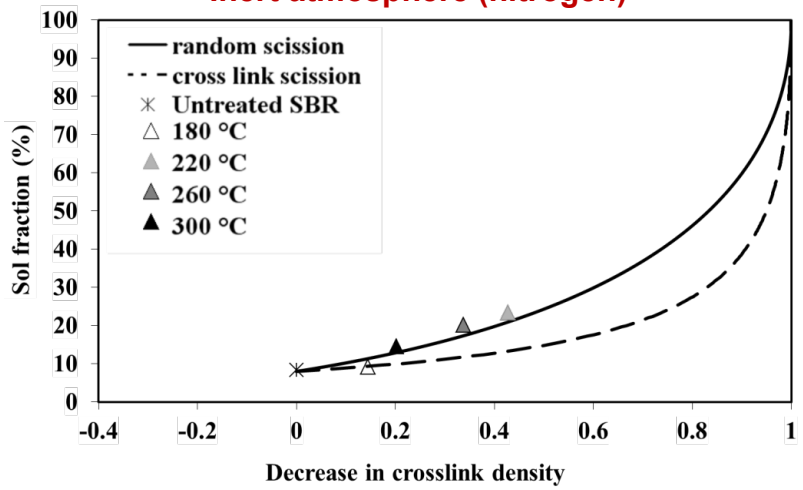
What is the effect of presence of oxygen?

Thermo-mechanical
In air



Discontinuous devulcanization
(internal mixer)
TCU mixer: varied
Screw speed: 50 rpm
Residence time: 5 minutes
SBR model compound
No devulcanization aid (DA)
TDAE: 5 wt%

Thermo-mechanical
Inert atmosphere (nitrogen)



High temperature & air → degradation & fragmentation of polymer →
The lower the temperature & the less oxygen the better

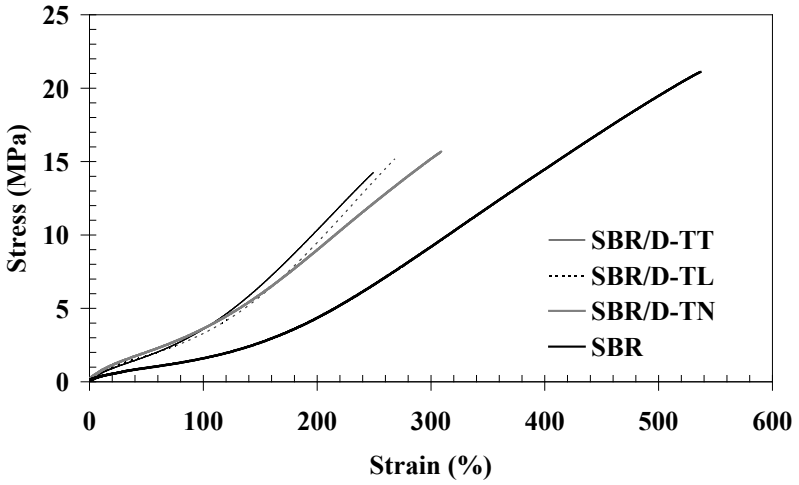
Elastomer Technology and Engineering

PhD Thesis: Sitisaiyidah Saiwari, University of Twente, 2013

Devulcanization process

What is the effect of presence of oxygen?

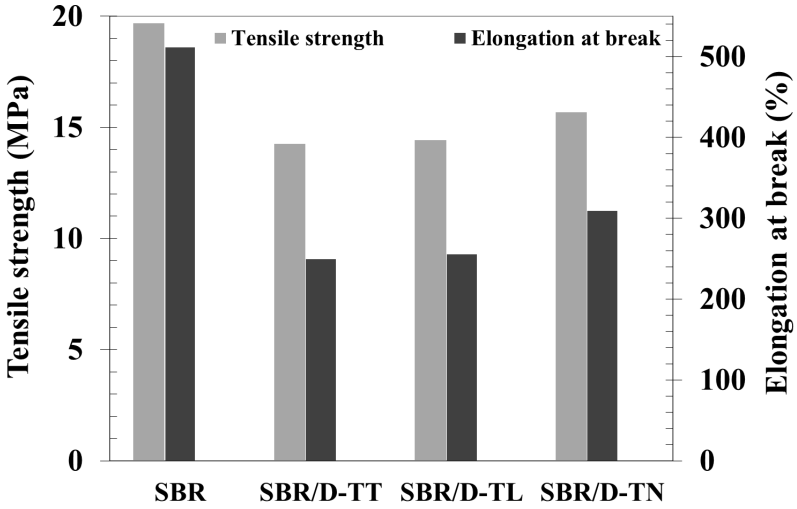
Discontinuous devulcanization
(internal mixer)
TCU mixer: varied
Screw speed: 50 rpm
Residence time: 5 minutes
SBR model compound
No DA
TDAE: 5 wt%



SBR/D-TT: air

SBR/D-TL: air & quenching in liquid nitrogen

SBR/D-TN: nitrogen & quenching in liquid nitrogen



The lower the temperature & the less oxygen the better

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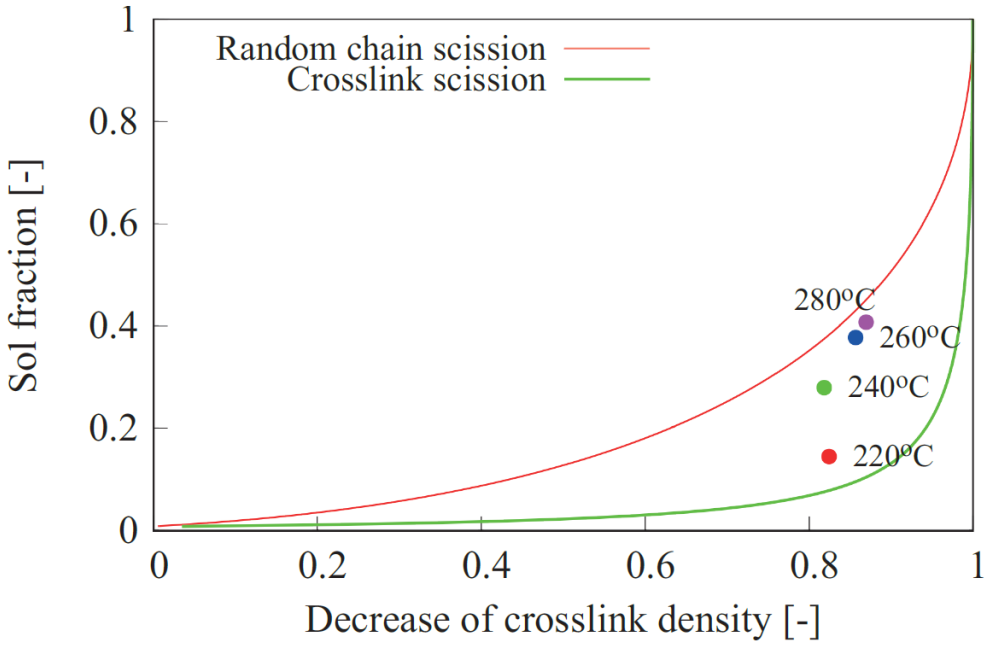
Devulcanization process

What is the effect of temperature?



Continuous devulcanization

(KrausMaffei ZE 25 UTX co-rotating)

TCU extruder: varied

Screw speed: 30 rpm

Residence time: 2 minutes

Whole passenger car tire rubber

DA: DPDS, 15mmol/100g

TDAE: 5 wt%

Anti-ox: 1 wt%

High temperatures → degradation & fragmentation of polymer

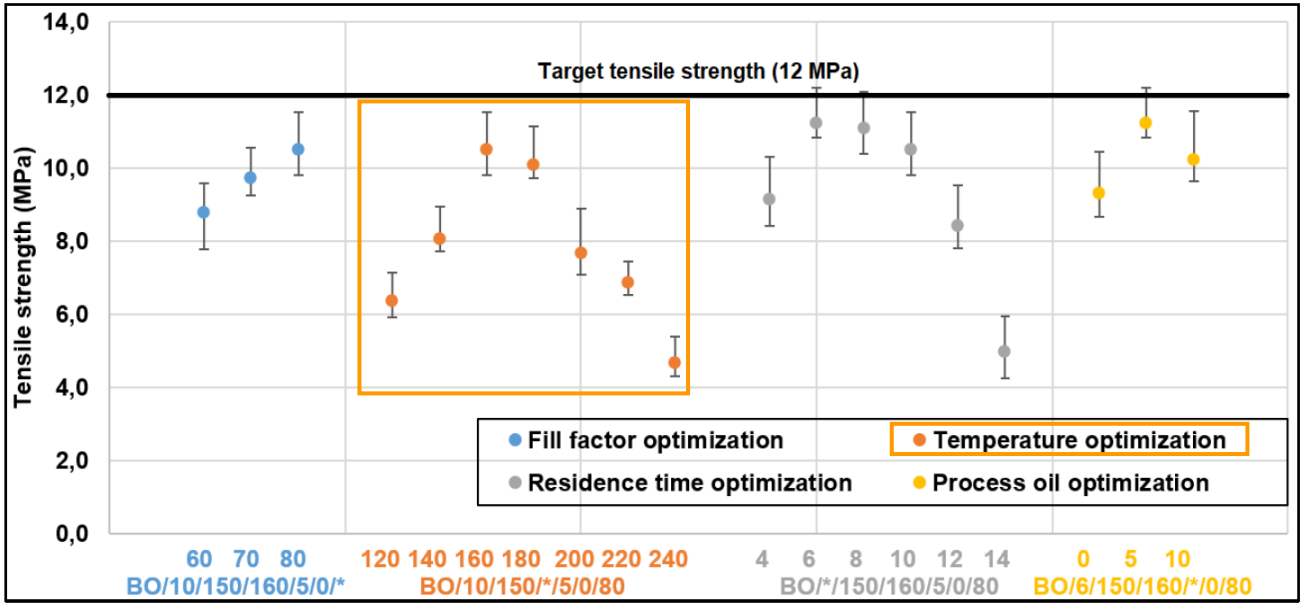
Presence of DA and stabilizer cannot overcome it

The lower the temperature the better

PhD Thesis: Hans van Hoek, University of Twente, 2022

Devulcanization process

What is the effect of temperature?



Discontinuous devulcanization (internal mixer)
TCU mixer: varied (120 - 240°C)
Screw speed: 50 rpm
Residence time: 5 minutes
NR (aircraft tire treads)
No DA
TDAE: 5 wt%

Increasing temperature → higher degree of network breakdown
High temperature → more random polymer breakdown
Optimum in terms of temperature

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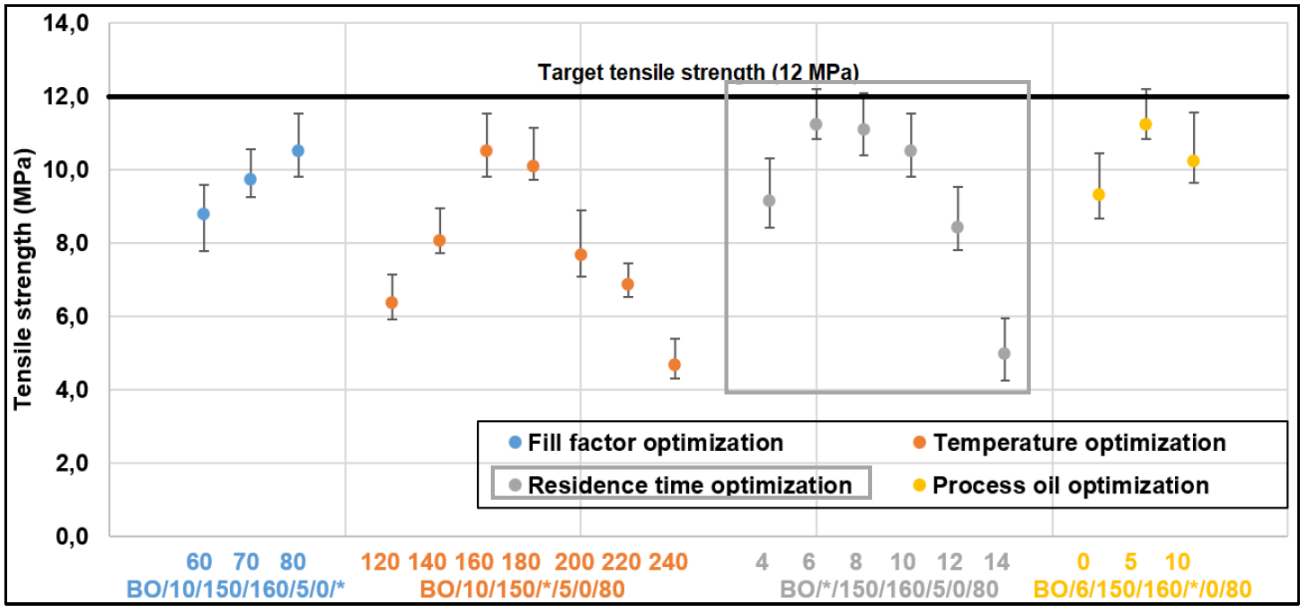
Devulcanization process

What is the effect of residence time?



Discontinuous devulcanization (internal mixer)
TCU mixer: 160°C
Rotor speed: 150 rpm
NR (aircraft tire treads)
No DA
TDAE: 5 wt%

Increasing residence time → higher degree of network breakdown
Optimum in terms of residence time

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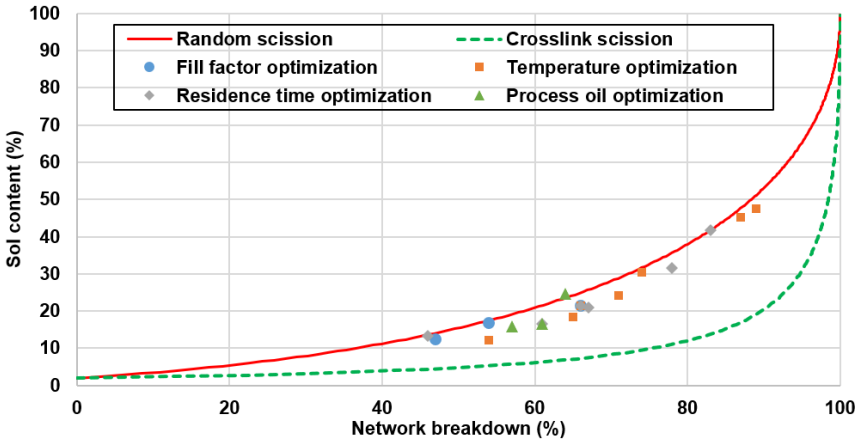
Devulcanization process

What is the effect of a devulcanization aid (DA)?

No devulcanization aid



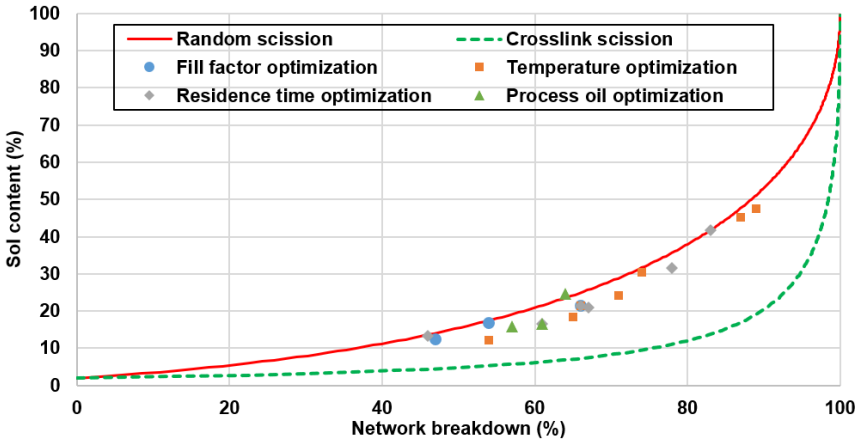
Feedstock: aircraft tire treads (NR)
Mixer volume: 50 ml
Parameter range:

- **Temperature: 120°C - 240°C**
- **Residence time: 4 - 14 minutes**
- **Fill factor: 60 - 80%**
- **Oil concentration: 0 - 10%**

Devulcanization process

What is the effect of a devulcanization aid (DA)?

No devulcanization aid



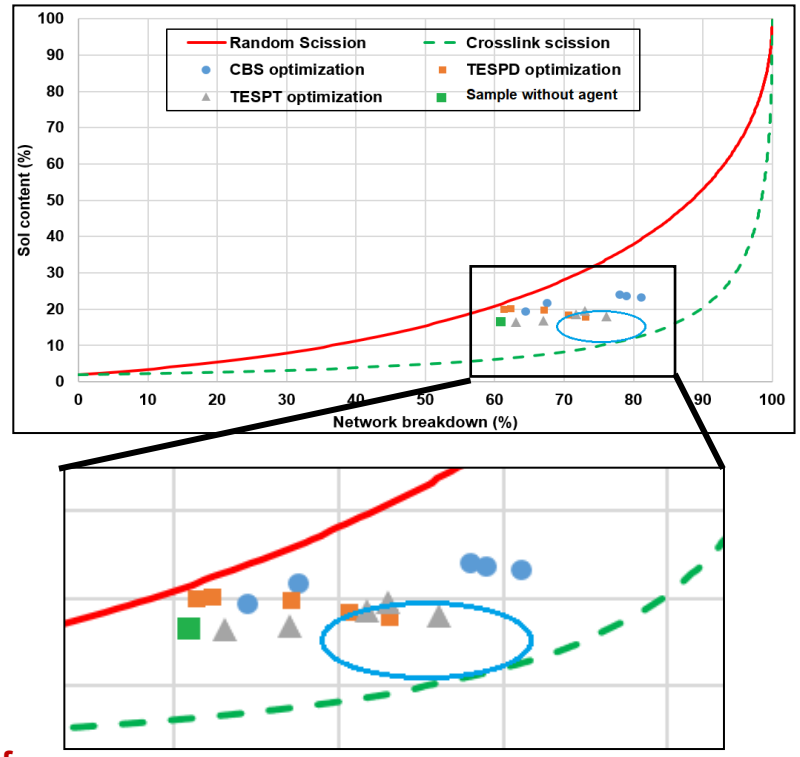
Feedstock: aircraft tire treads (NR)
Mixer volume: 50 ml
Parameter range:

- Temperature: 120°C - 240°C
- Residence time: 4 - 14 minutes
- Fill factor: 60 - 80%
- Oil concentration: 0 - 10%

DA boosts devulcanization reaction in terms of

- Degree of network breakdown
- Crosslink vs polymer breakdown
- Less recombination

With devulcanization aid



DA: regular rubber chemicals
CBS: vulcanization accelerator
TESPD & TESPT: coupling agents for silica filler

Concentration: app. 1,5 – 2,5 % (w/w)

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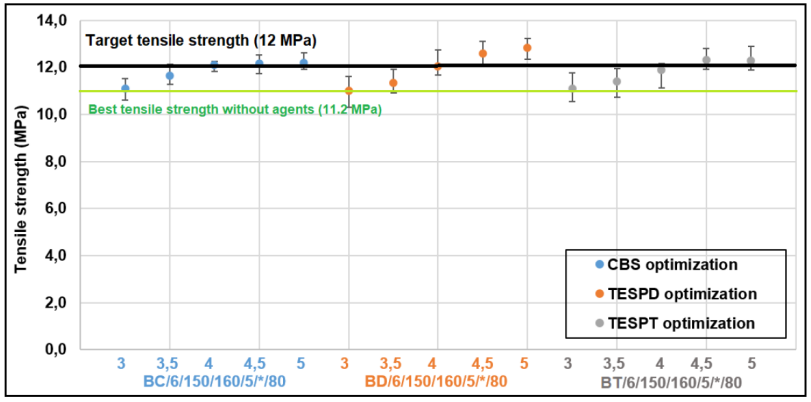
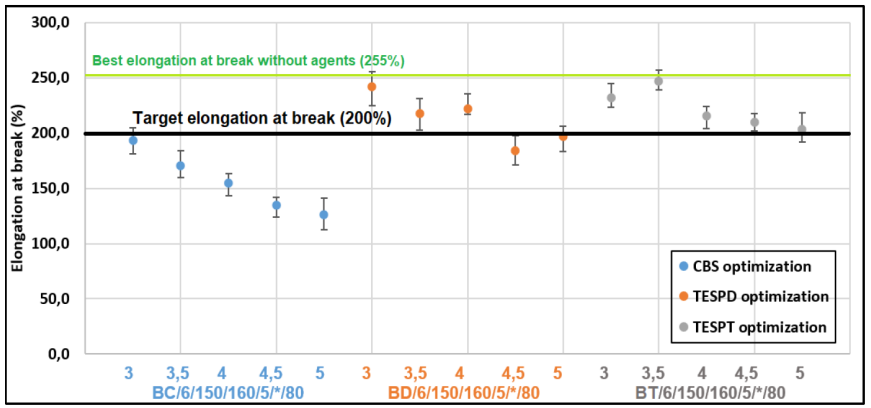
Devulcanization process

What is the effect of a devulcanization aid (DA)?





Feedstock: aircraft tire treads (NR)
Mixer volume: 50 ml
Parameter range:

- **Temperature: 120°C - 240°C**
- **Residence time: 4 - 14 minutes**
- **Fill factor: 60 - 80%**
- **Oil concentration: 0 - 10%**

Presence of DA leads to increase in strength

DAs: regular rubber chemicals
CBS: vulcanization accelerator
TESPD & TESPT: coupling agents for silica filler

Concentration: % (w/w)

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Devulcanization process

What's important?

Selected feedstock

- High NR content
- Single source rubber
- Carbon black filled rubber
- Tailored process for silica-filled rubber (under development)

Clean feedstock

Tailored devulcanization process

- Low temperature
- Low shearing forces
- Presence of DA
- Absence of oxygen

Tailored compounding with devulcanizate

Comparison with pyrolysis

What are the differences?

	Devulcanizate	Pyrolytic Carbon
Composition	All components of the original rubber compound	Carbon and inorganics
Processing	Like a virgin rubber compound Blended with a virgin rubber compound	Used as an additive like virgin carbon black
Degree of reuse	The full material for new rubber	Solid residu: additive for polymers Oils and condensables: fuel, chemicals Gas: energy carrier
Way of reuse	Blended with a virgin compound Adjustment of the filler and curatives	Replacing of a part of the filler in a virgin compound
Advantages compared to virgin material	Processing: lower energy consumption Properties: increase in ageing resistance, potentially higher tear strength More sustainable additive	More sustainable additive

We need both technologies to be able to recycle and reuse as much ELV tire rubber as possible

Who contributed to these studies?

TECH FOR FUTURE

Centre of Expertise HTSM Oost
Een initiatief van Saxion en Windesheim
mede mogelijk gemaakt door provincie Overijssel

Windesheim

aliancys QUALITY RESINS

NWO
Netherlands Organisation for Scientific Research

Schill+Seilacher

STW

Prince of Songkla University

RecyBEM B.V.
BAND & MILIEU

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