DESIGNING OF CRADLE-TO-CRADLE LOOPS FOR ELASTOMER PRODUCTS

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University of Twente
Elastomer Research Testing B.V.
Prince of Songkla University
Introduction
Material from end-of-life tires

Tires in the EU annually = 4,670,000 tons

Raw materials needed for producing these tires
(passenger cars, buses, light trucks):
  Rubber: 50% = 2,380,000 tons
  Filler (carbon black, silica): 26% = 1,167,500 tons
  ZnO: 2% = 100,000 tons
  Other ingredients: 4% = 280,200 tons
  Steel and wire: 15% = 681,820 tons
  Textile cord: 3% = 140,400 tons

Total: 3,838,740 tons
Introduction
What are the trends?

R&D: Number of patents on...

Legislation

USA
ACME TIRE COMPANY
WILEY RR-S

Korea

Japan

EU

Introduction
Recycling alternatives

Cradle to Cradle

DEVULCANIZATION

FINE GRINDING

PYROLYSIS or other processes

Cradle to ...

http://wdo.ca/Portals/_default/Skins/wdo/sliderimg/usedtires.jpg

Introduction
Status of recycling alternatives

‘Tires back into tires’: The only way to considerably broaden the market for recycled rubber

- Technology Readiness Levels (TRL):
  - Passenger car tire rubber: TRL 5-6 (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)

- Technology Readiness Levels (TRL):
  - No significant development potential of conventional technologies (batch, long residence time, high temperatures)
  - Improvements by after-treatments
  - New technologies?

- Large-scale application in tires only possible with significant quality improvements

- Technology available, also for very fine powder
- No further quality improvements possible
- Very limited application in virgin compounds
Introduction
Devulcanization versus reclamation

DEVULCANIZATION:
Crosslink scission $\Rightarrow$ properties of devulcanisate similar to properties of original material

REGENERATION:
Polymer scission $\Rightarrow$ shorter polymer chains $\Rightarrow$ poor properties
EPDM roof sheeting
Optimization the devulcanization process

Influence of devulcanization conditions:
- Concentration devulcanization aid (hexadeclyamine)
- Temperature
- Rotor speed
- Time

Influence on
- Mooney viscosity
- Insoluble fraction
- Overall XLD
- Monosulfidic XLD

Thesis Kuno Dijkhuis, ‘Recycling of vulcanized EPDM rubber’, University of Twente, 2008
### EPDM roof sheeting

**Optimization the devulcanization process**

<table>
<thead>
<tr>
<th>Influence of devulcanization conditions:</th>
</tr>
</thead>
<tbody>
<tr>
<td>▪ Concentration devulcanization aid</td>
</tr>
<tr>
<td>(hexadeclyamine)</td>
</tr>
<tr>
<td>▪ Temperature</td>
</tr>
<tr>
<td>▪ Rotor speed</td>
</tr>
<tr>
<td>▪ Time</td>
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<tr>
<td>• Overall XLD</td>
</tr>
<tr>
<td>• Monosulfidic XLD</td>
</tr>
</tbody>
</table>

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#### Diagrams

**Figure (a):**
- Insoluble fraction (%)
- HDA-concentration (wt%)
- Temperature (°C)

**Figure (b):**
- Insoluble fraction (%)
- Rotor speed (rpm)
- Time (min)

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- Monosulfidic XLD

(a) Overall crosslink density \( \times 10^4 \text{ mol/cm}^3 \)

(b) Overall crosslink density \( \times 10^4 \text{ mol/cm}^3 \)

HDA-concentration (wt%)
Temperature (°C)
Rotor speed (rpm)
Time (min)

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## EPDM roof sheeting

Optimization the devulcanization process

### Table 1: Optimization Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mooney viscosity</th>
<th>Insoluble fraction</th>
<th>Overall XLD</th>
<th>Mono-sulfidic XLD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration DA</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Temperature</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
<td>Rotor speed</td>
<td>↑</td>
<td>↓</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Time</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td>↑</td>
</tr>
</tbody>
</table>

### Table 2: Feedstock Properties

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Crosslink density ($\times 10^{-4}$ mol/cm$^3$)</th>
<th>Insoluble fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional cured</td>
<td>Overall 2.39</td>
<td>75.1</td>
</tr>
<tr>
<td></td>
<td>Monosulfidic 0.36 (15%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Di- plus polysulfidic 2.03 (85%)</td>
<td></td>
</tr>
</tbody>
</table>
**EPDM roof sheeting**  
*Conventionally versus efficiently cured rubber*

<table>
<thead>
<tr>
<th>Feed stock</th>
<th>Crosslink density ($\times 10^{-4}$ mol/cm$^3$)</th>
<th>Insoluble fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Overall</td>
<td>Monosulfidic</td>
</tr>
<tr>
<td>Conventionally cured</td>
<td>2.39</td>
<td>0.36 (15%)</td>
</tr>
<tr>
<td>Efficiently cured</td>
<td>0.97</td>
<td>0.51 (52%)</td>
</tr>
</tbody>
</table>
EPDM roof sheeting
Application study

Currently implemented at several roof sheeting companies

Thesis Kuno Dijkhuis, ’Recycling of vulcanized EPDM rubber’, University of Twente, 2008
Devulcanization versus reclamation
Analytics

Sol fraction (%)

- Random main chain scission
- Crosslink scission

Decrease in crosslink density

Devulcanization versus reclamation
Horikx Model

\[ 1 - \frac{v_f}{v_i} = 1 - \frac{v_f \left(1 - s_f^{1/2}\right)^2}{v_i \left(1 - s_i^{1/2}\right)^2} \]

\[ \gamma_i, \gamma_f: \text{average number of crosslinks per chain in the insoluble network after/ before reclamation} \]
\[ s_i: \text{soluble fraction of the rubber network before reclaiming} \]
\[ s_r: \text{soluble fraction of the reclaimed vulcanizate} \]
\[ v_i: \text{crosslink density of the network prior to treatment} \]
\[ v_f: \text{crosslink density of the reclaimed vulcanizate} \]

Passenger car tire rubber: SBR
Thermo-mechanical treatment

(a) TT: thermal treatment without exclusion of oxygen

S. Saiwari: Post-consumer tires back into new tires; thesis; University Twente, 2013
Passenger car tire rubber: SBR
Thermo-mechanical treatment

(a) TT: thermal treatment without exclusion of oxygen
(b) TL: thermal treatment and quenching in liquid nitrogen after treatment

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Passenger car tire rubber: SBR
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(a) TT: thermal treatment without exclusion of oxygen
(b) TL: thermal treatment and quenching in liquid nitrogen after treatment
(c) TN: thermal treatment under nitrogen atmosphere; quenching devulcanizate in liquid nitrogen
Passenger car tire rubber: SBR
Thermo-mechanical treatment

TT: thermal treatment without exclusion of oxygen
TL: thermal treatment and quenching in liquid nitrogen after treatment
TN: thermal treatment under nitrogen atmosphere; quenching devulcanizate in liquid nitrogen
SBR devulcanization
Effect of stabilizers

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Brand name</th>
<th>Type</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentaerythritol tetraakis (3-(3,5-di-tert-butyl-4-</td>
<td>Irganox</td>
<td>Hindered</td>
<td></td>
</tr>
<tr>
<td>hydroxyphenyl)propionate)</td>
<td>1010</td>
<td>Phenolic</td>
<td>![chemical_structure_1.png]</td>
</tr>
<tr>
<td>Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)</td>
<td>Irganox</td>
<td>Hindered</td>
<td>![chemical_structure_2.png]</td>
</tr>
<tr>
<td>propionate</td>
<td>1076</td>
<td>Phenolic</td>
<td></td>
</tr>
<tr>
<td>Tris(2,4-diter-</td>
<td>Irgafos</td>
<td>Phosphite</td>
<td>![chemical_structure_3.png]</td>
</tr>
<tr>
<td>butylphenyl)phosphite</td>
<td>168</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Decrease in crosslink density without additional sol fraction indicates less polymer scission
- Stabilizers allow to work at higher temperatures, thus faster processes

S. Saiwari: Post-consumer tires back into new tires; thesis; University Twente, 2013
Passenger car tire elastomers
Devulcanization mechanisms

Devulcanization aid: DPDS, 15 mmol/100 g
Oil: TDAE, 5%wt
Temperature: 220°C
Time: 6 minutes
Atmosphere: N₂ purging
Cooling: Liquid nitrogen
Passenger car tire rubber
Devulcanization conditions

<table>
<thead>
<tr>
<th>Factors</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>De-vulcanization aids</td>
<td>DPDS 30 mmol/100 g compound</td>
</tr>
<tr>
<td>De-vulcanization oil</td>
<td>TDAE 5% w/w</td>
</tr>
<tr>
<td>Swelling time</td>
<td>30 minutes</td>
</tr>
<tr>
<td>Swelling temperature</td>
<td>65 °C</td>
</tr>
<tr>
<td>De-vulcanization time</td>
<td>6 minutes</td>
</tr>
<tr>
<td>De-vulcanization temperature</td>
<td>220 °C</td>
</tr>
<tr>
<td>De-vulcanization atmosphere</td>
<td>With nitrogen gas purging</td>
</tr>
<tr>
<td>Dumping condition</td>
<td>Exclusion from air/oxygen</td>
</tr>
</tbody>
</table>

Addition of stabilizer
## Passenger car tire rubber
### Internal mixer versus extruder devulcanization

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Brabender internal mixer</th>
<th>Extruder</th>
</tr>
</thead>
<tbody>
<tr>
<td>DA</td>
<td>DPDS, 15 mmol/100g</td>
<td>DPDS, 18 mmol/100g</td>
</tr>
<tr>
<td>TDAE</td>
<td>5 %wt</td>
<td>6 %wt</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>TDTBP, 1 %wt</td>
<td>TDTBP, 1 %wt</td>
</tr>
<tr>
<td>Swelling temperature</td>
<td>65°C</td>
<td>65°C</td>
</tr>
<tr>
<td>Swelling time</td>
<td>30 minutes</td>
<td>30 minutes</td>
</tr>
<tr>
<td>Devulcanization time</td>
<td>6 minutes</td>
<td>Min. 6 minutes</td>
</tr>
<tr>
<td>Rotor/screw speed</td>
<td>50 rpm</td>
<td>10 rpm</td>
</tr>
<tr>
<td>Devulcanization temperature</td>
<td>220°C</td>
<td>220°C</td>
</tr>
<tr>
<td>Devulcanization atmosphere</td>
<td>N$_2$ gas purging</td>
<td>N$_2$ gas purging</td>
</tr>
<tr>
<td>Screw configuration</td>
<td>High shear</td>
<td>Low shear with kneading elements in devulcanization zone</td>
</tr>
<tr>
<td>Extrudate handling</td>
<td>Quenching in LN$_2$</td>
<td>Cooling calender</td>
</tr>
</tbody>
</table>
Application study in a blend
Different tire compounds

- No adjustment of compound composition
- ‘First shot’ D-GTR; not optimized
- Decrease in tensile strength of up to 55% for 50/50 blend
- Elongation at break increased for base, carcass and apex

- Compound adjustment gave an increase in tensile strength of 60% in a 50/50 blend
- Absolute improvement for apex, slight decrease for the other compounds
- In a 30/70 blend, the original tensile value will be reached except for the base compound
Limitations
Silica compounds
Limitations
Silica compounds

Reference samples
plain white rubber  5% powder  5% compound

Smoothest surface
96 h swelling,
two passes @ 150°C & 220°C

TGA residue
20 %wt
compound: 6 %wt
### Challenges

<table>
<thead>
<tr>
<th>Contaminations</th>
<th>Fibres</th>
<th>Steel</th>
<th>Sand</th>
<th>Glass ...</th>
</tr>
</thead>
<tbody>
<tr>
<td>Different polymers</td>
<td>SBR</td>
<td>BR</td>
<td>NR</td>
<td>IIR</td>
</tr>
<tr>
<td>Fillers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica, carbon black become less active</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Curing agents and acitvity</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Remains of curing agents &amp; reduced curing activity of the polymers influence new curing process</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aging during first lifecycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Summary

EPDM roof sheeting – the easy one
- Degree of devulcanization strongly depends on network structure
- Amines are the DA’s of choice
- Risk of re-combination at high concentrations and high temperatures
- Rotor speed and devulcanization time have minor influence
- 40% of virgin rubber can be replaced by devulcanizate

Passenger car tire rubber – the difficult one
- Most critical devulcanization parameter: temperature $\Rightarrow 220^\circ$C
- Screw: low shear design
- Protective atmosphere during and after devulcanization:
  - absence of oxygen
  - efficient cooling
- Maximum degree of devulcanization
  - batch mixer: $< 80\%$
  - extruder: 80% - 90%
- 90% Limit: bound rubber, stable monosulfidic crosslinks
- Visible particles, even for fine powder
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Project partner

NWO
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PhD scholarship for teachers

Schill + Seilacher
Sponsor and chemicals supplier

TECH FOR FUTURE
Incentive fund from Windesheim – Saxion

aliancys
Usage of process equipment

Thank you for your attention

RecyBEM B.V.

Band & Milieu

STW

UNIVERSITY OF TWENTE.