DESIGNING A CIRCULAR ECONOMY FOR PASSENGER CAR TIRES

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Improvement drivers

Improving tires:
Labeling systems with respect to tire performance, safety and environmental impact.

Improvement of recycling:
Number of patents on recycling of rubber.
Recent developments in tire compounds

Carbon black based
car tire compounds

Silica based
tire compounds

Improvements on:

Rolling resistance
Wet skid resistance
Without decreasing wear resistance.

http://www.apollotyres.com/uploads/Aspire.png
Devulcanization vs reclaim

Devulcanization
- Lower temperature, lower shear
- Granulated Tire Rubber
- High temperature, high shear
- Crosslink scission

Reclaim
- High temperature, high shear
- Polymer scission
Devulcanization vs reclaim

- **Devulcanization:** Lower temperature, lower shear. Crosslink scission > properties of devulcanize similar to properties of original material.

- **Reclaim:** Granulated Tire Rubber, High temperature, high shear. Polymer scission > shorter polymer chains > poor properties.

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Challenges of devulcanization of Granulated Tire Rubber (GTR)

Remaining dirt, fibres and steel
Mix of different elastomers
SBR difficult to devulcanize
Mix of different compounds
Mix of different fillers
Granulate size

Component | Polymer
---|---
Tread | SBR, BR
Belt | NR
Sidewall | NR, BR
Carcass | SBR, NR, BR
Bead | NR
Apex | SBR, NR, BR
Cap-ply | NR, BR
Innerliner | SBR, NR, IIR

Granulate size: 1-3.5mm
Initial results

Devulcanization
KrausMaffei ZE 25 UTX 42D co-rotating twin screw extruder

Process parameters:
- Residence time: 6-12-17-20 minutes
- Devulcanization temperature: 180°C and 220°C

Recipe:
- DBD (2,2'-DiBenzamidoDiphenyldisulfide): 3.9 and 6.85%wt
- TDAE (processing oil): 2 and 5%wt
- TDTBP (Tris(2,4-Di-Tert-Butylphenyl)Phosphate): 1%wt

Revulcanization

<table>
<thead>
<tr>
<th>Component</th>
<th>(phr)</th>
<th>CB-based vulcanization recipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
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<td>2.0</td>
<td></td>
</tr>
<tr>
<td>6PPD</td>
<td>1.0</td>
<td>The compounds were vulcanized for t90 +2 minutes at 170°C under 100 bar</td>
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<tr>
<td>TMQ</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>TBBS</td>
<td>1.5</td>
<td></td>
</tr>
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Range of results of revulcanizates
For all experiments 100% devulcanizate was used for better discrimination.

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[ JWvHoek ] 6/21
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Silica in GTR - TGA analysis

TGA analysis of the GTR to distinguish:
- the amount of volatiles (~21%wt),
- polymers (~35%wt),
- carbon black (~34%wt),
- silica + ash (~10%wt).

(amount of ash typically 2-3%wt)

Conclusion 1:
This GTR of scrap car tires contains up to 8%wt silica.
Effect silica on devulcanization - Horikx-Verbruggen-silica

![Graph showing the effect of silica on devulcanization](image)

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<td>SSBR</td>
<td>103</td>
</tr>
<tr>
<td>BR</td>
<td>25</td>
</tr>
<tr>
<td>Zeosil 1165</td>
<td>80</td>
</tr>
<tr>
<td>TESPT</td>
<td>7.0</td>
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<tr>
<td>TDAE</td>
<td>5.0</td>
</tr>
<tr>
<td>ZnO</td>
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<tr>
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</tr>
<tr>
<td>Sulfur</td>
<td>1.4</td>
</tr>
<tr>
<td>TBBS</td>
<td>1.7</td>
</tr>
<tr>
<td>DPG</td>
<td>2.0</td>
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Decrease in crosslink density [-]

Degree of devulcanization of silica based rubber as shown by a Horikx-Verbruggen diagram: Limited decrease of crosslink density for a silica based SBR-BR tread compound.
Effect silica on devulcanization - Horikx-Verbruggen-carbon black

Random main chain scission
- Crosslink scission
- No devulcanization
- TESPT 220 °C
- TESPT 250 °C

Decrease in crosslink density [-]

Normal range for devulcanizates of carbon black based rubber.
Effect silica on revulcanization - silica-silane-rubber

Silica:
Surface chemistry of silica.

Silica:
Chemical bound between silica and rubber by a silane bridge.
Effect silica on revulcanization - interpenetrating networks

Sulphide bonds in carbon black rubber

Physically bound rubber

Polymer - polymer network

Sulphide bonds in silica-silane based rubber

Polymer - polymer
&
polymer - silica network

High amount of (mono)sulphidic bonds between silica and rubber

Conclusion 2:
The chemical bond between the silica and the rubber has a large influence on the devulcanizability.
Effect silica on revulcanization - silica + DPG surface chemistry

DPG

Common secondary accelerator for carbon black based rubber

Strong base

Silica particle

High acidity hinders (re)vulcanization

DPG = 1,3-DiPhenylGuanidine

DPG reacts with hydroxyl moieties, decreasing the acidity.
Effect silica on revulcanization - DPG - silica surface chemistry

Silica:  Silane:  Rubber:
Silane bridge between silica and rubber. Part of the hydroxyl moieties are still unoccupied.

DPG occupies the remaining hydroxyl moieties, decreasing the overall acidity.
Effect silica on revulcanization - influence of DPG-TESPT

Tensile strength and strain @ break of DGTR, after revulcanization with:
- DPG (2.8phr)
- Silane (TESPT, 3.2phr) and DPG (2.8phr)

Conclusion 4:
After devulcanization free hydroxyl moieties on the silica surface exists.
These hydroxyl moieties:
- can be neutralized with DPG
- can be used for an additional silanization
both steps improve revulcanization.
Effect silica on revulcanization - comparison of tread compounds

- Compounds with 80phr CB and 90phr silica.
- Virgin material and devulcanize.
- Revulcanization with the similar recipe as virgin material.

Tensile strength of revulcanizates:

Conclusion 5:
- For CB based tread compound: about 14MPa

Conclusion 6:
- For silica based tread compound: about 13MPa
Effect silica on revulcanization - microscopy

Fracture surfaces of dumbbells after tensile test, samples 4*2mm before testing.

(a) Virgin Carbon black based (80phr)  (b) Devulcanizate

(a) Virgin Silica based (90phr)  (b) Devulcanizate

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Summary

Tensile strength [MPa] vs. Strain at break [%]

- CB tread
- Si tread
- Silane + DPG
- DPG

Improvement of devulcanization
Summary

The diagram shows the relationship between tensile strength [MPa] and strain at break [%]. The data points are categorized into different samples:

- **Silane + DPG**
- **DPG**
- **Si tread**
- **CB tread**

An arrow indicates an improvement of revulcanization. The tensile strength is plotted on the y-axis, while the strain at break is on the x-axis. The data points are scattered across the graph, with some trends visible.
Summary

Tensile strength [MPa]

Strain at break [%]

Potential of separation of compounds

Silane + DPG

Silica in GTR

Silica on devulcanization

Silica on revulcanization

CB tread

Si tread

DPG
Summary

1. GTR of recent scrap passenger car tires, age 5 year or less, can contain a considerable amount of silica, circa 8% wt.

2. The silica change the way GTR devulcanizes because of the chemical bond with the rubber.

3. Using DPG in revulcanization compensates for the acidity of silica, improving the tensile strength to 6.5MPa.

4. After adjusting the revulcanization of devulcanized GTR with an additional silanization step, making use of the available silica in the devulcanizate, a tensile strength of 8MPa was obtained.

5. Experiments with a silica based tread compound has shown that the remaining tensile strength of the revulcanizate is 13MPa.
Overall conclusions

- Result by optimizing the devulcanization: tensile strength up to 5MPa

- Effect of adjustment of revulcanization recipe, using the silica content: additional tensile strength 3MPa

- Potential of separation of tread: additional tensile strength 7MPa
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