NEW OPPORTUNITIES TO REDUCE THE CO$_2$-CONTENT BY USING INNOVATIVE MATERIALS

KANNIKA SAHAKARO$^1$, AMNUWA BERAHENG$^1$, M. SATO$^3$, C. YAMADA$^4$, WILMA K. DIERKES$^2$, JACQUES W.M. NOORDERMEER$^2$, ANKE BLUME$^2$

$^1$ PRINCE OF SONGKLA UNIVERSITY, PATTANI CAMPUS, THAILAND
$^2$ UNIVERSITY OF TWENTE, ENSCHEDE, THE NETHERLANDS
$^3$ THE YOKOHAMA RUBBER CO., LTD., JAPAN
$^4$ ASAHI KASEI CORP., JAPAN

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Spanish Rubber Industry Association (COFACO)
Estimated worldwide automobile production from 2000 to 2020

Automobile production in million vehicles


58

+ 67%

97

- 31%

Increase of Greenhouse Gas (GHG) Emissions

EU legislation from 2013: Reduction of Emissions

EU legislation: tolerable emission of a car

- 35 g CO₂ = - 3.5 balloons / km

1 l CO₂ = 1.96 g
one balloon = 2.5 l
→ 10 g = 5.1 l

“Kunststoffe im Auto – was geht noch?”, GAK 4/2013 Jg. 66, p. 248-258
Reality in 2019: Average specific CO₂ emissions from new passenger cars

Numbers from individual manufacturers that registered more than 300,000 new cars in 2019

Lowest number: 108 g CO₂ / km
Driving force: Reduction of Emissions

Solutions for the future for further reduction of CO$_2$?

One possible solution: Reduction of rolling resistance of tires

Another possible solution: Lightweight construction
CO$_2$ emission reduction and safety awareness throughout the world

★ Tire labeling:
mainly about wet grip and rolling resistance

Goal: To improve the performance balance of rolling resistance and wet grip without having a negative effect on abrasion resistance
Fuel Efficiency

Fuel saving per 100 km per label class
(based on example of Ø 6.6 l fuel consumption vehicle)

Change from G (least efficient) to A (most efficient) tires:
Reduction of 0.66 l/100 km fuel =
- 16.5 g CO₂/ km

European Commission; Continental: EU tire label, April 2011
A vs F grade for 40 tons five-axle articulated truck

F to A grade tires:

- reduce fuel consumption by up to 4.8 l / 100 km = 120 g CO₂/ km

→ saving of up to 7125 euros / year*

*Average fuel consumption of vehicle 32.3l/100km → 323l/1000km → 14.7% potential savings = 47.5 l less fuel consumption per 1000 km → fuel price 1.50 EUR/liter = 71.25 EUR/1000km → 100,000 km mileage/year = 7125 EUR savings/year

Contribution of Different Tire Parts to the Rolling Resistance (RR)

The main influence on RR comes from the tread.
Further Reduction of the Rolling Resistance (RR)

Use of Innovative Materials

New innovative materials in the tire tread:

- Functionalized polymers
- New silica / silane system
- Bio-based oils
Further Reduction of the Rolling Resistance (RR)

Use of Innovative Materials

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Functionalized Polymers for Reduced RR

![Image of a tire with text: “Excellent”]

**Graph: Rolling resistance vs. Wet grip index**

- **Rolling resistance index:** $50 \degree C \tan \delta$
- **Wet grip index:** $0 \degree C \tan \delta$

Legend:
- Excellent
- 5th
- 4th
- 3rd
- 2nd
Functionalized Polymers for Reduced RR

Functionalization Technology

1. Functionalization of the chain end

\[ \text{C} \cdot \text{Li}^+ + \text{SBR} \rightarrow \text{Functional Group} \]

2. Functionalization of initiator

\[ \text{-Li}^+ + \text{Styrene} + \text{Butadiene} \rightarrow \text{Initiator} \rightarrow \text{Polymerization} \]

3. Functionalization of main chain with functionalized monomer

\[ \text{Styrene} + \text{Butadiene} + \text{Functionalized monomer} \rightarrow \text{Polymerization} \]

4. Functionalization of side chain

\[ \text{SBR} + \text{Functional Group} \rightarrow \text{Functionalized SBR} \]
Functionalized Polymers for Reduced RR

Formulation and mixing procedure

<table>
<thead>
<tr>
<th>SBR Name</th>
<th>Ref.</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer structure</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound code</td>
<td>R1</td>
<td>A1</td>
<td>B1</td>
<td>C1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Master batch (MB1) Brabender</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
</tr>
<tr>
<td>0:00 Add Polymers</td>
</tr>
<tr>
<td>0:20 Mix</td>
</tr>
<tr>
<td>1:20 1/2 Silica, 1/2 TESPT, Oil</td>
</tr>
<tr>
<td>1:50 Mix</td>
</tr>
<tr>
<td>2:50 1/2 Silica, 1/2 TESPT, Stearic Acid, Zinc Oxide</td>
</tr>
<tr>
<td>3:10 Mix (Control rpm. up to target temp.)</td>
</tr>
<tr>
<td>4:10 Ram sweep</td>
</tr>
<tr>
<td>6:40 Discharge (145-150 C°)</td>
</tr>
</tbody>
</table>

Master batch (MB2) Brabender

<table>
<thead>
<tr>
<th>Time</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:00</td>
<td>Add MB1</td>
</tr>
<tr>
<td>4:00</td>
<td>Discharge (145-150 C°)</td>
</tr>
<tr>
<td></td>
<td>Mill Blend</td>
</tr>
</tbody>
</table>

Final Mix (Productive) Roll (50°C)

MB2 + Sulfur and Accelerators
Introducing functional group results in higher Mooney viscosity.
Functionalized Polymers for Reduced RR

$\tan\delta$ as predictor for the rolling resistance: the lower the better

![Graph showing $\tan\delta$ at 70°C for different polymers.]

- **Alkoxy group**: improving $\tan\delta$
- **Amine group**: No effect on $\tan\delta$
## Functionalized Polymers for Reduced RR

<table>
<thead>
<tr>
<th>Effect</th>
<th>Analytical Technique</th>
<th>Amine group</th>
<th>Alkoxy group</th>
<th>Amine and alkoxy group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica dispersion</td>
<td>TEM, USAX</td>
<td>+</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Flocculation of filler</td>
<td>RPA2000</td>
<td>+</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Filler-polymer interaction</td>
<td>Bound rubber Payne effect</td>
<td>+</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Tanδ (RR)</td>
<td>RPA2000</td>
<td>No effect</td>
<td>++</td>
<td>+</td>
</tr>
</tbody>
</table>

- Alkoxy group can improve silica dispersion and filler-polymer interaction
- Effect of amine group is small
- Functional group deteriorates the processability
- **Alkoxy group leads to improved RR**
Further Reduction of the Rolling Resistance (RR)

Use of Innovative Materials

New innovative materials in the tire tread:

- Functionalized polymers
- New silica / silane system
- Bio-based oils
Modern Passenger Car Tire: Green Tire

- 30% lower rolling resistance
- 5% less fuel consumption
- 7% improved wet grip
- better winter performance

Green Tire

- S-SBR: Solution Styrene Butadiene Rubber
- BR: Butadiene Rubber
- Highly dispersible Silica
- Silane: Si 69°

© EP 501227
Silica / Silane System in the Tire Tread for improved RR

Use of Silane as Coupling Agent

[Diagram showing the interaction between silica surface, silane coupling, triethoxysilyl group, propyl spacer, organo functional group, and rubber coupling during mixing and vulcanization]

Further Reduction of the Rolling Resistance (RR)

Use of Mercapto-Silane vs. Sulfur Silane

<table>
<thead>
<tr>
<th>Property Index</th>
<th>Si 69</th>
<th>Si 363</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mooney Viscosity</td>
<td>100</td>
<td>□ 112</td>
</tr>
<tr>
<td>Scorch time</td>
<td>100</td>
<td>□ 143</td>
</tr>
<tr>
<td>$\Delta G'(0.56%-10%)$</td>
<td>100</td>
<td>□ 50</td>
</tr>
<tr>
<td>tan$\delta$ at 60°C</td>
<td>100</td>
<td>□ 75</td>
</tr>
</tbody>
</table>

*Lower value is better.

Which mechanism is responsible for improved dispersion but worse processing?
**Possible mechanism for mercaptosilanes like Si 263**

- **Addition reaction**
- **Hydrogen abstraction**

Combination of addition reaction and radical propagation reaction → quick generation of large amount of dense chemical bound rubber
Mercapto-Silane for Reduced RR

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Oil content [phr]</th>
<th>Styrene (wt.%)</th>
<th>Cis (wt.%)</th>
<th>Trans (wt.%)</th>
<th>Vinyl (wt.%)</th>
<th>Mooney visc. ML1+4 [MU]</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLR6430</td>
<td>Trinseo</td>
<td>37.5</td>
<td>41</td>
<td>16</td>
<td>28</td>
<td>15</td>
<td>72</td>
</tr>
<tr>
<td>HP755B</td>
<td>JSR</td>
<td>37.5</td>
<td>40</td>
<td>13</td>
<td>23</td>
<td>24</td>
<td>65</td>
</tr>
<tr>
<td>BUNA VSL5025-2</td>
<td>Arlanxeo</td>
<td>37.5</td>
<td>28</td>
<td>6</td>
<td>16</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

- Three different unmodified SBRs with different vinyl contents
- Sulfur-Silane Si 69 vs Mercapto-Silane Si 263
## Mercapto-Silane for Reduced RR

### Mixing Procedure

<table>
<thead>
<tr>
<th>1st stage (Intermesh mixer (1.5L), revolution varied)</th>
<th>dump condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  20s</td>
<td>Polymers</td>
</tr>
<tr>
<td>2  45s</td>
<td>silica, St-Ac, antioxidant, silane, TDAE</td>
</tr>
<tr>
<td>3  120°C</td>
<td>raise ram and clean</td>
</tr>
<tr>
<td>4  135°C</td>
<td>raise ram and clean</td>
</tr>
<tr>
<td>5  150°C</td>
<td>raise ram</td>
</tr>
<tr>
<td>6  60s at 150°C</td>
<td>raise ram</td>
</tr>
<tr>
<td>7  60s at 150°C</td>
<td>raise ram</td>
</tr>
<tr>
<td>8  60s at 150°C</td>
<td>raise ram</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2nd stage (Intermesh mixer (1.5L), 30rpm (fixed))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  20s</td>
</tr>
<tr>
<td>2  30s</td>
</tr>
<tr>
<td>3  30s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3rd stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Add curatives on a two roll mill</td>
</tr>
</tbody>
</table>
Mercapto-Silane for Reduced RR

\( \tan \delta \) as predictor for the rolling resistance: the lower the better

Si 263 compounds show lower \( \tan \delta \) values than Si 69 compounds.
Mercapto-Silane for Reduced RR

ML as indicator for the processing: the higher the worse

Developed bound rubber network for Si 263 decreases chain mobility

→ Worse processability
Mercapto-Silane for Reduced RR

- Characteristics in mercapto-silane system:
  - possible to react directly with a double bond in a rubber polymer chain
  - possible to trigger the polymer radical chain reaction by abstracting an allylic hydrogen radical from the polymer
  
  \[ \Downarrow \]

  - leads to quick generation of large amount of dense chemical bound rubber
  
  \[ \Downarrow \]

  - suppression of silica flocculation during vulcanization
  
  \[ \Downarrow \]

  - maintenance of a better dispersed state of silica clusters
  \[ \rightarrow \] lower tanδ at 60°C value = lower RR

  - decreased chain mobility in uncured compound
  \[ \rightarrow \] worse processability
Further Reduction of the Rolling Resistance

Use of Innovative Materials

New innovative materials in the tire tread:

- Functionalized polymers
- New silica / silane system
- Bio-based oils
Alternative Oils for Reduced RR

Natural oils

- Epoxidized palm oil (EPO)
- Epoxidized soybean oil (ESBO)
Alternative Oils for Reduced RR

Standard: DAE
- Tudalen 65
- H&R

EPO
- Oilflex 222,
- Magnechem

ESBO
- Kaohsiung plant (Taiwan)

Epoxidized palm oil (EPO)

Epoxidized linolein, a major component of ESBO
## Alternative Oils for Reduced RR

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NR</td>
</tr>
<tr>
<td>RSS3</td>
<td>100.0</td>
</tr>
<tr>
<td>SBR 1502</td>
<td>-</td>
</tr>
<tr>
<td>HAF (N330)</td>
<td>60.0</td>
</tr>
<tr>
<td>Oil (DAE, EPO or ESBO)</td>
<td>10.0</td>
</tr>
<tr>
<td>ZnO</td>
<td>5.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.5</td>
</tr>
<tr>
<td>6PPD</td>
<td>1.5</td>
</tr>
<tr>
<td>TMQ</td>
<td>2.0</td>
</tr>
<tr>
<td>Microcrystalline wax</td>
<td>0.5</td>
</tr>
<tr>
<td>Phenolic resin</td>
<td>2.0</td>
</tr>
<tr>
<td>CBS</td>
<td>0.8</td>
</tr>
<tr>
<td>DPG</td>
<td>0.25</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.9</td>
</tr>
</tbody>
</table>
Alternative Oils for Reduced RR

Two mixing step process:

Mixing of rubber and all chemicals except curatives in kneader (30 rpm, fill factor 0.75 and initial mixing temperature 50 °C)

Mixing of accelerator and sulfur on a two roll mill
Alternative Oils for Reduced RR

ML as indicator for the processing: the higher the worse
Alternative Oils for Reduced RR

Modulus as indicator for a good reinforcement

ESBO leads to a strong deterioration of M100
Alternative Oils for Reduced RR

tanδ at 60ºC as predictor for the rolling resistance: the lower the better

Improvement of the RR for the compound with EPO
Alternative Oils for Reduced RR

- EPO and DAE oil filled compounds have similar cure characteristics, mechanical and dynamic properties, filler dispersion
- EPO leads to a lower RR
  → DAE can be replaced by EPO
Further Reduction of the Rolling Resistance

New innovative materials in the tire tread

- Functionalized polymers: Alkoxy-functionalization
- New silica / silane system: Mercapto-silane
- Bio-based oils: Epoxidized palm oil (EPO)

Processing issues have to be solved!
CO₂ Reduction as a Common Goal!

Bridgestone

Goodyear

Nokian Tires

Michelin

Continental

Yokohama

Pirelli

http://www.michelin.de/unternehmen/challenge-green
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