Enhanced silica-NR tread performance by hybrid fillers and polymers

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1. BACKGROUND
NATURAL RUBBER (NR)
Basic properties, applications and consumption

General:
• Renewable material
• Good mechanical and dynamic properties (high fatigue resistance, low hysteresis, low heat build-up)

Applications: anti-vibration mountings, heavy duty tires, conveyor belts, etc.

World consumption of NR is 47%
70% of NR is for tire products
Radial tires require a higher percentage of NR

Protein: bonds with \( \omega \)-end, acts as a crosslink point (hydrogen bonds)
Phospholipids: branching point (hydrogen and ionic bonds)

Granulated Non-granulated (fluffy)

Applications: mostly in tires and high-mechanical products

Improved performances compared to carbon black tire compounds:
- Tear resistance
- Wet traction
- Low rolling resistance
- Low heat build-up

Isolated silanol $\rightarrow$ most reactive, highly polar

Problem: NR is non-polar, whereas silica is polar.
- Difficult to disperse the silica
- Deterioration of the end-product properties

Solution: silane coupling agent

Primary particles $\xrightarrow{K_{12}}$ Small cluster $\xrightarrow{K_{21}}$ Large cluster
SILICA-TO-RUBBER INTERACTIONS
Silanization and coupling mechanism

Requirements:
• High temperature (T >130°C)
• Time

By-product: ethanol

Output:
• Good interaction between filler and rubber

Silanization reaction

TESPT coupling agent

ETOH

Coupling reaction

SILICA PARTICLE

RUBBER CHAIN

RESEARCH MOTIVATION
To improve abrasion resistance

How to improve the abrasion resistance of silica-filled compounds while maintaining the other tire performances?

Motivation for the current study!!
SECONDARY FILLERS
Carbon black and organo-nanoclay

https://www.alibaba.com/product-detail

https://www.indiamart.com

M. Galimberti et al., Rubber-clay nanocomposites, 2011.
SECONDARY POLYMERS
Styrene-butadiene rubber (SBR) and butadiene rubber (BR)

SBR
- Good wet grip, while NR gives good strength
- Reduced rebound resilience
- Better resistance to thermal and oxidative degradation

BR
- High elasticity, low $T_g$, good rolling resistance
- Might provide good abrasion resistance
- Low strength
2. RESEARCH OBJECTIVES
OBJECTIVES

➢ To investigate the effects of secondary polymers and secondary fillers on the properties of silica-filled NR tread compounds

➢ Different levels of microstructure of secondary rubbers such as cis-content, vinyl-content, \( t_g \) in BR, as well as styrene content in SSBR were studied

➢ Two secondary fillers were selected:
  ➢ Carbon black grade N134
    ➢ CTAB and BET specific surface area of 134 and 145 m\(^2\)/g, respectively
  ➢ Organo-nanoclay (Dellite 67G)
    ➢ Functionalized with 47 wt% of dimethyl dehydrogenated tallow ammonium chloride (2HT)
    ➢ Interlayer distance of 34.3 Å
3. EXPERIMENTS
# COMPOUND FORMULATION

## Effects of secondary polymers

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Amount (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reference</td>
</tr>
<tr>
<td>Natural rubber (RSS3)</td>
<td>100.0</td>
</tr>
<tr>
<td>BR(^a)</td>
<td>-</td>
</tr>
<tr>
<td>SSBR(^b)</td>
<td>-</td>
</tr>
<tr>
<td>ULTRASIL 7005</td>
<td>55.0</td>
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<tr>
<td>TEPD(^c)</td>
<td>5.0</td>
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<tr>
<td>TDAE oil</td>
<td>8.0</td>
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<tr>
<td>ZnO</td>
<td>3.0</td>
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<tr>
<td>Stearic acid</td>
<td>1.0</td>
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<tr>
<td>TMQ</td>
<td>1.0</td>
</tr>
<tr>
<td>DPG(^c)</td>
<td>1.1</td>
</tr>
<tr>
<td>CBS</td>
<td>1.5</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.5</td>
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</tbody>
</table>

\(^a\)BR was CB22, CB60 and HV80, containing vinyl-contents of <1%, 11% and 77%, respectively.

\(^b\)SSBR was SLR3402, SL563 and SLR4602, containing vinyl-contents of 30%, 55% and 62%, respectively.
## COMPOUND FORMULATION

Effects of secondary fillers

<table>
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<tr>
<td>TESPD&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>TDAE oil</td>
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<td>Sulfur</td>
<td>1.5</td>
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<td>1.5</td>
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</tbody>
</table>

<sup>a</sup>Secondary polymers were BR (HV80) and SSBR (SL563), containing vinyl-contents of 77% and 55%, respectively.

<sup>b</sup>Secondary fillers were carbon black (N134) and organoclay (Dellite 67G).
COMPOUND PREPARATION
Effects of secondary polymers and fillers

**Masterbatch compound**
- NR, BR or SSBR
- ½(Silica+TESPD+DPG)
- ½ (Silica+TESPD), TDAE oil
- ZnO, Stearic acid, TMQ

- Fill factor: 70%
- Rotor speed: 60 rpm
- Initial temperature setting of mixer: 120°C

**Final compound**
- CBS, Sulfur, ½ DPG

- Fill factor: 70%
- Rotor speed: 30 rpm
- Initial temperature setting of mixer: 70°C
CHARACTERIZATIONS

- Mooney viscosity
- Cure characteristics
- Payne effect
- Bound rubber
- Mechanical properties i.e. tensile properties and abrasion resistance
- Dynamic mechanical properties
Higher vinyl-contents in BR and SSBR shows positive influences on Payne effect, higher 300% modulus, reinforcement index. This is due to improvement of the interaction of TESPD silane coupling with the vinyl-groups in the BR or SSBR. Further study would be necessary to elucidate the BRC result.
Increasing amounts of vinyl-contents in BR and SBR shows positive influences on tan delta at -20°C and 0°C, but reduced DIN abrasion resistance.

The ice and wet traction are related to the $T_g$, where higher $T_g$ means a better ice and wet traction.
For rolling resistance, the tan delta at 60°C shows no significant change.

The pure silica-filled NR shows the lowest tan delta at 60°C, the lowest rolling resistance.

High cis-content BR and high vinyl-content BR and SSBR give positive effect in maintaining the rolling resistance.

A study on the effects of microstructures of secondary rubbers and blending would be interesting!!
When the hybrid polymers are combined with hybrid fillers, all show an increase in cure rate, i.e. reduced optimum cure time and scorch time.
EFFECT OF JOINT HYBRIDIZATION
Silica-silica interaction and tire performance

- For **carbon black**, a slightly changed Payne effect, tan delta at -20°C, tan delta at 0°C, compared to the pure NR compound with silica alone.

- For **organoclay**, the use of organoclay shows enhancements in Payne effect and dynamic properties i.e. tan delta indicators.
The abrasion patterns agree well with the DIN abrasion resistance indices.

A slightly higher tendency for Schallamach waves could be seen for the OC-filled compounds.

EFFECT OF JOINT HYBRIDIZATION

Overall tire performances

Note: The higher the indices, the better the performances!
6. CONCLUSIONS
CONCLUSIONS

- Increasing vinyl-contents in BR in combination with NR, a better Payne effect, 300% modulus, reinforcement index, and tan delta at -20°C and 0°C are obtained, whereas the tensile strength, elongation at break and DIN abrasion resistance index decrease.

- Higher vinyl contents in SSBR give improvements in Payne effect, 300% modulus, tan delta at -20°C and tan delta at 0°C but only a little in DIN abrasion resistance index.

- When the hybrid polymers are combined with hybrid fillers, silica/CB-filled NR/BR and NR/SSBR, respectively silica/OC-filled NR/BR and NR/SSBR all show positive effects on scorch time, optimum cure time, a slightly changed Payne effect, tensile properties, tan delta at -20°C, tan delta at 0°C, as well as DIN abrasion resistance, compared to the pure NR compound with silica alone.

- Overall the combination of BR and OC shows the best performance.
UNIVERSITY OF TWENTE.

Elastomer Technology and Engineering

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THANK YOU!

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