Can “organoclay” enhance abrasion resistance of silica-reinforced NR tread compounds?

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INTRODUCTION

Heavy vehicle tire treads

Typical compositions in truck tire treads
- Natural Rubber (NR) / Butadiene Rubber (BR)
- Carbon black as reinforcing filler
- Curing, processing and antidegrading packages

Why is silica replacing carbon black?
- Carbon black is produced from ‘petroleum’ – more costly and less available.
- Silica is from sand – cheap and more sustainable.
- Some key tire performance can be improved by silica.

General requirements of heavy-duty tire treads
- Wear resistance
- Rolling resistance
- Wet and ice traction
- Cut, chip and chunk resistance


INTRODUCTION

Benefits and challenges of silica/silane

- **Silica reduces tire “rolling resistance”**:  
  - ~30% for passenger car tires → 3-6% fuel savings;  
  - ~20% for truck tires → 6% fuel savings;  
  - Less CO₂ emission

- **It provides benefits to winter tires and all-season tires**.  
  - silica-based compounds are more elastic and flexible at low temperatures → better grip and braking.

- **Challenges in processing and optimizing!**

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INTRODUCTION

Inferior “abrasion resistance” of silica-NR tire treads

Current problem!

Rolling resistance

Carbon black tires
Silica tires

Abrasions resistance

Wet traction

MOTIVATION

Ways to improve wear resistance of heavy vehicle treads

Factors affecting wear resistance

- Elastomers
  - Blend ratio of NR/BR
  - Rubber type
  - Secondary polymers

- Reinforcement
  - Reinforcing fillers
  - Mixture of carbon black and silica
  - Hybrid fillers / nanofillers

- Crosslinking
  - Curing systems
  - Curing packages

MOTIVATION
Using nanoclay as a wear resistance enhancer

Why nanoclay?
Attractive
- Good reinforcement performance due to high aspect ratio
- Good interaction with rubber is achievable
- Increased **tearing energy** → Improved crack-growth and abrasion resistance

Nanoclay gives enhanced polymer orientation and highly stretched ligaments

“Crack tips become blunt”

**MOTIVATION**

Using nanoclay as a wear resistance enhancer

**Why nanoclay?**

Attractive
- Good reinforcement performance due to high aspect ratio
- Good interaction with rubber is achievable
- Increased tearing energy → Improved crack-growth and abrasion resistance

**Challenges**
- Dispersing nanoclay in rubbers is difficult.
- Intercalation/exfoliation of clay platelets is required.

**How?**

Organic modification:
47 wt% of dimethyl dihydrogenated tallow ammonium chloride

A state-of-the-art solution: Clay modification

MOTIVATION
Using nanoclay as a wear resistance enhancer

Why nanoclay?
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- Good reinforcement performance due to high aspect ratio
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Challenges
- Dispersing nanoclay in rubbers is difficult.
- Intercalation/exfoliation of clay platelets is required.

How?
Desired clay dispersion in a polymer

A.I. Khalaf, et. al., KGK, 69 (2016) 22.
**EXPERIMENTAL**

Formulation and compound preparation

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Amount (phr)</th>
<th>Reference</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR (RSS3)</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
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<tr>
<td>Silica (ULTRASIL 7005)</td>
<td>55.0</td>
<td>52.5</td>
<td>50.0</td>
<td>47.5</td>
<td>45.0</td>
<td>40.0</td>
<td>35.0</td>
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<tr>
<td>Organoclay (OC, Dellete 67G)</td>
<td>-</td>
<td>2.5</td>
<td>5.0</td>
<td>7.5</td>
<td>10.0</td>
<td>15.0</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>TESPD</td>
<td>5.0</td>
<td>4.8</td>
<td>4.5</td>
<td>4.3</td>
<td>4.1</td>
<td>3.6</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>DPG</td>
<td>1.1</td>
<td>1.1</td>
<td>1.0</td>
<td>1.0</td>
<td>0.9</td>
<td>0.8</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>

Sulfur 1.5, CBS 1.5, ZnO 3.0, Stearic acid 1.0, TDAE oil 8.0, TMQ 1.0 phr

**Mixing:**
Internal mixer

**OC** = 0, 4.6, 9.1, 13.6, 18.2, 27.3, 36.4 wt% rel. to total filler content

Variable in relation to silica content

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**Masterbatch compound**

- NR
  - ½(Silica+TESPD+DPG) + OC
  - TDAE oil, ½(Silica+TESPD)
  - ZnO, Stearic acid, TMQ

- Fill factor: 70%
- Rotor speed: 60 rpm
- Initial temperature setting of mixer: 100°C

**Final compound**

- Masterbatch compound
  - CBS, Sulfur, ½ DPG

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

Organoclay reduces compound viscosity during mixing!
Why does the organoclay change the properties?
RESULTS: FILLER-FILLER INTERACTION

➢ Organoclay can further hydrophobize the silica surface.

➢ Amine modifier of the nanoclay can boost the silanization.

➢ Reduced filler solid content does not decrease filler-filler interaction linearly.

Why?

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RESULTS: SPACING DISTANCE OF CLAY PLATELETS

Optimum d-spacing at OC from 9-18 wt%
RESULTS: CURE TIMES

➢ Organoclay, to a certain amount, significantly shortens cure time.

➢ Clay modifier is an amine derivative → accelerates sulfur vulcanization.

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RESULTS: MECHANICAL PROPERTIES

OC at 4.6-13.6 wt% improves abrasion resistance indicator, while maintaining tear resistance.
RESULTS: OVERALL COMPARISON

Big impact of organoclay on uncured compound properties, but not on stress-strain data

S. Sattayanurak, PhD Thesis, University of Twente, the Netherlands and Prince of Songkla University, Thailand, 2020.
RESULTS: DYNAMIC PROPERTIES FROM DMA

Optimum tire performance indicators at OC of 9 wt%
Why does “organoclay” improve both rolling resistance and wet/ice skid resistance?
RESULTS: MOLECULAR CHARACTERISTICS

![Graph showing the molecular characteristics of elastomer systems](Image)

- Black line: Without OC
- Blue dashed line: OC-9%
- Green dashed line: OC-18%
- Red dashed line: OC-36%

RESULTS: MOLECULAR CHARACTERISTICS

Organoclay significantly lowers filler-filler interaction →:
• less chain mobility at low temperatures;
• enhanced reinforcement.

The overloading of organoclay diminishes overall properties due to reagglomeration effect.
CONCLUSIONS

Silica/TESPD-filled NR

with 9 wt% of organoclay
rel. to total filler content

Role of organoclay:

Uncured compound
✓ reduces viscosity
✓ reduces filler-filler interaction
✓ shortens cure and scorch times

Vulcanizate
✓ maintains tensile and tear properties
✓ improves key tire performance
THANK YOU

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