Incorporating Silica into Natural Rubber

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Content

1. INTRODUCTION
2. QUESTIONS
3. EXPERIMENT
4. RESULTS & DISCUSSION
5. ANSWERS
1. INTRODUCTION
Natural Rubber (NR)

- Renewable material
- Good dynamic properties
  (high fatigue resistance, low hysteresis, low heat build-up)

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

\[ \text{Repeating unit: cis-1,4-polyisoprene} \]

\[ \omega\text{-end} \]

**Protein:** bonds with \( \omega\)-end, acts as a crosslink point (hydrogen bonds)

**Phospholipids:** branching point (hydrogen and ionic bonds)

Silica

Applications: tires and automotive products

Improved performances compared to carbon black filled tire tread compounds:

- Tear resistance
- Wet traction
- Low rolling resistance
- Low heat build-up

Functional groups

Isolated and geminal silanol groups \(\rightarrow\) most reactive, highly polar

Problem: NR is non-polar, whereas silica is polar.
- Difficult to disperse the silica
- Use of silane supports compatibility to polymer

Coupling Mechanisms

Requirements for coupling TESPT to silica:

- Temperature >130°C
- Sufficient reaction time

By-product: Ethanol

![Chemical diagram showing coupling mechanisms between silica and rubber, with triethoxysilyl-group and propyl spacer.](attachment:image.png)
Silica

Applications: tires and automotive products

Improved performances compared to carbon black filled tire tread compounds:

- Tear resistance
- Wet traction
- Low rolling resistance
- Low heat build-up

Problem: NR is non-polar, whereas silica is polar.
  - Difficult to disperse the silica
  - Use of silane supports compatibility to polymer
  - But even after reacting with silane ca. 75% of all Si-OH remain
  - Presence of silane decreases viscosity which results in worse dispersion

Dispersion Mechanisms

Conventional Mixing and the Alternatives

Mixing constraints:
- High temperature for the coupling reaction (T>130°C)
- NR starts to degrade at this temperature

Conventional or dry mixing

<table>
<thead>
<tr>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>rubber</td>
<td>silica</td>
<td>compound</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>silane</td>
<td></td>
<td>curing agents</td>
</tr>
</tbody>
</table>

- Time-consuming, ethanol emission, mixing + chemical reaction at the same time

Presilanized silica

- Rubber + Pre-silanized silica
- 2nd step required?
- Compound + curing agents

Presilanized silica in a masterbatch

- Rubber with presilanized silica
- 2nd step required?
- Compound + curing agents

Alternatives

- Second mixing step might not be necessary → save time
- No ethanol emission
- Silica is already dispersed in the masterbatch
NR-Silica Masterbatch

1. (Presilanized) silica slurry
2. NR latex is added
3. After coagulation
4. NR-silica masterbatch (dried & compacted)

SEM observation of NR / 30phr silica / 3phr TESPT:
Silica is better dispersed in a masterbatch

2. QUESTIONS
Questions

**Mixing time**
- 3 mixing cycles were applied: long (L), short (S) and very short (VS).

Q1. Which is the most suitable mixing cycle for each compound?

**Mixing problems**
- 2 processing aids were used: PA1 and PA2. Polarity: PA1 < PA2.

Q2. Does a processing aid supports the mixing?

**Mixing procedure**
- Evaluations on the mixing behavior and the mechanical properties.

Q3. Which is the best solution: in-situ, presilanized or masterbatch?
3. EXPERIMENT
## Compound Formulation

<table>
<thead>
<tr>
<th>Method</th>
<th>DRY MIX (DM)</th>
<th>PRESILANIZED (PS)</th>
<th>MASTERBATCH (MB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing cycle</td>
<td>L</td>
<td>VS</td>
<td>VS</td>
</tr>
<tr>
<td>NR</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>NR-silica masterbatch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ULTRASIL VN3 GR</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>TESPT coupling agent</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>PS1: BM Silica COS 8569 MH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA1 (Ultra-flow 700S)</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>PA2 (Ultra-DFR 900)</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound number</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

**Chemicals:** ZnO, stearic acid, 6PPD, TMQ, wax, TDAE oil  
**Curatives:** Sulfur, CBS, TBzTD  

*Amount in phr (part per hundred part of rubber)*
Mixing Procedure

Mixer: Brabender 390 ml
Fill factor: 70%
Starting speed: 60 rpm

STAGE 1
(T dump = 140°C)
- Long (L): 0.5, 2, 1.5, 4
- Short (S): 0.5, 2, 1.5, 4
- Very short (VS): 0.5, 0.5, 1, 2
- Very short (VS) for MB: 0.5, 0.5, 1, 2

STAGE 2
(T dump = 140°C)
- 18:50

STAGE 3
(T dump < 100°C)
- 14:20
- 10:20

Add NR / ½ NR-silica masterbatch
Add silica, silane / ½ NR-silica masterbatch
Add chemicals and PA1 or PA2
Sweep (ram opened)
Shearing (ram closed)
Add ½ NR-silica masterbatch and ½ PA2
Add chemicals and ½ PA2
Measurements

Mixed compound (uncured) → Cure characteristics
- Mooney viscosity
- Filler-filler interaction
- Bound rubber

Cure

Compound (cured) → Heat aging 70°C
- Dispersion
- Hardness
- Tensile

Compression set
4. RESULTS AND DISCUSSION
Mixing

NR-silica masterbatch $\rightarrow$ tough material

- High silica content
- Absence of processing additives
- Higher mixing energy

Different incorporation times of the chemicals

- Presilanized silica has poor flowability
  (DM: granulated; PS1: fluffy; MB: dispersed)
- Presence of silica between the mixer wall and the compound $\rightarrow$ slippage
Mixing

Similar profiles for different processing additives in the dry mix (2) and (3)

DM = dry mix
PS1 = presilanized
MB = masterbatch
Mooney Viscosity

Dry mix: Longer mixing = higher viscosity:
- Better silanization expected (=lower viscosity)
- Pre-scorch by premature crosslinking of TESPT

Presilanized silica and masterbatch:
- Silanization reaction shouldn’t have an influence
- Higher decrease of filler-filler network = better dispersion
- Higher cleavage of NR chains
Payne Effect: Indicator for Micro-Dispersion

- Shorter mixing cycle → higher filler-filler network and less cleavage of polymer chains
- Masterbatch compounds → lowest filler-filler interaction
- PA1 leads to lower Payne effect than PA2

Bound Rubber

DM and PS1: long cycle $\rightarrow$ higher bound rubber content
- Higher coupling possibility?
- Premature crosslink

MB: long cycle $\rightarrow$ lower bound rubber content
- Better dispersion of silica: release of occluded rubber

Processing aids
- PA2 is more polar than PA1: Supports PA2 silica – silane – polymer coupling?

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Cure Characteristics at 160°C

DM: very short mixing $\rightarrow$ marching modulus (2) and (3)
- Long cure time
- Inadequate silanization

MB: close results regardless of their mixing cycles

DM, PS1: long mixing $\rightarrow$ reversion (1) and (4)
- NR chain degradation
## Macro Dispersion

<table>
<thead>
<tr>
<th></th>
<th>DM</th>
<th>PS1</th>
<th>MB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long cycle (L)</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>&amp; PA1</td>
<td>1 (97%)</td>
<td>4 (97%)</td>
<td>9 (96%)</td>
</tr>
<tr>
<td>Very short cycle (VS)</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>&amp; PA1</td>
<td>2 (93%)</td>
<td>5 (96%)</td>
<td>Short (S) cycle 10 (97%)</td>
</tr>
<tr>
<td>Very short cycle (VS)</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
<tr>
<td>&amp; PA2</td>
<td>3 (97%)</td>
<td>11 (98%)</td>
<td></td>
</tr>
</tbody>
</table>

Worse dispersion:
- VS mixed dry mix with PA1
- PA2 improves dispersion in the very short mixing time (by improved silica – silane – polymer coupling?)
5. ANSWERS
Answers

Q1. Which is the most suitable mixing cycle for each compound?
• Dry mix → long mixing
• Pre-silanized and NR-silica masterbatch → very short mixing cycle possible

Q2. Does a processing aid support the mixing?
• Yes. PA2 (Ultra-DFR 900, higher polarity than PA1) is preferable for a shorter mixing time
• Supports the silica – silane – polymer coupling but leads to higher Payne effect in the green compound

Q3. Which is the best solution: in-situ, presilanized or masterbatch?
Overall, NR-silica masterbatch with very short mixing:
• In-rubber properties are as good as the conventionally mixed one but with shorter mixing time
All in all, different influences have to be considered:

Level of
- dispersion
- silanization
- polymer degradation
- premature crosslink
- Polymer-polymer coupling
- Polymer – silane – silica coupling

Challenging!