Achieving better processing of silica filled compounds

Schill + Seilacher “Struktol” GmbH Hamburg, Germany
Sebastian Fritsch, Colin Clarke, Manfred Hensel, Dr. Herbert Schulze

SGF Conference 23th - 24th April 2015 Jönköping, Schweden
Schill + Seilacher “Struktol” GmbH

- Founded in 1877
- Family owned and independent group
- 4 plants in Europe and the United States
- More than 600 employees worldwide
- Rubber division: About one third of total Group Turnover
Product Portfolio

Wide range of products for the Rubber and Latex industry:

- Lubricants
- Peptizers
- Homogenizers and tackifiers
- Plasticizers
- Vulcanization activators
- Metal oxide preparations
- Sulphur preparations
- Mould release agents
- Mandrel release agents
- Mould cleaning compounds
- Trade products

Represented in Sweden by ERTECO !!!
Silica Compound Processing Issues

- High compound viscosity as loading silica is increased
- High mixer torque $\Rightarrow$ rapid, uncontrolled heat rise
- Batch off compactness, poor dispersion and low green strength
- Multiple mixing steps needed to complete silane reaction
- Viscosity increase during storage after mixing
- Excess silane needed for viscosity reduction
- Slow extrusion rate
- Poor extrudate appearance
- Scorchy compound behaviour
Trends in Silica Compounds

**Increased loadings of silica (eg. in passenger tread)**
- 80 parts loading is commonly used in EU, now expanding in Asia
- 100 ⇒ 120 parts silica compounds introduced / under development
- Higher silica levels?
- Increased development of all-silica truck tread compound (NR)

**New generation materials**
- Functionalised polymers (sSBR, high Mwt. high cis BR)
- New coupling agent technologies
- Changes in process oil type
- New silica types (surface modifications)
**Struktol Lubricants of Interest**

Struktol HT 207: Mixture of soaps and fatty acids
Strongly adsorbed to filler thus supporting filler dispersion and breaking up of filler agglomerates

Struktol HT 254 / HT 257: Compound of fatty acid amides and amino acid derivatives
Surface active properties, distribution of fillers

Struktol HT 276: Blend of fatty acid zinc soaps (mainly aliphatic)
Reduces compound viscosity, enhances flow properties
**Motivation**

Improve Processing and Properties of SBR/BR compound

Application of Process Additives
**SBR/BR Compound**

- 80 phr SBR, 20 phr BR
- 60 phr Silica
- 5 phr Carbon Black
- 11 phr TESPT
- 3 phr Struktol 40 MS Flakes
- 3 phr Struktol HT 207 / Struktol HT 254
- Sulfur curing system

**Steps:**

1. First step
2. Second step
3. Third step
Mooney Viscosity After Mixing and Ageing

- 2nd stage mixing
- final stage mixing
- After 2 weeks storage
- After 4 weeks storage

Low viscosity change after mixing because less silica re-agglomeration due to better dispersion
Payne Effect Following Final Stage Mixing

RPA strain sweep 100 °C / 0,1 Hz  final pass

- G' 1 control
- G' 2 Struktol HT 207
- G' 3 Struktol HT 254

Lower Payne effect
Indicator for better silica dispersion and good polymer – silica interaction
Mooney Scorch and Cure Curves

Mooney scorch MS 135 °C

- Control
- Struktol HT 207
- Struktol HT 254

Struktol HT 207 and Struktol HT 254 have higher scorch times compared to the control.

MDR 2000 160°C

- Control
- Struktol HT 207
- Struktol HT 254

The torque (dNm) increases over time (min) for all samples, with Struktol HT 207 and Struktol HT 254 reaching a higher torque than the control.

Struktol HT 207 and Struktol HT 254 show improved performance in terms of scorch and cure characteristics.
# Physical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Control</th>
<th>Struktol HT 207</th>
<th>Struktol HT 254</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore hardness A (Sh.U)</td>
<td>67</td>
<td>66</td>
<td>67</td>
</tr>
<tr>
<td>rebound (%)</td>
<td>36</td>
<td>35</td>
<td>36</td>
</tr>
<tr>
<td>tensile strength (MPa)</td>
<td>14.2</td>
<td>16</td>
<td>16.1</td>
</tr>
<tr>
<td>elongation at break (%)</td>
<td>220</td>
<td>254</td>
<td>259</td>
</tr>
<tr>
<td>modulus 100 % (MPa)</td>
<td>4.1</td>
<td>4.1</td>
<td>4.3</td>
</tr>
<tr>
<td>dispersion (%)</td>
<td>97.53</td>
<td>97.44</td>
<td>97.9</td>
</tr>
<tr>
<td>abrasion loss (cmm)</td>
<td>69</td>
<td>66</td>
<td>73</td>
</tr>
</tbody>
</table>
Extrusion Output and Head Pressure

Trials with constant screw speed in 10D laboratory extruder
cold feed extruder GS 30/K-10D Troester (80/90/90/100) °C 60 1/min

Lower extruder pressure and better extrusion rate with additives
Surface Appearance of Extrusions (Garvey Die)

- Control compound
  - Pressure 93 Bar
  - Garvey rating D3

- Struktol HT 207
  - Pressure 72 Bar
  - Garvey rating C3

- Struktol HT 254
  - Pressure 59 Bar
  - Garvey rating B4
**Conclusions**

**Struktol HT 207 Benefits**
- Reduced Viscosity
- Better Extrusion
- Lower tan δ

**Struktol HT 254 Benefits**
- Much Reduced Viscosity
- Stable viscosity
- Best extrusion
- Highest dynamic stiffness
**Motivation – NR Compound**

Use conventional silane TESPT

Achieve good silanisation within shortest mixing time → increase properties

Reduce the mixing time in order to protect NR exposure to high temperature

Limit the adsorption of NR impurities onto silica surface → increase properties

**Classes of Struktol additive studied**

- Zinc salt based – Zn salts are widely used in NR compounds
- Metal free additive having high polarity → interaction with OH groups

**Addition together with silica silane systems**

- Promote dispersion and facilitate optimisation of silanisation
- Maintain processability by stabilisation of silica surface reactivity
# Formulations and mixing

<table>
<thead>
<tr>
<th></th>
<th>1st pass</th>
<th>2nd pass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber (SIR 20)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black N-330</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Silica (165m² /g)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Struktol SCA 98 (TESPT)</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Struktol HT 257 (metal free)</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Struktol HT 276 (zinc salt)</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>6PPD</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Zinc oxide (adjust for HT 276)</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CBS</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>DPG</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

1st pass - internal mixer Gk 1,5N - start 85°C, 65 1/min, factor: 9,5

- 0'   NR
- 0' 45" 80% silica, silane
- 100°C 20% silica, 6PPD, Struktol, ZnO, stearic acid (rotor speed to max.)
- 130°C dump

aim to dump at 130°C with diff. mixing times as needed - note temp., energy, time

2nd pass – cure addition stage internal mixer dump at 90°C
**Mixing performance**

Mixing profile designed to reach peak rapidly and dump at shortest time

No significant differences in mixing characteristics for each compound

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>Struktol HT 257</th>
<th>Struktol HT 276</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy consumption (kJ)</td>
<td>1630</td>
<td>1545</td>
<td>1579</td>
</tr>
<tr>
<td>Dump temperature (°C)</td>
<td>130</td>
<td>131</td>
<td>131</td>
</tr>
<tr>
<td>Sample temperature (°C)</td>
<td>166</td>
<td>161</td>
<td>163</td>
</tr>
<tr>
<td>Mixing time (min:sec)</td>
<td>02:32</td>
<td>02:27</td>
<td>02:30</td>
</tr>
</tbody>
</table>

Ca. 100 seconds of silica / silane mixing used

Significant reduction of Payne effect is noted

Additives have a significant influence towards suppression of silica flocculation, even when applied during very short mixing cycles.

Short mixing cycle is beneficial in order to minimise thermal degradation of the polymer
**Extrusion data**

Garvey die according to ASTM D-2230

Laboratory cold feed extruder Brabender 19/10 DW 60 1/min 120°C

<table>
<thead>
<tr>
<th>material pressure (bar)</th>
<th>material temperature (°C)</th>
<th>extrusion rate (g/min)</th>
<th>extrusion swelling (g/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>Struktol HT 257</td>
<td>Struktol HT 276</td>
<td></td>
</tr>
</tbody>
</table>

Improved extrusion performance obtained using Struktol additives:

- Reduce extruder head pressure by 25%
- Lower extrudate temperature by 8°C
- Lower die swell by 11%
**Curing data**

Zinc salt product *Struktol HT 276* has influence towards lowering reversion, such influence from zinc salt additive is well known, in this case even when equivalent zinc content (reduction from 2.5 phr → 1.99 phr zinc oxide was made) the positive influence of *Struktol HT 276* was maintained.

Such benefit will contribute towards lower hysteresis → reduced heat build up and lower rolling resistance.
Physical properties

DIN abrasion loss is reduced by use of Struktol additives, this is driven by increased dispersion and promotion of polymer – filler interaction, together with influence on reduced flocculation.

Use of Struktol additives does not result in compound softening - no loss of modulus. Tensile strength is maintained at acceptable values and tear strength is increased.
Summary of results

Short mixing cycles are possible with NR silica, when Struktol additives are used

- Silanisation efficiency is increased (lower Payne effect and flocculation change following annealing)
- Struktol additives reduce viscosity and increase scorch time (HT 276)
- Improved extrusion performance was obtained – low head pressure, low die swell
- Reduction of ZnO is possible (in the case of Struktol HT 276)
- Longer reversion time is possible, especially in the case of Struktol HT 276
- Abrasion loss is reduced by use of Struktol additives (physical properties were equivalent)
- Lower HBU as evidenced by longer blow-out time was achieved
- Tangent $\delta$ was directionally improved for both traction and low R.R.I
- Dynamic stiffness was maintained
Motivation

Highly filled SBR/BR Compound
4 Stage Mixing

Reduce Mixing Time +
Energy Consumption
<table>
<thead>
<tr>
<th>INGREDIENT</th>
<th>MIX STAGE</th>
<th>CONTROL</th>
<th>HT207</th>
<th>HT276</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buna VSL 5025-2HM</td>
<td>110</td>
<td>110</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>Lanxess CB24</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Zeosil Premium 200MP</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>TDAE Oil</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Struktol SCA985</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>N330</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Struktol HT207</td>
<td></td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total phr</strong></td>
<td>268.7</td>
<td>274.7</td>
<td>274.7</td>
<td></td>
</tr>
<tr>
<td>Buna VSL 5025-2HM</td>
<td>110</td>
<td>110</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>Lanxess CB24</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Zeosil Premium 200MP</td>
<td>30</td>
<td>50</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>TDAE Oil</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Struktol SCA985</td>
<td>2.4</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Struktol HT207</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Struktol HT276</td>
<td></td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AOz Wax</td>
<td></td>
<td>1.5</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>2.5</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>6PPD</td>
<td></td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td><strong>Total phr</strong></td>
<td>274.7</td>
<td>274.7</td>
<td>274.7</td>
<td></td>
</tr>
<tr>
<td>Zeosil Premium 200MP</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Struktol SCA985</td>
<td>1.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AOz Wax</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6PPD</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total phr</strong></td>
<td>274.7</td>
<td>274.7</td>
<td>274.7</td>
<td></td>
</tr>
</tbody>
</table>

**NOT INCLUDED**

<table>
<thead>
<tr>
<th>INGREDIENT</th>
<th>MIX STAGE</th>
<th>CONTROL</th>
<th>HT207</th>
<th>HT276</th>
</tr>
</thead>
<tbody>
<tr>
<td>Santocure CBS</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Perkacit DPG</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

**Final**

| Total phr | 268.7 | 274.7 | 274.7 |
Batch-Off Condition for Control Compound

PASS #1

total silica = 50 phr / energy = 0.35 kW-hr

PASS #2

total silica = 80 phr / 0.37 kW-hr

PASS #3

total silica = 100 phr / 0.41 kW-hr

FINAL PASS

total silica = 100 phr / 0.14 kW-hr
Mooney Viscosity Profile – Control Compound

Mooney Small Rotor = very high viscosity in 2\textsuperscript{nd} and 3\textsuperscript{rd} pass
3-Pass Mixing of Compounds with Struktol HT 276

PASS #1

- Total silica = 50 phr / energy = 0.35 kW-hr

PASS #2

- Total silica = 100 phr / energy = 0.36 kW-hr

PASS #3

- Total silica = 100 phr / energy = 0.12 kW-hr

35% Saving in Mix Energy
Mooney Viscosity Profile Achieved Using Process Additives

- 2nd pass Mv of control is above 120 MS 1+4 (100°C)
- Both Struktol batches give lower 2nd pass viscosity (even with 100 phr silica loading)
Dispersion Kinetics* - Control Batch at Each Mixing Stage

* Dispergrader alpha View courtesy of Alpha Technologies
Dispersion Kinetics – Process Additives at Each Mixing Stage

<table>
<thead>
<tr>
<th></th>
<th>PASS 1</th>
<th>PASS 2</th>
<th>PASS 3</th>
<th>FINAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>Z = 45%</td>
<td>Z = 64%</td>
<td>Z = 83%</td>
<td>Z = 89%</td>
</tr>
<tr>
<td>HT207</td>
<td>Z = 61%</td>
<td>Z = 83%</td>
<td>N/A</td>
<td>Z = 94%</td>
</tr>
<tr>
<td>HT276</td>
<td>Z = 61%</td>
<td>Z = 84%</td>
<td>N/A</td>
<td>Z = 94%</td>
</tr>
</tbody>
</table>

- Process additives achieve good dispersion in 2 mixing stages
- Can easily eliminate 3rd mixing stage (viscosity also sufficiently reduced)
Garvey Die Extrusion – Brabender Cold Feed

All zones of extruder barrel maintained at 125 °C
Screw speed = 60 rpm
# Compound Performance - Summary

<table>
<thead>
<tr>
<th>TEST PARAMETER</th>
<th>CONTROL</th>
<th>HT207</th>
<th>HT276</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mooney Scorch t5 @125 C°</td>
<td>11.7</td>
<td>21.6</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>Spiral Mold Flow @ 160 C° (g)</td>
<td>1.29</td>
<td>1.42</td>
<td>1.39</td>
</tr>
<tr>
<td>Tensile (MPa)</td>
<td>13.2</td>
<td>17.2</td>
<td>14.3</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>268</td>
<td>427</td>
<td>468</td>
</tr>
<tr>
<td>Sh. A Hardness</td>
<td>78</td>
<td>74</td>
<td>75</td>
</tr>
<tr>
<td>DIN Abrasion loss</td>
<td>215</td>
<td>164</td>
<td>166</td>
</tr>
<tr>
<td>Tear Strength Die C (N/mm)</td>
<td>28.1</td>
<td>33.0</td>
<td>34.1</td>
</tr>
<tr>
<td>G* 10 % @50 C° (MPa)</td>
<td>3.20</td>
<td>2.48</td>
<td>2.66</td>
</tr>
<tr>
<td>tan δ max @50 C° (0.5-20 % strain)</td>
<td>0.241</td>
<td>0.209</td>
<td>0.266</td>
</tr>
</tbody>
</table>

- **= IMPROVEMENT**
- **= DRAWBACK**
Conclusions

- A silica loading of 100 phr is easily achieved when a Struktol silica dispersant is incorporated into the recipe.

- A mixing stage can be removed allowing for significant time and energy savings of 30-35% due to Struktol additive use.

- The high viscosity is due to 100 phr of silica, this can be much reduced by ~50 ML1+4 points through each mixing step with additives use.

• Struktol HT207 is recommended for lowest tan d (low RRI).
• Struktol HT 276 is recommended for use best extrusion performance.
Summary

A small addition can have a huge impact!
Thank you very much for your attention!

For more Info visit us at www.struktol.de