Introduction ERT

• Start October 1\textsuperscript{st}, 2003
• Currently 13 employees
• Independent research and test laboratory
• Complete range of equipment
• Qualified employees
• Extensive academic and practical knowledge and experience
• ISO 17025 accredited
Main activities:

Elastomers

- Research and Development
- Testing
- Failure Analysis
- Consultancy
- Training and education
Our customers

- Raw material suppliers
- Producers of rubber-parts
- Trading companies
- End-users of rubber-parts
- Recycling, engineers, research institutes, universities

- From raw materials to applications and back to raw materials.

ELASTOMER RESEARCH TESTING B.V.
ERT: Compounding and analysis for the rubber industry

Dr. Ir. Kuno Dijkhuis
VKRT & DKG joint seminar
Deventer, the Netherlands
September 8th, 2016

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Compounding

Producing of a processable mixture of an elastomer with the correct fillers and chemicals, that after vulcanization results in a rubber having the required properties and requirements and which can be manufactured for an acceptable price.

The 3 P’s:
- Processable
- Properties
- Price
Radial tyre

Grip, rolling resistance, abrasion resistance

- Tread
- Plies
- Carcass
- Liner
- Flipper
- Sidewall
- Chafer
- Bead
  - hard, ≥90° Shore
  - High modulus

flexible, ozone resistant

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## Rubber recipe

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>phr</th>
<th>function</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR 1502</td>
<td>80</td>
<td>synthetic rubber</td>
</tr>
<tr>
<td>SMR 20</td>
<td>20</td>
<td>natural rubber</td>
</tr>
<tr>
<td>Carbon black</td>
<td>60</td>
<td>filler</td>
</tr>
<tr>
<td>Naphthenic oil</td>
<td>10</td>
<td>plasticizer</td>
</tr>
<tr>
<td>Zink oxide</td>
<td>4</td>
<td>activator</td>
</tr>
<tr>
<td>Stearic zuur</td>
<td>1</td>
<td>activator</td>
</tr>
<tr>
<td>6PPD</td>
<td>3</td>
<td>anti-ozonant</td>
</tr>
<tr>
<td>TMQ</td>
<td>1</td>
<td>anti-degradant</td>
</tr>
<tr>
<td>Wax</td>
<td>2</td>
<td>anti-ozonant</td>
</tr>
<tr>
<td>PVI</td>
<td>0,2</td>
<td>retarder</td>
</tr>
<tr>
<td>TBBS</td>
<td>1,2</td>
<td>accelerator</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2,5</td>
<td>curative</td>
</tr>
</tbody>
</table>
Types of elastomers

- General purpose rubbers: NR, IR, BR, SBR, IIR
- Special purpose rubbers: CR, NBR, EPDM, VMQ, FKM, etc.

- high temperature resistance
- low temperature resistance
- swelling in organic solvents
- weathering resistance
- flex properties
- price
ASTM/ISO nomenclature of rubbers

ASTM D1418 and ISO 1629:

- **M** Rubbers with a saturated carbon main chain of the polymethylene type
- **N** Rubbers with carbon and nitrogen in the main chain
- **O** Rubbers with carbon and oxygen in the main chain
- **Q** Rubbers with silicium and oxygen in the main chain
- **R** Rubbers with an unsaturated carbon main chain
- **T** Rubbers with carbon, oxygen and sulphur in the main chain
- **U** Rubbers with carbon, oxygen and nitrogen in the main chain
- **Z** Rubbers with phosphor and nitrogen in the main chain
Filler classification

Primary particle size (nm)

- 5000 nm: non-reinforcing
  - ground marble
  - soft clay

- 1000 nm: semi-reinforcing
  - precipitated CaCO$_3$
  - Al silicate
  - Ca silicate

- 500 nm: reinforcing
  - precipitated silica
  - carbon blacks

- 100 nm: semi-reinforcing
  - whiting

- 50 nm: reinforcing
  - calcined clay

- 10 nm: non-reinforcing
  - precipitated silica
  - fumed silica
Influence of fillers on some properties:

- Tensile strength
- Abrasion
- Hardness

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Types of plasticizers

• Mineral oils
  – parafinic
  – naftenic
  – aromatic
  - TDAE (Treated Distilled Aromatic Extract)
  - MES (Mildly Extracted Solvent)
Mineral oils compatibility with some rubbers

<table>
<thead>
<tr>
<th></th>
<th>Parafinic</th>
<th>Naftenic</th>
<th>Aromatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIR</td>
<td>excellent</td>
<td>moderate</td>
<td>bad</td>
</tr>
<tr>
<td>EPM</td>
<td>excellent</td>
<td>good</td>
<td>bad</td>
</tr>
<tr>
<td>EPDM</td>
<td>excellent</td>
<td>excellent</td>
<td>moderate</td>
</tr>
<tr>
<td>NR</td>
<td>good</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>BR</td>
<td>good</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>SBR</td>
<td>good</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>CR</td>
<td>bad</td>
<td>moderate</td>
<td>excellent</td>
</tr>
<tr>
<td>NBR</td>
<td>bad</td>
<td>moderate</td>
<td>excellent</td>
</tr>
</tbody>
</table>
Curing additives

- Sulphur
- Sulphur donors
- Peroxides
  - saturated elastomers
  - specific properties
- Miscellaneous
  - only specialty elastomers
  - i.e. Pt-curing: VMQ, FVMQ
Sulphur curatives

• Sulphur
  – most used curative
  – only unsaturised elastomers
  – ZnO and stearic acid as activator
  – Adjustable curing with accelerators
  – CV, SEV and EV system

• Sulphur donors
  – high percentage monosulfidic crosslinks
  – no reversion
  – good compression set and ageing resistance
  – more necessary, more expensive
Cross-link density vs. properties

Vulcanizate Property

Tear Strength
Fatigue Life
Toughness

Tensile Strength

Hysteresis
Permanent Set
Friction

Elastic Recovery
Stiffness

Crosslink Density

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Different types of crosslinks

• Polysulfidic crosslinks:
  \[ \text{----C-}S_X\text{-C-----} \]

• Disulfidic crosslinks:
  \[ \text{----C-S}_2\text{-C-----} \]

• Monosulfidic crosslinks:
  \[ \text{----C-S-C-----} \]

• Carbon-carbon crosslinks (peroxide):
  \[ \text{----C-C-----} \]

• unreacted sulphur-accelerator groups
# Vulcanization systems

<table>
<thead>
<tr>
<th></th>
<th>CV</th>
<th>SEV</th>
<th>EV</th>
<th>Donor</th>
</tr>
</thead>
<tbody>
<tr>
<td>phr sulphur</td>
<td>2 - 3.5</td>
<td>1 - 2</td>
<td>0.3 - 1</td>
<td>-</td>
</tr>
<tr>
<td>phr accelerator</td>
<td>0.5 - 1</td>
<td>1 - 2.5</td>
<td>2 - 6</td>
<td>4 - 6</td>
</tr>
<tr>
<td>% poly-S</td>
<td>90</td>
<td>50</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>% mono/di</td>
<td>10</td>
<td>50</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>reversion</td>
<td>much</td>
<td>little</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>flex-prop.</td>
<td>good</td>
<td>moderate</td>
<td>bad</td>
<td>bad</td>
</tr>
<tr>
<td>ageing res.</td>
<td>bad</td>
<td>moderate</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>compression set</td>
<td>bad</td>
<td>moderate</td>
<td>good</td>
<td>excellent</td>
</tr>
</tbody>
</table>
Acellerators

- Increase vulcanization speed
- More effective use of sulphur, adjustment of vulcanizate properties via CV, SEV and/or EV systems
- Less side reactions, larger degree of vulcanization, less reversion
- Adjustment of scorch and/or optimum curing time via combinations of accelerators
- Retarders only for increase of scorch time
Effect of accelerators in NR at 150°C

Rheograms at 150°C during 60 min. MDR 2000E, arc 0.5°, max. torque 1.0 Nm

Compound: phr
- NR SMR CV 100
- Zinc oxide 5
- Stearic acid 2
- Accelerator 0.6
- Sulphur 2.5

Torque

0.00 0.25 0.50 0.75

0.00 15.00 30.00 45.00

TBBS
TMTD
ZDMC
DPG
MBTS
Effect of accelerators in SBR at 170°C

Compound: phr
- SBR 1509 100
- Zinc oxide 5
- Stearic acid 2
- **Accelerator** 0.8
- Sulphur 1.2

Rheograms at 170°C during 60 min.
MDR 2000E, arc 0.5°, max. torque 0.8 Nm
Effect of retarders in NR at 150°C

Rheograms at 150°C during 30 min. MDR 2000E, arc 0.5°, max. torque 1.2 Nm

Compound:         phr
NR SMR CV          100
Zinc oxide         5
Stearic acid       2
CTP                as given
TMTD               as given
CBS                 0.6
Sulphur            2.5

+ 0.2 TMTD  + 0.3 CTP
Control CBS

Rheograms at 150°C during 30 min.
MDR 2000E, arc 0.5°,
max. torque 1.2 Nm
## Properties sulphur vs. peroxide

<table>
<thead>
<tr>
<th></th>
<th>sulphur</th>
<th>peroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>+</td>
<td>—</td>
</tr>
<tr>
<td>Tear resistance</td>
<td>+</td>
<td>—</td>
</tr>
<tr>
<td>Compression set</td>
<td>—</td>
<td>+</td>
</tr>
<tr>
<td>Thermal ageing</td>
<td>—</td>
<td>+</td>
</tr>
<tr>
<td>Flex properties</td>
<td>+</td>
<td>—</td>
</tr>
<tr>
<td>Dynamical behaviour</td>
<td>+</td>
<td>—</td>
</tr>
<tr>
<td>Reversion</td>
<td>—</td>
<td>+</td>
</tr>
</tbody>
</table>
Miscellaneous

Ingredients which give a special property to the rubber compound:

- Anti-degradants
- Processing aids
- Pigments
- Blowing agents
- Flame retarders
- Anti-static fillers
- Etc. etc. etc.
Chemical analysis

“Reversed engineering”
Chemical analysis

Qualitative (type) and Quantitative (concentration) analysis

Methods often used for rubber:
- Infra red analysis (FTIR)
- Gas chromatography mass spectrometry (GC-MS)
- Thermogravimetric analysis (TGA)
- Extraction (Soxhlet)
- Scanning Electron Microscopy (SEM-EDX)
Application of FTIR

- Polymer identification
- Determination of presence of organic additives and fillers
- Observation of degradation
- Analysis of (in)organic polutions
Chemical analysis: (H)NBR

![Chemical analysis graph]

NBR

HNBR

1232, 1110, 1066 and 1016 - phthalate plasticiser

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TGA
ISO 9924

• Thermal gravimetrical analysis
• Relative simple determination content of polymer, carbon black and ash and volatile matter
TGA

- 105 - 110 °C: moisture
- 110 – 300 °C: volatile matter like plasticisers, processing aids, anti-oxidants
- 300 – 600 °C: polymer
- 600 – 950 °C: N₂ replaced by O₂, oxidation, carbon black
- Residue is ash: mineral fillers, pigments, metal oxides
Extraction
ISO 1407

- Suitable solvent
- Extractable matter like low molecular weight components, plasticisers, antioxidants, waxes, processing aids, degradation products of the curing system.
Pyrolysis GC-MS

- Method to separate organic mixtures, to identify and quantify

- Existing decomposition products are characteristic for the analysed material

- GC-MS analysis releases the different components
Pyrolysis GC-MS

- The same as for FTIR, also for GC-MS creating a material specific reference library is of the biggest importance to be able to identify materials with certainty.
Fingerprint

- Prevent failure, know what you supply your customers:
  - Density, FTIR and TGA analysis
  - Consistency in material composition
  - Hardness and compression set
  - Optimal curing conditions

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Thanks for your attention?

Are there any questions?