Energy-saving Tires with Low Rolling Resistance: Example of Major Breakthrough in Rubber Technology

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Introduction

US Department of Transportation:
± 2/3 out of the total consumption of petroleum resources is used for transportation.
Introduction

Automotive transportation accounts for about $\frac{1}{2}$ of this segment.

In 2004 this consumed globally $1.1 \times 10^{12}$ liters of fuel, and created $2.61 \times 10^9$ M Tons of CO$_2$ emissions.


Clearly, any developments that can reduce that consumption will have an impact on global energy consumption and reduction of CO$_2$ emissions!
Introduction

Energy efficiency of fuel consumed for traction of a vehicle running at constant speed:

± only 30 % is effectively used for motion of the vehicle, of which:

- 1/3 is consumed to overcome the aerodynamic drag of the vehicle;
- 1/3 for mechanical friction in the vehicle;
- 1/3 to overcome the Tires Rolling Resistance.

± 70% is lost in the form of heat via the exhaust.
Rolling Resistance of Tyres

**Tire Rolling Resistance** is the Amount of Heat (dH) dissipated by internal hysteresis within the tire, per Unit of Distance (dl) traveled:

\[
\frac{dH}{dl}: \text{[Joule/m]} = \text{[N.m/m]} = \text{[N]}
\]

It has the dimension of a force, though it is a scalar, not a vector: a constant resistance to motion.

**Rolling Resistance** is indeed experienced as a force, ref. e.g. driving on under-inflated bicycle tires.
New legislation

A Triple, Seven-level Labeling System for Tires, starting 1 July 2012 in Europe on:
- Rolling Resistance;
- Wet Skid Resistance;
- Tire Noise;
will definitely increase the awareness on energy-saving tires!


Japan, USA and Canada are following.
Impact Assessment Study on Possible Energy / Labeling of Tires:
European Policy Evaluation consortium (EPEC); July 31, 2008

Tire EU Labeling Criteria:

<table>
<thead>
<tr>
<th>Wet Grip Rating</th>
<th>Roll. Resist. Rating</th>
<th>Sum (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>A/B</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>C/D</td>
<td>5</td>
</tr>
<tr>
<td>C</td>
<td>E/F</td>
<td>57</td>
</tr>
<tr>
<td>D</td>
<td>G</td>
<td>38</td>
</tr>
</tbody>
</table>

38% of current summer replacement passenger car tires do not meet the 2012 standard; about 50% of winter replacement tires don’t either!
Origin of Rolling Resistance

Silica filled rubber blend

Reinforced Rubber is composed of two co-continuous networks:
- the POLYMER network;
- the FILLER network.
Origin of Rolling Resistance

Upon deformation, the polymer network co-deforms, the filler network is destroyed and only slowly reforms upon release.

The polymers (more or less attached to the filler surface) slide along the surface and don’t fully return to their original configuration.

Mullins: Molecular slippage model of reinforcement mechanism
Origin of Rolling Resistance

The continuous disruption and restoration of the filler network (filler-filler interaction) causes the hysteretic effects in rubber:

the Payne Effect

the decrease of the dynamic modulus with strain causes the energy dissipation.
Reinforcing Fillers

- **Carbon Black**: most commonly used. **Polymer-Filler Interaction** is mainly physical in nature; thermodynamically based. Polymers attach along (part of) their contour to the carbon black primary particles (20 – 30 nm).

- **Silica (SiO₂)**: strongly polar relative to rubber. **Polymer-Filler Interaction** must be chemically established, otherwise the silica and rubber will not mix or interact.

**Compatibility Polarity Match**

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Fillers</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM</td>
<td>Carbon black</td>
</tr>
<tr>
<td>SBR</td>
<td>Silica</td>
</tr>
<tr>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>NBR</td>
<td></td>
</tr>
</tbody>
</table>

Surface tension [mJ/m²]

- 16.4
- 16.6
- 17.5
- 19.7
- 70.0

Coupling Silica and Rubber

By:
- chemically reacting the silica with coupling agents (silanes of different sorts), hydrophobation, during mixing of the rubber compound;
- during the vulcanization stage couple the silane to the rubber molecules.


J.-B. Donnet
U. Görl
A. Hunsche
H.D. Luginsland
T.F.E. Materne
A. Vidal
S. Wolff
Laboratory evaluations:

Laboratory evaluations of **Rolling Resistance**
and **Wet Skid Resistance/traction**:

\[ \tan \delta \@ 60^\circ C \sim \]
Rolling Resistance
\[ \tan \delta \@ 0^\circ C \sim \]
Wet skid resistance

Chemical polymer-filler interaction is greatly preferred!

Ref.: Cabot Corporation
Silica in rubber history

- **Silica and silicates as replacement of carbon black**
- **Precipitated silica** (lower costs than pyrogenic silica)
  - First applications: shoe soles (colored, transparent)
- **Silica in heavy-service tires** (improvement of cutting and chipping resistance, better adhesion to textile and metal), 10-25 phr silica
- **Silica-silane technology** for passenger car tire treads

1950 - 1970 - 1990 - 2010

- **Rolling resistance**
- **Abrasion resistance**
- **Wet grip**
Silica/silanes in rubber

1970

Organofunctional silanes as adhesion promoters for glass fiber – polymer systems

1990

Introduction of bifunctional silanes as coupling agents

Best silanes for highest reinforcing effect and minimal influence on scorch
F. Thurn, S. Wolff, KGK 28, 733ff, 1975

Bis-(triethoxysilyl propyl)tetra- and disulfides as coupling agents

Current silica consumption in rubber:
app. 0.5 mill. tons/year

Combinations:
-SCN
-S-CS-OR
-S-CS-NHR
-S-C(NH)(NH$_2$)
-SH
-S-S-
-S-S-S-
-S-S-S-S-

S-moieties

Si-moieties

-Si(OCH$_3$)$_3$
-Si(OC$_2$H$_5$)$_3$
-Si(i-OC$_3$H$_7$)$_3$
-Si(n-OC$_3$H$_7$)$_3$
-Si(CO$_4$H$_9$)$_3$
-Si(OC$_8$H$_17$)$_3$
Silica-rubber coupling reactions

Technological challenges involved:

- Coupling the silane with silanol-groups on the silica surface during mixing: requires a temperature of $>140^\circ$C, and a long reaction time; $145^\circ$C = vulcanization temp.: risk of pre-vulcanization or scorch during mixing;


H.D. Luginsland et al.
Technological challenges involved (cont.d):

- Tendency of the silica to de-mix during pre-scorch phase;
- Controlled addition-reaction of the silane to the polymers during the vulcanisation stage.

Silica-silane coupling

Common Internal Rubber Mixer technology is optimized for physical carbon black mixing, not as a chemical reactor for:

- Extremely good temperature control;
- Long duration of mixing;
- Devolatilization and removal of large amounts of ethanol.

Silane-rubber coupling

Silanes make use of the large reactivity of \(-\text{SH}\) (thiol) or \(-\text{S-S}:\) radicals towards unsaturated C=C-functionalities in the polymers:

Most reactive are pendant 1,2-vinyl groups in the polymers.

Combinations:

-SCN
-S-CS-OR
-S-CS-NHR
-S-C(NH)(NH\(_2\))
-SH
-S-S-
-S-S-S-
-S-S-S-S-

-\text{Si(OCH}_3\text{)}_3
-\text{Si(OC}_2\text{H}_5\text{)}_3
-\text{Si(i-OC}_3\text{H}_7\text{)}_3
-\text{Si(n-OC}_3\text{H}_7\text{)}_3
-\text{Si(CO}_4\text{H}_9\text{)}_3
-\text{Si(OC}_8\text{H}_{17}\text{)}_3
Amount of 1,2-vinyl groups in polymers used for tyres

**Natural rubber: 0%!**

Natural rubber by itself is a CO$_2$-sequestering polymer: it represents 45% of world rubber consumption and is growing in market share! However, NOT for energy saving tires.

**Emulsion-SBR:**

~ 10%

**Solution-SBR:**

~ 20 – 70%.
Polymer selection

- NR and Emulsion-SBR additionally suffer from preferential adsorption of proteins and emulsifiers on silica, precluding reaction of the coupling agent with the silica;

- Solution-SBR with high vinyl-content;

- Tg of S-SBR with high vinyl is too high: addition of 25% high-cis BR (Tg ~ -90°C);

- Solution-SBR is anionically polymerised: simple to modify at the end of the molecule: not effective, need reactivity all along the molecular chain;

- Grafting functional groups along the chain would be an option: requires additional operation, expensive, commercially not a viable option.

P. Robert, IUPAC Conf. June 2004
A.F. Halasa et al., German Rubber Conf., July 2006
Consequences for silica-developments

- S-SBR and BR are “low viscosity” polymers relative to NR and E-SBR;
- Silica is by virtue of its polar nature hard to mix with non-polar rubber;
- “Older” types silica were tunnel-dried: aggregates are heavily agglomerated: extra difficult to mix;

**Low Rolling Resistance** tire technology required development of special spray-drying technique:
- Rhodia Silices
- Degussa/Evonic
- PPG.
Continuous Developments

Ongoing developments in coupling agents:
- Less or no ethanol generation;
- Higher scorch stability during mixing: blocked silanes;

Ongoing developments in polymers:
- Effect is limited;

Ongoing developments in equipment:
- Adjustments to mixers for the chemical reactions;
- Efficiency of ethanol removal.
In combination with design changes of tires, the silica technology has achieved:

50% Rolling Resistance Reduction over the last 20 years.

More to follow!
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