



Elastomer Technology & Engineering



University of Twente
The Netherlands

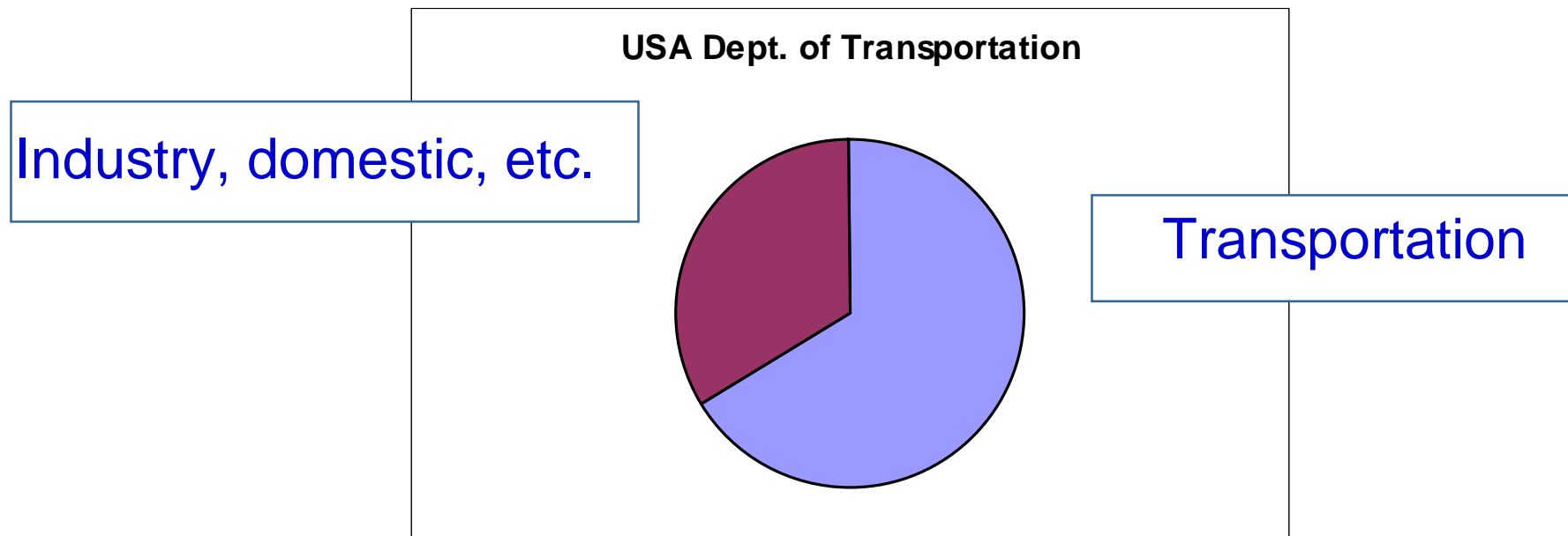
Enhanced Polymer-Filler Interactions: the Basis for Low Energy Consuming, Low Rolling Resistant Tyres

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Introduction

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



Introduction

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

In 2004 this consumed globally 1.1×10^{12} liters of fuel, and created 2.61×10^9 M Tons of CO₂ emissions.

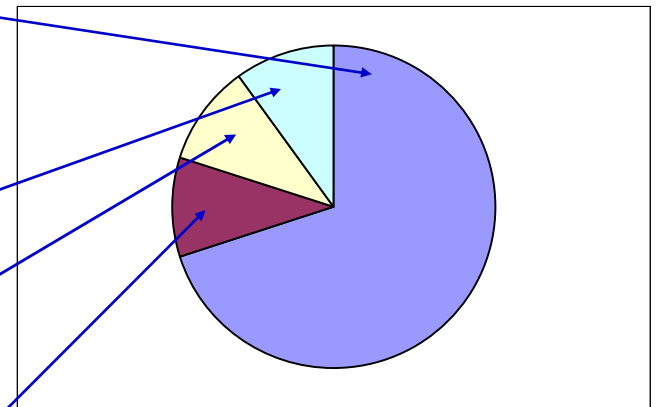
Clearly, any developments that can reduce that consumption will have an impact on global energy consumption and reduction of CO₂ emissions!



Introduction

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

- $\pm 70\%$ is lost in the form of heat via the exhaust;
- \pm 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 **Tyres Rolling Resistance.**



Rolling Resistance of Tyres

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

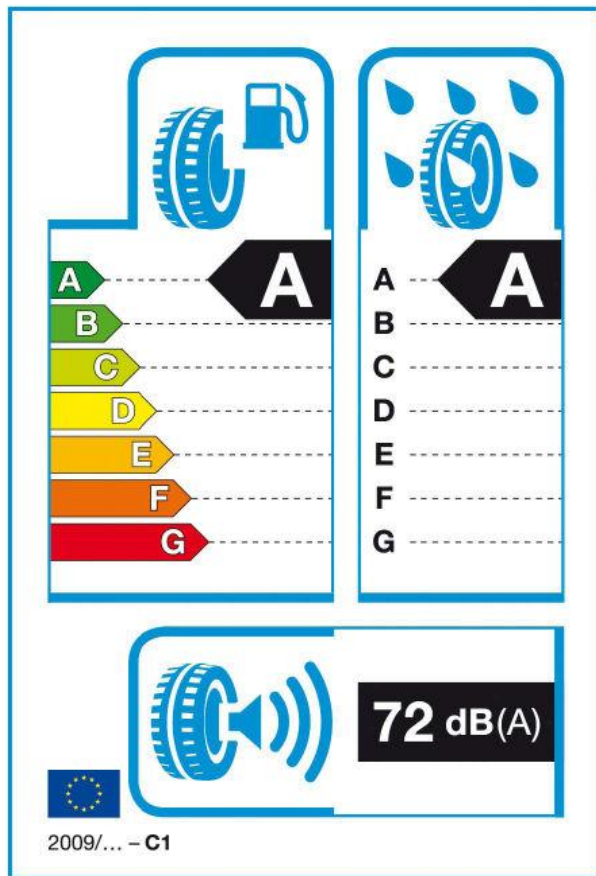
$$dH/dl: [\text{Joule/m}] = [\text{N.m/m}] = [\text{N}]$$

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 tyres.



New legislation



A Triple, Seven-level Labeling System for Tyres, starting end of 2012 in Europe on:

- **Rolling Resistance;**
- **Wet Skid Resistance;**
- Tyre Noise;

will definitely increase the awareness on energy-saving tyres!

Japan is following.

USA is considering to follow also.

New Legislation

Impact Assessment Study on Possible Energy / Labeling of Tyres;
European Policy Evaluation consortium (EPEC); July 31, 2008:

Tire EU Labeling Criteria:

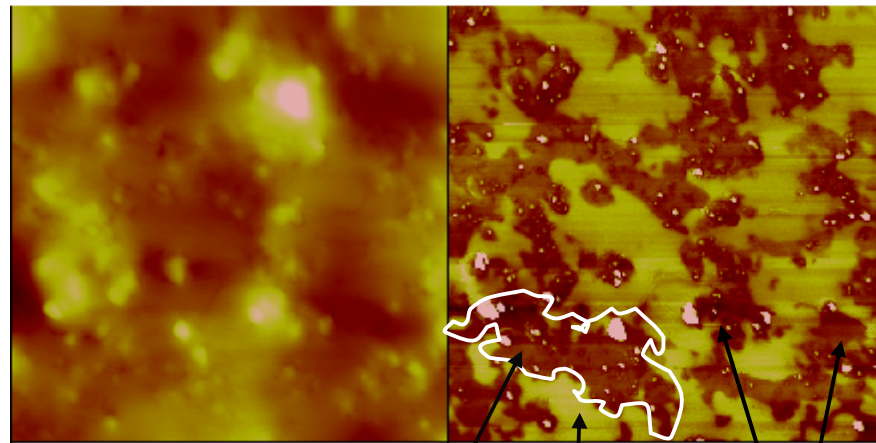
Wet Grip Rating	Roll. Resist. Rating	Sum (%)
A	A/B	0
B	C/D	5
C	E/F	57
D	G	38

38% of current summer replacement passenger car tyres do not meet the 2012 standard; about 50% of winter replacement tyres don't either!



Origin of Rolling Resistance

Silica filled rubber blend



Occluded
Polymer

Polymer

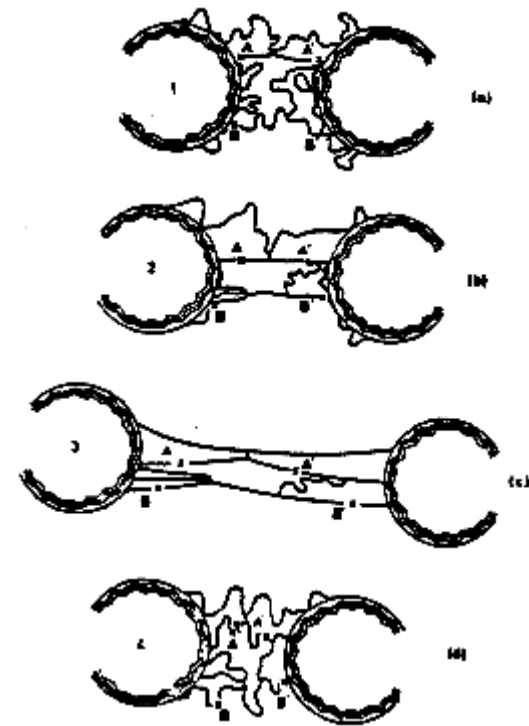
Reinforcing Filler

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

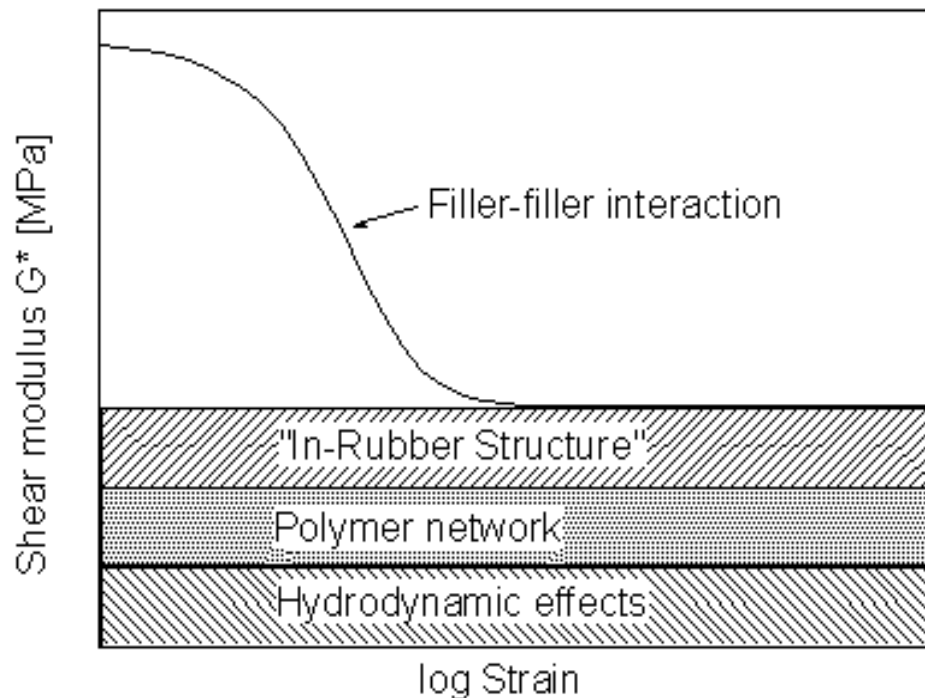
Origin of Rolling Resistance

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



Origin of Rolling Resistance



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

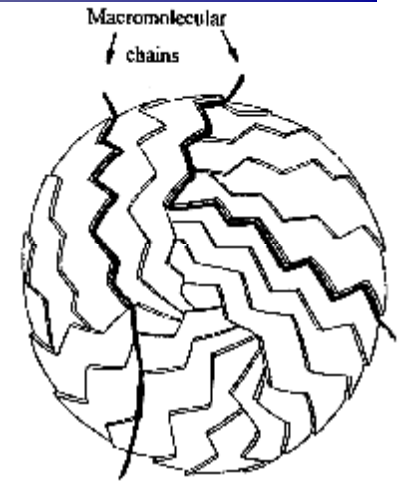
the Payne Effect

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

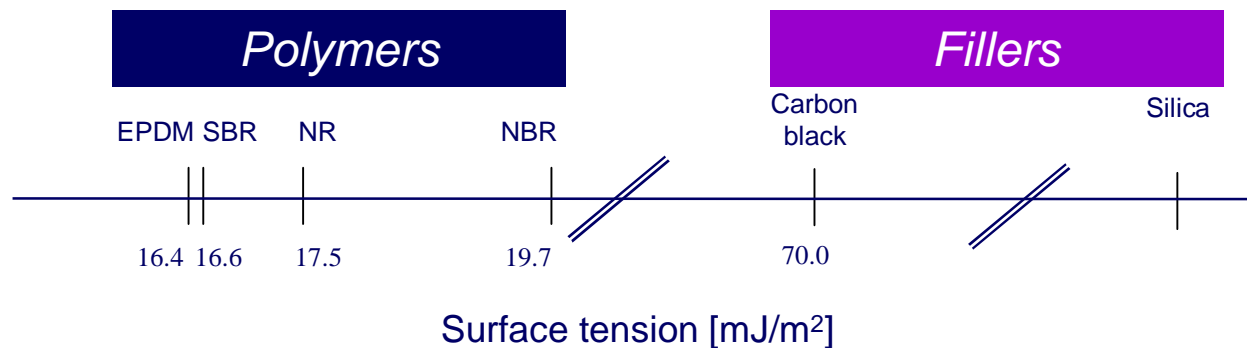


Reinforcing Fillers

- **Carbon Black:** most commonly used. **Polymer-Filler Interaction** is mainly physical of nature; thermodynamically based.
Polymers attach along (part of) their contour to the carbon black primary particles (20 – 30 nm).
- **Silica (SiO₂):** strongly polar rel. to rubber. **Polymer-Filler Interaction** must be chemically established, otherwise the silica and rubber will not mix nor interact.



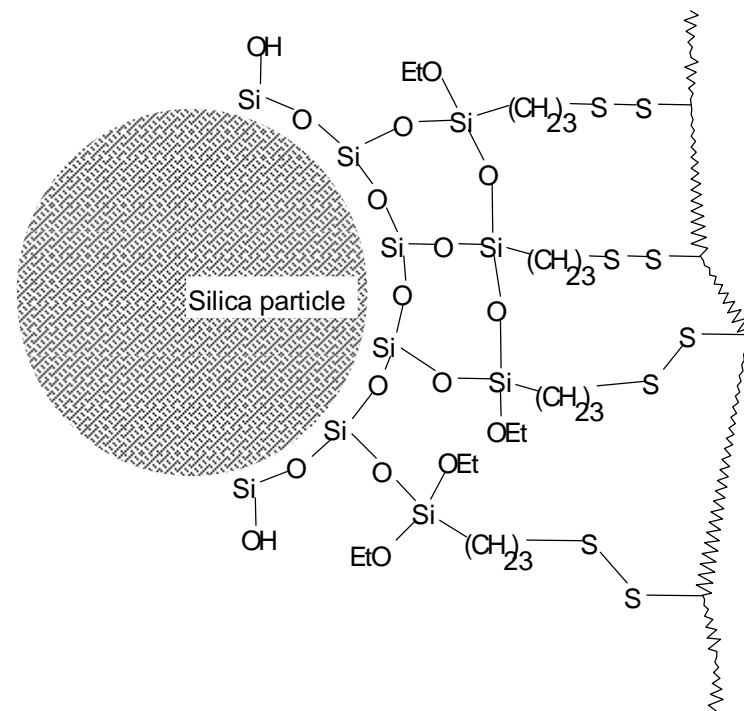
Compatibility Polarity Match



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 vulcanisation stage couple the silane to the rubber molecules.



Laboratory evaluations:

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

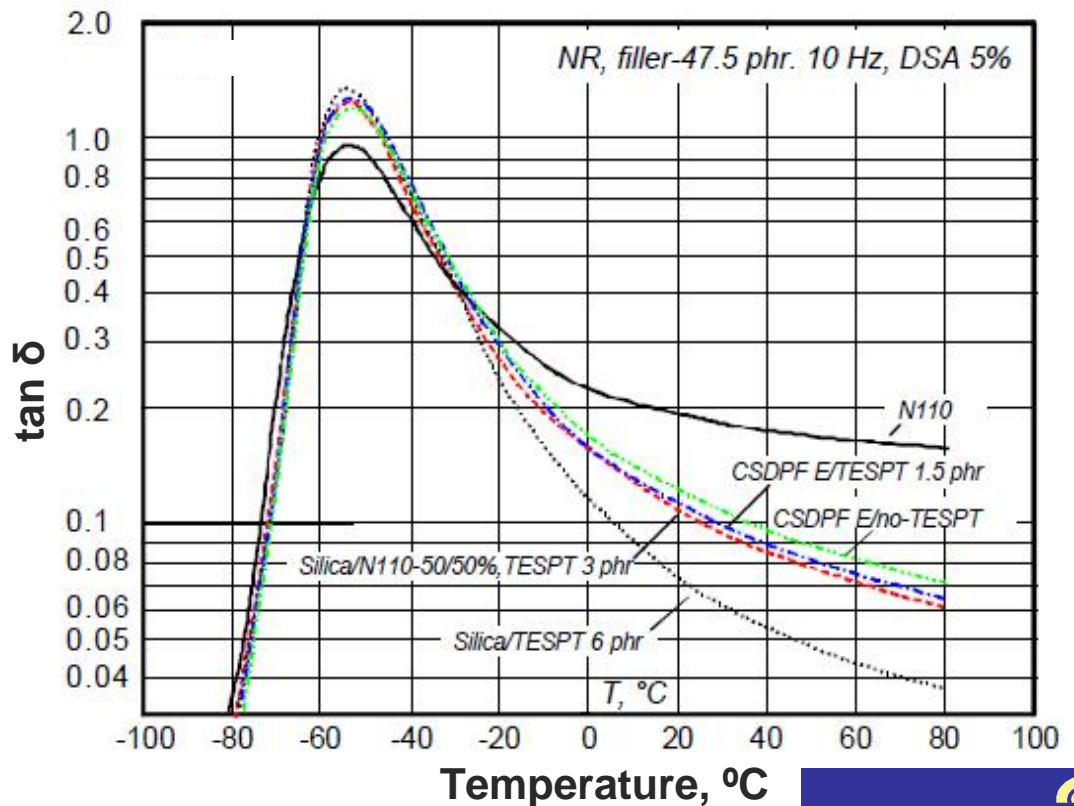
Tan δ @ 60°C ~

Rolling Resistance

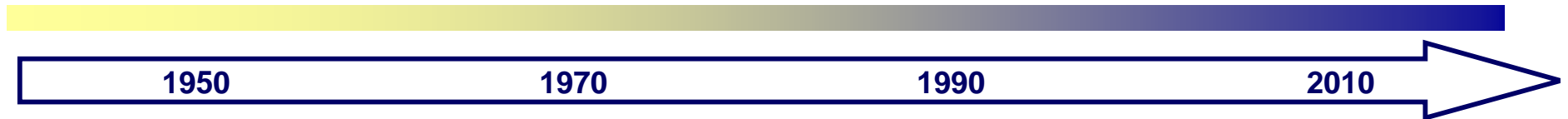
Tan δ @ 0°C ~

Wet skid resistance

Chemical
polymer-filler
interaction is greatly
preferred!



Silica in rubber history



Silica and silicates as replacement of carbon black

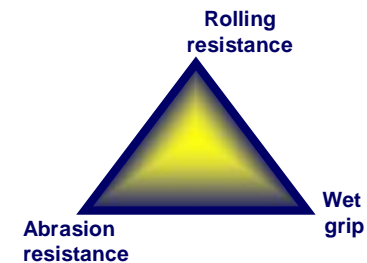
Precipitated silica (lower costs than pyrogenic silica)
First applications: shoe soles (colored, transparent)



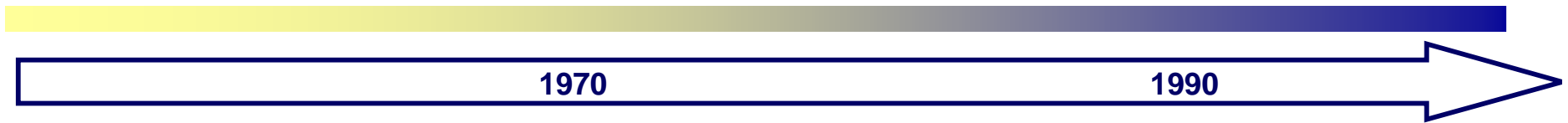
Silica in heavy-service tires (improvement of cutting and chipping resistance, better adhesion to textile and metal), 10-25 phr silica



Silica-silane technology for passenger car tire treads



Silica/silanes in rubber history



Organofunctional silanes as adhesion promoters for glass fiber – polymer systems

Introduction of bifunctional silanes as coupling agents

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

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

**Current silica consumption in rubber:
app. 0,5 mill. tons/year**

Combinations:	
S-	Si-
moieties	
-SCN	
-S-CS-OR	-Si(OCH ₃) ₃
-S-CS-NHR	-Si(OC ₂ H ₅) ₃
-S-C(NH)(NH ₂)	-Si(i-OC ₃ H ₇) ₃
-SH	-Si(n-OC ₃ H ₇) ₃
-S-S-	-Si(CO ₄ H ₉) ₃
-S-S-S-	-Si(OC ₈ H ₁₇) ₃
-S-S-S-S-	



Silica-rubber coupling reactions

Technological challenges involved:

- Coupling the silane with silanol-groups on the silica surface during mixing:
 - requires a temperature of $>140^{\circ}\text{C}$, and a long reaction time;
 - 145°C = vulcanisation temperature: risk of pre-vulcanisation or scorch during mixing;
- Generation and removal of enormous amounts of ethanol from the mixture;
- Controlled addition of the silane to the polymers during the vulcanisation stage.



Silica-silane coupling

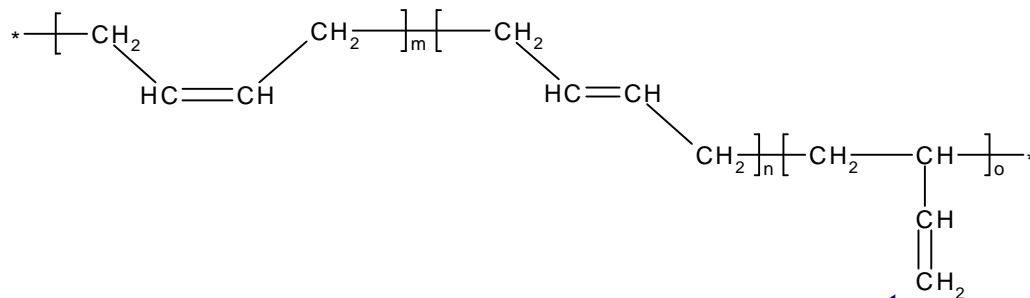
Common Internal Rubber Mixer technology is optimised for physical carbon black mixing, not as a chemical reactor for:

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



Silane-rubber coupling

Silanes make use of the large reactivity of $-SH$ (thiol) of $-S-S\cdot$ radicals towards unsaturated $C=C$ functionalities in the polymers:

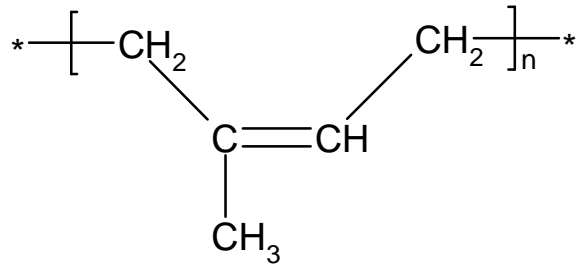


Most reactive are pendant 1,2-vinyl groups in the polymers.

S-	Combinations: Si-
moieties	
-SCN	-Si(OCH ₃) ₃
-S-CS-OR	-Si(OC ₂ H ₅) ₃
-S-CS-NHR	-Si(i-OC ₃ H ₇) ₃
-S-C(NH)(NH ₂)	-Si(n-OC ₃ H ₇) ₃
-SH	-Si(CO ₄ H ₉) ₃
-S-S-	-Si(OC ₈ H ₁₇) ₃
-S-S-S-	
-S-S-S-S-	

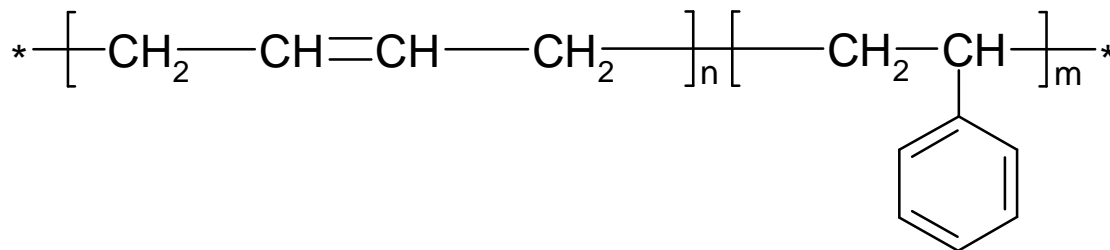


Amount of 1,2-vinyl groups in polymers used for tyres



Natural rubber: 0%!

Natural rubber by itself is a CO₂-sequestering polymer: it represents 45% of world rubber consumption **and is growing in market share!** However, NOT for energy saving tyres.



Emulsion-SBR:

~ 10%

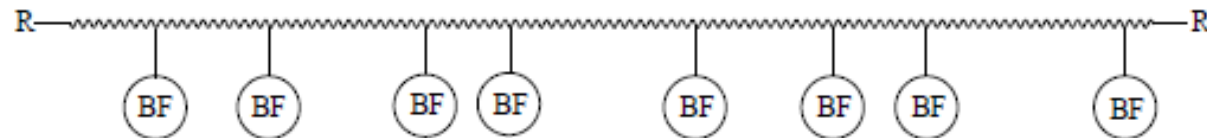
Solution-SBR:

~ 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.



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 tyre 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:

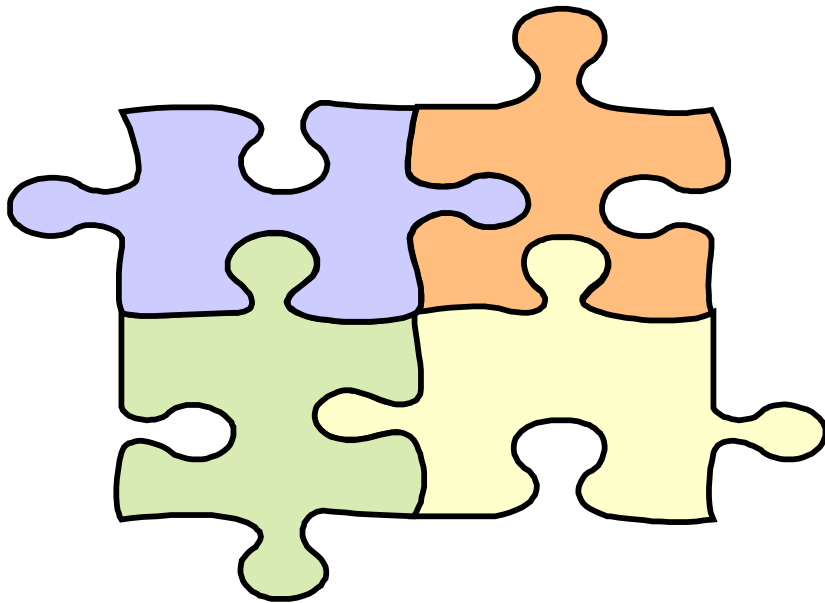
- Adjustments to mixers for the chemical reactions;
- Efficiency of ethanol removal.



Summary

Polymers

Silica



Coupling
agent

Mixing
equipment

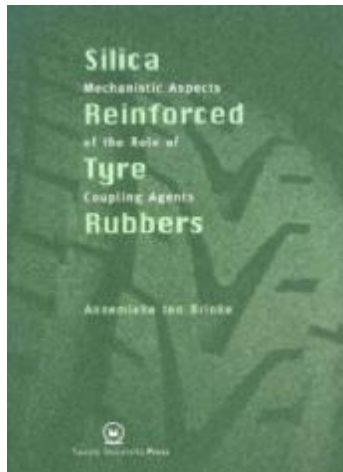
In combination with design changes of tyres, the silica technology has achieved :

**60% Rolling
Resistance
Reduction over the
last 20 years.**

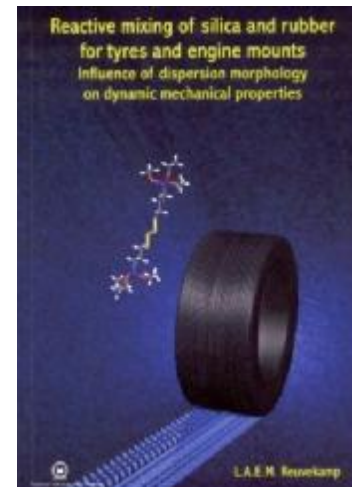
More to follow!



Relevant theses of Elast. Techn. and Eng., Univ. of Twente

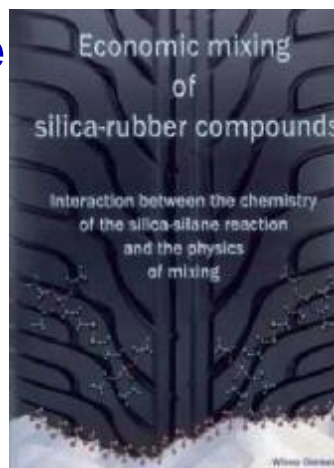


Coupling agents



Mixing and vulcanisation

Practical scale mixing



Rubber-filler interactions

