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## Epoxidized Natural Rubber Combined with Silica Fillers for Low Rolling Resistance Passenger Tires: an Overview

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# Introduction: Green Tire

**1992: Michelin introduced the „green tire“**




- 30 % lower rolling resistance
- 5 % less fuel consumption
- 7 % improved wet grip
- better winter performance



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The year 1992 marked the introduction of a revolutionary new tire technology by Michelin, shortly designated as "the Green Tire". Not so much because the tire was green colored, but because of its approx. 30% reduction of Rolling Resistance, thanks to the use of High-Dispersion Silica reinforcing filler in combination with high-vinyl S(olution)-SBR elastomer and high-cis polybutadiene elastomer used primarily in the tread of passenger car tires. This specially designed combination resulted in approx. 5% fuel savings in driving, approx. 7% improved wet grip (for safety) and also some better abrasion/wear resistance, so durability of tires in comparison with "older tires" made with traditional carbon black as reinforcing filler in tire treads.



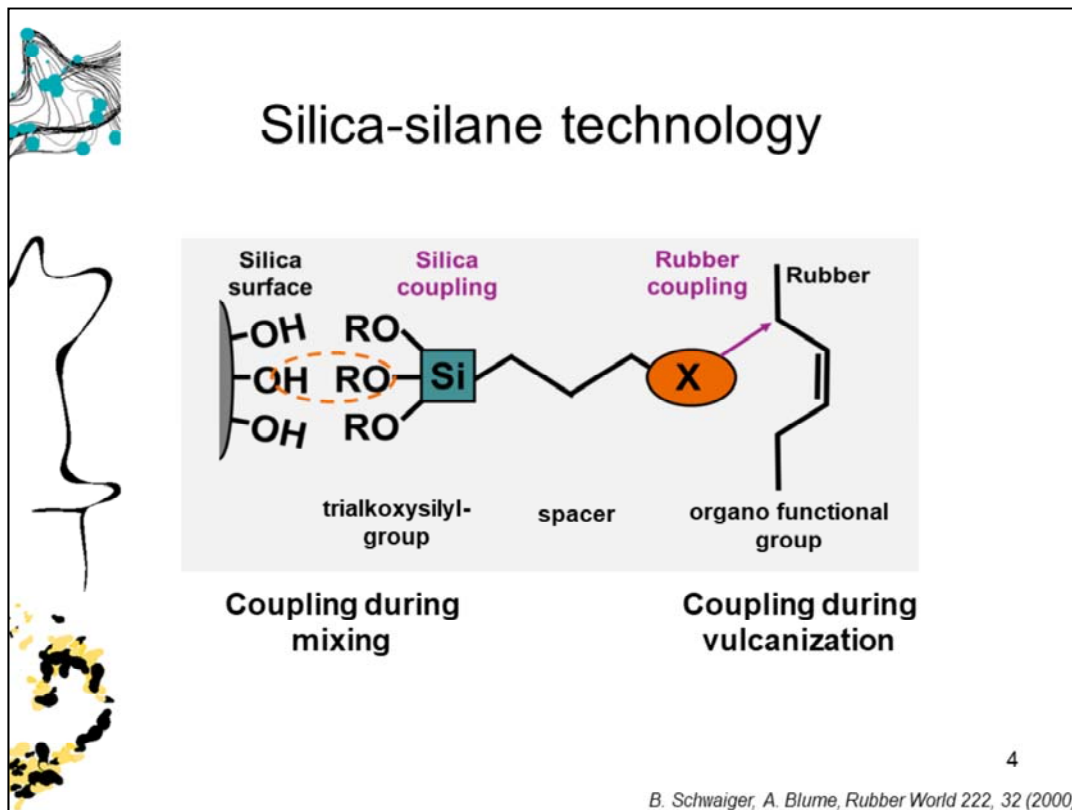
## Introduction: Challenges

**Silica is in comparison to carbon black a polar filler!**  
→ **different in-rubber behavior and properties**

- Silica distribution
  - Mixing procedures/conditions
  - Characteristics of filler and polymer
- Compatibility
  - Polar silica vs. Non-polar rubber
  - Use coupling agents
  - Use of functionalized elastomers
  - Application of compatibilizers
- Compound stability
  - Re-agglomeration or flocculation of silica
  - Undesired high compound viscosity


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However, this “green tire” technology established unprecedented challenges to rubber compounders and tire manufacturers. Silica is a polar filler, much more polar than carbon black and therefore does not have a natural tendency to mix with non-polar elastomers. The present slide summarizes the various problems encountered with silica-mixing and the stability of the obtained compounds afterwards. Commonly so-called coupling agents are used to stabilize the mixtures, next to the potential application of compatibilizers which generally tend to equilibrate polarity differences between the various phases: the elastomers vs. silica.




The present slide provides a pictorial view of how a commonly applied silane coupling agent establishes a chemical bridge/bond with silanol-groups on the surface of a silica-particle during the mixing stage, followed by a reaction from the other side with the elastomer molecules during the vulcanization lateron. Once both reactions have taken place, a strong chemical bond has been established between the silica particles and the rubber molecules, which stabilizes the mixture of these two ingredients with such opposed polarities.

The technology as presented in this slide, although looking nice on paper, has many disadvantageous aspects. In particular, the chemical coupling of the silanes to the silica particles must be achieved during the mixing stage: a chemical reaction in a physical mixer, which has not been designed (and is not really usefull) for chemical reactions. As a consequence, significant amounts of ethanol (alcohol) need to be removed from the mixer evolved from the condensation reaction of the silane with the silica; and when the temperature during mixing may unadvertently rise a bit too high, the second reaction between the coupling agent and the elastomers may already begin, resulting in too early vulcanization or scorch and killing the processability of the obtained compounds.



## Alternatives to *in situ* silanization for enhancing the silica-rubber compatibility

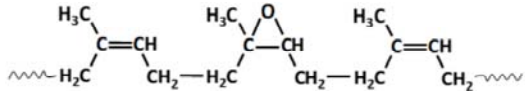


Modification of silica surfaces

- Plasma treatment
- Admicellar polymerization
- Silane pretreatment
- Grafting of functional groups

Use of polar rubber as compatibilizer

- Chloroprene rubber (CR)
- Acrylonitrile butadiene rubber (NBR)
- Epoxidized Natural Rubber (ENR)**

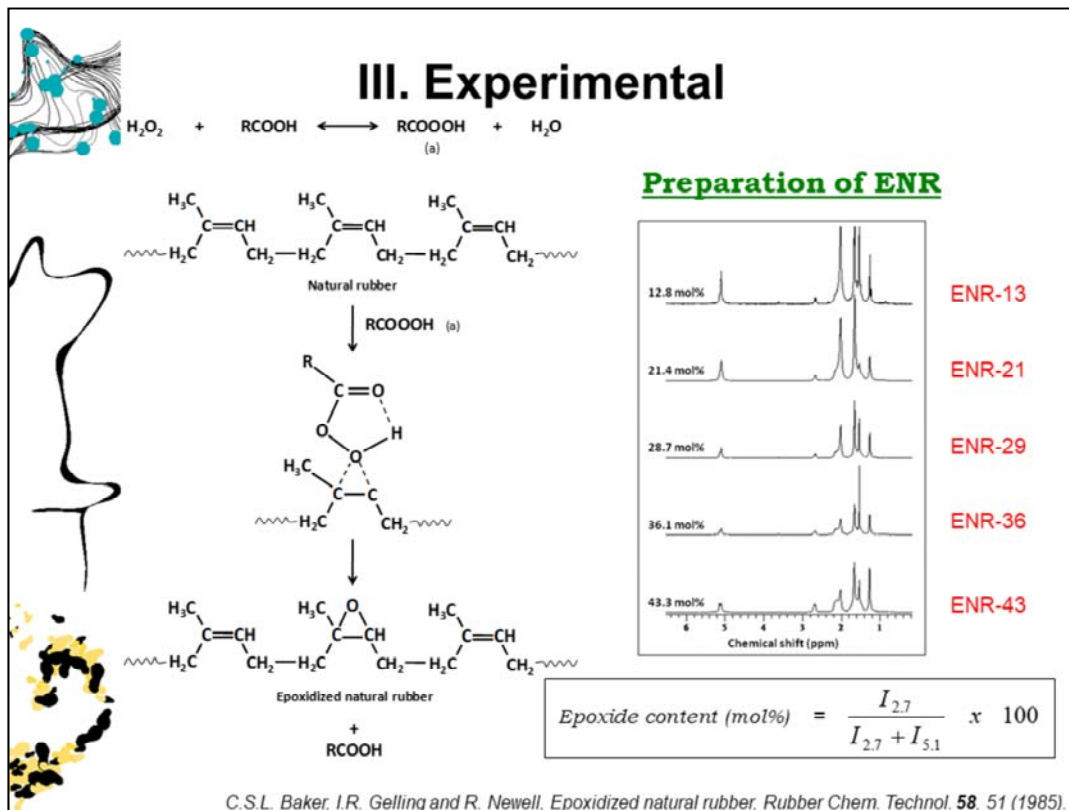


Epoxidized natural rubber

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Consequently, there are constantly new technologies developed in order to alleviate these problems, respectively to help/enhance the compatibilization and reaction of the silica with the elastomers. The present slide shows several examples: Modification of the silica surfaces before the mixing stage in order to enhance its compatibility with the elastomers beforehand; resp. use of polar rubbers/elastomers as compatibilizers, either in small quantities or as sole/full elastomers.

The present presentation deals with Epoxidized Natural Rubber in these two modalities: either as sole elastomer, or in smaller quantities together with unmodified Natural Rubber as the main elastomer component.



Epoxide modification of Natural Rubber elastomers has been known for quite some time already (e.g. 1985), whereby the pristine Natural Rubber molecules are epoxidized by the reaction product of hydrogen-peroxide and formic acid into formyl-peroxyde according to the above chemical reaction, which in turn creates epoxide groups on the Natural Rubber chains in variable quantities, depending on the relative amounts of the various reactants. By measuring the relative peak areas in Nuclear Magnetic Resonance (NMR) the content of epoxide groups in mol% (molar percents) can be quantified, ranging from very low, but practically from 10 mol% till as high as 50 mol%. , although the latter is a bit “too much”: the polymer starts to show unwanted disadvantages, like e.g. gel formation which we do not want.

These epoxidized Natural Rubbers are presently commercially available in limited quantities, waiting until a commercial breakthrough may occur in the near future. Again, they can be used either in pure form to fully replace other elastomers, in particular pristine Natural Rubber, or as compatibilizers in limited quantities only. I will cover an example of both options on basis of 2 PhD-studies executed at the University of Twente in the latter years:

- Pure Epoxidized Natural Rubber: W. Kaesakul: “Silica-Reinforced Natural Rubber for Low Rolling Resistance Tires, aspects of mixing, formulation and compatibilization”, PhD-thesis, Univ. of Twente, April 18, 2013;
- ENR as compatibilizer: K. Sengloyluan: “Silica-Reinforced Natural Rubber, use of natural rubber grafted with chemical functionalities as compatibilizer”, PhD-

thesis, Univ. of Twente, June 25, 2015.

## Experimental

### Compound formulation

Ingredients	phr
ENR <sup>[1]</sup>	100
ZnO	3.0
Stearic acid	1.0
TMQ	1.0
Silica ULTRASIL 7005	55
TESPT	X <sup>[2]</sup>
TDAE oil	8.0
CBS	1.5
DPG	1.1
Sulfur	1.5

[1] Epoxide contents: 10 - 45 mol%, reference NR (RSS3)


[2] Varying amounts from 0 – 12 wt% rel. to silica content

- ❖ **500 cm<sup>3</sup> internal mixer**
  - Controlled dump temperature at 140 – 145°C
  - Fill factor = 0.7
  - Rotor speed = 60 rpm
- ❖ **Two-roll mill**
  - Adding curatives: accelerators and sulfur
- ❖ **Determination of properties**
  - Mooney viscosity
  - Payne effect
  - Dynamic and mechanical properties

W. Kaesaku: "Silica-Reinforced Natural Rubber for Low Rolling Resistance Tires, aspects of mixing, formulation and compatibilization", PhD-thesis, Univ. of Twente, April 18, 2013 7

As a first example I would like to present the full use of Epoxidized Natural Rubber (ENR) with different degrees of epoxidation in comparison with unmodified NR in a typical truck tire tread formulation with 55 parts per hundred rubber (phr) easy dispersion silica. This is part of the PhD-thesis of one of the co-authors of this presentation: Wisut Kaewsaku at our University of Twente, defended in 2013. The degrees of epoxidation of the ENR-samples varied from 10-45 mol%. As we will see later on, the epoxidation of the ENR does not fully replace the role of the coupling agent Bis(Triethoxy-silyl-propyl) tetrasulfane (TESPT), so the latter was added in variable amounts to find the optimal synergistic performance of both.



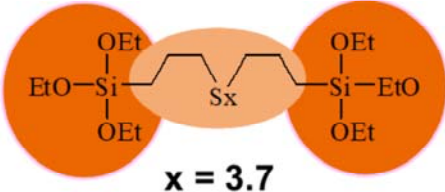


## Experimental

**Used silica:**

	<b>ULTRASIL 7005®</b>
BET	190 m <sup>2</sup> /g
DOA	225 g/100g
Moisture	5.0 %
pH	6.0

**Used silane: Bis-triethoxysilylpropyl-tetrasulfane (TESPT, Si 69®)**

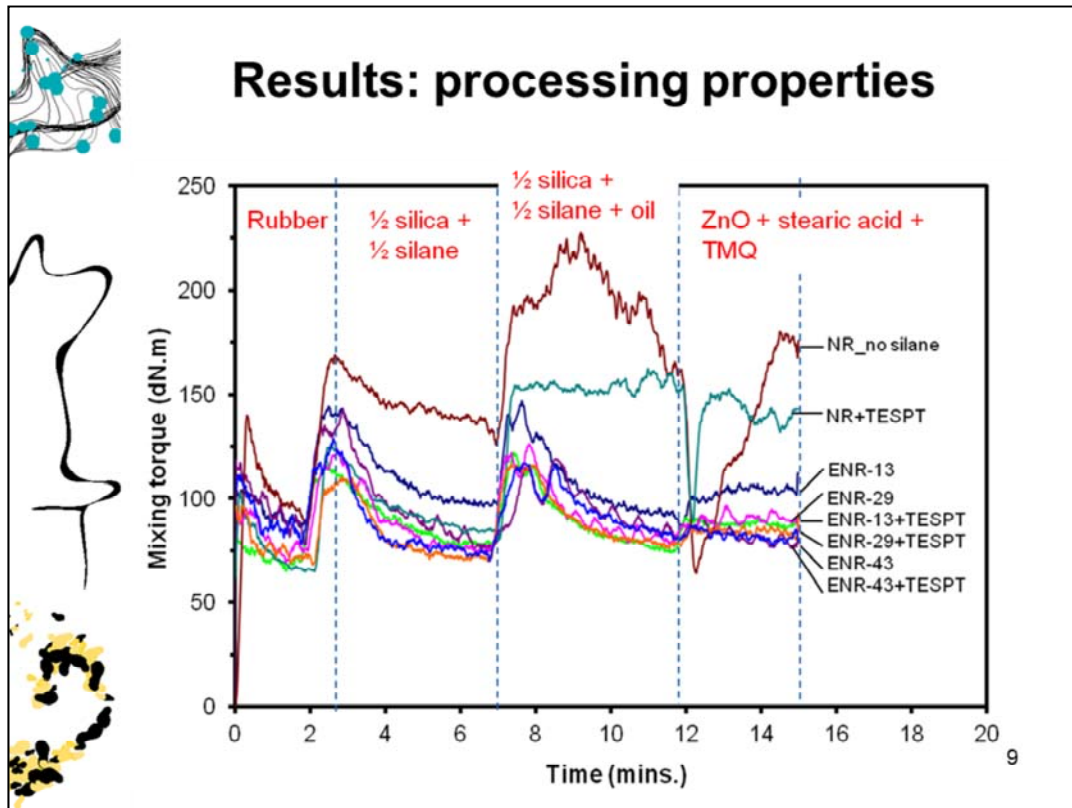


$x = 3.7$

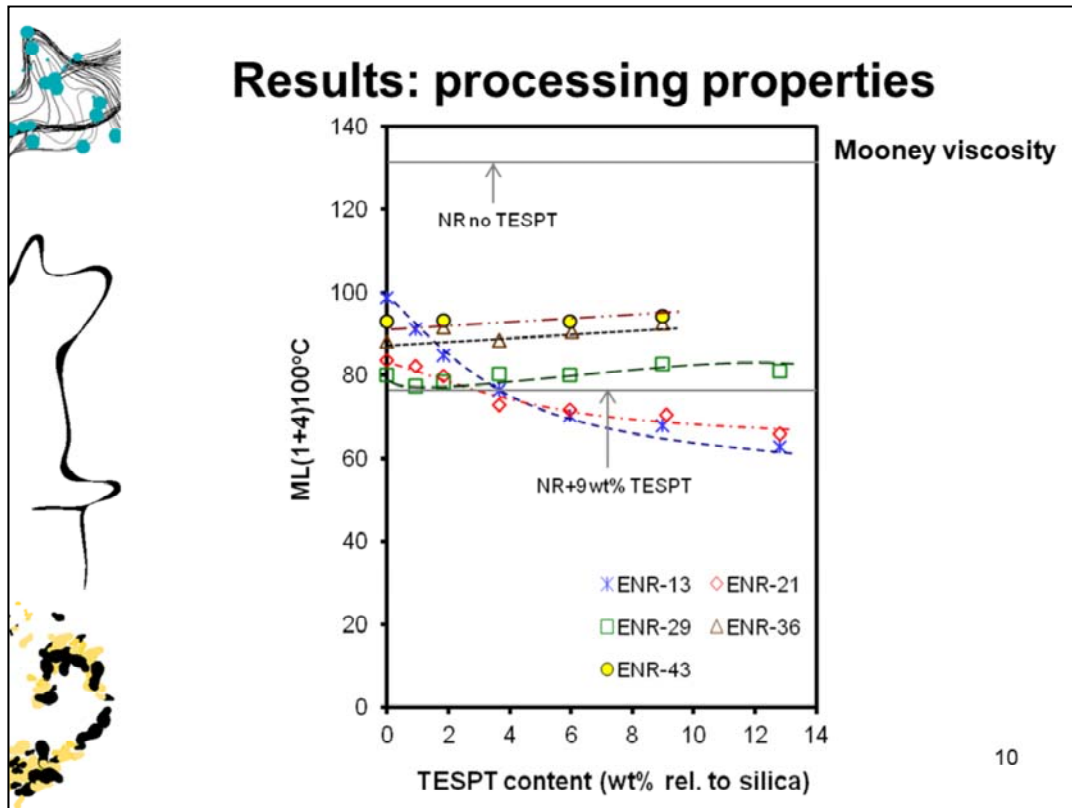
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ULTRASIL® and Si 69®: Trade names of Evonik Resource Efficiency GmbH

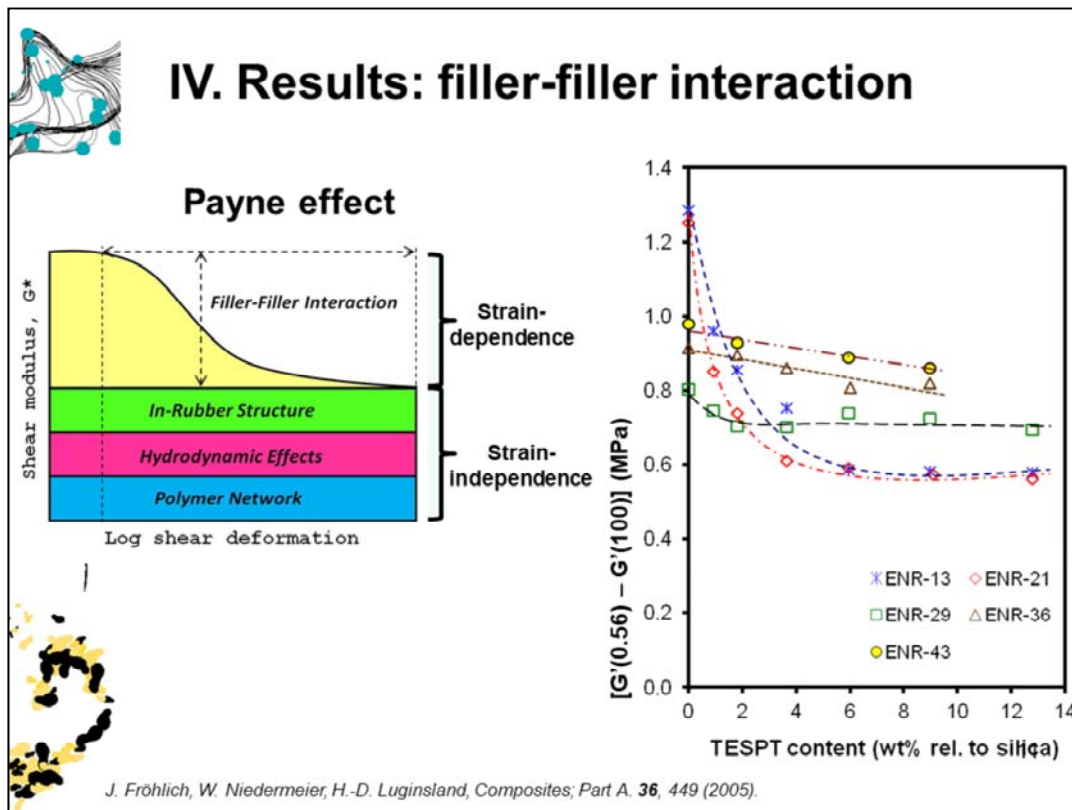
The easy-dispersion silica used was Ultrasil 7005, well known in the green tire technology world, with its typical specifications. The silane coupling agent TESPT is more commonly known as Si69. Both Ultrasil 7005 silica and TESPT/Si69 are available from Evonik Resource Efficiency GmbH, Germany.



To begin with, the present diagram shows typical mixing curves for pure NR without and with 9 wt% of TESPT silane relative to the 55 phr silica in the formulation (so 5 phr in the total formulation, the common amount), respectively ENR 13, 29 and 43 without further addition of TESPT and with the same 9 wt% of TESPT relative to the silica amount. Most conspicuous here is the mixing torque at the end of the mixing cycle of 15 minutes. The height of this end-torque is an indirect measure for the viscosity of the compounds, the lower the better the extrudability. Clearly, the torque decreases with higher degrees of epoxidation of the NR's, resp. by the additional dosage of TESPT coupling agent in all cases.



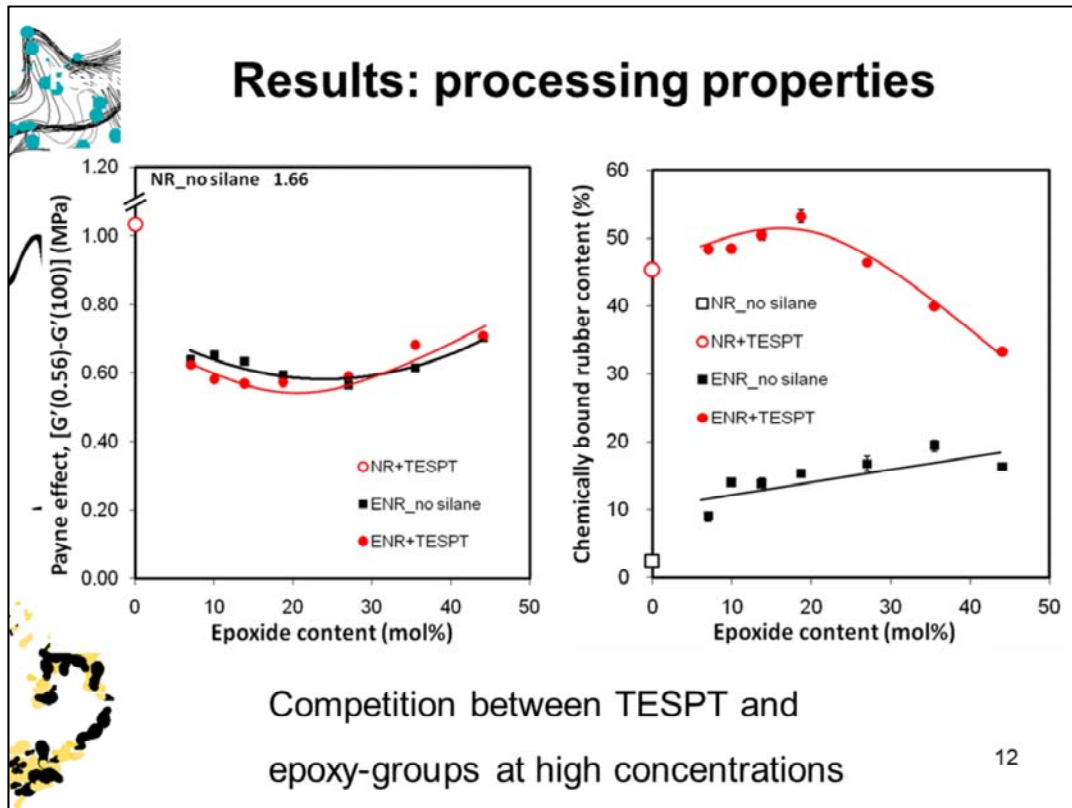
The present figure depicts the obtained Mooney viscosities in more detail: Very high at an unpractical level of 130 Mooney units for pure NR without coupling agent, being reduced to 75 Mooney units with 9wt% TESPT coupling agent relative to the silica. The epoxidized NR's position themselves halfway at no coupling agent added (left side of the figure) between NR without coupling agent and with. Only for the low epoxidized ENR's (13 and 21 mol%) there is a decrease in Mooney viscosity obtained at progressive amounts of TESPT coupling agent added. At higher degrees of epoxidation the Mooney viscosity is independent of the addition of extra coupling agent, or even has a slight tendency to increase.



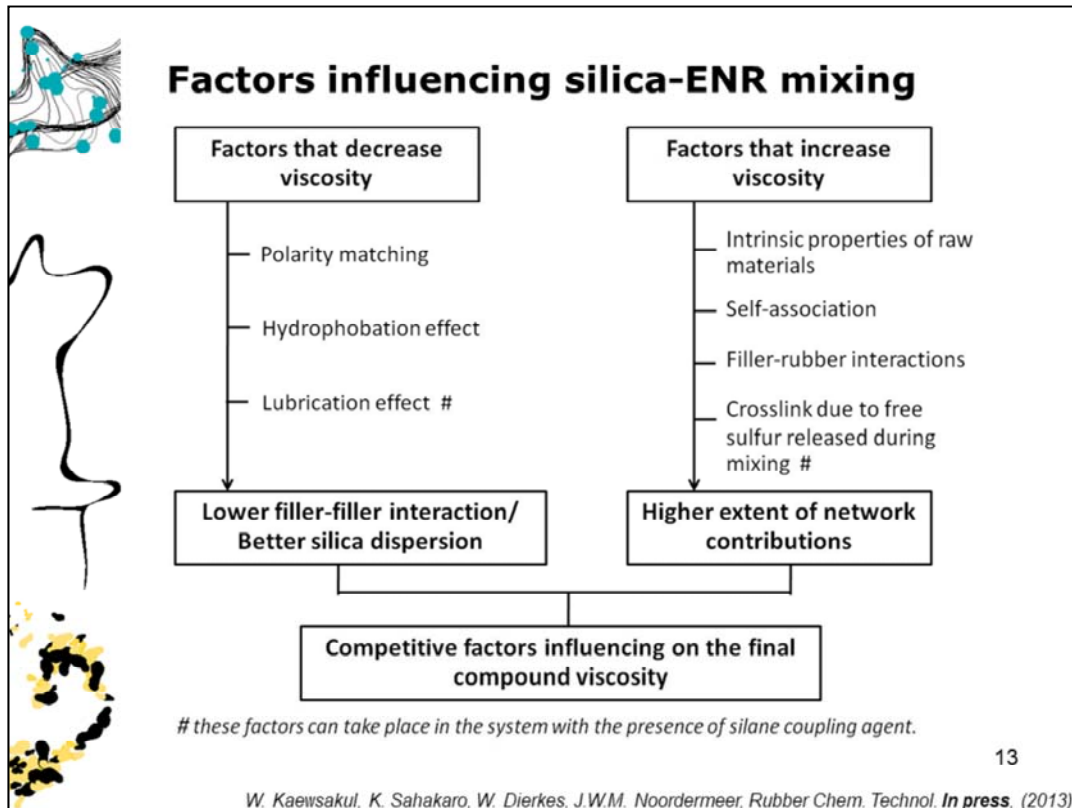
For silica technology it is common practice to interpret the silica-filler/rubber interaction versus the mutual filler-filler interaction in terms of the so-called Payne effect. Registering the strain dependence of e.g. the shear modulus of a silica-filled compound till strains of max. 100% shows a decrease of the modulus. The overall modulus being composed of 4 components: 1. the crosslinked polymer network; 2. the so-called hydrodynamic effect, the increase in modulus according to Einstein and Smallwood due to the presence of the hard/undeformable silica particles; and 3. the in-rubber structure: the silica particles acting as multifunctional crosslinkers by their bonding to the elastomer molecules via the coupling agents. All these three show little strain dependence in the range till 100% deformation. However, the mutual attraction of the silica particles, their coming loose and reformation of the bonds, upon deformation and subsequent release, give a strong shear dependence of the modulus: the Payne effect, which at the same time causes hysteretic dissipation resulting in – amongst others – the rolling resistance. The smaller the Payne effect, the less filler-filler interaction, the better in terms of less hysteresis.

This Payne effect as the difference in storage moduli e.g. measured at 0.56% strain vs. 100% strain, for the compounds containing the various ENR's with different degrees of epoxidation and with different amounts of coupling agent TESPT added, correspond somehow with the Mooney data in the previous slide. Only the low epoxidized grades show a dependency of the Payne effect on the addition of coupling agent, to eventually reach the lowest values of the Payne effect; while the higher epoxidized ENR's are little deformation/strain dependent

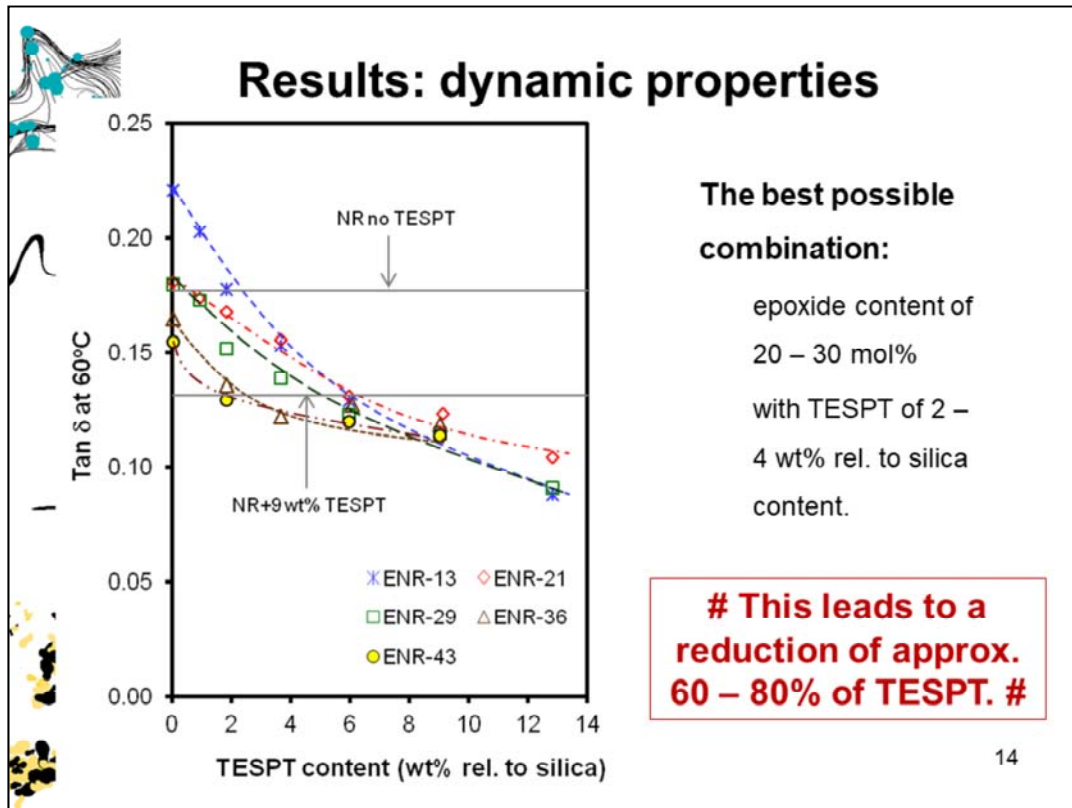
anymore. The transition is somewhere at 25 mol% epoxidation.



This is more clearly demonstrated in the present figure, where the Payne effect is plotted for NR without silane coupling agent (1.66 (Mpa), very bad), and for the various ENR's without and with extra 9 wt% silane coupling agent added relative to the silica content. In either case, the minimum (best performance) occurs somewhere around 25 mol% epoxide content. In the right hand figure we plotted the so-called Bound Rubber: the amount of elastomer which somehow gets chemically bound to the silica during mixing, but before vulcanization: for NR without and with silane present; resp. for ENR without and with extra silane added, plotted vs. their epoxide contents. Particularly for the ENR plus silane, the optimum at around 25 mol% epoxidation is again nicely visible.

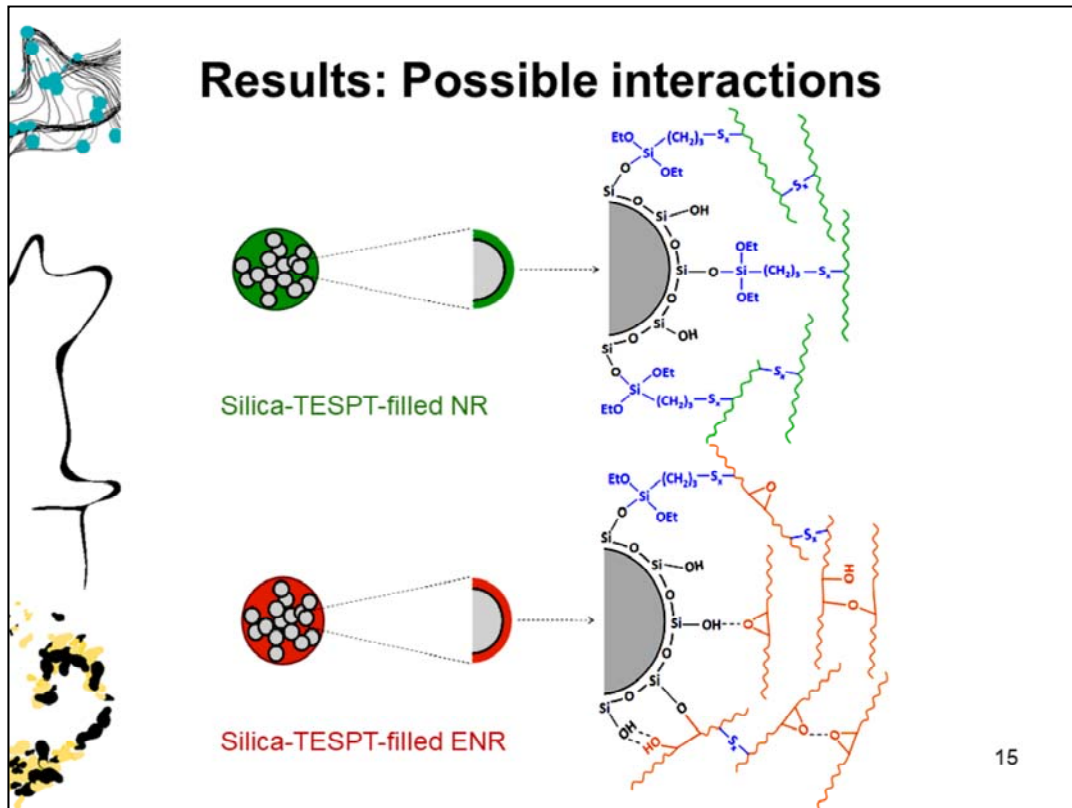


The previous results nicely demonstrate that there is a sort of competition going on in silica-ENR compounds mixing, as demonstrated in this slide. Positive factors that decrease the viscosity and decrease the Payne effect: matching of the polarity between elastomer and silica by higher epoxidation; making the silica more hydrophobic, as opposed to its hydrophilic nature; an internal lubrication (smearing) effect due to the silane coupling agent. These lead to lower filler-filler interactions and better silica dispersion. Versus negative factors that increase the viscosity and raise increase the Payne effect: the intrinsic polarity difference between the elastomers and the silica; the tendency of the silica to self-associate or re-agglomerate; lack of sufficient filler-rubber interactions; premature crosslinking due to sulfur released from the coupling agent TESPT; all leading to higher network contributions or scorch in a too early stage. Both competitive sets of factors together establish the quality of the compound before we can proceed with vulcanization, to measure the vulcanized properties.

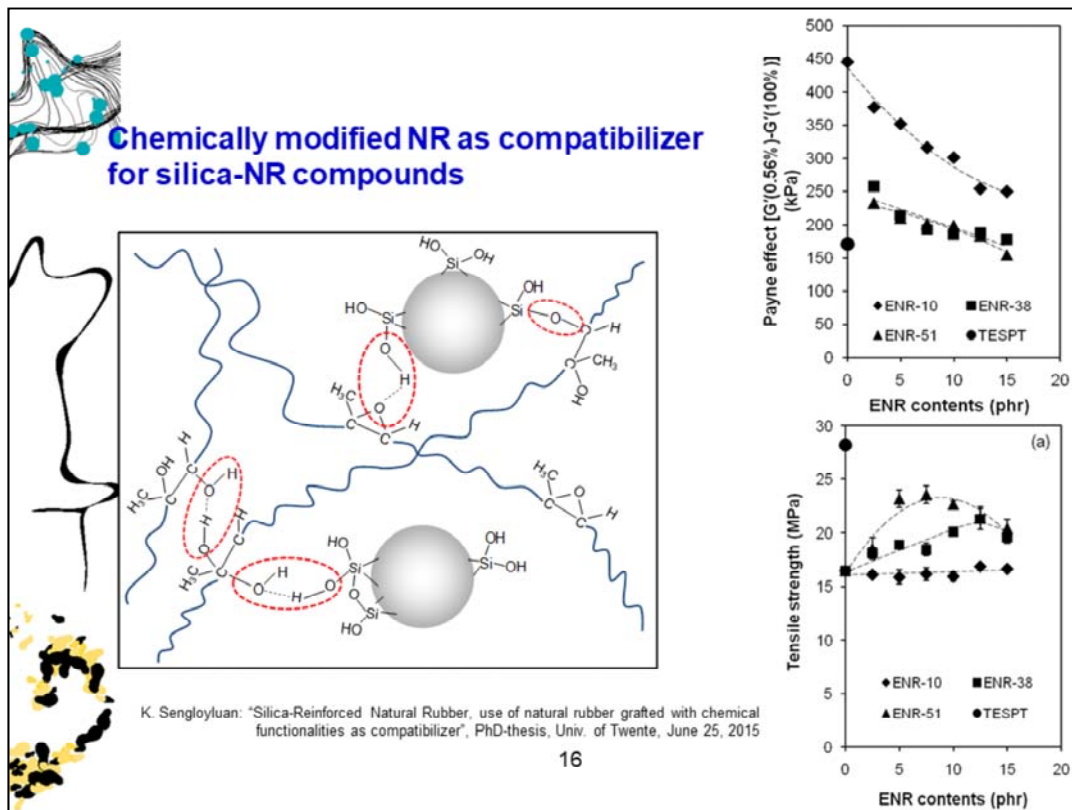


In short, to show the result of all this on the dynamic mechanical properties of the final vulcanizates as an indication for the hysteretic properties: the tangent of the phase angle measured at 60 °C as an indication for the Rolling Resistance of a passenger tire tread made of such compounds: the lower, the better. It shows that the lowest values are achieved with ENR's in the range of 20-30 mol% epoxidation, with extra addition of 2-4 wt% of TESPT coupling agent relative to the silica amount. This represents a reduction of 60-80% of the TESPT silane relative to the amount needed for pure NR: much less problems with e.g. ethanol generation and mixing: processing in general.

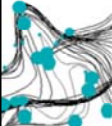




To sort of visualize what happens on a molecular scale on the silica surface: in the case of pure NR filled with silica in the presence of silane coupling agent, the latter has to account for all the chemical (and physical) interactions between the silica and the elastomer, as good as possible. In the case of ENR filled with silica, the epoxide-groups react with the silica surface and so play partially (but not completely) the role of the silane coupling agent, of which now much less is needed relative to the first case, to achieve more or less the best results.




The present slide taken from the PhD-thesis of Karnda Sengloyluan presents an example of the “Compatibilizer” approach of epoxidized Natural Rubber in basically the same truck tire tread compound formulation with 55 phr silica, but now with pure Natural Rubber as main elastomer component, but much lower amounts of epoxidized NR added. The idea (or hope) here is that the ENR preferentially settles at the interface between silica and NR and so acts in a way as coupling agent and/or as compatibilizer. In the present case there is no additional coupling agent TESPT added. Seeing the Payne effect on the non-vulcanized compounds as a function of the amounts of ENR added, with the degree of epoxidation as additional variable, the Payne effect indeed decreases (good) with more ENR added; the more the higher the epoxidation level of the ENR. But unfortunately still not as good as pure NR with TESPT coupling agent. The same is visible in the tensile strength obtained after optimal vulcanization: pure NR with TESPT coupling agent performs better than at any of the ENR contents. However, we see a new optimum again here, where a highly epoxidized ENR (51 mol%, twice as high as the optimal ENR epoxidation in the previous case) acting as compatibilizer peaks at appr. 8 phr ENR addition and one with 38mol% epoxidation at about 14% addition. It looks like the amount of epoxide groups added is in effect the governing factor, and less so the actual amount of ENR added.



**Use of ENR as compatibilizer in combination with TESPT and sulfur compensation**

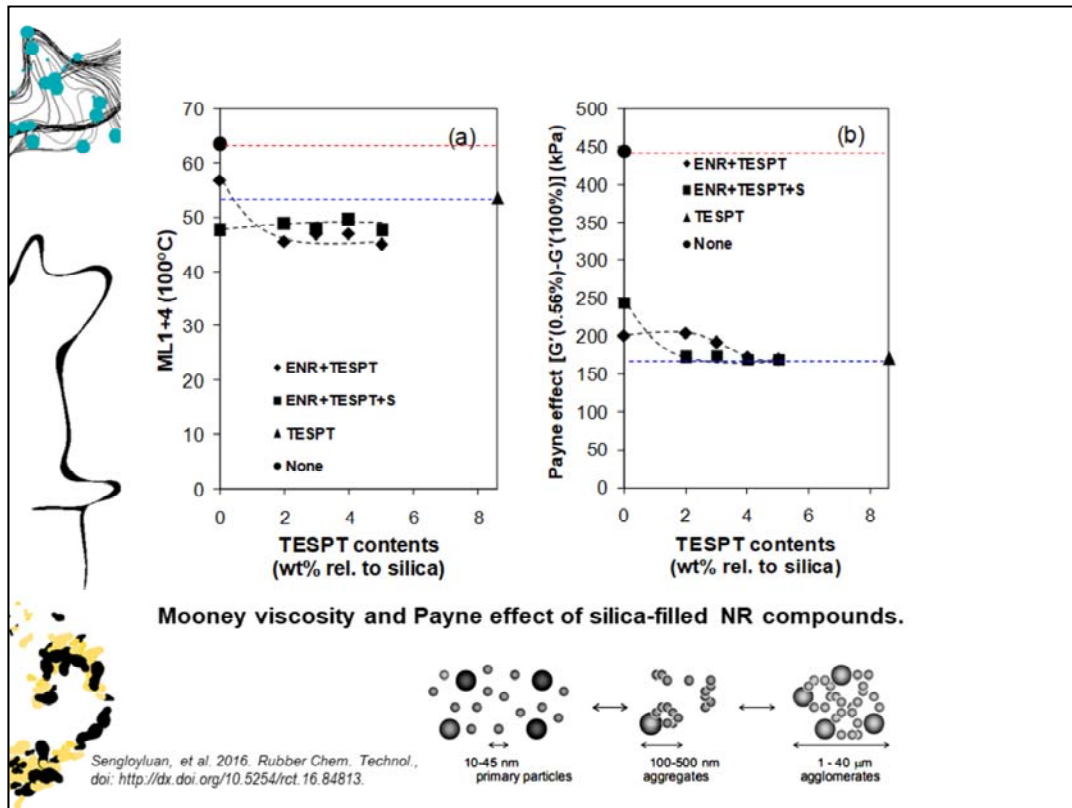
Ingredients	Parts per hundred parts of rubber (phr)			
	None	TESPT	ENR+TESPT	ENR+TESPT+S
NR (RSS3)	100.0	100.0	92.5	92.5
<b>ENR-51</b>	-	-	<b>7.5</b>	<b>7.5</b>
<b>TESPT</b>	-	<b>4.7*</b>	<b>1.1-2.7**</b>	<b>1.1-2.7**</b>
Zeosil1165MP	55.0	55.0	55.0	55.0
TDAE oil	8.0	8.0	8.0	8.0
ZnO	3.0	3.0	3.0	3.0
TMQ	1.0	1.0	1.0	1.0
Stearic acid	1.0	1.0	1.0	1.0
DPG	1.0	1.0	1.0	1.0
CBS	1.5	1.5	1.5	1.5
<b>Sulfur</b>	<b>1.5</b>	<b>1.5</b>	<b>1.5</b>	<b>2.3-1.9***</b>



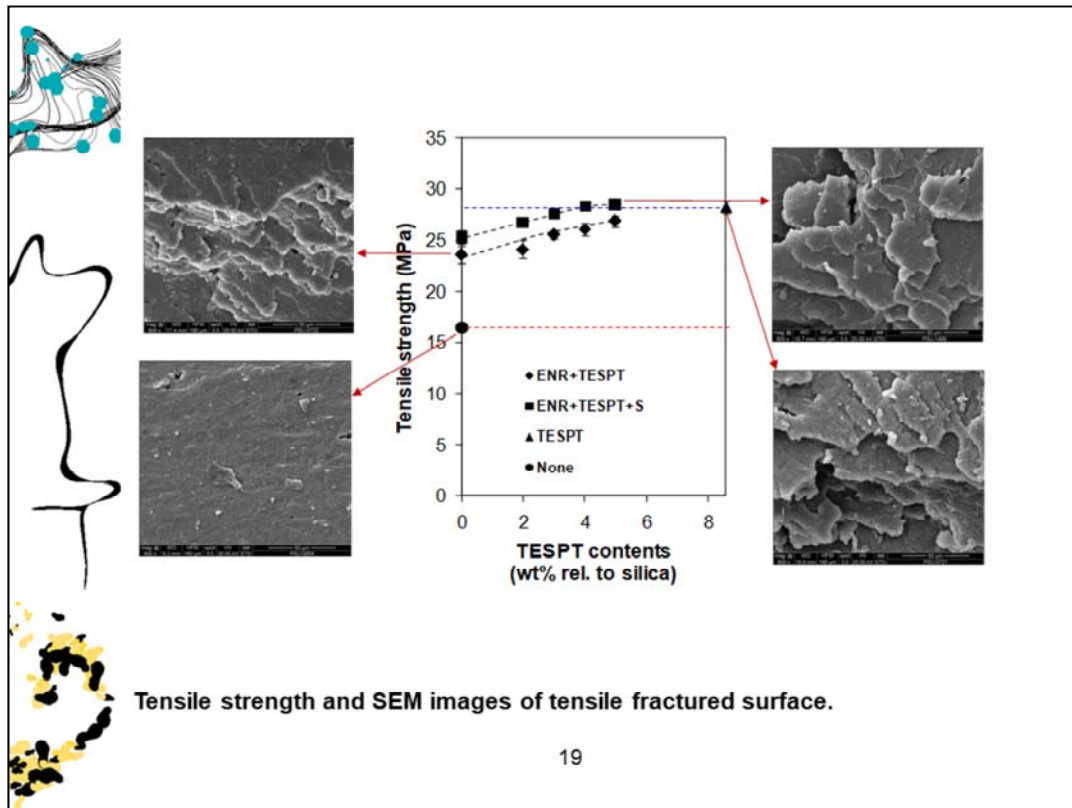
Remarks: \* TESPT 4.7 phr equals 8.6 wt% relative to silica; \*\* TESPT<sup>17</sup> 1.1-2.7 phr equals 2.5 wt% relative to silica; \*\*\* sulfur contents were adjusted to compensate for sulfur in TESPT molecules by taking the compound with 4.7 phr TESPT as reference.

In an attempt to compensate for the short-comings of the ENR as compatibilizer, and attempt was made to add TESPT coupling agent extra. As ENR the “best” performing one was taken with 51 mol% epoxidation, at the optimal dosage of 7.5 phr. However: a complicating factor in the present case is, that the TESPT brings along some extra sulfur (appr. 2 atoms per TESPT molecule) into the formulation, which later on in the vulcanization adds to the properties. In order to make a fair comparison therefore, a correction has to be made in the amount of elementary sulfur added in the vulcanization formulation, to reduce the sulfur in the same amount as added extra via the coupling agent.

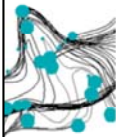
Therefore there are basically four different compound formulations compared: 1. Of pure NR without any ENR as compatibilizer or TESPT coupling agent; 2. NR with 4.7 phr TESPT: the optimal amount relative to 55 phr silica; 3. NR with 7.5 phr ENR-51 and changing amounts of TESPT coupling agent, but no changes in the amount of sulfur in the vulcanization formulation; 4. the same as 3, but now with reduction of the amount of elementary sulfur to equilibrate the amount of molar sulfur in the formulation, as if all sulfur atoms in the TESPT also participate in the vulcanization.



The present slide presents the results of all these combinations. Clearly, NR plus silica without ENR nor TESPT gives the highest Mooney viscosity and Payne effect: bad. NR plus silica and the optimal amount of TESPT at 8.6 wt.% relative to the silica (4.7 phr) is the second alternative. 7.5 phr of ENR-51 with some extra TESPT gives even some lower Mooney viscosity, where sulfur compensation does play a role indeed (left figure). As to the Payne effect, the combination of 7.5 phr EN-51 and just a little TESPT coupling agent results in equal values as obtained with the pure NR with TESPT reference.

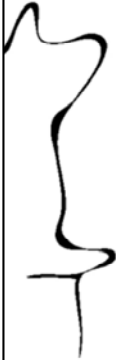


Similar as it comes to the vulcanized properties, where we take the tensile strength as criterion: 7.5 phr ENR-51 in combination with low amounts of TESPT in NR achieve the same tensile strength as when 8.7 wt% TESPT silane had been employed in pure NR. So again a great reduction in the amount of TESPT needed, with reduced processing problems during mixing due to lower amounts of ethanol generated.

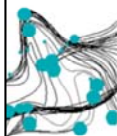


## Summary and Conclusions

- Epoxidized NR may play a double role in reducing the amount of TESPT coupling agent in 55 phr silica reinforced Natural Rubber based truck tire treads: in pure form as modified NR, and/or as compatibilizer.
- In case of full replacement of NR by ENR, the balance of properties can be matched or even slightly improved at 20-30 mol% epoxidation of the ENR. ENR cannot completely compensate for TESPT, but may function with only 20 - 40% of the TESPT needed otherwise.
- In case of use of ENR as compatibilizer in otherwise pure NR, 7.5 phr ENR with 51 mol% epoxidation is optimal and again 20 – 40 % of TESPT is needed for approximately the same properties as for pure NR with 8.6 wt%% of TESPT relative to the silica amount.
- Epoxidized NR **cannot** fully replace NR+TESPT without the help of the coupling agent. Some remains necessary.
- These reductions in TESPT usage help overcome processing problems, in particular during mixing, reducing the amounts of ethanol generated by the silane reaction with silica.



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## Relevant publications in the present context from PhD-students from the University of Twente:

W. Kaewsakul, K. Sahakaro, W.K. Dierkes and J.W.M. Noordermeer: "Cooperative Effects of Epoxide Functional Groups on Natural Rubber and Silane Coupling Agents on Reinforcing Efficiency of Silica"; **Rubber Chemistry and Technology**, **87.2**, 291-310 (2014).

Wisut Kaewsakul, Kannika Sahakaro, Wilma K. Dierkes, Jacques W.M. Noordermeer: "Optimization of Epoxidation Degree and Silane Coupling Agent Content for Silica-Filled Epoxidized natural Rubber Tire Tread Compounds"; **Advanced Materials Research** **844**, 243-246 (2014).

Wisut Kaewsakul, Kannika Sahakaro, Wilma K. Dierkes, Jacques W.M. Noordermeer, Anke Blume: "Interactions between Silica and Epoxidized Natural Rubber with and without Silane"; **Tire Technology International** **2016**: 96-99

Karnda Sengloyluan, Kannika Sahakaro, Wilma K. Dierkes, Jacques W.M. Noordermeer: "Silica-Filled natural Rubber Compounds Compatibilized by Using Epoxidized Natural Rubber"; **European Polymer Journal** **51**, 69-79 (2014).

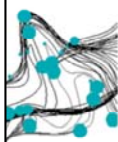
K. Sengloyluan, K. Sahakaro, W.K. Dierkes, J.W.M. Noordermeer: "Synergistic Effects in Silica-Reinforced Natural Rubber Compounds Compatibilized by ENR in combination with Different Silane Coupling Agents"; **Journal of Rubber Research** **19**(3), 170-189 (2016).

Karnda Sengloyluan, Kannika Sahakaro, Wilma K. Dierkes, Jacques W.M. Noordermeer: "Reduced ethanol emissions by a combination of epoxidized natural rubber and silane coupling agent for silica-reinforced natural rubber-based tire treads"; **Rubber Chemistry and Technology**, **89**(3), 419-435 (2016).

Saramolee P., Sahakaro K., Lopattananon N., Dierkes W.K. and Noordermeer J.W.M.: "Property enhancement of silica-filled natural rubber compatibilized with epoxidized low molecular weight rubber by extra sulfur"; **Advanced Materials Research** **844**, 235-238 (2014).

Saramolee P., Sahakaro K., Lopattananon N., Dierkes W.K. and Noordermeer J.W.M.: "Comparative properties of silica- and carbon black-reinforced natural rubber in the presence of epoxidized low molecular weight polymer"; **Rubber Chemistry and Technology**, **87.2**, 320-339 (2014).

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# Acknowledgments

## UNIVERSITY OF TWENTE.

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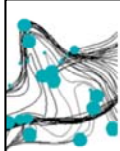


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# Thank You !



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