

A Review on Reinforcement of Natural Rubber by Silica Fillers for Use in Low-Rolling Resistance Tyres

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High dispersion silica has recently become the preferred alternative to carbon black for low rolling resistance tyres. However, the combination of natural rubber with silica and a coupling agent remains a challenge, but also offers a tremendous potential for reduction of energy consumption of transport. This paper gives an overview of the recent studies on silica reinforcement in natural rubber (NR) and its importance in tyre technology. Recent work on optimisation of the mixing process of silica in NR compounds and the influence of non-rubber constituents such as proteins on silica reinforcement are highlighted. The utilisation of modified NR such as epoxidised NR, and deproteinised NR are the methods of choice to enhance the compatibility between NR and silica, as well as to minimise the interference of proteins with coupling agents. A better understanding of the problems encountered with NR/silica systems will facilitate the further development of silica technology for NR, especially for use in highly filled silica tyre compounds.

Keywords: Natural rubber; silica; silane; rolling resistance

Silica technology for energy saving tyres has started in the early 1990's since the introduction of the "Energy Tyre" by Michelin¹. This technology claims to give automotive fuel savings of approximately 3% corresponding to a 20% reduction in rolling resistance compared to tyres with carbon black-reinforced treads^{2,3}. In the past, it was a difficult challenge to find a proper balance in the magic triangle properties as shown in *Figure 1*⁴. The magic triangle of tyre properties refers to the three most important properties

required for tyre performance, which are wet traction, wear resistance and rolling resistance. Silica significantly reduces rolling resistance and improves wet traction of tyre tread compounds compared to carbon black⁴. However, a major drawback of using silica is difficulties in processing which come from the polarity difference between silica and rubber.

The development of technology using silica in modified natural rubber has been reported well before the Michelin energy

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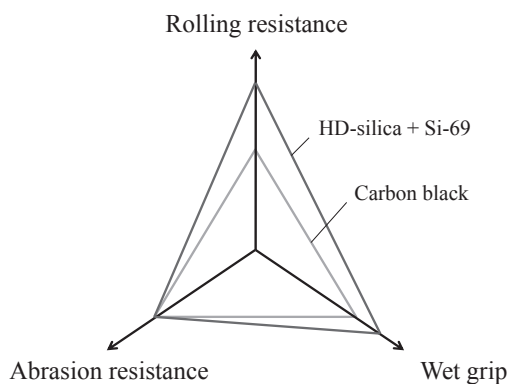


Figure 1. Magic triangle of tyre properties⁴.

tyre technology. Baker *et al.* has reported that the use of epoxidised natural rubber (ENR) filled with silica in tyre treads provides a combination of lower rolling resistance and higher wet grip⁵⁻⁷. The recent uptake of this technology is applied in ENASAVE tyres by Sumitomo on the development of the fossil resource-free tyre⁸⁻⁹.

The key of the silica technology is the high interaction and bonding between the silica and the rubber matrix where it can be directly in the case of functionalised polar rubber or indirectly in the case of non-functionalised non-polar rubber. For non-functionalised non-polar rubber reinforced with high-dispersion-silica, the chemical reaction of silica with a silane coupling agent is required. The coupling agent such as bis(triethoxysilylpropyl) tetrasulphide (TESPT) eventually creates a chemical link between the primary silica particles and the rubber molecules. This reaction reduces the hydrophilic character of the filler and increases its compatibility with the rubber polymer^{10-12,5-7}.

Silica technology as it is used today employs solution-polymerised synthetic elastomers like

solution styrene-butadiene rubber (S-SBR) and solution butadiene rubber (BR). On the other hand, the great majority of rubber polymers used for carbon black reinforced tyre applications are emulsion-polymers such as natural rubber (NR) and emulsion styrene-butadiene rubber (E-SBR). Up until now, the reason for not utilising NR in silica technology and its ineffectiveness for silane coupling agents still remains a challenge with limited documented evidence¹³⁻¹⁴.

The present review gives an overview of the work carried out on silica reinforcement of NR. The mixing conditions are the key parameters for silica reinforcement, and have been recently explored for NR compounds. An attempt to understand the mixing parameters which influence the properties of silica-filled NR compounds is discussed. The main difference between NR and synthetic polymers is the presence of a considerable amount of non-rubber constituents in the former. The influence of non-rubber constituents such as proteins on silica reinforcement in the presence and absence of a silane coupling agent is demonstrated. Morphology of silica-filled NR provides a better insight into filler-to-rubber interactions. The utilisation of epoxidised NR (ENR) and deproteinised NR (DPNR) is a possibility to enhance the compatibility between silica and NR, as well as to minimise protein adsorption on the silica surfaces, respectively. This enables the rubber compounder to use this natural polymer for truck tyre treads, making the ENR/silica and DPNR/silica systems green materials in terms of composition as well as application.

Silica as Reinforcing Filler for Rubber

The reinforcement of rubber by silica is different from the reinforcement by carbon black. The use of conventional silica has

been limited to white filler for coloured rubber compounds¹⁵ such as shoe soles, until the introduction of bifunctional silanes as coupling agents back in 1970's¹⁶. About two decades ago, a full replacement of carbon black by silica in tyre treads became an option, and nowadays silica is widely used for reinforcement of passenger car tyre treads¹. This is derived from the breakthrough in tyre technology: the introduction of the "Green Tyre" from Michelin with a tread based on a high-vinyl solution SBR and a high-cis BR as well as silica from Rhodia and a silane from Degussa^{1,15}. However, in truck tyre treads silica is employed only in small quantities together with carbon black in order to improve traction. Silica is a strongly polar and hydrophilic reinforcing filler¹⁷⁻¹⁸. The specific silanol group density and the surface activity are important parameters for the improvement of the dispersion behaviour, the dynamic stiffness and cure rate of a silica-filled compound¹⁹. The reinforcing potential is determined by the characteristic structure of silica, which can be divided into agglomerates, aggregates and primary particles (*Figure 2*)²⁰. The dimensions of agglomerates are typically in the range of 1 to 40 μm , and they are formed by clustering of silica aggregates by hydrogen bonding and van der Waals forces. The typical dimensions of silica aggregates

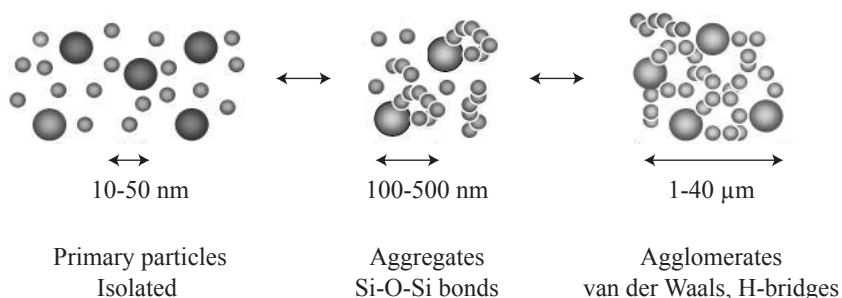
are 100 to 500 nm, and these units are formed by condensation of primary particles during the silica precipitation process²¹. Within the aggregates, the nano-sized primary particles are linked together *via* Si-O-Si bonds²¹. The size of the primary particles is between 10 and 50 nm²¹⁻²².

The silica surface is composed of siloxane and silanol groups as shown in *Figure 3*²¹. The silanol groups present on the surface of silica can be divided into three different types depending on arrangement of the hydroxyl groups, which are:

- Isolated silanol : a single hydroxyl group on a silicon atom
- Vicinal silanol : two hydroxyl groups on adjacent silicon atoms
- Geminal silanol : two hydroxyl groups on the same silicon atom

In addition, a siloxane bridge is formed when one oxygen atom is shared by two silicon atoms as shown in *Figure 3*²³.

The silica surface covered with a large number of silanol and siloxane groups can be characterised by the surface energy. The surface free energy of filler particles such



*Figure 2. The characteristic structure of silica*²⁰⁻²¹.

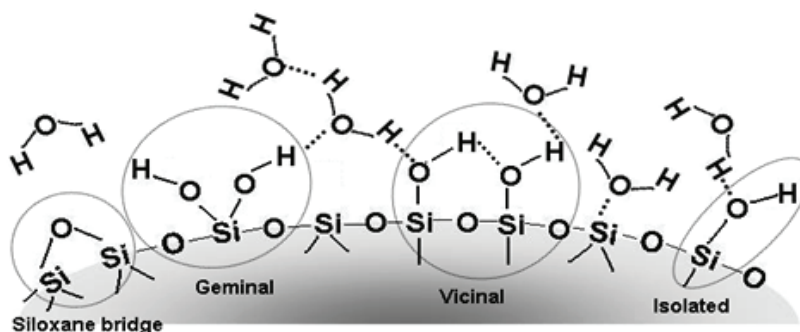


Figure 3. The siloxane and silanol groups present on a silica surface^{21–22}.

as silica can be quantified using inverse gas chromatography (IGC)²⁴. The surface free energy of a solid or filler, B_s , can be represented as²⁴:

$$B_s = B_s^d + B_s^{sp} \quad \dots 1$$

where, B_s^d is the dispersive component and B_s^{sp} is the specific component of the surface free energy.

Specific interactions measure the filler-filler interactions, which include hydrogen bonding, polar and acid-base interactions. The dispersive interactions between rubber and filler are non-specific interactions like Van der Waals forces.

In comparison with carbon black, the surface energy of silica is characterised by a lower dispersive component, B_s^d and a higher specific component, B_s^{sp} ^{25–26}. The low B_s^d of silica results in low filler to rubber interactions, whilst high B_s^{sp} of silica leads to strong agglomeration of silica in the rubber matrix. In contrast, the high B_s^d of carbon black gives strong filler to rubber interactions.

Easy incorporation of silica into a rubber mixture and good dispersion of silica are important parameters as they affect the

processing and compound properties. Silica can be classified according to its ease of dispersion into three categories, namely conventional, easily dispersible or semi-highly dispersible (HD) and HD silicas¹⁵.

Silanisation of silica leads to fundamental changes in its reinforcing characteristics. The dispersive component of the surface energy of modified-silica drops below the value of unmodified silicas and the polar component becomes negligible^{24–26}.

Organofunctional silanes used for sulphur-cured rubber compounds can be categorised into the following three types¹⁵.

Di- and polysulphidic silanes : $[(RO)_3 - Si - (CH_2)_3 - S]_2 - S_x$

Mercaptosilanes : $(RO)_3 - Si - (CH_2)_3 - SH$

Blocked Mercaptosilanes : $(RO)_3 - Si - (CH_2)_3 - S-B$

where R = CH₃ or C₂H₅ or other groups; B = CN or C₇H₁₅C=O; x = 0–8

Coupling agents may be premixed or pre-reacted with the silica filler or added to the rubber compound during the rubber and silica mixing stage^{15,21}. If the coupling agent and silica are added simultaneously to the

rubber compound during mixing, the coupling agent combines *in situ* with the silica²⁷. To date, the commonly and effectively used silane coupling agents in rubber systems are TESPT²⁸ and bis(triethoxysilylpropyl) disulphide (TESPD)¹⁵. The structure of TESPT is shown in Figure 4. Although described as a tetrasulphide, TESPT is actually a silane mixture with different sulphur ranks, ranging from S₁ to S₆ and an average sulphur rank around 3.83²⁹. During mixing of a silica-filled rubber compound, the silane coupling agent reacts with the silica resulting in hydrophobation of the silica surface. This hydrophobation inhibits the formation of a silica-silica network and makes silica more compatible with the non-polar rubber^{10–12}.

The reaction mechanism between silica, TESPT silane coupling agent and rubber has been extensively reviewed^{10,15,21,30–33}. On one side, the triethoxysilyl group of the TESPT reacts with the silanol groups of silica during compounding with loss of ethanol^{10,31}. On the other side, the rubber reactive group of the silane (*e.g.* tetrasulphane) has a strong tendency to form rubber-to-filler bonds during curing of the rubber compounds^{32–33}. The primary and secondary reaction of TESPT and silica, as well as the reaction of TESPT and rubber are shown in Figures 5–7, respectively^{30,33}.

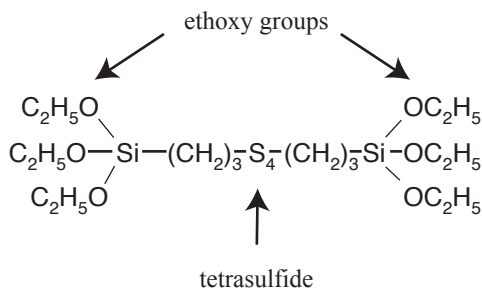
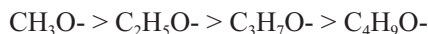


Figure 4. TESPT.

The reactivity of a silane coupling agent is generally influenced by the hydrolysable group of the silane. By comparing methoxy, ethoxy, propoxy and butoxy derivatives, the rate of the silanisation reaction decreases in the following order²¹:



The reaction rate with propoxy and butoxy groups is too slow to be acceptable. The methoxy group reacts too rapidly, and it is not used as a silanisation agent for toxicological reasons as it evolves methanol. Thus, the ethoxy group is the preferable one as silanisation agent, as it reacts sufficiently fast, and when proper precautions are taken, it is toxicologically harmless²¹.

Silica Technology in Tyre Rubbers

The first use of silica in truck tyre treads based on NR had shown an improvement in tear properties in terms of cut and chip behaviour, but the amount used was limited to 25 phr in order to avoid negative effects on tread wear. Higher amounts of silica require coupling agents, which at that time were not used for silica²¹. In 1992, Michelin patented the silica filled rubber compound for the production of high performance tyres in all seasons¹, which provide an excellent compromise of low rolling resistance, good traction on wet and snow covered roads, as well as noise reduction. In the rubber compound, a blend of high vinyl solution SBR and high-cis BR filled with highly dispersible silica³⁴ was used at a loading of 80 phr and an organosilane coupling agent. Since then, a lot of work on reinforcement of silica in SBR-based passenger car tyres has been investigated^{15,21,22,35–37}.

The optimisation of the mixing conditions of NR compounds with conventional silica and a silane was studied by Wolff³⁸. The

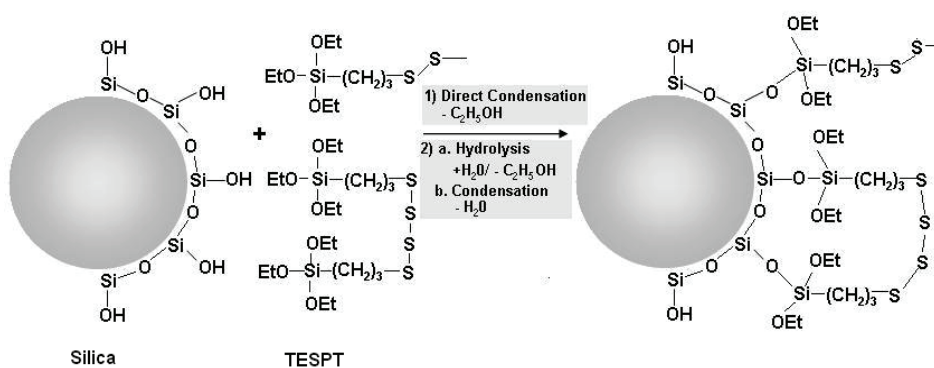


Figure 5. Primary reaction between silica and TESPT^{30,33}.

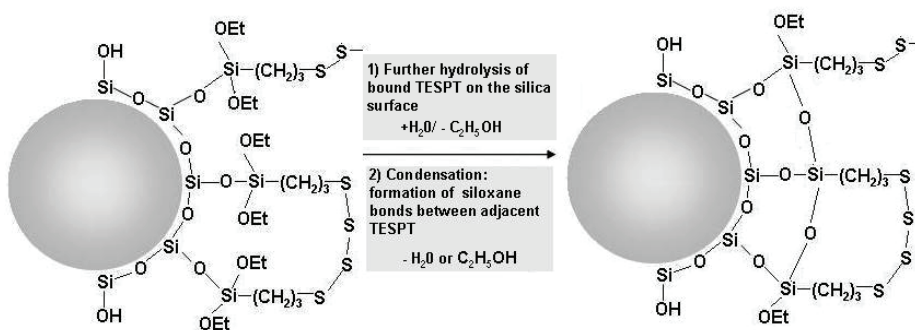


Figure 6. Secondary reaction between silica and TESPT^{30,33}.

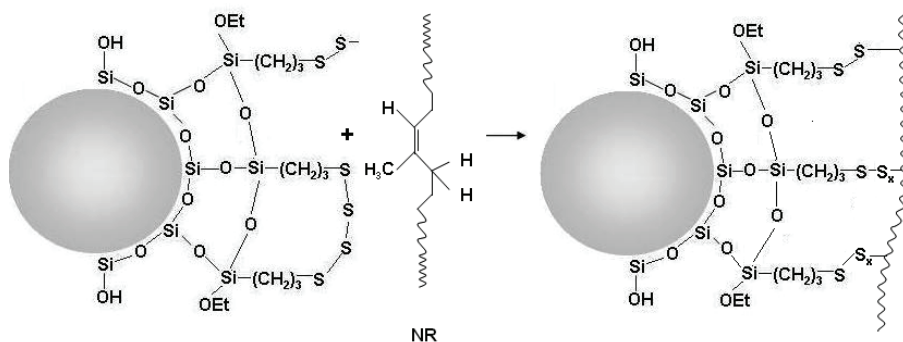


Figure 7. Reaction between rubber and TESPT^{30,33}.

author concluded that an increase of mixing temperature and time for the silica modification with silane enhances the compatibility between silica and NR through a chemical bond between TESPT and rubber. The overall properties are dependent on the extent of this interaction.

Investigations by Wolff³⁵ in field tests with truck treads demonstrated that the rolling resistance can be improved by as much as 30% when TESPT-modified silica is used in comparison to N220 carbon black. The tread wear index (abrasion resistance) decreases by no more than 5% and wet traction shows little change.

Silica has a superior performance concerning rolling resistance ($\tan \delta$ at 60°C) and heat build-up (ΔT_{centre}) compared to carbon black in NR compounds, as shown in Figure 8³⁹. Even silica with a lower BET surface area offers lower $\tan \delta$ values and less heat build-up in combination with better reinforcing behaviour compared to a low reinforcing carbon black³⁹.

Silica and TESPT were also applied in an earth mover tyre tread recipe⁴⁰. Based on 100 phr natural rubber and 66 phr of a mixture of conventional silica UltrasilVN3 and TESPT in 10:1 ratio; the properties were compared with a conventional carbon black reinforced Earth Mover tread compound. It was illustrated that the properties of silanised-silica reinforced rubber exceed those of carbon black reinforced rubber especially with regard to tear resistance and heat build-up (Goodrich Flexometer test). The scorch time and cure time are slightly shortened, but still remain in a range suitable for industrial practice. The reduction in Mooney viscosity of the compound is also an added advantage for easier processing and lower production costs.

Silica-Reinforced Natural Rubber Compounds

Mixing of Silica-Filled NR Compounds. Most of the work in this area was focused on synthetic rubbers, in particular SBR/BR-based compounds for passenger car tyres.

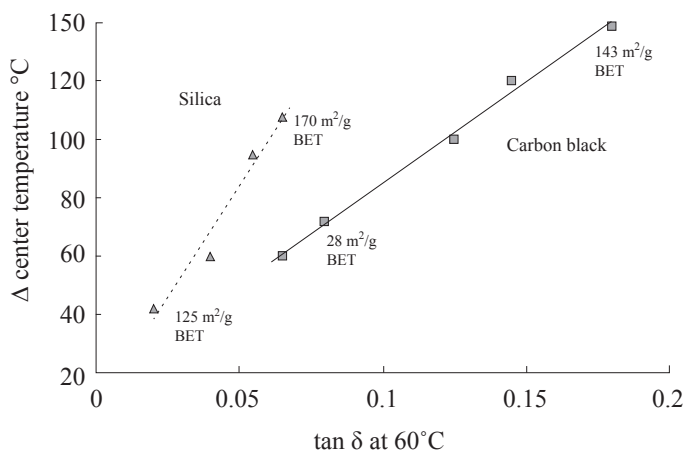


Figure 8. Influence of silica and carbon black on $\tan \delta$ at 60°C and heat build up in NR, 50 phr filler³⁹.

The investigation was carried out under the assumption that the final temperature reached when the compound is discharged, (dump temperature) is the main parameter influencing the mixing efficiency and silanisation reaction. Based on a study with NR³⁸, the dump temperature should be in the range of 145 to 155°C to achieve good silanisation and to avoid pre-crosslinking. Furthermore, a mixing time of at least 10 min is needed for the silanisation reaction during the first mixing step.

For the NR and silica combination, the optimisation of mixing conditions, *i.e.* mixing temperature and silica-silane-rubber mixing interval, which may have an influence on mixing quality and silanisation efficiency of silica-filled natural rubber compounds, was recently investigated. The compound formulation used for this study has been described elsewhere^{41,34}, which consists of silica/TESPT:55/5 phr with sulphenamide/diphenylguanidine accelerated sulphur vulcanisation.

Figure 9 shows that, with increasing mixing dump temperatures, the compound Mooney viscosities initially increase, then reach a maximum for a dump temperature range of 135–150°C. For dump temperatures above 150°C, the compound viscosity drops. This phenomenon is different from the work reported by Wolff³⁸, in which a steady decrease of viscosity with increasing dump temperature from 110 to 170°C for silica-filled NR compounds was observed. However, it was stated that the *in-situ* modification reaction of silica with TESPT should not be considered as an optimum reaction, since the recipe was composed of only 20 phr of silica in combination with 40 phr of carbon black. In the case of silica-TESPT filled SBR/BR compounds, Reuvekamp *et al.*⁴² reported a rather constant viscosity with increasing dump temperatures from 120–150°C, but an increased Mooney viscosity when dump

temperatures above 150°C were obtained, caused by premature scorch of the rubber by sulphur contained in the TESPT. It is clear that the NR and SBR/BR compounds display remarkably opposite trends of compound viscosities with varying mixing conditions.

The mixing torque gives insight in the processes happening during mixing. The mixing intervals between 120–720s, as given in Figure 10, represent the first and second incorporation step of silica, silane and processing oil. In these periods, the mixing torque decreases with increasing temperature, especially during the first incorporation, which is due to several factors. These include softening of the rubber at high temperatures, as well as

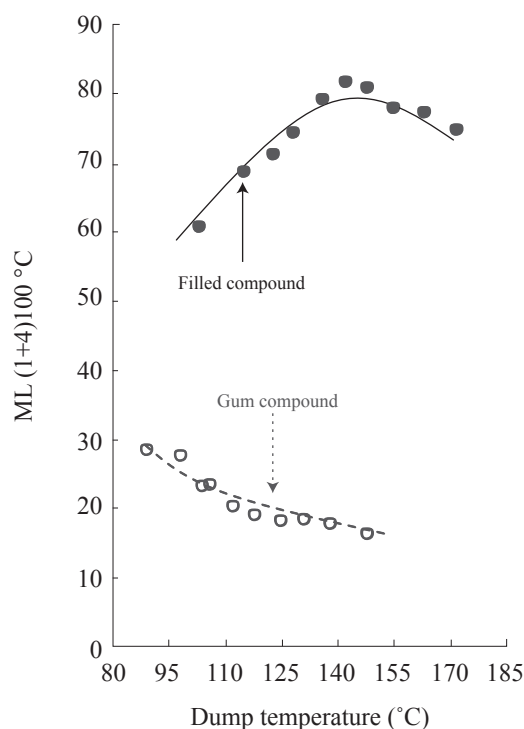


Figure 9. Effect of dump temperature on Mooney viscosity of gum and silica-filled NR compounds⁴¹.

breakdown of NR chains and silica structures by the mixing due to mechanical energy input, in combination with the hydrophobation effect of the TESPT silica surface modification. However, interestingly, a crossover of mixing torques is noticed at the second incorporation step of mixing. It demonstrates that, besides the silanisation reaction between silica and silane, a crosslinking or scorch reaction of NR with sulphur released from TESPT is simultaneously taking place, *i.e.* silica-silane-rubber and rubber-rubber bonds are created in the compound and consequently cause a rise in the compound viscosity. In industrial use, shorter cycle times are preferable for commercial production so that greater outputs can be obtained, leading to savings in energy-input as well as lowering processing costs. Under the assumption that further silanisation reactions potentially occur during a second mixing (remixing) step with an elevated starting temperature and/or

during the vulcanisation process, the silica-silane reaction times adjusted for an industrial compounding process can be shortened.

In order to prove the explanation given for the increase in mixing torque (*Figure 10*), the cure characteristics of NR and TESPT were investigated in comparison with the characteristics of SBR as shown in *Figure 11*. The test was performed with compounds of TESPT and diphenylguanidine (DPG) added, but without CBS (N-cyclohexyl-2-benzothiazolesulphenamide) and elemental sulphur as curing agents. The DPG is capable of boosting the silanisation reaction as reported by Mihara *et al.*⁴³ thus, it was included during the silica-silane-rubber mixing interval. It is clearly seen that NR readily reacts with TESPT at a temperature as low as 120°C, and the reaction rate increases rapidly at higher temperatures, as seen from a change of the cure curves. SBR shows a different behaviour

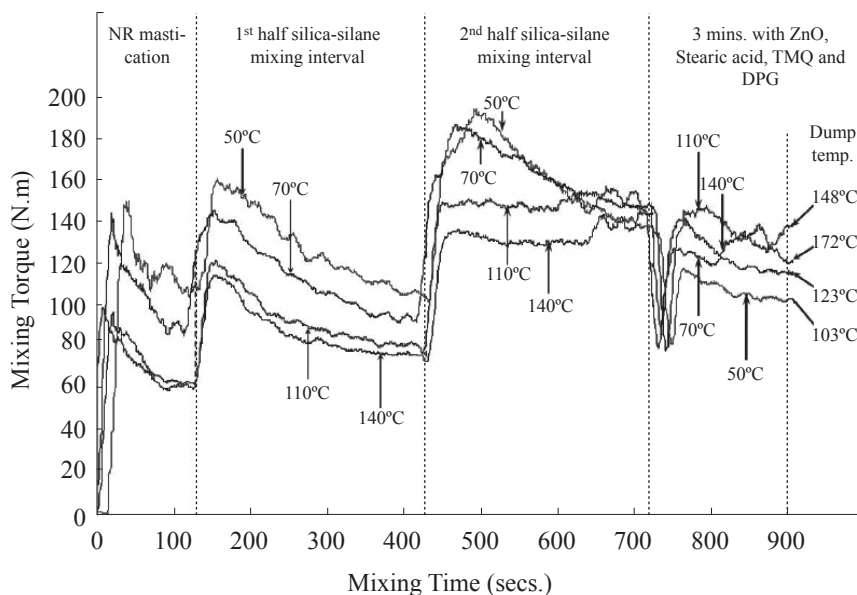


Figure 10. Mixing torques for silica-filled NR compounds prepared with various mixer temperature settings, as indicated for each line. The silica-silane-rubber total mixing interval was 10 minutes⁴¹.

since it starts to react with TESPT only at a higher temperature, *i.e.* 150°C. The rheometer torque differences, commonly used to indicate the extent of crosslinking, of both compounds are shown in *Figure 12*. The value for the NR and TESPT compound substantially increases from a test temperature of 120°C up to 150°C, and then gradually decreases at higher temperatures, a sort of reversion. On the other hand, the torque difference for the SBR and TESPT compound slightly increases until a temperature of 140°C, and then increases rapidly when the cure temperature exceeds 150°C. These results indicate that the viscosity of silica-TESPT filled rubber compounds significantly depends on a premature cross-linking reaction which takes place during the mixing process due to the sulphur in TESPT, in addition to the silanisation reaction and the thermo-mechanical shearing action.

The large torque scale variation for SBR and NR in *Figures 11* and *12* arises from the difference in molecular structures of NR and SBR. The torque increase observed in these rheometer curves is due to the rubber crosslinks caused by sulphur in TESPT only. A combination of partial crosslinking and bulky phenyl groups in the styrene part of SBR causes a larger restriction of movement of molecular chains under shear and hence a larger torque increase for SBR, compared to NR. In this context it is worth to mention that TESPT was first developed as a sulphur-cure accelerator with sulphur-donor properties, before it became commonly accepted as a coupling agent^{40,44}. Therefore, the increase of the silica-filled NR compound viscosities for dump temperatures in the range of 100–145°C: (*Figure 9*), is to a large extent due to the silica-silane-NR coupling reaction that occurs during the mixing process, and reaches its maximum at a dump temperature of 135–150°C. This premature crosslinking reaction dominates

over the breakdown of rubber chains and silica structures.

As seen from *Figure 9*, the viscosities of the silanised silica-filled NR compounds tend to decrease again at dump temperatures above 150°C. This may be attributed to an optimum degree of silica-rubber and rubber-rubber interactions/reactions induced by the TESPT. Furthermore, breakdown and degradation of rubber chains and/or polysulphide linkages becomes prominent. This observation can also be confirmed by the changes of bound rubber content in the compounds (*Figure 13*). In this experiment, the ammonia treatment was used to cleave the physical linkages formed by physical adsorption [ii], so that only the amount of chemically bound rubber, *i.e.* strong filler-rubber interactions and covalent bonds, were determined. The chemically bound rubber rapidly increases as a function of dump temperature, and then rises gradually after a dump temperature of approximately 135°C, indicating that the silica-silane-rubber and rubber-rubber interactions/reactions remain intact at higher temperatures and shear forces. Meanwhile, the physically bound rubber content in the compounds prepared at dump temperatures over 150°C decreases slightly, suggesting a reduction of chain entanglements or the physical network of rubber molecules due to a chain shortening by the degradation reaction.

During mixing of silica-silane and NR this premature crosslinking when TESPT is used as coupling agent cannot be avoided, as the NR starts to react with sulphur present in TESPT at a temperature as low as 120°C (*Figure 12*). The increased Mooney viscosity is normally an undesired processing property since it leads to processing difficulties in extrusion and calendering. Surprisingly, this phenomenon does not have an adverse effect on other properties of the compounds and vulcanisates as shown in *Figure 14*.

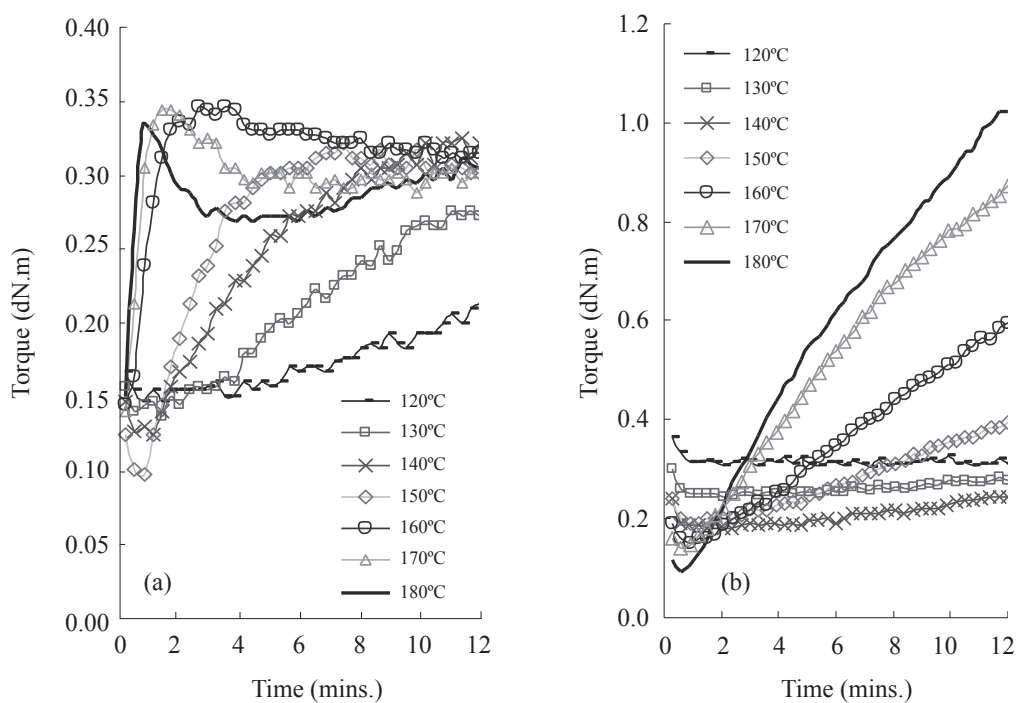


Figure 11. Cure characteristics of (a) NR and (b) SBR compounds, in the presence of TESPT (5.0 phr) and DPG (1.5 phr) at different cure temperatures⁴¹.

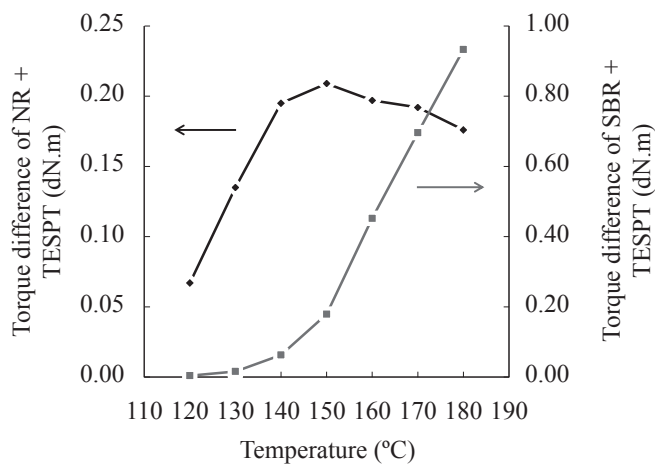


Figure 12. Rheometer torque difference of NR and SBR compounds as a function of cure temperature in the presence of TESPT (5.0 phr) and DPG (1.5 phr)⁴¹.

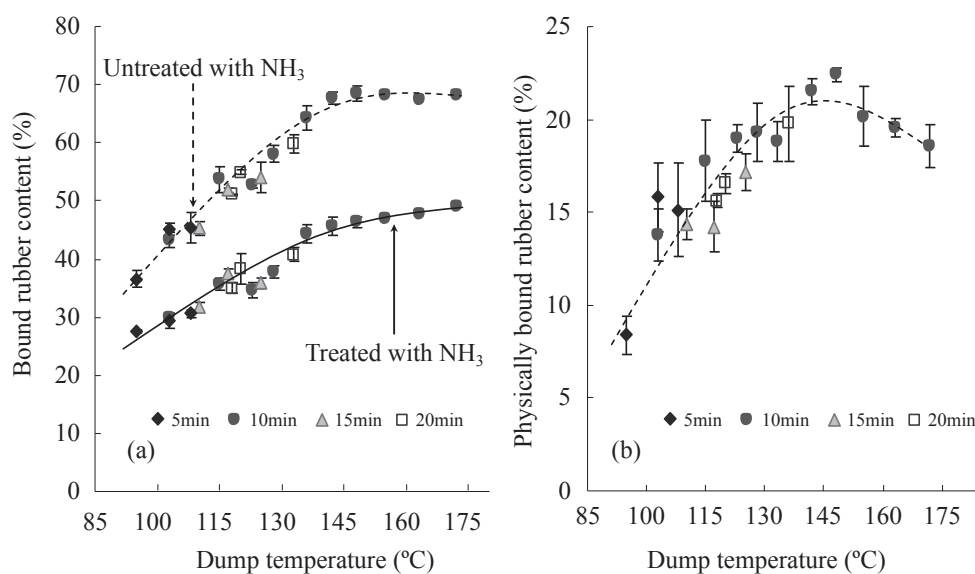


Figure 13. Influence of dump temperature on bound rubber contents of silica-filled NR compounds (a) Total and chemically bound rubber (treated with NH_3) and (b) Physically bound rubber content⁴¹.

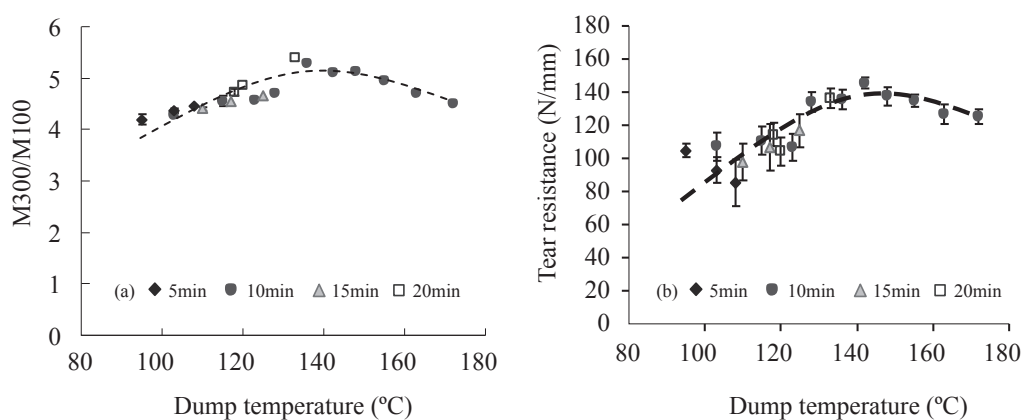


Figure 14. Effect of dump temperature and silica-silane-rubber mixing interval on mechanical properties of silica-filled NR vulcanisates (a) Reinforcement index $M300/M100$ and (b) Tear resistance⁴¹.

Filler-filler interaction is commonly measured by the so-called Payne effect: the drop in storage modulus in a dynamic mechanical test when the strain (deformation) is increased from low (0.56%) to a high value (100%) at constant frequency and temperature. The storage modulus of filled rubber drastically decreases as strain increases as the result of breakage of physical bonds between filler particles, for example van der Waals interactions, hydrogen bonds and London forces.

The improvement of the mechanical properties with increasing dump temperature to the optimum point, *i.e.* in the range of 135–150°C, especially in terms of reinforcement index (M300/M100) and tear resistance (Figure 14), is accounted for by better filler-rubber and lower filler-filler interactions as indicated by a higher bound rubber content

and a lower Payne effect of the compounds in Figures 13 and 15(a), respectively. The Payne effect or filler-filler interaction of silica/TESPT-filled NR compounds decreases with increasing dump temperature. This is not only due to higher degree of hydrophobation, greater extent of polymer-filler interaction, but also due to the lightly crosslinked network as a result of a small amount of crosslinking during mixing. Some rubber-rubber crosslinks formed at the later stage of mixing can restrict the re-agglomeration of silica particles. The results of this present work show a good agreement with the work reported by Lin *et al.*⁴⁵ in which the compounds comprising TESPT showed a reduction of re-agglomeration or flocculation of silica when they were mixed at higher dump temperature. The $\tan \delta$ at 60°C as depicted in Figure 15(b), a measure of rolling resistance of tyres based

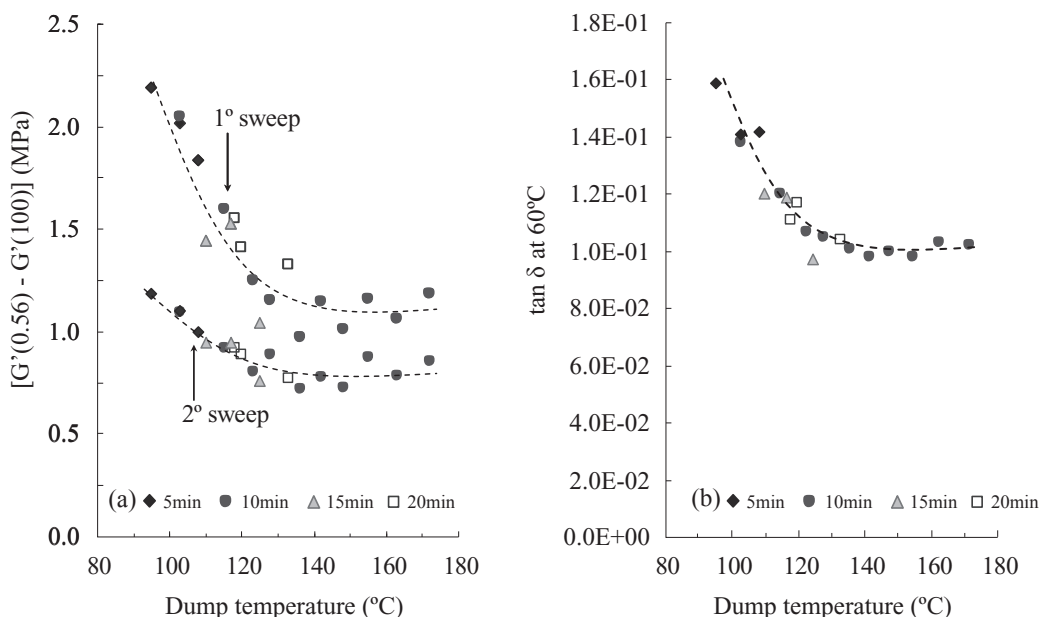


Figure 15. Influence of dump temperature on dynamic properties (a) Payne effect and (b) $\tan \delta$ at 60°C (frequency 10 Hz) of silica-filled NR vulcanisates prepared with various silica-silane-rubber mixing intervals⁴¹.

on silica-filled NR, is shown to improve when the compound dump temperatures are increased and the optimum temperature is in a range of 135–150°C, in agreement with all other properties.

Based on our investigations on the reinforcement parameter, (flocculation rate constant, bound rubber content, Payne effect, loss tangent at 60°C and mechanical properties) the optimal mixing conditions for silica-filled NR with TESPT as a coupling agent are at dump temperature in the range of 135–150°C, and 10 min mixing interval of silica-silane-rubber after mastication and before the addition of other ingredients (zinc oxide, stearic acid, polymerised 2,2,4-trimethyl-1,2-dihydroquinoline) and DPG). The decrease of reinforcement parameter, flocculation rate constant and Payne effect combined with the increase of bound rubber content can be taken as a proof for proper silanisation. However, it is worth to emphasize that the change in Mooney viscosity with dump temperature is different for NR and SBR when TESPT is used. The Mooney viscosity of the silica-filled NR compound increases due to sulphur in the TESPT to the maximum and thereafter decreases at higher temperatures as NR degradation starts to take place.

Effect of non-rubber constituents on silica-NR compounds. *Hevea brasiliensis* latex consists of rubber hydrocarbon, *cis*-1,4-polyisoprene, for about 25-40 weight percent⁴⁶ and non-rubber constituents for about 3-5 weight %⁴⁷ and water. The non-rubber constituents comprise proteins, amino acids, carbohydrates, lipids, amines, nucleic acids, as well as other inorganic and mineral components⁴⁸. Some of these constituents are dissolved in the aqueous serum during coagulation of NR latex.

Hevea latex can be separated using high speed centrifugation. After ultracentrifugation,

the *Hevea* latex has mainly three basic fractions: a rubber phase, C-Serum, and a bottom fraction⁴⁹. C-serum contains a large variety of proteins and enzymes, whilst the bottom fraction contains mainly the lutoids, the source of B-serum, and other minor organelles⁴⁹. B-serum is obtained *via* dialysis of the bottom fraction. Generally, the proteins from rubber particles and C-serum are acidic, whilst from B-serum there is a mixture of acidic and basic proteins. Most of the C-serum and B-serum proteins are water soluble, whilst, the proteins from rubber particles are mainly insoluble in water. The distribution of protein in the centrifuged latex fraction is listed in *Table 1*^{49,50}.

In order to illustrate the influence of non-rubber constituents in NR, particularly proteins on silica reinforced compounds in the presence and absence of coupling agent, truck tyre compounds based on NR with different protein contents were mixed⁵¹. The compound consisted of 55 phr Ultrasil 7005 silica and 5 phr TESPT. NR was compared with DPNR for reduced protein content, as well as skim rubber with high protein content. The protein contents of the different NR types based on their nitrogen content are shown in *Table 2*.

The influence of proteins in NR on the silica-silica interaction can be clearly observed from the vulcanisation curve as depicted in *Figure 16*. The clear two-step curve for NR-silica and DPNR-silica compounds without silane is due to silica flocculation or re-agglomeration^{45,53} and strong silica networking. With a high amount of proteins present in the compound, the silica-silica interaction is disrupted and this is visible at the beginning of the vulcanisation for the skim rubber-silica compound without silane where no sign of flocculation occurs. The use of a silane, TESPT in this case, in the NR-silica compound results in less pronounced silica flocculation and this is demonstrated by a small initial torque rise at the beginning

TABLE 1. PROTEIN DISTRIBUTION IN LATEX FRACTION^{49,50}

Latex fraction	Protein concentration (mg/ml latex)	% Distribution
Rubber phase	3.5	25
C-serum	6.0	43
B-serum	4.5	32
Total	14.0	100

TABLE 2. PROTEIN CONTENT OF NATURAL RUBBERS USED

Rubber Type	Nitrogen content, wt%	Protein content, wt %
NR (SMR 20)	0.21	1.3
DPNR (Pureprena)	0.07	0.4
Skim Rubber	2.06	12.9

It is generally accepted that the conversion factor from nitrogen to protein content is 6.25^{47,52}.

of vulcanisation (*Figure 16*). As compared to the silica compounds without silane, the flocculation of silica in the compounds with TESPT is small due to hydrophobation of the silica surface by TESPT. The effect of proteins on the cure behaviour of the silica compounds fades with the presence of TESPT.

The use of silica without silane modification in rubber results in a high Payne effect due to strong inter-aggregate interaction of silica. With TESPT modification, the Payne effect of the silica-filled compounds is greatly reduced as the silica surface is hydrophobised by TESPT, and the silica-silica network is disrupted as schematically shown in *Figure 17*. What is interesting in this study is that the same effect can be seen with protein. With a high amount of protein present in the rubber, the Payne effect of the silica compound without silane is lowered. There is a relation between the amount of protein and the decrease of silica-silica interaction. This indicates a strong interaction of proteins and silica, as well as the role of proteins in hydrophobising the silica surface.

For silica compounds with silane, the Payne effect decreases sharply with increasing mixing dump temperature, as is also seen in synthetic rubber/silica compounds and taken as a sign of reaction and consequent hydrophobation of the silica by the silane coupling agent^{41,54}. No effect of mixing temperature is perceived on filler-filler interaction for the skim rubber compound (*Figure 18*), this is observed for the unvulcanised as well as for the vulcanised compounds. This again indicates a strong interference of the proteins in skim rubber with the filler-filler network. For skim rubber, the silica-silica network is not influenced by dump temperature, even in the presence of silane, because silanisation is hindered. It can be seen in *Figure 18* that the Payne effect of vulcanised skim rubber compounds is higher than those of NR and DPNR compounds. The proteins in the skim rubber prevent the modification of the silica surface by the silane coupling agent. The logical explanation is that the interaction between silica and protein overrules the coupling agent and that the protein is shielding the silica surface.

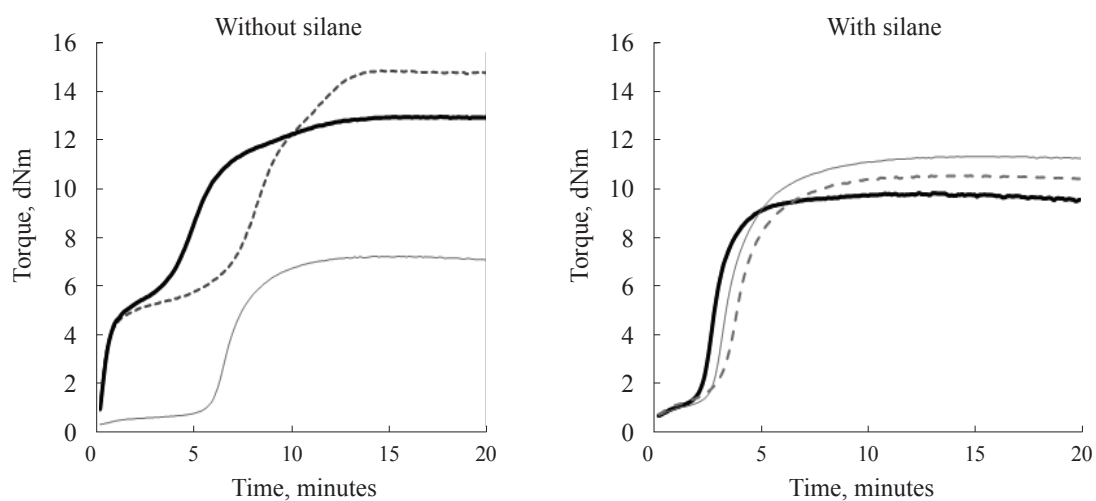


Figure 16. Comparison of vulcanisation curves of silica compounds with silane and without silane: NR(—), DPNR (---), Skim rubber (· · ·)⁵¹.

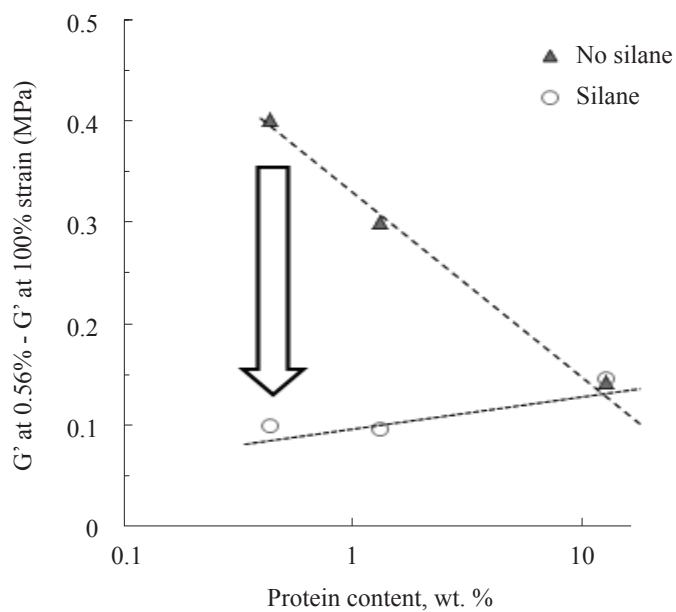


Figure 17. Influence of proteins on the Payne effect of NR-silica compounds⁵¹.

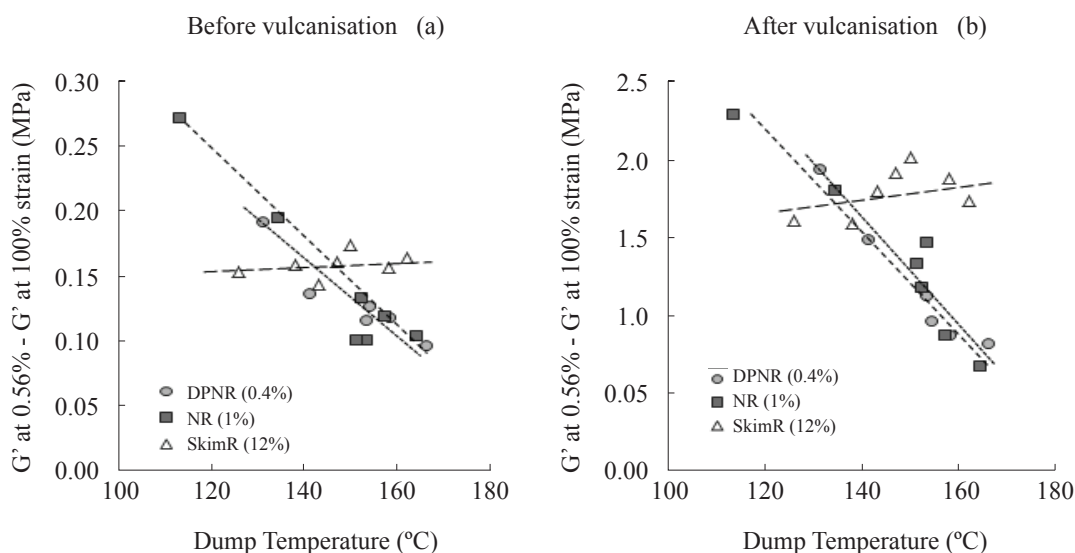


Figure 18. Payne effect of silica compounds with TESPT at varying protein contents in natural rubber (a) Unvulcanised samples (b) Vulcanised samples⁵¹.

The filler-to-rubber interaction of silica-filled NR with varying protein content can also be judged on basis of the chemically and physically bound rubber contents (BRC). Most of the bound rubber formed in a NR-silica-TESPT compound is chemically attached as shown in Table 3. This is obviously due to the hydrophobation of the silica surface as a result of silanisation with TESPT. The increase in silica-TESPT coupling consequently results in more filler-to-rubber interaction. This corresponds well with the lower Payne effect of the silica compounds with TESPT.

Without silane in the compounds, there is still silica-rubber interaction, as indicated by the physically bound rubber in Table 3. It demonstrates that the proteins contained in NR do interact with the silica, make it less hydrophilic and thus increase the rubber-silica interaction. However, no chemically bound rubber was obtained for the silica compounds without silane after ammonia treatment. This

means that without silane in the compound, only loosely or physically bound rubber is formed. This again indicates that the interaction of silica with NR in the absence of coupling agent is weaker than in a compound with silane.

Commonly, the dynamic mechanical loss angles $\tan \delta$ at 60°C of cured compounds are employed as indications for the rolling resistance of tyres. The lower $\tan \delta$ at 60°C, the lower the rolling resistance expected in real tyre performance. NR vulcanisates show a strong decrease in $\tan \delta$ at 60°C with increasing dump temperature regardless of the amount of protein in the rubber (Figure 19). Improvement in $\tan \delta$ at 60°C can still be achieved with higher mixing temperature, like with synthetic rubber. This must obviously be the result of more coupling of silica to the rubber with greater silanisation efficiency at high mixing temperatures. With low protein content, the DPNR vulcanisates exhibit the

TABLE 3. BOUND RUBBER CONTENT (BRC)

Rubber Type	Without silane		With silane	
	Physically BRC (%)	Chemically BRC(%)	Physically BRC (%)	Chemically BRC(%)
DPNR	45	0	11	76
NR	57	0	11	68
Skim Rubber	51	0	13	80

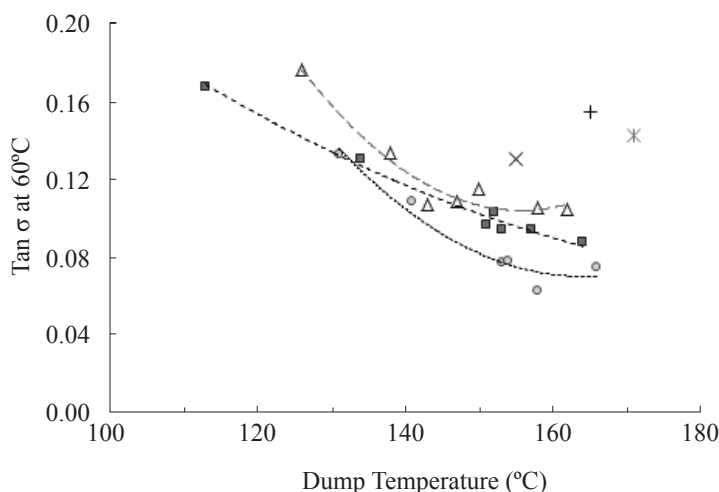


Figure 19. Comparison of $\tan \delta$ at 60°C for NR vulcanisates with varying protein content: (○) 0.4% (DPNR) (■) 1% (NR); (△) 12% (skim rubber) and silica-NR vulcanisate without silane (+): NR; (×) DPNR; (x) skim rubber⁵¹.

lowest $\tan \delta$ at 60°C at high dump temperature. This actually relates well with the higher chemically bound rubber content of DPNR compared to the NR compound. Still with all the protein contained in skim rubber, the $\tan \delta$ at 60°C is significantly lowered by mixing temperature history and only marginally worse than for NR and DPNR.

The silica-TESPT-rubber bonds created during vulcanisation improve the rubber-to-filler interaction. This is further supported with

the shift in the glass transition temperature (T_g) of vulcanisates with the use of the silane TESPT. In Figure 20, T_g of the vulcanisate increases from -49.5°C to -46.5°C when TESPT is used, indicating the restriction on the motion of rubber chains due to silica-TESPT-rubber coupling. In addition, the T_g is not affected by non-rubber constituents in the rubber. This is in agreement with the earlier observation that the interaction of protein with silica is weaker than the silica-TESPT coupling.

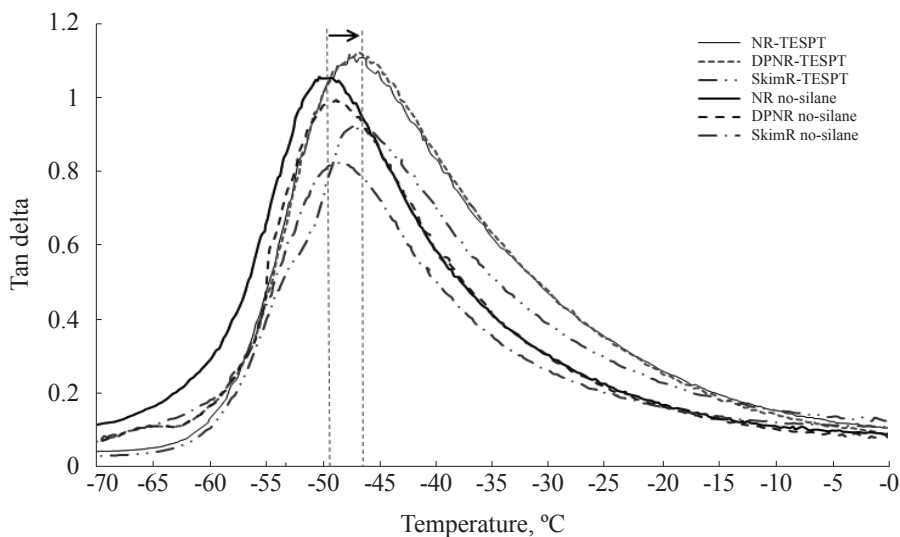


Figure 20. The effect of silane TESPT on the glass transition temperature, T_g of silica-filled vulcanisates. Measurement from dynamic mechanical analyser at 10 Hz.

Coupling agent and proteins show a complicated antagonistic effect in silica reinforcement of natural rubber. The effect of proteins is most pronounced when no silane is used in NR-silica compounds. When high amounts of proteins are present in NR, the interactions between proteins and silica are able to disrupt the silica-silica networking. A comparison of filler-to-rubber interactions in compounds with silane and without silane is graphically represented in Figure 21.

Morphology of NR-silica Systems. Transmission electron microscopy (TEM) was used by Julve *et al.* to evaluate the microdispersion of silica in a silica tyre tread compound with a high filler content⁵⁵. Reuvekamp found that a better silica microdispersion is obtained at high dump temperature after mixing, as characterised by an increase in the amount of segregated silica particles⁵⁶. A technique called network visualisation using TEM is a beneficial tool to study the rubber-to-filler interaction in

rubber compounds. This technique was first developed at the Tun Abdul Razak Research Centre (TARRC) to study rubber networks and was later used to investigate rubber-to-filler interactions⁵⁷. The TEM network visualisation process involves swelling of a vulcanisate in styrene, polymerisation of the styrene, staining the rubber network and visualisation using TEM⁵⁸. Using this method, the topology of a rubber network can be identified from the stained elastomer moieties and the unstained polystyrene matrix.

TEM network visualisations of silica-filled NR and silica-filled DPNR vulcanisates without coupling agent are depicted in Figure 22. In the micrographs, the silica is well dispersed in the rubber matrix and aggregates of around 50-100 nm size can be seen as dark particles throughout the sample. The vulcanised rubber network appears as a stained mesh structure, while polystyrene appears as unstained regions. Some silica aggregates in the NR vulcanisate are well bonded to the NR

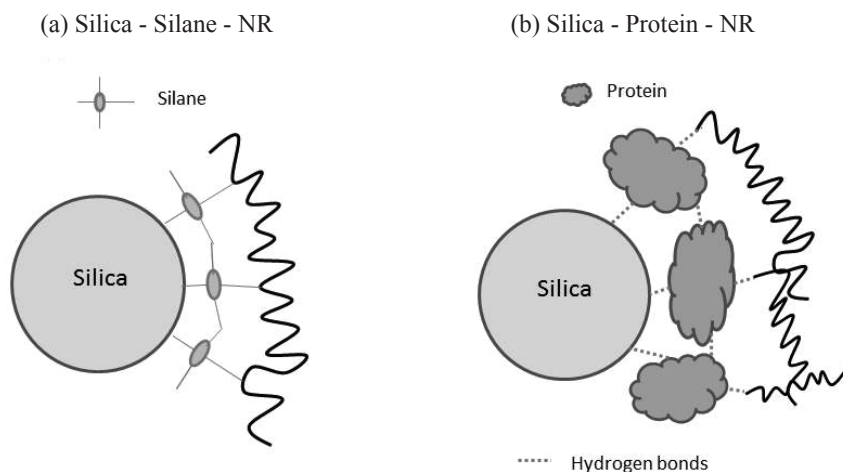


Figure 21. Illustration on the filler-to-rubber interaction for a silica compound (a) With silane (b) With protein and without silane.

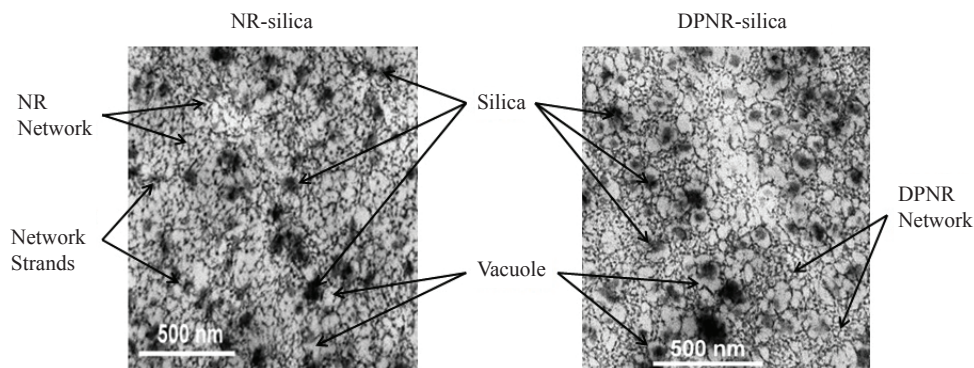


Figure 22. Comparison of TEM network visualisation micrographs of silica-filled NR and DPNR vulcanisates without coupling agent.

network as seen from the network strands from silica particles connected to the NR network. In addition, there are also vacuoles or voids surrounding the silica aggregates. The network visualisation of the DPNR vulcanisate is markedly different from the NR vulcanisate. There are clearly vacuoles surrounding the silica aggregates in the DPNR vulcanisate.

The styrene polymerises between the rubber network and the silica particles, and this results in the polystyrene vacuoles or voids surrounding the silica particles or aggregates. Ladouce-Stelandre *et al.* have suggested that the formation of such vacuoles is due to a weak interface between silica particles and rubber chains⁵⁷. The vacuoles are present in

the NR vulcanisate as well, but to a lesser extent, even though there is no silane coupling agent present in the compound. This points at more rubber-to-filler interactions in the NR vulcanisate than in the DPNR vulcanisate, and corresponds well with the results for the bound rubber.

A comparison of TEM network visualisation between NR and DPNR vulcanisates with the inclusion of the TESPT coupling agent is shown in *Figure 23*. Even though the micrographs are a bit less clear, it can be seen that there is strong attachment of the rubber network to the silica aggregates in both rubbers with TESPT present. Voids are scarcely visible in the TEM images. The aggregates of silica are also smaller as compared to those in the vulcanisate without silane. This agrees well with the earlier data that all silica compounds with TESPT exhibited a lower Payne effect and very high chemically BRC. It also shows that these compounds have high silanisation efficiency as a result of good mixing and reaction.

Silica-Reinforced Epoxidised Natural Rubber: Synergistic Effect between Epoxide Groups and Silane Coupling Agent

The silane chemistry is rather complicated because of the necessary *in-situ* reactions during rubber processing. The mixing temperature for silica/silane coupling agent filled rubber needs to be approximately 140–150°C^{12,41,42,59,60} which requires a rather high energy input. Alternative routes for improving processability and utility of silica-rubber mixes is therefore required. Polar modified natural rubber is of interest because it may lead to a reduction or a possible replacement of conventional silane coupling agents. The interaction between silica and rubber and its influences on material properties have been studied extensively for decades. Several published papers have revealed that the silanol groups on the silica surface have potential to form physical interactions or even chemical bonds with functionalised rubbers such as chlorosulphonated polyethylene (CSM)⁶¹, carboxylated nitrile rubber (XNBR)⁶² and

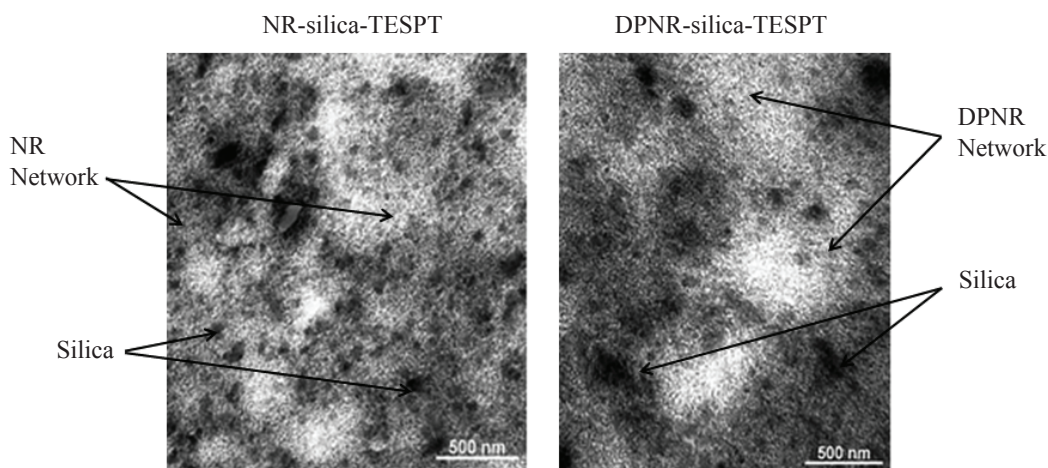


Figure 23. TEM network visualisation micrograph of silica-filled NR vulcanisate with TESPT silane coupling agent.

ENR⁶³⁻⁶⁵. The polar modified rubbers can be used either as raw material⁶⁶⁻⁶⁷ or as compatibiliser⁶⁸⁻⁶⁹. In this section⁷⁰, the influences of epoxide content in ENRs in the absence of a silane coupling agent, respectively a combination of ENRs with TESPT at varying loadings are evaluated on the overall properties of silica-filled ENR compounds. The epoxide content in ENRs used for this investigation was varied from 13-43 mol %, represented by ENR-13 to ENR-43, respectively. The ingredients used for the rubber formulation were the same as those described in earlier work⁴¹.

With regard to the changes in compound viscosity and Payne effect as shown in *Figures 24* and *25*, respectively, the phenomena apparently relate well to the overall properties of silica-filled ENR compounds and vulcanisates. There are several factors competitively influencing the compound viscosities of silica-filled polar-modified NR systems as summarised in *Scheme 1*.

The change in compound viscosities as indicated by Mooney viscosity (*Figure 24*) can be discussed by considering several factors which are simultaneously and competitively taking place in the compounds. "A better silica dispersion" resulting from a lower filler-filler interaction or Payne effect is a key factor that strongly reduces the viscosity of the compounds. Considering the ENRs with epoxide contents in the range of 13-29 mol% in *Figures 24* and *25*, the compounds without TESPT show a decrease in compound viscosity due to a dominant effect of silica dispersibility. Epoxide groups can result in polar-polar interactions with silanol functionalities on the silica, leading to better compatibility of the mixes resulting in a lower filler-filler interaction. Hence, a reduction of compound viscosity corresponds to the Payne effect (*Figure 25*). Apart from the

better polarity match between silica and ENR, the enhanced hydrophobation when TESPT is applied in the compounds and additional lubrication effects in the ENR-13 and ENR-21 compounds also lead to a strong reduction in compound viscosity. The only slight change of compound viscosity in ENR-29 with varying TESPT contents points to the fact that this level of epoxide content is just enough to hydrophobise the silica surface. The addition of TESPT has only a minor additional effect on the properties.

After the compounds show their optimum low compound viscosities due to the presence of appropriate combinations of either epoxide functionality or TESPT, other factors play a dominant role towards increased compound viscosities. The rise of compound viscosity can mainly be attributed to the increment of network contributions (*Scheme 1*). The ENRs with different levels of epoxide functionality have variable basic properties which certainly affect their compound viscosities. As shown in *Figure 26*, the Mooney viscosities of the ENRs increase with increasing epoxide content, as the ENRs themselves possess a relatively high polarity in their structures. They tend to form self-association *via* hydrogen bonding or polar interactions between either the same or neighbouring molecules, and even self-crosslink due to the opening of the oxirane rings⁷¹. *Figure 27* shows the possible self-crosslinking of ENR. This network generation contributes to the increase in compound viscosity.

In addition to the possibility of physical interactions generated between ENR and silica *via* polar-polar interactions, chemical silica-to-ENR coupling has been proposed⁶⁴⁻⁶⁵. For the compounds with TESPT coupling agent, strong chemical filler-rubber interaction can be formed through silane chemistry contributing to network structures. Moreover, TESPT can additionally release free sulphur

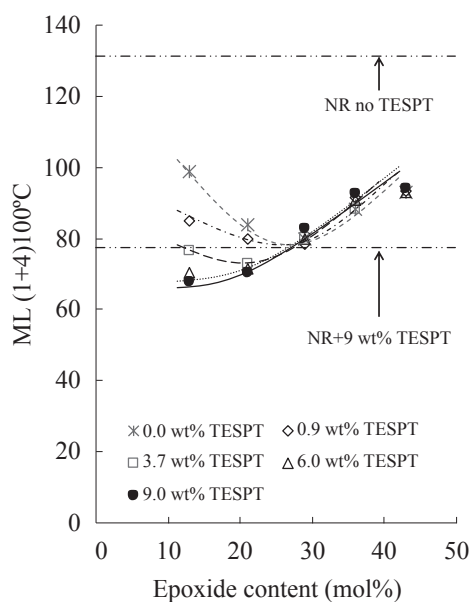


Figure 24. Mooney viscosities as functions of epoxide content in ENRs. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to the silica content are shown as references by dashed lines⁷⁰.

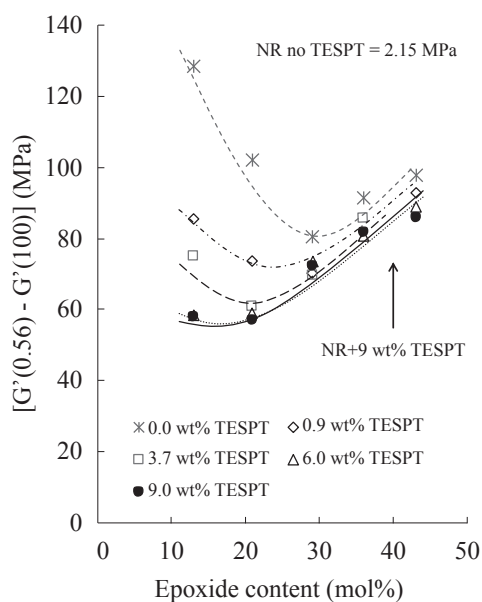
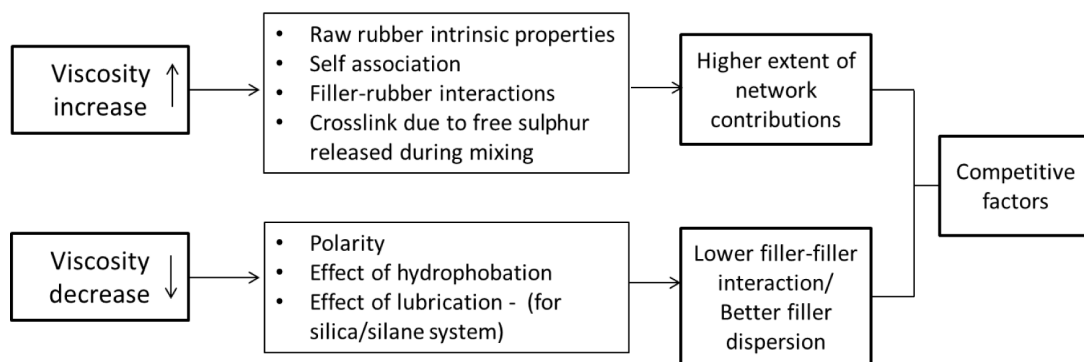


Figure 25. Payne effect as functions of epoxide content in the ENR compounds⁷⁰.



Scheme 1. Competitive factors influencing compound viscosities of silica-filled ENR compounds with and without silane coupling agent⁷⁰.

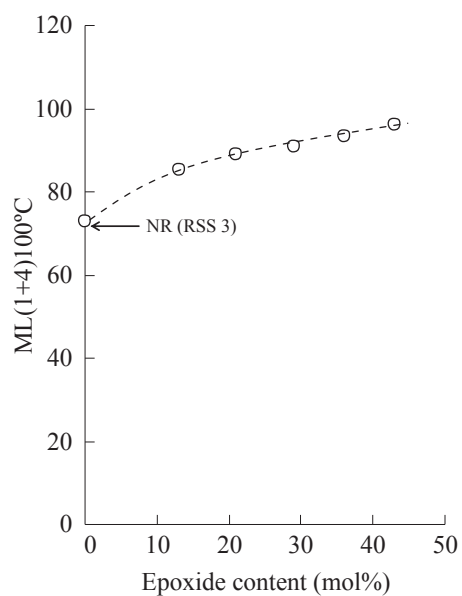


Figure 26. $ML(1+4)100^{\circ}C$ of unmodified NR and ENRs with various levels of epoxide functionality.

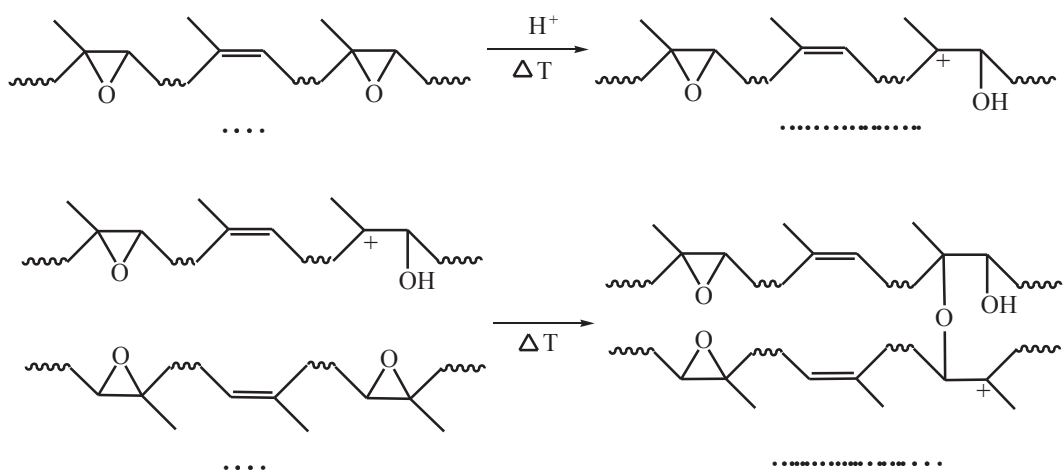


Figure 27. Self-crosslinking of ENR under acidic and thermal conditions⁷¹.

into the system, and then cause light rubber-rubber crosslinking during the high thermo-mechanical mixing conditions⁴¹. The combination of these factors which involve network formation leads to the increase in compound viscosities of silica-filled ENR systems.

Figure 28 displays that the increase of the TESPT loading results in a sharp decrease in $\tan \delta$ at 60°C of the compounds based on ENRs with 13, 21 and 29 mol% epoxide content, and a slight decrease for ENR-36 and ENR-43. Basically, $\tan \delta$ relates strongly to network contributions in the compounds. The dynamic mechanical test was performed at 3.5% strain and a frequency of 10 Hz, where

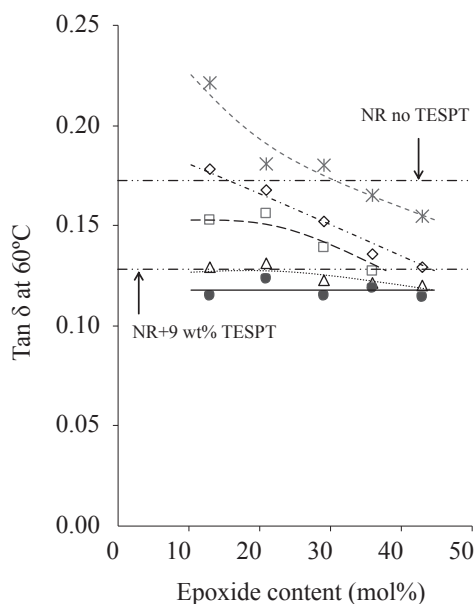


Figure 28. $\tan \delta$ at 60°C as functions of epoxide content in ENRs of the compounds added with different levels of TESPT. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to the silica content are shown as references by dashed lines⁷⁰.

the filler network begins to break. The results are therefore strongly influenced by network contributions originating from filler-rubber interactions and physical/chemical crosslinks. Without TESPT, the increase of epoxide contents leads to a strong decrease in $\tan \delta$ at 60°C. This can be linked to the greater filler-rubber interaction/network formation as reflected by the higher storage modulus at high strain. The combination of epoxide functionality with TESPT silane coupling agent jointly improve the $\tan \delta$ at 60°C or rolling resistance of tyres. Therefore, there is a possibility to reduce the amount of TESPT needed in silica-filled ENR formulations.

The compounds based on ENR-13, ENR-21 and ENR-29 show their optimum reinforcement indices when TESPT amounts at 9.0, 6.0, and 3.7 wt% relative to the silica content are combined, respectively, as shown in Figure 29. A further increase of TESPT loading results in a decrease in reinforcement index. The ENR compounds without TESPT show an increase of reinforcement index with increasing epoxidation degree up to 29 mol% to match more or less the same level as that of an unmodified NR compound in the presence of TESPT. However, a further increase of epoxide content leads to a decrease again in reinforcement index. This reflects a good synergistic effect between epoxide groups and TESPT towards enhanced reinforcing efficiency of silica in ENR compounds.

Based on the results in this investigation, the Payne effect and compound viscosity remarkably decrease with the presence of epoxide functional groups up to 29 mol% on ENR compared to silica-filled normal NR compounds. A high content of epoxide groups, e.g. ENR-36 and ENR-43, adversely affects the processibility and most of the properties. Addition of TESPT into silica-filled ENRs with epoxide contents of 13 and 21 mol% further enhances compound

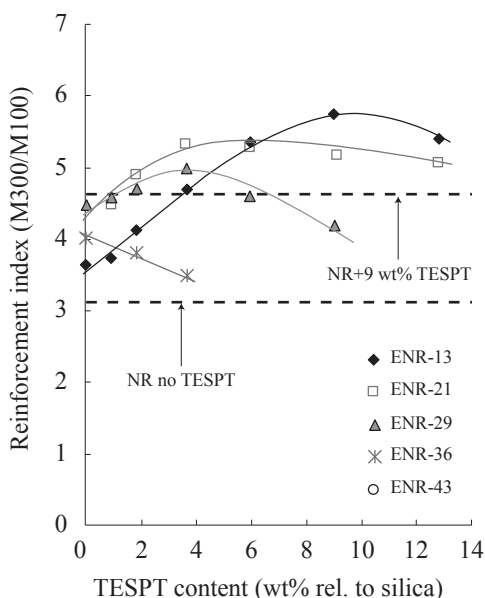


Figure 29. Reinforcement index as functions of TESPT content of ENR compounds containing different epoxidation degrees. Silica-filled unmodified NR compounds without and with TESPT at 9 wt% relative to silica content are included as references⁷⁰.

processibility and vulcanisate properties, whilst the use of TESPT has the least effect on the ENR 29 compound. The overall properties demonstrate that epoxide groups on ENR alone can not provide the properties to match those of silica-TESPT filled unmodified NR. But, the right combination of epoxide groups and TESPT as silane coupling agent leads to a similar level of properties compared to the TESPT-unmodified NR system. With the synergistic effect of polar epoxide groups, the silane coupling agent loading needed can be reduced down to half or even lower compared to conventional silica-filled NR compounds. Overall, the ENR with the epoxide content in the range of 20-30 mol% gives optimum properties for silica-filled ENR compounds. This finding is in good agreement with the

previous works reported by the TARRC⁵. In addition, for tyre applications, ENR-25 gives the most preferable properties, in particular rolling resistance and wet grip^{72,73}.

CONCLUSIONS

The properties of silica-filled compounds show a strong dependence on dump temperature, since the silanisation reaction and silica dispersion are key parameters in this system. The optimal mixing conditions for silica-filled NR compounds with TESPT as a coupling agent are a dump temperature in the range of 135–150°C, and a 10 min mixing interval of silica-silane-rubber prior to addition of the other ingredients (ZnO, stearic acid, TMQ and DPG). Mixing performed till dump temperatures above 150°C leads to a decrease in vulcanisate properties as a result of NR degradation. During mixing of silica-filled NR compounds with TESPT as coupling agent, it is evident that, in addition to the silanisation reaction, premature crosslinking reactions take place since NR can start to react with sulphur coming from TESPT molecules at a temperature as low as 120°C. However, this phenomenon does not have an adverse effect on the vulcanisate properties.

Natural rubber is a durable natural resource, but has the disadvantage of containing a variety of non-rubber components such as proteins. An in-rubber study of the interaction of silica with proteins present in natural rubber shows that the latter compete with the coupling agent during the silanisation reaction. The presence of proteins makes the silane less efficient for improving dispersion and filler-polymer coupling, and thus, negatively influences the final properties of the rubber material. Furthermore, the protein content influences the rheological properties as well as filler-filler and filler-polymer interactions. With high amounts of proteins present in NR,

the interactions between proteins and silica are able to disrupt the silica-silica network and improve silica dispersion. The effect of proteins is most pronounced when no silane is used, but proteins are not able to replace a coupling agent. In order to achieve a good balance of properties, the presence of a coupling agent is still essential.

Rubber-to-filler interactions in vulcanised NR-silica compounds are greatly improved with the use of silane TESPT as coupling agent. This is the result of a reduced silica-silica networking, following the chemical reaction between silica and TESPT, as demonstrated by a lower Payne effect and higher content of chemically bound rubber. The TEM network visualisation confirmed the strong rubber-to-filler interaction in the silica compounds with silane.

Polar functionality grafted onto natural rubber has a significant impact on the reinforcing efficiency of silica. Parallel studies involving various levels of epoxidation on natural rubber (ENR) in the absence of TESPT coupling agent, as well as a combination of ENRs with different loadings of TESPT, provide a better understanding of the various factors which influence the properties of silica-filled ENR compounds. Based on the overall properties, it can be concluded that the best possible combination to optimise processibility, to reduce filler-filler interaction, and improve vulcanisate properties, is to utilise ENR with an epoxide content in the range of 20–30 mol%, together with a small portion of TESPT, *i.e.* 2–4 wt% relative to the silica content. This leads to a reduction of approximately 60–80% of TESPT when compared to the conventional NR compounds, where the optimal loading of TESPT was 9.0 wt% relative to the silica content.

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