

## ***Synergistic Effects in Silica-Reinforced Natural Rubber Compounds Compatibilised by ENR in Combination with Different Silane Coupling Agent Types***

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*Bis-(3-triethoxysilyl-propyl)tetrasulfide (TESPT), 3-mercaptopropyl-di(tridecan-1-oxy-13-penta(ethyleneoxide)) ethoxysilane (VP Si-363<sup>TM</sup>) and 3-octanoyl-thio-propyltriethoxysilane (NXT<sup>TM</sup>) are comparatively studied at varying amounts from 2 to 5 wt% relative to the silica, in combination with 7.5 phr of epoxidised natural rubber (ENR) with 51 mol% of epoxide (ENR51), as compatibilisers for silica-filled NR compounds. The compounds with ENR and VP Si-363 or NXT show a lower Mooney viscosity and reduced bound rubber contents and moduli at 100% and 300% elongations when compared to the one with TESPT. The presence of ENR51 at 7.5 phr already effectively reduces the filler-filler interactions. The addition of silane on top of the ENR has only little influence on Mooney viscosity and Payne effect, but clearly enhances filler-rubber interactions as indicated by an increased chemically bound rubber content. The tensile properties of the silica-filled NR vulcanisates are increased with increasing silane contents, in which state-of-the-art TESPT still provides better properties than the other silanes, while VP Si-363 and NXT give more or less the same properties. At a fixed silane content of 4 wt% relative to silica and 7.5 phr of ENR51, sulphur compensation added into the compounds by taking the mix with optimal content of TESPT as reference, enhances the tensile modulus and strength. In the presence of ENR, the dynamic mechanical properties of the silica-filled NR compounds are influenced by the glass transition temperature of the ENR. With respect to tyre rolling resistance, the use of TESPT provides the lowest loss tangent at 60°C.*

**Keywords:** Natural rubber; ENR; silane; silica; tyre compounds

Incorporation of fillers into rubber compounds has an important effect on the physical properties of the rubber vulcanisates that result

from the development of stress concentration, which in turn depends on several factors such as shape of the fillers, the specific filler surface

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area, particle size, particle size distribution and nature of the boundary layer between filler and matrix<sup>1-3</sup>. Silica is a non-black filler which consists of a great number of silanol groups on its surface, leading to high polarity, acidity and low adhesion between silica and elastomers<sup>2</sup>. Use of silica as a reinforcing filler in rubber compounds needs some chemical functional groups or silane coupling agents to increase the reinforcing efficiency by means of increased silica-rubber interactions and improved silica dispersion. The use of epoxidised natural rubber (ENR) as compatibiliser in silica-filled NR compounds has demonstrated that it could enhance the reinforcing efficiency of silica to some extent but the final properties were still somewhat inferior to the use of state-of-the-art TESPT silane coupling agent<sup>4</sup>. It is known that the properties of ENR itself depend on the epoxide-group content and that there is a decrease of strain-induced crystallisation at high levels of epoxidation<sup>5,6</sup>. Various studies on silica-filled ENR compounds<sup>7-9</sup> reported good reinforcement and improved properties compared to silica-filled NR without silane coupling agent, due to chemical interactions between the polar epoxide-groups of the ENR and the silanol-groups on the silica surface<sup>8,9</sup>.

The most widely used method to optimise the silica reinforcing efficiency in rubber compounds is the use of a silane coupling agent. The silane modified silica surface has a reduced specific surface energy, leading to improvement of the compatibility between silica and hydrocarbon rubber, better silica dispersion, improved compound processability and vulcanisation properties<sup>10</sup>. Sulphur-containing silane coupling agents have more influence on the overall properties of silica-filled rubber than a sulphur-free silane<sup>11</sup>. Bis-(3-triethoxysilyl-propyl)tetrasulphide (TESPT) gives better scorch safety and lower compound viscosity when compared to

$\gamma$ -mercaptopropyltriethoxysilane (MPS) due to the highly reactive thiol end-group of the MPS which has a catalytic effect on accelerated sulphur vulcanisation<sup>12</sup>. TESPT with its tetrasulphide moiety is known to donate free sulphur to the compounds, and the use of a silane with lower sulphur rank or a sulphur-free silane needs correction of the sulphur-content relative to the sulphur contained in the reference compound with TESPT. It has been reported that the extra sulphur added either in the first step of mixing in an internal mixer or in the second step on a two-roll mill can react with the coupling agent to some extent, leaving a large part in the system to participate in the vulcanisation reaction<sup>11</sup>. A recent study based on the use of small amounts of TESPT in combination with 10 phr epoxidised low molecular weight natural rubber with 28 mol% epoxide groups (ELMWNR-28) in the silica-reinforced NR compounds showed that by adding TESPT at only 1.5 phr, the compounds show superior processability and only slightly lower modulus compared with the use of the optimal content of TESPT at 4.5 phr<sup>13</sup>.

While silica is constantly gaining more importance for energy-saving low rolling resistance tyres, there is a steady development of alternative silanes. 3-Octanoyl-thio-propyltriethoxysilane (NXT) has been introduced as a silane coupling agent offering a better scorch safety than TESPT, because of its bulky blocking end-group on the mercapto function<sup>14-16</sup>. The blocked silane will couple with NR only during the curing period<sup>15,16</sup> and it has been reported that the NXT-silane needs a mixing temperature above 130°C to react with the silanol groups on silica. The longer scorch time of NXT compounds is in accordance with the higher activation energy for premature scorch compared to that of TESPT<sup>15</sup>. A study on SBR compounds filled with silica that were modified by NXT in comparison with TESPT showed that the NXT compounds gave lower

Payne effects and lower viscosities due to better filler dispersion, but poorer modulus because the silane contains only one sulphur atom in its structure<sup>17</sup>. Another new silane that was proposed for tyre compounds is VP Si-363 which is a bifunctional organosilane having long dialkoxy-ethoxy-silyl groups and a mercapto-function<sup>18</sup>. The “scorchy” nature of the mercapto-function of this silane is suppressed by steric hindrance by the large side-arms<sup>18</sup>. As the silica-silane reaction proceeds *via* the ethoxy-group, this silane type produces less ethanol emission during processing compared to the conventional TESPT or Si-69. A kinetic study by Blume<sup>19</sup> using a model system showed that the presence of –SH and long alkoxy groups enhances the rate of reaction. Furthermore, the oxygen atoms inside the long alkoxy chain of VP Si-363 may increase the possibility of silane adsorption onto the silanol groups of the silica *via* hydrogen bonding and shield the remaining free silanol groups.

Based on the work reported earlier<sup>4</sup>, the use of ENR containing 51 mol% of epoxide (ENR51) at 7.5 phr gave the best overall improvement in the Payne effect, bound rubber content, mechanical and dynamic mechanical properties. With the aim to reduce the use of silane coupling agent and ethanol emission, this present work explores combinations of ENR51 at 7.5 phr with three different types of silane: TESPT, VP Si-363 and NXT in silica-filled NR-compounds. The amount of ENR51 is fixed at 7.5 phr based on the optimum properties<sup>4</sup> and the silane contents are varied from 2.0 to 5.0 wt% relative to the silica amounts. Later on, with fixed amounts of both ENR51 and silane, compensations are applied in the compound with elemental sulphur relative to the total sulphur contained in the reference TESPT-compound, and the resulting properties are investigated in comparison with the normal formulation.

## EXPERIMENTAL

### Materials

The rubbers used were natural rubber (Ribbed Smoked Sheet (RSS #3), locally produced in Thailand, and epoxidised natural rubbers (ENR) with 51 mol% of epoxide, denoted as ENR51, that was prepared as described previously<sup>4</sup>. The compounding ingredients were highly dispersible silica (Zeosil 1165MP, Solvay, France), treated distillate aromatic extract oil (TDAE oil) (Hansen & Rosenthal, Germany), N-cyclohexyl-2-benzothiazole sulphenamide (CBS), diphenyl guanidine (DPG) and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) (all from Flexys, Belgium), ZnO, stearic acid and sulphur (all from Sigma-Aldrich Chemie, Germany). Three different types of silane coupling agents were bis-(3-triethoxysilyl-propyl)tetrasulphide (TESPT), 3-mercaptopropyl-di(tridecan-1-oxy-13-penta(ethyleneoxide))ethoxysilane (VP Si-363<sup>TM</sup>) (both from Evonik, Germany) and 3-octanoyl-thio-propyltriethoxysilane (NXT<sup>TM</sup>) (Momentive, USA). Their details are given in *Table 1*.

### Compound Formulations and Mixing Procedures

The first mixing step of silica-filled NR compounds was performed using an internal mixer, Brabender<sup>®</sup> 50EHT, (Brabender<sup>®</sup> GmbH & Co.KG, Germany) with a mixing chamber volume of 70 cm<sup>3</sup> at a rotor speed of 60 rpm. The initial mixer temperature setting was 100°C in order to reach a dump temperature in the range of 135-150°C, as recommended by Kaewsakul<sup>20</sup>, that is the temperature range providing optimal overall properties of the silica/silane-filled NR compounds. The dump temperature was recorded in the range of 144-149°C. This temperature range is required to ensure an effective silanisation

reaction that leads to good silica dispersion and thus, optimal overall physical properties<sup>20</sup>. The compound formulations are shown in *Tables 2* and *3*, and the mixing procedures are described in *Table 4*. The second step of curative addition was carried out on a two-roll mill.

### Mooney Viscosity, Payne Effect and Bound Rubber Content

Mooney viscosity [ML(1+4), 100°C] was tested by using a Visc Tech<sup>+</sup> (Tech-Pro Inc., USA) according to *ASTM D1646*. The Payne effect<sup>21</sup> or filler-filler interaction of the final compounds (with curatives) was analysed by using a rubber process analyser (RPA2000, Alpha Technologies, USA) at 100°C, frequency 0.5 Hz and varying strains from 0.56% to 100%. The difference of storage shear moduli at 0.56% and 100% strain was calculated and reported as the Payne effect.

For the bound rubber content determination, uncured compound (without curatives) was cut into small pieces of 0.25g, put into a metal cage and immersed in toluene at room temperature

for 72 h (renewed every 24 h). The sample was removed from the toluene, dried at 50°C for 24 h, then immersed in toluene again for 72 h at room temperature in either a normal or an ammonia atmosphere. The ammonia treatment was done to cleave the physical linkages between rubber and silica, in order to determine the chemically bound rubber *versus* bound rubber physical of nature. The sample was finally dried at 50°C for 24 hours. The bound rubber content was then calculated using the following equation<sup>22</sup>:

$$\text{Bound rubber content (\%)} = (m - m_s) \times \frac{100}{m_r} \quad \dots 1$$

where  $m$  is the weight of sample after extraction,  $m_s$  is the weight of silica in the sample taken from the formulation and  $m_r$  is the original weight of rubber in the sample.

### Cure Characteristics, Vulcanisation and Tensile Properties

Cure properties of the compounds were tested by using a moving die rheometer (MDR) (rheoTech MD<sup>+</sup>, Tech-Pro, Inc., USA)

TABLE 1. SILANE COUPLING AGENT INFORMATION

Trade names	Chemical names	Structures	MW (g/mol)
Si-69	Bis-(3-triethoxysilyl-propyl)tetrasulphide (TESPT)	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{O} \\   \\ \text{CH}_3\text{CH}_2\text{O}-\text{Si}-(\text{CH}_2)_3-\text{S}_x-(\text{CH}_2)_3-\text{Si}-\text{OCH}_2\text{CH}_3 \\   \qquad \qquad \qquad \text{with } x = 3.70 \qquad \qquad   \\ \text{CH}_3\text{CH}_2\text{O} \qquad \qquad \qquad \text{OCH}_2\text{CH}_3 \end{array}$	532.5
VP Si-363	3-Mercaptopropyl-di(tridecan-1-oxy-13-penta(ethyleneoxide))ethoxysilane	$\begin{array}{c} \text{CH}_3(\text{CH}_2)_{12}(\text{OC}_2\text{H}_4)_5\text{O} \\   \\ \text{CH}_3\text{CH}_2\text{O}-\text{Si}-(\text{CH}_2)_3-\text{SH} \\   \\ \text{CH}_3(\text{CH}_2)_{12}(\text{OC}_2\text{H}_4)_5\text{O} \end{array}$	987.5
NXT	3-Octanoyl-thio-propyltriethoxysilane	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{O} \\   \\ \text{CH}_3\text{CH}_2\text{O}-\text{Si}-(\text{CH}_2)_3-\text{S}-\text{C}(=\text{O})-(\text{CH}_2)_6\text{CH}_3 \\   \\ \text{CH}_3\text{CH}_2\text{O} \end{array}$	365.0

TABLE 2. COMPOUND FORMULATIONS WITHOUT EXTRA SULPHUR

Ingredients	Parts per hundred parts of rubber (phr)					
	References			No extra sulphur		
RSS3	100.0	100.0	92.5	92.5	92.5	92.5
ENR-51	-	-	7.5	7.5	7.5	7.5
TESPT	-	4.7*	-	1.1-2.7**	-	-
VP Si-363	-	-	-	-	1.1-2.7**	-
NXT	-	-	-	-	-	1.1-2.7**
Zeosil 1165MP	55.0	55.0	55.0	55.0	55.0	55.0
TDAE oil	8.0	8.0	8.0	8.0	8.0	8.0
ZnO	3.0	3.0	3.0	3.0	3.0	3.0
TMQ	1.0	1.0	1.0	1.0	1.0	1.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0
DPG	1.0	1.0	1.0	1.0	1.0	1.0
CBS	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5

Remarks: \* TESPT 4.7 phr equals to 8.6 wt% rel. to the silica; \*\* Amounts of silane were varied at 2, 3, 4, 5 wt% rel. to silica, which are respectively equal to 1.1, 1.65, 2.2, 2.7 phr.

TABLE 3. COMPOUND FORMULATIONS WITH SULPHUR COMPENSATION

Ingredients	Parts per hundred parts of rubber (phr)			
	Extra sulphur*			
RSS3	92.5	92.5	92.5	92.5
ENR-51	7.5	7.5	7.5	7.5
TESPT	-	2.2	-	-
VP Si-363	-	-	2.2	-
NXT	-	-	-	2.2
Zeosil 1165MP	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
Sulphur	2.6	2.1	2.5	2.4

Remarks: \* Sulphur content was compensated relative to the sulphur contained in the reference compound with 4.7 phr TESPT.

at 150°C for 30 min as per *ASTM D 5289* at a frequency of 1.67 Hz and 13.95% strain. Then, the compounds were cured to their respective optimum cure times ( $t_{c90}$ ) at 150°C with a compression mould (Chaicharoen Karnchang Ltd, Thailand). Vulcanised sheets

of 2 mm thickness were cut into dumbbell specimens using die type C, and tensile testing was carried out using a Hounsfield tensile tester (H10KS, Hounsfield Test Equipment, England) at a crosshead speed of 500 mm/min according to *ASTM D412*.

TABLE 4. MIXING PROCEDURES

Mixing procedures	Cumulative time (mins)
Step 1 : Internal mixer	
- NR and ENR mastication	2
- Addition of a first half of silica (and ½ of silane)	7
- Addition of a second half of silica( and ½ silane) and TDAE oil	12
- Addition of ZnO, stearic acid, and TMQ	15
Step 2 : Two roll mill	
- Addition of DPG, CBS, and sulphur (+ extra sulphur)	5

### Dynamic Mechanical Properties

Storage modulus, loss modulus and  $\tan \delta$  of the silica-filled NR vulcanisates containing different compatibilisers were determined using a dynamic mechanical thermal analyser, DMTA V (Rheometrics Scientific, USA). The samples were tested in tension mode in a temperature range from -80°C to 80°C, at a frequency of 10 Hz under two strain deformations: 0.001% strain at -80°C to -30°C and 0.01% strain from -30°C to 80°C.

## RESULTS AND DISCUSSION

### Mooney Viscosity and Payne Effect of ENR-Silane Compatibilised Silica-Filled NR

Mooney viscosities of the silica-filled NR compounds with different types and amounts of silane coupling agents added on top of 7.5 phr of ENR51 as compatibiliser are shown in *Figure 1a*. The silica-filled compound without compatibiliser shows by far the highest compound viscosity due to hindrance of rubber flow by the filler network and silica agglomerates. The presence of ENR51 as compatibiliser significantly reduces the Mooney viscosity as a result of interactions between the epoxy groups of ENR and silanol groups on the silica surface<sup>4</sup>. The addition of an increasing amount of silane further decreases the Mooney viscosity slightly, indicating an

improvement of silica dispersion, as a small amount of free silanol groups may still exist in the system after the silica-ENR interactions. An excess amount of silane coupling agents helps to lubricate the rubber molecular chains and facilitates the flow for the rubber compounds, and thus, reduces the compound viscosity.

The compounds with VP Si-363 and NXT silane coupling agents show lower Mooney viscosities than those with TESPT. The long alkoxy groups with polyethylene glycol units of VP Si-363 enhance the hydrophobation and so improve silica dispersion as well as to promote the rubber chain mobility around the silica surface<sup>18</sup>, whereas the blocking group in the NXT molecules should also have the same role in enhancing chain mobility and flexibility around the silica particles or aggregates that may result in a reduction of compound viscosity. Furthermore, the bulky side-groups of VP Si-363 and the blocking group of NXT prevent a reaction between the mercapto group and rubber during processing. This is different from TESPT that has polysulphidic linkages which can disproportionate and donate sulphur atoms into the system to generate premature crosslinking during processing and may cause a higher compound viscosity<sup>11,20</sup>. The Payne effect of the silica-filled NR compounds with different compatibilisers is shown in *Figure 1b*. All the compatibilised compounds show similar Payne effects close



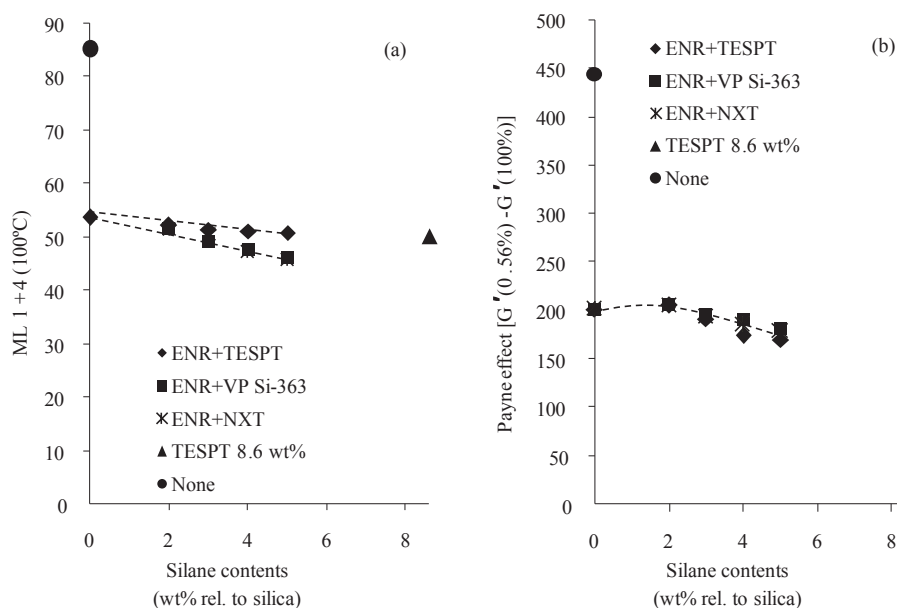


Figure 1. (a) Mooney viscosity and (b) Payne effect of silica-filled NR compounds with 7.5 phr of ENR51 in combination with varying amounts of TESPT, VP Si-363 and NXT.

to that of the reference TESPT compound, indicating that the filler-filler interactions are efficiently replaced by interactions between the epoxy groups of ENR and alkoxy groups of the silanes with the silanol groups on the silica surface. The increase of silane coupling agents to 4-5 wt% relative to silica results in the same level of Payne effect as the compound with optimal TESPT dosage, and all the three types of silanes show no different effect on this property.

### Filler-Rubber Interaction of ENR-Silane Compatibilised Silica-Filled NR

Bound rubber content is a general parameter used to determine the degree of filler-rubber interaction in still unvulcanised compounds. The effects of silane types and concentrations on the bound rubber content of the ENR-compatibilised silica-filled NR compounds are

shown in Figure 2. Therein, Figure 2a shows the chemically bound rubber contents after the treatment with ammonia for cleaving physical interactions, and Figure 2b displays the results of physically bound rubber content.

The addition of ENR51 as compatibiliser in the silica-filled NR compounds increases the chemically bound rubber but decreases the physically bound rubber, attributed to generation of interactions *via* hydrogen bonding and/or chemical bonding during mixing at high temperature between the epoxy groups of ENR and the silanol groups of silica, as schematically displayed in our previous report<sup>4</sup>. The chemically bound rubber contents of the compounds clearly increase with increasing amount of TESPT, NXT and VP Si-363, indicating that remaining silanol groups further interact with the additional functional groups of the silanes, leading to a further increase of silica-rubber interactions.

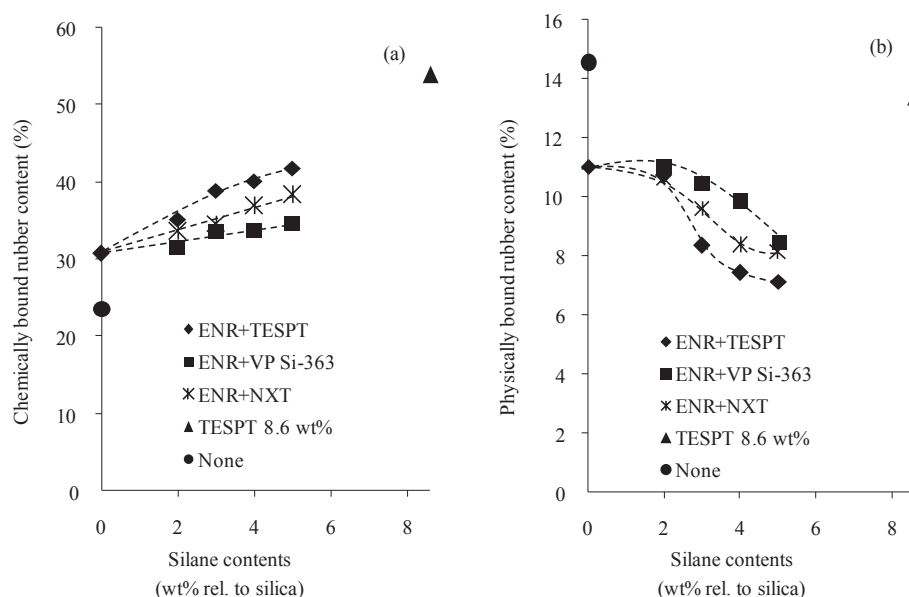


Figure 2. (a) Chemically and (b) Physically bound rubber contents of silica-filled NR compounds with 7.5 phr of ENR51 as compatibiliser in combination with varying amounts of TESPT, VP Si-363 and NXT.

The use of TESPT gives the highest chemically bound rubber content and the lowest physically bound rubber content, while the VP Si-363 gives the lowest chemically bound rubber content and the highest physically bound rubber content of the three silanes. TESPT has a bis-(triethoxy)-structure in which there are more ethoxy groups available to react with the silanol groups of silica. Moreover, the tetrasulphide part may introduce premature scorch during mixing at high temperature<sup>20</sup>. NXT has a triethoxy group and the lowest molecular weight among the three types of silane used in this work. Hence, more ethoxy groups are available for silanisation compared with VP Si-363 which has only 1 ethoxy group in a molecule and the highest molecular weight due to the bulky long alkoxy substituents, as shown in Table 1. As reported by Klockmann<sup>18</sup>, for VP Si-363 the silica-silane reaction proceeds *via* the ethoxy group, while the long dialkoxy groups

with polyethylene glycol parts lead to fast adsorption on the silica surface and increased hydrophobation. This results in the lowest chemically bound rubber content, but the highest physically bound rubber content of the three silanes.

### Cure Properties of ENR-Silane Compatibilised Silica-Filled NR without Sulphur Compensation

Shorter optimum cure times (Figure 3a) are observed when silanes were added to the compound with ENR as compatibiliser, and increasing the silane content of all types leads to a further reduction of the optimum cure time. This is due to a further decrease of free silanol groups by the silanisation reaction on the silica. In the presence of mercaptosilane VP Si-363, the largest reduction of optimum cure times was observed. The bulky substituents



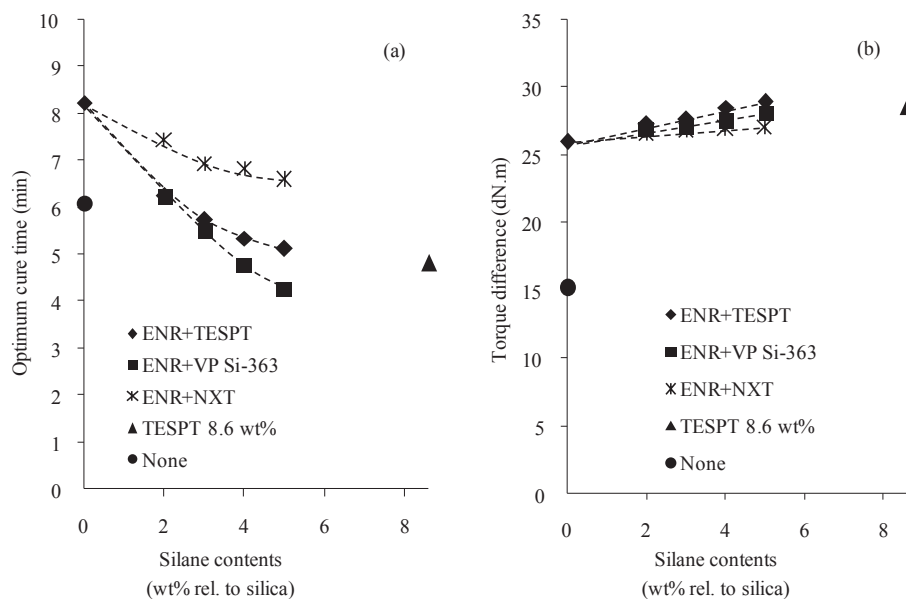


Figure 3. (a) Optimum cure time ( $t_{90}$ ) at 150°C and (b) Torque difference ( $M_H - M_L$ ) of silica-filled NR compounds with 7.5 phr of ENR-51 as compatibiliser in combination with varying amounts of TESPT, VP Si-363 and NXT.

of VP Si-363 prevent the “scorchiness” of the mercapto-group by steric hindrance<sup>18</sup>, but this mercapto-group provides a more efficient coupling with rubber during the vulcanisation reaction when compared with the compounds with ENR and TESPT or NXT. In the presence of TESPT, the vulcanisation reaction is also accelerated by its sulphur donor effect, so it gives shorter optimum cure times when compared to the use of the blocked NXT silane. The compounds with NXT show the longest cure times due to the mercapto-group blocked by the long aliphatic blocking group in the NXT structure, (Table I) that reduces the silane-NR reactivity during processing, so that the silane-NR coupling occurs only during vulcanisation<sup>15</sup>. Figure 3b shows the cure torque difference ( $M_H - M_L$ ) which is closely related to crosslink density in the materials, including both chemical bonds and interactions. It is clearly seen that the use of all compatibiliser types

strongly increases the cure torque difference compared to the non-compatibilised one, and the use of the silane containing a higher sulphur rank, *i.e.* TESPT, gives the highest torque differences, indicating more crosslinks in the vulcanisates.

### Tensile Properties of ENR-Silane Compatibilised Silica-Filled NR

The silica-filled NR vulcanisates with ENR/TESPT combinations as compatibilisers show a remarkable increase of the 100% modulus with increasing TESPT content, as shown in Figure 4a, whereas the ENR/VP Si-363 and ENR/NXT combinations show only a small change in tensile modulus with increasing silane contents. The substantially higher modulus of the vulcanisates with TESPT is caused by the highest filler-rubber interactions in the silica-filled compounds as

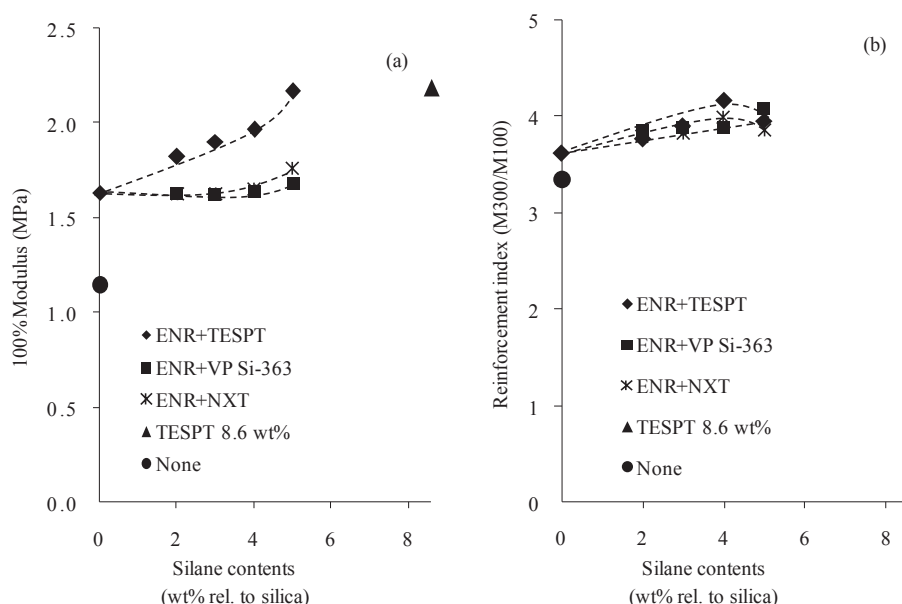


Figure 4. (a) Modulus at 100% and (b) Reinforcement index of silica-filled NR vulcanisates with 7.5 phr of ENR51 as compatibiliser in combination with varying amounts of TESPT, VP Si-363 and NXT.

was indicated by the bound rubber content before vulcanisation (Figure 2), and the higher crosslink density resulting from sulphur released from the TESPT molecule.

The ratio of tensile moduli at 300% to 100% elongation is often used for determining the reinforcement index of silica-filled rubber vulcanisates. As shown in Figure 4b, the reinforcement index of the silica-filled NR vulcanisate with reference TESPT only is remarkably higher than that of all other vulcanisates, and the compatibilisation by using ENR results only in a slightly higher reinforcement index than the fully non-compatibilised one. The introduction of silanes combined with ENR increases the reinforcement index somewhat, but not to the level of TESPT alone. The reinforcement index relates to filler-rubber interactions which were indicated by the chemically bound rubber content before vulcanisation as shown

in Figure 2a. A higher silica-rubber interaction increases the modulus of vulcanisates due to more restriction of chain movement. For the ENR/silane combination, the use of TESPT silane gives the highest reinforcement index among the three types of silanes studied and an optimum value is observed at 4.0 wt% of TESPT relative to silica.

Tensile strength and elongation at break of the silica-filled NR vulcanisates with ENR51/silane combinations as compatibiliser are increased slightly with increasing silane concentrations, as shown in Figure 5. The use of 7.5 phr of ENR51 as compatibiliser apparently leaves some free silanol groups in the system and so the addition of just a small amount of silane coupling agent can further enhance the interaction between the silica and rubber phase through the silanisation reaction. Tensile strength of the silica-filled vulcanisate with optimal content of TESPT is the highest,

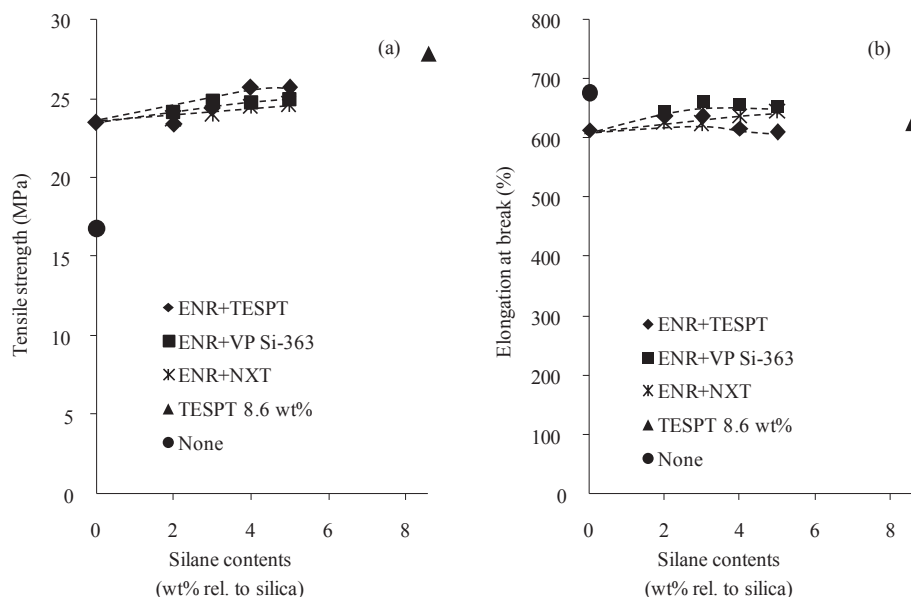


Figure 5. (a) Tensile strength and (b) Elongation at break of silica-filled NR vulcanisates with 7.5 phr of ENR51 as compatibiliser in combination with varying amounts of TESPT, VP Si-363 and NXT.

and the ENR/TESPT combination gives a higher tensile strength than the use of the other two types of silane. The ENR/TESPT system shows an optimum tensile strength when 4.0 wt% of TESPT relative to silica was used, which is still inferior to that of the reference compound with TESPT alone. Overall, the use of different silanes in combination with 7.5 phr of ENR51 results in only small differences in tensile strength and elongation at break, where both properties are only slightly increased with increasing silane loadings.

### Sulphur Compensation for Silica-Filled NR Compatibilised with the ENR51/Silane Combination

Due to the structural differences between the three silane types as shown in Table 1, in which TESPT has average sulphur rank of

3.7 whereas VP Si-363 and NXT have only 1 sulphur atom per molecule, the amount of total sulphur in the compounds which affects the network formation is therefore different. By taking the compound with TESPT of 8.6 wt% relative to silica as a reference, corrections are applied for the other compounds with extra elemental sulphur added together with other curatives on a two-roll mill in the second step of mixing. The silica-filled NR compounds for this study are compatibilised with ENR51 at 7.5 phr and silane at 4.0 wt% relative to silica, *i.e.* 2.2 phr in the formulation (Table 3). The three types of silane coupling agents are used with a sulphur correction to compensate for the sulphur content in the reference compound with TESPT alone. The properties are reported in comparison with those without compatibiliser, with reference TESPT (*i.e.* 8.6 wt% rel. to silica), and with 7.5 phr of ENR51 only.

### Cure Properties of ENR-Silane Compatibilised Silica-Filled NR with Sulphur Compensation

When extra sulphur was added into the silica-filled NR compounds, all of the compounds show a faster cure times and an increase of maximum cure torques as seen in *Figures 6a-b*. The compounds with sulphur corrections show reduced optimum cure times due to an increase of sulphur concentration available during the curing reaction. As previously reported by Kaewsakul<sup>20</sup> that sulphur in TESPT can create premature crosslinks in the NR compounds at a temperature as low as 120°C. The amount of free sulphur available during the curing step can be different even though the total amount of sulphur in the final compound is expected to be the same. The cure behaviours therefore are not the same, as the sulphur released from TESPT can be activated in the internal mixer already, while the corrected sulphur

was added on two roll mill. The correction of the compounds with elemental sulphur relative to the sulphur contained in the reference TESPT system content leads to an increase of crosslink density in the rubber matrix and consequently to an increase of torque differences, as shown in *Figure 6b*. The torque values of the compounds with sulphur correction increase to match or nearly match the level obtained by the use of TESPT in the reference compound. The effect of increasing sulphur content on the increase of maximum torque due to the increased total crosslink density also resulted in an increased glass transition temperature ( $T_g$ ) and decreased fractional free volume of the material, as has been reported<sup>23</sup>. Comparing the three silane types that were used in combination with ENR51, the use of VP Si-363, TESPT and NXT gives optimum cure times in ascending order like in the case of the compounds without sulphur compensation, as previously discussed.

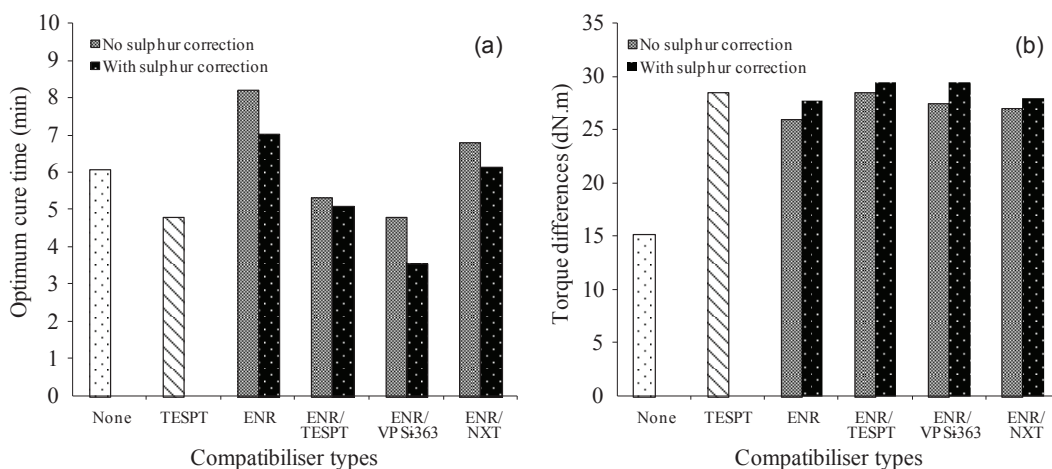


Figure 6. (a) Optimum cure time and (b) Torque differences of silica-filled NR vulcanisates with different combinations of ENR51 (7.5 phr)/silanes (2.2 phr) without and with extra sulphur, compared to the ones without compatibiliser, respectively, with reference TESPT only and with ENR51 alone.

### **Tensile Properties of ENR-Silane Compatibilised Silica-Filled NR with Sulphur Compensation**

The tensile modulus at 100% elongation and reinforcement index of the silica-filled NR vulcanisates with different types of compatibilisers with and without sulphur compensation are shown in *Figures 7a* and *b*. For the combination system, the use of ENR51/TESPT shows the highest 100% modulus and reinforcement index, while the ENR51/VP Si-363 and ENR51/NXT show similar properties. All the compatibilised compounds show very much higher moduli than the compounds without compatibiliser, where the benchmark TESPT gives the highest properties. With the correction of sulphur content in the silica-filled NR compounds relative to the reference TESPT compound, a significant increase of tensile modulus of the vulcanisates is obtained due to an increase in crosslink density. The reinforcement index is also slightly increased by sulphur correction.

Tensile strength of the vulcanisates is also improved somewhat by applying the sulphur correction relative to the reference TESPT compound as shown in *Figure 8a*. In accordance with the modulus, the use of TESPT together with ENR51 gives the highest tensile strength among the three different ENR/silane combinations due to the number of ethoxy groups for interaction with the silanol groups on the silica surface to increase the silica-filler interactions, and the sulphur donated from TESPT molecules to contribute to network formation in the vulcanisates. When compared to the compounds that contain TESPT and the same total sulphur content, the use of TESPT 8.6 wt% relative to silica gives a higher tensile strength than the use of ENR/TESPT with sulphur correction. This may indicate a more effective use of sulphur released from the TESPT molecules during the mixing at high temperature, when compared to the corrected

sulphur that was added on the cold two-roll mill. Due to the higher network density that causes a higher modulus, elongation at break decreases as shown in *Figure 8b*.

### **Dynamic Mechanical Properties of ENR-Silane Compatibilised Silica-Filled NR with Sulphur Compensation**

Storage moduli ( $E'$ ) of the silica-filled NR vulcanisates containing different compatibilisers show only small differences in the glassy region, where the molecular motions are largely restricted. However, the vulcanisates do show their different behaviours in the rubbery region, which is determined by the segmental mobility of the rubber chains. Comparing the silica-filled NR with only TESPT and without compatibiliser, the silica/TESPT system shows higher storage modulus ( $E'$ ) but lower loss modulus ( $E''$ ) after the glass-to-rubber transition as shown in *Figures 9a* and *b*. As previously discussed, the silica/TESPT compound has the strongest filler-rubber interactions by its highest chemically bound rubber content in *Figure 2a* and an increase of crosslink points through silane bridges. This vulcanisate therefore shows higher elastic modulus and better elasticity that leads to lower energy loss under dynamic conditions. The silica-filled NR without compatibiliser that has the highest filler-filler interaction or Payne effect (*Figure 1b*), leads to less elasticity of the material as the rubber being trapped in the filler-filler network and low interfacial interaction between the silica and rubber phases causes loss of energy as dissipated in heat<sup>24</sup>. The incorporation of ENR51 and ENR51/silanes combinations introduces the secondary transition in the range of -10 to 10°C as observed in both the storage and loss moduli curves. This second transition is due to the higher  $T_g$  of ENR vs NR and the damping behaviour of the ENR in the  $T_g$ -transition range. The presence of two  $T_g$ 's

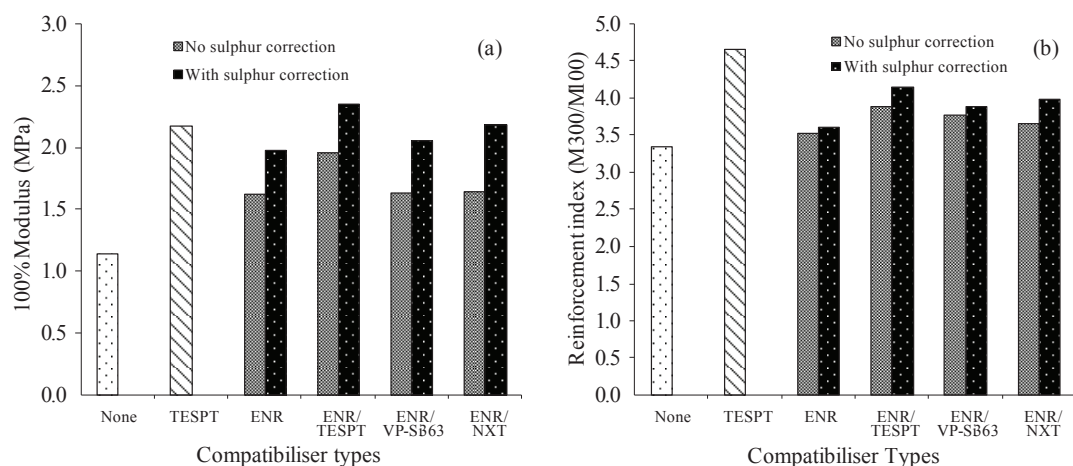


Figure 7. (a) 100% Modulus and (b) Reinforcement index of silica-filled NR vulcanisates with different combinations of ENR51 (7.5 phr)/silanes (2.2 phr) without and with extra sulphur, compared to the ones without compatibiliser, respectively, with reference TESPT only and with ENR51 alone.

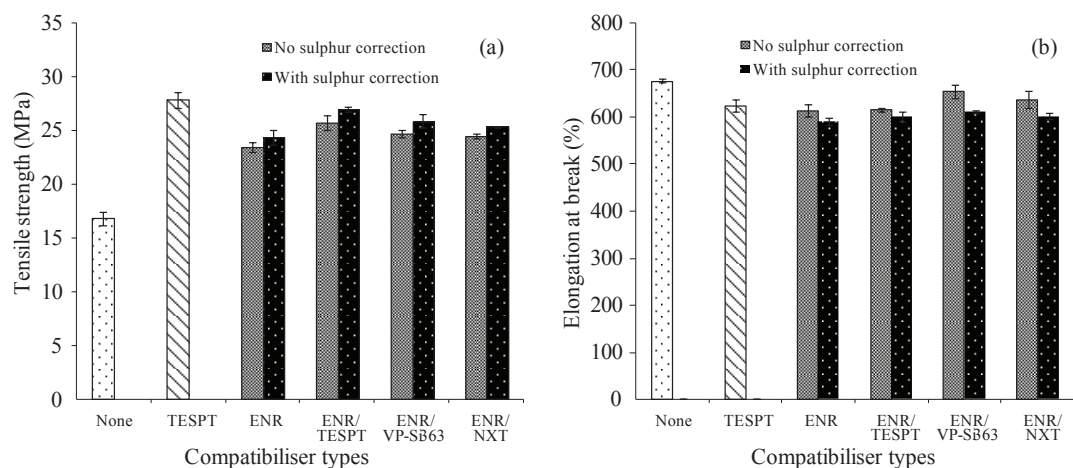


Figure 8. (a) Tensile strength and (b) Elongation at break of silica-filled NR vulcanisates with different ENR51 (7.5 phr)/silanes (2.2 phr) combinations without and with extra sulphur, compared to the ones without compatibiliser, with reference TESPT only and with ENR51 alone.

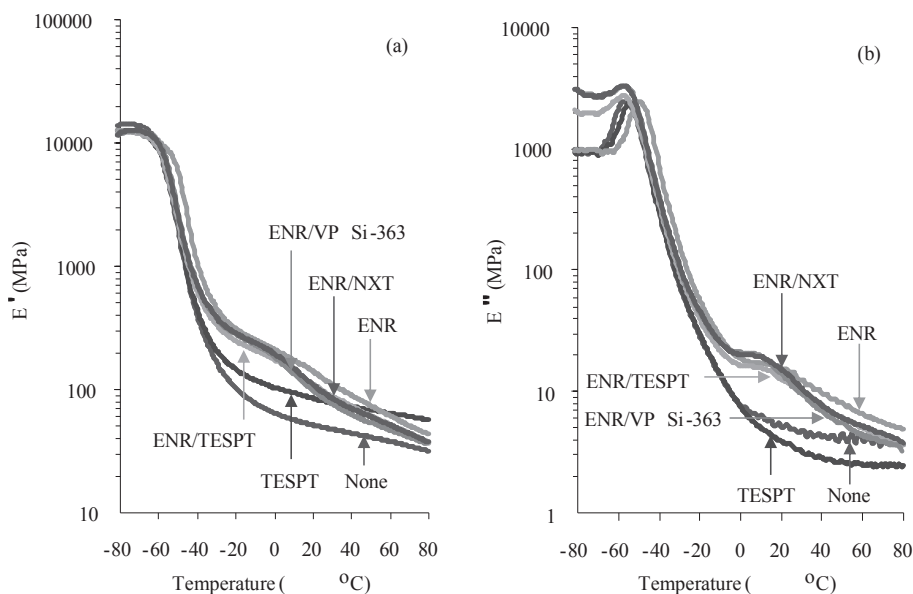


Figure 9. (a) Storage and (b) Loss moduli of silica-filled NR vulcanisates compatibilised with 7.5 phr of ENR51 and 4.0 wt% of silanes relative to silica, with sulphur compensation, in comparison with those vulcanisates without compatibiliser, respectively, with reference TESPT and with ENR51 alone.

confirms that NR and ENR51 are basically immiscible.

The results of  $\tan \delta$  in Figure 10 show that the silica-filled NR with TESPT has the highest  $\tan \delta$  peak due to the improved silica dispersion and less rubber trapped in the silica network, leading to more rubber segments available to be involved in the polymer segmental relaxation in the glassy region<sup>25</sup>. The addition of ENR as compatibiliser in the silica-filled NR decreases the intensity of  $\tan \delta$  peak, as also shown in the values in Table 5. This reduction is caused by the silica-ENR interactions and intermolecular interactions between epoxy groups of adjacent ENR molecules, which results in a restriction of polymer chain relaxations and an increase in the material stiffness. The addition of silane coupling agents together with ENR51 increases the  $(\tan \delta)_{\max}$  values slightly when compared to the

vulcanisate with only ENR51, as summarised in Table 5, because of a further improvement of filler dispersion and less occluded rubber. Among the different compatibiliser types, the  $\tan \delta$  peak of the TESPT-compound is broader towards the rubbery region compared to that of the others as a result of a greater extent of filler-rubber interactions in this material.

The second glass transition peak corresponding to ENR51 is clearly observed for the compounds that are compatibilised with either ENR alone or with ENR/silane. According to Manna<sup>26</sup> ENR with 50 mol% of epoxy groups and 60 phr of silica has a  $T_g$  of about -3 to 1°C. It is observed in Figure 10 that in the presence of silane coupling agents, the second  $\tan \delta$  peak intensity is increased and the peak position shifted toward lower temperature in comparison with ENR51 alone. In the systems with ENR/silane



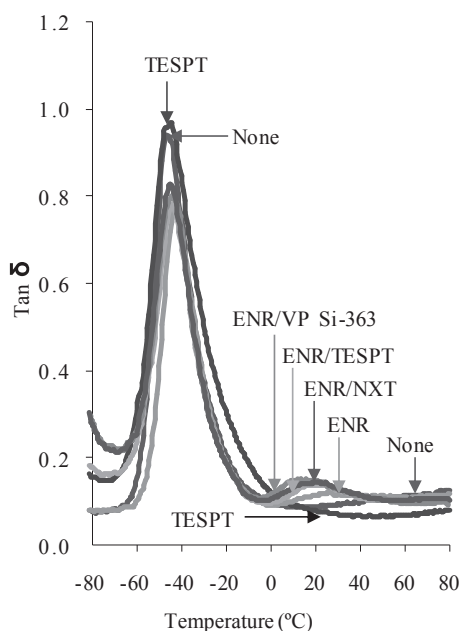


Figure 10. Loss tangent ( $\tan \delta$ ) of silica-filled NR vulcanisates compatibilised with 7.5 phr of ENR51 and 4.0 wt% of silanes relative to silica with sulphur compensation, in comparison with those vulcanisates without compatibiliser, respectively, with reference TESPT only and with ENR51 alone.

TABLE 5.  $T_g$  AND  $\tan \delta$  VALUES AT DIFFERENT POSITIONS TAKEN FROM FIGURE 9

Compatibiliser types	$T_g(^{\circ}\text{C})$		Values of $\tan \delta$		
	at $\tan \delta$ peak	at $E''$ peak	at peak	at $5^{\circ}\text{C}$	at $60^{\circ}\text{C}$
Without compatibiliser	-47	-58	0.94	0.09	0.11
TESPT	-45	-54	0.97	0.10	0.07
ENR-51	-44	-52	0.77	0.09	0.11
ENR-51 +TESPT+S	-45	-57	0.79	0.12	0.10
ENR-51 +VP Si-363+S	-45	-57	0.80	0.13	0.09
ENR-51 +NXT+S	-45	-57	0.82	0.11	0.10

combinations, the silica-silane interactions are promoted together with epoxide-silica interactions. In these cases, there is competition leading to more free epoxide groups in the ENR compared to the silica-filled NR with only ENR as compatibiliser. In the combination system, ENR therefore exhibits its characteristic peak in a more prominent

manner. For the compound with only ENR as compatibiliser, the second  $\tan \delta$  peak is broader and less pronounced because of more interactions between epoxide groups of ENR and silanol groups on the silica, leading to a weaker characteristic peak of ENR. This observation of the change of  $\tan \delta$  peak of ENR as compatibiliser in silica-filled NR due

to the level of filler-rubber interactions was also reported by Saramolee<sup>27</sup>.

The  $T_g$  values taken at both  $\tan \delta$  and loss modulus peaks are summarised in *Table 5* together with the  $\tan \delta$  values at different temperatures. On comparing with the non-compatibilised material, the  $T_g$ 's of the vulcanisates with compatibilisers shift slightly to higher temperature, due to an increase of silica-rubber interactions that restrict the rubber segmental relaxations in the transition region.

For the  $\tan \delta$  values at 5°C and 60°C, the results are plotted in *Figure 11*. According to UNECE regulation no. 117<sup>28</sup>, wet grip grading of tyres should be tested in the temperature range of 5-35°C. *Figure 11a* shows the  $\tan \delta$  values at 5°C of the silica-filled vulcanisates containing different compatibilisers and without. The use of ENR51 together with silane coupling agents gives the highest  $\tan \delta$  values in the temperature range of 5-35°C

which is in the range of the second glass transition associated with the ENR, when compared to the use of TESPT, ENR only and no compatibiliser, respectively. The increased  $\tan \delta$  at low temperature indicates a better wet grip of tyre tread compounds made thereof.

The  $\tan \delta$  value at high temperature, commonly in the range of 40-80°C, indicates tyre rolling resistance. As shown in *Figure 11b*, the incorporation of ENR either with or without silane results in high  $\tan \delta$  values at 60°C which are just slightly lower than that of the compound without compatibiliser. This damping property is again related to the  $T_g$  of ENR51. The high mol% of epoxide groups on the ENR introduces chain stiffness and lower elasticity. Moreover, the different polarity of the two rubber phases leads to blend incompatibility which causes an energy loss at their interface under dynamic deformation. Among the different compatibilisers studied, the use of conventional TESPT in silica-filled NR compounds provides a remarkably low

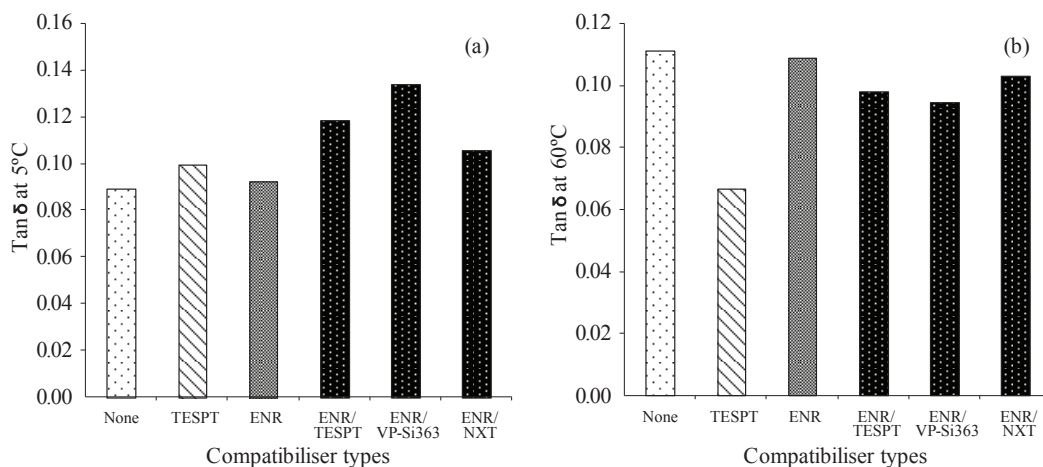


Figure 11.  $\tan \delta$  values at (a) 5°C and (b) 60°C of silica-filled NR vulcanisates with different combinations of ENR51 (7.5 phr)/silanes (2.2 phr) with sulphur correction, compared to the ones without compatibiliser, respectively, with reference TESPT only and with ENR51 alone.

$\tan \delta$  at 60°C, indicating superior low rolling resistance expected for tyre tread compounds.

## CONCLUSIONS

The properties of silica-filled NR compounds compatibilised with 7.5 phr of ENR51 can be further enhanced by the addition of silane coupling agents at a smaller amount compared to the normal use of TESPT. The addition of silanes; TESPT, NXT and VP Si-363, at varying amounts in the range of 2 to 5 wt% relative to silica together with 7.5 phr of ENR51 reduces the compound viscosity slightly but clearly enhances the chemically bound rubber content. Among the three different ENR51/silane combinations, the use of ENR/TESPT gives the highest chemically bound rubber content and tensile properties, whereas the ENR/NXT combination gives higher chemically bound rubber content but similar tensile properties compared to the ENR/VP Si-363 system. The optimum tensile strength is obtained when 7.5 phr of ENR51 with TESPT at 4.0 wt% relative to silica are used. When the amount of silane coupling agent is fixed at 4.0 wt% relative to silica in combination with 7.5 phr of ENR51 as compatibilisers in the silica-filled NR compound, the addition of extra sulphur to correct the total sulphur content relative to the reference compound with TESPT leads to increases of modulus and tensile strength, while elongation at break decreases. The enhanced interactions and bonding between the silica and rubber phases by means of compatibilisers, either without or with sulphur correction, shift the  $T_g$  of the silica-filled NR to higher temperature when compared to the rubber without any compatibiliser. The use of an ENR/silane combination increases the  $\tan \delta$  at 5°C and reduces the  $\tan \delta$  at 60°C compared to the use of ENR51 alone, indicating an improvement in wet traction and rolling resistance of tyre treads made thereof.

Among the three types of silanes studied in combination with ENR51 and sulphur compensation, the use of 2.2 phr TESPT together with 7.5 phr ENR51 provides the best overall properties, but it does not fully match the properties of a compound with TESPT alone at optimal quantity, *i.e.* 4.7 phr. However, in the perspective of the “Magic Triangle of Tyre Technology” where wet skid resistance, rolling resistance and wear are to be optimised, the combination of ENR51, TESPT and sulphur compensation may become a better option for winter tyres that demand good wet grip, providing that this result has yet to be confirmed by real tyre tests.

## ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from the Netherlands Natural Rubber Foundation (Rubber Stichting) and Graduate School of Prince of Songkla University.

*Date of receipt: November 2015*

*Date of acceptance: May 2016*

## REFERENCES

1. WADDELL, W.H. AND EVANS, L.R. (1996) Use of Nonblack Fillers in Tyre Compounds. *Rubber Chem. Technol.*, **69**(3), 377–423.
2. VOET, A., MORAWSKI, J.C. AND DONNET, J.B. (1977) Reinforcement of Elastomers by Silica. *Rubber Chem. Technol.*, **50**(2), 342–355.
3. WOLFF, S. (1996) Chemical Aspects of Rubber Reinforcement by Fillers. *Rubber Chem. Technol.*, **69**(3), 325–346.
4. SENGLOYLUAN, K., SAHAKARO, K., DIERKES, W.K. AND NOORDERMEER, J.W.M. (2014) Silica-Reinforced Tyre Tread

- Compounds Compatibilised by Using Epoxidised Natural Rubber. *Eur. Polym. J.*, **51**, 69–79.
5. GELLING, I.R. (1985) Modification of Natural Rubber Latex with Peracetic Acid. *Rubber Chem. Technol.*, **58**(1), 86–96.
6. BANDYOPADHYAY, A., SARKAR, M.D. AND BHOWMICK, A.K. (2004) Epoxidised Natural Rubber/Silica Nanoscale Organic-Inorganic Hybrid Composites Prepared by Sol-Gel Technique. *Rubber Chem. Technol.*, **77**(5), 830–846.
7. BAKER, C.S.L., GELLING, I.R. AND NEWELL, R. (1985) Epoxidised Natural Rubber. *Rubber Chem. Technol.*, **58**(1), 67–85.
8. MANNA, A.K., DE, P.P., TRIPATHY, D.K., DE, S.K. AND PEIFFER, D.G. (1999) Bonding between Precipitated Silica and Epoxidised Natural Rubber in the Presence of Silane Coupling Agent. *J. Appl. Polym. Sci.*, **74**(3), 389–398.
9. ROCHA, T.L.A.C., ROSCA, C., ZIEGLER, J. AND SCHUSTER, R.H. (2005) Influence of Polymer Polarity on Phase Morphology of NR Blends. *Kautsch. Gummi Kunstst.*, **58**(1-2), 22–29.
10. WANG, M.J. AND WOLFE, S. (1992) Filler-Elastomer Interactions. Part V. Investigation of the Surface Energies of Silane-Modified Silicas. *Rubber Chem. Technol.*, **65**(4), 715–735.
11. TEN BRINKE, J.W., DEBNATH, S.C., REUEKAMP, L.A.E.M. AND NOORDERMEER, J.W.M. (2003) Mechanistic Aspects of the Role of Coupling Agents in Silica-Rubber Composites. *Comp. Sci. Technol.*, **63**(8), 1165–1174.
12. POH, B.T. AND NG, C.C. (1998) Effect of Silane Coupling Agents on the Mooney Scorch Time of Silica-Filled Natural Rubber Compound. *Eur. Polym. J.*, **34**(7), 975–979.
13. SARAMOLEE, P., SAHAKARO, K., LOPATTANANON, N., DIERKES, W.K. AND NOORDERMEER, J.W.M. (2016) Compatibilization of Silica-Filled Natural Rubber Compounds by Combined Effects of Functionalized Low Molecular Weight Rubber and Silane. *J. Elast. Plast.*, **48**(2), 145–163.
14. YAN, H., TIAN, G., SUN, K., ZHANG, Y. AND ZHANG, Y. (2005) Effect of Silane Coupling Agent on the Polymer-Filler Interaction and Mechanical Properties of Silica-Filled NR. *J. Polym. Sci., Part B: Polymer Physics*, **43**(5), 573–584.
15. YAN, H., SUN, K., ZHANG, Y., ZHANG, Y. AND FAN, Y. (2004) Effects of Silane Coupling Agents on the Vulcanisation Characteristics of Natural Rubber. *J. Appl. Polym. Sci.*, **94**(4), 1511–1518.
16. YAN, H., SUN, K., ZHANG, Y. AND ZHANG, Y. (2004) Effects of Mixing Conditions on the Reaction of 3-Octanoylthio-1-propyltriethoxysilane during Mixing with Silica Filler and Natural Rubber. *J. Appl. Polym. Sci.*, **94**(6), 2295–2301.
17. VALENTÍN, J.L., MORA-BARRANTES, I., RODRÍGUEZ, A., IBARRA, L. AND GONZALEZ, L. (2007) Effect of oleyl amine on SBR compounds filled with silane modified silica. *J. Appl. Polym. Sci.*, **103**(3), 1806–1814.
18. KLOCKMANN, O. (2006) Processing of New Rubber Silane VP Si363. *The International Tyre Exhibition & Conference (ITEC) 2006, September 12-14, Akron, OH, paper no. 29B*.
19. BLUME, A. (2011) Kinetics of the Silica-Silane Reaction. *Kautsch. Gummi Kunstst.*, **64**(4), 38–43.
20. KAEWSAKUL, W., SAHAKARO, K., DIERKES, W.K. AND NOORDERMEER, J.W.M. (2012) Optimization of Mixing Conditions for Silica-Reinforced Natural Rubber Tyre Tread Compounds. *Rubber Chem. Technol.*, **85**(2), 277–294.

21. PAYNE, A.R. (1965). A Note on the Conductivity and Modulus of Carbon Black-Loaded Rubbers. *J. Appl. Polym. Sci.*, **9(3)**, 1073–1082.
22. WOLFF, S., WANG, M.J. AND TAN, E.H. (1993) Filler-Elastomer Interactions. Part VII. Study on Bound Rubber. *Rubber Chem. Technol.*, **66(2)**, 163–177.
23. SALGUEIRO, W., MARZOCCA, A., SOMOZA, A., CONSOLATI, G., CERVENY, S., QUASSO, F., GOYANES, S. (2004) Dependence of the Network Structure of Cured Styrene Butadiene Rubber on the Sulphur Content. *Polym.*, **45(17)**, 6037–6044.
24. DA COSTA, H.M., VISCONTE, L.L.Y., NUNES, R.C.R. AND FURTADO, C.R.G. (2002) Mechanical and Dynamic Mechanical Properties of Rice Husk Ash-Filled Natural Rubber Compounds. *J. Appl. Polym. Sci.*, **83(11)**, 2331–2346.
25. QU, L., YU, G., WANG, L., LI, C., ZHAO, Q. AND LI, J. (2012) Effect of Filler–Elastomer Interactions on the Mechanical and Nonlinear Viscoelastic Behaviors of Chemically Modified Silica-Reinforced Solution-Polymerized Styrene Butadiene Rubber. *J. Appl. Polym. Sci.*, **126(3)**, 116–126.
26. MANNA, A.J., DE, P.P. AND TRIPATHY, D.K. (2002) Dynamic Mechanical Properties and Hysteresis Loss of Epoxidised Natural Rubber Chemically Bonded to the Silica Surface. *J. Appl. Polym. Sci.*, **84(12)**, 2171–2177.
27. SARAMOLEE, P., SAHAKARO, K., LOPATTANANON, N., DIERKES, W.K. AND NOORDERMEER, J.W.M. (2014) Comparative Properties of Silica- and Carbon Black-Reinforced Natural Rubber in the Presence of Epoxidised Low Molecular Weight Polymer. *Rubber Chem. Technol.*, **87(2)**, 320–339.
28. UNECE Regulation No 117 (2011) Testing Method for Measuring the Wet Grip Index of C1 Tyres Proposed Amendments. *GRRF 71<sup>st</sup> session, September 13-15*.