Reinforcement Efficiency of Silica in Dependence of different Types of Silane Coupling Agents in Natural Rubber-based Tire Compounds

Introduction

Bis(triethoxysilylpropyl)tetrasulfide (TESPT) has become the state-of-the-art in silica-silane reinforced tire-rubber compounds. The silanization reaction of the ethoxy-groups in TESPT molecules with silanol groups of silica during mixing, and the coupling reaction between silica and rubber molecules during the Vulcanization reaction lead to generation of chemical bonds between silica and rubber [1,2], introducing a double network structure in the filled rubber, i.e. a network between filler and rubber via silane bridges and a crosslinked network generated by the curatives. The use of TESPT provides a good silica dispersion, low Payne effect, good abrasion resistance and mechanical properties, and low tire rolling resistance [2-4]. TESPT itself has some drawbacks however, as the tetrasulfide structure can lead to “scorch” problems and the silanization reaction emits large amounts of ethanol during mixing, being an environmental issue. Alternative silanes such as 3-octanoylthio-1-propyltriethoxysilane (NXT) and 3-mercaptopropyl-di(tridecan-1-oxy-13-penta(ethyleneoxide)) ethoxysilane (VP Si-363) have been introduced. NXT is an octanoyl-blocked mercaptosilane developed to provide a better scorch safety than TESPT [5]. However, the apparent activation energy of the vulcanization reaction of an NXT-containing compound is lower than that of a TESPT-based one, and the apparent activation energy of both compounds decreases with increasing silica concentration [6]. VP Si-363 or 3-mercaptopropyl-di(tridecan-1-oxy-13-penta(ethyleneoxide)) ethoxysilane is a mercaptosilane containing one ethoxy-group and two long alkyl groups. It has been reported that the presence of the thiol-group or the mercaptosilane structure can increase the possibility of adsorption of this silane on the silica surface leading to a faster silane-silica reaction when compared to a mercaptosilane with short chain alkyl groups [7]. Compared with the use of TESPT, the incorporation of VP Si-363 into silica-filled styrene-butadiene rubber (SBR)/butadiene rubber (BR) blends for tire compounds improved the rolling resistance of a tire by 13% and reduced Volatile Organic Compounds (VOC): ethanol emission by 80% [8,9]. A study on nanoclay-filled rubber showed that VP Si-363 has a smaller effect on tensile modulus than TESPT, which is possibly due to the bulky alkyl groups of VP Si-363 that take more space when bonded to the clay surface and restrict the number of bonds between silane and filler [10].

Naturkautschuk · Silane · Silan-Haftvermittler · Verstärkung · Reifen

Verstärkungseffizienz von Kieselsäure in Abhängigkeit verschiedener Silan-Koppelungsagenzien in Naturkautschuk-basierenden Gummi-mischungen

Introduction

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Authors

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In addition to the mercapto-silanes, there are many other types of silane coupling agents that have been tested for silica-filled polymers, and also for some other purposes, to include amino-silanes, cyano-silanes, vinyl silanes, etc. Vinyl silanes such as vinyltrimethoxysilane (VTMS) and vinyltriethoxysilane (VTES) are applied for moisture crosslinking of polyolefins in order to improve their properties and expand the applications of these materials [11-14]. In rubber, vinyl-silanes are commonly used to improve the properties of inorganic filler-filled ethylene-propylene rubber (EPM) and ethylene-propylene-diene rubber (EPDM) with a peroxide vulcanization system. Vinyl-silane containing formulations show a remarkable improvement in modulus, tensile and tear properties, filler dispersion and dynamic mechanical properties of these materials [15,16]. Besides a good interaction between filler and rubber as a result of the silanization reaction, the vinyl-group in the silane structure can also react with free radicals on rubber molecules during peroxide vulcanization [16] leading to strong bonding between filler and rubber, as reflected in good static and dynamic properties of the filled rubber.

This present work studies the effect of different types of silane coupling agents: NXT, VP Si-363 and VTES, on the properties of silica-filled NR by applying two sets of compounds based on equal molar and on equal alkoxy-functional groups relative to the reference compound with TESPT. The reinforcing efficiency of silica in combination with the different silanes in NR compounds is compared.

**Experimental Materials**

The compounding ingredients were natural rubber (Ribbed Smoked Sheet (RSS) #3), locally produced in Thailand; highly dispersible silica (Zeosil 1165MP, Solvay, France), treated distillate aromatic extract oil (TDAE-oil, Hansen & Rosenthal, Germany), N-cyclohexyl-2-benzothiazole sulfenamide (CBS), diphenyl guanidine (DPG) and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) (all from Flexys, Belgium), ZnO, stearic acid and sulfur (all from Sigma-Aldrich Chemie, Germany). Four different types of silanes were used: bis-(triethoxysilyl)propyltetrasulfide (TESPT) (Evonic, Germany), 3-Octanoylthio-1-propyltriethoxysilane (NXT) (Momentive, USA), 3-Mercaptopropyl-di(tridecan-1-oxy-13-penta(ethyleneoxide))ethoxysilane (VP Si-363) (Evonik, Germany) and Vinyltriethoxysilane (VTES) (Evonik, Germany). All ingredients were used as received. The chemical names, structures and molecular weights of the silanes used in this study are shown in Table 1.

**Compound formulations and mixing procedures**

Compound formulations are shown in Table 2. The amounts of NXT, VP Si-363 and VTES silanes were calculated to either molar or alkoxy-groups equivalents to that of the reference compound with TESPT. All the compounds were mixed following the mixing procedures as described in previous work.
The first mixing step of silica-filled NR compounds was performed using an internal mixer, Brabender® 50EHT, (Brabender® GmbH & Co.KG, Germany) with a mixing chamber volume of 70 cm³. The initial mixer temperature setting was 100 °C in order to reach a discharge temperature in the range of 135–150 °C, as required by Kaewsakul et al. [17], that is the temperature range providing optimal overall properties of the silica/silane-filled NR compounds.

**Testing of compound and vulcanizate properties**

**Mooney viscosity and Payne effect.** Mooney viscosity [ML(1+4), 100 °C] was tested by using a Visc Tech+ (Tech-Pro Inc., USA) according to ASTM D1646. The Payne effect [18] or filler-filler interaction of the final compounds (with curatives) was analyzed by using a Rubber Process Analyzer (RPA2000, Alpha Technologies, USA) at 100 °C, frequency 0.5 Hz and varying strains from 0.56% to 100%

**Bound rubber content.** Uncured compound (without curatives) was cut into small pieces for 0.25 g, 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 h. The bound rubber content was then calculated using the following equation [19]:

\[
\text{Bound rubber (¥)} = \frac{(m_0 - m_f)}{m_f} \times 100
\]

Where \(m_0\) is the weight of sample after extraction, \(m_f\) is the weight of silica in the sample and \(m_i\) is the original weight of elastomer in the sample.

**Cure characteristics, vulcanization and tensile properties.** Cure characteristics of the silica-filled NR compounds were analyzed by using a Moving Die Rheometer (MDR) (RheoTech MD+, Tech-Pro Inc., USA) at 150 °C for 30 minutes at a frequency of 1.67 Hz and 14% strain. The compounds were cured to their respective optimal cure times (\(t_90\)) at 150 °C with compression molding (Chaicharoen Karnchang Ltd., Thailand). The vulcanized 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.

**Dynamic mechanical analysis.** The loss tangent or tan \(\delta\) as function of temperature of the silica-filled NR vulcanizates was determined using a dynamic mechanical thermal analyzer, DMTA V (Rheometric Scientific, USA). The samples were tested in tension mode in the temperature range from -80 °C to 80 °C at a frequency of 10 Hz and 0.01% strain.

**Results and discussion**

**Mixing behavior**

The processability of the rubber compounds can be determined by their mixing behavior and the torques generated during mixing, which is associated with the compound viscosities. The plots of mixing torques versus mixing time of the compounds with equal molar or alkox-y-functional groups of NXT, VP Si-363 and VTES compared to TESPT respectively, are shown in Figs. 1–3. The mixing torque of the filled compounds largely depends on the level of filler dispersion. By using a bifunctional silane with alkox-y groups, the silanization reaction between the alkoxy groups of the silane and the silanol groups of the silica takes place in the mixer. A TESPT-molecule contains on average 3.7 sulfur atoms and two sides of triethoxy groups that can effectively react with the silanol groups on the silica surface under optimum mixing conditions. It has been reported that premature crosslinks created by the sulfur in TESPT in silica-filled NR compounds showed a positive effect on silica dispersion as it helped to suppress
filler flocculation [17]. The NXT, VP Si-363 and VTES are also bifunctional silanes with different chemical structures, which may have an influence on the reactivity towards the silanization and later on the coupling reaction with the rubber. Fig. 1 shows the mixing torques of silica-filled NR compounds without silane coupling agent, with TESPT, and with NXT at two different contents based on equal molar and equal ethoxy-groups relative to TESPT. As expected, the silica-filled NR compound without silane coupling agent clearly shows the highest mixing torque, related to the highest compound viscosity due to strong filler-filler interactions that cause formation of a filler-filler network of silica aggregates and restricts the mobility of the elastomers. Moreover, some parts of elastomer are trapped inside the silica network, i.e. occluded rubber. The silica-silica network and a high amount of occluded rubber contributes to the shear modulus of the uncured compounds [20], that reflects in the mixing torque. The incorporation of silane coupling agents in the silica-filled compounds clearly improves the compound processability as seen in the reduction of mixing torques especially after the addition of the second half of the filler plus silane and oil, as a result of improved silica dispersion and presence of the process oil. At the beginning, the silane addition is comparable to a plasticizer: it reduces the viscosity. At the end of the mixing cycle, the compound with NXT at equal ethoxy-functional groups to TESPT shows a slightly lower mixing torque compared to the reference compound with TESPT. The use of VP Si-363 at both loadings in the silica-filled NR compounds results in a much lower mixing torque than the compound with TESPT, as seen in Fig. 2. The mixing torque decreases with increasing amount of VP Si-363 and the difference in mixing torques can be clearly observed in the second interval of silica addition already, indicating a very fast dispersion of silica in the rubber matrix. As reported by Blume [7], the presence of the SH-group and two long alkoxy groups in VP Si-363 increases the rate of reaction with the silica due to the increase of adsorption possibilities to the silanol-groups which can occur via the ethoxy-group and different oxygen atoms inside the alkoxy chain through hydrogen bonding, as proposed in Scheme 1. Besides the reaction between the ethoxy-group and the silanol-group, the long alkoxy chains that shield the silica surface promote the silica dispersion and improve the processability of the silica-filled rubber compound. In contrast to the other two silanes, the addition of vinyl-silane VTES results in final mixing torques which are higher than for the compound containing TESPT, but still lower than without silane, as shown in Fig. 3. As the silane molecule reacts with the silica via the ethoxy groups and the chemical structure of the whole silane influences its kinetic behavior [7], the VTES with the short vinyl function that gives less steric hindrance compared to NXT and VP Si-363, should provide a better reactivity towards the silanol groups. According to the study by Blume [7] with a model compound, the rate of the beginning reaction of VTES is slightly higher than for VP Si-363 and clearly higher than for TESPT. Despite this higher rate, the compound with VTES shows a higher mixing torque, i.e. higher viscosity. The smaller steric effect of VTES molecules leads to a lesser shielding effect on the silica surface. Moreover, there may be a loss of some ethoxy-groups of VTES through the hydrolysis-reaction with moisture and a subsequent condensation reaction with neighboring ethoxy-groups due to their high reactivity, as shown in Scheme 2. For TESPT the bulky molecule introduces steric hindrance and reduces the rate of condensation between its own molecules, and in addition TESPT has a larger shielding effect on the silica surface compared to VTES, resulting in the possibly better silanization efficiency and filler dispersion. The incorporation of rigid filler particles into rubber compounds increases the viscosity and impedes the flow of elastomer molecules, causing a higher mixing energy and an increase of compound temperature due to generated heat. The silanization reaction between the alkoxy-groups of the

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Silane content (mmol)</th>
<th>Specific energy (kJ/g)</th>
<th>Discharge temperature (°C)</th>
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<tbody>
<tr>
<td>Without silane</td>
<td>-</td>
<td>4.37</td>
<td>156</td>
</tr>
<tr>
<td>TESPT</td>
<td>8.8</td>
<td>3.43</td>
<td>144</td>
</tr>
<tr>
<td>NXT 1x</td>
<td>8.8</td>
<td>3.48</td>
<td>144</td>
</tr>
<tr>
<td>VP Si-363 1x</td>
<td>8.8</td>
<td>3.13</td>
<td>138</td>
</tr>
<tr>
<td>VTES 1x</td>
<td>8.8</td>
<td>3.89</td>
<td>148</td>
</tr>
<tr>
<td>NXT 2x</td>
<td>17.6</td>
<td>3.32</td>
<td>142</td>
</tr>
<tr>
<td>VP Si-363 2x</td>
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<td>2.94</td>
<td>134</td>
</tr>
<tr>
<td>VTES 2x</td>
<td>17.6</td>
<td>3.80</td>
<td>146</td>
</tr>
</tbody>
</table>
silanes and the polar silanol groups of silica leads to less filler-filler interaction and improvement of silica dispersion in the rubber matrix, and consequently affects compound viscosity and mixing torque [3]. Based on the mixing torque data, the mixing energy (kJ/m/kg) was obtained and the specific energy in units of (kJ/g) for each compound was calculated: the values are summarized in Table 4. As already observed in the mixing torque curves in Figs. 1-3, the use of silane coupling agents reduces the mixing torques and the specific energy is lower in accordance with the mixing torques or compound viscosity. Lower viscosity generates less shearing heat during mixing and results in a lower discharge temperature, as also shown in Table 4. Among the four types of silanes, VP Si-363 gives the lowest specific mixing energies and discharge temperatures. The use of higher silane contents in the compounds in case of functional groups-equivalence to TESP leads to less mixing energy and lower discharge temperature. 

An additional factor to be considered is the large difference in absolute amounts of silanes added on basis of the equi-molar or equal alkoxy-functional groups. Some of the mixer-torque differences and corresponding viscosity effects can also be related to different plasticizer effects. Mooney viscosity, Payne effect and bound rubber content

The properties of filled uncured compounds generally correspond to the levels of filler dispersion, filler-rubber interaction and the occurrence of a filler-filler network. Mixing of silica into NR or other hydrocarbon rubbers is known to face difficulties arising from the strong silica-silica interactions and poor silica-rubber compatibility. Different compatibilizers or silane coupling agents will have a different efficiency in silica-filled NR compounds which affects the properties of the compounds.

Mooney viscosities of the silica-filled NR compounds silanized with different types of silane coupling agents are shown in Fig. 4. The silica-filled NR compound without silane shows a significantly higher Mooney viscosity than all other compounds in accordance with the mixing torque results, as discussed previously. At the same molar content, the compound with TESP shows the lowest Mooney viscosity indicating its superior flow due to the good silica shielding by the six ethoxy-groups. Among the compounds with silanes, the use of VTES gives the highest compound Mooney viscosity, independent of whether it was used at either molar or ethoxy-functional equivalents to TESP. This poorest efficiency of VTES to enhance filler dispersion, by means of silanization and shielding of the silanol groups, despite its high reactivity due to less steric effects, may be attributed to the possibility of self-reaction between the VTES molecules as discussed before. Moreover, after the silanization of the silica the short vinyl-group on the other side of the VTES molecule cannot promote molecular chain movement like in the case of the long fragments of NXT and VP Si-363 molecules.

At equal molar basis, the Mooney viscosity of the compound with TESP is lower than with VP Si-363 and NXT, but at equal ethoxy-functional groups content the compound with VP SI-363 shows the lowest Mooney viscosity of all. The addition of VP Si-363 results in a lower Mooney viscosity than the use of NXT, because besides the silanization reaction of the silica, two long alkoxy groups with different oxygen atoms promote the adsorption of silane on silica via hydrogen bonding, as shown in Scheme 1 [7]. The efficient shiel-
ding of the silica surface and the long alkyl chains enhance the mobility of rubber chains around silica aggregates leading to the low compound viscosity. Furthermore, this compound contains the largest amount of coupling agent in absolute weight terms. Fig. 5(a) shows the Payne effect or filler-filler interaction of the silica-filled NR compounds. The difference of storage modulus $G'$ at 0.56% and 100% strain is presented, which clearly shows a strong filler-filler interaction of the compound without silane and only a small reduction of the Payne effect by the use of VTES. Increasing the VTES-content reduces the Payne effect, but it remains still very much higher than with the use of TESPT, VP Si-363 and NXT which can effectively diminish the filler-filler interactions in the compounds. The lower filler-filler interaction, i.e. less filler-filler networking and better dispersion of the silanized silica-filled compounds with TESPT, NXT and VP Si-363 is in good agreement with the compound viscosities: Fig. 4, and mixing torques: Figs. 1-3, as previously discussed. With equal alkoxy-group content, NXT gives even a lower Payne effect compared to TESPT. This difference may be caused by the smaller size and less steric hindrance of the NXT molecules compared to TESPT, which leads to an easier reaction between the alkoxy-group of NXT-silane and the silanol groups of silica. Another effect is that TESPT can couple two silica-aggregates which increases the viscosity again. The interactions between silica and the rubber phase promoted by silane can be proved by the chemically bound rubber content [19] in the silica-filled NR compounds as shown in Fig. 5(b). Among the various types of silane studied, the silica-filled NR compound with TESPT shows the highest chemically bound rubber content, whereas the compounds with NXT and VP Si-363 display similar values lower than for TESPT but still higher than for the mixes with VTES and without silane. The good filler-rubber interactions in the compounds with the sulfur containing silanes, i.e. TESPT, NXT and VP Si-363, is not only the result of an efficient silanization reaction but also because of an increase of the adsorption possibility on the silica surface by thiols. The exceptionally high chemically bound rubber content in the TESPT compound can be attributed to the tetra-sulfide structure that can donate free sulfur into the system to generate some crosslinks in the compound during mixing, as previously demonstrated by Kawsakul et al. [17] The lowest chemically bound rubber contents of the compound with VTES confirms that it has the lowest efficiency due to its minor shielding effect for use with silica in NR-compounds. The decrease of the chemically bound rubber contents in the VP Si-363 silanized silica-filled NR compounds when the amount of silane was increased could be due to its molecular structure that has long alkoxy-groups. The ethoxy-groups will react with silanol-groups of the silica, although the oligomeric poly(ethylene-oxide) side arms will also react to some extent, in the same manner as poly(ethylene-oxide) by itself can act as a shielding agent for silica.
The two long alkoxy chains per molecule should also improve the rubber chain mobility around the silica aggregates and cause more loose chains to be dissolved in toluene during the bound rubber content measurement. The different structures of silanes on the silica surface after silanization and the linkages between silane and rubber chains caused by either premature scorch in the TESPT compound or after vulcanization in the compounds with TESPT, NXT and VP Si-363, are proposed in Scheme 3. The lateral condensation of silanes attached to adjacent isolated silanol-sites as depicted in this Scheme has often been quoted in literature. But, based on molecular modeling, for steric reasons [21] this reaction can only take place for a minimum distance >4 Å, which surpasses the distance between adjacent silanol-sites by a factor of appr. 2.

Cure characteristics

NXT silane is a mercapto silane with a carboxylic blocking group to retard the reactivity of the mercapto-group. Basically, the NXT-compound is more stable at high temperature than TESPT, providing a better scorch safety. As reported by Yan et al. [6], the scorch time of a NR compound with NXT is longer than that with TESPT due to the bonding dissociation energy of NXT, which is higher than that of TESPT. However, the apparent activation energy of vulcanization of the compound with NXT is lower than that with TESPT at a given concentration due to the steric hindrance of NXT which is less than for TESPT. From the cure curves of silica-filled NR compounds in Fig. 6(a) the compound without silane coupling agent clearly shows silica flocculation which means re-agglomeration of silica under shear conditions at high temperature [22]. The addition of TESPT and NXT suppresses silica flocculation and so decreases the filler-filler interaction. The use of NXT and TESPT silanes at the same molar contents results in a similar rheometer minimum cure torque (ML) in which the NXT compound shows a little silica flocculation, but after vulcanization, the maximum cure torque (MH) and torque difference (MH-ML) of the NXT compound is lower than that of the TESPT compound, as shown in Fig. 6(b). Increase of the NXT silane loading in order to have the same amount of alkoxy-groups as TESPT leads to a significant decrease of ML without a sign of silica flocculation and longer induction period prior to vulcanization, as well as a lower MH due to its plastization in combination with silanization-effects. The scorch time of the silica-filled NR compound without silane is longer than that of the compound with TESPT due to the polar character of the silica surface that adsorbs the polar curatives and results in cure retardation as well as a lower vulcanization efficiency. In contrast, the addition of NXT-silane gives a longer scorch time than the compounds without silane and with TESPT, respectively, due to the carboxylic blocking groups in the NXT-structure that results in more thermal stability than the TESPT silane. The higher sulfur rank of TESPT with lower bom-
ding energy of S-S in TESPT compared to the C-S in NXT also leads to a higher reactivity of TESPT towards coupling with rubber during the vulcanization reaction. TESPT may “donate” some of its sulfur to the compound, to implicitly raise the amount of free sulfur and consequently give extra crosslinking. NXT cannot do that. Fig. 7(a) shows the cure curves of silica-filled NR compounds with two different amounts of VP Si-363 in comparison with that of the compounds with TESPT and without silane. The reactive mercapto-group in the VP Si-363 molecule leads to a very fast curing reaction as seen by the shorter scorch and cure times compared to the compound with TESPT, as can be seen in Fig. 7(b). The compounds with VP Si-363 show a lower minimum torque than that with TESPT and no silica flocculation. Increasing the amount of VP Si-363 drastically reduces the cure torque maximum and torque difference, which may be caused by the plasticizing effects of the large absolute amount of VP Si-363 and the long alkoxy-groups, leading to a reduction of stiffness of the final vulcanizate. Again, TESPT outperforms VP Si-363 in maximum torque due to its sulfur donating effect. The silica-filled NR compounds with VTES silane show a reduction of silica flocculation with increasing VTES content, but the flocculation phenomenon still clearly exists even in the compound with ethoxy-groups equivalent to TESPT in accordance with the high Payne effect: Fig. 5(a), and low chemically bound rubber content: Fig. 5(b). As discussed previously, the small molecule of VTES can easily react with the silanol groups of silica but not properly shield the silica surface. As observed in Figs. 8(a) and (b), increasing the amount of VTES has only little effect on the cure behavior of the compounds. The absence of sulfur in the VTES/silica compound leads to a lack of coupling reactions via the sulfur atoms and consequently lower network density, resulting in a lower maximum cure torque and torque difference compared to the TESPT compound. The compound without silane has a filler-filler network that results in a higher maximum torque $M_h$, compared to the one with VTES, but due to its higher minimum torque $M_l$, the torque differences ($M_h-M_l$) of the compounds without silane and with VTES are similar. During vulcanization via a radical mechanism, the vinyl-part may be bound to the rubber molecules, but this apparently does not happen to a significant extent as sulfur vulcanization is not a radical reaction.

**Tensile and dynamic mechanical properties**

Fig. 9 shows the 100%-modulus and reinforcement index of the silica-filled NR vulcanizates containing different types of silanes in which the one with TESPT shows the highest modulus, in correspondence with its highest chemically bound rubber: Fig. 5(b), and maximum cure torques: Figs. 6-8. Compared with NXT and VP Si-363 silanes, either at equal molar or number of alkoxy-groups, TESPT gives a much higher tensile modulus due
to a higher crosslink density, because of its higher sulfur content and sulfur donating ability. The lower bonding dissociation energy of TESP compared to NXT and VP Si-363 leads to a faster and easier reaction with rubber. The bonding dissociation energy in sulfur-containing silanes is: C-S-C 285 kJ/mol; C-Sx-C (where x ≥ 2) < 268 kJ/mol; S-S ≈ 134 kJ/mol [6,23]. Consequently, there are more chemical bonds between TESP and rubber and a higher crosslink density because of the extra sulfur donated by TESP leading to a higher modulus. At equal moles of silanes used, the vulcanizates with NXT and VP Si-363 silanes show significantly lower moduli compared to that with TESP, but clearly higher than that with VTES. The differences in tensile modulus of the vulcanizates containing different silane types resemble the differences in chemically bound rubber content, as shown in Fig. 5(b). The inferior modulus of the vulcanizate with VTES demonstrates that it suffers from absence of coupling reaction even though it shows some improvement in the properties of uncured compounds such as the Payne effect, compared to the compound without silane. The tensile strength of the silica-filled NR vulcanizates having different types of silane coupling agents as shown in Fig. 10(a), shows the same trend as that of the 100 % modulus: Fig. 9(a) in accordance with the chemically bound rubber content: Fig. 5(b). TESP gives the highest tensile strength compared to the other silanes. However, the addition of NXT silane at equal amount of alkoxyl groups also results in a tensile strength at the same level as the use of TESP. At the same molar equivalents to TESP, NXT and VP Si-363 give vulcanizates with the same level of tensile strength, slightly lower than TESP. But an increasing amount of VP Si-363 decreases the tensile strength like for the 100 % modulus. The use of TESP, NXT and VP Si-363 significantly increases the chemically bound rubber content compared to the non-compatibilized compound, and consequently there is a large increase seen in tensile strength and 300 %-modulus. The use of TESP gives the highest chemically bound rubber content and the highest tensile strength and 300 %-modulus of the silica-filled NR vulcanizates. The addition of VTES causes no change in the chemically bound rubber content and even slightly lowers the tensile strength and 300 %-modulus.
compared to the compound without silica. It is worth to note that the use of NXT and VP Si-363 gives comparable tensile strengths but lower moduli compared to the use of TESPT. For tire applications or mechanical goods for use under dynamic conditions, dynamic mechanical properties are of great importance. The key tire performances, i.e. wet grip, rolling resistance and wear, are all related to these dynamic mechanical properties. Basically, wet grip refers to breaking ability for tires [24], and rolling resistance is a measure of the amount of energy consumed over distance travelled. Herein, tan δ values at 5 °C and 60 °C may respectively be used to indicate wet grip and rolling resistance, as shown in Figure 12. Fig. 12(a) shows the tan δ at 5 °C of the silica-filled NR compounds with different types of silane coupling agents in which the use of TESPT gives the highest tan δ at 5 °C, whereas the addition of VTES results in the lowest tan δ at 5 °C, even below the value of the compound without silica. The Vulcanizates with NXT and VP Si-363 show a higher tan δ at 5 °C compared to the one without silica, and the values are increased with increasing concentration of the silanes. The results indicate that silica-filled NR vulcanizates with TESPT, NXT, and VP Si-363 should provide a better wet grip than that without silica. It should be noted though that based on a recent study [25] on the correlation between tan δ at 0 °C and factual friction performance of tire compounds, in spite of the commonly accepted assumption that the tan δ at 0-20 °C is indicative of wet grip, this has to be taken with reserve and does not generally hold. The tan δ values at 60 °C of the silica-filled NR vulcanizates are shown in Fig. 12(b). For energy saving tires, this value should be low for reduction of heat build-up and decreased hysteresis loss of tires. The results in Fig. 12(b) clearly demonstrate that the silica-filled NR without silica coupling agent shows the highest tan δ value at 60 °C due to poor filler-rubber interactions and thus inferior energy transfer as well as poor reinforcing efficiency. The use of TESPT gives the best low tan δ at 60 °C, implying the best low rolling resistance of a tire compound. Several factors contribute to this. The best filler-rubber interactions as indicated by the chemically bound rubber content: Fig. 5(b); and the highest crosslink density as implied by the highest cure torque difference: Figs. 6-8, due to the earlier mentioned “sulfur donation” of TESPT. The use of NXT and VP Si-363 lowers the tan δ value at 60 °C compared to the filled rubber with no silica, where both types of silanes give similar tan δ values. Increasing the NXT and VP Si-363 contents in order to provide equal amounts of alkyox groups to the reference TESPT slightly decreases the tan δ at 60 °C, which may be caused by a better filler dispersion. Based on the overall results, TESPT is the best silane coupling agent in this study for silica-filled NR compounds providing outstanding filler-rubber interaction, mechanical and dynamic properties. The mercaptosilanes NXT and VP Si-363 also efficiently reduce the filler-interaction, enhance the compound properties, i.e. lower Mooney viscosity and improve cure behavior, but give somewhat inferior mechanical and dynamic properties compared to TESPT, most likely due to a lower degree of crosslinking than for TESPT, which “donates extra sulfur” to the curing package. The difference could probably partly or totally be overcome by adding some extra sulfur to the pertinent formulation. VTES is not an effective silane coupling agent for this sulfur-cross-linked system as it results in no improvement in properties compared to the compound without silica.

Conclusions
The comparative study of the compound and vulcanize properties of silica-filled NR compounds silanized by four types of silane coupling agents, i.e. TESPT, NXT, VP Si-363 and VTES, shows their different effects on the reinforcement of silica in NR. Among the four silane types, VTES gives the poorer overall properties due to its poor shielding efficiency and the vinyl group that is difficult to couple with NR rubber chains in the presence of sulfur. The use of NXT and VP Si-363 shows a good improvement in compound properties, i.e. mixing energy, Mooney viscosity, cure behaviors, bound rubber content, and an increase of mechanical and dynamic mechanical properties compared to that without silica, but the properties are somewhat inferior to the use of TESPT, mainly due to lower crosslink densities compared with TESPT which has an intrinsic “sulfur donating” effect.

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References