# Silane grafted natural rubber and its compatibilization effect on silica-reinforced rubber tire compounds

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**Abstract.** Natural Rubber (NR) grafted with 3-octanoylthio-1-propyltriethoxysilane (NXT) was prepared by melt mixing using 1,1′-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane as initiator at 140 °C with NXT contents of 10 and 20 parts per hundred rubber [phr] and initiator 0.1 phr. The silane grafted on NR molecules was confirmed by Fourier transform infrared (FTIR), proton nuclear magnetic resonance ($^1$H-NMR) and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM-EDX). Based on $^1$H-NMR, the use of 10 and 20 phr (parts per hundred resin) of silane resulted in grafted NXT onto NR of 0.66 and 1.32 mol%, respectively, or a grafting efficiency of approx.38%. The use of NXT-grafted NR as compatibilizer in silica-filled NR compounds, to give a total amount of NXT in both grafted and non-grafted forms in the range of 0.8–6.1 wt% relative to the silica, decreases the Mooney viscosity and Payne effect of the compounds, improves filler-rubber interaction, and significantly increases the tensile properties of the silica-filled NR-compounds compared to the non-compatibilized one. At the same silane-content, the use of silane-grafted NR gives slightly better properties than the straight use of the same silane. With sulfur compensation, the use of NXT-grafted-NR with about 6 wt% NXT relative to the silica gives technical properties that reach the levels obtained for straight use of bis-(3-triethoxysilyl-propyl)tetrasulfide (TESPT) at 8.6 wt% relative to the silica.

*Keywords: rubber, reinforcement, natural rubber, silica, silane grafted NR*

## 1. Introduction

Silica has a hydrophilic surface by its specific character of a large number of surface silanol groups, i.e. 4.9 OH·nm$^{-2}$ [1], leading to strong hydrogen bonding between silica particles and poor filler-rubber interactions in non-polar elastomers. In general, a silane coupling agent is added together with silica into a rubber during the mixing process to enhance the silica-rubber compatibility. Under suitable mixing conditions, the silane coupling agent undergoes a silanization reaction with silanol groups on the silica involving primary and secondary reactions [2]. To complete the reaction between silica and, for example,

bis-(3-triethoxysilylpropyl)tetrasulfide (TESPT) silane during mixing, the discharge temperature of a silica-filled Styrene-Butadiene Rubber (SBR) compound should be above 130 °C. But at a temperature above 160 °C the silane starts to react with the elastomer to form premature crosslinks [3]. For silica-filled NR compounds with TESPT as coupling agent, a discharge temperature is recommended in the range of 135–150 °C while a higher temperature leads to degradation of the NR [4]. All silanes with alkoxy functional groups may react with the silanol groups on the silica and so shield the silica surface to make it more hydrophobic [5]. Different silanes show distinct

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effects on the properties of silica-filled elastomers. A sulfur-free silane shows a good improvement in the Payne effect, but gives poorer mechanical and dynamic mechanical properties compared to sulfur-containing silanes such as TESPT [6].

Surface modification of silica prior to mixing is an alternative method to improve silica reinforcement in the rubber matrix. Modification of silica with a silane coupling agent can change the characteristic surface from hydrophilic to hydrophobic. Surface modification with vinyl- and mercapto-silanes reduces the silica aggregate size without re-agglomeration of the silica, but modification with an amino-silane tends to increase the silica agglomerate size because of its hydrophilicity that leads to the formation of hydrogen bonds between particles/aggregates [7, 8]. Organic monomers such as styrene, isoprene, and butadiene have been used to modify the silica surface to obtain a hydrophobic character through *in situ* polymerization of the monomers adsorbed on the surface *via* bilayers of surfactants [9–11].

Silane-modified polymers are another route employed for improvement of silica reinforcement in polymeric materials. Polypropylene (PP) grafted with vinyltriethoxysilane (VTES) was used in PP/silica nanocomposites in which the grafted PP could attach to the silica surface through VTES moieties, leading to a decrease of chain mobility and diffusion, as proven by a shift of crystallization and melting behaviors to a higher temperature [12]. The use of VTES-grafted SBR for a silica-filled compound led to improved cure and tensile properties [13, 14], and a shift of the glass transition temperature [13] ($T_g$) to a higher temperature due to the good interactions between silica and SBR-graft-VTES, that restrict movement of the SBR chains. A liquid low molecular weight polybutadiene (PB) was grafted with mercaptopropyltrimethoxysilane through radical addition of the thiol group to the double bonds on the polymer molecule at 75 °C. The grafted PB was later silanized onto silica surfaces at 135 °C, allowing the alkoxy-groups of the silane fragments to react with the silanol groups of the silica [15]. Modified-silica with the grafted PB showed a decrease in the number of OH-groups on the surface to the same level as that of silica with TESPT, due to the influence of the shielding effect of the grafted PB. The decrease of hydrophilic character of the surface modified silica further lead to a reduction of filler-filler interaction and an improvement of filler dispersion in the rubber matrix [16].

Grafting of silane onto polymers has been reported employing different reaction conditions. Silane grafted onto polybutadiene was done in solution under nitrogen atmosphere [15–17]. The solution state is known to provide a better control of the reaction compared to the melt state, but is environmentally unfriendly and provides only a small amount of grafted polymer per batch. The reaction in solution is therefore not preferred for industrial scale. VTES grafted onto SBR has been studied in the latex state using benzoic peroxide as initiator [13]. Furthermore, silane grafting in the melt state is well known for vinyl-silane-grafted polyolefins like polyethylene [18–20] and polypropylene [21].

Grafting of 3-octanoylthio-1-propyltriethoxysilane (NXT) onto NR molecules is done in the present work. For practical purposes, the NXT-grafted-NR is prepared by melt mixing in an internal mixer using 1,1′-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane or Luperox® 231XL40 as an initiator. The half-life time of Luperox® 231 at 140 °C is about 5 minutes which is shorter than that of the more common dicumyl peroxide (DCP) with its half-life time of about 30 minutes at the same temperature. The shorter half-life time of Luperox® 231 allows the grafting process to be conducted at lower temperature and shorter reaction time compared to the use of DCP, to prevent thermal degradation of the NR. Prior optimization of grafting conditions gave an optimal temperature of 140 °C and initiator concentration of 0.1 phr, which gave grafted material with a very low content of gel (<5%). The NXT-grafted-NR is prepared using 10 and 20 phr of NXT, and characterized by Fourier-transform infrared (FTIR) and proton nuclear magnetic resonance ($^1$H-NMR) spectroscopic techniques, and elemental analysis by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX). This silane-grafted-NR is then used as a compatibilizer for silica-reinforced NR compounds. The non-purified silane-grafted-NR is used in a range of 5–20 phr. For comparison, compounds are produced with the pure silane in the non-grafted form, in the same amounts as contained in the grafted NR. The properties of both types of compounds and vulcanizates compatibilized with silane and silane-grafted-NR are discussed in comparison with those without any compatibilizer and with reference bis-(3-triethoxysilyl-propyl)tetrasulfide TESPT. Further, the sulfur in the silanes plays a dual role: one as part of the coupling agent to attach to the

elastomer, the other as direct curative, causing a difference in sulfur amounts in the compounds. Therefore, this work also investigates the effect of sulfur compensation relative to the sulfur contained in the reference TESPT-containing compound in order to further improve the properties of the silica-filled NR compounds with NXT-grafted-NR as compatibilizer.

## 2. Experimental
### 2.1. Materials
Natural rubber was ribbed smoked sheet (RSS) #3, locally produced in Thailand. 3-Octanoylthio-1-propyltriethoxysilane (NXT) (Momentive, USA) and 1,1′-di(tert-butylperoxy)3,3,5-trimethylcyclohexane (Luperox® 231XL40) (Arkema, USA) 40% extended on calcium carbonate and silica, were used for the melt grafting reactions. The initiator and the NXT silane coupling agent details are given in Table 1. The compounding ingredients were RSS#3, NXT, highly dispersible silica (Zeosil 1165MP, Solvay, France), bis-(3-triethoxysilylpropyl)tetrasulfide (TESPT) (Evonik, Germany), 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, sulfur (all from Sigma-Aldrich Chemie, Germany).

### 2.2. Preparation of silane-grafted-NR
NR, previously cut into small pieces, was mixed with the silane coupling agents and the initiator in an internal mixer, Brabender® 50EHT (Brabender® GmbH & Co.KG, Germany), for 12 minutes with a rotor speed of 60 rpm using the formulations and mixing steps as shown in Table 2. The predetermined optimized grafting temperature of 140 °C and initiator concentration of 0.1 parts per hundred rubber (phr) were used for preparing the NXT-grafted-NR by using silane amounts of 10 and 20 phr.

### 2.3. Characterization of silane-grafted-NR
### 2.3.1. Structural characterization by Fourier-transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance ($^1$H-NMR) spectroscopy
An attenuated total reflection (ATR) – FTIR spectrometer (Tensor 27, Bruker, UK) was used to characterize

**Table 1.** Initiator and silane coupling agent

| Trade names | Chemical names | Structures | $M_W$ [g/mol] |
|---|---|---|---|
| Luperox® 231XL40 | 1,1′-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane | | 302.4 |
| NXT | 3-Octanoyl-thio-propyltriethoxysilane | | 365.0 |

**Table 2.** Formulations and mixing procedures for preparing the silane-grafted NR

| Formulation | Chemicals | Amount [phr] |
|---|---|---|
| | RSS3 | 100.0 |
| | NXT | 10.0–20.0 |
| | Luperox® 231XL40 | 0.1 |
| **Grafting procedures** | | **Cumulative time [min])** |
| | NR mastication | 0 |
| | Addition of NXT | 1 |
| | Addition of Luperox® 231XL40 | 2 |
| | Discharge | 12 |

purified grafted NR samples. Purification of the silane-grafted NR samples was performed for the purpose of structural characterizations by dissolving the materials in toluene under continuous stirring for 72 h, then filtering to remove any insoluble part, and subsequently precipitating the soluble part in ethanol to remove free or ungrafted silane. The purified sample was finally dried at 60 °C for 24 h and kept in a desiccator before the analysis. The extent of silane grafting ($R$) onto the NR molecules was obtained by using the peak height ratios according to Equation (1) [19]:

$$R_{1075} = \frac{A_{1075}}{A_{1375}} \text{ and } R_{1035} = \frac{A_{1035}}{A_{1375}} \quad (1)$$

where $R_{1075}$ and $R_{1035}$ are the extents of silane-grafting determined at 1075 and 1035 cm$^{-1}$, $A_{1075}$ is the peak height of Si–O–C deformation at 1075 cm$^{-1}$, $A_{1035}$ is the peak height of Si–OSi vibration and $A_{1375}$ is the peak height of –CH$_3$ in NR at 1375 cm$^{-1}$.
The purified and dried grafted NR samples were dissolved in deuterated chloroform (CDCl$_3$) and characterized by NMR spectroscopy (Varian Unity Inova 500 MHz, Varian, USA). The amount of NXT grafted onto NR molecules in mol% can be quantified by using Equation (2):

$$\text{mol\% of grafted NXT on NR} = \frac{\frac{A_{3.8}}{6}}{\frac{A_{3.8}}{6} + A_{5.1}} \cdot 100 \quad (2)$$

where $A_{3.8}$ is the integrated peak area of methylene protons of the alkoxy group (–Si–O–C$\underline{\text{H}}_2$–CH$_3$) of the NXT at 3.8 ppm, and $A_{5.1}$ is the integrated peak area of alkene protons $\left(\begin{smallmatrix} \text{CH}_3 \\ | \\ \text{–C=C}\underline{\text{H}} \end{smallmatrix}\right)$ of NR at 5.1 ppm.
There are 6 alkoxy-methylene protons in each NXT molecule and 1 alkene proton in each isoprene unit.

### 2.3.2. Grafting efficiency of silane-grafted NR
Based on mol% of grafted silane on the NR obtained from the calculations according to Equation (2), the weight% of grafted silane can be calculated by using Equation (3):

$$\text{wt\% of grafted silane on NR} = \frac{\text{mol\%}_{\text{silane}} \cdot M_{W_{\text{silane}}}}{\text{mol\%}_{\text{silane}} \cdot M_{W_{\text{silane}}} + \text{mol\%}_{\text{NR}} \cdot M_{W_{\text{NR}}}} \cdot 100 \quad (3)$$

where mol%$_{\text{silane}}$ is the mol% of grafted silane on NR, $M_{W_{\text{silane}}}$ is the molecular weight of the silane,

mol%$_{\text{NR}}$ is the mol% of NR and $M_{W_{\text{NR}}}$ is the molecular weight of the NR repeating unit (68 g/mol). Then, the grafting efficiency can be calculated according to Equation (4):

$$\text{Grafting efficiency [\%]} = \\ = \frac{\text{wt\% of grafted silane on NR}}{\text{wt\% of silane for the reaction}} \cdot 100 \quad (4)$$

### 2.3.3. Elemental analysis by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX)
The purified silane-grafted-NR was analyzed for the chemical elements carbon (C), oxygen (O) and silicon (Si) by using SEM-EDX spectroscopy (Quanta 400, FEI, USA).

### 2.4. Compounds preparation
The NXT-grafted-NR was used without purification in order to simplify the process. To study the effect of NXT-grafted-NR as a compatibilizer in silica-filled NR, the grafted-NR was added at 5, 10, 15 and 20 phr as part of the rubber matrix. Total silane contents based on calculation, either in the form of free silane and of grafted silane in the compatibilizer are summarized in Table 3. The silica-filled NR compound formulations with the various amounts of NXT-grafted-NR and the straight silane, i.e. pure silane in non-grafted form, are shown in Table 4 together with the references. The compound formulations with sulfur compensation are shown in Table 5. The compounds were mixed in an internal mixer with the initial mixer temperature setting of 100 °C to complete the silanization of silica and silane, following

**Table 3.** Total amount of NXT involved in NR-grafted and non-grafted forms added per phr of non-purified NXT-grafted NR, used as compatibilizer in the silica-filled NR compounds

| Amount of NXT-grafted-NR | Amount of total silane [wt% rel. to silica] |
|---|---|
| **NXT-grafted-NR with 10 phr of silane** | |
| • 5 phr | 0.8 |
| • 10 phr | 1.7 |
| • 15 phr | 2.5 |
| • 20 phr | 3.4 |
| **NXT-grafted-NR with 20 phr of silane** | |
| • 5 phr | 1.5 |
| • 10 phr | 3.0 |
| • 15 phr | 4.6 |
| • 20 phr | 6.1 |

**Table 4.** Compound formulations with the use of NXT-grafted-NR and straight NXT in comparison with TESPT and without any compatibilizer, without sulfur compensation

| Ingredients | Parts per hundred parts of rubber [phr] | | | |
|---|---|---|---|---|
| | References | | Silane-grafted-NR | Straight use of silane |
| RSS3 | 100.0 | 100.0 | 95.0–80.0 | 100.0 |
| TESPT | – | 4.7[*] | – | – |
| NXT-grafted-NR[**] | – | – | 5.0–20.0 | – |
| NXT | – | – | – | 0.8–6.1[***] |
| Silica | 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 |
| Sulfur | 1.5 | 1.5 | 1.5 | 1.5 |

[*]TESPT 4.7 phr equals 8.6 wt% rel. to silica;
[**]NXT-grafted-NR was prepared by using silane contents at 10 and 20 phr;
[***]Silane contents for straight use were calculated based on silane loadings in the non-purified silane-grafted-NR as shown in Table 3.

**Table 5.** Compound formulations with the use of NXT-grafted-NR with sulfur compensation

| Ingredients | Parts per hundred parts of rubber [phr] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | NXT-grafted-NR with silane 10 phr | | | | NXT-grafted-NR with silane 20 phr | | | |
| RSS3 | 95.00 | 90.00 | 85.00 | 80.00 | 95.00 | 90.00 | 85.00 | 80.00 |
| TESPT | – | – | – | – | – | – | – | – |
| NXT-grafted-NR | 5.00 | 10.00 | 15.00 | 20.00 | 5.00 | 10.00 | 15.00 | 20.00 |
| Silica | 55.00 | 55.00 | 55.00 | 55.00 | 55.00 | 55.00 | 55.00 | 55.00 |
| TDAE oil | 8.00 | 8.00 | 8.00 | 8.00 | 8.00 | 8.00 | 8.00 | 8.00 |
| ZnO | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| TMQ | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Stearic acid | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| DPG | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| CBS | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 |
| Sulfur[*] | 2.59 | 2.55 | 2.51 | 2.47 | 2.56 | 2.48 | 2.41 | 2.33 |

[*]Sulfur content was compensated towards the amount of sulfur contained in TESPT in the reference compounds with 4.7 phr TESPT in Table 4.

**Table 6.** Mixing procedures for compounds preparation

| Mixing procedures | Cumulative time [min] |
|---|---|
| **Step 1: Internal mixer** | |
| – NR and silane-grafted-NR (or NR only) mastication | 2 |
| – Addition of first half of silica (and ½ of silane if any) | 7 |
| – Addition of second half of silica (and ½ silane if any) and TDAE oil | 12 |
| – Addition of ZnO, stearic acid and TMQ | 15 |
| **Step 2: Two roll mill** | |
| – Addition of DPG, CBS and sulfur(plus extra sulfur if any) | 5 |

the mixing procedures as shown in Table 6. The properties of the silica-filled NR compounds with the silane-grafted-NR as compatibilizer were studied in comparison with the results of silica filled NR with straight silane at different amounts.

## 2.5. Measurements of Mooney viscosity, Payne effect, and bound rubber content

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 [22] 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%. 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 0.25 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 elastomer 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 Equation (5) [23]:

$$\text{Bound rubber content } [\%] = \frac{m - m_s}{m_r} \cdot 100 \qquad (5)$$

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.

## 2.6. Measurements of cure characteristics, vulcanization and tensile properties

Cure properties of the compounds were tested by using a Moving Die Rheometer (MDR) (rheoTech MD$^+$, Tech-Pro, Inc., USA) at 150 °C for 30 minutes 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 molding press (Chaicharoen Karnchang Ltd., Thailand). 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.

## 2.7. Analysis of dynamic mechanical properties and tensile-fractured surface topography

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

Tensile fractured surfaces of silica-filled NR vulcanizates were analyzed by using the scanning electron microscopy (SEM) technique. The fractured surface was gold-coated before being analyzed by SEM (Quanta 400, FEI).

## 3. Results and discussion
### 3.1. Grafting of NXT onto NR molecules
Under the grafting conditions, the peroxide initiator is decomposed giving reactive radicals as shown in Figure 1, and a possible reaction mechanism of the NXT grafting onto NR molecules in the presence of radicals is shown in Figure 2. The Luperox® 231XL40 is a diperoxide initiator that can be thermally decomposed to give two free radicals or radical species (•OC(CH$_3$)$_3$) per molecule. The tert-butoxy radicals can further split to create more reactive methyl radicals (•CH$_3$) under the high grafting temperature, as shown in Figure 1. Both types of reactive free radicals formed in the system [24] can initiate the grafting reaction on the NR which may proceed through two different pathways *via* H-abstraction and addition [25], as shown in Figure 2. The reactive initiator transfers its radical to the sulfur on the coupling agent which subsequently attacks a double bond of the polymer molecule. The grafting reaction tends to proceed then through an abstraction reaction at the allylic position of the NR structure, more than through the addition reaction like with common sulfur vulcanization [26]. Upon successful grafting a covalent C–S–C bond between rubber and silane is generated with the pendant alkoxy groups.
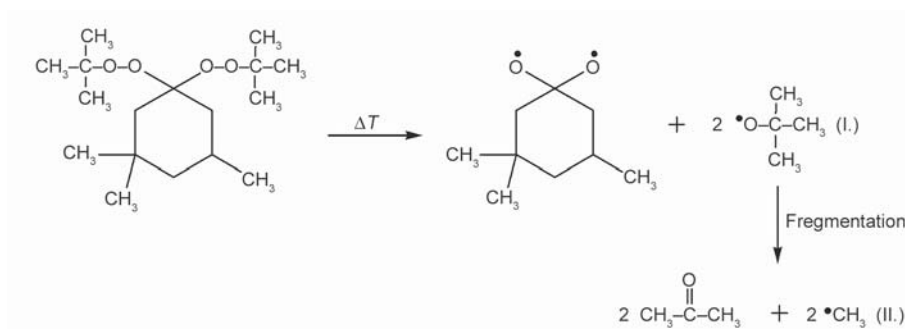
**Figure 1.** Decomposition of 1,1′-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane (Luperox® 231XL40)
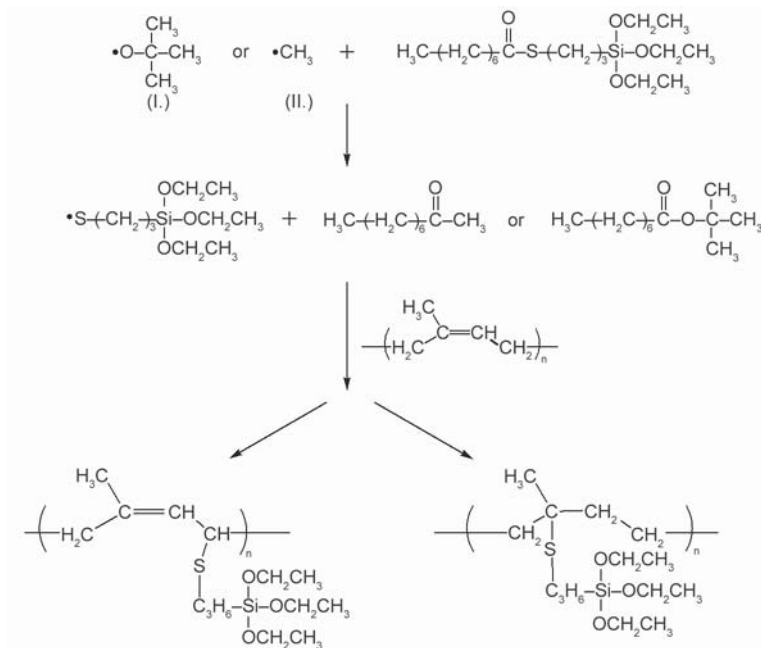


**Figure 2.** Postulated reaction mechanism of NXT grafting onto NR molecules in the presence of radical species

The FTIR spectra of the purified NR grafted in presence of 10 and 20 phr of NXT are shown in comparison with that of virgin NR in Figure 3. Jiao *et al.* [27] studied silane grafted ethylene-octene copolymer and reported that the peaks at 1167, 1105, 1082 and 958 $cm^{-1}$ could be assigned to the deformation of Si–O $CH_2CH_3$ of the silane coupling agent. The FTIR spectra in Figure 3 clearly show absorption bands at 1075 and 1035 $cm^{-1}$ assigned to Si–O–C and Si–OSi deformations, respectively. In this fingerprint region as seen in Figure 3, virgin NR also shows absorption bands in the range of 1400–700 $cm^{-1}$, so it is not easy to identify the Si–O–C deformations of the silane grafted NR. However, the peak intensity at 1075 $cm^{-1}$ relative to the neighboring peaks at 1125 and 1035 $cm^{-1}$ has changed, indicating that reactions have taken place between silane and rubber. There are absorption bands at 3270 $cm^{-1}$ from O–H stretching deformations due to hydrolysis of the alkoxy-group in the silane structure during the grafting reaction or during the post-treatment; respectively

at 1010 $cm^{-1}$ which may be assigned to the Si–OH group [28] due to hydrolysis of the ethoxy groups. The hydrolysis of ethoxy groups by moisture during the grafting reaction leads to hydroxyl groups Si–OH which can further form a crosslink Si–O–Si in the grafted rubber. By taking the peak heights at 1075 and 1035 $cm^{-1}$ relative to the peak at 1375 $cm^{-1}$ as internal standard, the increased amount of the silane used for the grafting reactions with NR results in the increase of peak height ratios or R values as shown in Table 7, indicating the presence of more grafted silane fragments.

Figure 4 shows $^1$H-NMR spectra of the purified NXT-grafted-NRs prepared by using two different NXT amounts of 10 and 20 phr in comparison with that of virgin NR. The grafted rubber shows a characteristic peak of NXT-silane at a chemical shift of 3.8 ppm assigned to the proton of the ethoxy-groups of the silane. This peak is intensified with increasing silane amount and the mol% of NXT-silane in the grafted NR as calculated according to Equation (2) is shown
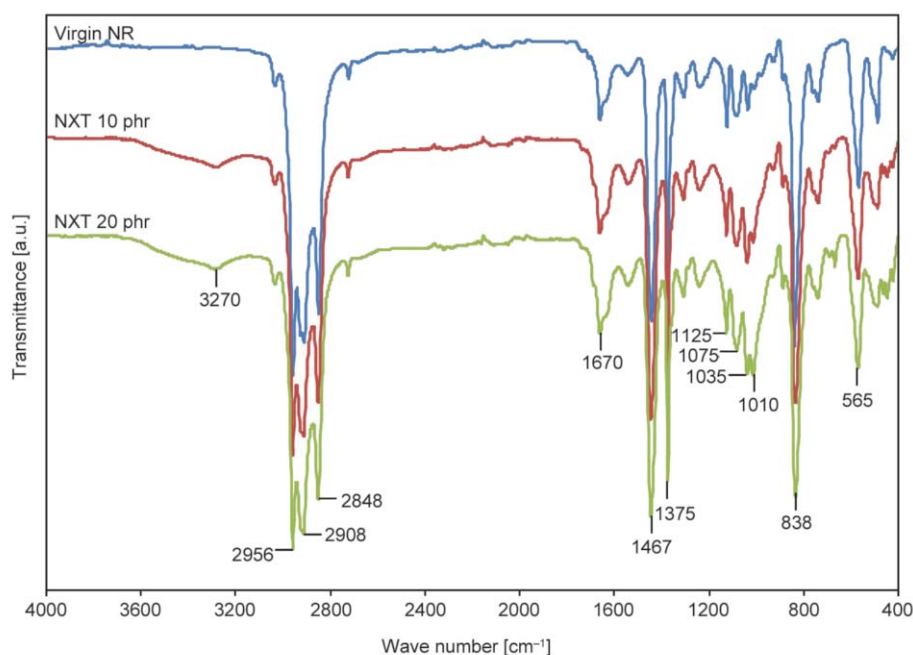
**Figure 3.** ATR-FTIR spectra of virgin NR and NR grafted with NXT at 10 and 20 phr

**Table 7.** The extent of NXT grafting ($R$) onto NR molecules from ATR-FTIR, mol% of NXT on NR molecules from ^{1}H-NMR, grafting efficiency and chemical elements from SEM-EDX

| Analysis results | Amount of NXT [phr] | | |
|---|---|---|---|
| | 0 (virgin NR) | 10 | 20 |
| **$R$ value from ATR-FTIR** | | | |
| $R_{1075} = A_{1075}/A_{1375}$ | 0.31 | 0.49 | 0.55 |
| $R_{1035} = A_{1035}/A_{1375}$ | 0.22 | 0.42 | 0.49 |
| **Mol% of NXTfrom ^{1}H-NMR** | 0.00 | 0.66 | 1.32 |
| Amount of grafted NXT [wt%] | – | 3.43 | 6.68 |
| Amount of NXT used [wt%] | – | 9.09 | 16.67 |
| **Grafting efficiency [%]** | – | 37.70 | 40.10 |
| **Chemical elements from SEM-EDX** | | | |
| C [wt%] | 98.20 | 97.50 | 96.8 |
| O [wt%] | 1.80 | 2.40 | 3.00 |
| Si [wt%] | – | 0.10 | 0.20 |

in Table 7. The grafted silane on the NR molecules increases with increasing amount of silane used for the reaction. The presence of the silane grafted on the NR molecules is also confirmed by elemental analysis, as reported in Table 7. The grafting of silane fragments on the NR molecules is proved by the presence of silicon atoms in the modified NR; the increase of silane content used for the reaction results in an increase of Si and O components in the grafted materials.

## 3.2. Effect of silane-grafted-NR as compatibilizer and of straight non-grafted silane on the properties of silica-filled NR compounds, without sulfur compensation

### 3.2.1. Mooney viscosity, bound rubber content and Payne effect

For filled rubber compounds, the viscosity increment depends on several factors, to include mastication time [29], mixing time [30], filler types [31, 32], filler contents [32, 33], compatibilizer or coupling
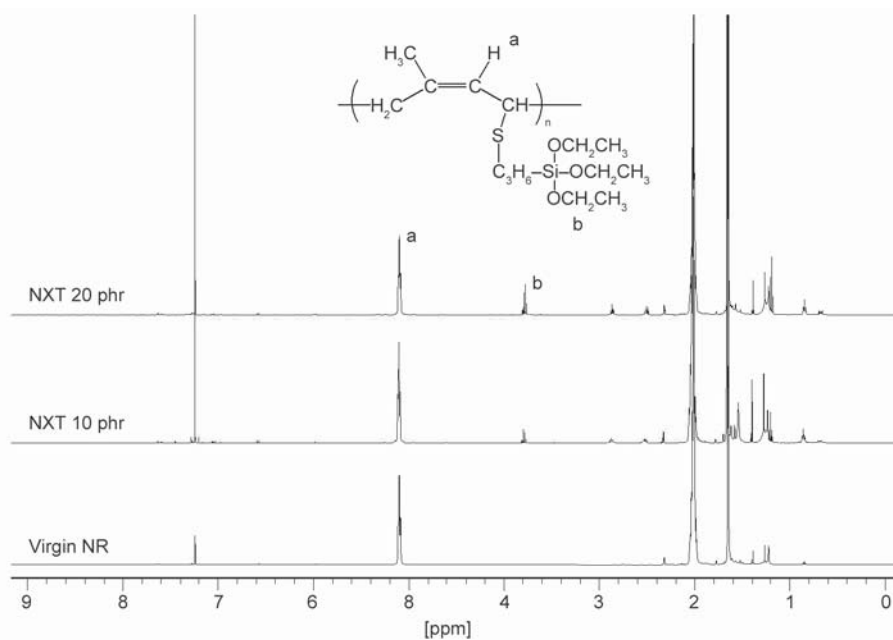
**Figure 4.** ¹H-NMR spectra of virgin NR and NR grafted with NXT at 10 and 20 phr

agent [34, 35] and storage time [36]. The change of compound viscosity is strongly influenced by the levels of filler-filler and filler-rubber interactions which consequently have an influence on the final properties of the filled rubber. The decrease of compound viscosity results in a lower mixing torque and consequently less heat generation or lower compound temperature after mixing.

Mooney viscosities of the silica-filled NR compounds decrease with increasing amounts of silane, either in the form of NR-*g*-silane or straight non-grafted silane, and both sets of compounds show similar Mooney viscosities, as shown in Figure 5. The Mooney viscosity of the filled-NR with 6 wt% of silane relative to the silica, decreases to almost the same level as that of the reference compound with TESPT at 8.6 wt% relative to the silica. This level of 8.6 wt% of TESPT relative to the silica was found to be the optimum, as calculated based on the work described by Guy *et al.* [37]. For silica-filled compounds, the viscosity reduces when filler dispersion is improved [35]. Thus, the incorporation of NXT and NXT-grafted-NR improves the silica dispersion and consequently reduces the Mooney viscosity due to a diminished hydrophilic character of the silica after the silanization reaction. As expected, the silica-filled NR compound without any compatibilizer shows the highest Mooney viscosity because of the strong filler-filler interactions *via* hydrogen bonding of the silanol groups on the silica surfaces that lead to poor dispersion and agglomerates to obstruct flow.
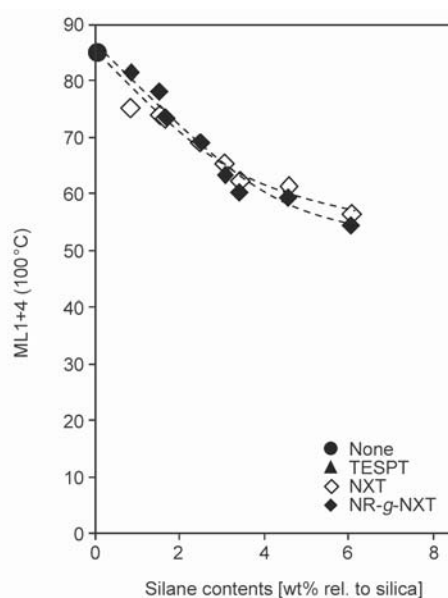


**Figure 5.** Mooney viscosity of silica-filled NR compounds with use of (a) straight NXT (open symbols) and NXT-grafted-NR (closed symbols)

Figure 6a shows the chemically bound rubber contents after treatment in ammonia atmosphere to cleave all weak physical filler-rubber interactions [23] of silica-filled NR compounds. The use of either silane-grafted-NR or straight non-grafted silane significantly increases the bound rubber, i.e. increased silica-rubber interaction compared to the non-compatibilized one. But the increased bound rubber content is still to a significantly lower level compared with the reference compound with TESPT. The chemically bound rubber contents increase with rising

amount of NXT up to approx. 3 wt% relative to the silica, thereafter the values tend to level off. As only some of the silanol groups will react with the ethoxy groups of silane, the adsorbed silane on the silica surface will also act as a shielding agent that only forms physical interactions between filler and rubber. The chemically bound rubber content therefore reaches a saturated point, as observed in Figure 6a. The use of silane-grafted-NR tends to show a marginally higher chemically bound rubber content than the use of non-grafted silane. The partially pre-grafted silane to NR may enhance the compatibility between rubber and silica and allow the ethoxygroups of NXT to react more effectively with the silica during the silanization reaction, compared to the straight non-grafted silane. However, the use of TESPT in the silica-filled NR compound still gives an outstanding chemically bound rubber content, which is due to its tetrasulfide structure that results in premature crosslinking with the NR molecules [38] and the bis-triethoxy-groups to react with the silanol groups during silanization.

The filler-filler interaction or Payne effect of the silica-filled NR compounds with both non-grafted silane and silane-grafted-NR is remarkably decreased with increasing silane content to meet the same level of Payne effect of the compound with 8.6 wt% of TESPT, as shown in Figure 6b. The ethoxy-groups of the silanes undergo a silanization reaction with the silanol-groups of the silica and reduce the filler-filler interactions. The use of NXT-grafted-NR gives slightly lower Payne effects than the straight use of NXT. At 6.1 wt% of NXT, the compound shows a slightly lower Payne effect compared to the reference compound with 8.6 wt% of TESPT.

### 3.2.2. Tensile properties

The modulus at 300% elongation and reinforcement index (M300/M100) of the silica filled NR vulcanizates compatibilized by straight use of silane in comparison with the use of silane-grafted-NR are shown in Figure 7. The modulus of the vulcanized silica-filled NRs significantly increases with rising silane amounts due to an increase of the silica-rubber interactions. The use of silane-grafted-NR as compatibilizer clearly gives a higher modulus than the straight use of silane. The reinforcement index of the silica-filled NR vulcanizates also increases as a function of silane content: Figure 7b, to reach an optimum at about 4–5 wt% of silane relative to the silica, above which the addition of either more non-grafted silane or silane grafted-NR results in more or less the same values. In both cases the property level of the TESPT-filled compound is not reached. The increasing filler-rubber interactions as derived from the chemically bound rubber contents: Figure 6a, lead to a higher resistance to deformation, but because there are no additional crosslinks generated by sulfur donated to the compounds by the silane molecules like in the case of TESPT, the NXT silanized compounds therefore have a significantly lower modulus.
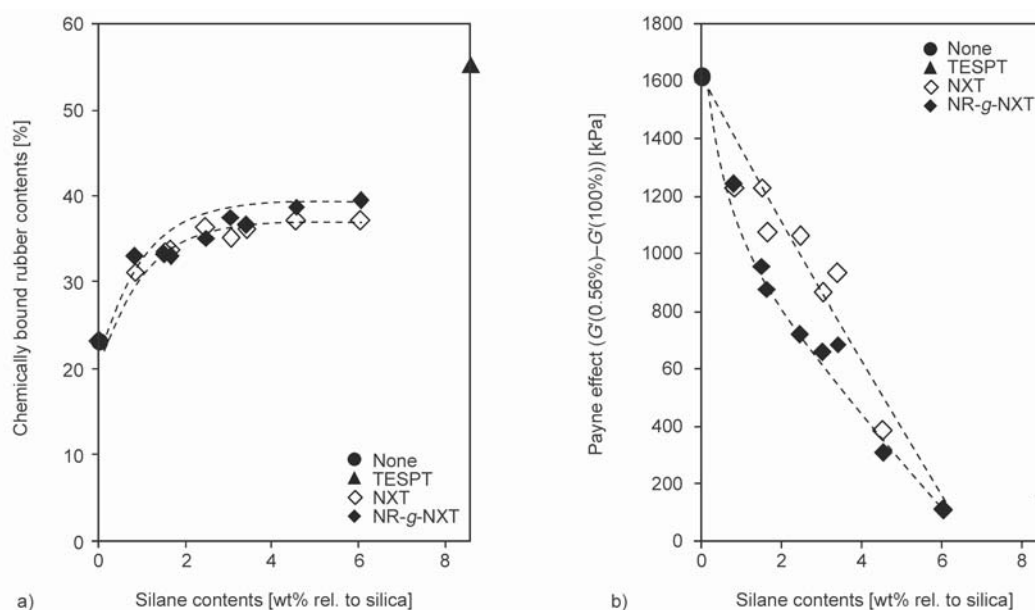


**Figure 6.** Chemically bound rubber contents (a) and Payne effect (b) of silica-filled NR compounds with use of (a) straight NXT (open symbols) and NXT-grafted-NR (closed symbols)
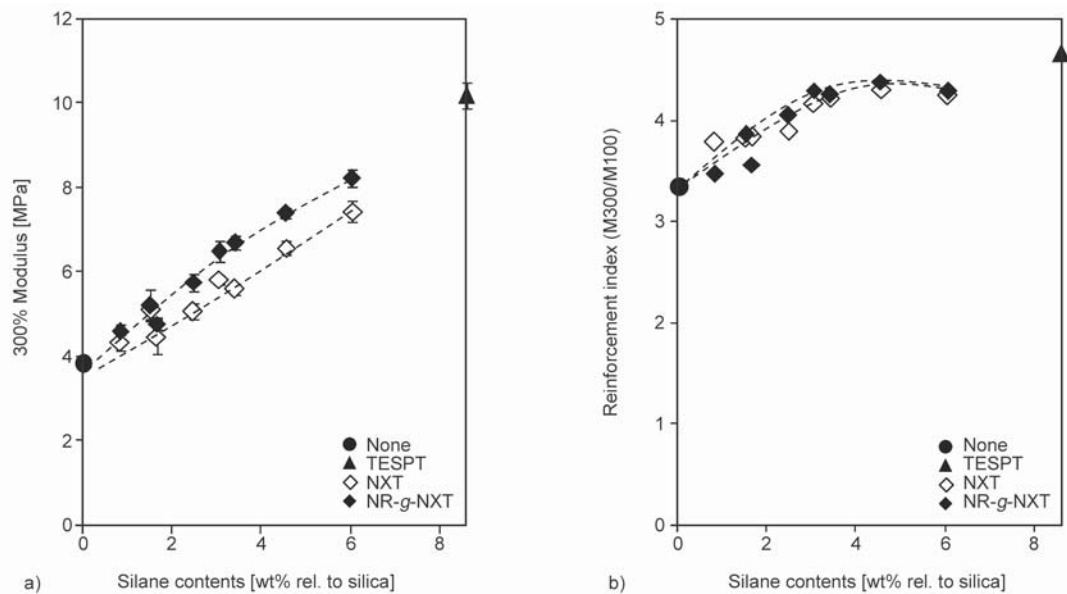
**Figure 7.** 300% Modulus (a) and reinforcement index (b) of silica-filled NR compounds with use of (a) straight NXT (open symbols) and NXT-grafted-NR (closed symbols)

The tensile strength and elongation at break of the silica-filled NR vulcanizates with silane-grafted-NR and straight non-grafted silane as compatibilizers show only small differences, where the tensile strength reaches a level slightly lower than that of the vulcanizate with 8.6 wt% of TESPT relative to the silica: Figure 8. The use of either straight silane or silane-grafted-NR clearly improves the tensile strength of the silica-filled NR, as a result of the increased silica-rubber interactions by the coupling reaction of the silanes. The correlations of 300% modulus and tensile strength with filler-rubber interactions as determined by chemically bound rubber contents are clearly demonstrated in Figures 9. Like the 300% modulus in Figure 7a, the use of NXT-grafted-NR as compatibilizer gives a higher tensile strength than the straight use of NXT-silane, but the value is still lower than for TESPT that provides the best silica reinforcement for the NR compounds. The coupling between silica and rubber that leads to the increased modulus and tensile strength affects the elongation at break slightly, decreasing a little as shown in Figure 8b. A small reduction of elongation at break despite a large increase in modulus and tensile strength derives from
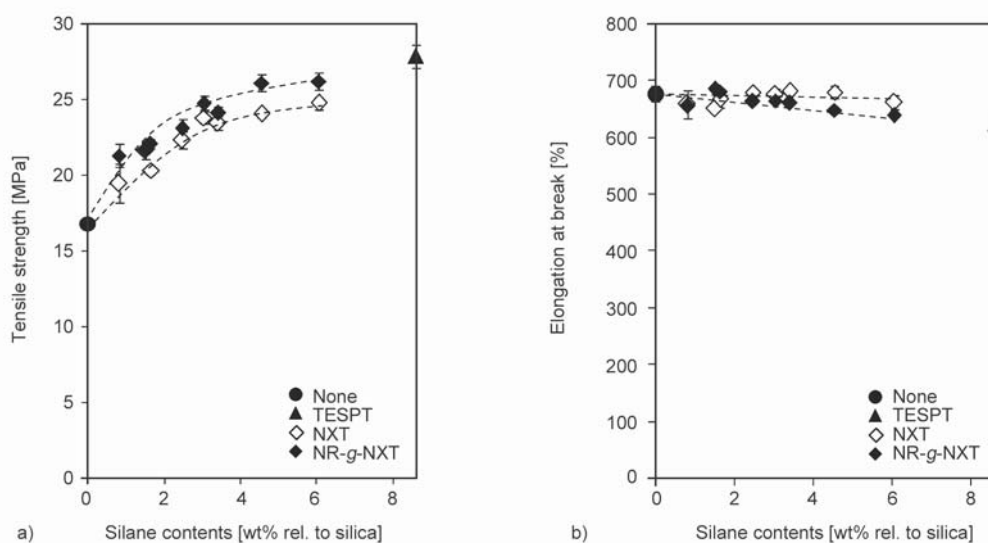


**Figure 8.** Tensile strength (a) and elongation at break (b) of silica-filled NR compounds with use of (a) straight NXT (open symbols) and NXT-grafted-NR (closed symbols)
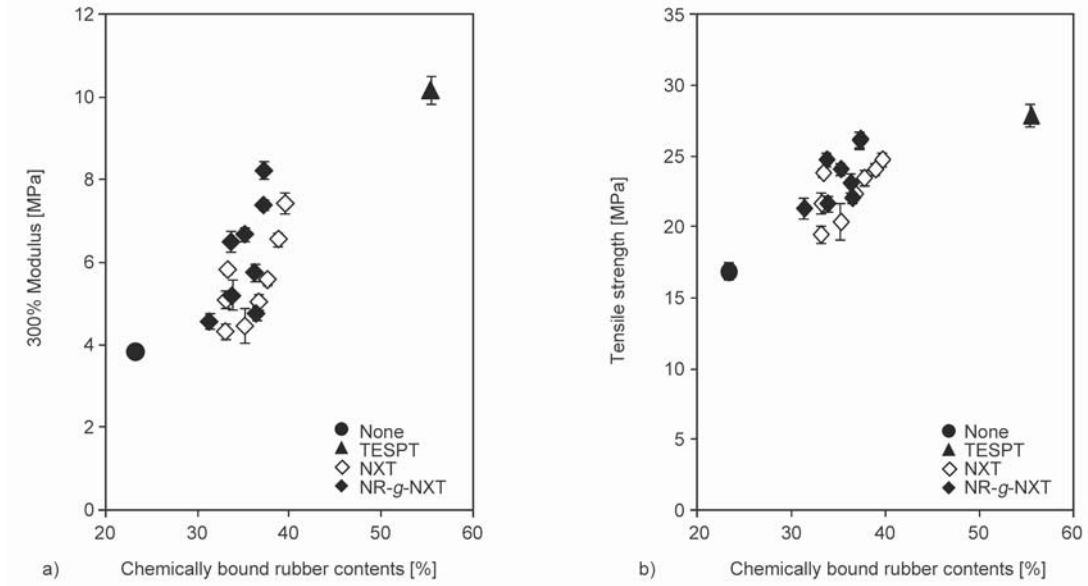
**Figure 9.** Correlation between 300% modulus (a) and tensile strength (b) with chemically bound rubber content of silica-filled NR compounds

the good elasticity of natural rubber matrix. The incorporation of silane promotes interfacial adhesion between filler surface and rubber without sacrificing the toughness of the cured rubber.

### 3.2.3. Dynamic mechanical properties

The storage modulus ($E'$) and loss tangent or tan δ as a function of the temperature of the silica-filled NR vulcanizates are shown in Figures 10, respectively. In the glassy region, the silica-filled vulcanizate with TESPT shows only a small difference in storage

modulus compared to the mixes with NXT-grafted-NR. However, in the rubbery region, the silica/TESPT system shows the highest storage modulus while the other vulcanizates show similar levels of lower moduli. For filled rubbers, the modulus depends on filler content, crosslink density, filler-filler and filler-rubber interactions that affect the segmental mobility of the rubber chains. The modulus normally increases with increasing amount of filler [39] or degree of filler-rubber interaction [40]. The silica-filled NR with TESPT has the highest storage modulus, indicative
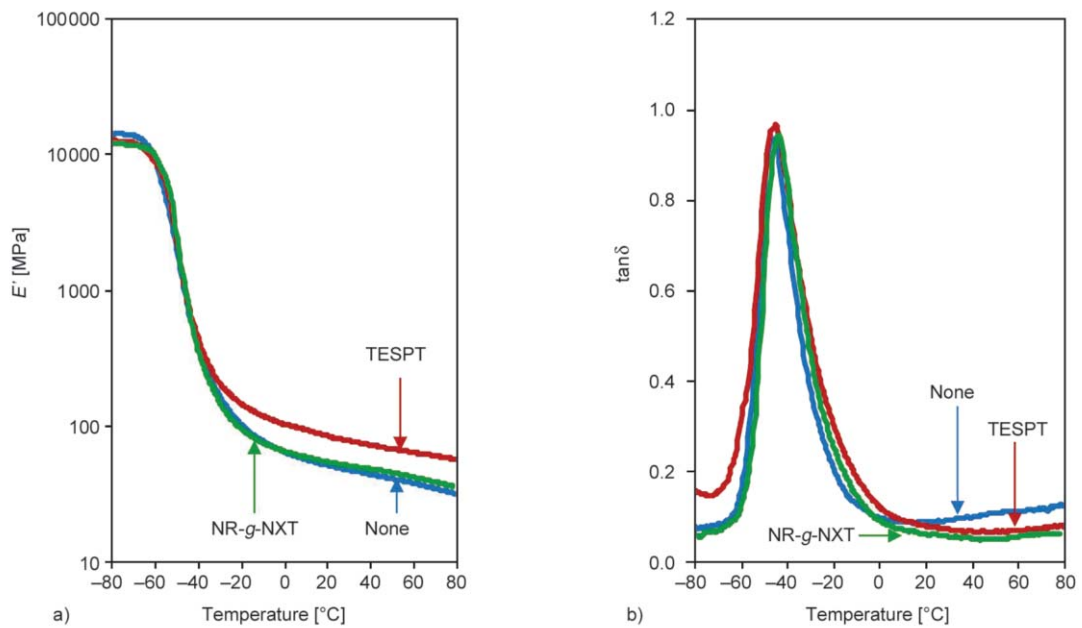


**Figure 10.** Storage modulus ($E'$) (a) and loss tangent (tan δ) (b) of silica-filled NR with NXT-grafted-NRs, both with total silane of 6.1 wt% relative to the silica; TESPT at 8.6 wt% relative to silica

**Table 8.** $T_g$ and tan δ values of silica-filled NR vulcanizates with a total silane content of 6.1 wt% relative to the silica for NR-*g*-NXT; and 8.6 wt% for TESPT

| Compatibilizer types | $T_g$ [°C] | Values of tan δ | | |
|---|---|---|---|---|
| | at tan δ peak | at peak | at 5 °C | at 60 °C |
| Without compatibilizer | –47 | 0.94 | 0.09 | 0.11 |
| TESPT | –45 | 0.97 | 0.10 | 0.07 |
| NR-*g*-NXT | –44 | 0.95 | 0.08 | 0.05 |
| NR-*g*-NXT + sulfur | -42 | 0.93 | 0.08 | 0.06 |

of most filler-rubber interactions and highest cross-link density contributed from sulfur in the TESPT molecules.

The rubber with TESPT shows a slightly higher tan δ peak intensity over the other vulcanizates, which indicates that there is less trapped rubber in the silica network and so more flexible rubber chains to respond to the dynamic deformation in the transition region. In the rubbery region where the rubber chains are in motion, the compatibilized systems show lower tan δ values compared to the non-compatibilized one, due to their better filler-rubber interactions and so less energy loss during deformation. The values of tan δ at different positions are summarized in Table 8, together with the values of $T_g$ taken from the tan δ peaks.

The glass transition temperature ($T_g$) is the temperature of the glass-to-rubber softening transition which can be observed as a large drop in modulus. Although the $T_g$ is often taken at the peak of tan δ, the $T_g$ of a polymer may also be reported by using the temperature at either the loss modulus ($E''$) peak, where the value at the $E''$ peak corresponds to segmental relaxation processes only and is not affected by different levels of filler-rubber interaction [41]. This present work compares the $T_g$'s of the silica-filled NRs with different compatibilizers taken from the tan δ peak, as shown in Table 8. The $T_g$'s of the silica-filled vulcanizates with TESPT and NXT-grafted-NR are shifted to a higher temperature compared to the one without compatibilizer, due to an increased degree of filler-rubber interactions which restrict the mobility of the polymer chains. Although the compounds with NXT-grafted-NR as compatibilizer show lower chemically bound rubber content and inferior mechanical properties than for TESPT, their $T_g$'s are slightly higher than the one with TESPT. The use of silane grafted-NR with some silane molecules already grafted to rubber may result in a higher extent of the coupling reaction between rubber

and silica. In the transition region, the free volume between polymer molecules rapidly increases leading to an increase of polymer chain mobility to respond to dynamic deformation. The better chain flexibility in the compatibilized compounds and good filler-rubber interactions lead to lower energy losses and so lower tan δ in the rubbery region.

The tan δ values at low temperature, i.e. 5–35 °C for summer tires and 2–20 °C for winter tires [42], and at higher temperatures commonly at 60 °C can be used to indicate tire wet grip and rolling resistance, respectively. The results in Table 8 shows that the use of NXT-grafted-NR as compatibilizer gives slightly lower tan δ values at 5 °C, indicating a small decrease in wet grip, respectively a lower tan δ at 60 °C implying an improvement in rolling resistance compared to the reference compound with TESPT. The lower tan δ at 60 °C in the vulcanizates containing the silane-grafted-NR again may be attributed to efficient coupling or bridging between rubber and silica *via* the pre-grafted silane fragments and some additional linkages created by self-crosslinking between the grafted moieties.

### 3.2.4. SEM micrographs

SEM micrographs of tensile fractured surfaces of silica-filled NR vulcanizates without compatibilizer, with TESPT, with non-grafted NXT and with NXT-grafted-NR are compared in Figures 11. A smooth failure surface of a silica-filled vulcanizate is due to a weak filler-rubber interaction and poor silica dispersion, whereas a rough failure surface with many tear lines from ductile failure indicates a good silica-rubber interaction and high tensile strength [43, 44]. The SEM micrographs of the vulcanizates with no compatibilizer and with reference TESPT, as shown in Figure 11a and 11b respectively, clearly correspond to their different tensile strengths: Figure 8a. The addition of NXT silane, both in pure silane form and NXTgrafted-NR, improves the silica-rubber
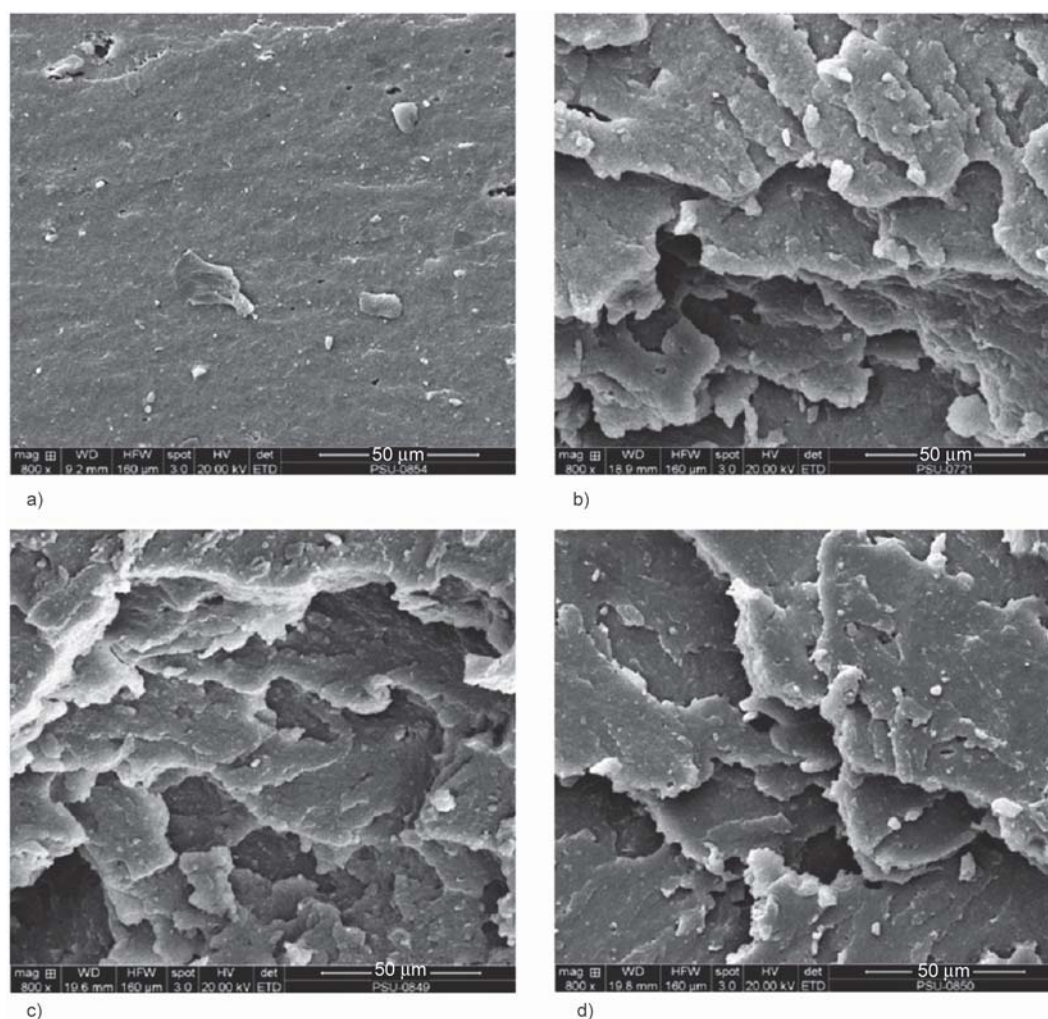
**Figure 11.** SEM micrographs of tensile fractured surfaces of silica-filled NR vulcanizates at 800× magnification: (a) without compatibilizer; (b) with TESPT at 8.6 wt% rel. to silica; (c) with NXT at 6.1 wt% rel. to silica; and (d) with NXT-grafted-NR containing total NXT of 6.1 wt% rel. to silica

interactions to lead to more surface roughness and tear lines on the failure surfaces when compared to the filled vulcanizate without compatibilizer, and the surface topography resembles more that of the reference compound with TESPT. However, there is no clear difference in the failure surface patterns of the filled vulcanizates prepared by the straight use of silane and by the use of silane-grafted-NR.

## 3.3. Effect of silane-grafted-NR as compatibilizer with sulfur compensation on the properties of silica-filled NR compounds

Some previous studies reported the influence of sulfur content in the silica-reinforced rubber compounds, such as ten Brinke *et al*. [45] who showed that, with sulfur correction, all sulfur containing silanes behaved more like TESPT; such as bis-(3-triethoxysilylpropyl)disulfide (TESPD) with sulfur

correction could give final properties similar to those of TESPT. The correction of sulfur deficiency in silica-filled NR compared to the TESPT-based system also leads to enhanced properties which are related to extra network formation [46]. Therefore, the sulfur compensation relative to the sulfur contained in the reference TESPT compound was also applied in this part to improve the properties of the silica-filled NR compounds with NXT-grafted-NR as compatibilizer.

## 3.3.1. Mooney viscosity, Payne effect and cure properties

The Mooney viscosities of the silica-filled NR compounds with NXT-grafted-NR as compatibilizer with sulfur compensation show slightly lower viscosities than the non-sulfurcompensated ones, as shown in Figure 12a. The change of Mooney viscosities is mainly affected by the amounts of NXT-silane in the grafted-NR, and the compounds containing NR-*g*-NXT
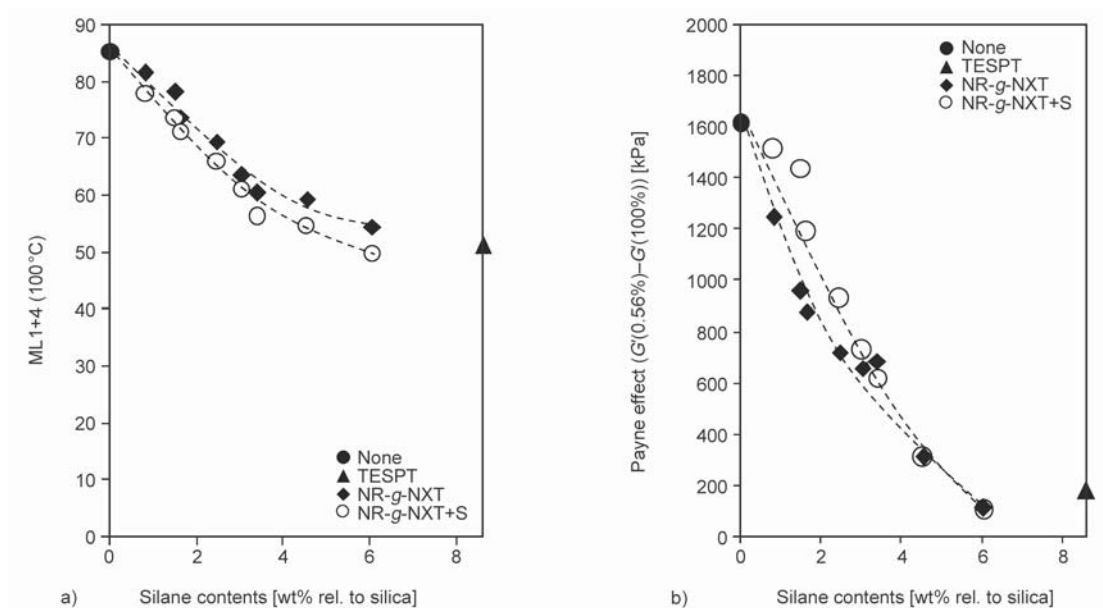
**Figure 12.** Mooney viscosity (a) and Payne effect (b) of silica-filled NR compounds with NXT-grafted-NR as compatibilizer without and with sulfur compensation, in comparison with the reference compounds with TESPT and without compatibilizer

at 6.1 wt% silane relative to the silica show more or less the same level of the Mooney viscosity to that of the reference compound. Also, the Payne effect of the silica-filled NR compounds without and with sulfur compensation shows no significant difference, as shown in Figure 12b. The Payne effect dramatically decreases with the addition of NXT-grafted-NR as compatibilizer and the silica-filled compounds with NXT 4–6 wt% relative to the silica show similar level of the Payne effect to the reference one with 8.6 wt% TESPT.

In Figure 13a, the silica-filled NR-compound with TESPT shows the shortest optimum cure time as the silane has efficiently reacted with the silanol groups on the silica surface, leading to more hydrophobicity and less curative adsoption on the silica surface. Moreover, TESPT is a sulfur donor [47]. The TESPT-compound therefore has a faster cure time compared to the other compounds. The optimum cure times of the silica-filled NR compounds with NXT grafted-NR as compatibilizer decrease with increasing NXT amounts due to more reactive ethoxy-groups available
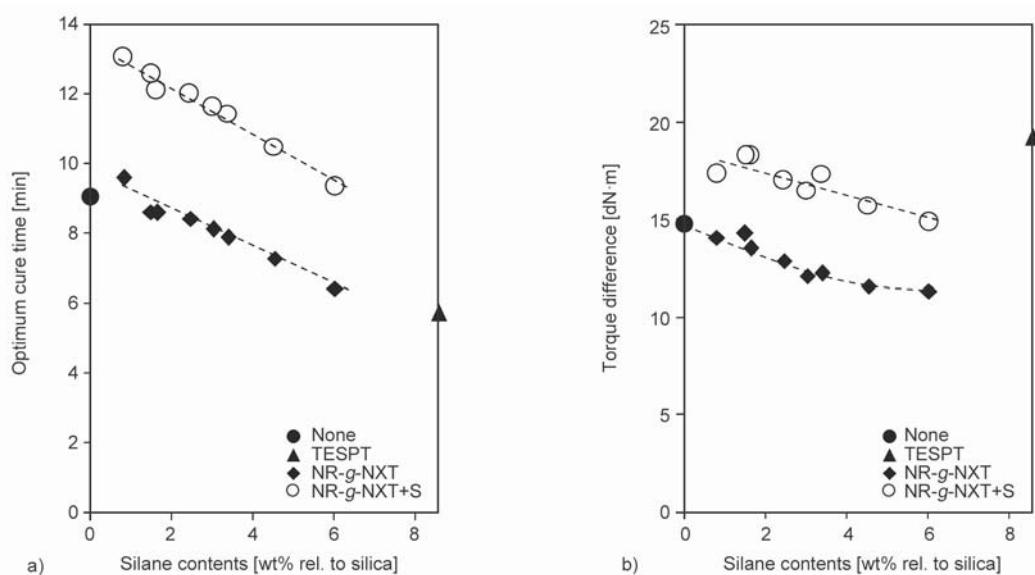


**Figure 13.** Optimum cure time (a) and torque difference (b) of silica-filled NR compounds with NXT-grafted-NR as compatibilizer without and with sulfur compensation, in comparison with the reference compounds with TESPT and without compatibilizer
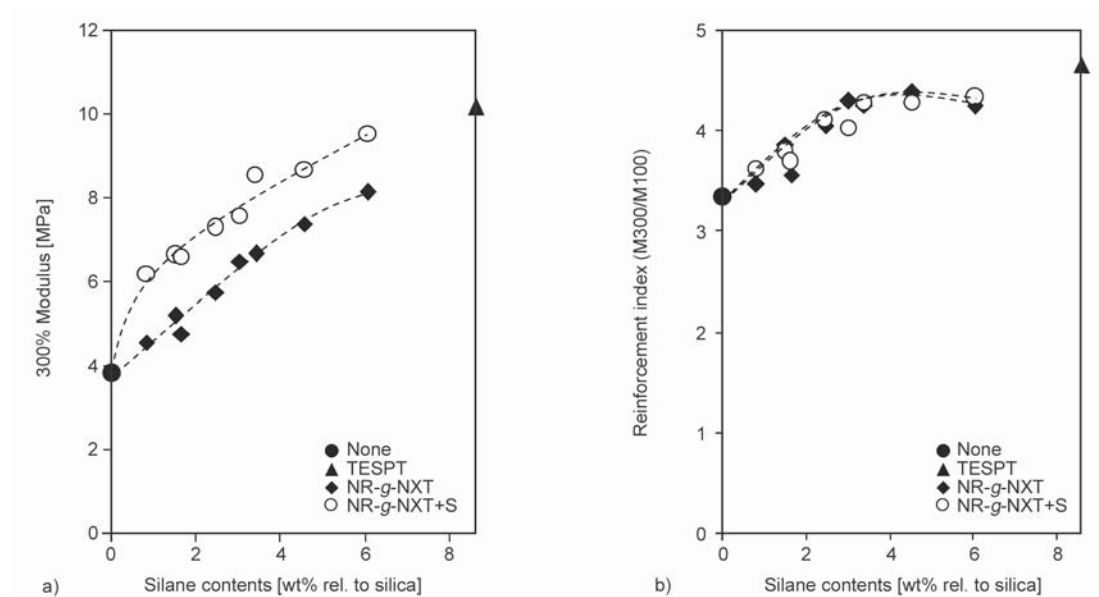
**Figure 14.** Modulus at 300% elongation (a) and reinforcement index (b) of silica-filled NR compounds with NXT-grafted-NR as compatibilizer without and with sulfur compensation, in comparison with the reference compounds with TESPT and without compatibilizer

to react with the silanol groups resulting in less interference with the curatives in the vulcanization reaction. The addition of more elemental sulfur to correct the total sulfur content towards the sulfur contained in the TESPT compound results in longer cure times, indicating that the change of sulfur-to-accelerator ratio has an influence on the crosslinking reaction in the rubber. In this case, the increase of sulfur content, while the accelerator and activator contents remain the same, leads to a longer time required to complete the vulcanization reaction.

The silica-filled NR-compounds with NXT-grafted-NR as compatibilizer show a decrease of torque difference with increasing amounts of NXT-silane which might be caused by the presence of NXT-fragments that can act as a plasticizer. The compounds with sulfur correction show a higher torque difference compared to the compounds with non-adjusted sulfur content, as seen in Figure 13b, due to the increased crosslink density in the rubber matrix.

**3.3.2. Tensile and dynamic mechanical properties**

The 300% modulus, reinforcement index and tensile strength of the silica-filled NR vulcanizates with NXT-grafted-NR as compatibilizer, with and without sulfur correction, increase with rising silane contents as shown in Figures 14 and 15a, respectively. Sulfur compensation increases the modulus of the vulcanizates due to an increase of the crosslink density *via*

sulfur crosslinks as indicated by the increase of torque difference in Figure 13b. However, the sulfur correction in the NXT-grafted-NR compatibilized vulcanizates has no effect on the reinforcement index, as seen in Figure 14b. The decrease in torque difference with increasing NXT-grafted-NR contents in Figure 13b does not reflect in the 300% modulus, as would have been expected: on the contrary, the 300% modulus increases, as does the reinforcement index. The ultimate 300% modulus and reinforcement index for the sulfur compensated compounds almost reach the level obtained for straight TESPT. The presence of 4.6 wt% NXT relative to the silica in the NXT-grafted-NR used as compatibilizer combined with sulfur correction increases the tensile strength to the same level as that for the optimum TESPT content. With sulfur correction and increasing NXT content, the elongation at break of the vulcanizates, as shown in Figure 15b, tends to decrease slightly as a result of more filler-rubber interactions and a higher crosslink density.

Storage modulus ($E'$) and tan δ of the silica-filled NR with NXT-grafted-NR, with and without sulfur correction, with TESPT and without compatibilizer are compared in Figures 16. In the glassy state, all the filled vulcanizates show a similar level of $E'$ even though they have different degrees of filler-rubber interaction as reflected in the bound rubber contents in Figure 6a, but in the rubbery region, the sulfur compensation slightly increases the storage modulus of
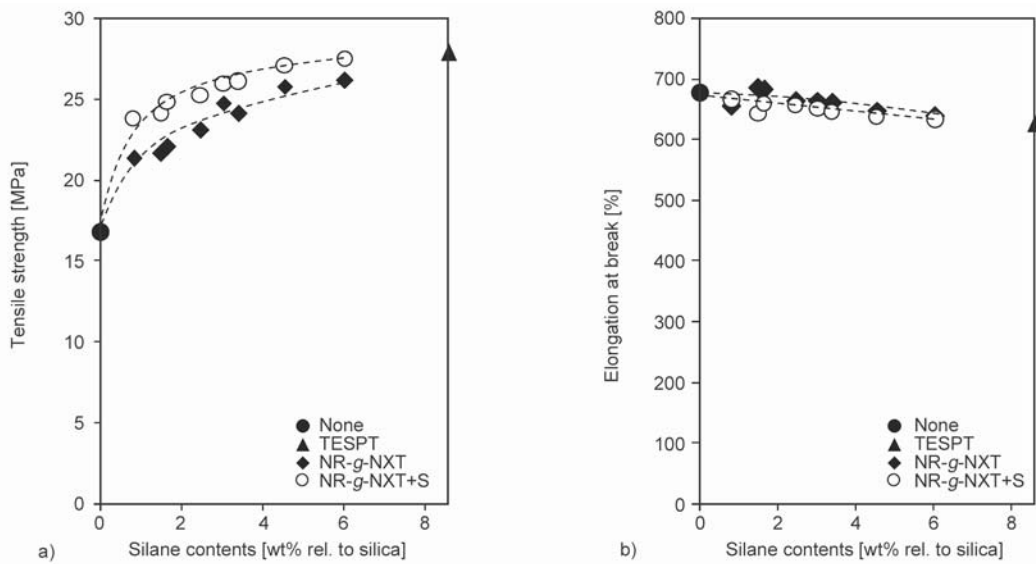
**Figure 15.** ensile strength (a) and elongation at break (b) of silica-filled NR compounds with NXT-grafted-NR as compatibilizer without and with sulfur compensation, in comparison with the reference compounds with TESPT and without compatibilizer

the silica-filled NR vulcanizate due to the increase of crosslink density: Figure 13b. The $\tan\delta$ peak of the silica-filled NR with NXT-grafted-NR is slightly shifted to a higher temperature compared to the silica-filled NR with TESPT and without compatibilizer, respectively. The increase of sulfur content due to the sulfur compensation towards to the level for TESPT compound results in a slight further shift of the $\tan\delta$ peak due to the increase of crosslink density, which restricts the segmental motion of the rubber chains. The $\tan\delta$ value at peak is also reduced after

the sulfur compensation, as more crosslink points restrict the relaxation and reduce chain flexibility. The $\tan\delta$ values at different temperatures are summarized in Table 8. The use of TESPT in the silica-filled NR vulcanizate gives the highest $\tan\delta$ at 5°C, that suggests the best wet grip for a tire-tread made thereof; and significantly lower $\tan\delta$ at 60°C compared to the non-compatibilized vulcanizate, indicative for rolling resistance of tire treads. However, the $\tan\delta$ at 60°C of the silica/TESPT system is slightly higher when compared to the vulcanizate containing NR-*g*-NXT.
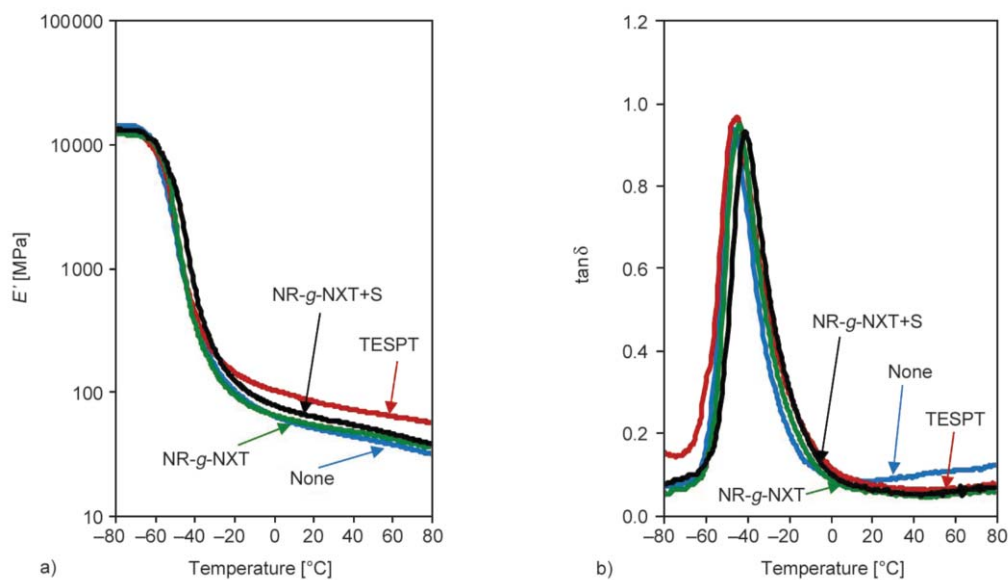


**Figure 16.** Storage modulus (a) and $\tan\delta$ (b) of silica-filled NR compounds with NXT-grafted-NR as compatibilizer without and with sulfur compensation, in comparison with the reference compounds with TESPT and without compatibilizer

The use of NR-*g*-NXT as compatibilizer suggests therefore somewhat inferior tire wet grip compared to the use of TESPT, but the lowest tan δ values at 60 °C imply the lowest tire rolling resistance. The inclusion of sulfur compensation relative to the reference compound with TESPT has practically no influence on tan δ at both 5 and 60 °C.

## 4. Conclusions

NXT-grafted-NR is successfully prepared under melt mixing conditions in an internal mixer at 140 °C using 0.1 phr of 1,1′-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane (Luperox® 231XL40) as initiator. The NXT-grafted NR is confirmed by FTIR infrared absorption bands at 3270, 1075 and 1035 cm$^{-1}$ which can be assigned to the deformations of OH, Si–O–C and Si–O–Si, respectively; by 1H NMR as indicated by the presence of methylene protons of the alkoxy groups (–OCH$_2$–C–) from the fragment of the silane that were attached to the NR molecule; and by elemental analysis *via* the SEM-EDX technique as indicated by the amounts of oxygen and silicon in the grafted NR.

Increasing amounts of NXT-grafted-NR as compatibilizer in silica-filled NR compounds decrease the Mooney viscosity, Payne effect, and increase the chemically bound rubber contents, 300% modulus, reinforcement index and tensile strength. Tensile fractured surfaces of the silica-filled NR vulcanizates indicate ductile failure with surface roughness and many tear lines when the NXT-grafted-NR is used, similar to the compound with TESPT. At the same silane loading, the use of NXT-grafted-NR as compatibilizer gives a better improvement in Payne effect, chemically bound rubber content, 300% modulus and tensile strength compared to the straight use of non-grafted silane, but the properties are still somewhat lower than for the use of TESPT at its optimum content, i.e. at 8.6 wt% relative to the silica. The sulfur-compensated-compounds with the NXT-grafted-NR of about 6 wt% NXT relative to the silica show a significantly higher cure torque difference compared to the counterparts without sulfur compensation that leads to the increase of the modulus and tensile strength of the vulcanizates to reach the level obtained for straight TESPT.

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