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SILANE-GRAFTED NATURAL RUBBER AS COMPATIBILIZER IN SILICA-REINFORCED NATURAL RUBBER

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Abstract

In spite of the wide application of silica and silanes in tires, this filler system still has its shortcomings. The main drawback is the elaborative processing, as the silica-silane as well as the silane-polymer bond have to be formed in situ during mixing and curing. Besides, this filler system does not work properly in natural rubber (NR), mainly due to the non-rubber components. Approaches to circumvent these disadvantages are the application of pre-treated silicas or grafted polymers.

In this study, the latter approach is chosen by grafting NR with different types of silanes: 3-octanoyl-thio-propyltriethoxysilane (OTPS) and 3-mercaptopropyl-di(tridecan-1-oxy-13-penta(ethyleneoxide))ethoxysilane (MPDTS). These silane-grafted NRs were used as compatibilizers in silica-filled NR compounds in concentrations of 5-20 phr, representing 0.8-6.1 wt% silane functionality relative to the silica, and compared to compounds with straight use of a silane ([(3-triethoxysilylpropyl)tetrasulfide, TESPT).

The use of the silane-grafted NRs as compatibilizers decreases Mooney viscosity, Payne effect and silica flocculation, improves filler-rubber interaction and significantly increases the tensile moduli, reinforcement index and tensile strength of the silica-filled NR-compounds compared to the non-compatibilized ones. At the same silane-content, the use of silane-grafted-NRs gives slightly better properties than the straight use of the silane, and the use of OTPS-grafted NR as compatibilizer shows a better overall performance than the use of MPDTS-grafted NR. In the presence of silane-grafted NRs as compatibilizers, the tan δ values at 60ºC decreased compared to the compounds with TESPT and without compatibilizer, posing a significant advantage over the conventional TESPT-filler technology.

When sulfur compensation was applied to the silica-filled NR compounds with the OTPS-grafted NR, the Mooney viscosity was slightly lower compared to the compounds without sulfur compensation, and a higher cure torque difference was measured as a consequence of the higher concentration of sulfur. After vulcanization, the rubber with 6% OTPS-grafted NR shows similar 300% modulus, reinforcement index, tensile strength and elongation at break compared to the reference compound with 8.6 wt% TESPT relative to the silica. Tensile fractured surfaces of the vulcanizates with sulfur compensation show more tear lines, which correlates with their higher tensile strength values. Therefore, the OTPS-grafted NR with sulfur compensation is an alternative to the straight use of TESPT in silica compounds.

Introduction

Several attempts are made in the recent past to increase the compatibility between natural rubber (NR) and silica. Chemical modification of natural rubber by epoxidation[1] is one approach and is widely used to increase the polarity, improve some properties of the rubber and enhance the compatibility with polar substances including silica. The silanol-groups on the silica surface interact with the epoxide groups of ENR through hydrogen bonds during processing and ring opening of the epoxide groups can form chemical bonds with silica via a condensation reaction with the silanol groups.[2,3] Silica-filled epoxidized polybutadiene (EpBR) and epoxidized styrene-butadiene rubber (EpSBR) show improvement in the chemical interaction between the rubbers and silica as well as improved filler dispersion.[4,5] A restriction of polymer chain movement by presence of the chemical bonds between the epoxide-groups and silica resulted in a shift of the glass transition temperature (T_g) of the silica-filled epoxidized rubber.[4-6]

An alternative pathway to enhance the compatibility between polymer and silica is to use silane modified polymers instead of straight use of a silane. Grafting of silane coupling agents onto polymer molecules are reported by using different types of silanes such as vinyltrimethoxysilane (VTMS)[7-9], vinyltriethoxysilane (VTES)[9-12] and mercaptopropyl-trimethoxysilane.[12-13] Vinylsilanes such as VTMS and VTES are widely used to modify polyolefins to improve the strength properties of the pure polymers via a self-crosslinking reaction. The grafting of vinylsilanes onto the polyolefins was carried out in a melt using dicumyl peroxide (DCP) as initiator[7-10], and under inert conditions at low temperature with azobisisobutyronitrile (AIBN) as initiator.[11] Increased crosslink density in the silane-grafted polyolefins leads to improvement of thermal stability and tensile properties.[8,9] Polypropylene (PP) grafted with VTES and PP-graft-VTES/silica nanocomposites were investigated in which the grafted silane affects the crystallization temperature of PP and the impact strength of the composites.[11] VTES was grafted onto styrene-butadiene rubber at a temperature of about 60-70°C by using potassium persulfate (KPS)[12] or benzoyl peroxide (BPO)[13] as initiators under nitrogen atmosphere. The use of SBR-g-VTES for a silica-filled compound led to improved cure and tensile properties,[12,13] and a shift of the glass transition temperature[12] (T_g) to higher temperatures due to the good interactions between silica and SBR-g-VTES, that restrict movement of the SBR-chains. Further, liquid polybutadiene (PB) has been modified with mercaptopropyltrimethoxysilane and mercaptopropyltriethoxysilane to improve the reinforcing efficiency of silica in this rubber.[14-15] The mercapto-silane-modified PB was prepared in solution at 75°C under inert atmosphere with AIBN as initiator, and the grafting reaction proceeded through radical addition of the thiol group of the silane to the double bond of PB, introducing alkoxy groups on the rubber chains. After a silanization reaction of silica with the silane-grafted PB, the silica characteristics showed a more hydrophobic surface, which was proven by an increase of contact angle[14] and a decrease of the number of hydroxyl groups on the silica surface.[15] The covalent bond Si-O-C of the silanized PB was analyzed by proton-, carbon- and silicon nuclear magnetic resonance spectroscopy (^{1}H-NMR, ^{13}C-NMR and ^{29}Si-NMR).[14,16] The better interaction of silica and rubber via silane-grafted PB improved the silica dispersion and tensile strength.[15] Therefore, the use of silane-modified polymer chains is an alternative method to improve bonding between hydrophilic silica and hydrophobic hydrocarbon rubber.

This paper reports the influence of 3-octanoyl-thio-propyltriethoxysilane (OTPS) grafted-NR and 3-mercaptopropyl-di(tridecan-1-oxy-13-penta(ethyleneoxide)ethoxysilane (MPDTS) grafted-NR, i.e. NR-g-OTPS and NR-g-MPDTS, respectively, as compatibilizers in silica-filled NR. The non-purified silane-grafted-NRs were used in a range of 5-20 phr and the respective amount of silanes was also straightly used in another set of compounds, for comparison. The properties of both compounds and vulcanizates compatibilized with silane and silane-grafted-NR are discussed in comparison with those without compatibilizer and with reference TESPT.

Experimental

Materials and compound preparation

The compounding ingredients, i.e. NR (RSS3), TESPT, silica (Zeosil 1165MP), TDAE oil, ZnO, TMQ, stearic acid, DPG, CBS and sulfur, used for preparation of the silica-filled NR compounds, were as follows:

- Natural Rubber: Ribbed Smoked Sheet (RSS) #3, locally produced in Thailand
- Highly dispersible silica: Zeosil 1165MP, Rhodia, France
- Bis-(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): Flexys, Belgium
- ZnO, stearic acid and sulfur: Sigma-Aldrich Chemie, Germany

Two different types of silane coupling agents were used for grafting onto NR: 3-mercaptopropyl-di(tridecan-1-oxy-13-penta(ethyleneoxide))ethoxysilane - MPDTS (VP Si-363, Evonik, Germany) and 3-octanoyl-thio-propyltriethoxysilane - OTPS (NXT, Momentive, USA).

For the grafting procedure, NR was mixed with the silane coupling agent and the initiator (0.1 phr of 1,1′-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane - Luperox® 231XL40, Arkema, USA; 40% extended on calcium carbonate and silica) in an internal mixer, Brabender® 50EHT (Brabender® GmbH & Co.KG, Germany), for 12 minutes with a rotor speed of 60 rpm at 140°C.

The OTPS- and MPDTS-grafted-NRs, pre-prepared by using 10 and 20 phr of silane, were used without purification in order to simplify the process. The amount of grafted OTPS is 3.43 wt% and 6.68 wt% respectively, and for the grafted MPDTS is 1.57 wt% and 3.10 wt%, respectively. To study the effect of OTPS- and MPDTS-grafted-NRs as compatibilizers in silica-filled NR, the silane-grafted-NRs were varied 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 compatibilizers are summarized in Table I.

Table I
Total OTPS and MPDTS contents used as compatibilizers in the silica-filled NR compounds

Amount of OTPS- and MPDTS-grafted-NR	Amount of total silane (wt% rel. to silica)
Silane-grafted-NR with 10 phr of silane	
• 5 phr	0.8
• 10 phr	1.7
• 15 phr	2.5
• 20 phr	3.4
Silane-grafted-NR with 20 phr of silane	
• 5 phr	1.5
• 10 phr	3.0
• 15 phr	4.6
• 20 phr	6.1

The silica-filled NR compound formulations with the various amounts of silane-grafted-NRs and the straight silanes are shown in Table II together with the references. The properties of the silica-filled NR compounds with the silane-grafted-NRs as compatibilizers were studied in comparison to the results of silica-filled NR with straight silanes at different amounts, as calculated based on the silane contents used in the preparation of the silane-grafted rubber, as shown in Table I. The mixing procedures are given in Table III. The first mixing step was performed using an internal mixer, Brabender® 50EHT, (Brabender® GmbH & Co.KG, Germany) with a mixing chamber volume of 70 cm^3. The initial mixer temperature setting was 100°C in order to reach a dump temperature in the range of 135-150°C. The second step of curative addition was carried out on a two-roll mill.

Table II
Compound formulations

Ingredients	Parts per hundred parts of rubber (phr)					
	References		Silane-grafted-NRs		Straight use of silane	
RSS3	100.0	100.0	95.0-80.0	95.0-80.0	100.0	100.0
TESPT	-	4.7*	-	-	-	-
OTPS-grafted-NR**	-	-	5.0-20.0	-	-	-
MPDTS-grafted-NR**	-	-	-	5.0-20.0	-	-
OTPS	-	-	-	-	0.8-6.1***	-
MPDTS	-	-	-	-	-	0.8-6.1***
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
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5

Remarks: * TESPT 4.7 phr equals 8.6 wt% rel. to silica; ** OTPS- and MPDTS-grafted-NRs were prepared by using silane contents of 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 I.

Table III
Mixing procedures

Mixing procedures	**Cumulative time (mins.)**
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	5

Property testing and characterization

Mooney viscosity of the compounds after step 2 were measured using a Visc Tech+ device (Tech-Pro Inc., USA) according to ASTM D1646, and cure characteristics were tested 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 13.95% strain.

The Payne effect or filler-filler interaction of the uncured silica-filled compounds were studied by using a Rubber Process Analyzer (RPA 2000, Alpha Technologies) at 100°C, frequency 0.5 Hz and varying strains in the range of 0.56 to 100%. The difference of storage moduli at low strain (i.e. 0.56%) and high strain (i.e. 100%) is reported. The flocculation rate constant (k_a) of the uncured silica-filled compounds was studied by using the RPA 2000 at 100°C, strain 0.56%, frequency 1.00 Hz, and test time 12 minutes.

For the bound rubber test of the non-productive compounds after step 1, 0.25 g of uncured compound (without curatives) was cut into small pieces, 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 the physically bound one. The sample was finally dried at 50°C for 24 h.

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 13.95% strain. The compounds were later cured to their respective cure times (tc90) with a compression mold (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.

The dynamic properties 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°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.

For the Scanning Electron Microscopy (SEM) analysis, the freshly tensile-fractured test pieces were surface-coated with gold before being analyzed in a Quanta 400 (FEI).

Results and discussion

Effect of OTPS-grafted-NR as compatibilizer and straight use OTPS on the properties of silica-filled NR compounds

Mooney viscosity, bound rubber content, Payne effect and flocculation rate constant: For filled rubber compounds, the viscosity depends on several factors, to include mastication time[17], mixing time[18], filler types[19,20], filler contents[20,21], compatibilizer or coupling agent[22,23], and storage time[19,24]. 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.

Mooney viscosities of the silica-filled NR compounds decrease with increasing amounts of silane either in the form of NR-g-OTPS or straight used OTPS, and both sets of compounds show similar properties, as shown in Figure 1(a). The Mooney viscosity of the filled-NR with OTPS and OTPS-grafted-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.*[25] For silica-filled compounds, the viscosity reduces when filler dispersion is improved.[23] Thus, the incorporation of OTPS or OTPS-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 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 large agglomerates to obstruct flow.

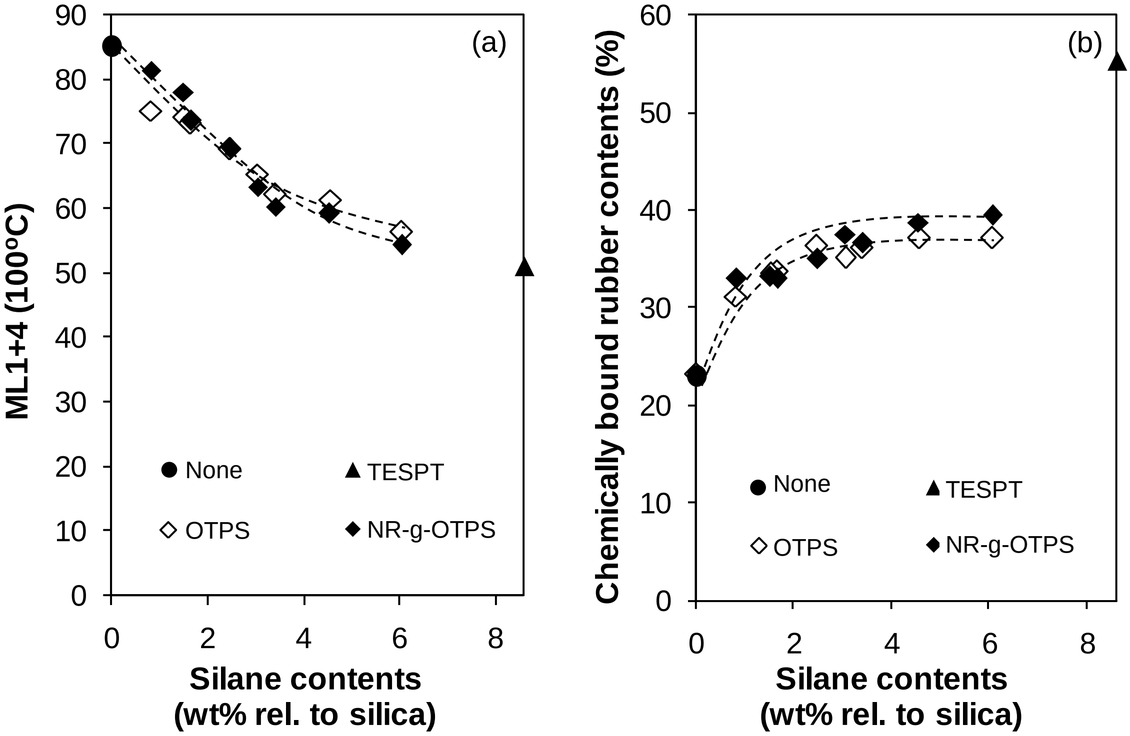

Figure 1 Mooney viscosity (a) and bound rubber content (b) of silica-filled NR compounds with use of straight OTPS (open symbols) and OTPS-grafted-NR (closed symbols)

Figure 1(b) shows the chemically bound rubber content of silica-filled NR compounds with different compatibilizers, in which the use of either NR-g-OTPS or straight OTPS significantly increases the bound rubber, i.e. increased silica-rubber interaction compared to the non-compatibilized one, but still to a significantly lower level compared to the reference compound with TESPT. The chemically bound rubber contents increase with rising amount of OTPS silane up to 3.4 wt% relative to the silica, thereafter the values level off. The use of OTPS-grafted-NR tends to show a marginally higher chemically bound rubber content than the straight use of OTPS, in accordance with the Payne effect in Figure 2(a). The partially to NR pre-bonded silane may enhance the compatibility between rubber and silica and allow the ethoxy-groups of OTPS to react more effectively with the silica during the silanization reaction. 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 moeity that results in pre-mature crosslinking with the NR molecules[26] 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 OTPS and OTPS-grafted-NR is remarkably decreased with increasing silane content to finally meet the same level of Payne effect of the compound with TESPT, as shown in Figure 2(a). The ethoxy-groups of the OTPS-silane undergo a silanization reaction with the silanol-groups of the silica and reduce the filler-filler interactions. Increasing amounts of OTPS-silane further decrease the Payne effect of the compounds and the use of OTPS-grafted-NR gives even slightly lower Payne effects than the straight use of OTPS.

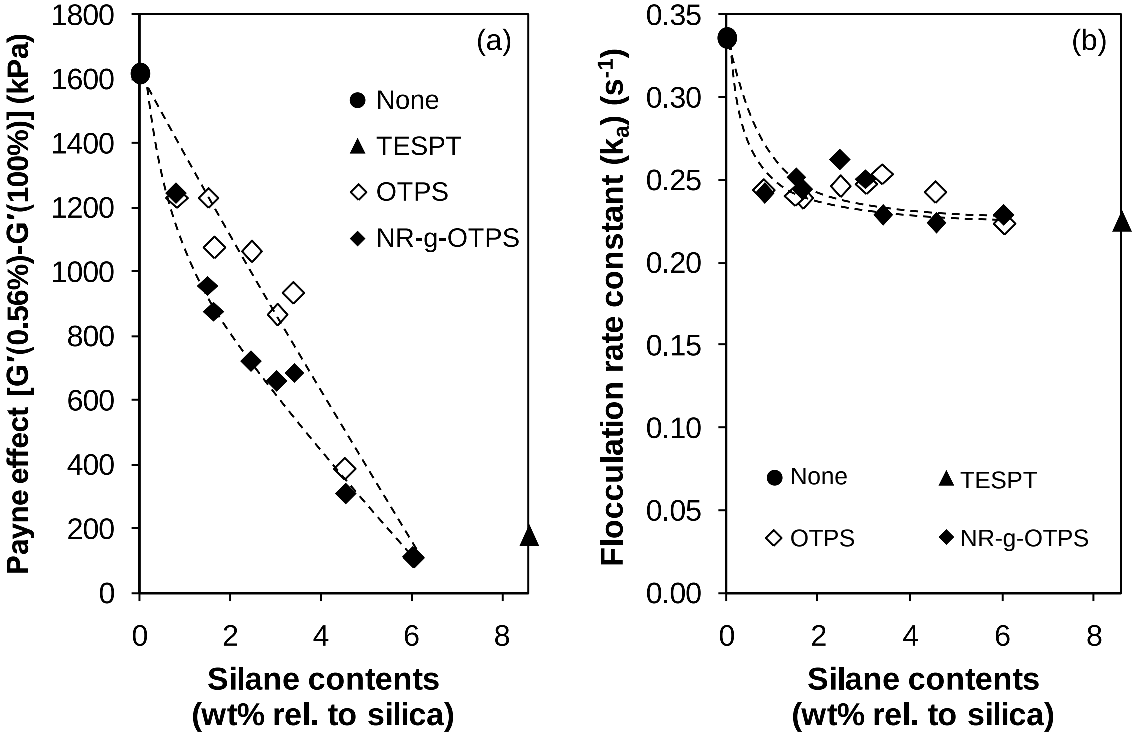

Figure 2 Payne effect (a) and flocculation rate constant (b) of silica-filled NR compounds with straight use of OTPS (open symbols) and OTPS-grafted-NR (closed symbols)

The flocculation behavior of the silica in the rubber matrix is due to the difference in polarity between silica and rubber causing re-agglomeration of silica aggregates or de-mixing, which will influence the properties of the material.[27] The flocculation rate constant (k_a) is used to determine the degree of re-agglomeration of the silica to form a silica-silica network under heat treatment.[28] At higher temperatures, silica aggregates can move easier within the rubber matrix to reform agglomerates and re-create a filler-filler network. The silica-filled compound without silane shows a strong silica flocculation tendency as shown in Figure 2(b) due to hydrogen bonding between the silanol groups on the silica surface. The addition of both, OTPS and OTPS-grafted-NR, at only a small amount already reduces the flocculation rate of the silica-filled compounds, like in the case of TESPT, due to reduction of the silica polarity by attaching of the silane onto the silica surface. However, further increase of OTPS-content has no additional effect on the silica flocculation rate constant.

Tensile properties: The modulus at 300% elongation and reinforcement index of the silica-filled NR vulcanizates compatibilized by straight use of OTPS in comparison to the use of OTPS-grafted-NR are shown in Figures 3(a) and (b). The modulus of the vulcanized silica-filled NRs significantly increases with rising OTPS-contents in both cases due to increase of the silica-rubber interactions. The use of OTPS-grafted-NR as compatibilizer gives a higher modulus than the straight use of OTPS, in accordance with the higher chemically bound rubber content: Figure 1(b), and lower Payne effect: Figure 2(a). The reinforcement index of the silica-filled NR vulcanizates also increases as a function of OTPS-content: Figure 3(b), to reach an optimum at about 4.5 wt% of OTPS relative to the silica, above which the addition of either more OTPS or OTPS-grafted-NR results in more or less the same values. In both cases the property levels of the TESPT-filled compound are not, respectively nearly, reached.

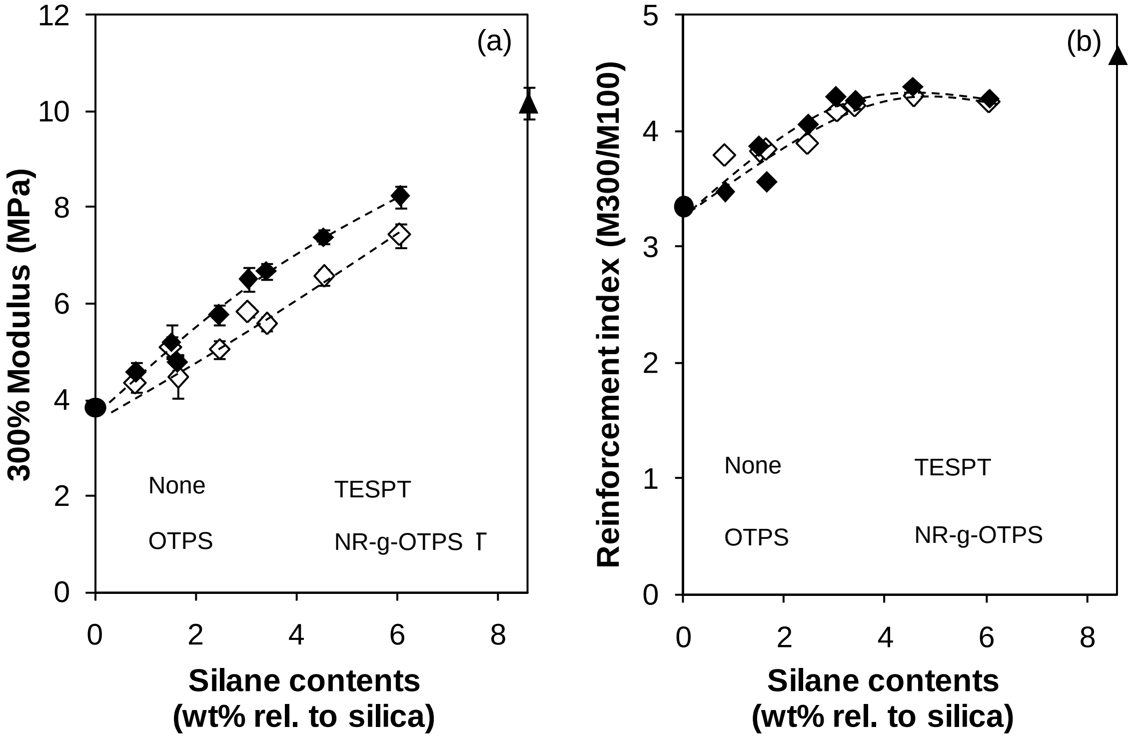

Figure 3 300% Modulus (a) and reinforcement index (b) of silica-filled NR with straight use of OTPS (open symbols) and OTPS-grafted-NR (closed symbols)

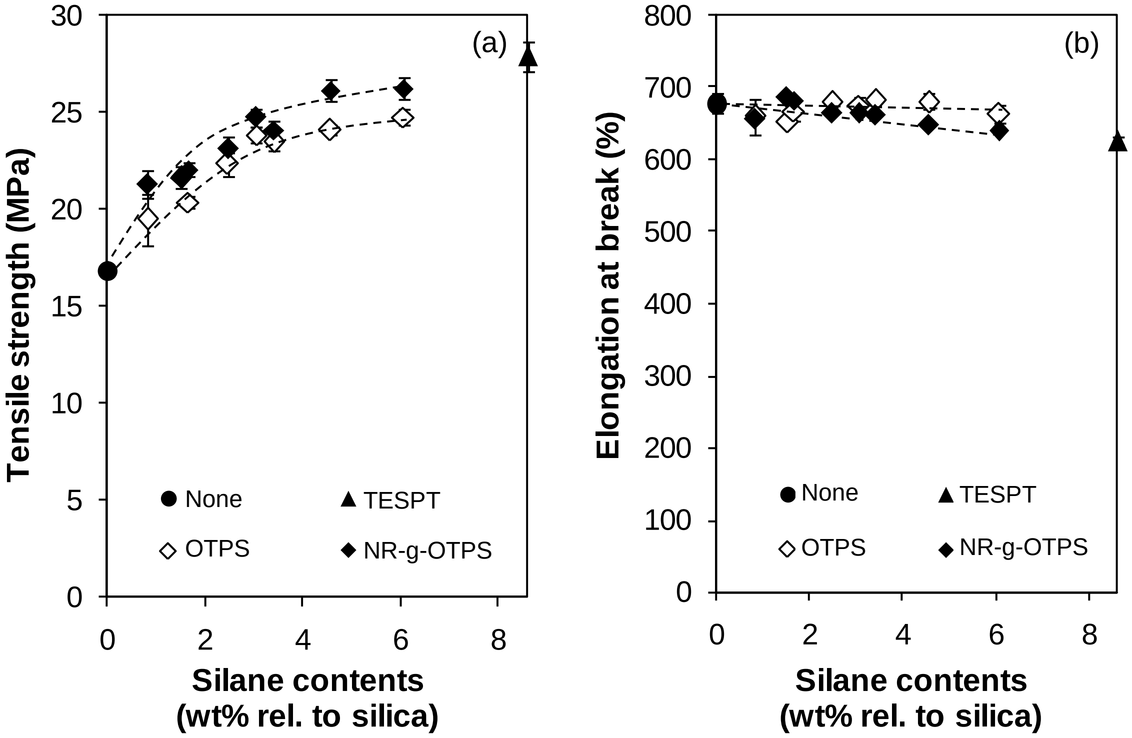

Figure 4 Tensile strength (a) and elongation at break (b) of silica-filled NR compounds with straight use of OTPS (open symbols) and OTPS-grafted-NR (closed symbols)

The tensile strength and elongation at break of the silica-filled NR vulcanizates with OTPS-grafted-NR and straight OTPS 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. The use of either OTPS or OTPS-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 OTPS-silane. The tensile strength rises progressively when the OTPS-content is increased up to about 3.5 wt% relative to the silica, and thereafter tends to level off. Like the 300% modulus in Figure 3(a), the use of OTPS-grafted-NR as compatibilizer gives a higher tensile strength than the straight use of OTPS-silane. 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 4(b).

Surface topography: SEM micrographs of tensile fractured surfaces of silica-filled NR vulcanizates without compatibilizer, with TESPT, with OTPS and OTPS-grafted-NR are compared in Figures 5(a)-(f). 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. The SEM micrographs of the vulcanizates with no compatibilizer and with reference TESPT, as shown in Figure 5(a) and (b) respectively, clearly correspond to their different tensile strength values: Figure 4(a). The addition of OTPS improves silica-rubber interactions to lead to more surface roughness and tear lines on the failure surfaces when compared to the filled vulcanizate without compatibilizer. The increasing amount of OTPS silane from 3.4 to 6.1 wt% relative to the silica results in ever more tear lines on the failure surfaces of the filled vulcanizates, as shown in Figure 5(c)-(f), due to more filler-rubber interaction and higher strength, and the surface topography resembles to 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 OTPS and by the use of OTPS-grafted-NR.

Effect of MPDTS-grafted-NR as compatibilizer and straight use of MPDTS on the properties of silica-filled NR compounds

Mooney viscosity, bound rubber contents, Payne effect and flocculation rate constant: The Mooney viscosities of the silica-filled NR compounds are different depending on the types and amounts of compatibilizers; as shown in Figure 6(a). The incorporation of compatibilizers either in the form of straight MPDTS silane or MPDTS-grafted-NR dramatically decreases the Mooney viscosity because of the improvement in silica-rubber interactions after the silanization reaction. This leads to improved silica dispersion, but there is no difference in Mooney viscosity between the two sets of compounds.

Figure 6(b) shows the chemically bound rubber content after treatment in ammonia atmosphere cleaving all weak physical filler-rubber bonds.[29] The results are similar to what was observed in Figure 1(b) for the OTPS-silane: an increasing amount of MPDTS increases the chemically bound rubber content in the compounds to just a slightly lower level compared to the effect of OTPS. 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 forms physical interactions between filler and rubber. The chemically bound rubber content therefore reaches a saturation point, as observed in Figures 1(b) and 8.6(b). The use of MPDTS-grafted-NR shows a slightly higher chemically bound rubber content than the straight use of MPDTS in the range of high silane contents, i.e. > 3.5 wt% relative to the silica, due to some thiol-groups of the MPDTS molecules already bonded to NR molecules prior to use, causing the higher extent of silica-rubber interactions.

The filler-filler interaction or Payne effect of the silica-filled NR compounds with various amounts of MPDTS silane is shown in Figure 7(a). Increasing MPDTS contents progressively reduce the Payne effect, and the use of silane either in its original form or in the silane-grafted-NR form results in similar properties. The flocculation rate constant (k_a) or re-agglomeration rate of the silica under heat treatment is reduced after applying the compatibilizers, as shown in Figure 7(b), but the scatter in the data due to the measurement error is too large to significantly discriminate between the two different forms of silane. During the silanization reaction, the ethoxy groups of the silane are condensed with the silanol groups of silica to form a covalent bond between silica and silane if straight silane is used, or to possibly form a link between silica and rubber if silane-grafted-rubber is used. Moreover, the bulky alkoxy-groups with oxygen atoms of MPDTS can adsorb on the silica surface giving a shielding effect on the polar surface. Therefore, the filler-filler interactions as well as flocculation rate constant are decreased.

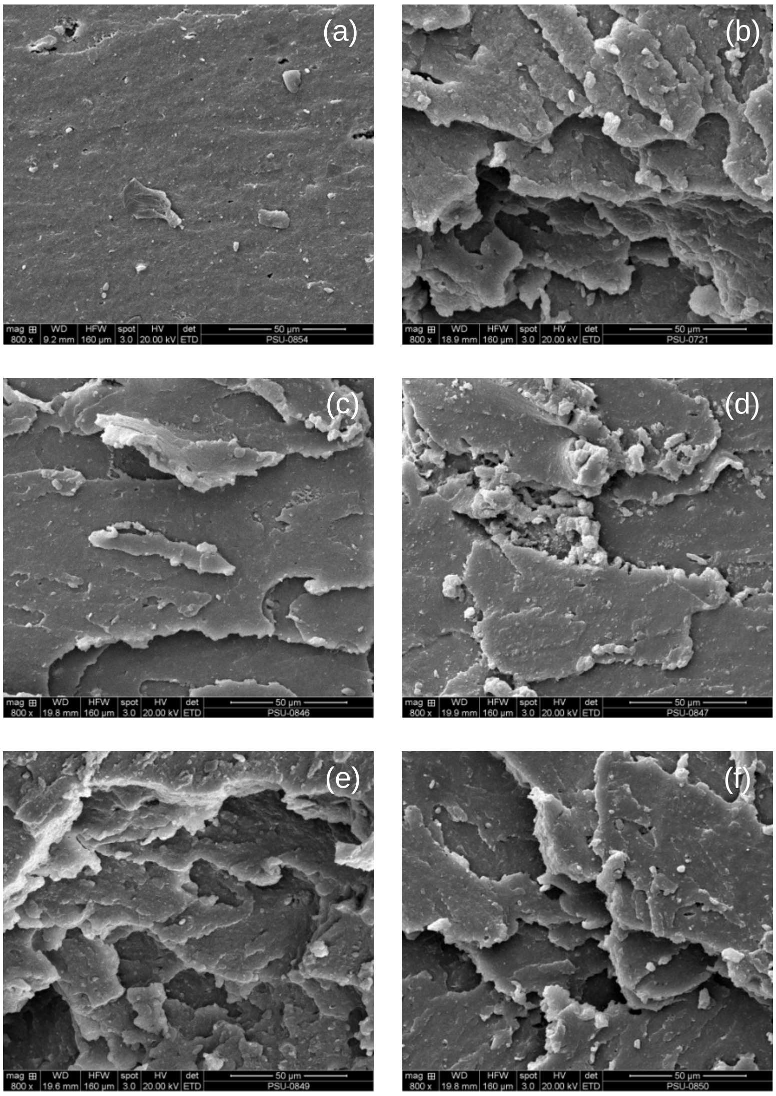

Figure 5 SEM micrographs of tensile fractured surfaces of silica-filled NR vulcanizates at 800x magnification: (a) no compatibilizer; (b) with TESPT at 8.6 wt% rel. to silica; (c) with OTPS at 3.4 wt% rel. to silica; (d) with OTPS-grafted-NR containing total OTPS of 3.4 wt% rel. to silica; (e) with OTPS at 6.1 wt% rel. to silica; and (f) with OTPS-grafted-NR containing total OTPS of 6.1 wt% rel. to silica

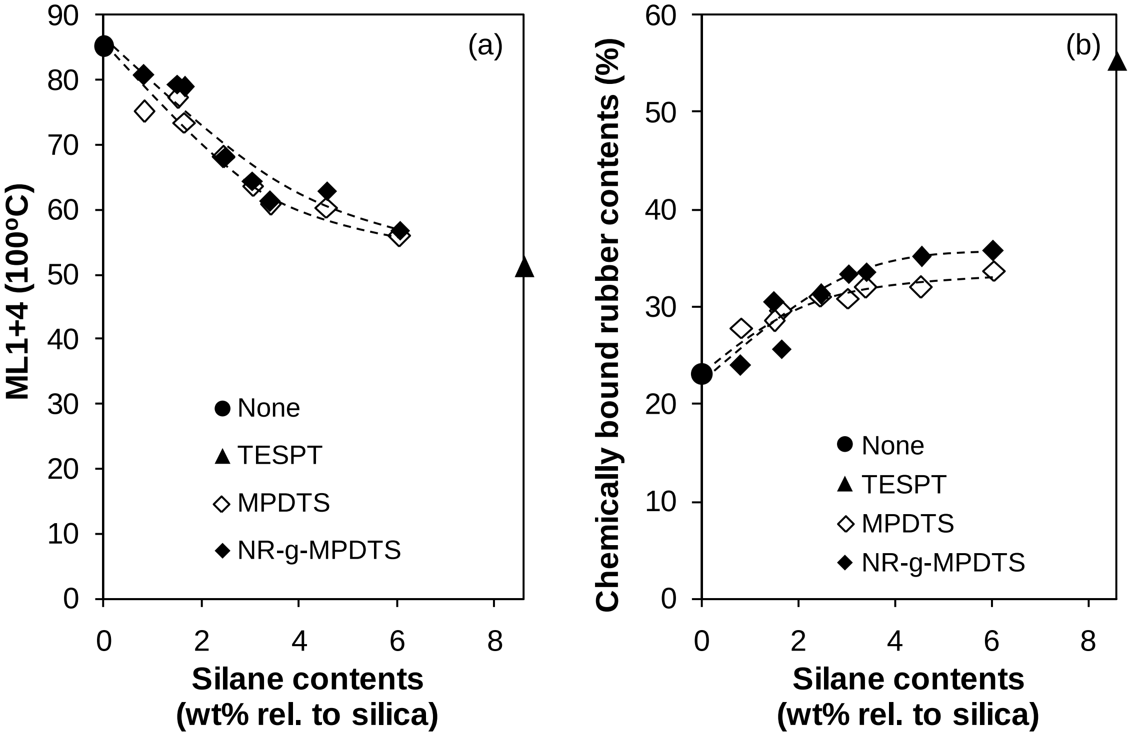

Figure 6 Mooney viscosity (a) and chemically bound rubber contents (b) of silica-filled NR with straight use of MPDTS (open symbols) and MPDTS-grafted-NR (closed symbols)

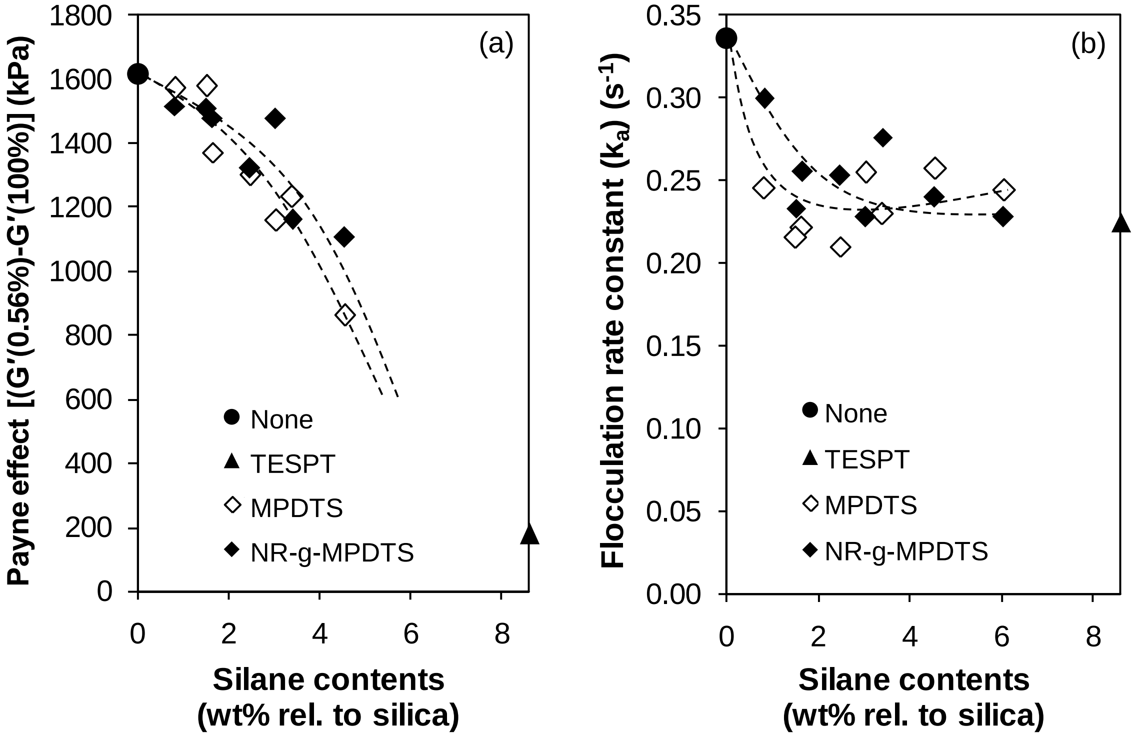

Figure 7 Payne effect (a) and flocculation rate constant (b) of silica-filled NR with straight use of MPDTS (open symbols) and MPDTS-grafted-NR (closed symbols)

Tensile properties: The 300% modulus and reinforcement index (M300/M100) of the silica-filled NR vulcanizates containing different amounts of MPDTS in the form of straight silane and silane grafted NR, are shown in Figures 8(a) and (b) in comparison to those containing TESPT and no compatibilizer. The two sets of compounds that contain MPDTS and MPDTS-grafted-NR show no significant difference in 300% modulus and reinforcement index. The values increase with increasing MPDTS contents but to a lower level compared to the use of TESPT. The increasing filler-rubber interactions as derived from the chemically bound rubber contents: Figure 6(b), lead to a higher resistance to deformation, but as there are no additional crosslinks generated by sulfur donated to the compounds by the silane molecules like in the case of TESPT, the MPDTS silanized compounds have a significantly lower modulus.

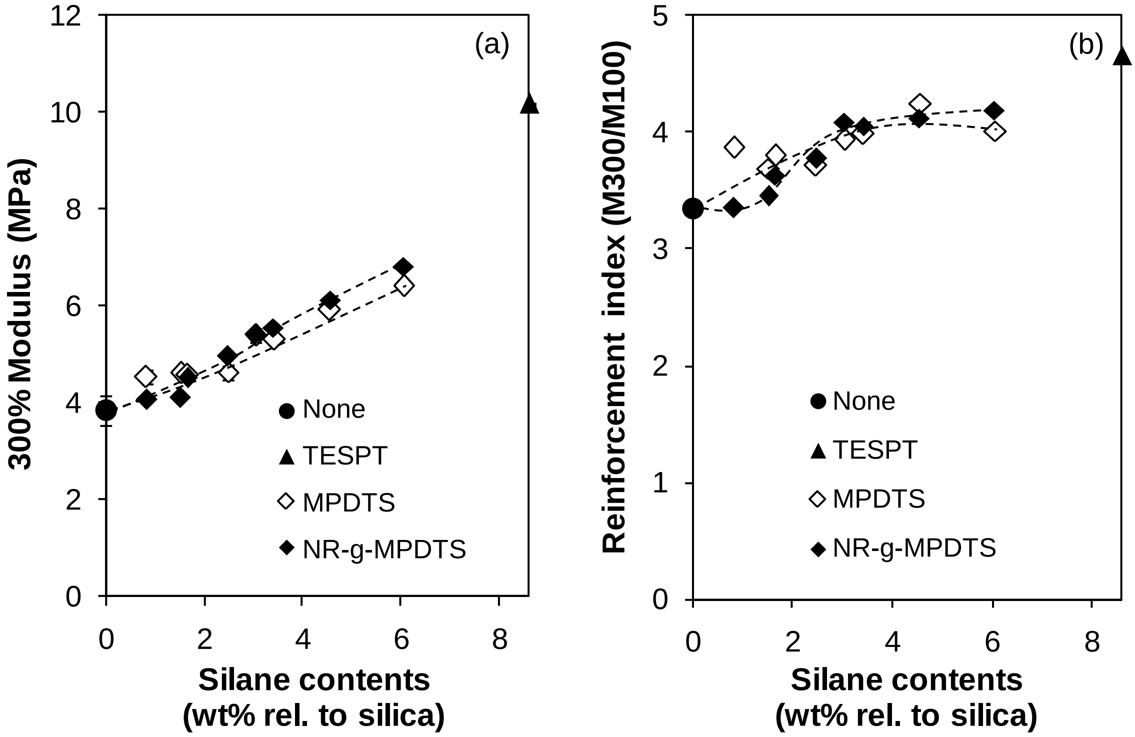

Figure 8 300% Modulus (a) and reinforcement index (b) of silica-filled NR with straight use of MPDTS (open symbols) and MPDTS-grafted-NR (closed symbols)

The tensile strength of the silica-filled vulcanizates increases as a function of MPDTS content due to the effect of the coupling reaction, where the use of MPDTS-grafted-NR as compatibilizer shows a better improvement in tensile strength especially at high MPDTS-grafted-NR content compared to the use of straight silane, as seen in Figure 9(a). The elongation at break of the silica-filled NR vulcanizates marginally decreases with increasing amount of MPDTS, as shown in Figure 9(b), due to deformation restriction by silica-to-rubber linkages but the vulcanizates show slightly higher elongation at break than the reference TESPT vulcanizate that has more crosslinks by the sulfur released from its tetrasulfide structure.

Surface topography: SEM images of the tensile fractured surface of silica-filled NR vulcanizates with the use of straight MPDTS and MPDTS that was partially bonded to NR are shown in Figures 10(c) and (d) in comparison to that of reference vulcanizates with no compatibilizer and with TESPT in Figures 12(a) and (b). The vulcanizates with TESPT and MPDTS-grafted-NR show similar failure surfaces with many tear lines in accordance with their similar tensile strength, whereas the one with the use of MPDTS shows a slightly less complicated fracture surface indicating a somewhat less ductile behavior. The weakest silica-filled NR vulcanizate without compatibilizer in Figure 10(a) shows a smooth fracture surface due to its poorer filler-rubber interactions that lead to easy sample rupture.

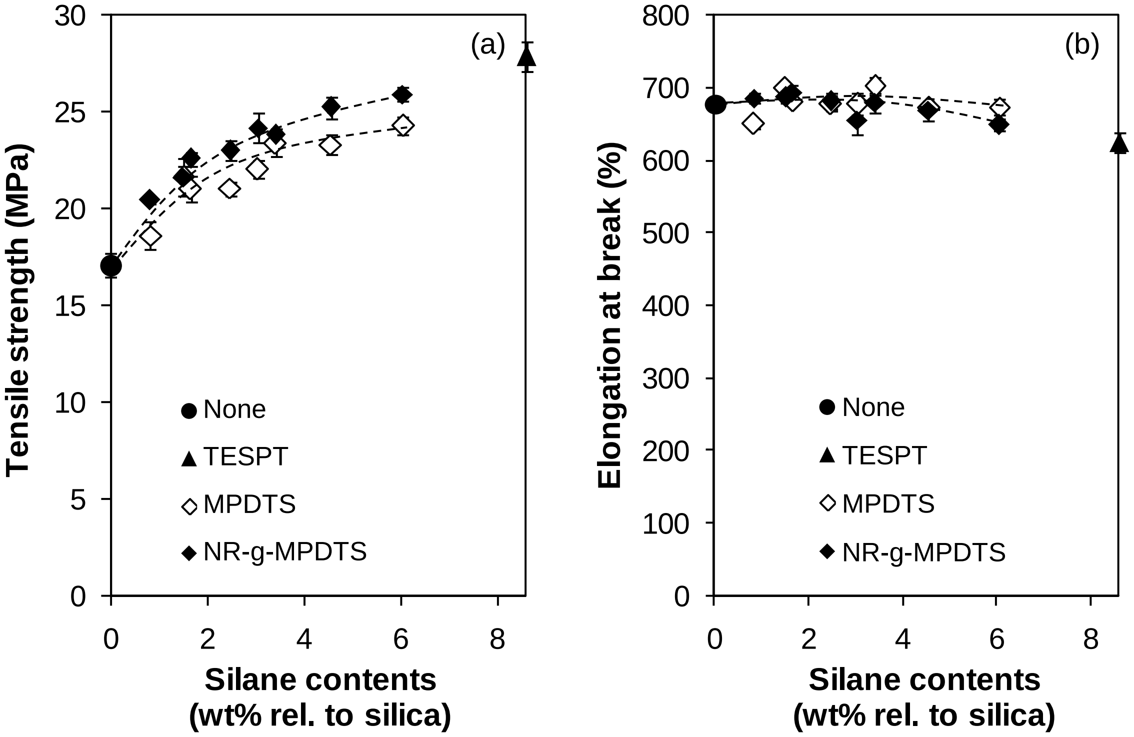

Figure 9 Tensile strength (a) and elongation at break (b) of silica-filled NR with straight use of MPDTS (open symbols) and MPDTS-grafted-NR (closed symbols)

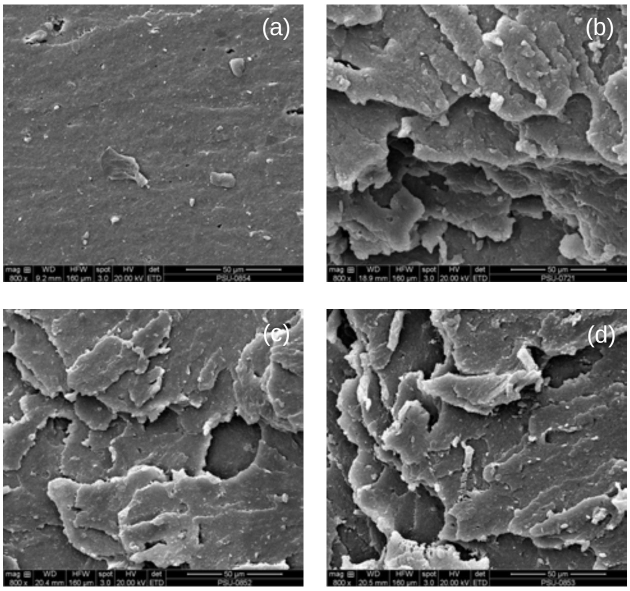

Figure 10 SEM micrographs of tensile fractured surfaces of silica-filled NR vulcanizates at 800x magnification: (a) without compatibilizer; (b) with TESPT at 8.6 wt% rel. to silica; (c) with MPDTS at 6.1 wt% rel. to silica; (d) with MPDTS-grafted-NR containing total silane of 6.1 wt% rel. to silica

Comparative properties of silica-filled NR containing OTPS-grafted-NR and MPDTS-grafted-NR as compatibilizers: The use of silane-grafted NRs, i.e. OTPS-grafted-NR and MPDTS-grafted-NR, as compatibilizers give slightly better overall properties of the silica-filled NR compounds compared to the straight use of free silane. In the silane-grafted NRs, part of the silane is already grafted onto the NR-molecules, and another part remains free in the material. The improvement in the filled-rubber properties results from a good filler-rubber interaction, as the pre-bonded silane and rubber may lead to a better coupling and network formation reaction during vulcanization. Mooney viscosity, chemically bound rubber content, Payne effect, flocculation rate constant, 300% modulus, reinforcement index, tensile strength, elongation at break and dynamic mechanical properties are presented in comparison to those of the reference compounds with TESPT and without compatibilizer.

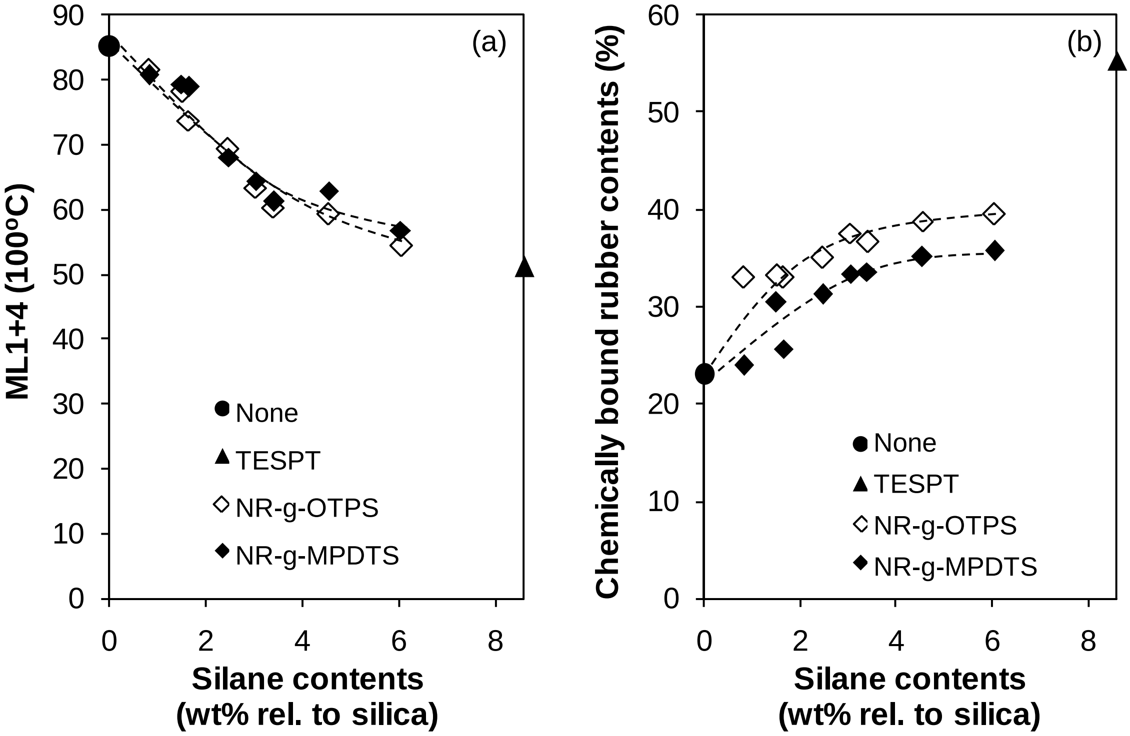

Figure 11 Mooney viscosity (a) and chemically bound rubber content (b) of silica-filled NR with OTPS-grafted-NR (open symbols) and MPDTS-grafted-NR (closed symbols)

Mooney viscosities of the silica-filled NR compounds with OTPS- and MPDTS-grafted-NRs decrease with increasing amounts of the compatibilizers, and both types of the silane-grafted NRs give very similar viscosity levels as shown in Figure 11(a). Figure 11(b) shows the chemically bound rubber contents of the silica-filled NR compounds in which the compounds with OTPS-grafted-NR show a higher chemically bound rubber content than those with MPDTS-grafted-NR. The filler-filler interaction or Payne effect of the silica-filled NR compounds remarkably decreases with increasing silane contents in the OTPS- and MPDTS-grafted-NRs, as shown in Figure 12(a). The use of OTPS-grafted-NR results in a significantly lower Payne effect of the filled compounds compared to the use of MPDTS-grafted-NR. At 6.1 wt% of OTPS, the compound shows a slightly lower Payne effect compared to the reference compound with 8.6 wt% of TESPT. Different silanes have different efficiencies for silica-reinforced compounds. At equal weight, OTPS that has a lower molecular weight and three ethoxy-groups per molecule, shall have more functional groups available on a molar basis to react with the silanol groups of silica. Even at the same amount of functional groups, the use of OTPS silane still provides a better improvement in the Payne effect than MPDTS due to its smaller molecule and less steric hindrance for the silanization reaction. Figure 12(b) shows the flocculation rate constants of the silica-filled compounds with different types of compatibilizer. The addition of both types of compatibilizer at only a small amount reduces the flocculation rate of the compounds to a similar level as that of the TESPT-compound. However, the scatter in the data is too large to discriminate between the NR-g-OTPS and NR-g-MPDTS.

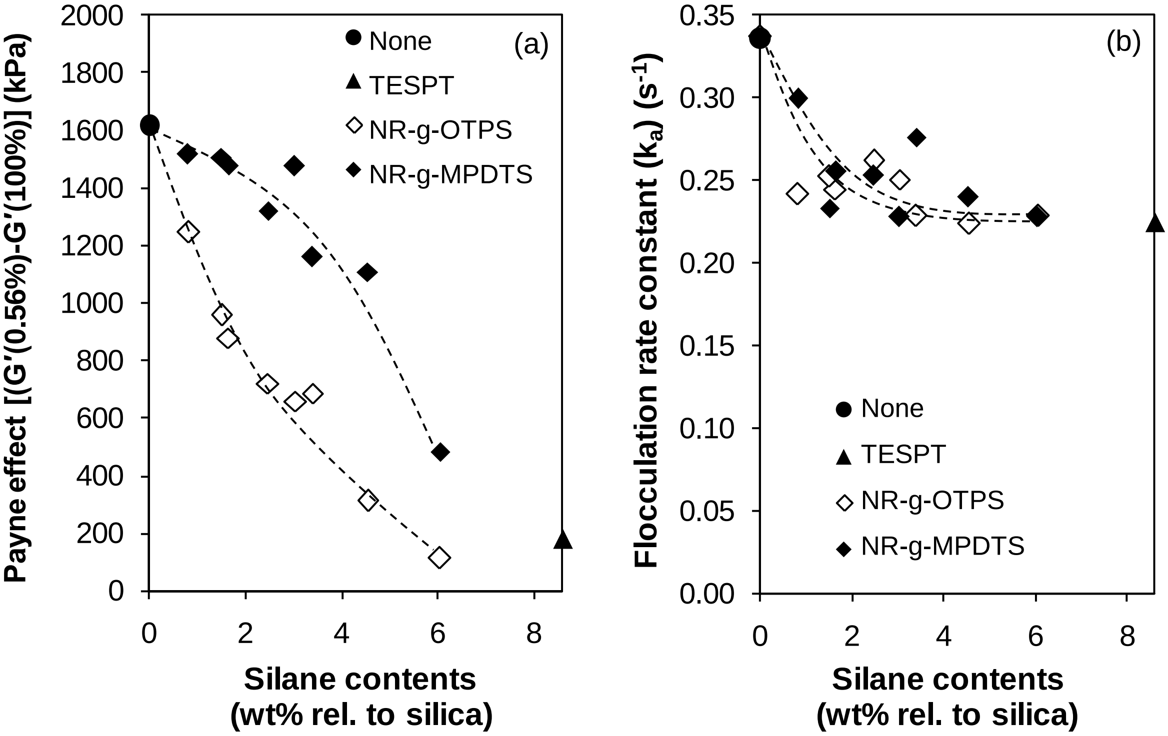

Figure 12 Payne effect (a) and flocculation rate constant (b) of silica-filled NR with OTPS-grafted-NR (open symbols) and MPDTS-grafted-NR (closed symbols)

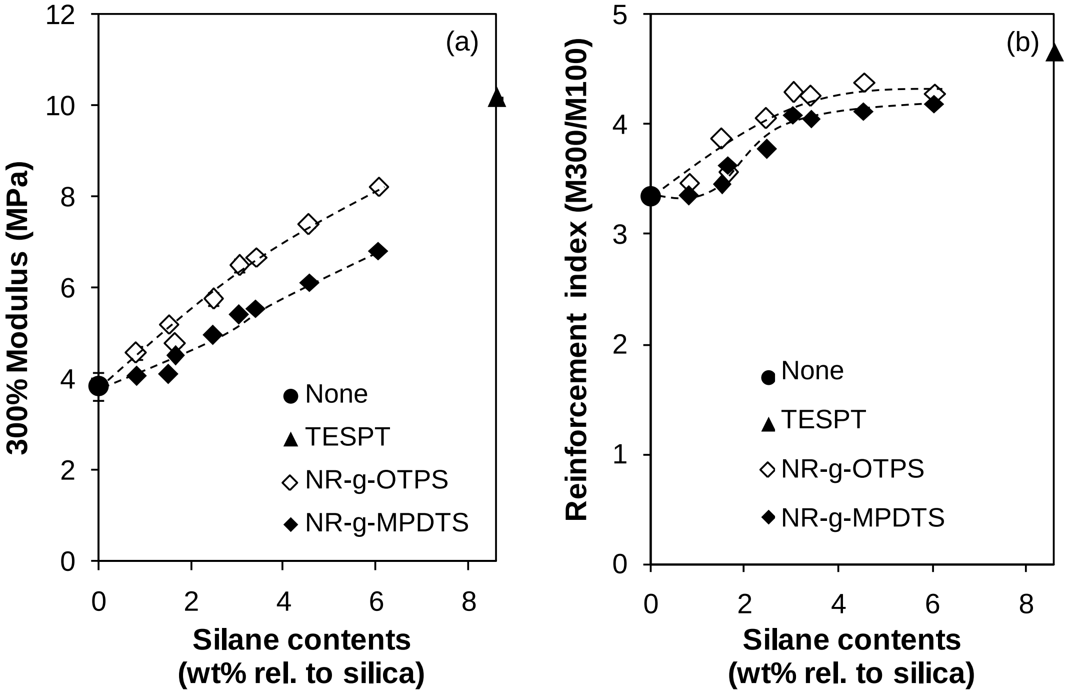

Figure 13 300% Modulus (a) and reinforcement index (b) of silica-filled NR with OTPS-grafted-NR (open symbols) and MPDTS-grafted-NR (closed symbols)

The 300% modulus and reinforcement index of the silica-filled NR vulcanizates increase with the addition of increasing amounts of silane in the grafted NRs as displayed in Figures 13(a) and (b), respectively. This corresponds with the increased filler-rubber interaction and decreased Payne effect. The incorporation of OTPS-grafted-NR leads to a clearly higher 300% modulus than the use of MPDTS-grafted-NR, indicating a higher reinforcement efficiency of OTPS for silica-reinforced NR. The OTPS silane consists of more reactive ethoxy-groups to form a bond with the silanol-groups on the silica surface compared to the MPDTS silane. Moreover, at equal total silane content in the compounds, the higher grafting efficiency of the OTPS on NR should result in a higher level of crosslinks or chemical bonds between rubber and filler, leading to a higher 300% modulus and reinforcement index.

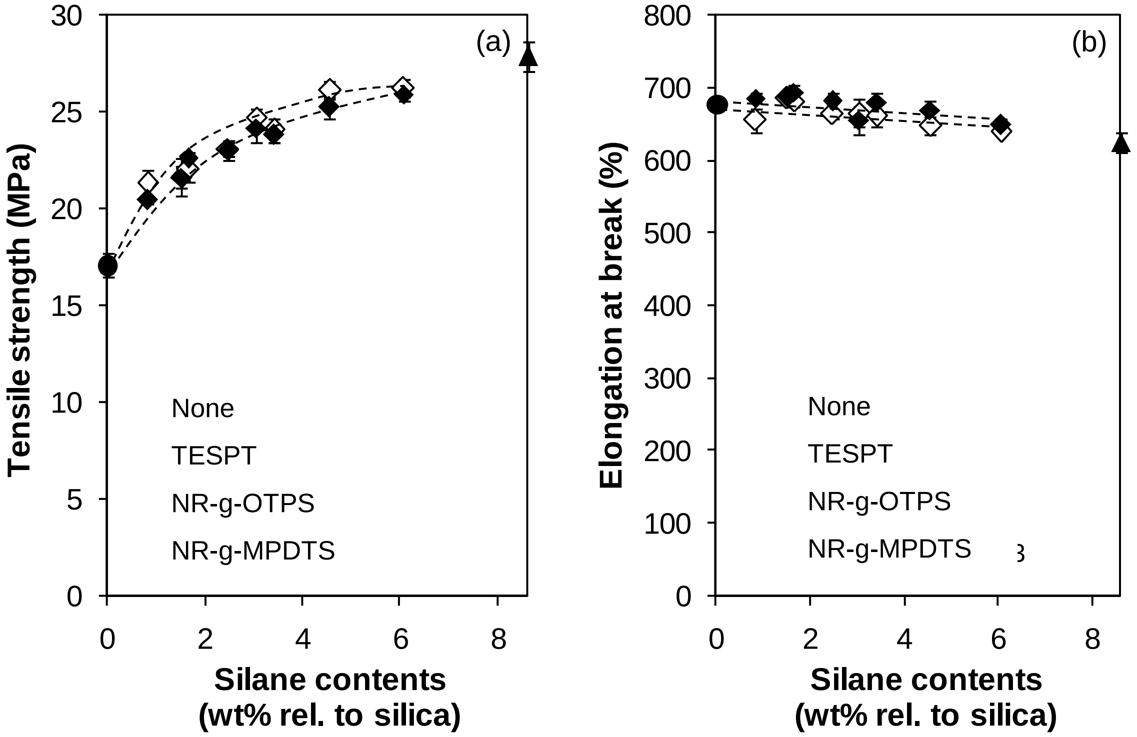

Figure 14 Tensile strength (a) and elongation at break (b) of silica-filled NR with OTPS-grafted-NR (open symbols) and MPDTS-grafted-NR (closed symbols)

The tensile strength of the silica-filled NR vulcanizates is enhanced with increasing total silane content in the grafted-NRs in correspondence with the increased modulus and reinforcement index as shown in Figure 14(a). However, amongst the silane types studied, TESPT still provides the best silica reinforcement for the NR compounds. The use of NR-g-OTPS and NR-g-MPDTS as compatibilizers results in more or less the same elongation at break, and increasing the total silane content decreases the extensibility of the vulcanizate to the level of the reference TESPT system as shown in Figure 14(b), due to the increase of linkages within the materials.

For the vulcanizates containing a total silane content of 6.1 wt% relative to the silica, with NR grafted by using 20 phr of silane, the dynamic mechanical properties were analyzed and the results are shown in Figures 15 and 8.16 in comparison with the ones with TESPT at 8.6 wt% relative to the silica and without compatibilizer.

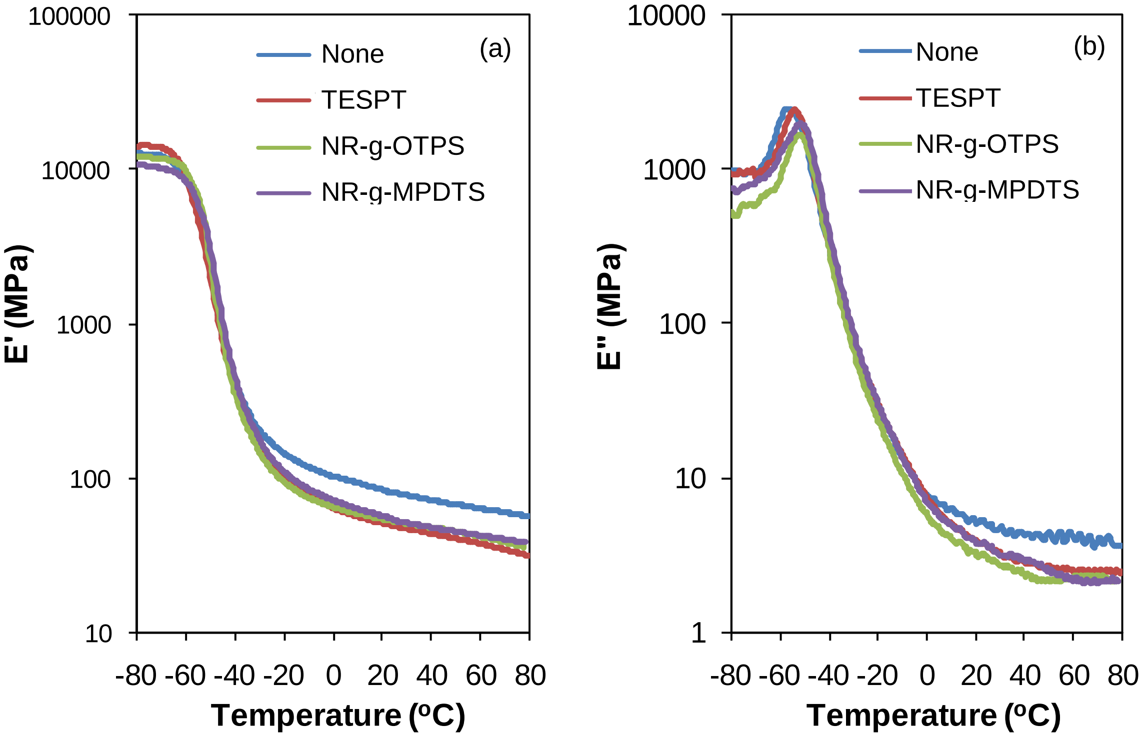

Figure 15 Storage modulus (E′) (a) and loss modulus (E") (b) of silica-filled NR with OTPS- and MPDTS-grafted-NRs, both with total silane of 6.1 wt% relative to the silica; TESPT at 8.6 wt% relative to silica

The storage (E′) and loss (E") moduli of the silica-filled NR vulcanizates as function of temperature are shown in Figures 15(a) and (b), respectively. In the glassy region, the silica-filled vulcanizate with TESPT shows a higher storage modulus compared to the mixes with OTPS- and MPDTS-grafted-NRs, respectively. But in the rubbery region, the filled rubber without compatibilizer shows the highest storage and loss moduli while the other vulcanizates with different compatibilizers show similar levels of the moduli. For filled rubbers, the modulus of the materials depends on filler content and filler-rubber interactions that affect the segmental mobility of the rubber chains, and the modulus normally increases with increasing amount of filler[30] or degree of filler-rubber interaction.[31] In the glassy region, the rubber with TESPT that has the highest filler-rubber interaction shows the highest storage modulus, i.e. the hardest vulcanizate. In the rubbery region, the highest storage and loss moduli of the silica-filled NR without compatibilizer are due to the highest filler-filler interactions that cause a filler-filler network with trapped or occluded rubber and less flexibility of the chains to relocate under deformation.[31] The incorporation of TESPT, OTPS- or MPDTS-grafted-NRs results in less filler-filler interaction which leads to lower storage and loss moduli due to the presence of more mobile rubber segments and less trapped rubber after the silanization reaction.

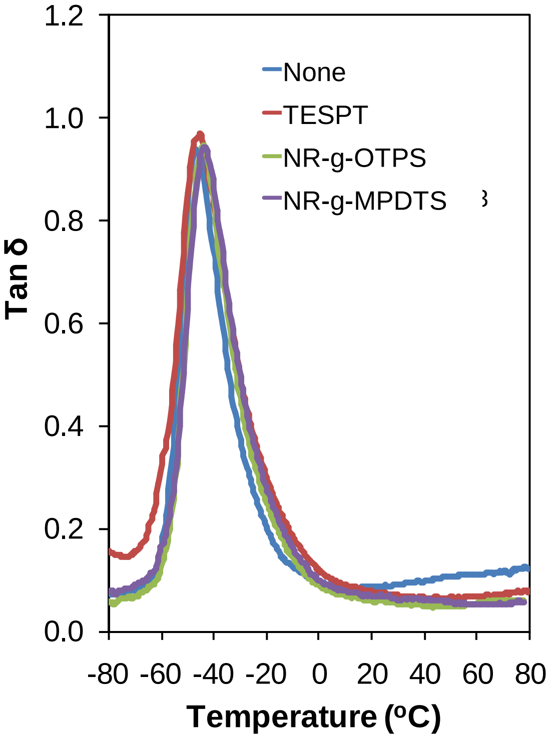

Figure 16 Tan δ of silica-filled NR with OTPS- and MPDTS-grafted-NRs, both with total silane of 6.1 wt% relative to the silica; TESPT at 8.6 wt% relative to silica

The loss tangent or tan δ values as a function of temperature of the silica-filled NR vulcanizates with different compatibilizers are shown in Figure 16, wherein the rubber with TESPT shows a slightly higher tan δ peak intensity over the other vulcanizates. This 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 with the three types of compatibilizers show lower tan δ values compared to the non-compatibilized one, due to their better filler-rubber interactions and therefore less energy loss during deformation. The values of tan δ at different positions are summarized in Table IV together with the values of T_g taken from the tan δ and E" peaks.

The glass transition temperature (T_g) is the temperature of the glass-to-rubber softening which can be observed as a large drop in modulus. Even though the T_g is often taken at the peak of tan δ, the T_g of a polymer can be reported by using the temperature at either the loss modulus (E") peak or at the tan δ peak, in which the value at the E" peak corresponds to segmental relaxation processes only and is not affected by different levels of filler-rubber interaction.[32] This present work compares the T_g's of the silica-filled NRs with different compatibilizers taken from both, the E" and tan δ peaks, which show the same trend, as shown in Table V: The T_g's of the silica-filled vulcanizates with TESPT, OTPS- and MPDTS-grafted-NRs 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 OTPS- and MPDTS-grafted-NRs as compatibilizers show lower chemically bound rubber content and inferior mechanical properties than the ones with TESPT, their T_g's are slightly higher than the latter. The use of silane grafted NR with silane molecules already bonded 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 response to dynamic deformation. The better chain flexibility in the compatibilized compounds and good filler-rubber interactions lead to lower energy losses and thus lower tan δ in the rubbery region.

Table IV

T_g and tan δ values of silica-filled NR vulcanizates at 6.1 wt% relative to the silica for NR-g-OTPS and NR-g-MPDTS; and 8.6 wt% for TESPT

Compatibilizer types	T_g(°C)		Values of tan δ		
	at tan δ peak	at E″ peak	at peak	at 5°C	at 60°C
No compatibilizer	-47	-58	0.94	0.09	0.11
TESPT	-45	-54	0.97	0.10	0.07
NR-g-OTPS	-44	-52	0.95	0.08	0.05
NR-g-MPDTS	-44	-52	0.95	0.08	0.05

The tan δ values at low temperature, i.e. 5-35°C for summer tires and 2-20°C for winter tires[33], and at higher temperatures commonly at 60°C, can be used to indicate tire wet grip and rolling resistance, respectively. The results in Table IV show that the use of OTPS- and MPDTS-grafted-NRs as compatibilizers give slightly lower tan δ values at 5°C, i.e. a small decrease in wet grip, but 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.

Overall, the use of silane-grafted-NRs as compatibilizers in the silica-filled NR compounds without sulfur compensation can effectively enhance the properties compared to the non-compatibilized system. By taking the compound with 8.6 wt% TESPT relative to the silica as reference, the use of OTPS-grafted-NR that gives better performance than MPDTS with 4-6 wt% of silane relative to the silica, gives similar Mooney viscosity, Payne effect and flocculation rate constant, but inferior chemically bound rubber content, modulus and tensile strength. However, a slight shift in the T_g of the vulcanizate in the presence of OTPS-grafted-NR gives a positive effect on tire rolling resistance as indicated by the lower tan δ at 60°C.

Conclusions

Increasing amount of OTPS- and MPDTS-grafted-NRs as compatibilizers in silica-filled NR-compounds result in a decrease in Mooney viscosity, filler-filler interaction or Payne effect, flocculation rate constant and in an increase of the chemically bound rubber content, 300% modulus, reinforcement index and tensile strength. The reinforcement index and tensile strength of the silica-filled NR vulcanizates level off when the silane content in the silane-grafted-NRs, which includes free and grafted silane, exceeds 3.0 wt% relative to the silica. Tensile fractured surfaces of the silica-filled NR vulcanizates indicate ductile failure with surface roughness and many tear lines, when the silane-grafted-NRs are used, similar to the compound with TESPT. At the same silane loading, the use of silane-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 a silane. Comparing the two types of silane-grafted-NRs, the use of OTPS provides a better improvement of overall properties than MPDTS, 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. In the presence of the silane-grafted-NR as compatibilizer, the T_g of the silica-filled NR vulcanizates is shifted to higher temperature. Tan δ at 5°C, that relates to wet grip, is slightly decreased, but the tan δ at 60°C is clearly reduced indicating a lower tire rolling resistance for tire treads made thereof, compared to the reference compound with TESPT.

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