



INFLUENCE OF SILANE MODIFIERS WITH DIFFERENT FUNCTIONALITIES ON SILICA-FILLED NR COMPOUNDS

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Wisut Kaewsakul¹, Kannika Sahakaro^{1,2}, Wilma K. Dierkes¹, Jacques W.M. Noordermeer¹, and Anke Blume¹

¹ Elastomer Technology and Engineering, Department of Mechanics of Solids, Surfaces & Systems, Faculty of Engineering Technology, University of Twente, The Netherlands

² Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani Campus, Thailand

E-mail: w.kaewsakul@utwente.nl

Abstract

To gain better insight into the chemical mechanisms of bifunctional organosilanes, especially TESPT in reaction with silica and natural rubber (NR), different types of modifying agents are employed to investigate the role of key functionalities contained in the modifying chemicals. The properties of silica-filled NR compounds and vulcanizates prepared with different silane agents are correlated with the phenomena of reinforcement.

The mechanisms of the reactions that take place during processing of the silica-based NR compounds are defined in this work. The investigation clarifies that when organosilanes bearing alkoxy- and sulfide-functional groups are used, there are three reaction mechanisms competitively taking place during primary compound mixing or in the non-productive mixing process. These mechanisms are all temperature dependent: 1) the silane-to-silica or silanization/hydrophobation reaction; 2) silane-to-rubber or coupling reaction; and 3) rubber-rubber crosslinking originating from active sulfur released by the polysulfide-based silanes. These simultaneous reactions reach an optimum at a dump temperature of approximately 140-150°C, as determined by filler-filler and filler-rubber interactions, and mechanical properties.

The network structures between silica-silane-rubber and rubber-rubber primarily account for an increase of the Mooney viscosity and chemically bound rubber content, as well as improved silica dispersion with less filler-filler interaction. The silane bearing only alkoxy groups show that it can improve the processing properties: lower Mooney viscosity, better silica dispersion, lower Payne effect and mechanical properties compared to the one without coupling agent. However, the best possible overall properties are only obtained when bifunctional coupling agents: TESPT and TESPd are used.

Introduction

Silica has become a strong alternative for carbon black fillers in tires after it was reported that it provides a better balance in tire properties, in particular rolling resistance, heat build-up, and wet grip, compared with those for the classical carbon black [1]. The introduction of silica into rubber compounds brought some disadvantages, generally with regard to processing and vulcanization aspects. The most widely used method to maximize the reinforcing efficiency of silica is the use of bifunctional organosilanes as coupling agents of which bis-(triethoxysilylpropyl) tetrasulfide (TESPT) is the common silane coupling agent for silica-filled rubber compounds [2].

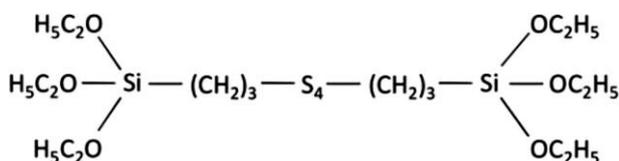
In practical mixing procedures, the silica, TESPT, and rubber are simultaneously introduced into an internal mixer, in which various complicated reactions simultaneously take place [3,4]. Within this mechanistic complexity, the extents of two important reactions need to be optimized: (1) the silanization or hydrophobation reaction between silane and silica; and (2) the coupling reaction between silane and rubber. Both reactions are dependent on time and temperature. The hydrophobation reaction is rather slow at moderate temperatures of, for example 120°C [4]. Thus, a high compound mixing temperature which is often determined as the dump temperature is required to obtain a short processing cycle. At elevated temperatures, on the other hand, the coupling reaction between silane and rubber can be triggered, resulting in premature scorch and hence an undesired high compound viscosity [5].

Based on a study with SBR/BR tread compounds [6], the dump temperature should be in the range of 145-155°C to achieve good silanization and to avoid precrosslinking. For silica-filled natural rubber system [7], in addition to the silanization reaction, precrosslinking reactions take place during NR compound mixing as NR can start to react with sulfur released from TESPT molecules at a temperature as low as 120°C. However, this phenomenon does not have an adverse effect on the NR vulcanizate properties. Hence, based on the overall properties, it was suggested that a dump temperature in the range of 135-150°C is still the most appropriate condition for silica-filled NR compounds with TESPT as coupling agent.

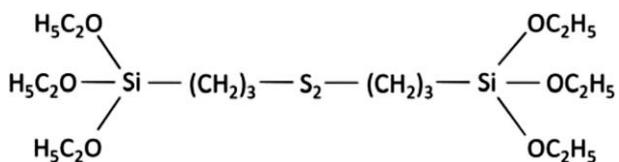
To render insight in the chemical mechanism of bifunctional organosilanes in reaction with NR, especially TESPT, this study was then executed. The properties of silica-filled NR compounds and vulcanizates prepared with different silane agents are investigated and correlated with the phenomena of reinforcement. Various factors influencing the reinforcing ability of silanized silica in NR are discussed.

Experimental

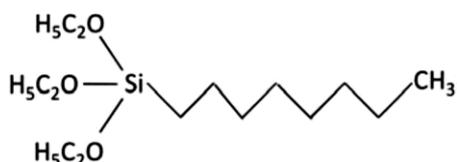
Conceptual. – The experiments are designed to observe the phenomena of the key functionalities, the quantities of silane used in this study are based on equimolar concentrations of alkoxy- or sulfur-functionalities with reference to a certain amount of TESPT. Hence, the number of alkoxy groups in alkoxy-based silanes is equalized so that the silanization or hydrophobation effects can be compared for each compound. A silane carrying only tetrasulfide groups (without alkoxy groups) is included comparable to the active sulfur content assumed to be available in the TESPT-added compound system. The effect of average sulfur-chain length of silane coupling agents on the reinforcement efficiency is also studied to obtain information about whether the tetrasulfide group of TESPT is the optimal sulfur rank, or whether other (lower) sulfur ranks give comparable or even better performance. In addition, a vinyl type silane is included to investigate the effects of different alkoxy type functionalities, and whether the vinyl-site can also react with NR. Figure 1 shows the chemical structure and some technical data of five silane modifiers with their dosage used for the compound formulation in this study.



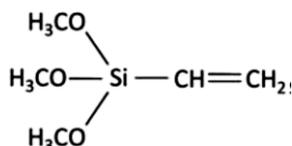
(i) Bis-triethoxysilylpropyl tetrasulfide or TESPT: Mw = 539 g/mol, Dose = 9.0 wt% or 5.0 phr, Supplied by Ben Meyer, Germany, Trade name Couplink-69.



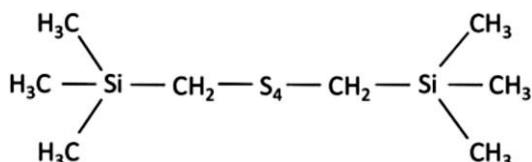
(ii) Bis-triethoxysilylpropyl disulfide or TESPDP: Mw = 475 g/mol, Dose = 7.9 wt% or 4.4 phr, Supplied by Evonik, Germany, Trade name Si-266.



(iii) Octyltriethoxysilane, OTES: Mw = 539 g/mol, Dose = 9.2 wt% or 5.1 phr, Purchased from Merck KGaA, Germany.



(iv) Vinyltrimethoxysilane, VTMS: Mw = 539 g/mol, Dose = 4.9 wt% or 2.7 phr, Purchased from Merck KGaA, Germany.



(v) Bis-trimethylsilylmethyl tetrasulfide, TMSMT: Mw = 539 g/mol, Dose = 5.0 wt% or 2.8 phr, Synthesized in-house following the procedure described elsewhere [8].

Figure 1. Chemical structure of silane modifiers.

Compound preparation. – The compound formulations used in this study are shown in Table 1. The qualities of silanes were based on equimolar concentrations of alkoxy- or sulfur-functionalities with reference to the optimal amount of TESPT at 5.0 phr or 9.0 wt% relative to the silica amount. Hence, the number of alkoxy groups in alkoxy-based silanes, that is TESPT, TESP, OTES, and VTMS, was equalized so that the silanization or hydrophobation effect can be compared for each compound. Meanwhile, the TMSMT amount was adjusted with respect to the active sulfur content assumed to be available in the system. Based on the equimolar calculation, the dosage of each silane used in the formulation is indicated in Figure 1.

Table 1. Compound formulation.

Ingredients	Amount (phr)	Technical data; Supplier
NR (RSS3)	100.0	Ribbed Smoked Sheet, grade 3; locally produced in Pattani, Thailand
Silica (Ultrasil 7005)	55.0	CTAB-specific surface area 171 m ² /g, Evonik, Germany
TESPT (or other)	5.0 (or variable)	See Figure 1(i)
Process oil (TDAE)	8.0	Treated distillate aromatic extract, Vivatec 500; Hansen & Rosenthal, Germany
Zinc oxide	3.0	Imperial Chemical, Thailand
Stearic acid	1.0	
TMQ	1.0	Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline; Flexsys, Belgium
DPG	1.1	Diphenylguanidine; Flexsys, Belgium
CBS	1.5	N-cyclohexyl-2-benzothiazolesulfenamide; Flexsys, Belgium
Sulfur	1.5	Siam Chemical, Thailand

The mixing was performed using an internal mixer with a mixing chamber of 500 cm³ (Charoen Tut, Thailand). The mixer was operated at a fill factor of 70% and a rotor speed of 60 rpm. The initial mixer temperature settings were adjusted from 50 to 140°C to reach final dump temperatures in the range of 100-170°C. NR was initially masticated for 2 min, then half of the silica and silane

were added and mixed for 5 min, prior to adding the second half of silica and silane together with TDAE oil. The mixing was continued to the full silica-silane-rubber mixing interval of 10 min. Subsequently, ZnO, stearic acid, TMQ, and DPG were added and mixed for 3 min. The compounds were then discharged, sheeted out on a two-roll mill, and kept overnight prior to the incorporation of CBS and sulfur on a two-roll mill.

Property determinations. – The compounds were tested for their Mooney viscosities by using a Mooney viscometer (ViscTech+, TechPro, USA) according to ASTM D1646. The cure characteristics were determined using a Moving Die Processability Tester or MDPt (TechPro, USA) with the testing condition of a frequency 0.833 Hz and 2.79% strain. The optimum vulcanization time (t_{c90}) was determined and used for press-curing of the samples at 150°C.

Payne effect which determines the extent of filler-filler interaction was measured under shear deformation using a Rubber Process Analyzer (RPA, Alpha Technologies, USA). The compound samples were cured to t_{95} at 150°C, prior to performing a strain sweep test in the range of 0.56-100% at 0.50 Hz and 100°C.

Chemically bound rubber contents were measured with ammonia treatment. 0.2 g of sample, that is uncured masterbatches (without curatives), was extracted by toluene for 72 h at room temperature. The toluene was renewed every 24 h. The sample was removed from the toluene, dried at 105°C for 24 h. The sample was immersed again in toluene for 72 h at room temperature in an ammonia atmosphere with renewing toluene every 24 h. The sample was finally dried at 105°C for 24 h and weighed. The bound rubber content was calculated according to the equations demonstrated elsewhere [7].

The compounds were press-vulcanized at 150°C to t_{c90} . The vulcanized sheets having a thickness of about 2 mm were die-cut to dumbbell-shaped specimens for tensile tests. Tensile tests were performed at a crosshead speed of 500 mm/min according to ASTM D412 using a Hounsfield Tensile Tester. The mean values of tensile properties taken from five specimens are reported.

Results and discussion

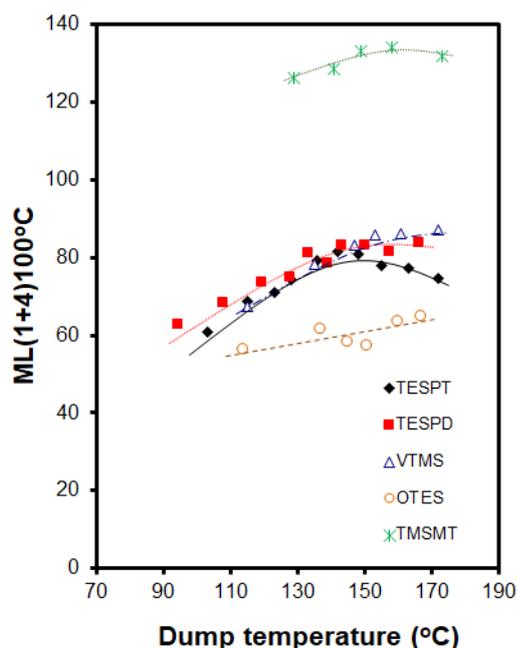


Figure 2. Mooney viscosity of compounds.

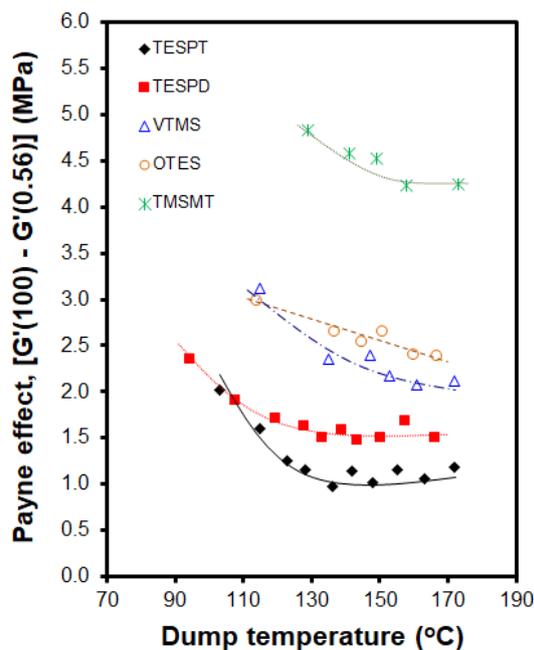


Figure 3. Payne effect of compounds.

Figure 2 shows that, with increasing mixing dump temperature, the Mooney viscosity of the compounds prepared with TMSMT, a sulfidic (nonalkoxy)-silane, gradually increases and reaches an optimum at dump temperatures in the range of 140-150°C. TESPT and TESP, which are

sulfidic alkoxy-type silanes, show a similar trend, but at lower values. After the Mooney viscosities have reached the maximum value, the compounds show some sort of reversion which could be linked to a change within the polysulfide linkages.

According to the conclusion given in our previous studies [7], this result is in good agreement with the fact that, apart from the silanization reaction, a certain amount of coupling and crosslinking reactions of active sulfur toward NR also takes place during mixing in the mixer, which results in a rise of the Mooney viscosity. Basically, all these reactions are temperature dependent. Higher mixing temperatures lead to a higher potential for silanization as well as for crosslinking. This points to a dominant effect of network contributions toward the compound viscosity.

For the sulfide-based silanes, that is TESPT, TESP, and TMSMT, the crosslinks are formed via sulfur that is released and activated at the high temperature. For vinyl silane, that is VTMS, the crosslinks can also occur via C=C and active radicals generated during mixing.

Figure 3 shows that the change of the Payne effect with dump temperature of the different compounds shows a good agreement with the Mooney viscosities. The lowest filler-filler interactions or Payne effects are achieved by using TESPT and TESP as silica surface modifying agents. OTES and VTMS show higher levels but a similar extent of filler-filler interaction, whereas TMSMT gives the highest level of Payne effect in accordance with the highest compound viscosities as shown in Figure 1.

It is clear that alkoxy-based organosilanes reduce filler-filler interaction for silica-filled NR compounds, indicating that they can effectively transform the hydrophilic into a more hydrophobic silica surface to provide better compatibility between the silica and the NR. However, the different alkoxy-silanes show variable efficiency because of their differences in functionalities on the other side of the silane molecules as illustrated in Figure 1.

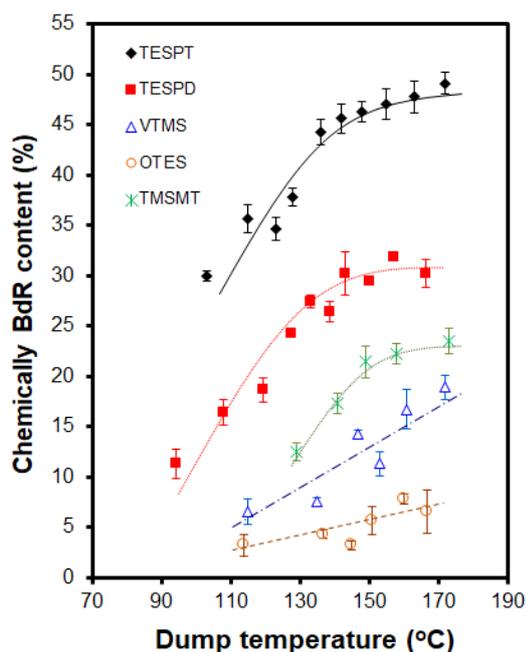


Figure 4. Bound rubber content of compounds. vulcanizates.

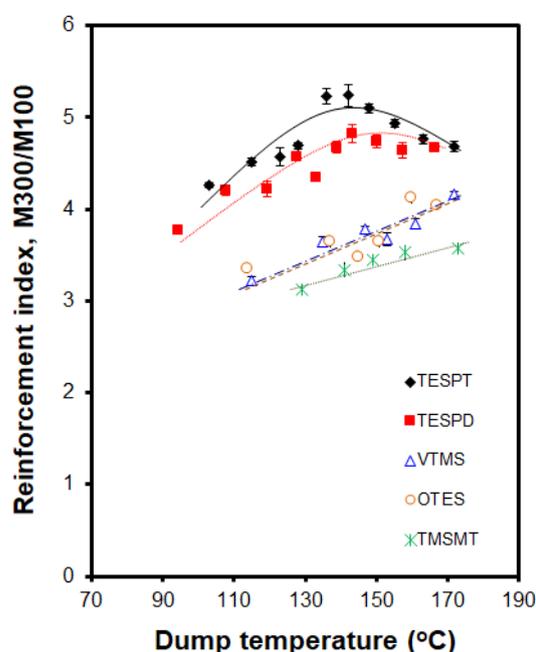


Figure 5. Reinforcement index of vulcanizates.

The chemically bound rubber content of compounds as shown in Figure 4 reflects that TESPT and TESP which possess sulfur functionalities can create silica-to-rubber coupling and rubber-rubber crosslink during mixing at high temperature and hence strongly affect the compound viscosity (Fig. 2) and filler-filler interaction (Fig. 3). The alkoxy nonsulfur silanes, that is OETS and VTMS, show

somewhat less reactivity compared to the sulfide types. Free sulfur released from TESPT can produce lightly crosslinked rubber during the non-productive mixing step [6,7].

The use of TMSMT which has no alkoxy groups but only a sulfur functionality clearly demonstrates the ineffectiveness of this silane type as it provides very high extent of filler-filler interaction in the NR compounds (Fig. 3). Not being able to silanize, TMSMT cannot chemically hydrophobize the silica surface and hence the large difference in polarity between silica and NR is not overcome. The results demonstrate that it is necessary to utilize bifunctional organosilanes for silica-filled compounds. However, TMSMT shows a rise of chemically bound rubber content with increasing dump temperature, attributed to the crosslink between rubber and free sulfur released from its structure at elevated temperature. This confirms the lightly crosslinking mechanism of free sulfur observed for tetrasulfide silane or TESPT.

The reinforcement index, i.e. the ratio of modulus at 300% strain to modulus at 100% strain, is shown in Figure 5. TESPT gives the highest reinforcement efficiency, followed by TESP. The vulcanizates containing TESPT and TESP show more or less the same maximum region of reinforcement index with regard to the dump temperature in the range of 140-150°C. The alkoxy-silanes without sulfur moiety, that is VTMS and OTES, show a considerably lower reinforcement efficiency, whereas the nonalkoxy silane, TMSMT, provides the lowest values. However, the filler-filler interaction is decreased with increasing dump temperature as a consequence in an improved reinforcement index.

Concluding remarks

- Sulfide-alkoxy-based silane coupling agents give the most practical and technical benefit for silica-reinforced NR compounds as they can effectively reduce compound viscosity, filler-filler interaction, while providing high filler-rubber interaction, and hence lead to much better improvement in mechanical properties when compared to the only alkoxy- or sulfide-based silanes.
- TMSMT confirms that tetrasulfide silane, the commonly used one is TESPT, can liberate free sulfur into the system during nonproductive mixing step, generating the lightly crosslinked rubber networks which significantly increase the compound viscosity and chemically bound rubber content.
- There are three reaction mechanisms competitively taking place during compound mixing which are all temperature dependent: 1) the silanization reaction; 2) the coupling reaction; and 3) rubber-rubber crosslinking originating from active sulfur released by the polysulfide-based silanes.

Acknowledgements

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