

Influence of silane modifiers with different functionalities on silica-filled NR compounds

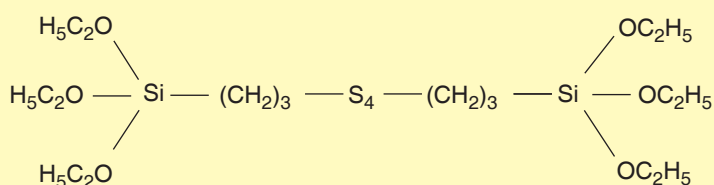
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Silica has become a strong alternative for carbon black fillers in tires after it was reported that it provides a better balance in tire properties, in particular rolling resistance, heat build-up and wet grip, compared with those for the classical carbon black (ref. 1). The introduction of silica into rubber compounds brought some disadvantages, generally with regard to processing and vulcani-

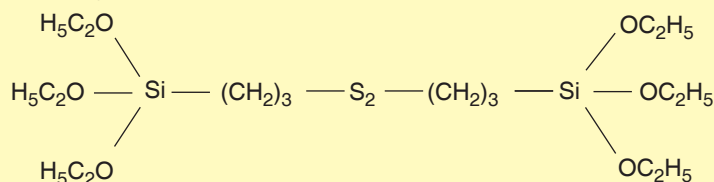
zation aspects. The most widely used method to maximize the reinforcing efficiency of silica is the use of bifunctional organosilanes as coupling agents, of which bis-(triethoxysilylpropyl) tetrasulfide (TESPT) is the common silane coupling agent for silica-filled rubber compounds (ref. 2).

In practical mixing procedures, the silica, TESPT and rubber are simultaneously introduced into an internal mixer, in which various complicated reactions simultaneously take place (refs. 3 and 4). Within this mechanistic complexity, the extents of two

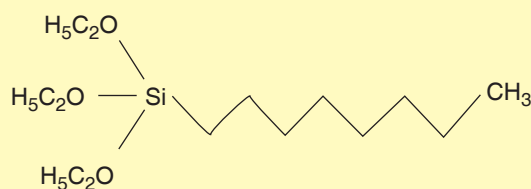
Figure 1 - chemical structure of silane modifiers



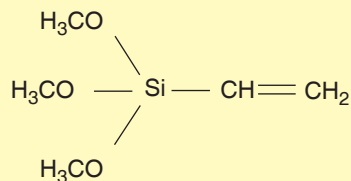
(i) Bis-triethoxysilylpropyl tetrasulfide or TESPT: Mw = 539 g/mol, dose = 9.0 wt% or 5.0 phr, supplied by Ben Meyer, Germany, trade name Couplink-69.



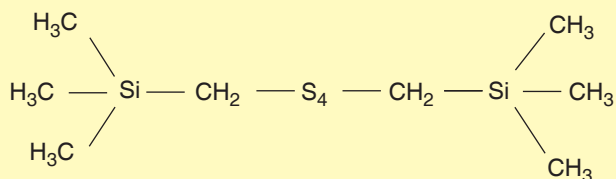
(ii) Bis-triethoxysilylpropyl disulfide or TESPD: Mw = 475 g/mol, dose = 7.9 wt% or 4.4 phr, supplied by Evonik, Germany, trade name Si-266.



(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 (ref. 8).

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 (ref. 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 (ref. 5).

Based on a study with SBR/BR tread compounds (ref. 6), the dump temperature should be in the range of 145-155°C to achieve good silanization and to avoid precrosslinking. For a silica-filled natural rubber system (ref. 7), in addition to the silanization reaction, precrosslinking reactions take place during natural rubber (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.

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, Vivatex 500; Hansen & Rosenthal, Germany
Zinc oxide	3.0	Imperial Chemical, Thailand
Stearic acid	1.0	Thailand
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

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.

Compound preparation

The compound formulations used in this study are shown in table 1. The quantities 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, OTE 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.

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 minutes, then half of the silica and silane were added and mixed for 5 minutes, 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 minutes. Subsequently, ZnO, stearic acid, TMQ and DPG were added and mixed for 3 minutes. 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) according to ASTM D1646. The cure characteristics were determined using a moving die processability tester or MDPT (TechPro) with the testing condition of a frequency 0.833 Hz and 2.79% strain. The optimum vulcanization time (t_{90}) was determined and used for press curing of the samples at 150°C.

Payne effect, which determines the extent of filler-filler inter-

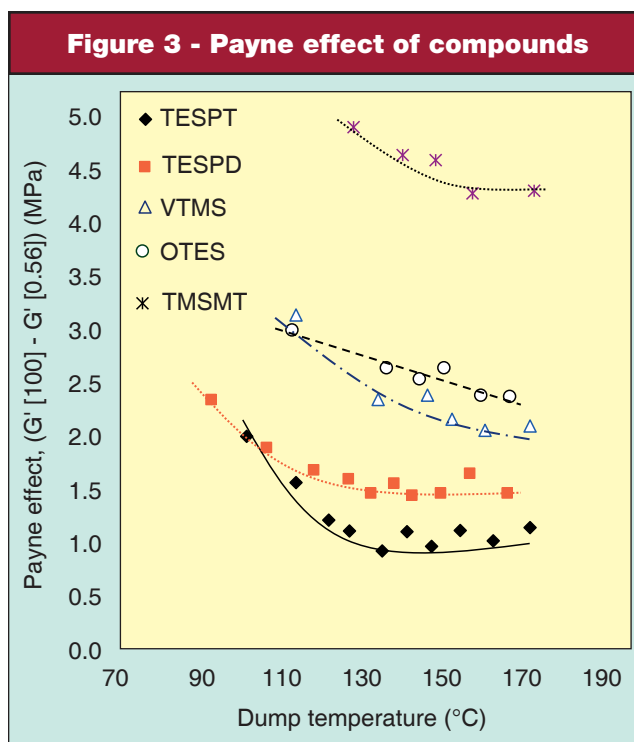
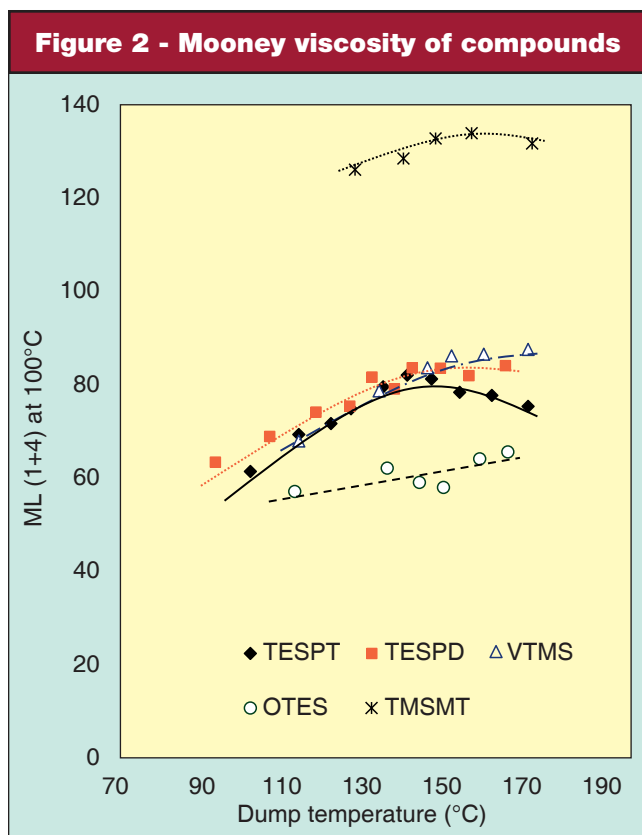
action, was measured under shear deformation using a rubber process analyzer (RPA, Alpha Technologies). The compound samples were cured to t_{95} at 150°C, prior to performing a strain sweep test in the range of 0.56-100% at 0.50 Hz and 100°C.

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

The compounds were press-vulcanized at 150°C to t_{90} . 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/minute 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 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 (ref. 7), this result is in good agreement with the fact that, apart from the silanization reaction, a certain amount of coupling and cross-linking 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.

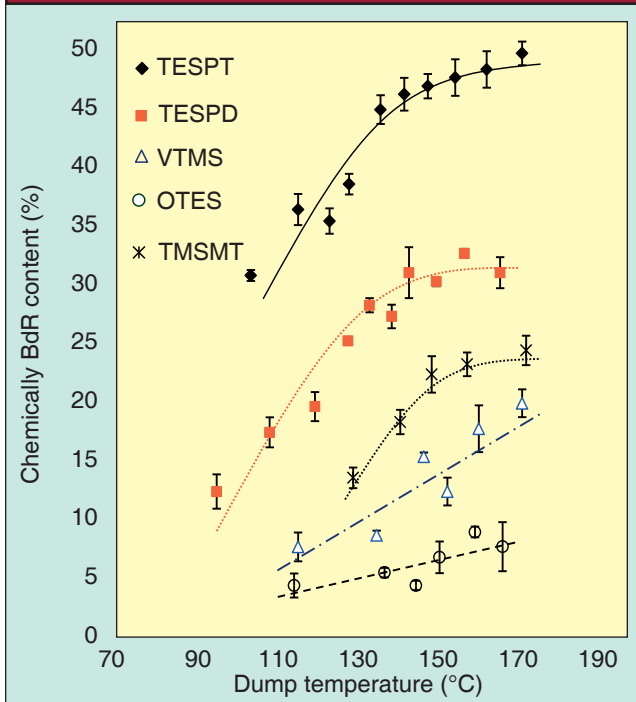
For the sulfide-based silanes, that is TESPT, TESP and TMSMT, the crosslinks are formed via sulfur that is released and activated at the high temperature. For vinyl silane, that is VTMS, the crosslinks can also occur via C = C and active radicals generated during mixing.

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.

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

Figure 4 - bound rubber content of compounds

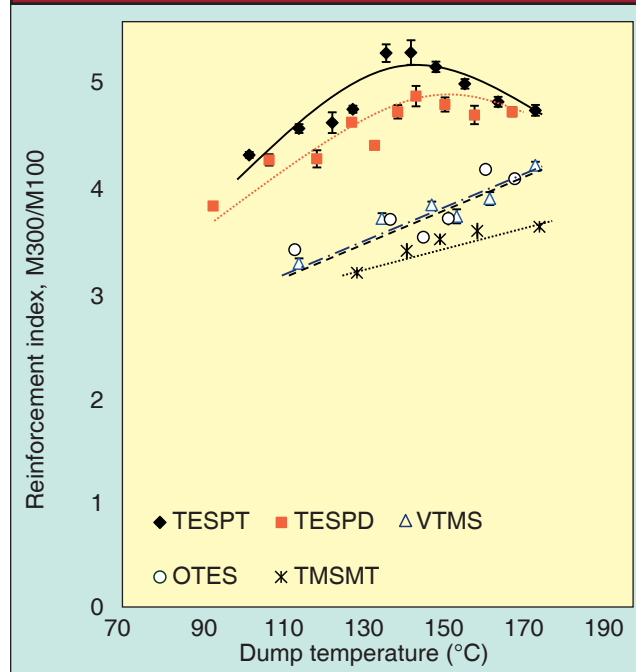


and a rubber-rubber crosslink during mixing at high temperature, and hence strongly affect the compound viscosity (figure 2) and filler-filler interaction (figure 3). The alkoxy non-sulfur silanes, that is OTES and VTMS, show somewhat less reactivity compared to the sulfide types. Free sulfur released from TESPT can produce lightly crosslinked rubber during the non-productive mixing step (refs. 6 and 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 (figure 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.

Figure 5 - reinforcement index of vulcanizates



Conclusion

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.

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 a non-productive mixing step, generating the lightly crosslinked rubber networks which significantly increase the compound viscosity and chemically bound rubber content.

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