Varying Si-Substituents for Rubber Silanes

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Abstract

The market share of silica filled tire tread compounds for passenger cars is continuously growing. New developments are being introduced focusing on environmental aspects, like reduced fuel consumption since ecological requirements become more and more stringent. Compared to carbon black the use of silica and silanes reduces fuel consumption but requires a more controlled mixing procedure because this is crucial for the bonding of the silane to the silica surface. The structure of silanes is in general characterized by three different parts. A silica reactive side with an Si-unit, a rubber reactive moiety and a spacer part connecting the reactive units. Traditionally the Si-unit is substituted by three alkoxy groups like three methoxy or three ethoxy groups. These are cleaved and released out of the compound during the mixing process and allow formation of a covalent bond between the silica surface and the silane. Hence, for the controlled bonding of the silane to the silica the kind of substitution on the Si-unit is important for this chemical reaction. A variety of different Si substituents are known and described in literature and patents [1 – 4, 24, 25]. This article focuses mainly on ethoxy groups and alkyl polyethers as substituents. It is shown, that the latter allow a very efficient hydrophobation of the silica surface, reducing the agglomeration tendency of the silica.

Keywords: Silica/Silane system, filler dispersion, rolling resistance indicator, VOC-reduction, patent protection, poly ether substituent

Introduction

An essential condition for optimum reinforcing properties is a good filler dispersion in the rubber compound as this allows best interactions between rubber and the filler. The reinforcing properties have a fundamental influence on the physical properties of the compound and determine the application of all rubber goods.

Rubber, usually used for tire tread compounds, and silica are not compatible due to their different polarity. This is where bifunctional organosilanes come into play, acting as coupling agents between rubber and silica, hydrophobating the silica and building a

covalent bridge between the two materials. The introduction of bifunctional organosilanes in rubber application in the seventies of the last century was the beginning of the chemical reinforcement [5 – 7]. This opened completely new application fields for mineral fillers, particularly for highly active precipitated silica. In many applications, but especially in the tire industry, an evolution started which is far from being completed. Although the Silica/Silane technology entered the tire industry in the early nineties of the last century [2, 8 – 12], only a decade later, almost all passenger cars in Europe were equipped with tires whose treads contain silica and silane. The reason was the particular property profile which can only be achieved with the so-called "Green Tire" technology. Compared to the formerly used carbon black filled systems the Magic Triangle of rolling and abrasion resistance and wet grip was extended (Figure 1). By then the assertion that important properties could only be improved on cost of the others – was not valid anymore. The Silica/Silane technology allowed a simultaneous significant improvement of rolling resistance and wet grip without having negative influence on abrasion resistance and hence on the tire lifetime.
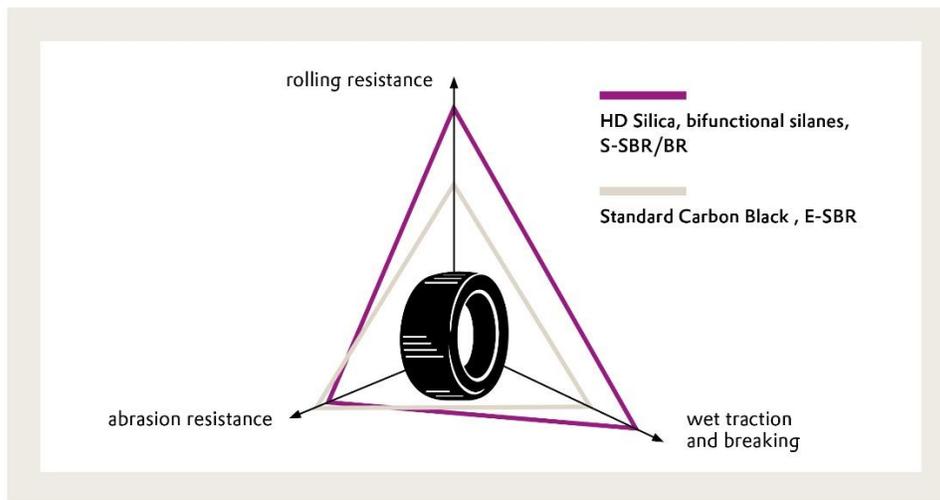

Figure 1: Extension of the Magic Triangle thanks to the Silica/Silane technology

The rolling resistance was reduced by approximately 25 percent and the fuel consumption by approximately five percent. However, the improvement was paid by a deteriorated processing compared to the conventional carbon black system. In addition to dispersion and distribution of the fillers and the need for additional ingredients, the control of a chemical process was now dominating the mixing process. Hence, it was and is still indispensable to know the influence of the various factors on the reaction such as temperature, time, concentration etc. and to optimize the compound mixing process.

To fulfil the task of bonding the silica to the rubber the bifunctional organosilanes use two reactive groups in their molecule (Figure 2) [13-15].
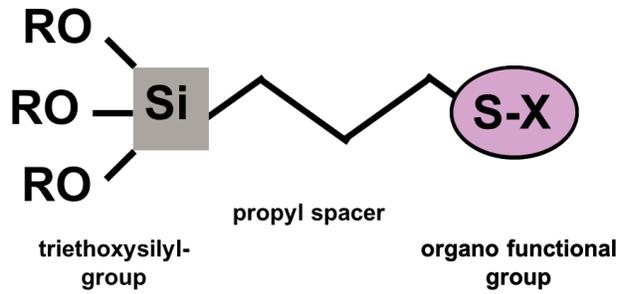
Figure 2: Schematic structure of organosilanes

The alkoxy silyl group, the silica active site can react with the silanol groups of the silica to build stable siloxane bonds (filler modification). This should proceed during the compound manufacturing and is accompanied by a cleavage of alcohol [16]. The sulfur-functional group, the rubber active one, reacts with the polymer during the vulcanization and develops covalent filler-rubber-bonds. These chemical bonds are responsible for the high reinforcing potential of the Silica/Silane filler system [17, 18].

To achieve the best processing and performance of the vulcanizate it is important to bond the coupling agent to the silica as effective as possible without the reaction with the polymer matrix. Both chemical reactions must be carefully controlled.

The silanization of the silica surface is mainly determined by the Si–substituents on the silica active site of the silane. The silanization reaction proceeds via two single steps as visualized in Figure 3 [19 – 21]

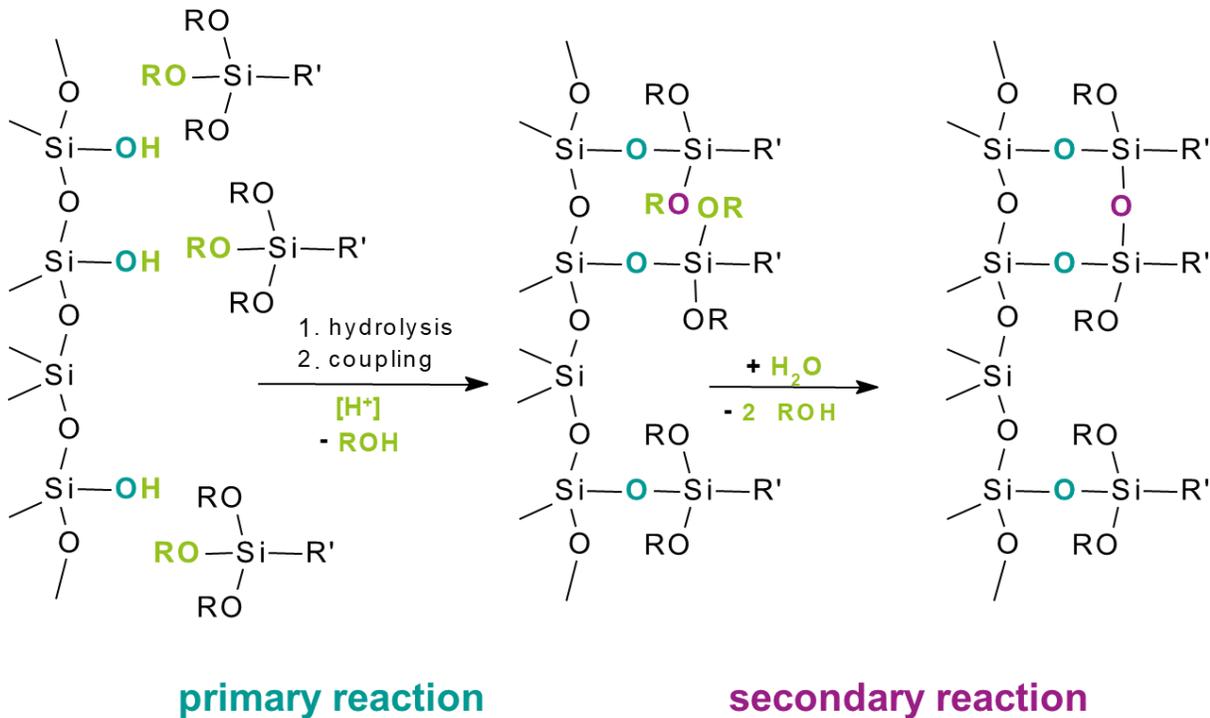primary reaction   secondary reaction

Figure 3: Silanization mechanism

In the primary reaction the silane couples to the silica surface. In the secondary reaction, adjacent silanes on the surface condensate under the development of siloxane bonds. both reactions proceed under cleavage of the Si–substituents (Fig 3). It is obvious, that the nature of the substituents plays a decisive role for the silanization.

Simple alkyloxy substituents
Short chain alkoxy groups like methoxy or ethoxy are the most elementary alkyloxy substituents. Both types are the most widespread in silanes for the rubber industry. But during the silanization methanol or ethanol will be emitted (Fig 3). Due to the toxicity of methanol the application of methoxy substituted silanes is more restricted, especially in tire plants with partly open systems. Most commercially available rubber silanes are based on ethoxy substituents. For Evonik the ethanol is derived in its majority from sustainable resources. The most prominent member used in the rubber industry is the bis-triethoxy silyl propyl polysulfide with the trade name Si 69® (Figure 4).

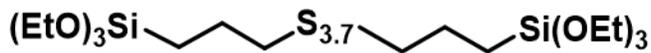$$(EtO)_3Si \diagdown\diagup\diagdown S_{3.7} \diagdown\diagup\diagdown Si(OEt)_3$$

Figure 4: Molecular structure of Si 69®

Ethanol is emitted during the silanization which proceeds during the whole mixing process. In Figure 5 the ethanol emission of an exemplary two-stage mixing process with different dump temperatures is depicted. It can be shown that in this process regarding the ethanol release temperatures a little above 140 °C are already as enough as dump temperatures around 155 °C.
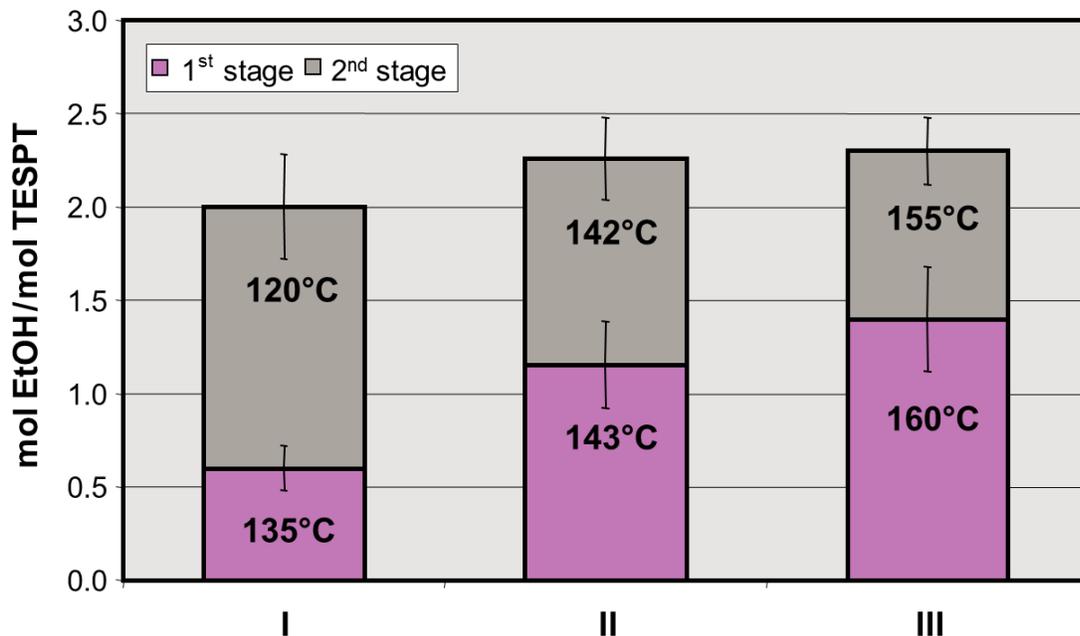

Figure 5: Formation of ethanol during a two-stage mixing process

With the ongoing silanization process the polar silica surface is hydrophobized because the hydroxy groups on the silica react with the silane. In addition, the alkoxy substituents act as shielding agents and reduce the polar character of adjacent hydroxy groups. The

silica becomes compatible with the non-polar rubber matrix. The strong filler network, characteristic for silica filled systems, becomes weaker. The mixing time together with the temperature profile in the internal mixer is an important parameter for the chemical reaction of the silane with the hydroxyl groups on the surface of the silica.

Not hydrophobized silica is characterized by a pronounced Payne-effect [22]. This is reduced increasingly with progressing hydrophobation with the silane.

Size and polarity of the Si-substituents of the silane play an important role. The affinity towards the silica surface depends on the polarity of the silane, whereas transportation processes depend on the size of the silane. Both effects are determined by the substituents on the Si-unit. To illustrate this alkoxy substituted silanes with varying chain length were synthesized: methoxy, ethoxy and propoxy substituted sulfur silanes. They were tested iso molar, that means all with the same amount of Si units, in a highly silica filled S-SBR / BR blend, mixed in a three-stage mixing process. The silanization was followed by means of RPA measurements. A reduction of the filler network by the proceeding hydrophobation reduces the Payne-effect. The shear modulus at low strain is continuously reduced indicating the ongoing silanization. Figure 6 shows the RPA curves after the first and the last mixing stage.
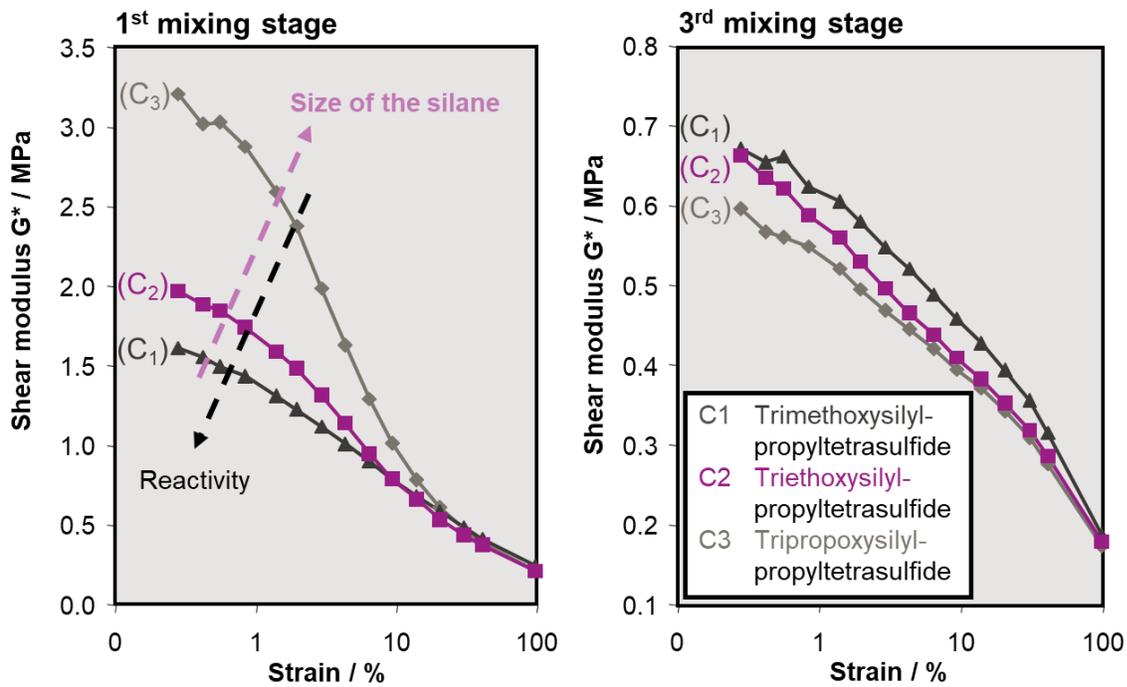

Figure 6: RPA curves after the first (left) and last (right) mixing stage

After the first stage, the strongest reduction of the silica network is reached by the smallest silane. In the beginning of the mixing procedure the reactivity of the moiety and the transportation process dominate. The silane with the shortest alkoxy substituent has the highest reactivity and diffusion rate and therefore the highest silanization and hydrophobation result. However, this changes after the third and last mixing stage. It can be assumed, that all silanes had enough time to reach the silica surface. Also, the silanization yield should be comparable. But then the hydrophobation quality dominates

as effect. The silane with the longest alkoxy substituents can also shield adjacent hydroxyl groups on the silica surface. Its polar character gets further reduced resulting in higher hydrophobation. The filler network is less strong, which can be seen in the lowest Payne-effect.

According to the proposed mechanism (Figure 3), alkyloxy substituents are cleaved during the silanization process and depending on its chain length released as volatile organic compound (VOC) into the environment. The large majority is emitted during the mixing process. But due to ongoing condensation some emission is happening even during the lifetime of finished articles [23]. With increasing chain length the substituents become less volatile. To prove this, an Si 69® derivate was prepared, where 2/3 of the ethoxy substituents were replaced by a mixture of dodecanoxy and tetradecanoxy (70 / 30 w% blend). In the following called Si69-12/14. The emission of ethanol was measured during the mixing process. Formulations and the mixing procedure are given in tables 1 and 2:

Table 1: Formulations for the ethanol measurements

1st stage	phr	phr
Buna VSL 5025-2	96	96
Buna CB 24	30	30
ULTRASIL® 7000 GR		80
Si 69-12/14	**15.7**	-
Si 69®	-	**6.4**
ZnO	3	3
Stearic acid	2	2
Process oil	10	10
6PPD	1.5	1.5
Wax	1	1
Protektor	1	1
2nd stage		
Batch 1st Stage		
3rd stage		
Batch 2. Stage		
DPG	2.0	2.0
TBzTD	0.2	0.2
CBS	1.5	1.5
Sulfur	1.5	1.5

Table 2: Mixing procedure for the ethanol measurements

1st stage		**GK 4 N**
	0 - 1 min	Polymers
	1 - 3 min	½ filler, silane, ZnO, oil, stearic acid
	3 - 4 min	½ filler, antioxidant, wax
	4 min	lift ram and clean
	4 - 5 min	continue mixing
	5 min	lift ram
	5 - 6 min	mix and dump (150°C)
2nd stage		**GK 4 N**
	0 - 2 min	plastify batch stage 1
	2 - 5 min	mix at target temperature
	5 min	dump (150°C)
3rd stage		**GK 4 N**
	0 - 2 min	plastify batch 2, sulfur, accelerators
	2 min	dump on open mill (110°C)
		homogenize
		cut 3 x left, 3 x right with 3 mm nip
		roll up and pass through a 3 mm nip 3 x
		sheet off

The emitted ethanol is reduced with XP SI 69-12/14 by 80 % compared to the Si 69® compound (fig 8).
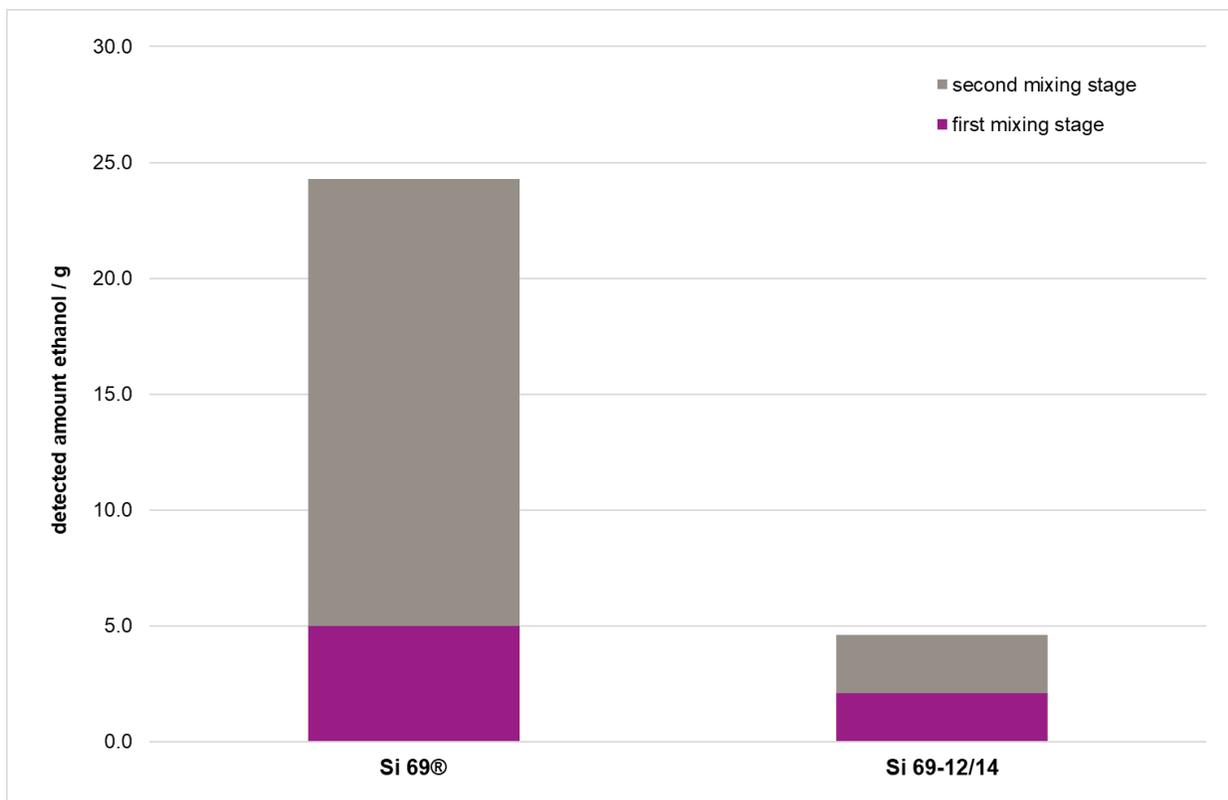
Figure 8: Ethanol emitted of the compounds

In a standard mixing process the main emission of ethanol proceeds in the second mixing stage. According to Figure 3 the silanization reaction starts with the coupling to the silica under cleavage of the corresponding alcohol followed by subsequent condensation reactions. It must be assumed that during the first mixing stage mainly the primary reaction proceeds. For Si 69-12/14 further condensation reactions are obviously inhibited. The chain length of the substituents provides a significant shielding effect. Once coupled to the silica, they sterically shield surrounding coupling sites on the silica surface. Remaining silane molecules still possessing ethoxy substituents are blocked from reaching the surface for coupling and releasing ethanol.

Alkylpolyethers as substituents

In 2003, a patent application of Degussa was published, disclosing partly long chain substituents [24]. In a further patent of Evonik in 2009 the benefit of long chain alkyl polyether substituents for applications in rubber compounds [25] was published. The molecular structure of the corresponding polysulfide silane, the Si 69® analogue, herein after called XP Si 369-2, is given in Figure 7:
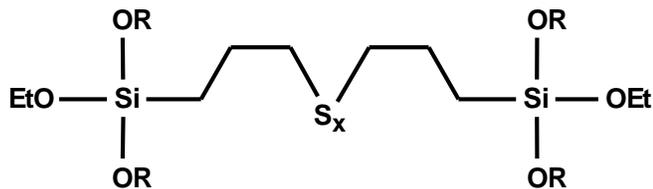

Figure 7: Molecular structure of XP Si 369-2, R= $C_nH_{2n+1}(O\text{-}CH_2\text{-}CH_2)_m$, x = 3,75

As the substituents of XP Si 369-2 are not volatile – and not dangerous to the environment – [26] they will stay in the rubber compound even when cleaved off the silane during the silanization of the silica surface. Again only the ethoxy substituents can be emitted as VOC. To elucidate the impact of such substituents a further Si 69® analogues were prepared, one, where only one of the three ethoxy substituents was replaced, so-called XP Si 369-1. Both XP Si 369-1 and XP Si 369-2 with two replaced ethoxy groups. Both were tested in an S-SBR/BR blend as shown in Table 3. The corresponding mixing procedure is given in Table 4:

Table 3: Formulations for the tests of XP Si 369-1 and XP Si 369-2

1. Stage	phr	phr	phr
BUNa VSL 5025-1	96	96	96
Buna CB 24	30	30	30
ULTRASIL® 7000 GR	80	80	80
Si 69©	**6.4**	-	-
XP Si 369-1	-	**15.5**	-
XP Si 369-2	-	-	**27**
ZnO	3	3	3
Stearic acid	2	2	2
process oil	10	10	10
6PPD	1.5	1.5	1.5
Wax	1	1	1
2. Stage			
Batch 1. Stage			
3. Stage			
Batch 2. Stage			
DPG	2	2	2
TBzTD	0.2	0.2	0.2
CBS	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5

Table 4: Mixing procedure

1. Stage	**Intermix 1.5 E, cooling temp. 70°C, rpm: 70**
0 - 1'	Polymers
1 - 2'	1/2 filler, silane, ZnO, oil, stearic acid
2 - 3'	1/2 filler, antioxidant, wax,
3 - 4'	mix and dump at 145°C
2. Stage	**Intermix 1.5 E, cooling temp. 80°C, rpm: 80**
0 - 2'	plastify batch stage 1
2 - 3'	mix at 145 °C and dump
3. Stage	**Intermix 1.5 N, cooling temp. 50°C, rpm: 40**
0 - 2'	plastify batch 2, sulfur, accelerators
2'	dump at 100°C on open mill
	homogenize

The silanes are compared on an isomolar basis. Here the increasing dosage reflects the increasing molecular weight. The obtained in-rubber test results are summarized in Table 5. It has already been mentioned, that the silanization depends on the size and polarity of the silane itself. The hydrophobation is mainly dominant in later stages of the mixing process. The Mooney-values after the second and the third mixing stages are shown in Figure 9. The complete data set is summarized in Table 5.
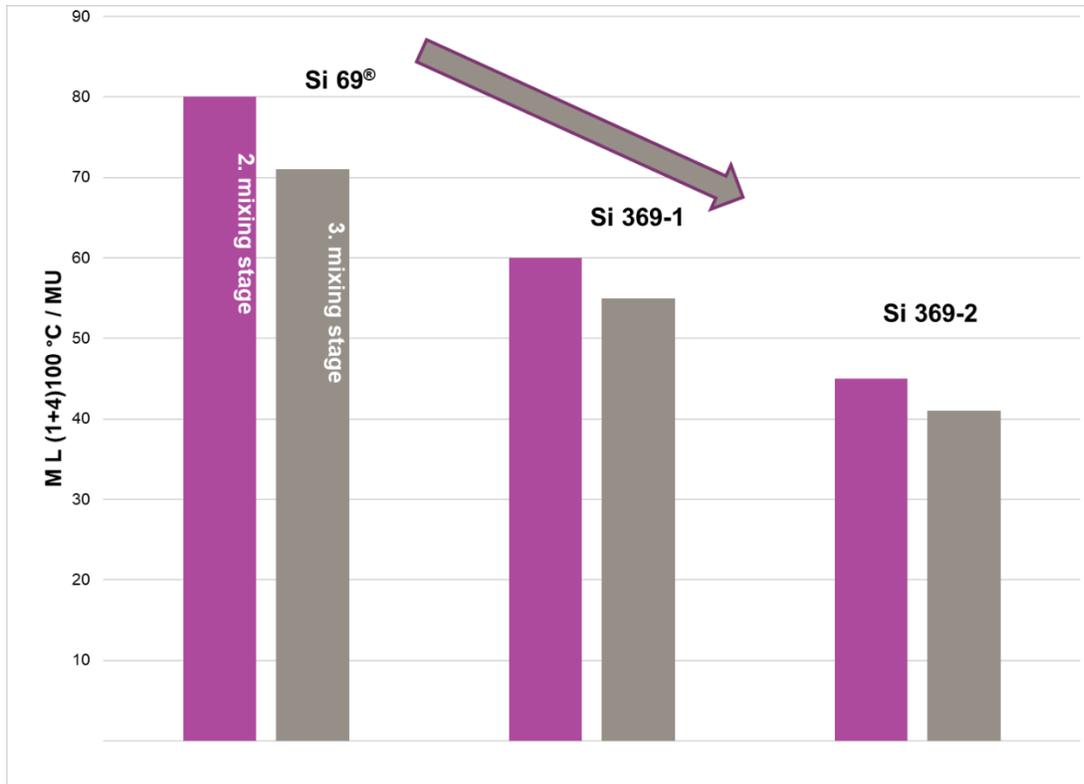u

Figure 9: Mooney-values of the test compounds

With the increasing degree of substitution, the values for the Mooney-value decrease. More substituents lead to a higher hydrophobation due to the higher shielding effect. These substituents also induce a certain bulkiness to the molecule. The molecular size increases, what should have an impact on the transportation processes and on the onset of the silanization.

Table 5: Results of in-rubber tests

		Si 69®	XP Si 369-1	XP Si 369-2
ML(1+4) at 100 °C 2nd stage	MU	80	60	45
ML(1+4) at 100 °C 3rd stage	MU	71	55	41
Mooney Scorch				
Scorch Time t5	min	33.0	19.0	15.0
Scorch Time t35	min	42.2	30.2	23.3
MDR: 165 °C; 0.5°				
M_L	dNm	2.5	1.7	1.1
Delta torque	dNm	18.4	16.7	13.3
t 10 %	min	1.7	1.8	1.8
t 90 %	min	8.3	7.8	7.2
t 80 % - t 20 %	min	3.1	2.9	2.8
Tensile strength (ring)	MPa	12.3	13,0	10.7
Modulus 100 %	MPa	1.9	1,6	1.4
Modulus 300 %	MPa	9.3	7,6	6.0
Modulus 300 % / 100 %	--	1.0	4.8	4.3
Elongation at break	%	435	445	350
Shore-A-hardness	SH	65	63	57
DIN-Abrasion, 10 N	mm^3	84	92	113
Ball-Rebound, 60 °C	%	61.5	61,8	65.2
MTS, 16 Hz, 50 N +/- 25 N				
E*, 0 °C	MPa	19.5	13.8	9.3
E*, 60 °C	MPa	8.3	7.4	6.1
tan δ, 0 °C	--	0.465	0.415	0.345
tan δ, 60 °C	--	0.115	0.105	0.093
Dispersion Topography				
Peak area (Topo)	%	1.8	1.1	5.1

To investigate the transportation processes during the mixing, a corresponding disulfide silane was prepared (x = 2 in Figure 7), herein after called XP Si 366. Higher sulfide ranks tend to release sulfur into the rubber matrix during the mixing, what can cause a pre-crosslink, a prescorch [28] in case the mixing temperatures are too high. By using a disulfide silane, overlaying effects of such a prescorch are avoided. It was compared to the triethoxy disulfide silane Si 266®. The hydrophobation speed of these silanes was compared by using time depending RPA-measurements of the first mixing stage. Both silanes were mixed in a single mixing step routine. Formulation and the mixing procedure are given in Tables 6 and 7.

Table 6: formulations for investigations of the hydrophobation speed

1st stage	phr	phr
Buna VSL 5025-2	96.25	96.25
Buna CB 24	30.00	30.00
Ultrasil© 7000 GR	80.00	80.00
Si 266®	**5.80**	
XP Si 366		**9.00**
CORAX N 330	5.00	5.00
ZnO	2.00	2.00
Stearic acid	1.00	1.00
Vivatec 500	8.75	8.75
Vulkanox HS/LG	1.50	1.50
Vulkanox 4020/LG	2.00	2.00
Protektor	2.00	2.00

Table 7: Mixing procedure

1st stage		GK 1.5 E, fill factor 0.54, 80 upm, chamber temp.: 80°C
		batchtemp.: 150°C - 160°C
1	0.0 - 0.5 min	polymer
2	0.5 - 1.0 min	add Vulkanox HS & Vulkanox 4020
3	1.0 - 2.0min	1/2 silica, ZnO
4	2.0 - 2.0 min	clean
5	2.0 - 3.0 min	a) add CB to the oil pouch and then the mixture to the mixer
		b) add 1/2 silica with silane
		c) add remaining chemicals
6	3.0 - 3.0 min	clean
7	3.0 - 3.5 min	mix and keep temp. at 155°C by adjusting RPM
8	3.5 - 3.5 min	dump, 2-4 sec on open mill (4 mm nip), sheet out; take 10 g. for RPA test, remaining compound back to kneading machine
9	3.5 - 4.5 min	mix and keep temp. at 155°C by adjusting RPM
10-30	4.5 - 14.5 min	repeat steps 7 to 9, take every minute 10 g for RPA test

Every minute a sample was taken and analyzed after vulcanization at 165 °C by means of RPA strain sweep. By this the reduction of the silica network can be followed and the hydrophobation speed of the silanes can be compared. The corresponding curves are shown in Figures 10 and 11.
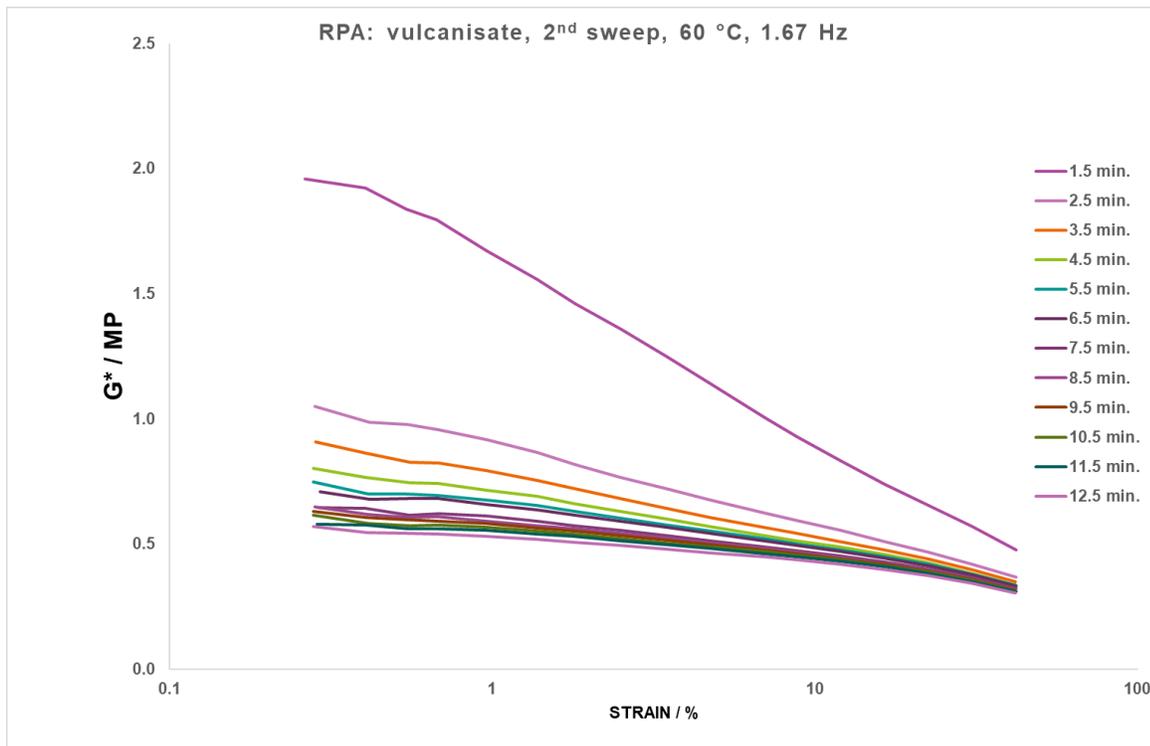

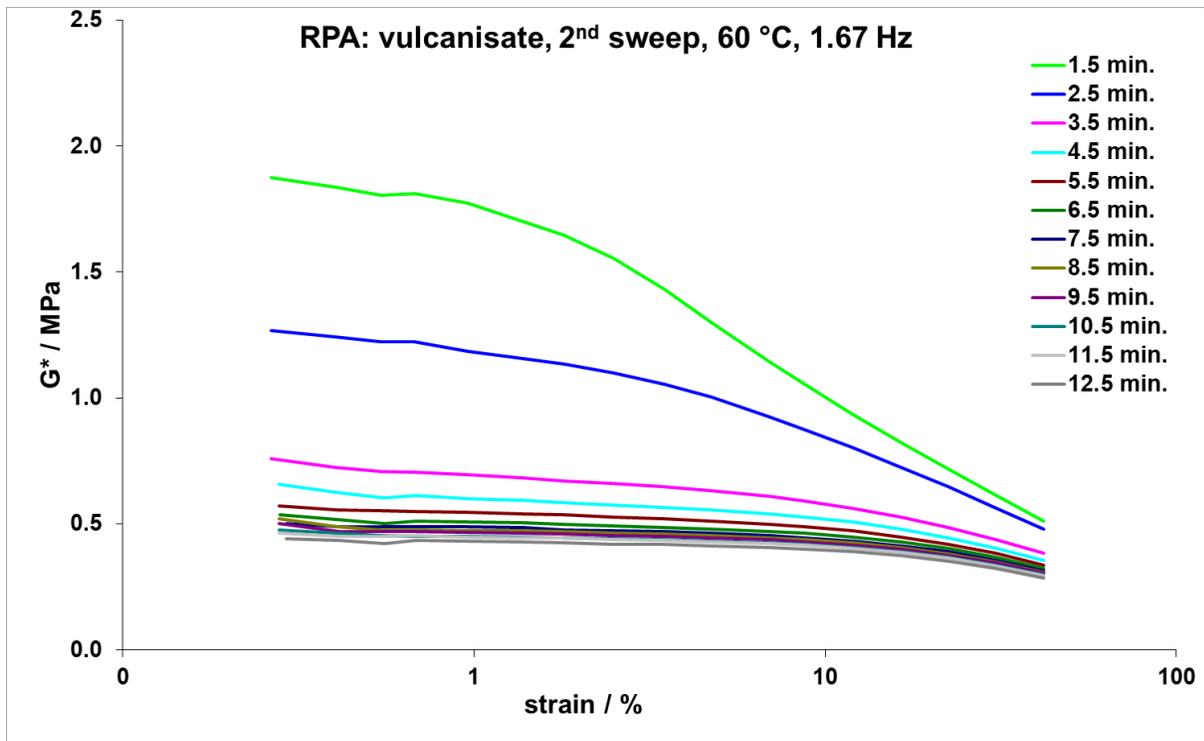Figure 10: RPA curves of the Si 266® compound

Figure 11: RPA curves of the XP Si 366 compound

The reduction of the Payne-effect is due to the reduction of the silica networking caused by hydrophobation during the mixing. The time necessary to reach the completion of the silanization process (e. g.: in above Figure 11 at 5,5 min) is indicated by levelling out of the Payne-effect. Hence, a comparison of the time needed to reach this final level can be used to compare the hydrophobation speed of the single silanes. To visualize the differences in silanization time the Payne–effect $\Delta G^* = (G^*_{0.3\%\ strain}) - G^*_{42\%strain})$ as an indicator for the reduction of the silica network was calculated. Results are given in Figure 12.

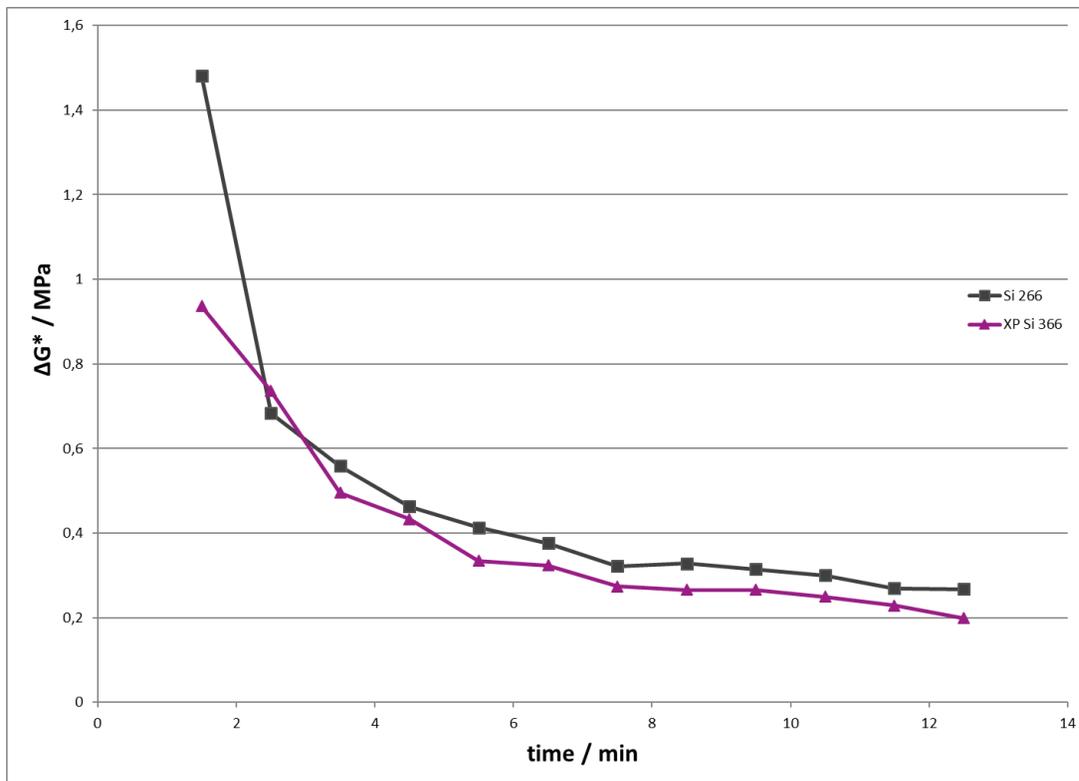Figure 12: Payne-effect ΔG^*(2nd strain sweep) as a function of mixing time for Si 266® and XP Si 366

The first sample for RPA measurements was taken 1.5 minutes after the silane was added to the mixer. Within this time XP Si 366 leads already to a more efficient reduction of the Payne-effect and therefore covers the free silanol groups faster than Si 266®. 3.5 minutes after the silane addition the change in Payne-effect over time is comparable for both silanes. However, XP Si 366 leads to a lower final Payne-effect. The two disulfidic silanes differ only in the alcohol units. This experiment demonstrates that the alkyl polyether substituents lead to a faster and more efficient hydrophobation reaction in comparison to the corresponding ethoxy substituents. It must be assumed that the slowdown of the transportation processes by the bulkiness of the molecule is overcompensated by the strong affinity of the polar polyethers of the amphiphilic substituents to the polar silica surface. In solution, where transportation processes are not of so much relevance, it was already reported, that these substituents provide an increased silanization rate [29]. Enough flexibility in the configuration of the backbone chain of the substituents can be assumed. As already shown by the results with XP Si 369 a certain shielding effect of the long chain substituents covers adjacent hydroxyl groups leading to a more efficient hydrophobation of the silica. In silane chemistry this shielding effect is also used to fulfill other tasks. The commercial mercapto silane Si 363® bears at its Si- core two alkyl polyether substituents. Here the shielding is used to protect the mercapto group in order to reduce its reactivity [30]. Figure 13 shows this schematically. The reduced VOC emission, as shown in Figure 8 for XP Si 369 is also a characteristic feature of this silane.
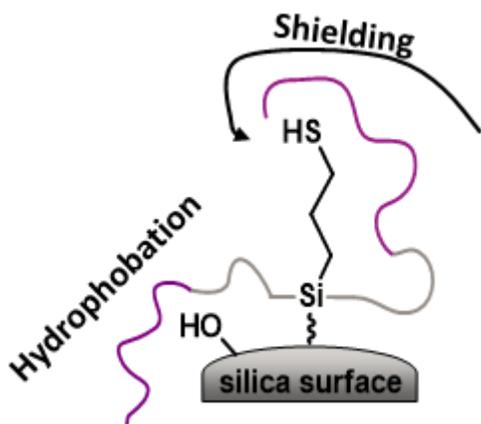
Figure 13: Shielding effect as used by Si 363[®]

Conclusions

When added to rubber mixtures, the substituents on the Si-core of rubber silanes have a major effect on processability and performance of the resulting rubber compounds. The modern low volatile alkyl polyether substituents, as already in use for the commercial silane Si 363[®] are characterized by a high silanization rate due to the polar polyether part. In addition, the non-polar alkyl part provides a shielding effect. A reduced VOC-emission is of further benefit.

References

[1] DE 2255577
[2] EP 0501227B1
[3] EP 1043357B2
[4] WO 2007085521
[5] *Schwaber, D. M., Rodriguez, F.:* Rubber and Plastics Age, 48 1967, 1081
[6] *Wolff, S.:* KGK, 30, 1977, 516
[7] *Wolff, S.:* KGK., 32, 1979, 312
[8] *Trono, A.:* TyreTech.'92, Paris/Frankreich, 1992
[9] *Agostini, G., Bergh, J., Materne, Th.:* Akron Rubber Group, Akron, Ohio/USA, Oct. 1994
[10] *Marwede, G.W., Eisele, U.G., Sumner, A.J.M.:* ACS, Cleveland, Ohio/USA, Oct. 1995
[11] *Ranney, M.W., Pagano, C.A.:* Rubber Chem. Technol. 44, 1971, 1080
[13] *Thurn, F., Wolff, S.:* KGK 28,1975, 733
[14] *Wolff, S., Wang, M.-J., Tan, E.-H.:* KGK. 47, 1994 102
[15] *Görl, U.:* KGK 51, 1998, 416
[16] *Kiselev, A.V., Lygin, V.J.:* Infrared Spectra of Surface Compounds. Wiley, New York/USA, 1975
[17] *Görl, U., Münzenberg, J., Luginsland, H.D., Müller, A.:* KGK, 1999, 52,588
[18] *Luginsland, H.-D.:* A review on the chemistry and the reinforcement of the Silica/Silane filler system for rubber applications, Shaker, Aachen, Germany 2002
[19] Görl, U., Hunsche, A, Müller., Koban, H.G., Rubber Chem. Technol. 1997, 70, 608
[20] A. Hunsche, A., Görl, U, Müller, M. Knaack, Th. Göbel, Th., KGK, 1997, 50, 881
[21] Hunsche, A., Görl, U., Koban, H.G. Lehmann, Th., KGK 1998, 51, 525

[22] Payne, A.R., Whittaker, R.E., Rubber Chem. Techno*l.* 1971, *44*, 440
[23] Klockmann*, O., Hasse, A.*: ACS, San Antonio Texas/USA, May 2005
[24] EP 1394167 B1
[25] EP 1829922 B1
[26] EU Directive 67/548/EEC
[27] Hasse, A., Klockmann, O. Wehmeier, A., Luginsland, H.D., KGK 2002, 55 (5), 236
[28] Blume, A., Fall rubber colloquium, Hanover, Germany, Nov. 2010
[29] Klockmann, O., Albert, P. Hasse, A., Korth, K., Rubber World 2006,234, 36