

Key factors influencing marching modulus in silica-silane compounds

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Abstract. Silica-silane became a very successful filler system for passenger car tire treads, as it considerably improves tire performance, mainly in terms of rolling resistance. However, this technology has its drawbacks in terms of processing: longer mixing cycles, 2 or 3 mixing stages, as well as influences on the curing behavior of the compound. One specific problem related to the latter is a marching modulus, which makes determination of the correct curing time difficult. As a consequence, the properties of silica compounds might be sub-optimal. Earlier studies describe various causes of marching modulus in silica compounds: filler-filler interaction [1], degree of silanization [2], filler-polymer and polymer-polymer coupling as well as sulfur donated by the silane [3,4]. These are also key factors in order to suppress marching behavior. In this study, filler-filler and filler-polymer interactions are varied and studied in depth on their influence on marching modulus and interference with other properties and processing parameters. Several types of silane coupling agents are used in order to vary the molecular structure of the filler-filler and filler-polymer interactions, and different silanization temperatures are applied to vary the degree of silanisation. These variations are correlated to the Marching Modulus Intensity (MMI) as well as bound rubber content and physical properties. In order to differentiate the influence of filler-filler and filler-polymer interaction on MMI of the silica-filled rubber compounds, the curing behavior was monitored in a rheometer at different strains. The results of this study clearly show, that both factors - filler-filler as well as filler-polymer interactions - are the main influencing parameters for the marching modulus, and are on their turn related to the degree silanization. A proper choice of compounding and processing parameters allows to suppress the marching modulus.

1. Introduction

The polarity difference between silica fillers and rubber polymers induces major difficulties in the mixing process such as poor dispersion and high Mooney viscosities. Therefore, silane coupling agents, which act as compatibilizers between silica and polymer, have become an inevitable component in the formulation of a silica filled rubber compound. Using a silane coupling agent significantly improves the processability and reinforcement of silica filled rubber through the chemical reaction between the silica and the silane, commonly denoted as “silanization”. [5-7]

The fact that this chemical reaction has to occur in a mechanical mixer which was not designed for that purpose, causes insufficient silanization resulting in problems with the vulcanization. The consequence of an incomplete silanization makes itself felt in a marching modulus during the vulcanization stage of such compounds. A marching modulus during vulcanometry is a problem often observed in silica-filled S-SBR/BR tire tread compounds. It is neither productive nor efficient to wait for a prolonged time in order to obtain a plateau in the vulcanization profile. Therefore, the marching modulus phenomenon should be avoided or at least minimized. In order to overcome this problem, understanding of the physicochemical mechanisms underlying the marching modulus phenomena of silica filled rubber compounds is required. However, the mechanisms are not clearly defined yet.

Several authors state that the curing behavior of silica filled rubber compounds is related to the degree of filler dispersion, the silanization and the filler-polymer coupling reaction, as well as the donation of free sulfur from the silane coupling agent. [2, 4, 8, 9] Within the present study, these factors are analyzed in order to differentiate the effect of filler-filler and filler-polymer interaction as well as sulfur donation on the marching modulus. Therefore, compounds with various silane coupling agents are mixed at various silanization temperatures. Subsequently, the vulcanization behavior of these compounds is measured at small (approx. 7%) and large (approx. 42%) strain. The results will be interpreted in terms of the degrees of silanization reached.

1. Sample preparation and analysis

Different types of silane with their characteristics and functions are given in Table I. With these silanes, all series of experiments were done based on a tire tread compound as shown in Table II. Bis-(triethoxysilylpropyl)tetrasulfide (TESPT) was used as the reference silane. The amount of TESPT applied in the formulations was adjusted according to Equation (1), based on the CTAB surface area of Zeosil 1165MP: 152 m²/g. [10]

$$TESPT (phr) = 5.3 \times 10^{-4} \times (CTAB)_{silica} \times (phr)_{silica} \quad (1)$$

Table I. characteristics and functions of the silanes

# ethoxy groups	Name of the silane		Sulfur rank	Function		
				Silanization	Coupling	Sulfur donation
2x3	Bis(triethoxysilylpropyl)tetrasulfide	TESPT	3.85	Yes	Yes	Yes
2x3	Bis(triethoxysilylpropyl)disulfide	TESPD	2	Yes	Yes	No
2x3	1,8-Bis(triethoxysilyl)octane	TESO	0	Yes	No	No
1X3	Propyltriethoxysilane	PTEO	0	Yes	No	No

Table II. Compound formulation

Mix. stage	Ingredient	Ref.	Mix A	Mix B	Mix C	Mix D	Mix E
Ma- ster batch	S-SBR(27.3wt% oil)/BR	103.2/25	→	→	→	→	→
	Silica	80	→	→	→	→	→
	TESPT/TESPD/TESO/PTEO	6.4/-/-/-	-/5.7/-/-	-/5.7/-/-	-/-/5.2/-	-/-/-/4.9	-/-/-/-
	TDAE Oil	7	→	→	→	→	→
	St. Acid/ZnO/DPG/6PPD	1/2/2/2	→	→	→	→	→
Final	Sulfur	-	-	0.7	-	-	-
	Sulfur	0.7	1.4	0.7	1.4	1.4	1.4
	ZBEC	0.2	0.2	0.2	0.2	0.2	0.2
	CBS	2.2	2.2	2.2	2.2	2.2	2.2

As the molar masses of the various silanes used in this study differ from the one of TESPT, the quantities of the silanes were adjusted to be equimolar. Additionally, the sulfur ranks of those silanes also differ from the one of TESPT; therefore the total amount of active sulfur was adjusted according to the amount of sulfur which can be released from TESPT. In case of Mix B, the extra amount of active sulfur was introduced in first mixing step. The compounds were mixed in two steps as shown in Table III. The master batch stage was done by using a lab scale internal mixer (Brabender Plasticorder) with 390 ml of chamber volume; the fill factor of the internal mixer was 75%. Three batches were mixed for each set of conditions in order to check the reproducibility.

Table III. Master batch mixing procedure

Master batch mixing procedure for internal mixer		Final mixing procedure on mill	
Action	time [mm:ss]	Action	time [mm:ss]
Add polymer	00:00~00:20	Add master batch	-
Mastication	00:20~01:20		
½ Silica, Silane	01:20~01:40	Mixing	00:00~02:00
Mixing	01:40~02:40		
½ Silica, remaining ingredients	02:40~03:10	Add curatives	02:00~02:30
Mixing till target temperature: 130, 140, 150, 160, 170°C	03:10~04:10		
Ram sweep	04:10~04:14	Mixing	02:30~09:00
Mixing (at target temperature)	04:14~06:40		
Discharge and sheet off	-	Discharge and sheet off	-

The Payne effect, Filler Flocculation Rate (FFR), filler-polymer Coupling Rate (CR) and the rheogram with small (~7%) and large (~42%) strain were measured using a Rubber Process Analyzer (RPA; RPA Elite, TA Instruments). The values of the Payne effect, FFR, CR and Marching Modulus Intensity (MMI) were calculated using Equations (2) to (5) in Table IV, respectively. Total and chemically bound rubber content were evaluated and calculated with the same method as stated in the work of Hayichelaeh. [11]

Table VI. Equations and meaning of the symbols

Equations	Meaning of the symbols
$Payne\ effect = G'(0.56\%) - G'(100\%)$ (2)	$G'(0.56\%), G'(100\%)$: Storage modulus (G') at a strain of 0.56% and 100%
$FLR = d \log \left(\frac{G'_{0.56}(t)}{G'_{0.56i}} \right) / d \log \left(\frac{t}{t_i} \right)$ (3)	$G'_{0.56}(t)$: at 0.56% strain at test time t $G'_{0.56i}$ is the initial storage modulus at t_i ; $t_i=1min$
$CR = d \log \left(\frac{T(t)}{T_{scorch}} \right) / d \log \left(\frac{t}{t_{scorch}} \right)$ (4)	$T(t)$: torque level at test time t T_{scorch} : $T(t)=T_{min}+1$ [dNm] t_{scorch} : the time at $T(t)=T_{scorch}$
$MMI = (T_{40} - T_{20}) / (40min - 20min)$ (5)	T_{40}, T_{20} : corresponding torque at 40 min. and 20 min.

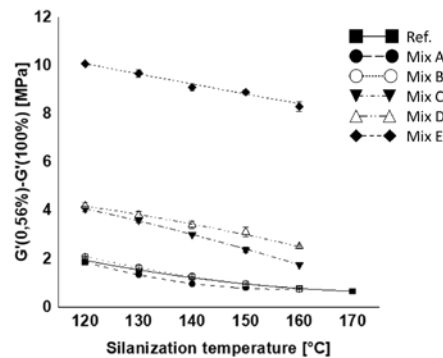


Fig. 1.— Payne effect as a function of silanization temperature

3. Results and discussion

3.1 Filler-filler interaction (Payne effect)

The Payne effects of the uncured compounds are plotted as a function of the silanization temperature for all mixing series, as shown in Figure 1. With increasing silanization temperature, a lower Payne effect was observed due to a higher degree of silanization for the silane-containing compounds. This trend was not expected for Mix E due to the absence of a silane coupling agent. The fact that still some decrease in Payne effect is seen for these compound can be explained by the micro-dispersion mechanism of silica, proposed by Blume and Uhrlandt. [12, 13] At higher temperature the polymer mobility is enhanced, either by lower viscosity or possibly some polymer breakdown. This means that the polymer can more easily penetrate into the voids of the agglomerates. Consequently, aggregates are better separated by the polymer, resulting in a better micro-dispersion of silica.

3.2 Bound rubber content

Figure 2 shows the amount of bound rubber. In case of the Ref. compound, Mix A and Mix B, the samples with sulfidic silanes, a higher amount of chemically bound rubber was observed when the compounds were mixed at a higher silanization temperature. It is well known that during mixing already some polymer-filler coupling via the silane may occur, in the worst case resulting in pre-scorch. Thus, the higher degree of polymer-filler coupling is established during mixing at a higher silanization temperature.

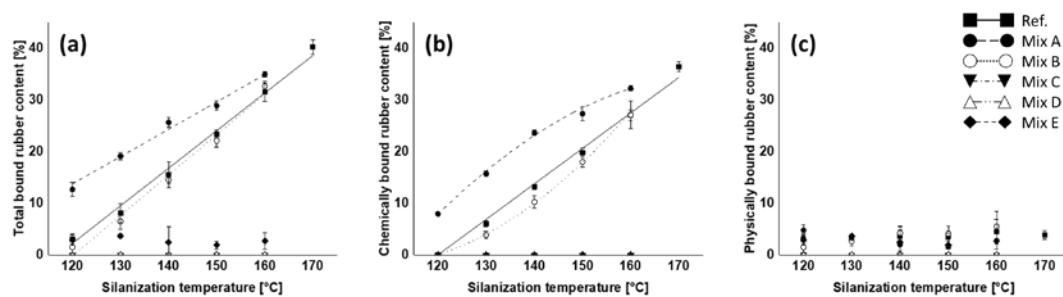


Fig. 2.— Bound rubber content vs. silanization temperature; (a): total; (b): chemical; (c): physical

3.3 Silica flocculation rate

The FFR values of Ref. compound, Mix A, and Mix B compounds are plotted as a function of the silanization temperature: Figure 3(a). A higher amount of bound rubber leads to lower filler-filler interaction and so a reduced tendency for flocculation.

The FFR of all mixing series are plotted against total bound rubber content of these compounds in Figure 4. The FFR values start to decrease when the total bound rubber content exceeds approx. 15%. The flocculation rate has an upper limit of 0.16. For Mix E, the compound without silane, the highest flocculation rates are expected. As the values here do not exceed 0.16, it is justified to assume that the maximum FFR limit is around 0.16. Besides, the curves of the samples containing TESPT and TESP in Figure 3(a) at low silanization temperatures also show this value.

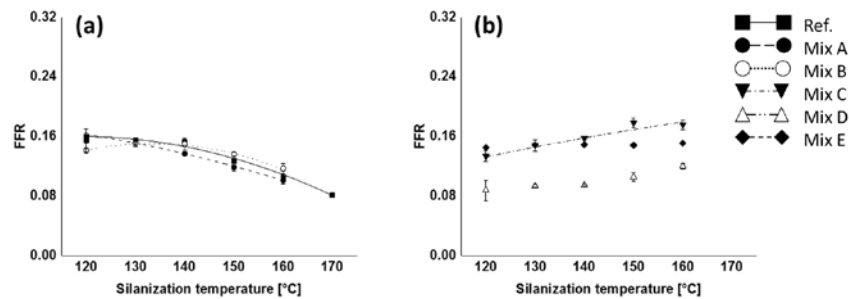


Fig. 3.— Silica flocculation rate (FFR) vs. silanization temperature; (a): Ref. to Mix B; (b): Mix C to E

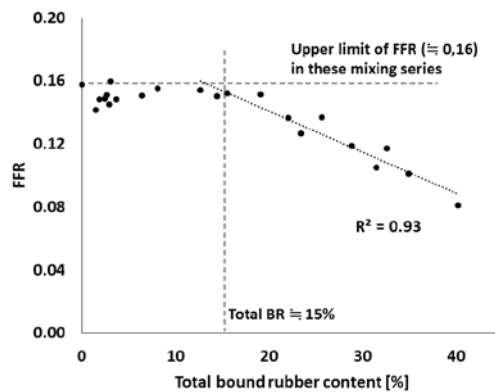


Fig. 4.— FFR versus total bound rubber content

3.4 Filler-polymer coupling rate

The filler-polymer Coupling Rates (CR) of all mixing series are shown in Figure 5. As expected, the CR is zero for Mixes C, D and E, as a coupling reaction was not possible. The CR of the Ref. compound and Mix B plotted as a function of the silanization temperature, show a decreasing trend with increasing temperature. In contrast to this, Mix A shows a constant and slow CR (approx. 0.05) for the whole temperature range. The trend of Mix A is clear when the sulfur rank of TESP_D is taken into account: app. 90% of disulfide, a rather pure material compared to a mixture of sulfur ranks in TESP_T. [14, 15] The disulfidic bridge is not reactive enough to give coupling to the polymer without additional sulfur added, as in Mix B. Therefore, the filler-polymer coupling reaction rate of Mix A remains low and constant at all silanization temperatures.

The results of the Ref. compound and Mix B clearly indicate that the presence of active sulfur enhances the speed and efficiency of the filler-polymer coupling reaction. The concentration of free sulfur will decrease when mixing is done at a higher temperature. Consequently, the CR will decrease due to the lowered concentration of active sulfur. Hasse et al. [16] reported that activation of the silane consumes free sulfur. Additionally, they reported that the addition of sulfur increases the speed and efficiency of the filler-polymer coupling reaction. In case of the compound Ref., no free sulfur was added in the first mixing stage. However, TESP_T is a mixture of silanes with various sulfur ranks from S₂ to S₁₀. [15] The longer sulfur bridges can donate active sulfur; this sulfur can in turn activate other silane molecules.

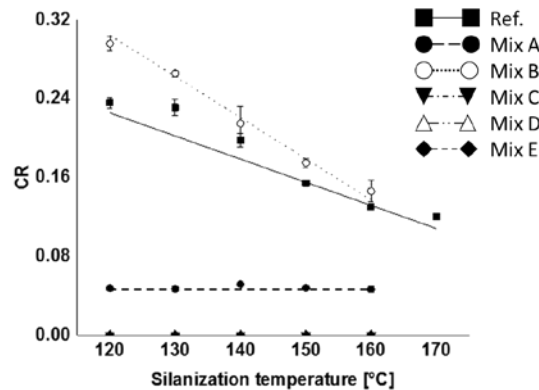


Fig. 5.— Filler-polymer coupling rate (CR) vs. silanization temperature

3.5 MMI at small (ASTM conditions, MMI 0.5°) and large strain (MMI 3°)

The Marching Modulus Intensities (MMI) measured at two different strains of all mixing series are plotted in Figure 6. Mix E has no silane which means that no reaction is possible between filler and polymer in this mixing series, and the highest MMI is observed in this mix. This indicates that the level of 0.5° strain is particularly affected by filler-filler interaction. In addition, the MMI of 0.5° of the Ref. compound and Mix A plotted as a function of the silanization temperature shows that increasing the latter lowers the MMI 0.5°.

However, the trend of MMI 0.5° cannot be explained with the intensity of filler-filler interaction for all mixing series. Except for Ref. compound and Mix A, MMI 0.5° shows an almost constant level for the whole temperature range for the other samples. In addition, it is interesting to note that Mix B does not follow the trend of Ref. compound and Mix A: the MMI 0.5° is constant at first and only tends to decrease for the highest silanization temperature of 160°C. This indicates that not only filler-filler interaction but also other factors affect the MMI 0.5°, as will be discussed later.

A different trend is observed in the MMI measurements done at a strain of 3° or 42%. Fröhlich and Luginsland [17] reported that the breakage of the silica network starts at a higher strain amplitude, and the breakage take place in a wider strain range than for a conventional filler such as carbon black. Therefore, it was expected that a large part of the filler-filler network will be broken when the filled rubber compound is subjected to large deformations. Consequently it may be stated that only filler-polymer and polymer-polymer interactions are active at the strain of 42%. As already seen in Figure 2, no filler-polymer interaction was found in Mixes C and D. So only polymer-polymer interaction seems to exist for these mixes. As a result, these samples show an almost constant MMI 3° for the whole silanization temperature range. Besides, the MMI values do not depend on the measurement strain: the levels of both MMI values are almost the same.

If there is at least some filler-polymer interaction present, as a consequence of active or free sulfur in the compound either released by TESPT or added (Mix B), there is an increase of the MMI 3° as a function of silanization temperature. A decreasing trend of the MMI 3° with increasing silanization temperature is observed for Mixes A and E. These combined results demonstrate that the presence of free sulfur in the compound influences the polymer-filler as well as polymer-polymer interaction, while in the absence only polymer-polymer interaction plays a role.

For the MMI 0.5°, a higher silanization temperature and consequently the degree of silanization has a positive effect on reducing the MMI irrespective of the presence of free sulfur.

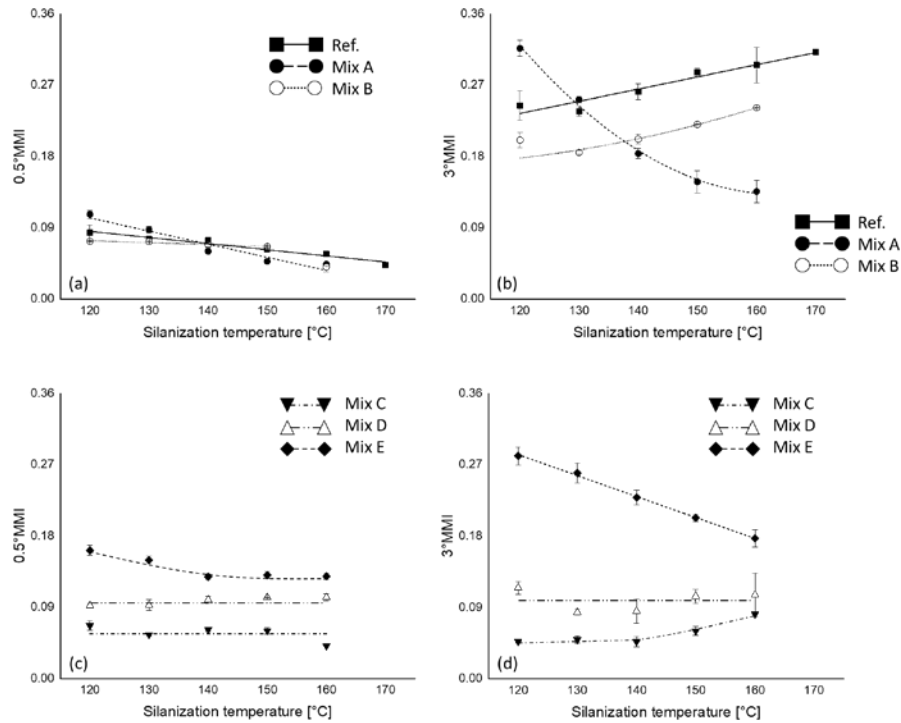


Fig. 6. — MMIs vs. silanization temperature; (a,b): S-silane; (c,d): non-S silane, no silane; (a,c): MMI 0.5°; (b,d): MMI 3°

3.6 Marching modulus intensity as a function of FFR and CR

A correlation can be made between the MMI and FFR and CR as shown in Figure 7. As was seen in Figure 3, in case of Mix C and Mix E, the FFR values were at the maximum level of 0.16. Therefore, no correlation could be made with both MMI, because the FFR values were fixed while the MMI varied along with silanization temperature. Samples Ref., Mix A and Mix B show a good correlation of MMI 0.5° with FFR values: an R^2 higher than 0.9. This indicates that silica flocculation is happening during the vulcanization process for all compounds, but mostly for the Ref. compound and Mixes A and B. The degree of agglomeration has an influence on the viscosity of the compounds. [18] The viscosity will increase faster, the quicker the filler particles flocculate. Due to this, shielding of the filler surface not only by a silane but also by bound rubber will strongly affect the rheogram of a silica compound. No correlation was found between FFR and MMI 3°.

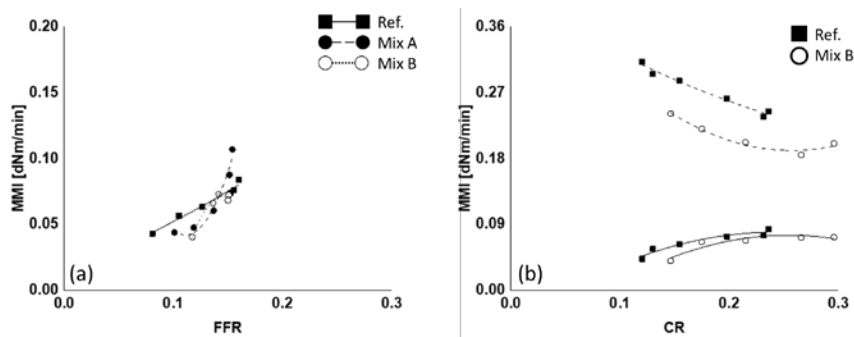


Fig. 7. — (a) MMI 0.5° versus FFR; (b): MMI 0.5° and MMI 3° versus CR.

CR is another important factor for the MMI 0.5° and MMI 3°, when the compounds satisfy two conditions. First, they should contain a silane with two functionalities: silanization and filler-polymer coupling. Second, additional active sulfur is required. Without active sulfur, the filler-

polymer coupling reaction rate will be limited to a low level (Figure 5, Mix A), and will not have a sizable effect on the MMI. When the filler-polymer interaction is established during the curing period, a fast filler-polymer reaction will lead to a quick increase of the torque level at the beginning of the measurement, overlying the torque increase due to the network formation.

4. Conclusions

The focus of this study was to elucidate the causes of marching modulus of silica filled S-SBR/BR rubber compounds. Three factors: the intensity of filler-filler interaction, the silica flocculation rate and the filler-polymer coupling rate are the major influencing factors for the marching modulus, in order of decreasing importance. All three factors are a consequence of improper silanization of the silica during mixing. While a silica-filled rubber compound undergoes vulcanization, silica flocculation occurs at the same time. There is a lower limit of total bound rubber of 15%, below which the flocculation is at its upper level and does not show a trend anymore in the marching modulus. The polymer-filler coupling rate during the curing process contributes as well to the marching modulus intensity. When the compound shows a fast coupling rate, the compound becomes quickly stiffer, limiting flocculation. However, the coupling rate is only an effective factor in the presence of active sulfur. The addition of free sulfur or its release from TESPT speeds up the filler-polymer coupling reaction, because the activation of the silane consumes free sulfur. Additionally, the reactivity of a sulfur-bridged silane increases with increasing sulfur moiety length beyond S₂.

All in all, both filler flocculation and polymer-filler coupling are strongly influenced by the mixing conditions. Mixing time and temperature are the crucial factors.

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