

**Paper# A12**

The Origin of Marching Modulus  
of Silica Filled Tire Tread Compounds

J. Jin<sup>1,2\*</sup>, J.W.M. Noordermeer<sup>1</sup>, W.K. Dierkes<sup>1</sup>, A. Blume<sup>1</sup>

<sup>1</sup> University of Twente, Enschede, the Netherlands

<sup>2</sup> Hankooktire Co., LTD., Daejeon, Republic of Korea

Presented at the Fall 192nd Technical  
Meeting of Rubber Division, ACS  
Louisville, KY  
October 9 - 11  
2018

ISSN: 1547-1977

\* Speaker

## THE ORIGIN OF MARCHING MODULUS OF SILICA FILLED TIRE TREAD COMPOUNDS

### ABSTRACT

Silica reinforced S-SBR/BR tire tread compounds often show characteristic vulcanization profiles that do not exhibit a distinct maximum in the cure curve, nor a plateau profile within acceptable time scales: marching modulus. In such a situation, it is difficult to determine the optimum curing time, and as a consequence the physical properties of the rubber compound may vary. Previous studies stated 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. This implies that these are the key factors for minimization of the marching modulus.

In the present work, various silane coupling agents with different sulfur ranks and functionalities, were mixed at varied silanization temperatures. The correlation between these factors and their effect on the Marching Modulus Intensity (MMI) were investigated. The MMI was monitored by measuring the vulcanization rheogram using a Rubber Process Analyzer (RPA) at small (approx. 7%) and large (approx. 42%) strains in order to discriminate the effects of filler-filler and filler-polymer interactions on marching modulus of the silica filled rubber compound. Both factors have an intricate influence on the marching modulus, determined by the degree of filler-filler interaction and the coupling agent.

## INTRODUCTION

It is well known that the polarity difference between silica and polymer induces major difficulties in the mixing process such as poor dispersion and high Mooney viscosities. Therefore, silane coupling agents, which also act as a compatibilizer between silica and polymer, became an inevitable component in the formulation of a silica filled rubber compound. Using a silane coupling agent significantly improves the processability and reinforcing properties of silica filled rubber compounds. However, the fact that a chemical reaction has to occur in a mechanical mixer also causes difficulties such as pre-scorch.

A marching modulus is one of the problems, which is often observed in silica filled S-SBR/BR tire tread compounds. This phenomenon makes it difficult to determine the curing time,  $t_{90}$ , from the rheogram.  $T_{90}$  is well known as the optimum curing time.<sup>1</sup> It is neither productive nor efficient waiting for a prolonged time in order to obtain a plateau in the profile. Therefore, the marching phenomenon should be avoided or at least minimized. In order to overcome this problem, understanding of the physicochemical mechanisms underlying the marching phenomenon of silica filled rubber compounds is required. However, this mechanism is 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. Earlier studies<sup>2</sup> also describe that the marching modulus intensity is related to the silica flocculation rate and filler-polymer coupling reaction rate after mixing.

In order to differentiate the effect of filler-filler and filler-polymer interaction as well as sulfur donation on the marching modulus, compounds with various silane coupling agents were mixed at various silanization temperatures. Subsequently, the vulcanization behavior of these compounds was measured at small (approx. 7%) and large (approx. 42%) strain.

## EXPERIMENTAL

### MATERIALS

Different types of silane were used in the present study as given in Table I. The silanes were chosen based on functionality and sulfur rank. 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 recipes was adjusted according to Equation 1<sup>3,4</sup>, based on the CTAB surface area of Zeosil 1165MP: 152 m<sup>2</sup>/g.

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

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.

## MIXING

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 mixing procedures are shown in Table III.

The fill factor of the mixer was fixed to 75%. The temperature of the mixer temperature control unit (TCU) was set at 50°C. In order to avoid the first batch effect, one initial batch (B0) was mixed and discarded before the regular mixing starts. After B0, the regular mixing was started when the mixing chamber reached at 55°C. After the first mixing step, the compounds were sheeted out immediately on a lab scale two-roll mill (Polymix 80T) in order to cool down the compound and prevent further reaction. Three batches were mixed for each set of conditions in order to check the reproducibility. All batches were mixed with good reproducibility as shown in Figure 1.

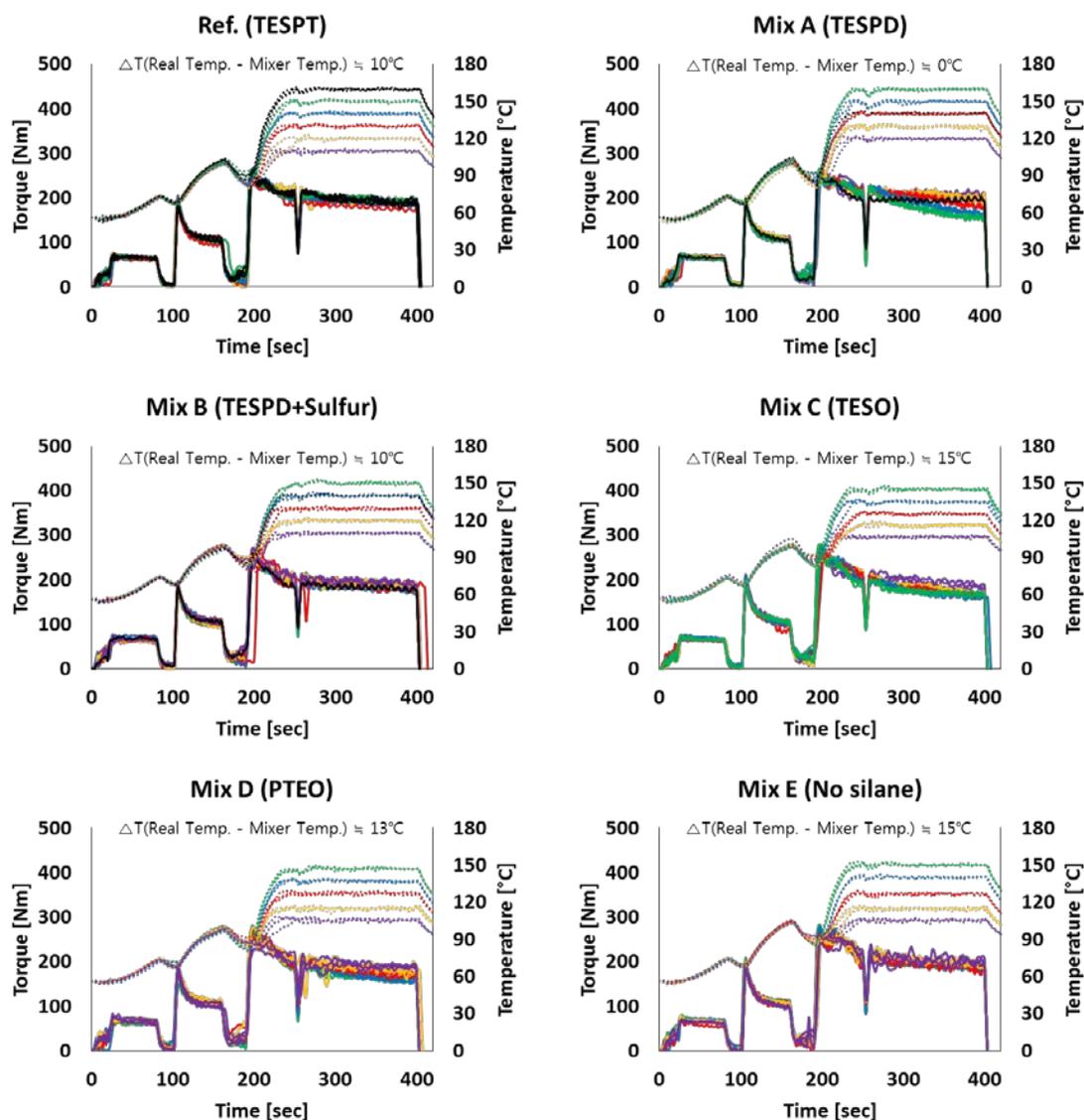


Figure 1 Mixing fingerprints (torque: solid lines; temperature: dashed lines)

### PAYNE EFFECT

The storage shear moduli ( $G'$ ) of the uncured and cured rubber compounds were evaluated by using a Rubber Process Analyzer (RPA; RPA Elite, TA Instruments). The Payne effect of the uncured rubber was measured at a temperature of 100°C, a frequency of 0.5 Hz and varying strains in the range of 0.56 - 200%. The Payne effect of the cured rubber was measured at a temperature of 100°C after 30 minutes of curing at 160°C, a frequency of 0.5 Hz and varying strains in the range of 0.56 - 120%. The uncured Payne effect was calculated from the difference in storage shear moduli at low strain (0.56%) and high strain (100%), i.e.  $G'(0.56\%) - G'(100\%)$ .

### FILLER FLOCCULATION RATE

The filler flocculation rate (FLR) of the uncured silica-reinforced S-SBR/BR compounds without curatives was studied by using the RPA mentioned above at 100°C, a strain of 0.56% and test time of 14 minutes including 2 minutes of pre-heating time. According to Mihara<sup>3,4</sup>, it is possible to observe the flocculation of silica particles by monitoring the change of storage modulus ( $G'$ ) at low strain under isothermal conditions.

The measurement temperature was selected according to the industrial extrusion temperature. In a previous study, Mihara<sup>3,4</sup> assumed that silica flocculation is a first order reaction; however, the silica flocculation rate measured here was best fitted using a power law indicating a higher order. The storage shear moduli were recorded at different measurement times, and the FLR was calculated using Equation 2.<sup>2</sup>

$$FLR = \frac{d \log \left( G'_{0.56}(t) / G'_{0.56i} \right)}{d \log \left( t / t_i \right)} \quad (2)$$

Where FLR is the dimensionless flocculation rate,  $G'_{0.56}(t)$  is the storage modulus at 0.56% strain at test time  $t$ ,  $G'_{0.56i}$  is the initial storage modulus at  $t_i$ , and  $t_i$  is 1 minute. In order to transform those rates into a linear correlation, ASTM D1646-04<sup>5</sup> was used.

### FILLER-POLYMER COUPLING RATE

The filler-polymer coupling rate (CR) of the uncured silica-reinforced S-SBR/BR compounds without curatives was studied by using a RPA (RPA Elite, TA Instruments) under the following conditions: 160°C, 1.677 Hz and 3 degrees ( $\approx 42\%$ ) of strain for 40 minutes. A large strain was applied for the CR measurement in order to break the filler-filler interaction. Therefore, only the filler-polymer interaction is taken into account in the CR. The torque levels at different times were recorded, and then the CR was calculated following Equation 3.<sup>2</sup>

$$CR = \frac{d \log \left( T(t) / T_{incu.} \right)}{d \log \left( t / t_{incu.} \right)} \quad (3)$$

Where CR is the dimensionless filler-polymer coupling rate,  $T(t)$  is the torque level at test time  $t$ ,  $T_{incu.}$  is the torque level at  $t_{incu.}$ , and  $t_{incu.}$  is the incubation time which corresponds to the time for the torque to increase by 1 dNm:  $T(t) = T_{min} + 1 \text{ dNm}$ .  $T_{min}$  is the minimum torque level which is observed during the measurement. The kinetics of the coupling reaction followed a power law starting from the incubation time. In order to transform

those rates into a linear correlation, ASTM D1646-04<sup>5</sup> was used.

#### CURE CHARACTERISTICS AND MARCHING MODULUS INTENSITY

The rheogram was measured at 160°C for 40 minutes under two different strain conditions as follows:

- 0.5 degrees ( $\approx 7\%$ ) of strain and 1.667 Hz of frequency: ASTM<sup>6</sup> conditions
- 3 degrees ( $\approx 42\%$ ) of strain and 1.667 Hz of frequency

The marching modulus intensity (MMI) is calculated from the rheograms by using Equation 4.<sup>2</sup>

$$MMI = \frac{T_{40} - T_{20}}{40min - 20min} \quad (4)$$

Where MMI is the marching modulus intensity,  $T_{40}$  and  $T_{20}$  is the corresponding torque at 40 minutes and 20 minutes.

#### TOTAL BOUND RUBBER CONTENT

Approximately 0.2 g of the rubber compounds without curatives, as obtained from the first mixing step, were cut into small pieces and immersed in toluene at room temperature for 5 days, while the toluene was renewed every day. Thereafter, the samples were removed from the toluene, dried at 105°C for 24 h and weighed. The bound rubber content was calculated according to Equation 5.<sup>7</sup>

$$\text{Bound rubber content (\%)} = \frac{W_{fg} - W \left( \frac{m_f}{m_f + m_p} \right)}{W \left( \frac{m_p}{m_f + m_p} \right)} \quad (5)$$

Where  $W_{fg}$  is the weight of filler and gel,  $W$  is the weight of specimen, and  $m_f$  and  $m_p$  are the weights of filler and polymer in the compound, respectively.

#### CHEMICALLY BOUND RUBBER CONTENT

The degree of filler-polymer coupling can be measured by the chemically bound rubber content. For this analysis, approximately 0.2 g of the rubber compounds without curatives, as obtained from the first mixing step, were cut into small pieces and immersed in toluene at room temperature for 5 days, this time under ammonia atmosphere in order to cleave physical linkages. The toluene was renewed every day. Then, the samples were removed from the toluene, dried at 105°C for 24 h and weighed. The chemical bound rubber content was also calculated according to Equation 5.

## RESULT AND DISCUSSION

#### FILLER-FILLER INTERACTION (PAYNE EFFECT)

The Payne effect of the uncured compounds is plotted as a function of the silanization temperature for all

mixing series, as shown in Figure 2.

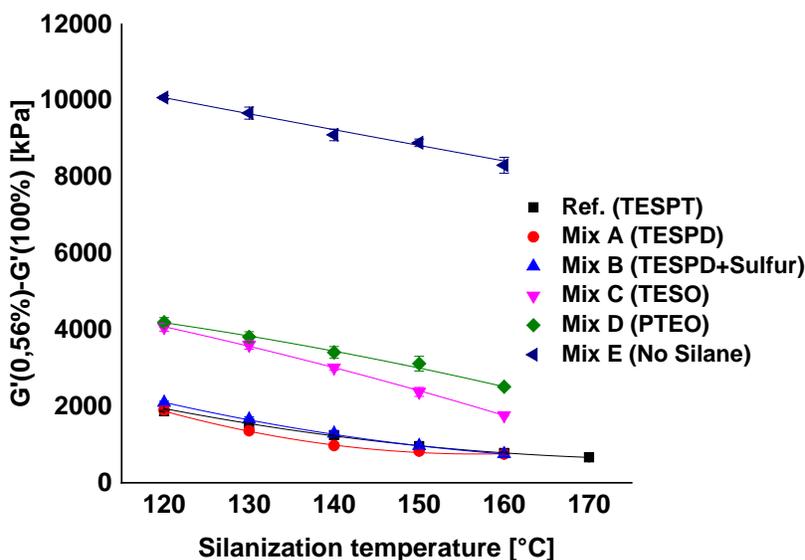


Figure 2 Payne effect as a function of silanization temperature

With increasing silanization temperature, a lower Payne effect was observed due to a higher degree of silanization. This trend was not expected for Mix E due to the absence of a silane coupling agent. No silanization reaction can occur in Mix E, thus it was expected that all compounds in Mix E would show a similar level of Payne effect. However, this phenomenon can be explained by the micro-dispersion mechanism of silica, as shown in Figure 3.

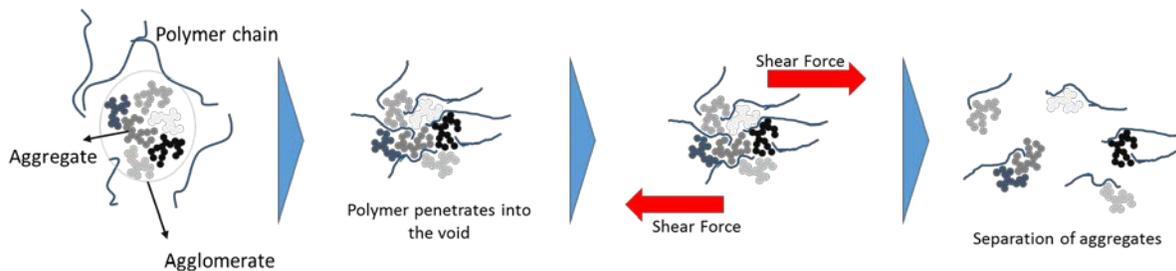


Figure 3 Micro-dispersion mechanism of silica <sup>8,9</sup>

At higher temperatures the polymer mobility is enhanced, which 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.

It is obvious that the highest Payne effect is observed in Mix E, because no silanization is possible without any silane coupling agent. Mix C and Mix D, which contains the silane without sulfur moiety, shows the second highest Payne effect. This effect can be explained by bound rubber contents which will be discussed later.

### BOUND RUBBER CONTENT

Figure 4 shows the amount of bound rubber.

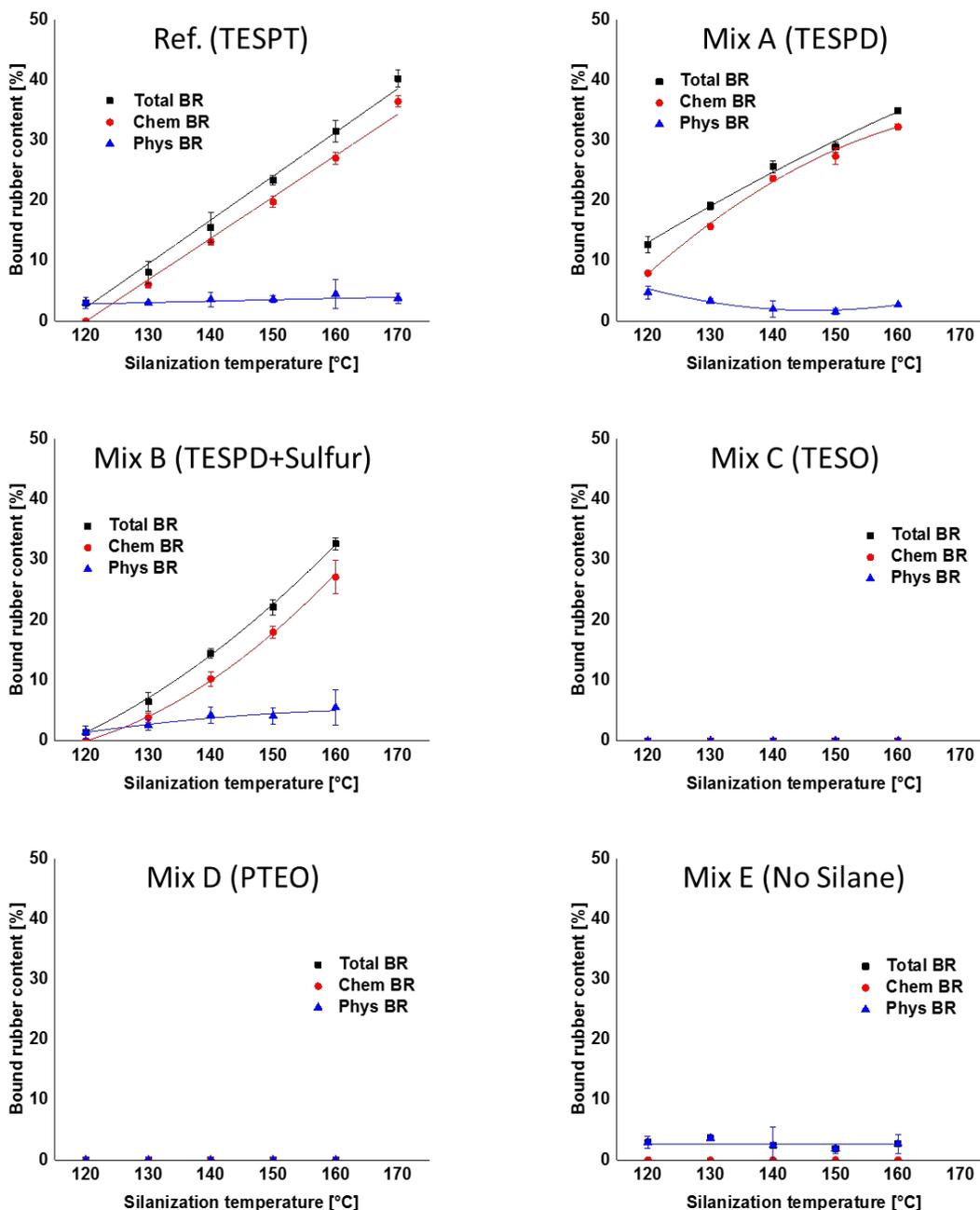


Figure 4 Bound rubber content of samples with different types of coupling agents

In case of Ref., Mix A and Mix B, the samples with TESPT, TESPD and TESPD with sulfur adjustment, a higher amount of chemically bound rubber was observed when the compounds were mixed at a higher silanization temperature. Mihara<sup>4</sup> and Choi<sup>10</sup> reported that polymer-filler coupling via the silane coupling agent can occur

during mixing. Thus, it is possible that the higher degree of polymer-filler coupling is established during mixing at a higher silanization temperature.

No bound rubber at all was found in the samples with sulfur-free silanes (TESO, PTEO). However, approximately 2% of physical bound rubber was formed in Mix E even though there was no silane.

### SILICA FLOCCULATION RATE

The flocculation rates (FLR) of all mixing series are shown in Figure 5.

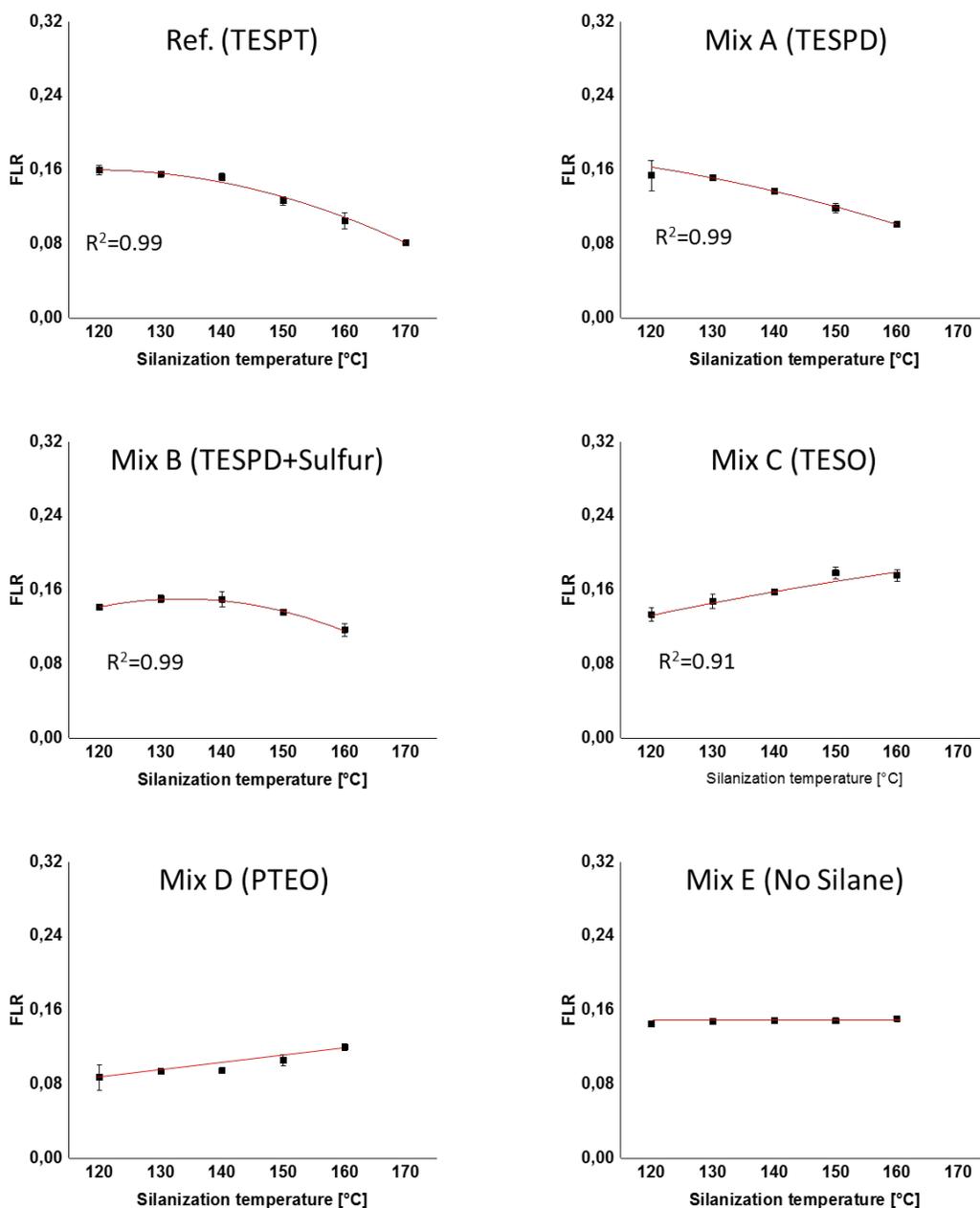


Figure 5 Silica flocculation rate (FLR) of samples with different types of coupling agents

In this figure, the FLR values of the compounds are plotted as a function of the silanization temperature. In general, there is a correlation between FLR and bound rubber in the case of compounds with a sulfur bridged silane: a higher amount of bound rubber, thus a higher degree of silanization, leads to lower filler-filler interaction.

According to earlier work <sup>2</sup>, the flocculation rate has an upper and lower limit. The lower limit was not found in this work, as the curves in Figure 5 do not reach a plateau value. For Mix E, the compound without silane, the highest flocculation rates are expected. As the values here do not exceed 0.16, it is assumed that the maximum FLR limit is around  $0.16 \pm 0.01$ . Besides, the curves of the samples containing TESPT and TESP reach a plateau at this value.

The total bound rubber content of all mixing series were plotted against FLR of these compounds in Figure 6. As can be seen in Figure 6, FLR values start to decrease when the total bound rubber content exceeds approx. 15%.

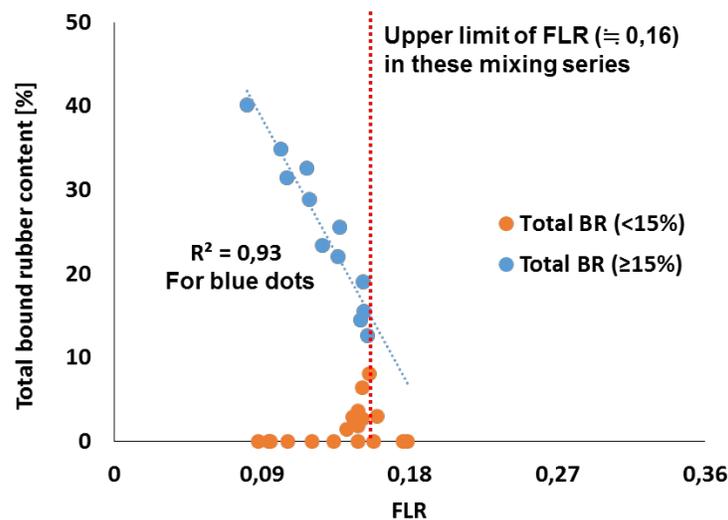


Figure 6 Total bound rubber versus FLR

#### FILLER-POLYMER COUPLING RATE AFTER MIXING

The filler-polymer coupling rates (CR) of all mixing series are shown in Figure 7. As expected, the CR is zero for Mix C, Mix D and Mix E, (TESO, PTEO and no silane) as a coupling reaction was not possible.

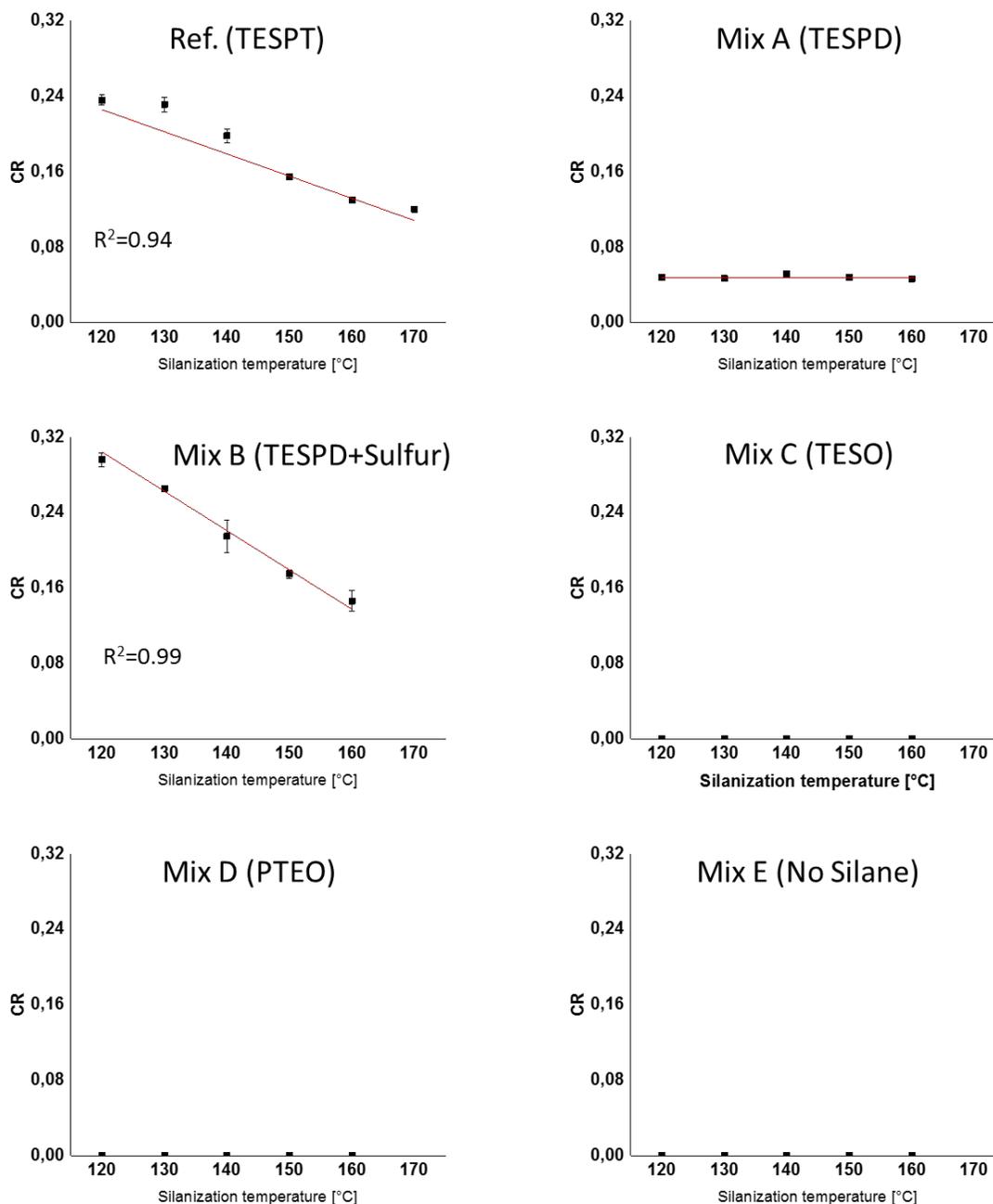


Figure 7 Filler-polymer coupling rate (CR) of samples with different types of coupling agents

The CR of Ref. (with TESPT) and Mix B (with TESP and sulfur adjustment), plotted as a function of the silanization temperature, show a decreasing trend with increasing temperature. In contrast to this shows Mix A, a constant and slow CR (approx. 0.05) for the whole silanization temperature range. The trend of Mix A is obvious when the sulfur rank of TESP is taken into account: the sulfur bridge in TESP consists of app. 90% of  $S_2$ <sup>11, 12</sup>, which means that it is a rather pure material compared to a mixture as TESPT. Therefore, the filler-polymer coupling reaction rate of Mix A will be the same at isothermal measurement conditions.

The results of Ref. and Mix B indicate that the presence of active sulfur enhances the speed and efficiency of the filler-polymer coupling reaction. At a higher silanization temperature, more active or free sulfur is consumed for filler-polymer bonding in this mixing step. As a result, the concentration of free sulfur will decrease when mixing is done at a higher temperature. Consequently, CR will decrease due to the lowered concentration of active sulfur. Hasse<sup>13</sup> reported that activation of the silane consumes free sulfur. Additionally, he reported that the addition of sulfur increases the speed and efficiency of the filler-polymer coupling reaction.<sup>13</sup> In case of Ref., no free sulfur was added in the first mixing stage. However, TESPT is a mixture of silanes with various sulfur ranks from S<sub>2</sub> to S<sub>10</sub>.<sup>12</sup> The longer sulfur bridges can donate active sulfur<sup>11, 13</sup>; this sulfur can in turn activate other silane molecules. This result agrees well with the results shown here.

#### **MARCHING MODULUS INTENSITY**

The marching modulus intensities (MMI) measured at two different strains of all mixing series are plotted in Figure 8.

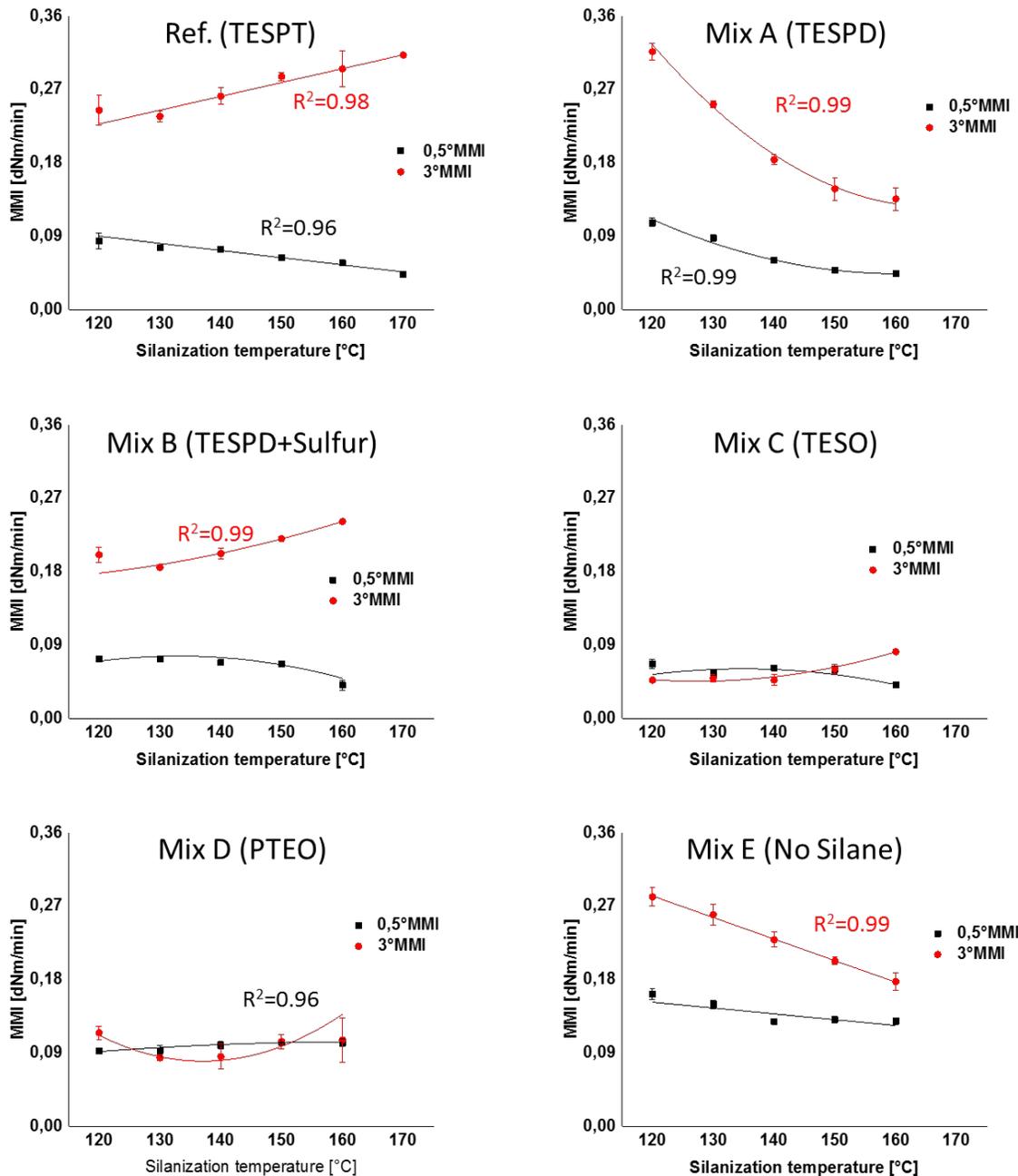


Figure 8 MMI of samples with different types of coupling agents

*Marching modulus intensity at small strain (ASTM conditions, 0.5° MMI).*— Mix E has no silane which means that no reaction is possible between filler and polymer in this mixing series, and the highest 0.5° MMI is observed in this mix. This indicates that the level of the 0.5° MMI is particularly affected by filler-filler interaction. In addition, 0.5° MMI of Ref. (with TESPT) and Mix A (with TESPD) plotted as a function of the silanization temperature shows that increasing the latter lowers the 0.5° MMI. However, the trend of 0.5° MMI of not all mixing series could be explained with the intensity of filler-filler

interaction. Except for Ref. and Mix A, 0.5° MMI shows an almost constant level for the whole silanization temperature range for the other samples. In addition, it is interesting to notice that Mix B did not follow the trend of Ref. and Mix A. This indicates that not only filler-filler interaction but also other factors, which will be discussed later, affect the 0.5° MMI.

*Marching modulus intensity at large strain conditions (3° MMI).*— A different trend was observed in the MMI measurements done at a strain of 3°. 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, as shown in Figure 9. Therefore, it is assumed that only filler-polymer and polymer-polymer interactions will affect these results.

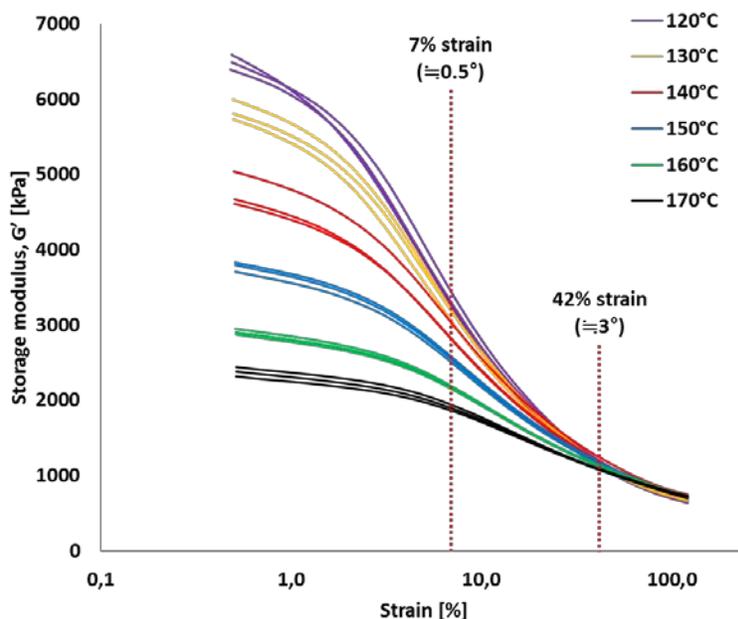


Figure 9 Examples of Payne effect curves: cured Ref. compound

As seen in Figure 4, no filler-polymer interaction was found in Mix C and Mix D. As a result, these samples showed an almost constant 3° MMI for the whole mixing temperature range. Besides, the MMI values of these compounds did not depend on the measurement strain intensity: the level of both MMI values are almost the same. This indicates that a certain polymer-filler interaction is required in order to affect 3° MMI.

Another interesting point was found in this plot: If there is at least some filler-polymer interaction present, as a consequence of active or free sulfur, it will also affect the 3° MMI. Indeed, a decreasing trend of the MMI along with increasing silanization temperature was observed in Mix A, but Ref. and Mix B, with active sulfur, show an opposite trend. Mix E, without any silane and sulfur, shows the same trend as Mix A. These trends indicate that not only filler-polymer interaction but also other factors, to be discussed as well later, affect the 3° MMI.

#### MARCHING MODULUS INTENSITY AS A FUNCTION OF FLR AND CR

A correlation is made between MMI and FLR and CR and shown in Figure 10.

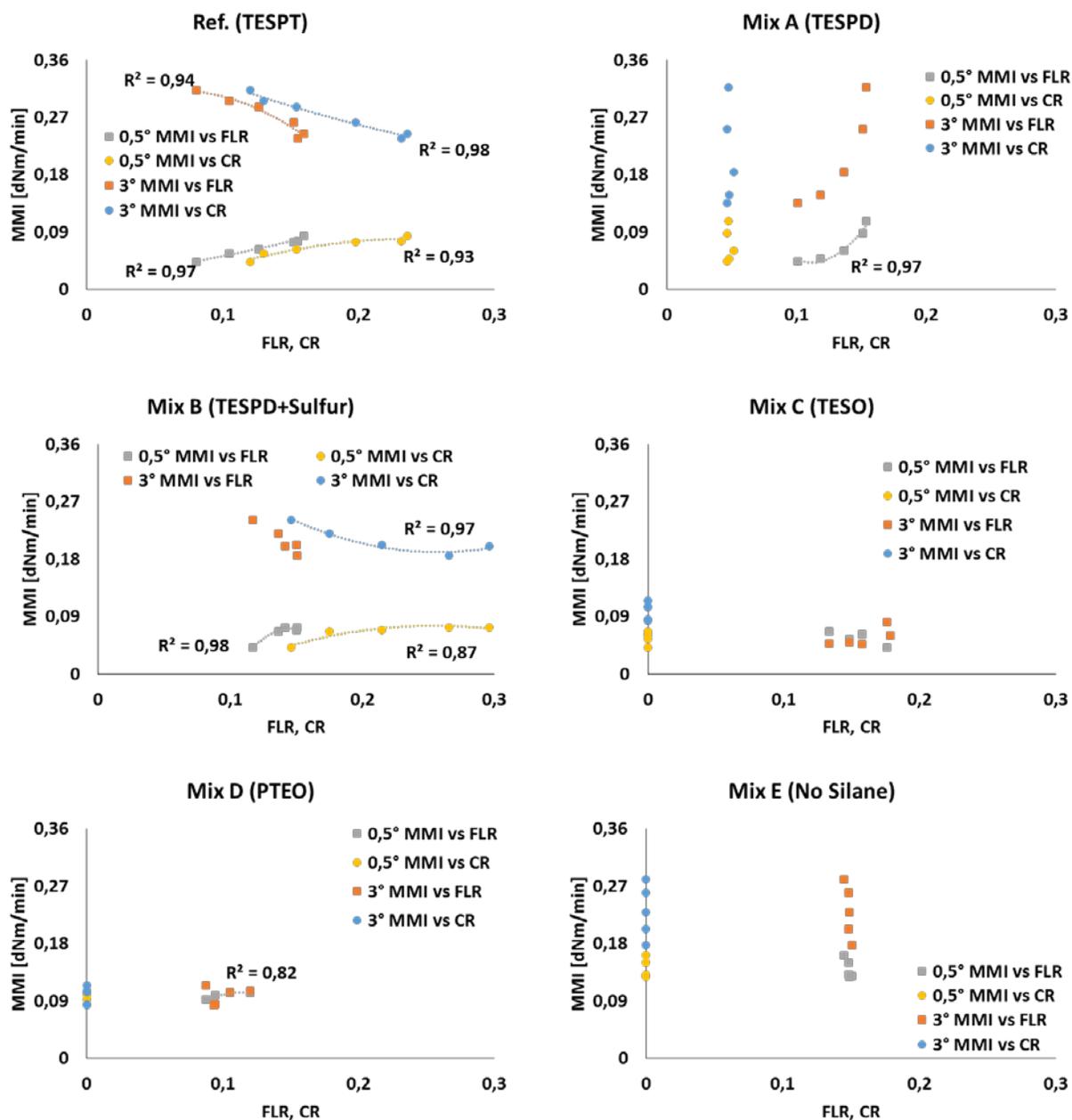


Figure 10 MMI versus FLR and CR

As seen in Figure 5, in case of Mix C and Mix E (TESO and no silane), the 0.5° MMI values reached the maximum FLR level; therefore, no correlation could be made. Samples Ref., Mix A and Mix B show a good correlation of 0.5° MMI with FLR values. This indicates that silica flocculation is happening during the vulcanization process. It is well known that the size of agglomerates has an influence on the viscosity of a rubber compound.<sup>14</sup> Thus, the viscosity will increase faster, the faster the filler particles flocculate. Due to this, the shielding of the silica surface by not only a silane coupling agent but also by bound rubber will strongly affect the rheogram of the silica compound.

CR becomes an effective factor for 0.5° MMI and 3° MMI when the compound satisfies two requirements.

Firstly, the compound should contain a silane with two functionalities: silanization and filler-polymer coupling. Secondly, additional active sulfur is required. Without active sulfur, the filler-polymer coupling reaction rate will be at a low level (Figure 7, Mix A with TESP) measured under isothermal conditions, and will not have any effect on the MMI.

When the filler-polymer interaction is established during the curing period, the compound gets stiffer and a higher torque is required in order to rotate the rheometer die. Therefore, a fast filler-polymer reaction will lead to a fast increase of the torque level at the beginning of the measurement, overlying the torque increase due to the network formation.

However, the trends are depending on the intensity of the measuring strain. In order to explain these conflicting results, the rheogram of the Ref. mixing series is shown in Figure 11 as an example.

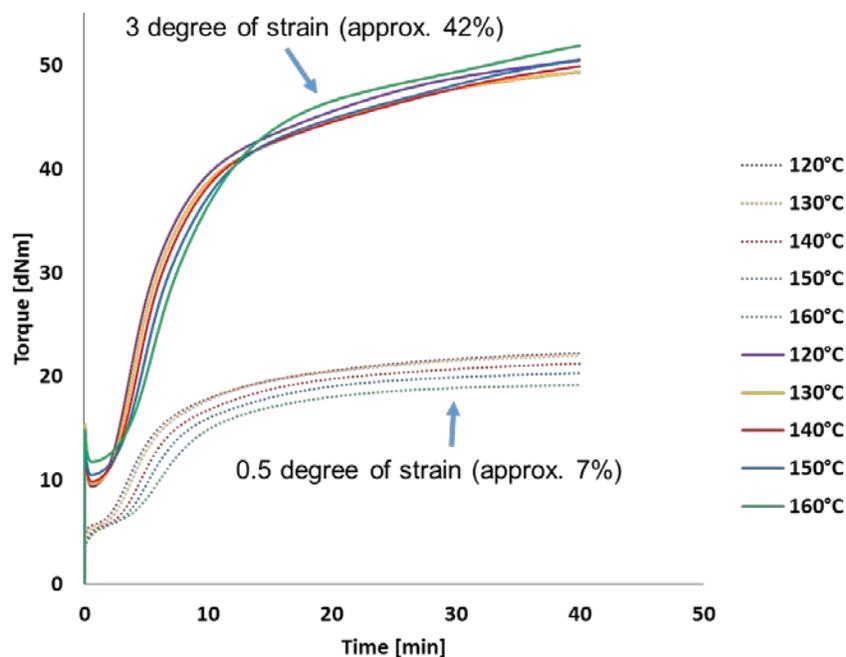


Figure 11 Rheograms of Ref. mixing series

At small strains (approx. 7%), a higher torque is measured for samples prepared at lower silanization temperatures, induced by filler-filler interaction and filler-polymer coupling. However, at large strain (approx. 42%), the level of torque at 40 minutes is almost the same (except for the sample silanized at 160°C), as the effect of filler-filler interaction becomes less at such a high deformation.

## CONCLUSIONS

The focus of this study was to elucidate the causes of marching modulus during curing of silica filled S-SBR/BR rubber compounds. The result showed that three factors – the intensity of the filler-filler interaction, the silica flocculation rate (FLR) and the filler-polymer coupling rate (CR) – are major influencing factors of the marching modulus phenomenon of silica compounds.

When measuring the curing behavior under ASTM conditions in a rheometer, the marching modulus of silica

filled rubber compounds is in first instance influenced by filler-filler interaction and FLR. While a silica filled rubber compound undergoes vulcanization, silica flocculation (FLR) occurs at the same time due to the strong filler-filler interactions. However, in cases where FLR reached its highest value, no trend in marching modulus is found.

The coupling rate (CR) during the curing process contributes as well to the marching modulus intensity. When the compound shows a fast CR, the compound gets stiffer and a higher torque is measured in the rheometer. As a consequence, a fast increase of the torque level at the beginning of the measurement is occurring, overlying the torque increase due to the network formation.

However, the CR is only an effective factor in the presence of active sulfur. The addition of free sulfur or the release of it from TESPT can speed up the filler-polymer coupling reaction, because the activation of the silane consumes free sulfur.<sup>13</sup> Additionally, the reactivity of the sulfur bridged silane increases with increasing sulfur moiety length beyond S<sub>2</sub>.<sup>12, 15</sup>

Both, FLR and CR, are strongly influenced by the mixing conditions such as the silanization temperature. When the silane is exposed to high mixing temperatures, more pre-coupling between the filler and polymer can happen. As a result, a higher amount of chemically bound rubber will form and lead to a reduction of the filler-filler interaction. As a consequence, flocculation of silica will slow down. In addition, CR will also slow down due to a higher consumption of free sulfur during mixing.

## ACKNOWLEDGEMENT

The authors gratefully acknowledge financial and materials support from HANKOOKTIRE CO., LTD. (Daejeon, Korea), Evonik Resource Efficiency GmbH. (Wesseling, Germany) and Solvay GmbH (Lyon, France).

## REFERENCES

- 1 "Vulcanization of Elastomers: Principles and Practice of Vulcanization of Commercial Rubbers", G. Alliger, I. J. Sjothun, Reinhold Pub. Corp., New York (1964)
- 2 J. Jin, J. W. M. Noordermeer, W. K. Dierkes, A. Blume, poster **28** at the Deutsche Kautschuk-Tagung (2018)
- 3 S. Mihara, R. N. Datta, J. W. M. Noordermeer, RUB. CHEM. TECHNOL. **82**, 524 (2009)
- 4 S. Mihara, PhD Thesis, University of Twente: Enschede (2009)
- 5 ASTM Standard D1646-04, "Standard Test Methods for Rubber—Viscosity, Stress Relaxation, and Pre-Vulcanization Characteristics (Mooney Viscometer)", ASTM International, West Conshohocken, PA (2004)
- 6 ASTM Standard D5289-95, "Standard Test Method for Rubber Property—Vulcanization Using Rotorless Cure Meters", ASTM International, West Conshohocken, PA, (2001)
- 7 S. Wolff, M. J. Wang, E-H. Tan, RUBBER CHEM. TECHNOL. **66**, 163 (1993)
- 8 A. Blume, S. Uhrlandt, 157th meeting Rub. Div. ACS Dallas, Texas, paper **32** (2000)
- 9 H-D. Luginsland, J. Fröhlich, A. Wehmeier, RUBBER CHEM. TECHNOL. **75**, 563 (2002)
- 10 S-S. Choi, E. Ko, Polymer Testing **40**, 170 (2014)
- 11 "Rubber compounding; Chemistry and applications, 2nd Edition", B. Rodgers, CRC Press, New York (2016)
- 12 H.-D. Luginsland, Kautsch. Gummi Kunstst. **53**, 10 (2000)
- 13 A. Hasse, O. Klockmann, A. Wehmeier, H.-D. Luginsland, Kautsch. Gummi Kunstst. **55**, 236 (2002)
- 14 N. Tokita, I. Pliskin, RUBBER CHEM. TECHNOL. **46**, 1166 (1973)
- 15 U. Görl, J. Münzenberg, D. Luginsland, A. Müller, M. Wolfgang, Kautsch. Gummi Kunstst. **52**, 588, (1999)

**TABLE I**  
**SILANE COUPLING AGENTS WITH THEIR**  
**CORRESPONDING SULFUR RANK AND FUNCTIONALITY**

Name of the silane	Sulfur rank	Possible functions		
		Silanization	Coupling	Sulfur donation
Bis(triethoxysilylpropyl)tetrasulfide (EtO) <sub>3</sub> -Si-(CH <sub>2</sub> ) <sub>3</sub> -S <sub>3.85</sub> -(CH <sub>2</sub> ) <sub>3</sub> -Si-(OEt) <sub>3</sub>	(TESPT) 3.85	O	O	O
Bis(triethoxysilylpropyl)disulfide (EtO) <sub>3</sub> -Si-(CH <sub>2</sub> ) <sub>3</sub> -S <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -Si-(OEt) <sub>3</sub>	(TESPD) 2	O	O	X
1,8-Bis(triethoxysilyl)octane (EtO) <sub>3</sub> -Si-(CH <sub>2</sub> ) <sub>8</sub> -Si-(OEt) <sub>3</sub>	(TESO) 0	O	X	X
Propyltriethoxysilane (EtO) <sub>3</sub> -Si-(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub>	(PTEO) 0	O	X	X

**TABLE II**  
**FORMULATION OF THE COMPOUND**

Mixing stage	Ingredient	Product name	Company	Ref., phr	Mix A, phr	Mix B, phr	Mix C, phr	Mix D, phr	Mix E, phr
Master Batch	S-SBR*	Buna VSL5025-2HM	Lanxess	103.2	103.2	103.2	103.2	103.2	103.2
	BR	Buna CB24	Lanxess	25	25	25	25	25	25
	HD Silica	Zeosil 1165MP	Solvay	80	80	80	80	80	80
	TESPT	Si69	Evonik	6.4	-	-	-	-	-
	TESPD	Si266	Evonik	-	5.7	5.7	-	-	-
	TESO	SIB1824.0	Gelest	-	-	-	5.2	-	-
	PTEO	VP Si203	Evonik	-	-	-	-	4.9	-
	TDAE Oil	VIVATEC 500	Hansen & Rosenthal	7	7	7	7	7	7
	Stearic acid	Stearic acid	Merck	1	1	1	1	1	1
	Zinc Oxide	ZnO	Merck	2	2	2	2	2	2
	DPG	Perkacit DPG	Flexsys	2	2	2	2	2	2
	6PPD	KUMANOX 13	Kumho Petrochemical	2	2	2	2	2	2
	Sulfur	S	J. T Baker	-	-	0.7	-	-	-
Final	Sulfur	S	J. T Baker	0.7	1.4	0.7	1.4	1.4	1.4
	ZBEC	Vulkacit ZBEC	Lanxess	0.2	0.2	0.2	0.2	0.2	0.2
	CBS	Santocure CBS	Flexsys	2.2	2.2	2.2	2.2	2.2	2.2

※27.3 wt% oil extended

**TABLE III**  
**MIXING PROCEDURE**

Masterbatch (first) step		Final (second) step	
Action	Action time, sec	Action	Action time, sec
Add polymer	20	Add master batch	-
Mastication	60		
½ Silica, Silane	30	Milling	120
Mixing	60		
½ Silica, other remains	20	Add curatives	30
Mixing (Up to 120~170°C)	60		
Ram sweep	4	Milling	350
Mixing (at target temp.)	150		
Discharge and sheeting	-	Discharge	-

Figure 1: Mixing fingerprints (torque: solid lines; temperature: dashed lines)

Figure 2: Payne effect as a function of silanization temperature

Figure 3: Micro-dispersion mechanism of silica

Figure 4: Bound rubber content of samples with different types of coupling agents

Figure 5: Silica flocculation rate (FLR) of samples with different types of coupling agents

Figure 6: Total bound rubber versus FLR

Figure 7: Filler-polymer coupling rate (CR) of samples with different types of coupling agents

Figure 8: MMI of samples with different types of coupling agents

Figure 9: Figure 9 Examples of Payne effect curves: cured Ref. compound

Figure 10: MMI versus FLR and CR

Figure 11: Rheogram of Ref. mixing series