

# Comparison of silica-NR masterbatches with in-situ silica/silane compounds

by Suyanti Hersanto, Wisut Kaewsakul, Wilma K. Dierkes and Anke Blume, University of Twente, The Netherlands; and Joachim Bertrand, Behn Meyer Europe GmbH

Natural rubber (NR) is a renewable material which offers superiorities over synthetic rubbers in terms of elasticity and mechanical performance. Therefore, natural rubber is generally used for anti-vibration mountings, conveyor belts, heavy-duty tires, high quality technical rubber products, and much more.

The filler is a vital part in rubber compounds. Silica-silane filled compounds have better tensile and tear strength, higher abrasion resistance, lower rolling resistance and hysteresis, as well as improved wet traction for winter tires when compared to carbon black filled compounds (ref. 1). Silica is rather polar compared to natural rubber; therefore, it builds up a strong filler network through hydrogen bonds. Addition of a coupling agent is essential to break these networks and bridge the silica to the rubber, leading to an optimized reinforcing efficiency.

In conventional mixing, in which rubber, silica and silane are separately added into the mixer, a second non-productive mixing stage is needed in order to achieve good hydrophobation of the silica surface and to control the thermal load of the compound. Consequently, this mixing method is time- and en-

ergy-consuming. Besides, ethanol is generated as a by-product of the silanization reaction, reducing mixing efficiency, hindering the silica-silane coupling yield in the compound, and being problematic when emitted in large amounts. Better alternatives to the dry mix are pre-silanized silica and pre-silanized silica in a masterbatch (ref. 2). For both options, the second re-mixing and silanization stage is no longer required, and ethanol emission is not an issue anymore. However, from the mixing point of view and considering the change of the material consistency from a more elastic to a stiffer silica-containing rubber, the addition of a processing aid could be useful to ease the mixing process.

More insight into the effect of mixing time and processing aid on the properties of NR-silica compounds is required to determine whether the alternative compounds are actually better than the conventionally mixed ones. The outcome of this research can lead to a shift in the preparation of NR-silica compounds to a more favorable method in terms of time- and cost-efficiency.

## Experimental

The pre-silanized silica and the NR-silica masterbatch (MB) offer the possibility of a shorter mixing time. Furthermore, the compound containing the silica masterbatch is supposed to have the highest dispersion quality and, as a consequence, the best mechanical properties. To confirm this hypothesis, silica-filled NR compounds were prepared by three methods: in a dry mix, used as pre-silanized silica and as an NR-silica masterbatch, and they were prepared using different mixing times and processing aids. The pre-silanized silica and NR-silica masterbatch were delivered by Behn Meyer, Germany. The technical information concerning these two products is described elsewhere (ref. 2). Both alternatives contain grades and contents of NR, silica and silane comparable to the conventional silica-silane system of the dry mix. The performance of the silica-filled NR compounds in terms of mixing efficiency and vulcanizate properties is evaluated.

The rubber formulations are presented in table 1. The total amount of silica and silane in the pre-silanized silica and in the silica-masterbatch was adjusted by taking into account the mass loss of water and alcohol in the silanization reaction. Table 2 shows the experimental design with a series of compounds assigned to different raw materials, mixing cycles and processing aids.

Mixing of the ingredients was done in a Brabender internal mixer with a capacity of 390 ml. For all mixing stages, a fill factor of 70% was chosen, together with a rotor

**Table 1 - compound formulations**

Ingredients	Dosage (phr)
NR or NR-silica masterbatch (MB) <sup>a)</sup>	100.0 or 152.0
Ultrasil VN3 or pre-silanized silica (PS)	50.0 or 52.0
TESPT	5.0 or 0.0 <sup>b)</sup>
Processing aid	2.0
TDAE oil	5.0
ZnO/stearic acid	4.0/1.5
6PPD/TMQ/wax	2.5/1.2/3.0
CBS/TBzTD	1.5/2.0
Sulfur	1.5

a) NR-silica masterbatch contains 52.0 phr of pre-silanized silica  
b) TESPT was not added in PS- and MB-based compounds

**Table 2 - experimental design of this study**

Compounds	Number	Mixing cycle	Processing aid	Notation
Conventional silica-silane system or Dry Mix (DM)	1	Long (L)	PA1 (Ultra-Flow 700S)	DM-PA1_L (1)
	2	Very short (VS)	PA1	DM-PA1_VS (2)
	3	Very short	PA2 (Ultra-DFR 900)	DM-PA2_VS (3)
Pre-silanized silica (PS)	4	Long	PA1	PS-PA1_L (4)
	5	Very short	PA1	PS-PA1_VS (5)
NR-silica masterbatch (MB)	6	Long	PA1	MB-PA1_L (6)
	7	Short (S)	PA1	MB-PA1_S (7)
	8	Very short	PA2	MB-PA2_VS (8)

**Table 3 - mixing procedure: long cycle (L: with three stages) and short cycle (S: without stage 2)<sup>a)</sup>**

Stage 1		Stage 2: Silanization <sup>a)</sup>		Stage 3: Final mixing	
Time <sup>b)</sup>	Action	Time	Action	Time	Action
0:00	Load STR 5L or ½ NR-silica MB	0:00	Load masterbatch	0:00	Load masterbatch
0:30	Close ram	0:30	Close ram	0:30	Close ram
1:00	Add silica, silane or ½ NR-silica MB	4:30	Discharge	1:00	Add curatives
3:00	Close ram			1:20	Close ram
5:00	Add chemicals and PA1 <sup>c)</sup>			1:50	Sweep
5:20	Close ram			2:10	Close ram
6:50	Sweep			3:10	Discharge
7:10	Close ram				
11:10	Discharge				
Shear duration: 8 minutes		Shear duration: 4 minutes		Shear duration: 2 minutes	

<sup>a)</sup> The long cycle is a three-step mixing, while the short cycle is a two-step mixing procedure of which the second mixing stage is eliminated <sup>b)</sup> The unit of time is min.:sec. <sup>c)</sup> Processing aid

According to the mixing sequence as detailed in tables 3 and 4. After addition of the chemicals, the rotor speed was adjusted manually to reach the dump temperature of 140°C as soon as possible. The three mixing cycles employed are called long (L), short (S) and very short (VS) cycles.

Vulcanization of the compounds was done in a curing press at a temperature of 160°C for the

**Table 4 - mixing procedure: very short cycle (VS)**

Stage 1		Stage 2: Final mixing	
Time <sup>a)</sup>	Action	Time	Action
0:00	Load STR 5L or ½ NR-silica MB	0:00	Load masterbatch
0:30	Close ram	0:30	Close ram
1:00	Add silica, silane or ½ NR-silica MB and ½ PA2	1:00	Add curatives
3:00	Close ram	1:20	Close ram
3:30	Add chemicals and PA1 or ½ PA2	1:50	Sweep
3:50	Close ram	2:10	Close ram
4:50	Sweep	3:10	Discharge
5:10	Close ram		
7:10	Discharge		
Shear duration: 4 minutes		Shear duration: 2 minutes	

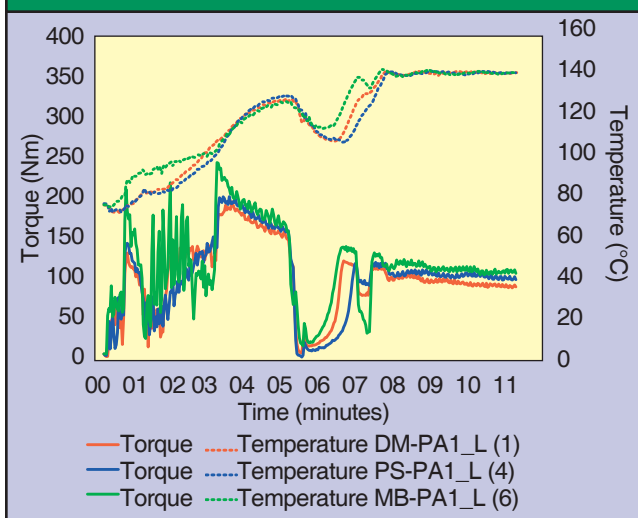
<sup>a)</sup> The unit of time is min.:sec.

curing time  $t_{95}$  determined from the cure characteristics test. The Payne effect was analyzed using a rubber process analyzer (RPA 2000) from Alpha Technologies. The change in modulus was recorded during a strain sweep from 0.56% to 100% at 100°C and 5 Hz. The bound rubber measurement is comprised of two parts, total and chemically bound rubber. In the latter, ammonia treatment is needed to break down the physical bonding between the filler and polymer. The measurement was conducted according to the procedure described in ear-

lier work (ref. 3). The dispersion level of the filler in the vulcanized rubber matrix was evaluated with a DisperGrader Alpha View from Alpha Technologies. Tensile properties were measured with a Zwick Roell Z1.0 machine using a crosshead speed of 500 mm/minute according to ISO 37 with a type 2 dumbbell.

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**Figure 1 - mixing fingerprints of the compounds prepared with the same long mixing cycle, but different silica forms**



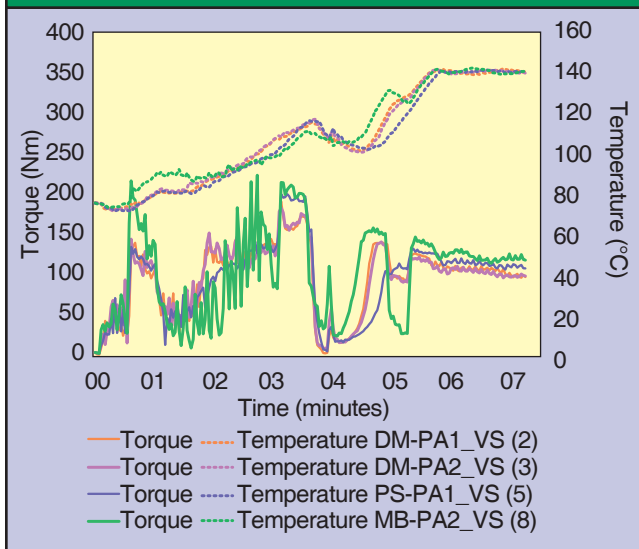
## Results and discussion

### Mixing

Figure 1 shows that from minutes 1 to 3, the NR-silica masterbatch is a tough material due to its silica content and the absence of processing additives; thus, higher energy is required to mix the masterbatch compounds. These conditions appear as irregularity and wide fluctuation in the mixing torque of the masterbatch compound in this timescale.

Immediately after the addition of the chemicals at 5:20 minutes (figure 1), the torque increases to its maximum point at a different rate, depending on the type of compounds. The time needed to reach the maximum torque is one minute for the dry mix and the masterbatch compounds, and one-and-a-half minutes for the pre-silanized silica compound. The pre-silanized silica is a fluffy type; therefore, it is more difficult and time-consuming to incorporate compared to the granulated silica, e.g., Ultrasil VN3. As a consequence, other added chemicals are also slower to be incorporated. The masterbatch com-

**Figure 2 - mixing fingerprints of the compounds prepared with the same very short mixing cycle, but different silica forms and processing aids**

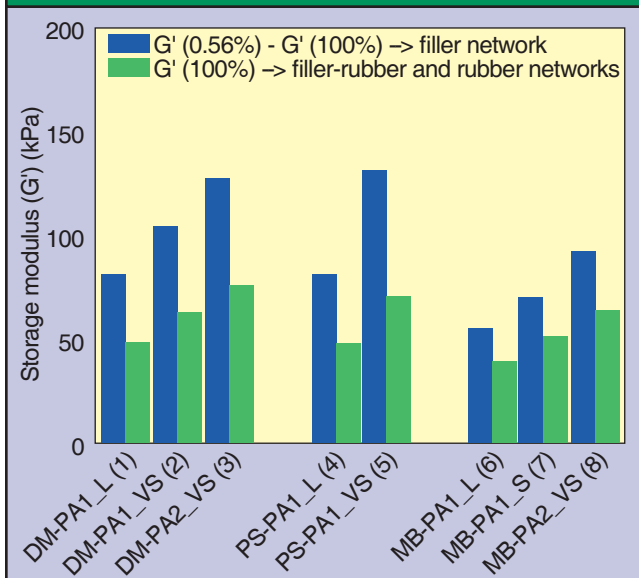


pounds, in which silica is already dispersed, show the fastest additive incorporation (figure 2).

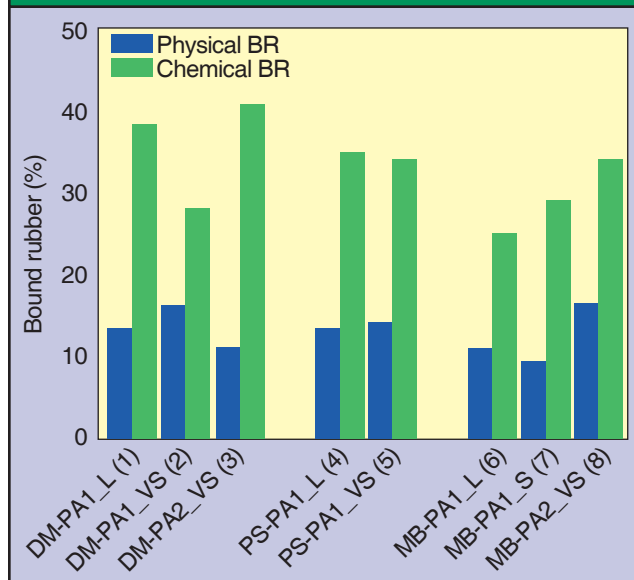
*Filler-filler and filler-rubber interactions*

The Payne effect ( $G'_{0.56\%} - G'_{100\%}$ ) or filler-filler interaction, as depicted in figure 3, was calculated from the difference between storage moduli at 0.56% and 100% strain. The influence of the mixing cycles on the filler-filler network is seen as a lower Payne effect for a longer mixing time, as more energy is put into mixing of the compounds, and the silica network is destroyed to a higher degree. This is very well demonstrated by the masterbatch

**Figure 3 - Payne effect of the compounds prepared with different raw materials, mixing cycles and processing aids**



**Figure 4 - bound rubber (BR) content of the compounds prepared with different raw materials, mixing cycles and processing aids**



groups, which are silanized and dispersed prior to the mixing. In addition, the masterbatch compounds show the lowest level of filler-filler interaction, which is expected and desired.

When the mixing time is prolonged, more silanization will occur, which improves the compatibility between silica and NR. Therefore, a higher chemical bound rubber content is expected. This is true for the compound pairs 1-2 and 4-5 (figure 4). However, a different tendency is found for the masterbatch compounds 6, 7 and 8. With an accomplished silanization and dispersion of the filler in the masterbatch compounds, the longer mixing causes more destruction of polymer chains/networks, leading to a decreased bound rubber content.

Compound 3 with PA2 (Ultra-DFR 900) shows a higher chemical bound rubber content than compound 2 with PA1 (Ultra-Flow 700S). The total bound rubber of compound 3 reaches a similar value as compound 1 with long mixing cycle. This suggests that PA2 supports the silanization reaction.

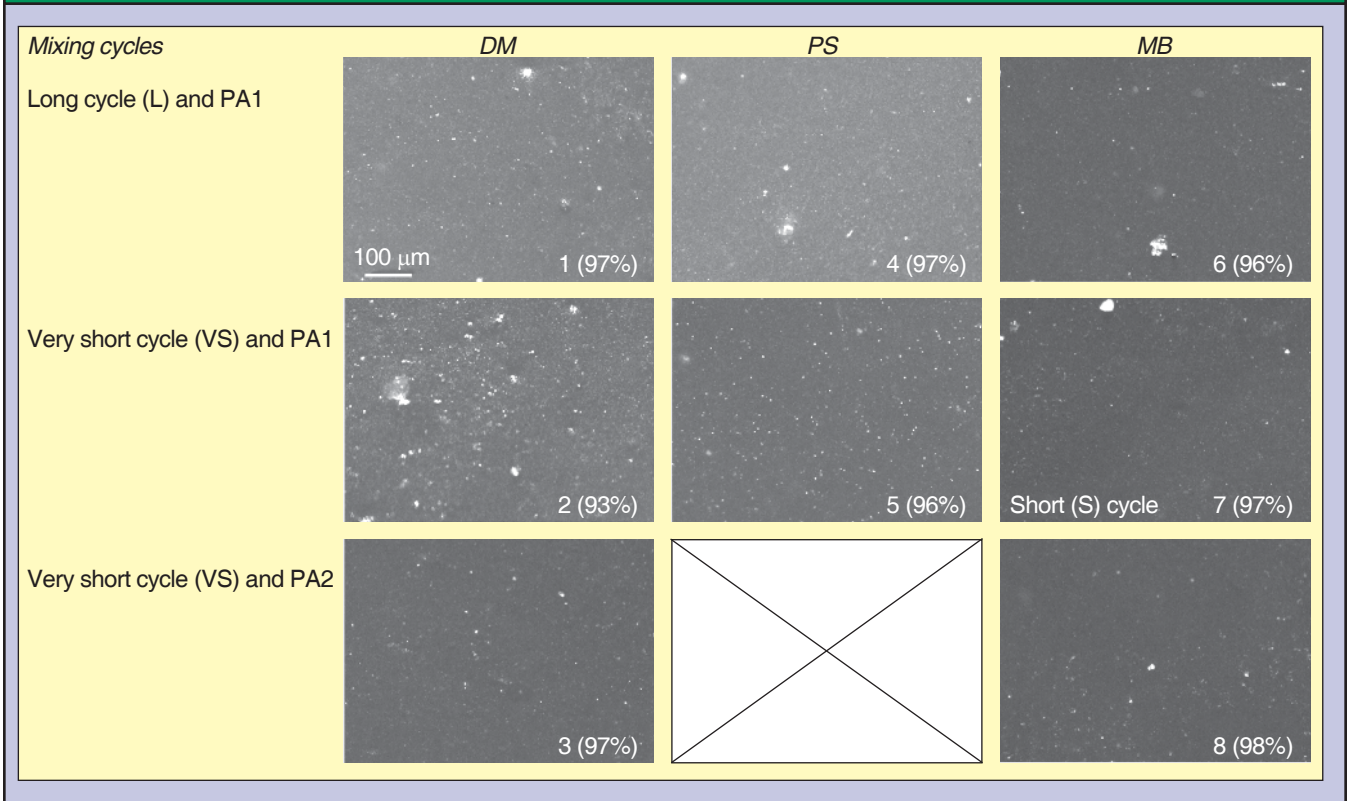
*Macro-dispersion*

Based on the DisperGrader evaluation, values below 95% are considered as poor dispersion. For the dry mix compounds (figure 5), switching from a long to a very short mixing cycle results in a worse dispersion. The shorter mixing time is insufficient for an adequate silanization reaction, so that the silica clusters remain due to the filler-filler interaction. Addition of PA2 (Ultra-DFR 900) improves the dispersion, though. It promotes silanization, which emerges from its higher polarity than PA1 (Ultra-Flow 700S). Therefore, a lower filler-filler interaction results in the breakdown of the silica aggregates.

*Mechanical properties*

The reinforcement index (M300/M100) is the highest for the masterbatch compounds, followed by the dry mix and the pre-silanized silica compounds (figure 6). The shorter the mixing

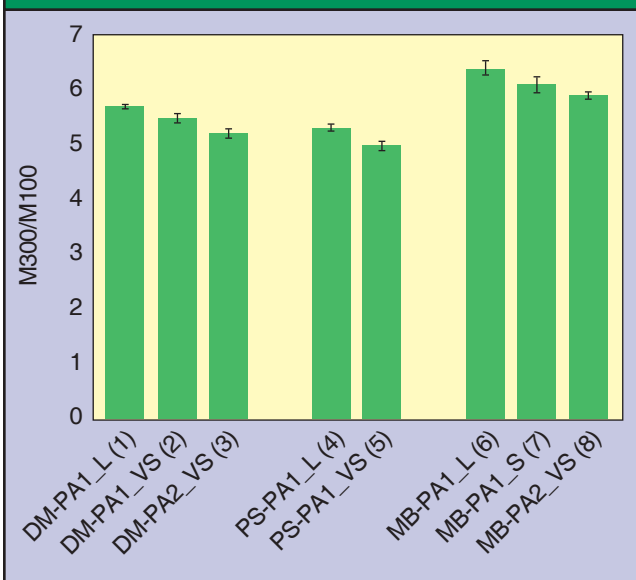
**Figure 5 - macro-dispersion images labeled with the dispersion degree of the vulcanizates prepared with different raw materials, mixing cycles and processing aids**



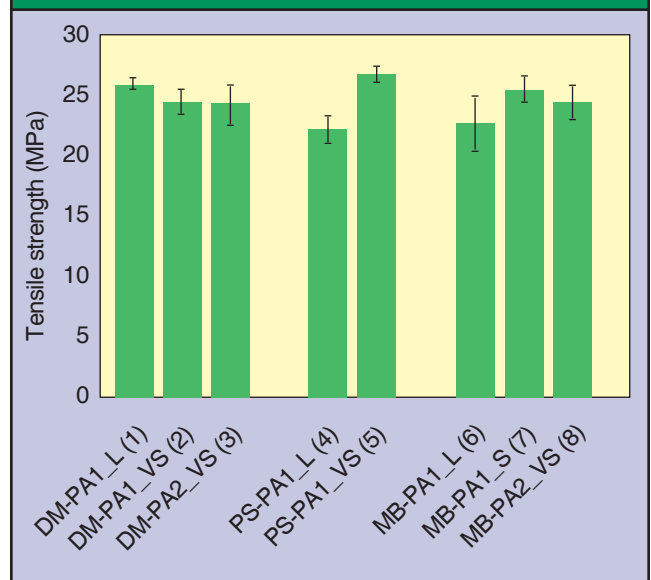
time, the lower the reinforcement index. There is an inverse correlation between the reinforcement index and the filler-filler interaction measured as the Payne effect (figure 3), indicating that the micro-dispersion of the silica has a strong impact on the strength properties of the compounds.

The tensile strength (figure 7) of the pre-silanzed and the pre-silanzed silica-NR masterbatch compounds are similar to the dry mix compounds; especially the very shortly mixed compounds 5 and 8, compared to the long-mixed compound 1. By taking the elongation at break into account (figure 8), it is

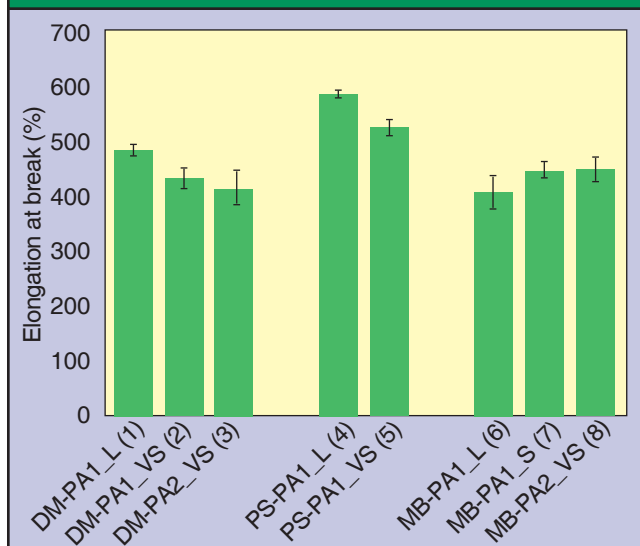
**Figure 6 - reinforcement index of the vulcanizates prepared with different raw materials, mixing cycles and processing aids**



**Figure 7 - tensile strength of the vulcanizates prepared with different raw materials, mixing cycles and processing aids**



**Figure 8 - elongation at break of the vulcanizates prepared with different raw materials, mixing cycles and processing aids**



best to have the long mixing for the dry mix and the very short mixing for the others. As portrayed by the macro-dispersion (figure 5), the very short mixing is not sufficient for the dry mix to achieve a good dispersion and hydrophobation, and thus results in a lower reinforcement. The shorter mixing cycle for silica-masterbatch compounds retains the rubber chains/networks, while the silica particles are well dispersed. This,

therefore, leads to the improved tensile strength and elongation at break.

### Conclusions

The best mixing cycles for each group of compounds are the long mixing cycle for the conventionally mixed compound, which requires silanization, and the very short mixing cycle for the pre-silanized and masterbatch compounds. Processing aid Ultra-DFR 900 with a higher polarity is more efficient than Ultra-Flow 700S, and especially suitable with the masterbatch compound which is very shortly mixed. Overall, the properties of the masterbatch compound with the very short mixing cycle are as good as the properties of the longer conventionally mixed compound. Combining this with the advantages of shorter production time and better material handling, the NR-silica masterbatch is obviously a better solution than the conventional silica/silane-based system.

This article is based on a paper presented at the 194th Technical Meeting of the Rubber Division, ACS, October 2018.

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