

Comparison of Silica-NR Masterbatches with in-situ Silica / Silane Compounds

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## **Abstract**

In a modern green tire tread compound, silica is added together with silane to the rubber matrix. A suitable mixing process has to be applied to guarantee an efficient coupling reaction between the silica and the silane in order to reach a good hydrophobation of the silica surface. Therefore, the adjustment and careful control of critical mixing parameters like mixing time and mixing temperature is essential. Alternative approaches to overcome these difficulties can be the use of pre-silanized silica or silica-NR masterbatches. In the present study the in-rubber performances of all three systems will be compared and the advantages and disadvantages discussed.

## **Introduction**

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

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 [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 energy-consuming. Besides, ethanol is generated as 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 presilanized silica and presilanized silica in a masterbatch [2]. For both options, the second re-mixing and silanization stage is no longer required and ethanol emission is not an issue any more. 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 way of preparation of NR-silica compounds to a more favorable method in terms of time- and cost-efficiency.

## **Experimental**

The presilanized 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 are prepared by three methods: in a dry mix, used as presilanized silica and as a NR-silica masterbatch, and they are prepared using different mixing times and processing aids. The presilanized silica and NR-silica masterbatch were delivered by Behn Meyer, Germany. The technical information concerning these two products is described elsewhere [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 presilanized 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.

**Table 1** Compound formulations.

Ingredients	Dosage (phr)
NR or NR-silica masterbatch (MB) <sup>a)</sup>	100.0 or 152.0
Ultrasil VN3 or presilanized 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

<sup>a)</sup> NR-silica masterbatch contains 52.0 phr of presilanized silica.

<sup>b)</sup> 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)
Presilanized 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)

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 speed of 60 rpm and a starting temperature of 80°C. 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 as long (L), short (S) and very short (VS) cycles. The details are shown in Tables 3 and 4.

**Table 1** Mixing procedure: long cycle (L: with 3 stages) and short cycle (S: without stage 2) <sup>a)</sup>.

Stage 1		Stage 2: silanization <sup>a)</sup>		Stage 3: final mixing	
Time	Action	Time	Action	Time	Action
0:00	Load STR 5L / 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 / 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>b)</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				
<i>Shear duration: 8 minutes</i>		<i>Shear duration: 4 minutes</i>		<i>Shear duration: 2 minutes</i>	

a) The long cycle is a 3-step mixing, while the short cycle is a 2-step mixing procedure of which the second mixing stage is eliminated.

b) Processing aid

**Table 4** Mixing procedure: very short cycle (VS).

Stage 1		Stage 2: final mixing	
Time	Action	Time	Action
0:00	Load STR 5L / ½ NR-silica MB	0:00	Load masterbatch
0:30	Close ram	0:30	Close ram
1:00	Add silica, silane / 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*

Vulcanization of the compounds was done in a curing press at a temperature of 160°C for the curing time  $t_{95}$  determined from the cure characteristics test. The Payne effect was analyzed using a Rubber Process Analyzer (RPA2000) 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 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 earlier work [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 under a crosshead speed of 500 mm/min according to ISO 37 with a type 2 dumbbell.

## 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.

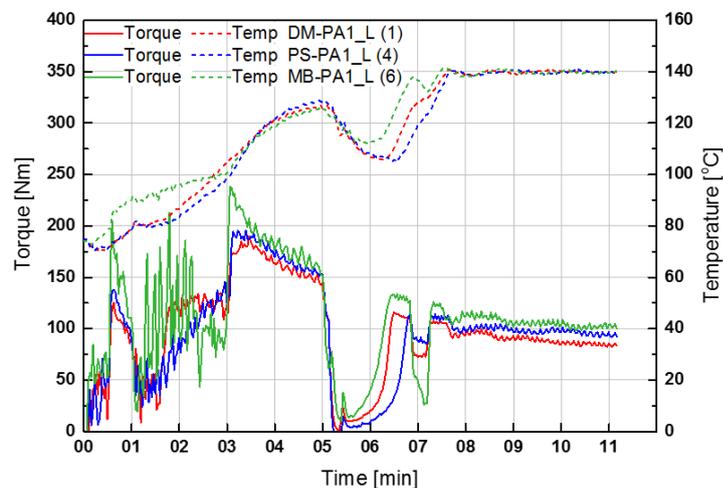


Fig. 1

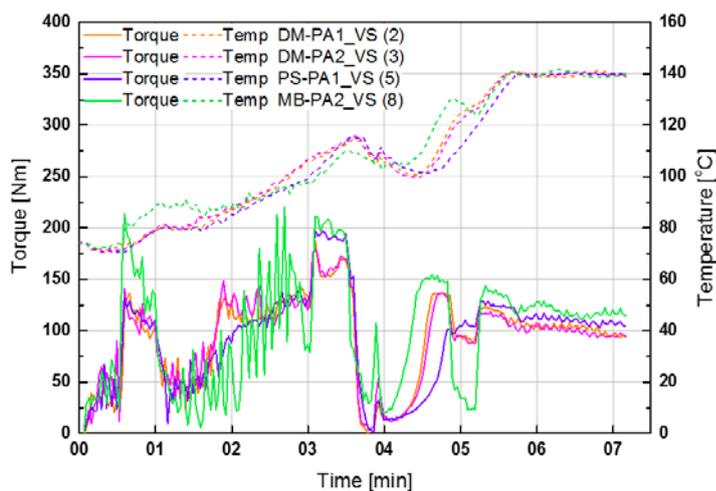


Fig. 2

**Figures 1-2** Mixing fingerprints of the compounds prepared with different silica forms, processing aids, and mixing times.

Immediately after the addition of the chemicals at 5:20 minutes (Fig. 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 1 minute for the dry mix and the masterbatch compounds, and 1.5 minutes for the presilanized silica compound. The presilanized 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 incorporated. The masterbatch compounds, in which silica is already dispersed, show the fastest additive incorporation: see also Fig. 2.

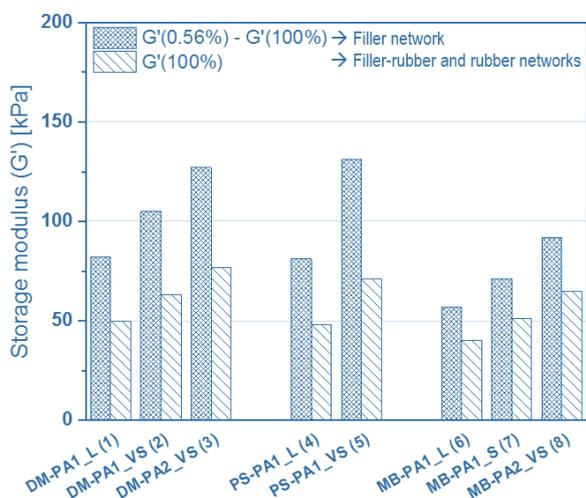


Fig.3

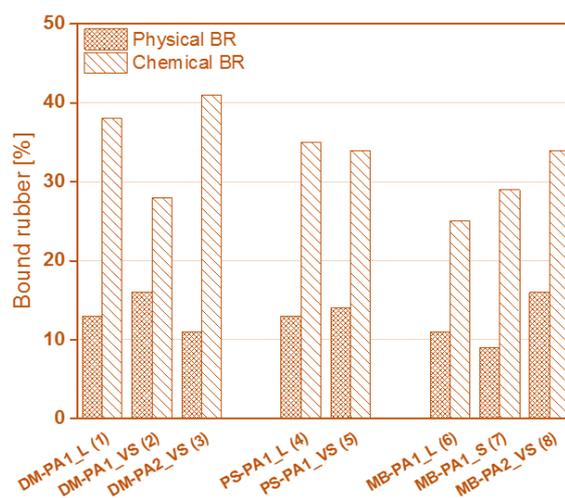


Fig.4

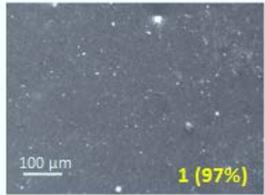
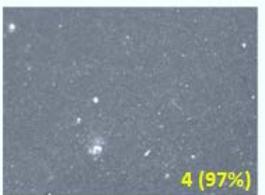
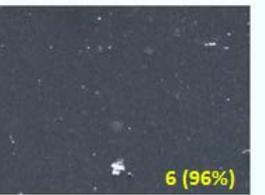
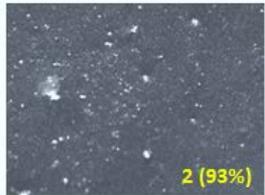
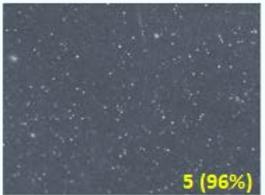
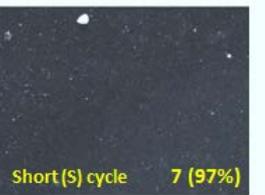
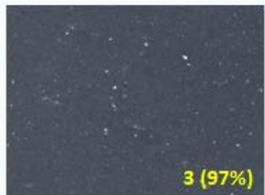
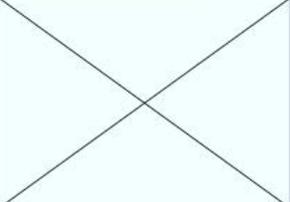
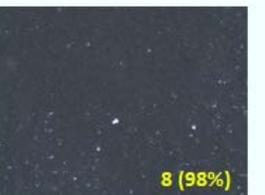
**Figures 3-4** Payne effect and bound rubber content of the compounds prepared with different raw materials, mixing cycles and processing aids.

**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 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: see Figure 4. However, a different tendency is found for the masterbatch compounds 6-7-8. With an accomplished silanization and dispersion of the filler in the masterbatch compounds, the longer mixing causes more destruction on 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.

Mixing cycles	DM	PS	MB
Long cycle (L) & PA1			
Very short cycle (VS) & PA1			
Very short cycle (VS) & PA2			

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

**Macro-dispersion.** – Based on the Dispergrader evaluation, values below 95% are considered as poor dispersion. For the dry mix compounds: see 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.

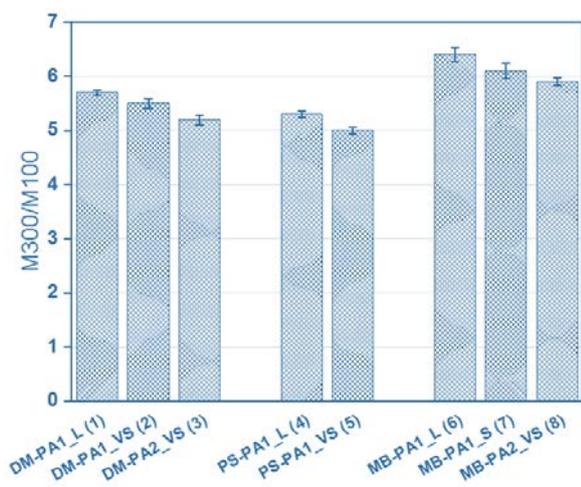


Fig. 6

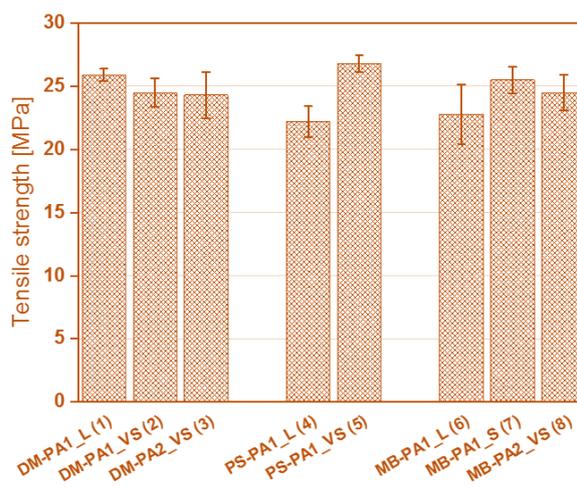


Fig. 7

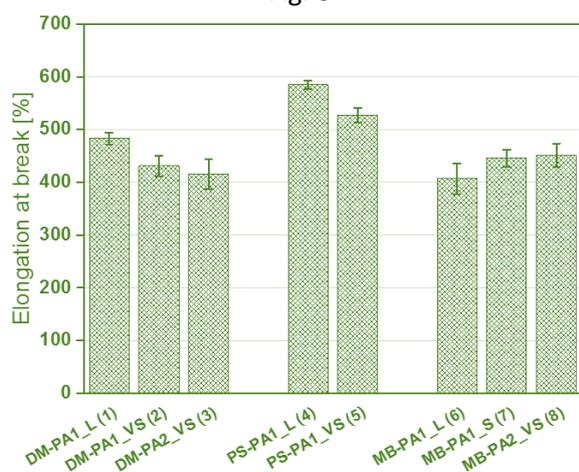


Fig. 8

**Figures 6-8** Mechanical properties of the vulcanizates prepared with different raw materials, mixing cycles and processing aids.

**Mechanical properties.** – The reinforcement index (M300/M100) is the highest for the masterbatch compounds, followed by the dry mix and the presilanized silica compounds: see Figure 6. The shorter the mixing 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 (Fig. 3), indicating that the micro-dispersion of the silica has a strong impact on the strength properties of the compounds.

The tensile strength (Fig. 7) of the presilanized and the presilanized 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 (Fig. 8), it is best to have the long mixing for the dry mix and the very short mixing for the others. As portrayed by the macro-dispersion (Fig. 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 presilanized 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.

### **Acknowledgements**

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