

# The relation between macro- and micro-dispersion of silica filler in rubber matrix

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**Abstract.** The dispersion of fillers in elastomers can be discriminated into two categories based on the dimensions of the filler clusters: macro- (2 to 100  $\mu\text{m}$ ) and micro- (smaller than 2  $\mu\text{m}$ ) dispersion. Both dispersion types are determining the final properties of the composite, but the micro-dispersion of fillers is crucial for good reinforcement of the rubber. Two basic dispersion mechanisms are proposed in literature for carbon black: agglomerate rupture and onion peel model. These filler dispersion mechanisms imply that micro-dispersion occurs only after agglomerate fragmentation of fillers, and that therefore these processes are strongly related. For silica fillers, Blume and Uhrlandt proposed a specific micro-dispersion mechanism: The polymer firstly penetrates into the voids of the agglomerates, followed by polymer chains pulling off fragments from the larger agglomerates under shearing conditions. This mechanism suggests that micro- and macro-dispersion of silica are independent.

In this study, the relation between micro- and macro-dispersion of silica in a rubber matrix was investigated. Different degrees of dispersion were achieved by variation of the mixing parameters (silanization temperature, time) and the amount of coupling agent. The degree of micro- and macro-dispersion was analyzed by measuring the Payne effect and using microscopic methods, respectively. No correlation was found between micro- and macro-dispersion. The results of this study confirm indeed that these filler dispersion processes happen simultaneously, but independently. Additionally, the factors affecting micro- and macro-dispersion will be discussed.

## 1. Introduction

Dispersion of rubber fillers such as silica, can be divided into two categories: macro- and micro-dispersion. Macro-dispersion can be defined as dispersion of agglomerates which are between the size range of 2 to 100  $\mu\text{m}$ . Micro-dispersion refers to dispersion of aggregates of silica with a size smaller than 2  $\mu\text{m}$ . [1] Both dispersions are important, however, in order to achieve the best reinforcement of rubber, micro-dispersion is most crucial. [2,3]

Blume and Uhrlandt [4] proposed a micro-dispersion mechanism of silica fillers: First, the polymer penetrates into the voids of the agglomerates; when the polymer has penetrated, silica clusters are situated in a shearing condition and the polymer chains pull off aggregates from the agglomerates. From this point of view, micro- and macro-dispersion seem to be independent.

In order to confirm correlation or independence between micro- and macro-dispersion of silica, four series of mixing trials are performed within the present study as follow:

- Series 1: The effect of silanization temperature (130°C~160°C) and presence of silane;
- Series 2: The effect of silanization time (0 sec ~ 250 sec);
- Series 3: The effect of the amount of silane at the typical silanization temperature (140°C, the temperature was selected based on the results of Series 1);
- Series 4: The effect of silica characteristics (surface area and structure).

The degree of micro- and macro-dispersion for all series is evaluated by measuring the Payne effect and using the Dispergrader, respectively. The Payne effect of silica-filled rubber compounds

is generally used as an indicator of the degree of filler-filler interactions. [2, 5, 6] When a rubber is filled with a reinforcing filler, filler-filler interactions take place. In general, the storage modulus of such filled rubber compounds decreases with increasing strain amplitude due to the breakdown of the filler network. This effect is commonly known as the Payne effect, which is obtained from the difference in storage modulus at low strain and high strain amplitude. [5, 6] Sarkawi et al. and Seo et al. compared the results of Payne effect and the images obtained from Transmission Electron Microscopy (TEM) and reported that both results are comparable. [7, 8] Thus, the Payne effect was used as an indicator of silica micro-dispersion in the present work. The results of this study confirm that these filler dispersion processes happen simultaneously, but independently. Additionally, major influencing factors on micro- and macro-dispersion of silica were investigated.

### 1. Sample preparation and analysis

All series of experiments were done based on a tire tread compound as shown in Table I. The silicas used in this work are listed in Table II with their specification and classification: Conventional (CV), and Highly-Dispersible (HD). Bis-(TriEthoxySilylPropyl)Tetrasulfide (TESPT) was used as silane coupling agent. The amount of TESPT applied in the formulations of COM4, COM5 was adjusted according to Equation (1), based on the CTAB surface area of the Silicas 2 and 3 as given in Table II: [9]

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

Table I. Compound formulation

Mixing stage	Ingredient	COM1 (phr)	COM2 (phr)	COM3 (phr)	COM4 (phr)	COM5 (phr)
Master batch	S-SBR* / BR	110 / 20	→	→	→	→
	Silica 1 / 2 / 3	90 / - / -	90 / - / -	90 / - / -	- / 90 / -	- / - / 90
	TESPT	8.0	-	4.0	7.3	8.0
	TDAE Oil	5	→	→	→	→
	St. Acid / ZnO / DPG	1 / 2 / 1.5	→	→	→	→
Final	Sulfur	0.7	→	→	→	→
	ZBEC	0.2	→	→	→	→
	CBS	2.2	→	→	→	→
Used for		Series 1, 2, 3	Series 1, 3	Series 3	Series 4	Series 4

\*27.3 wt% oil extended

Table II. Specification and classification of the silicas [2, 3]

Sample code	Class	BET [m <sup>2</sup> /g]	CTAB [m <sup>2</sup> /g]	DBP number [g/100g]
Silica 1	HD Silica	180	177	220
Silica 2	HD Silica	155	152	196
Silica 3	CV Silica	175	167	175

The compounds were mixed in two steps as shown in Tables III and IV. The master batch stage was done by using a lab scale internal mixer (Brabender Plasticorder) with a 390 ml of chamber

volume. The fill factor of the internal mixer was fixed to 63%. In Series 1, both COM1 and 2 were mixed with Mixing procedure A. In Series 2, COM1 was mixed with Mixing procedure B; in Series 3, COM1, 2 and 3 were mixed with Mixing procedure A, but with a fixed silanization temperature of 140°C for a purpose to be discussed later on. A short silanization time was applied for COM3, because the compound crumbled when the silanization time for COM3 exceeded longer than 50 seconds. In Series 4, COM4 and 5 were mixed with Mixing procedure A at a fixed silanization temperature of 150°C. Three batches were mixed for each set of conditions in order to check the reproducibility.

Table III. Master batch mixing procedure

Mixing procedure A		Mixing procedure B	
Action	time [mm:ss]	Action	time [mm:ss]
Add polymer	00:00~00:20	Add polymer	00:00~00:20
Mastication	00:20~01:20	Mastication	00:20~01:20
½ Silica, Silane	01:20~01:40	½ Silica, Silane	01:20~01:40
Mixing	01:40~02:40	Mixing	01:40~02:40
½ Silica, remaining ingredients	02:40~03:10	½ Silica, remaining ingredients	02:40~03:10
Mixing till target temperature: 130, 140, 150, 160°C	03:10~04:10	Mixing till 150°C	03:10~04:10
Ram sweep	04:10~04:14	Ram sweep	04:10~04:14
Mixing (at target temperature)	04:14~06:40	Mixing for various time laps: 0, 50, 100, ..., 250 sec	04:14~08:20
Discharge and sheeting	-	Discharge and sheeting	-

Table IV. Final mixing procedure on a mill

Mixing procedures A and B	
Action	time [mm:ss]
Add master batch	-
Mixing	00:00~02:00
Add curatives	02:00~02:30
Mixing	02:30~09:00
Discharge	-

The micro-dispersion of silica was evaluated by measuring Payne effect of the uncured rubber compounds using a Rubber Process Analyzer (RPA; RPA Elite, TA Instruments). The macro-dispersion of silica of the compounds was analyzed by using a Dispergrader (DisperGRADER Alpha View, Alpha Technologies). The average and standard deviation of macro dispersion values were calculated after 15 measurements per each set of condition.

### 3. Result and discussion

#### 3.1 Series 1: The effect of silanization temperature and presence of silane coupling agent

The micro- and macro-dispersions of COM1 (with TESPT) and 2 (without TESPT) with different silanization temperatures are compared in Figure 1. COM1 (with TESPT) shows a very low level of Payne effect for the whole range of silanization temperatures compared to COM2 (without TESPT). A decreasing Payne effect is observed in both series with increasing silanization temperature. The fact that still some decrease in Payne effect is seen even in absence of TESPT can be explained by the micro-dispersion mechanism of silica proposed by Blume and Uhrlandt. At higher temperatures, the polymer mobility is enhanced, either by lower viscosity or possibly by some polymer breakdown. This implies 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.

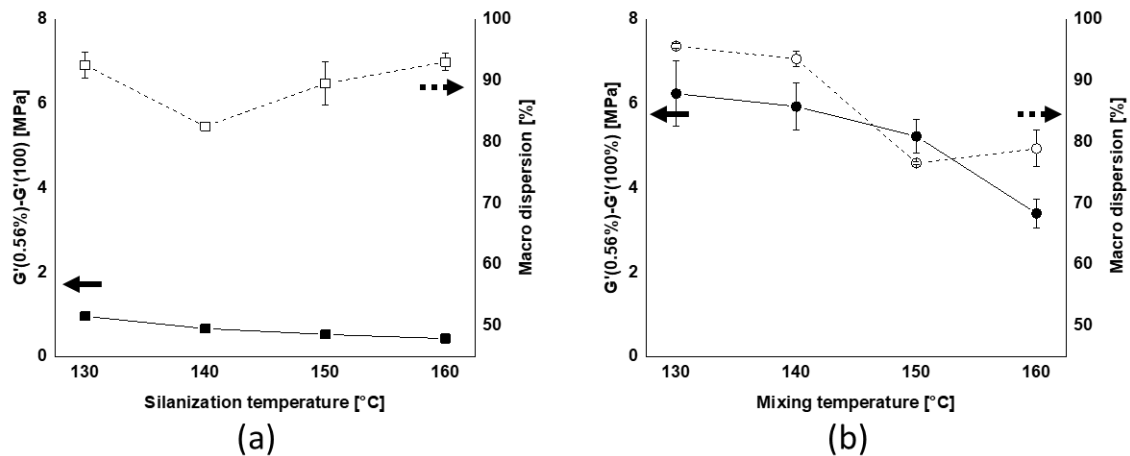


Fig. 1.— Micro-dispersion (Payne effect) and macro-dispersion of the compounds in Series 1; (a): COM1; (b): COM2.

A higher degree of macro-dispersion for COM1 (with TESPT) and an increasing trend in macro-dispersion along with increasing silanization temperature were expected. However, the highest macro-dispersion was observed for COM2 (without TESPT) mixed at the lower temperatures of 130 $^{\circ}\text{C}$  and 140 $^{\circ}\text{C}$ . At lower mixing temperatures, the viscosity of the polymer is higher, thus mechanical shearing is more enhanced. [10] There were no other obvious factors which affected the viscosity of the rubber polymer. The experiments show, that the macro-dispersion of the compounds without TESPT decreases with increasing the silanization temperature: Figure 1(b). However, it is more complex for COM1 (with TESPT): Figure 1(a). The level of macro-dispersion drops when the temperature rises from 130 $^{\circ}\text{C}$  to 140 $^{\circ}\text{C}$ , and gradually increases along with silanization temperature. In this case, the macro-dispersion of silica can be influenced not only by changes in compound viscosity induced by temperature, but also by the degree of silanization. When the silica is shielded by silane, the filler becomes more compatible with the polymer and this leads to reduction of the filler network. This will first result in a lower viscosity again. [10] When the starting temperature of silanization (130 $^{\circ}\text{C}$ ) is taken into account, it can be deduced that the viscosity of the rubber becomes relatively high at 130 $^{\circ}\text{C}$ : induced by the temperature and a lower degree of silanization. [10, 11] At 140 $^{\circ}\text{C}$ , the viscosity of the rubber polymer drops and results in a lower macro-dispersion like in the case of COM2, Figure 1(b). However, at a higher temperature, the efficiency of silanization enhances. Even though the polymer viscosity is reduced

with increasing mixing temperature, silica becomes more compatible with rubber polymer due to equilibration of their polarities. This does indeed enhance the macro-dispersion to some extent, together with the micro-dispersion. Macro-dispersion images for the compounds in Figure 1, obtained from the Dispergrader, are shown in Figure 2. As can be nicely seen in these figures, the macro-dispersion of silica changes with mixing temperature and presence of TESPT.

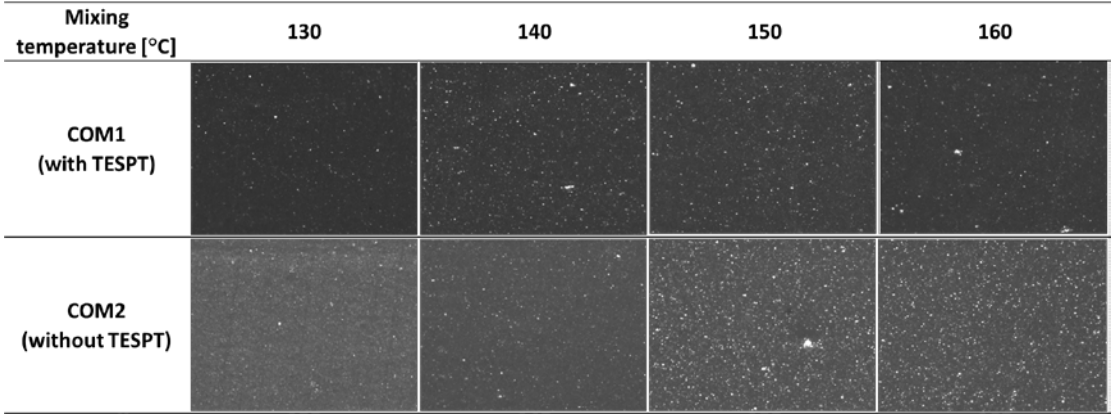


Fig. 2.— Macro-dispersion images for compounds of Figure 1.

3.2 Series 2: The effect of silanization time.

In this part of the study, the micro- and macro-dispersions of COM1 (with TESPT) with different silanization times are compared: Figures 3 and 4. The Payne effect is strongly reduced with increasing silanization time, while the level of macro-dispersion stays almost the same. This result indicates that the macro- and micro-dispersion processes of fillers during mixing happen simultaneously, but independently.

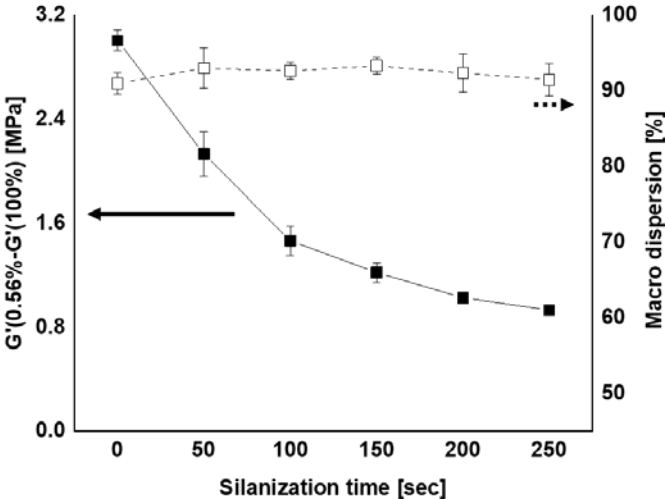


Fig. 3.— Micro-dispersion (Payne effect) and macro-dispersion of the compound in Series 2.

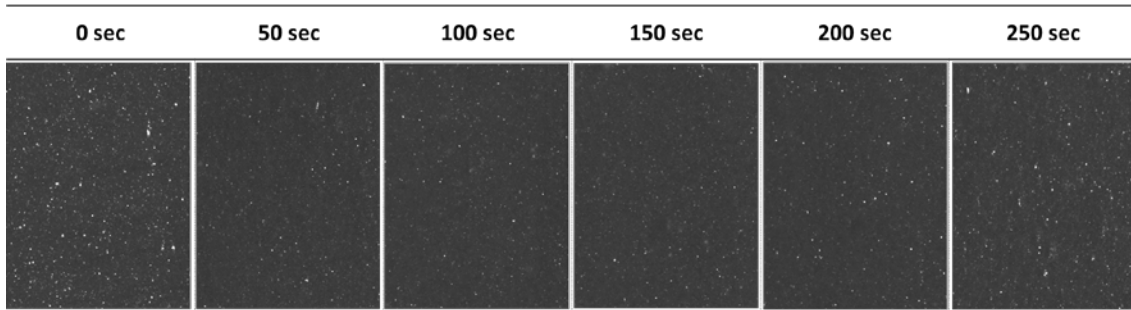


Fig. 4.— Macro-dispersion images corresponding to Figure 3.

### 3.3 Series 3: The effect of the amount of silane

COM1 (with 8 phr of TESPT), COM2 (without TESPT) and COM3 (with half (4 phr) of TESPT compared to COM1) are compared here to qualify the effect of the amount of coupling agent (TESPT) in more detail. 140°C was selected for the silanization according to Figure 1, where COM1 (with TESPT) showed the lowest macro-dispersion level of all series, while the macro-dispersion of COM2 (without TESPT) was close to the highest value. The results are shown in Figure 5. The compounds with half silane (COM3) or no silane at all (COM2) show a relatively higher macro-dispersion than the compound with the full amount of TESPT (COM1). Especially for COM3, a higher value of macro-dispersion was obtained even though less than 50 seconds of silanization time was applied, while the others had 150 sec of silanization time. However, the micro-dispersion is still greatly enhanced – Payne effect reduced – with increasing amount of TESPT.

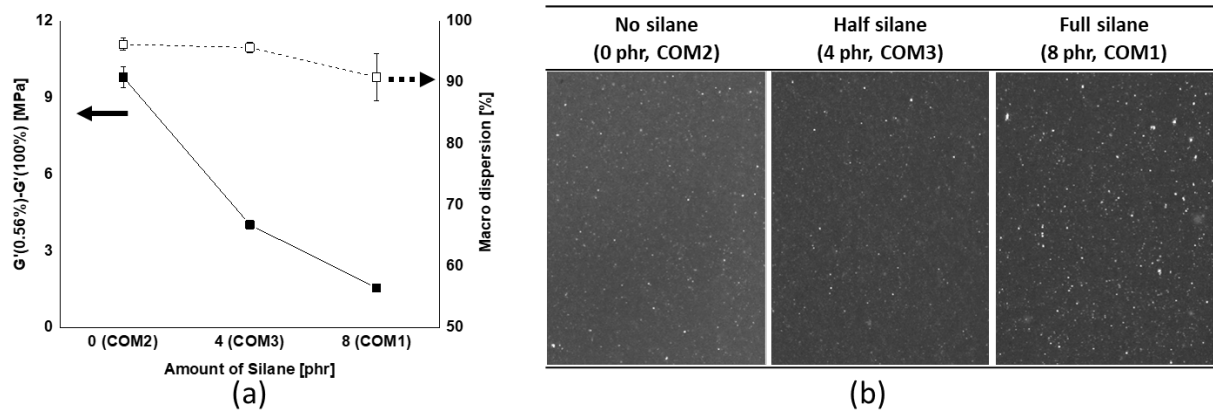


Fig. 5.— Micro-dispersion (Payne effect) and macro-dispersion of the compound in Series 3, (a); and their macro-dispersion images, (b).

### 3.4 Series 4: The effect of silica characteristics: specific surface area and structure.

In this series, the micro- and macro-dispersions of COM4 (HD silica) and COM5 (CV silica) mixed according to Mixing procedure A at 150°C are compared: Figure 6. Only a small difference in the storage moduli ( $G'$ ) at 100% strain — 0.15 and 0.16 MPa for COM4 and 5, respectively — are seen due to the reinforcement contribution of the hydrodynamic effect. Overall, the Payne effect is practically the same for both, COM4 and COM5.

However, a much better macro-dispersion is observed for COM4 (HD silica). These results again indicate that the micro-dispersion of silica is not related to the degree of macro-dispersion. Another important indication from this work is that the structure of the silica strongly influences the degree of macro-dispersion. The micro-/macro-dispersion results of COM4 can be explained as discussed in the previous paragraph (3.1 Series 1: The effect of silanization temperature and presence of silane). In case of HD-silica, when silane is present, both micro- and macro-dispersion improve at 150°C mixing temperature due to the silanization. However, this tendency is not observed for COM5: CV-Silica. This can be explained with the void volume or dense of packing of the CV-silica. Due to its denser packing, the breakage of silica agglomerates is less effective than for HD-silica; obviously because the latter was developed for that purpose. However, the surprising effect is that the micro-dispersion (Payne effect) was not influenced by this high-dispersion quality of the *silica*.

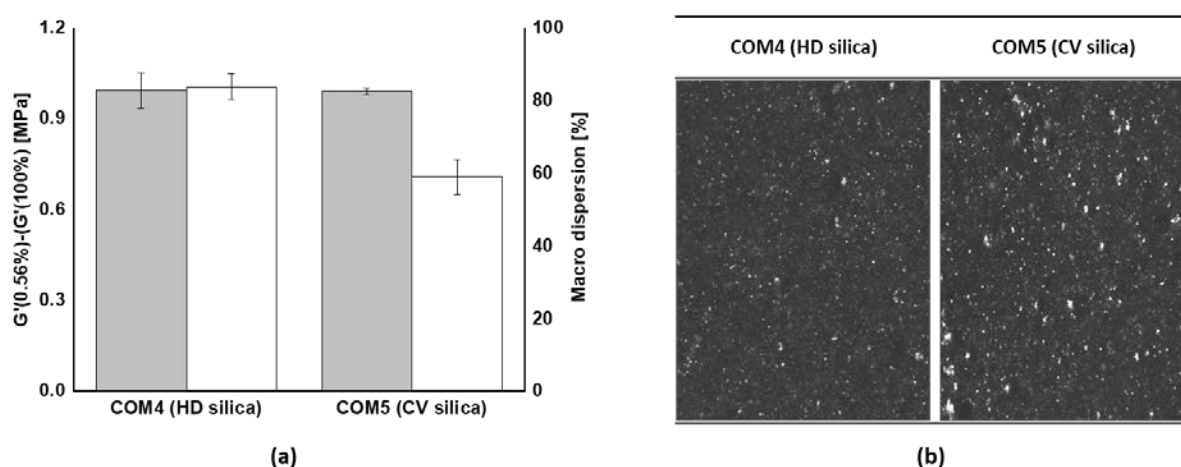


Fig. 6.— Micro-dispersion (Payne effect) and macro-dispersion of the compound in Series 4, (a); and their macro-dispersion images, (b); (■): Payne effect; (□): macro-dispersion.

#### 4. Conclusions

The focus of this study was to investigate the relationship between micro- and macro-dispersion of silica in rubber and its effect on reinforcement. No relation could be found between these two dispersions. The results of this study confirm that the micro- and macro-dispersion processes of silica happen simultaneously, but independently.

The second objective of this work was to investigate the major influencing factors on both silica dispersions. All the factors investigated in this work are summarized in Table V. On the one hand, the macro-dispersion of the silica filler is better at lower mixing temperatures, where the viscosity of the rubber polymer stays high. On the other hand, the micro-dispersion is better for a higher mixing temperature, because micro-dispersion is mainly influenced by the degree of silanization and the mobility of the polymer. However, even the level of macro-dispersion is enhanced when the degree of silanization reaches a higher level, in spite of the fact that the viscosity of the polymer is reduced. Overall, in case of silica-filled rubber compounds, the degree of silanization is crucial for both, macro- and micro-dispersion. From a material aspect, the structure of the silica has not much effect on the micro-dispersion of silica, but strongly influences the degree of macro-dispersion due to the degree of packing of silica aggregates.

Table V. Influencing factors on micro-/macro-dispersion of silica in a rubber matrix.

Dispersion categories	Main influencing factors
Macro-	- Structure of silica - Higher polymer viscosity - Degree of silanization (if silane is present)
Micro-	- Lower polymer viscosity - Presence of silane - Degree of silanization (if silane is present)

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