A New Rubber Silane for Future Requirements – Lower Rolling Resistance; Lower VOCs

Rubber silane • Free mercapto group • Low rolling resistance • VOC reduction

This contribution focuses on a new rubber silane for the tire industry – VP Si 363. It is shown that compared to traditional silanes a reduction of rolling resistance by more than 10 % is achievable while additionally the emission of volatile organic compounds (VOCs) is reduced by up to 80 %. Beside results of a tire test detailed in-rubber investigations are presented. Synergisms with different compounding ingredients are discussed and mechanistic explanations are given.

In the early 90s the request for enhanced tire performance resulted in the introduction of the silica-silane-filler system for passenger car tire treads [1]. Besides precipitated silica the sulfur-functional organosilane Si 69 was one of the key products for a new tire generation with significantly improved wet grip and rolling resistance [2, 3]. Nevertheless, today the automotive industry faces future requirements. Ecological and economical aspects gain more importance. The Kyoto Protocol and the Euro 5 norm indicate that in the future CO₂-emissions have to be reduced further. Additionally oil and gasoline prices reach higher and higher levels. As a consequence a further significant reduction of the fuel consumption of cars is necessary. One way to reach this goal is a reduced rolling resistance of tire tread compounds. Established silanes already available in the market can fulfill this requirement only to a limited extent. Furthermore, by the use of the well-known triethoxy silanes a certain emission of VOCs cannot be avoided. Therefore, VP Si 363, which can be seen as a successor of Si69, has been developed recently and is now introduced to the tire industry [4, 5]. With this new silane a further reduction of rolling resistance by more than 10 % is achievable and the emission of VOCs is reduced by more than 80 %.

Chemical structure and basic mechanism

The molecular structure of VP Si 363 is shown schematic in Figure 1. It is characterized by a free mercapto group on the rubber-active site and a combination of an ethoxy group and polymeric, amphiphilic substituents on the silica-active site. The silica-silane reaction proceeds via the ethoxy substituent on the silicon atom. It is cleaved during the mixing process and the silane bonds covalently to the silica-surface. The steric hindrance given by the bulky polymeric substituents is overcome by the polar part of these substituents. This ensures a high silica affinity which guarantees a fast adsorption and reaction on the silica-surface. Furthermore, free silanol groups on the silica-surface are also shielded by these non-volatile, long-chain substituents leading to an excellent hydrophobation of the silica. Additionally, the polar glycol part acts as an intrinsic activator function comparable to ethylene glycols.

The mercapto group is responsible for the efficient coupling of this silane to the polymer chains. As the use of sulfide silanes lead in general to a coupling yield silane-polymer of approx. 50 % [6, 7], a free mercapto group yields nearly 100 % due to a changed coupling mechanism. For this reason only half of the amount of silane (calculated on Si-units) is needed on a molar basis to reach a superior reinforcement.

The “scorchy” behavior often observed for silanes containing a mercapto group is prevented by the polymeric substituents on the Si-unit and a changed cure system, which will be described later. Due to the long-chain nature of the polymeric substituents a special shielding effect is provided as depicted in Figure 2. Beside the hydrophobation of the silica surface, the long-chain substituents generate a certain steric hindrance for the mercapto group. Its reaction with the accelerator and the sulfur is slowed down. A higher scorch

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safety together with an excellent reinforcement is obtained as shown in the following chapter.

**In-rubber behavior**

VP Si 363 is compared to Si 69 in a silica filled S-SBR/BR compound. As both silanes differ in molecular weight and coupling efficiency different dosages are applied. Furthermore as already mentioned the use of VP Si 363 requires a change in the cure system. The formulations and the results are shown in Table 1 and 2.

The reference compound is a typical Green Tire compound based on an S-SBR/BR blend filled with 80 phr HD performance silica Ultrasil 7000 GR together with 6.4 phr Si 69 (8 phr – parts per filler). The test compound is based on 9 phr (11 phr) VP Si 363. The cure system is adjusted. As known when comparing Si 69 to other silanes like e.g. the disulfide silane Si 266 a sulfur adjustment has to be done and the main accelerator CBS has to be kept on the same level. This measure guarantees the same overall crosslink-density. Regarding the relationship of the guanidine activator DPG to a “kicker” thiuram activator TBzTD an “inverse activator composition” (IAC) has to be established. In the VP Si 363 compound only small amounts of DPG are used in contrast to the reference. Instead a certain amount of TBzTD is introduced. In total, the overall amount of activators can be reduced due to the reduced filler network and a higher amount of TBzTD. The in-rubber properties are given in Table 2. Due to the adjusted activator composition and the intrinsic shielding effect, the VP Si 363 compound exhibits an even more pronounced incubation period as the reference compound, indicated by \( t_{90\%} \) and an increased vulcanization speed, expressed as \( t_{90\%} \times t_{20\%} \), respectively. The data in Table 2 reflect the above mentioned properties of VP Si 363 compounds: firstly, compared to the Si 69 reference compound, the silica network is decreased. This leads to a reduced Mooney-viscosity after the final mixing stage and a lower Shore-A-hardness. Secondly, the coupling efficiency of the silane towards the polymer is increased, resulting in an increased modulus at 300% strain and also an increased reinforcing index (modulus 300% / modulus 100%). The improvement in DIN-abrasion is a further consequence. The dynamic data show the influence of both effects: an outstanding increase in ball rebound and an enormous decrease of \( E' \) at 60°C of more then 40% are due to the reduced filler network and the high coupling efficiency. This is reached only by the application of the new silane and should lead to tires with a significant reduced hysteresis loss. Furthermore the complex moduli measured at 0°C and at 60°C display a lower temperature dependence over a wide range due to the reduced influence of the silica network in the Si 363 compound. A more detailed discussion of the dynamic behavior can also be found in [5].
The extreme low hysteresis loss is only one of the major advantages, which can be obtained with this new silane. Additionally a strong reduction in volatile organic compounds (VOC) is gained as shown in Figure 3. The VOCs emitted during the mixing process for compounds filled with 80 phr silica are measured. Three different compounds are investigated: a reference compound with no silane, a compound with 6.4 phr Si 69 and a compound with 10 phr VP Si 363. In average the Si-unit of VP Si 363 bears one ethoxy and two polymeric substituents where the latter ones are not volatile. Together with the reduced molar amount possible for this silane a VOC reduction of approx. 80% compared to the use of state-of-the-art-silanes is achieved.

This drastical reduction of VOCs helps to fulfill the requirements on the controlled VOC emission during the mixing process. Furthermore, also the emission out of the resulting rubber articles is reduced fulfilling requirements on environmental friendly products.

**Tire properties**

Reducing the emission of VOCs is one of the advantages of VP Si 363. Another key-advantage is the low hysteresis loss. To confirm the results of the lab studies a tire test was performed. Despite of the adjusted cure system for VP Si 363 compounds no further adjustment or optimization were done. 6.6 phr Si 69 were replaced by 9 phr VP Si 363 in a full silica compound. The mixing routine was not modified. Processing, e.g. compound viscosity, sheet appearance, extrusion process were comparable.

As shown in Figure 4 the rolling resistance is improved by 13 % in combination with balanced tire properties. Taking into account that the shift from carbon black to the silica-silane system as filler system counted for a reduction of rolling resistance by approximately 20 % the further improvement of 13 %, given by the use of VP Si 363, has to be seen as a further performance jump. Replacing Si 69 by VP Si 363 changes the properties of a resulting tire significantly.

**Summary**

VP Si 363, which can be seen as a successor of Si 69, has been developed recently and is now introduced to the tire industry. Replacing Si 69 with this new silane leads to a strongly improved rolling resistance as proven by a tire test. Despite of the adjusted cure system (IAC and sulfur adjustment) no further adjustment or optimization were done. Balanced tire properties were obtained and a performance jump for rolling resistance by an improvement of 13 % was gained. In addition VOC emissions were reduced by 80 %. A temperature stability of the dynamic modulus as well as the reduced amount of co-activators like DPG needed so far for silica compounds are further advantages.

Using VP Si 363 means to fulfill the requirements of the future – lower rolling resistance and lower VOCs.

**References**


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