The development of sulphur-functional silanes as coupling agents in silica-reinforced rubber compounds. Their historical development over several decades

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SUMMARY

Where silica is used as an active filler in rubber vulcanisates, a bifunctional silane has to be added to achieve the full reinforcement potential in almost all cases. Sulphur vulcanisation is the crosslinking method of choice in many fields of application, particularly because of the outstanding dynamic properties of the resulting parts. Since sulphur-functional silanes are able to participate directly in sulphur vulcanisation, this substance class has become the preferred coupling agent for the sulphur-based vulcanisation of silica-filled rubber compounds. This paper outlines in four stages the history of sulphur-silane development over the last few decades.

INTRODUCTION

Sulphur silanes and their use as coupling agents for bonding active silicas to polymers have been known in the rubber industry for decades. With the introduction of “green tyre technology”, greater demands have naturally been placed on these sulphur-functional silanes as the technology has developed. Looking back, the changing constraints associated with these developments and the progress achieved can be divided into four stages, as illustrated in Figure 1 [1]. The following sections will take a detailed look at the different generations of silanes.

THE FIRST GENERATION – TESPT

The first commercial sulphur silane, mercaptopropyl-trimethoxysilane (MTMO), was highly reactive and so its use was severely limited by the safety risks that this presented for processing. Its market penetration was also hindered by the unpleasant odour that sometimes occurred as a result of impurities. The success of sulphur silanes in the rubber industry only really took off in the early 1970s with the development of bis[triethoxysilylpropyl] tetrasulphide (TESPT) – known as Si 69 – by Evonik Industries AG (previously Degussa AG). The technical breakthrough came in 1992 when so-called green tyre technology came on to the market. The combination of the silica/silane system with a special rubber blend brought a significant improvement in car tyre properties in terms of fuel savings and wet grip compared with a conventional, carbon-black-filled tyre, with no change in wear characteristics.

Bifunctional silanes are generally made up of three structural units: (a) the silica-reactive unit, (b) the organic spacer and (c) the polymer-reactive unit. The properties of these three structural features will now be explained, using Si 69 as an example, to make it easier to understand the history of sulphur-based rubber silane development on the basis of this silane.

The silica-reactive unit (a) is generally a trialkoxysilyl group, of which the rate of reaction is controlled primarily by the alkoxy substituents. As a rule of thumb, the reactivity decreases as the length of the alcohol increases [2]. Although the sterically undemanding trimethoxysilane displays the highest reactivity, its use on a large scale should be avoided on toxicological grounds because of the methanol that is released during the silanisation reaction. Long-chain alcohols reduce reactivity with the silica surface and their evaporation from the rubber compound is delayed, so the less toxic ethanol represents...
the best choice. During silanisation, the alkoxy groups are not fully reacted and therefore alcohol groups remaining on the silane contribute to the hydrophobisation of the silica surface. The development of reduced-VOC or VOC-free silane compounds (VOC = volatile organic compounds) is based essentially on replacing ethanol with high-molecular-weight, non-volatile alcohols or on oligomerising the silanes without any significant reduction in silane reactivity.

The organic spacer (b) affects the hydrophobising action of the silane. Almost all rubber silanes have a propyl spacer for reasons relating to raw material availability and manufacturing processes [3]. The hydrosilylation of allyl chloride with trichlorosilane and subsequent esterification of the resulting 3-chloropropyltrichlorosilane gives 3-chloropropyltriethoxysilane (CIPTES) as a raw material for a silane portfolio with a wide variety of functional groups.

If further hydrophobisation is required without introducing any more rubber-active groups, it is possible to use processing auxiliaries or monofunctional alkyl silanes, such as propyltriethoxysilane (PTEO) or octyltriethoxysilane (OCTEO).

In the case of Si 69, the polymer-reactive unit (c) is a polysulphide group with an average sulphur chain length of 3.7. The disulphide and polysulphide portions are activated by adding free sulphur and form covalent bonds with the polymer during the vulcanisation process. The polysulphides are more reactive the longer the sulphur chains. Overall, TESPT acts increasingly as a sulphur acceptor rather than as a sulphur donor in the course of the vulcanisation process, although it performs both functions in parallel. The composition of the accelerator system – consisting of elemental sulphur and one or more accelerators – can be varied to manipulate the network structure as required and it therefore plays a fundamental part in activating the silane as well as in the properties of the finished product under dynamic load.

THE SECOND GENERATION – TESPD

Compared with carbon-black-based compounds, the production of highly filled silica-based compounds requires significant adaptations to the manufacturing process because of the chemical reaction that takes place inside the kneader when the silica/silane system is used. Accurate temperature control is essential for a successful silanisation reaction and for driving off the alcohol-water mixture that is liberated. TESPT has a significant content of polysulphides, which start to react with the polymer at high temperatures even when no vulcanisation system is present. A mixing temperature of less than 155°C should be maintained for TESPT in order to suppress undesirable scorching. The second generation of sulphur silanes met the industry's need for more thermally stable silanes with bis[triethoxysilylpropyl] disulphide (TESPD), which was introduced in the late 1990s and is available from Evonik with the trade names Si 266 and Si 75. This silane significantly extended the stable processing window into a higher temperature range.

Figure 2 shows a comparison of the temperature stability of compounds using TESPT and TESPD with various disulphidic silane contents. While there is a significant rise in torque due to the reaction of the polysulphides in TESPT at 180°C, this is very low for the TESPD species, where it is attributable to the remaining tri- and polysulphides. Pure disulphide silane (model silane) displays no torque increase, which demonstrates the high thermal stability of the disulphide bond in the absence of free sulphur and an accelerator.

The disulphide group has to be activated before it bonds to the rubber. This takes place during vulcanisation and can be illustrated by the cure curves for silica-filled compounds (Figure 3) [4]. The first increase in torque occurs through flocculation of the silica particles. In the case of TESPT, activation by the vulcanisation system takes place at the same time as crosslinking whereas the induction phase is longer with TESPD because activation has to take place beforehand. Once curing is complete, an
identical crosslink density is achieved for the two silanes provided that they were used in equimolar quantities and that the total quantity of sulphur was adjusted correctly. As a rule of thumb, 1.0 phr Si 69 is substituted by 0.9 phr Si 266 and 0.09 phr sulphur.

In this context, the relationship between activation and the resulting crosslink density requires closer examination. As mentioned above, both TESPD and TESPT act primarily as sulphur acceptors during vulcanisation and they require this additional sulphur in order to be activated for efficient vulcanisation. In contrast to carbon-black-filled compounds, two networks are created in parallel in silica-reinforced compounds: the polymer-polymer network (matrix crosslinking) and the silica-silane-polymer network. They cannot be separated from one another and they compete for sulphur and accelerator until these have been completely used up. Figure 4 illustrates the relationship between these two networks and their effects in terms of the overall crosslink density [2, 5]. The mutual dependency of the two networks means that it is impossible to achieve quantitative silane coupling efficiency with TESPD and TESPT. About 40 – 60% coupling efficiency is assumed, depending on the composition of the vulcanisation system.

THE THIRD GENERATION – PROTECTED MERCAPTOSILANE

Mercaptosilanes achieve very high coupling efficiency in sulphur vulcanisation, but their reactivity is too high to be controlled adequately for most applications in the rubber industry. One way of regulating mercaptosilane reactivity is to introduce a protecting group. In choosing a protecting group, a compromise is needed between achieving good processing characteristics and maintaining the mercaptosilane’s high coupling efficiency. The Momentive range includes a product with the trade name NXT, which is an octanoyl thio ester-protected mercaptosilane with improved processing characteristics and reduced reactivity compared with free 3-mercaptopropyl triethoxysilane (MPTES). Figure 5 shows selected properties of the protected mercaptosilane in a model compound in comparison with TESPD. Both the low viscosity and the improved hysteresis properties can be explained by reduced filler-filler interactions. The reinforcing effect is comparable with that of the TESPD reference compound.

A few years ago, Momentive launched the NXT Z family of products on to the market. In this product group, NXT and MPTES are combined as an oligomer to optimise the compromise between processing (NXT) and performance (MPTES). The oligomerisation also reduces ethanol emissions during compound production.
THE FOURTH GENERATION – SHIELDED MERCAPSILANE

As described above, free mercaptosilane is the substance class of choice when a further increase in coupling efficiency is required. In the fourth generation of silanes, the free mercaptosilane's reactivity is modulated by long-chain polyalkyl ether alcohols on the silane's silicon atom – a measure that has three positive effects:

- shielding of the reactive mercapto group, delaying its activation by N-cyclohexyl-2-benzothiazolesulphenamide (CBS) and sulphur
- efficient hydrophobisation of the silica surface and thus a reduction of the filler-filler network
- a huge reduction in silane-related VOC emissions of over 80% through substitution of two-thirds of the ethanol groups with high-molecular-weight alcohol (Figure 6).

The shielded mercaptosilane described above is available from Evonik with the trade name Si 363.

The assumed mechanism is that the accelerator CBS reacts rapidly and almost quantitatively with the silane’s mercapto group to form the activated silane-accelerator complex. This results in the release of highly reactive mercaptobenzothiazole (MBT), which again has an accelerating effect on the reaction. Since 1,3-diphenylguanidine (DPG), which is conventionally used in silica-filled compounds, shortens the scorch time, it is recommended that this be omitted in compounds with Si 363 and that 0.3 – 0.5 phr tetrabenzylthiuram disulphide (TBzTD) be used to increase the crosslink density to the desired level.

Zinc oxide and stearic acid are an integral part of rubber formulations. The point at which they are added can have a particularly marked effect on the processing and performance of Si 363 compounds. As well as stearic acid’s role in the accelerator system, it can also be regarded as a processing aid. If the system can tolerate relatively large quantities of stearic acid, these can have a positive effect on viscosity in the first mixing step and during induction. For Si 363, the point at which zinc oxide is added has a huge influence on the compound’s viscosity throughout all the mixing steps. It is recommended that zinc oxide and stearic acid should always be added as early as possible when Si 363 is used.

The rate of hydrophobisation of Si 363 – as for all silanes – is heavily dependent on the batch temperature during the mixing process. The optimum temperature window for Si 363 is between 155 and 170°C. It should be emphasised here that the upper temperature limit for compound production is determined by the polymer’s temperature resistance rather than by the silane. Like TESPD compounds, a non-accelerated Si 363 compound displays no rise in torque – and therefore no scorch – at high temperatures as observed e.g. for TESPT (Figure 7) [6]. It is essential to select sufficiently high (Translator’s note: context suggests that the word “temperature” may have been omitted from the original German at this point) and long silanisation times not just for Si 363 but for all compounds containing a silica/silane system. If the silanisation time is too short or the temperature too low, this has a highly detrimental effect on scorch behaviour.

Figure 8 shows the performance spectrum of Si 363 in a model compound. Compared with TESPD, the
The reinforcing effect is unchanged but the excellent hysteresis properties make it stand out. If, despite observing all the above influencing variables, the processing of Si 363 compounds is hampered by high viscosities, short scorch times or a lack of green strength, the use of processing aids is recommended [7]. Adding 2.0 – 2.5 phr of the processing aid has only a minor effect on performance but significantly improves the processing of the compounds. Evonik recommends the processing aids Struktol HT 276 from Schill + Seilacher and/or Sylvatraxx 1001 from Arizona Chemical. Another option for improving highly filled Si 363 compounds is to replace some of the Si 363 with TESPD. It is important to point out here that only the use of TESPD is recommended. Polysulphides and mercaptans can lead to H₂S formation at high temperatures when mixed in liquid form. However, it has not yet been possible to detect H₂S on a laboratory scale (1.5 litre kneader).

Increasing demands for better performance in the tyre industry with ever lower roll resistance values can be met successfully by using Si 363.

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REFERENCES


