

Perfect couple

Optimizing the use of Si69 coupling agent in tire formulations

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When precipitated amorphous white silica is used in tire compound reinforcement, it requires a bifunctional organosilane to disperse it well in the rubber matrix and chemically bond it to the rubber. Bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT), known also as Si69 coupling agent (Figure 1), is used extensively with precipitated silica in sulfur-cured tire compounds. Chemical bonding between rubber and silica via the sulfur in TESPT plays a major role in rubber reinforcement because it provides strong stable covalent sulfur bonds between the two. However, there is sufficient scientific evidence to suggest that TESPT may not be reacting with rubber during high-temperature curing when elemental sulfur is present, so its potential as a coupling agent is not fully exploited.

The raw rubber used was high-cis polybutadiene (96 wt % 1,4-cis content; Buna CB 24, Bayer, Newbury, UK; not oil extended). The reinforcing filler was Coupsil 8113, which is a precipitated amorphous white silica

Figure 1: Chemical structure of Si69 coupling agent (TESPT)

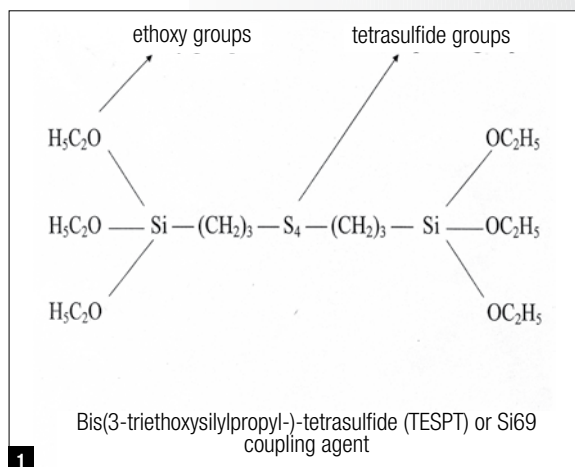
Figure 2: Typical torque vs time cure trace by ODR at 160°C showing minimum and maximum torques and Δtorque. Data for the rubber with 1.75phr CBS

(Evonik Ultrasil VN3), the surface of which was pretreated with TESPT. It has 11.3% by weight TESPT, 2.5% by weight sulfur (included in TESPT), a 175m²/g surface area (measured by N₂ adsorption), and a 20-54nm particle size. Evonik Industries of Germany supplied the Coupsil. The other ingredients were: N-cyclohexyl-2-benzothiazole sulphenamide (a fast-curing delayed action accelerator with a melting point of 105°C); Santocure CBS (Flexsys, Dallas, Texas); zinc oxide (ZnO, an activator, Harcros Durham Chemicals, Durham, UK); and elemental sulfur (curing agent: Solvay Barium Strontium, Hanover, Germany).

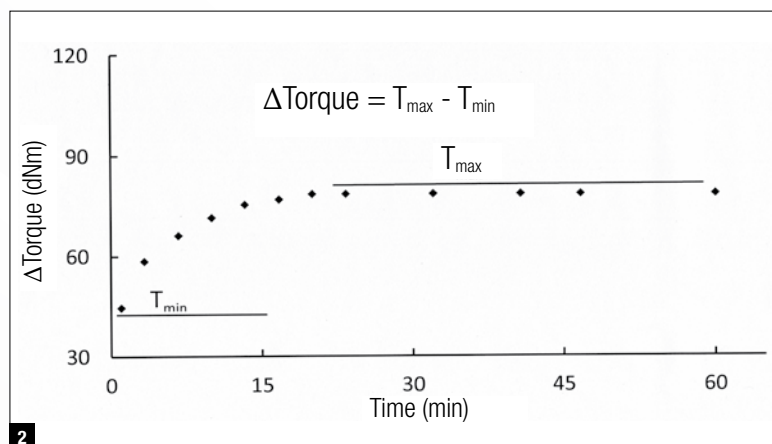
The compounds were prepared in a Haake Rheocord 90 (Berlin, Germany), a small laboratory mixer with counter-rotating rotors. The Banbury rotors and the mixing chamber were initially set at ambient temperature (25°C) and the rotor speed was set at 45rpm. The volume of the mixing chamber was 78cm³ and it was 74% full during mixing. Polylab monitor 4.17 software was used for controlling the mixing condition and storing data. All the rubber compounds had 50 parts per hundred rubber (phr) by weight pretreated silanized silica.

To prepare them, the raw rubber was introduced first in the mixer and then the silanized silica was added and mixed for 10 minutes. CBS, ZnO and elemental sulfur were subsequently mixed for another six minutes before the compound was removed from the mixer. The temperature of the compounds during mixing was 45-53°C.

The cure properties of the rubber compounds were measured



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at 160°C ($\pm 2^\circ$ C) in an oscillating disc rheometer curemeter (ODR, Monsanto, Swindon, UK) at an angular displacement of $\pm 3^\circ$ and a test frequency of 1.7Hz, according to the British Standard ISO 3417. From the cure traces, scorch time (t_{s2}), which is the time for the onset of cure, and the optimum cure time (t_{95}), which is the time for the completion of cure, were determined. The cure rate index, which is a measure of the rate of cure in the rubber, was calculated using the method described in British Standard ISO 3417, 2008. Results from these experiments are summarized in Table 1. Δ torque was subsequently plotted against the loading of CBS, zinc oxide, and elemental sulfur. Δ torque is the difference between the maximum and minimum torque values on the cure trace of the rubber, and is an indication of crosslink density changes in the rubber (Figure 2).

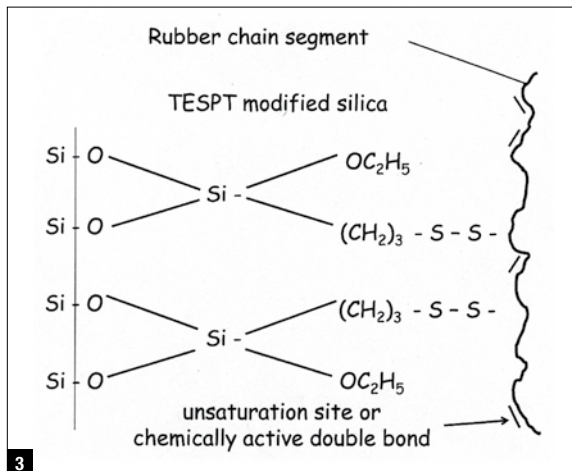
To activate the rubber reactive

tetrasulfide groups of TESPT (Figure 3), CBS was added. The loading of CBS in the rubber was increased to 1.75phr to fully react the sulfur in TESPT with the rubber to produce strong chemical bonds or crosslinks between the two.

Two compounds were made. The formation of crosslinks strengthened the rubber/silica interaction. Zinc oxide was used as an activator to improve the effectiveness of CBS during curing of the rubber. The loading of ZnO in the rubber with CBS was raised to 1.5phr to determine the amount required to further increase the efficiency of CBS and chemical bonding between the sulfur in TESPT and the rubber. In total, seven compounds were made. No stearic acid was included in the cure system because previous studies showed that the addition of up to 2.5phr stearic acid as a secondary activator to BR rubber filled with a high loading of silanized silica containing

Table 1: Formulations and cure properties of the rubber compounds

| Formulation (phr) | Compound 1 | Compound 2 |
|---------------------------------------|------------|------------|
| BR | 100 | 100 |
| Silanized silica | 50 | 50 |
| CBS | 1.75 | 1.75 |
| ZnO | 0 | 0 |
| Elemental sulfur | 0 | 2 |
| Scorch time, t_{s2} (min) | 2 | 2 |
| Optimum cure time, t_{95} (min) | 18 | 8 |
| Cure rate index (min^{-1}) | 6.3 | 16.7 |



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sulphenamide accelerator and ZnO had no effect on the Δ torque.

To evaluate the effect of elemental sulfur on the cure properties of the rubber with CBS and ZnO, seven compounds were prepared. The loading of elemental sulfur was raised gradually to 3phr to determine the amount necessary to fully crosslink the rubber phase. This was in addition to the crosslinks that formed between the sulfur in TESPT and the rubber.

To react the sulfur in TESPT with the rubber, 1phr of CBS was added. The cure trace of the rubber showed a marching cure over a 60-minute test time (Figure 4), which indicated incomplete reaction between the sulfur in TESPT and the rubber. Although the cure might have reached equilibrium with a much longer test time, this would have been of no practical benefit to the present work. The loading of CBS in the rubber was then raised

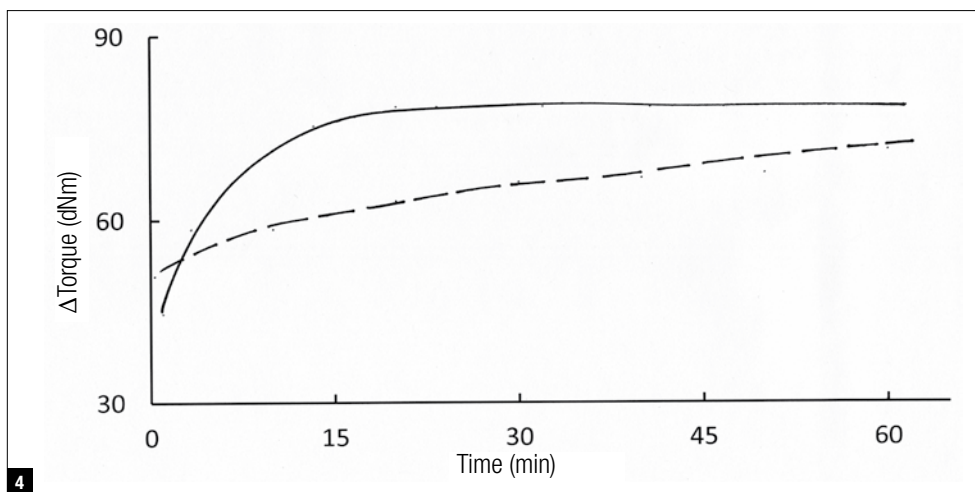
Figure 3: Silica pre-treated with Si69 coupling agent

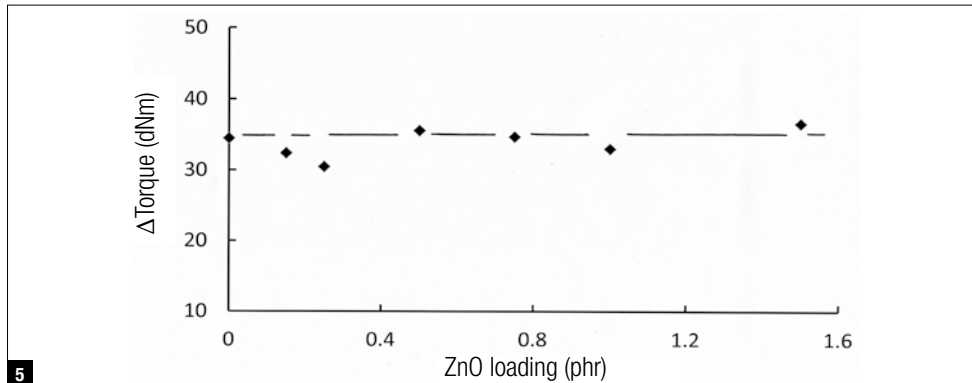
Figure 4: Typical torque vs time cure traces by ODR at 160°C for the rubbers with 1phr CBS (---) and 1.75phr CBS (—)

to 1.75phr until an equilibrium cure was produced (Figure 4). This indicated a complete reaction between TESPT and the rubber.

To increase the efficiency of CBS, ZnO was added. Figure 5 shows Δ torque versus ZnO loading for the rubber with 1.75phr CBS. Δ torque remained constant at about 34dNm, when the loading of ZnO was raised from 0phr to 1.5phr. The addition of ZnO had no added benefit for the Δ torque and the chemical bonding between the sulfur in TESPT and the rubber. Hence, only 1.75phr CBS was needed to fully react the sulfur in TESPT with the rubber (compound 1).

To cure the rubber phase in addition to the crosslinks formed between the sulfur in TESPT and the rubber, elemental sulfur was added to the rubber containing 1.75phr CBS. The loading of elemental sulfur was raised to 3phr to determine the amount necessary to fully cure the rubber. The Δ torque rose from 35-89dNm when 2phr elemental sulfur was incorporated in the rubber (Figure 6). Afterwards, there was no obvious increase in the value of Δ torque. When CBS was added, it dispersed throughout the rubber. Some of the CBS reacted with the sulfur in TESPT to produce chemical bonds between the rubber and the silica and the remaining CBS reacted with elemental sulfur to form crosslinks in the rubber phase. This in turn increased the Δ torque of the rubber, as shown in Figures 4 and 6. However, above 2phr elemental sulfur,





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the Δ torque remained fundamentally unchanged because there was no more CBS left in the rubber to react with elemental sulfur to produce more crosslinks. Evidently, to fully cure the rubber, 2phr elemental sulfur was sufficient and hence the cure system was 1.75phr CBS and 2phr elemental sulfur (compound 2).

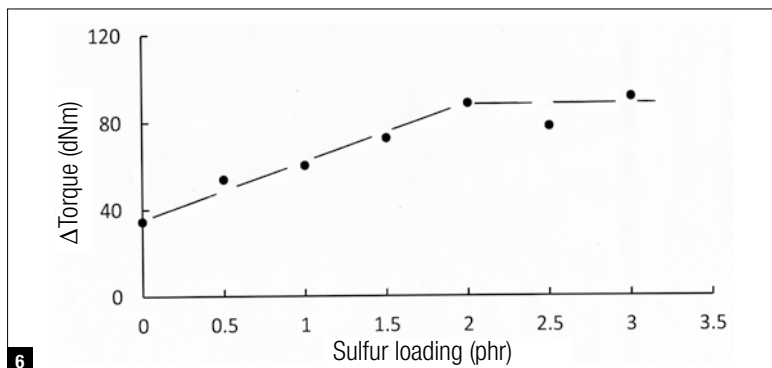
A number of interesting features emerged from this study. The addition of ZnO as a primary activator had no effect on CBS, given that the crosslink density between TESPT and the rubber as indicated by the Δ torque values was unaffected and remained essentially unchanged as a function of ZnO. This is remarkable because sulfur cure systems in tire compounds often contain primary and secondary accelerators, primary and secondary activators (ZnO and stearic acid), as well as elemental sulfur, sometimes adding up to 10-12phr. The sulfur in TESPT and elemental sulfur reacted quite differently with the rubber as shown in Table 1. The scorch and optimum cure times of the rubber with CBS were two minutes and 18 minutes, respectively (compound 1), whereas those for the rubber with elemental

sulfur were two minutes and eight minutes, respectively (compound 2). There was not sufficient time for the sulfur in TESPT to react fully with the rubber in compound 2. In addition, elemental sulfur reacted at a much faster rate with the rubber than the sulfur in TESPT did. This was well documented with the cure rate index, which was 16.7 min^{-1} for the former and 6.3 min^{-1} for the latter (Table 1).

In some road car tire compounds, sulfur cure systems are used in conjunction with silica and liquid TESPT. There is an indication that during high-temperature curing of tires when elemental sulfur is present, correct thermochemical conditions may not be present for the sulfur in TESPT to fully react with rubber to form stable covalent sulfur bonds, which is expected from a coupling agent such as TESPT. Therefore, contrary to what is believed, TESPT may in fact behave as a single functional rather than a bifunctional silane in tire compounds. If that is the case, then non-sulfur bearing silanes may well be more suitable for use in tires than TESPT. **tire**

Figure 5: Δ Torque vs ZnO loading for the rubber with 1.75phr CBS. Each point on the figure corresponds to one compound

Figure 6: Δ Torque vs elemental sulfur loading for the rubber with 1.75phr CBS. Each point on the figure corresponds to one compound



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