

# **Developing Ethylene-Propylene-Diene Rubber Compounds for Industrial Applications using a Sulfur-bearing Silanized Silica Nanofiller**

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# **Developing Ethylene-Propylene-Diene Rubber Compounds for Industrial Applications using a Sulfur-bearing Silanized Silica Nanofiller**

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## **ABSTRACT**

The loading of a sulfur-bearing silanized silica nanofiller in ethylene-propylene-diene rubber with 4.5 wt % of ethylidene norbornene diene content was increased progressively to 60 parts per hundred rubber by weight. The rubber compounds were cured via the tetrasulfane groups of the silane by adding sulfenamide accelerator and zinc oxide. The hardness, tensile strength, elongation at break, stored energy density at break, tear strength, Young's modulus, M50-M300, compression set, cyclic fatigue life and bound rubber content of the rubber vulcanizates were measured. With the exception of the elongation at break and compression set which deteriorated, the remaining properties improved and the rate of cure, optimum cure time and crosslink density benefitted also when the loading of silica was increased in the rubber. The bound rubber content was unchanged and the cyclic fatigue life of the rubber vulcanizate enhanced considerably when silica was added. Optimizing the chemical bonding

between the rubber and filler via the tetrasulfane groups of TESPT reduced the chemical curatives in the rubber. This was a major improvement in health, safety and environment.

**Key words:** Rubber, silanized silica, chemical bonding, reinforcement, mechanical properties

## INTRODUCTION

Sulfur curing produces rubber vulcanizates with exceedingly good mechanical and dynamic properties, which makes rubbers like EPDM suitable for industrial uses. Raw EPDM has poor strength because it does not strain crystallise like natural rubber (NR) does and thus must be reinforced with fillers. Reinforcement describes the physical effects produced in a rubber vulcanizate by the inclusion of a second solid phase [1].

Traditionally, carbon blacks (CB) with surface area ranging from 6 to 250 m<sup>2</sup>/g have been used to reinforce the dynamic and mechanical properties of EPDM [2,3]. However, there is a low level of polycyclic aromatic hydrocarbons (PAH) within the structure of CB. Many of these PAHs are tightly bound into the structure of the CB aggregate and are not free to migrate, but a small amount will be on the surface. PAHs are known to be highly carcinogenic (cause cancer), mutagenic (cause mutation) and teratogenic (cause birth defects) and therefore there is a considerable health risk associated with their use in rubber compounds [4]. There are a number of fillers which can replace CB in EPDM because of

their ability to improve the rubber properties. The most widely researched alternative fillers to CB are organoclays [5], synthetic silicas [6,7], white rice husk ash [8], kaolin [9], and quartz [9, 10]. However, silicas with surface areas ranging from 125 to 200 m<sup>2</sup>/g have shown to be very effective in improving the mechanical properties of rubber vulcanizates and have gained considerable importance in recent years [11]. For example, precipitated amorphous white silica is used largely in shoe soles, mechanical rubber goods, and low rolling resistance tires with excellent wet grip and good abrasion resistance [11, 12]. Normally, silica particles have a larger surface area than carbon black particles and therefore are more reinforcing [13].

Precipitated silica has silanol or hydroxyl groups on its surface which makes it acidic and moisture absorbing [14, 15]. Acidity and moisture are both detrimental to the cure of rubber compounds [16], and can also cause loss of crosslink density in sulfur-cured rubbers [13]. Bifunctional organosilanes such as bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT) remedy the problems aforementioned and are used to enhance the reinforcing capability of fillers with silanol groups on their surfaces, such as precipitated silicas, and also forms an integral part of curing systems to improve the crosslinking network properties. These silanes are used as primers for treating silica surfaces to make the filler more suitable for use in

rubber [13]. The silanization reaction of silica takes place when silica and silane are mixed together in the required ratio and homogenized in an additional, preliminary mixing stage.

The modification is carried out at the optimum temperature and reaction time [17]. TESPT combines silica and sulfur into one single product known as a “crosslinking filler”[18]. One such filler is silanized silica where the surface of precipitated silica is pre-treated with sulfur-bearing TESPT to chemically bond silica to rubber and prevent the filler from interfering with the reaction mechanism of sulfur-cure in rubber.

Crosslinking of EPDM rubber by silica filler has been the subject of some studies. Das and co-workers [7] investigated the effect of an increasing loading of liquid TESPT on the cure and mechanical properties of an EPDM vulcanizate containing up to 40 phr precipitated silica. Liquid TESPT was taken 5 % by weight with respect to silica and was added during the addition of silica to the rubber. The silanization was carried out *in situ*. The loading of TESPT was raised gradually to 2 phr. At a constant loading of the filler, the scorch and optimum cure times increased when TESPT was added. Furthermore, the M100 and M300 and tensile strength rose significantly, the hardness showed a marginal improvement, and elongation at break decreased when TESPT was incorporated in the filled rubber. The crosslink density rose noticeably when TESPT was mixed with the rubber. The bound rubber

content also increased as a function of the silica loading though the increase was more significant when TESPT was present in the rubber. A similar study by Kim [6] reported significant increases in the crosslink density of an EPDM rubber when a bifunctional silane was added. The silane-added compound showed a higher elongational modulus than the control one. It was concluded that the silane acted as a coupling agent, promoting crosslinking between the silica surface and double bonds in the rubber and this resulted in a strong three dimensional net-work structure in EPDM.

When effects of pre-treated silanized silica, and silica and liquid silane mixture on the vulcanization of a sulfur-cured polyisoprene rubber were measured, it was shown that the rubber mixed with the pre-treated silanized silica had a higher crosslink density and increased filler-rubber interaction both of which were beneficial to the mechanical properties of the cured rubber. When the silica was reacted with liquid TESPT *in situ*, it generated harmful ethanol during mixing [19,20].

The aim of this study was to measure effect of up to 60 parts per hundred rubber by weight (phr) of a TESPT pre-treated silanized precipitated amorphous white silica nanofiller on the viscosity, cure properties, hardness, tensile strength, elongation at break, stored energy density at break, tear energy, compression set, Young's modulus, M50-M300 and cyclic

fatigue life of an ethylene-propylene diene rubber. Since the formation of stable covalent sulfur bonds between silica and rubber produces strong rubber-filler interaction [16], the chemical bonding or crosslinks between the two was optimized by adding a sulfenamide accelerator and zinc oxide as an activator. Dispersion of the silica particles in the rubber matrix was also investigated by scanning electron microscopy and the bound rubber content was measured by swelling the rubber vulcanizates in an organic solvent in order to evaluate the filler-rubber interaction.

## **EXPERIMENTAL**

### *Materials and mixing*

The raw rubber used was ethylene-propylene-diene rubber (EPDM; 64 wt% ethylene and 4.5 wt% ethylenenorbornene (ENB), Vistalon 3666, ExxonMobil Chemical Europe, Belgium). Vistalon 3666 is extended with 75 parts per hundred rubber by weight (phr) of a paraffinic oil. The reinforcing filler was Coupsil 8113 (Evonik Industries AG, Germany). Coupsil 8113 is precipitated amorphous white silica (type Ultrasil VN3) the surface of which was pre-treated with TESPT before use in the rubber. It has 11.3% by weight TESPT, 2.5% by weight sulfur (included in TESPT), 175 m<sup>2</sup>/g surface area (measured by N<sub>2</sub> adsorption) and a 20-54 nm particle size. The loading of the silanized silica filler in the rubber was 30, 45

and 60 phr.

In addition to the raw rubber and fillers, the other ingredients were *N*-tert-butyl-2-benzothiazole sulfenamide (a safe-processing delayed action non-sulfur donor accelerator with a melting point of 109°C) (Santocure TBBS, Flexsys, Dallas, TX), and zinc oxide (ZnO; an activator, Harcros Durham Chemicals, Durham, UK). The cure system consisted of TBBS and ZnO which were added to fully crosslink the rubber. The melting points of ZnO and silica filler are greater than 1000°C.

The rubber compounds were mixed in a Haake Rheocord 90 (Berlin, Germany), a small size laboratory mixer with counter rotating rotors. The Banbury rotors and the mixing chamber were initially set at 23°C for mixing the rubber compounds. The rotor speed was set at 45 r.p.m. The volume of the mixing chamber was 78 cm<sup>3</sup>, and it was 46% full during mixing. Polylab monitor 4.17 software was used for controlling the mixing condition and storing data.

For preparing the rubber compounds, a total mixing time of 14 min was used, which was long enough to fully disperse the silica particles in the rubber. The fillers and rubber were mixed for 10 min, and then TBBS and ZnO were added and mixed for another 4 min. The temperature of the rubber compounds during mixing reached 48°C. Finally, when mixing



ended, the rubber was removed from the mixer and passed once through a gap between the rolls of a two-roll mill to produce sheets about 6-8 mm thick. The compounds were next stored at  $21\pm 2^\circ\text{C}$  for at least 24 h before their viscosity and cure properties were measured.

#### *Determination of the optimum amounts of TBBS and ZnO to crosslink the silica-filled rubbers*

To activate the rubber reactive tetrasulfane groups of TESPT, TBBS was added. The loading of TBBS in the rubbers with 30, 45 and 60 phr silanized silica was increased progressively to 9 phr to measure the amount needed to start the chemical bonding between the rubber and TESPT and to maximize the crosslink density in the rubber. In total, thirty three rubber compounds were made.

The loading of ZnO in the silica-filled rubbers with TBBS was raised to 3.0 phr to improve the efficiency of TBBS and optimize the chemical bonding between the filler and rubber. In total, twenty five rubber compounds were mixed.

#### *Measurement of the viscosity and cure properties of the rubber compounds*

The viscosity of the raw rubber and rubber compounds was measured according to British Standard 1673: Part 3; London, UK, 1969, and the results were expressed in Mooney Units (MU). The scorch time, which is the time for the onset of cure, and the optimum cure time, which is the time for the completion of cure, were determined from the cure traces

generated at  $160 \pm 2$  °C by an oscillating disc rheometer curemeter (ODR). This test was carried out according to British Standard 1673: Part 10; London, UK, 1977. 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 903: Part A60: Section 60.1; London, UK, 1996.  $\Delta$ Torque, which 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, was then plotted against the loading of TBBS and ZnO.

#### *Test pieces and test procedures*

After the viscosity and cure properties were measured (Table 1), the rubber compounds were cured in a compression mould at 160°C with a pressure of 11 MPa. Pieces of rubber, each ~50 g in weight, were cut from the milled sheets. Each piece was placed in the centre of the mould to enable it to flow in all the directions when pressure was applied to prevent anisotropy from forming in the cured rubber. For determining the mechanical properties of the rubbers, sheets 23 cm by 23 cm and approximately 2.6 mm thick were used, from which various samples for further tests were cut. For measuring the hardness and compression set of the rubbers, cylindrical samples 15 mm in diameter and 9 mm in height were cured. The rubber sheets and samples were kept in storage at  $21 \pm 2$ °C for one week before they were

tested.

*Assessment of the silica dispersion in the rubber vulcanizates*

In order to study dispersion of the silica particles in the rubber, a Cambridge Instrument Stereoscan 360 Tungsten filament scanning electron microscope (SEM) was used. Small pieces of the cured rubbers were placed in liquid nitrogen for 3 min. They were recovered and fractured into two pieces to create fresh surfaces. The samples, 7 mm<sup>2</sup> in area and 4 mm thick, were coated with gold, and then examined and photographed in the SEM. The degree of dispersion of silica in the rubber was subsequently studied from the SEM micrographs.

*Bound rubber measurement of the rubber vulcanizates*

The bound rubber is the rubber portion that cannot be separated from the filler when the rubber compound is extracted with a solvent (often toluene) in which the rubber is readily soluble. This is called coherent gel and include solvent, the solid filler, and (bound) higher molecular weight chains. The measurement of bound rubber is a practical means of evaluating the degree of rubber-filler adhesion or interaction. The formation of bound rubber increases with factors such as the surface activity of the filler [13].

The solvent used for the bound rubber determination was toluene. For the determination, 1.8 g of the rubber compounds were cured in a compression mold to produce cylindrical

samples, 15 mm in diameter and 9 mm in height. The samples were then placed individually in 20 ml of the solvent in labelled bottles and allowed to swell for up to 72 h at 21°C. The weight of the samples was measured every day until it reached equilibrium. It took up to 50 h for the rubber samples to reach equilibrium. The solvent was removed after this time elapsed, and the samples were dried in air for 9 h. The samples were subsequently dried in an oven at 85°C for 24 h and allowed to stand for an extra 24 h at 23°C before they were re-weighed.

The bound rubber was then calculated using the following expression [21,22]

$$R_B = \frac{W_{fg} - W\left[\frac{m_f}{(m_f + m_p)}\right]}{W\left[\frac{m_p}{(m_f + m_p)}\right]} \times 100 \quad (1)$$

where  $W_{fg}$  is the weight of silica and gel,  $m_f$  is the weight of the filler in the compound,  $m_p$  is the weight of the polymer in the compound, and  $W$  is the weight of the specimen.

*Determination of the hardness, modulus, tensile properties, tear strength, compression set and cyclic fatigue life of the rubber vulcanizates*

The mechanical properties and cyclic fatigue life of the rubber vulcanizates were measured according to the procedures described in the British Standards.

*Hardness:* Br Standard 903: London, UK 1995; Part A26, using a Shore A Durometer hardness tester (The Shore Instrument and MFG, Co., New York).

*Tear energy:* Br Standard 903: London, UK 1995; Part A3, using trouser test pieces in a LR50K Plus materials testing machine (Lloyd Instruments, UK).

*Tensile stress-strain properties:* Br Standard 903: London, UK 1995; Part A2, using Lloyd Nexygen 4.5.1 computer software to store and process the data.

*Compression set:* Br Standard 903: London, UK 1986; Part A51.

The cyclic fatigue life of the rubber vulcanizates  $N$  (number of cycles to failure) was measured in uniaxial tension in a Hampden dynamic testing machine (Northampton, UK) with standard dumbbell test pieces. The tests were performed at constant maximum deflections of 120% and test frequency of 3.72 Hz. The strain on each test piece was relaxed to zero at the end of each cycle. For each compound four test pieces were used. When the number of cycles exceeded 10,000 kilocycles (kc) and the samples did not fracture, the test was stopped. The test temperature was  $20 \pm 2^\circ\text{C}$ .

## **RESULTS AND DISCUSSION**

### *Effect of TBBS and ZnO on the $\Delta$ torque of the silanized silica-filled rubber compounds*

Figure 1 shows  $\Delta$ torque as a function of TBBS loading for the rubber with 30 phr silanized silica.  $\Delta$ Torque increased from 5 to 17 dN m as the loading of TBBS was raised to 2 phr, and it continued rising to about 19 dN m when the amount of TBBS reached 5.5 phr.

Similarly for the rubbers with 45 and 60 phr silanized silica,  $\Delta$ torque rose to 20 and 24 dNm when 4 and 5 phr TBBS, respectively were added and thereafter, the increases were at a much slower rate when the loading of TBBS reached 9 phr. Evidently, the addition of 2, 4 and 5 phr TBBS to the silica-filled rubbers was sufficient to react the rubber reactive tetrasulfane groups of TESPT with the rubber to form crosslinks or chemical bonds between the two.

To improve the efficiency of TBBS in the silica-filled rubbers, ZnO was added. For the rubber with 30 phr silanized silica and 2 phr TBBS,  $\Delta$ torque increased sharply to 30 dN m when 0.75 phr ZnO was included, and it continued rising at a much slower rate to around 32 dN m when the loading of ZnO reached 3 phr (Fig. 2). Likewise, for the rubbers with 45 silanized silica and 4 phr TBBS, and 60 phr silanized silica and 5 phr TBBS,  $\Delta$ torque increased to 34 and 42 dNm, respectively when 0.75 and 1 phr ZnO were added. It seemed that the addition of 0.75 phr ZnO to the rubbers with 30 and 45 phr silanized silica, and 1 phr ZnO to the rubber with 60 phr silanized silica, respectively was sufficient to improve the efficiency of TBBS and optimize the chemical bonding between TESPT and the rubber in these compounds.

After these measurements were completed, four rubber compounds were prepared for further tests. Compound 1 was made through the addition of 30 phr silanized silica, 2 phr

TBBS, and 0.75 phr ZnO, compound 2 by adding 45 phr silanized, 4 phr TBBS and 0.75 phr ZnO, and compound 3 by incorporating 60 phr silanized silica, 5 phr TBBS, and 1 phr ZnO in the raw rubber (Table 1). These compounds were chosen because they had the optimum amounts of TBBS and ZnO for curing. Finally, compound 4 (control compound) was prepared by adding 0.75 phr elemental sulfur, 2 phr TBBS, and 0.75 phr ZnO. As mentioned earlier, Coupsil 8113 has 2.5 wt% sulfur included in TESPT. Compound 1 had 30 phr silanized silica and the sulfur content in TESPT was equivalent to 0.75 phr. Hence, 0.75 phr elemental sulfur was added to make compound 4. No control compounds were made for compounds 2 and 3. Therefore, the cure systems (S/TBBS/ZnO) in compounds 1-4 were 0.75phr/2phr/0.75phr, 1.13phr/4phr/0.75phr, 1.5phr/5phr/1phr, and 0.75 phr/2phr/0.75phr, respectively.

Dispersion of the silica filler in the rubber is shown in Figures 3 and 4. The silica particles dispersed well in the rubber matrix down to about 35 nm after 14 min of mixing. The particle size of silica is 20-54 nm. The reinforcing effect of silica on the mechanical properties of an EPDM rubber vulcanizate was maximized because of the good dispersion of the silica filler in the rubber [23]. This was mainly due to the pre-treatment of the silica particles with TESPT, which reduced the filler-filler interaction and increased the rubber-

filler interaction [16].

*Effect of the additives on the viscosity and cure properties of the rubber*

The viscosity of the rubber increased from 65 MU (raw rubber) to 102 MU when up to 60 phr silanized silica, 5 phr TBBS, and 1 phr ZnO were incorporated in the rubber (compounds 1-3; Table 1). It was noted that the control compound (compound 4; Table 1) had a viscosity of 52 MU which was noticeably lower than those of the filled compounds and this showed that the addition of silica and the chemical curatives increased the rubber viscosity. Viscosity increases when solid additives such as fillers, accelerators and activators are mixed with rubber [11]. Mixing for long times, e.g. 14 min, breaks down the rubber chains and causes a reduction in the molecular weight and viscosity of the rubber [24]. The reduction is due to chain scission [25] or the mechanical rupture of the primary carbon-carbon bonds that are present along the backbone of the rubber chains. This is often compensated by the reinforcing effect of the filler as indicated by the higher viscosities measured for compounds 1-3. However, in the absence of filler (compound 4), the damage inflicted on the rubber chains by mixing was not compensated and therefore the viscosity decreased below that of the raw rubber which was 65 MU.

The rubber compound with the silanized silica had shorter scorch and optimum cure



times and a higher cure rate (cf. compound 1 and compound 4; Table 1). This was because the precipitated silica was pre-treated with sulfur-bearing TESPT, which prevented it from interfering with the curing reaction, and the sulfur in TESPT participated in the curing process [16]. Compound 3 had the largest  $\Delta$ torque value of 42 dN m, which indicated the highest crosslink density compared with other compounds, and it also had the fastest cure rate as shown by the cure rate index at  $5.3 \text{ min}^{-1}$ . This meant that a progressive increase in the loading of TESPT was beneficial to crosslink density and helped to shorten the cure cycle.

In compound 4 (control), the crosslinks or sulfur bridges formed between the rubber chains [26] whereas in compounds 1-3, there was silica-to-rubber coupling and at the same time, some of the sulfur in TESPT split off and matrix crosslinks were formed during the curing process[27]. When the loading of TESPT was increased progressively in an EPDM rubber filled with precipitated silica, the optimum cure time shortened and the rate of cure rose [7]. Our results showed a similar trend. Furthermore, the tetrasulfane groups of TESPT reacted at a much faster rate with the rubber chains than the equivalent loading of elemental sulfur did under the curing conditions. This also produced shorter scorch and optimum cure times and a lower crosslink density as indicated by the  $\Delta$ torque value (cf. compound 1 and compound 4; Table 1).

*Effect of an increasing loading of silanized silica on the mechanical properties and cyclic fatigue life of the rubber vulcanizate*

Mechanical properties of the rubber vulcanizate benefitted to a great extent from the addition and progressive increases in the loading of silica. The hardness, tensile strength, and Young's modulus were enhanced by 63%, 65%, and 306%, respectively when the full amount of silica was added (compound 1-3; Table 2). The modulus increased by 117% at 50% elongation and then continued rising by 268% at 300% elongation and the compression set rose by 59% when the full loading of silica was present in the rubber. Clearly, the compression set deteriorated after silica was added to the rubber. The properties related to fracture improved noticeably too. The tear energy and stored energy density at break rose by 36% and 26%, respectively at the optimum loading of silica. Probably, the most interesting results were for the cyclic fatigue of the rubber vulcanizate, which was 4.8 kc for the control compound and then exceeded 10,000 kc when the filler was added. This was a major improvement in the fatigue performance of the rubber. Obviously, the inclusion of silica was greatly beneficial to the rubber properties (cf. compound 1 and compound 4; Table 2). It is interesting that a similar behaviour was also reported by Kim [6] who showed major improvement in the mechanical properties of an EPDM rubber after adding precipitated silica

and a sulfur-bearing liquid silane similar to TESPT.

Many benefits of silane and silica in rubber reinforcement have been reported when the filler loading was increased progressively from 20 to 40 phr and liquid TESPT was added to silica. The M100 and M300, tensile strength and hardness rose but elongation at break deteriorated as a function of the silica loading. For the vulcanizate with 40 phr silica, the bound rubber content was about 34% which indicated strong interaction between the rubber and solid filler [7]. Our results confirmed the reported trend.

There are various factors which affect reinforcement of rubbers by solid fillers. They are filler-rubber interaction [28,29], filler-filler interaction [30], and formation of crosslinks in rubber [31]. The  $\Delta$ torque values of the rubber vulcanizates increased from 27 to 42 dN m (Table 1) and this confirmed contribution from the chemical bonding or crosslinks between the rubber and filler to the rubber properties [16,27]. The bound rubber content was somewhere between 59-63% which also indicated strong rubber/filler interaction. The silica particles were dispersed well in the rubber matrix (e.g. Fig. 4), and this was beneficial to the mechanical properties of the cured rubber [7]. Since the formation of stable covalent sulfur bonds between silica and rubber produces strong rubber-filler interaction [13, 16], it was essential to optimize the chemical bonding between the two. As the  $\Delta$ torque values in Table 1

indicate, when the tetrasulfane groups of TESPT reacted with the rubber chains to form stable covalent sulfur bonds and the reaction was maximized by using sufficient amounts of TBBS and ZnO, this optimized the rubber-filler interaction. At the same time, it helped to reduce the excessive use of these harmful chemicals, and eliminated elemental sulfur, stearic acid and secondary accelerator from the formulation altogether.

### *Health, safety, and the environmental issues related to rubber compounds*

The new European chemicals policy, Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) and various legislations for environment and safety restrict excessive use of chemicals in rubber which are harmful to health, safety and the environment. In order to address the health, safety and environmental concerns related to rubber compounds, it is essential to use chemical curatives and reinforcing fillers more efficiently. Currently, there are some deficiencies in using liquid TESPT and precipitated silica in rubber reinforcement. When silica compounds are modified *in situ* with liquid TESPT, un-reacted TESPT could sometimes be identified, indicating an incomplete and uneconomical modification process *in situ*. Also, plant trials with the same compound (but conducted with different internal mixing equipment, resulting in different mixing conditions) could give different properties from those experienced on the experimental compounds [17].

As mentioned earlier [21,22], when silica reacts with liquid TESPT *in situ*, it generates harmful ethanol during mixing. There is also a major concern about the cure systems in these compounds. For instance, in some EPDM vulcanizates where liquid TESPT and precipitated silica were used [6], the cure system consisted of 5 phr ZnO and 1 phr stearic acid (primary and secondary activators), 3.1 phr accelerators (primary and secondary) and 0.8 phr curing agents (sulfur substitute), adding up to 9.9 phr, which was too much. As this study has shown, the problems mentioned above was remedied when TESPT pre-treated silanized silica was used and the chemical bonding between the rubber and filler was optimized via the tetrasulfane groups of TESPT by using TBBS and ZnO. It seemed that reducing excessive amounts of the chemical curatives (e.g. one accelerator and one activator, compound 3; Table 1) had no detrimental effect on the rubber properties and in fact using TESPT pre-treated silanized silica filler produced better quality rubber compounds and ethanol free mixing. Therefore, this technology has the potential to produce safer, cost-effective and environmental-friendly industrial EPDM rubber goods and offers major advantages over the current methods.

## **CONCLUSIONS**

From this study, it was concluded that

- The hardness, tensile strength, stored energy density at break, Young's modulus, M50-M300, and tear strength of the rubber vulcanizate improved progressively when up to 60 phr silanized silica was added though the compression set and elongation at break deteriorated. The cyclic fatigue life enhanced significantly when silica was added but increase in the loading of silica did not seem to affect the fatigue life of the rubber vulcanizate.
- The amount of TBBS for optimizing the chemical bonding between the tetrasulfane groups of TESPT and rubber chains rose from 2 to 5 phr when the silica loading was increased from 30 to 60 phr.
- The optimum cure time decreased and the rate of cure and crosslink density of the rubber as indicated by the cure rate index and torque values, respectively increased when the loading of silica was raised from 30 to 60 phr.
- The use of the TESPT pre-treated sulfur-bearing silanized silica nanofiller helped to reduce excessive use of the chemical curatives in the rubber compound by eliminating stearic acid, elemental sulfur and secondary accelerator from the cure system without compromising the mechanical properties of the rubber vulcanizate.

Finally, the replacement of toxic carbon black with silanized precipitated silica was a major

step in reducing the health risk associated with the presence of PAHs in carbon black-filled

EPDM rubber compounds

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TABLE 1. Recipes, Mooney viscosity and cure properties of the rubber compounds.

|                                       | Compound                         |           |         |             |
|---------------------------------------|----------------------------------|-----------|---------|-------------|
|                                       | 1                                | 2         | 3       | 4           |
| EPDM                                  | 100                              | 100       | 100     | 100         |
| Silanized silica                      | 30                               | 45        | 60      | -           |
| TBBS                                  | 2                                | 4         | 5       | 2           |
| ZnO                                   | 0.75                             | 0.75      | 1       | 0.75        |
| Elemental sulfur                      | -                                | -         | -       | 0.75        |
|                                       | Cure system                      |           |         |             |
| S(phr)/TBBS(phr)/ZnO(phr)             | 0.75/2/0.75                      | 1.125/4/1 | 1.5/5/1 | 0.75/2/0.75 |
|                                       | Mooney viscosity ML (1+4, 100°C) |           |         |             |
|                                       | 80                               | 96        | 102     | 52          |
|                                       | Cure properties at 160°C         |           |         |             |
| Minimum torque (dN m)                 | 17                               | 19        | 24      | 11          |
| Maximum torque (dN m)                 | 44                               | 51        | 66      | 45          |
| $\Delta$ Torque (dN m)                | 27                               | 32        | 42      | 34          |
| Scorch time, $t_{52}$ (min)           | 7                                | 10        | 7       | 29          |
| Optimum cure time, $t_{95}$ (min)     | 36                               | 31        | 26      | 79          |
| Cure rate index ( $\text{min}^{-1}$ ) | 3.5                              | 4.8       | 5.3     | 2           |

The raw EPDM rubber had a viscosity of 65 MU.

Silanized silica composition:

30 phr: 26.61 phr silica, 3.39 phr TESPT, 0.75 phr tetrasulfane (in TESPT);

45 phr: 39.915 phr silica, 5.085 TESPT, 1.125 phr tetrasulfane (in TESPT);

60 phr: 53.22 phr silica, 6.78 phr TESPT, 1.5 phr tetrasulfane (in TESPT).

TABLE 2. Mechanical properties, cyclic fatigue life and bound rubber content of the rubber vulcanizates.

|   | Compound |         |         |         |
|---|----------|---------|---------|---------|
|   | 1        | 2       | 3       | 4       |
| Hardness (Shore A)                                  | 43       | 60      | 70      | 28      |
| Tensile strength (MPa)                              | 20       | 26      | 33      | 0.54    |
| Elongation at break (%)                             | 1475     | 1092    | 1041    | 160     |
| Stored energy density at break (mJ/m <sup>3</sup> ) | 106      | 105     | 133     | 0.5     |
| Tear energy (kJ/m <sup>2</sup> )                    | 25       | 23      | 34      | 1       |
| Range of values (kJ/m <sup>2</sup> )                | 19-26    | 21-28   | 29-53   | 0.8-1.1 |
| Compression set (%)                                 | 6.3      | 9       | 10      | 4.1     |
| Young's modulus (MPa)                               | 1.8      | 3.4     | 7.3     | 0.7     |
| Modulus at different strain amplitudes (MPa)        |          |         |         |         |
| 50%   | 0.60     | 0.98    | 1.3     | 0.36    |
| 100%  | 0.41     | 1.0     | 1.4     | 0.24    |
| 200%  | 0.41     | 1.2     | 1.7     | -       |
| 300%  | 0.57     | 1.4     | 2.1     | -       |
| Cyclic fatigue life (kc)                            | > 10,000 | >10,000 | >10,000 | 4.8     |
| Range of values (kc)                                | -        | -       | -       | 0.05-17 |
| Bound rubber content (%)                            | 63       | 60      | 59      | -       |

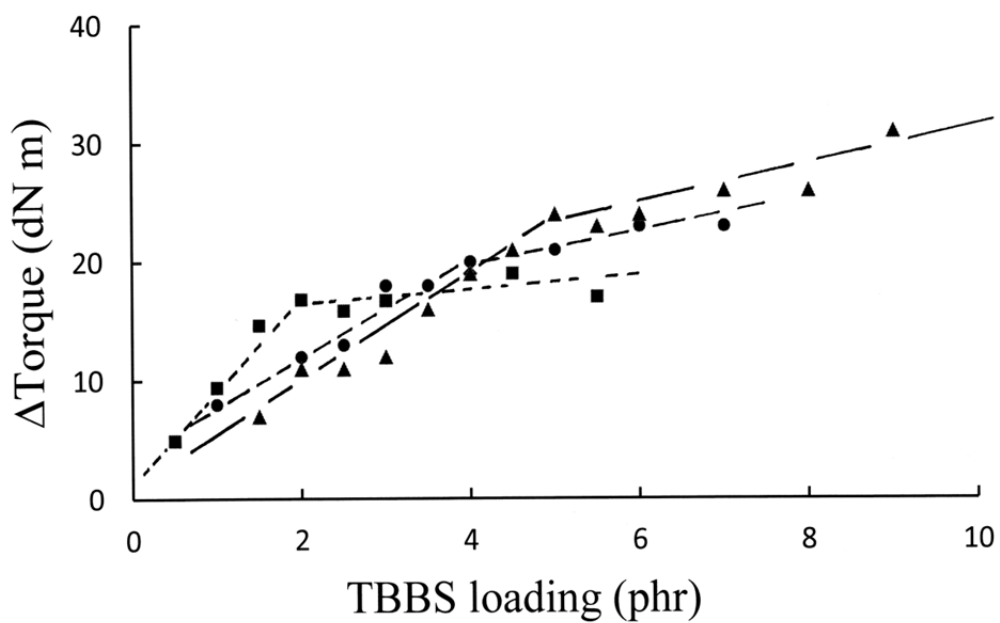


Figure 1 –  $\Delta$ Torque versus TBBS loading. (◆) rubber with 30 phr silanized silica, (●) rubber with 45 phr silanized silica, (▲) rubber with 60 phr silanized silica. Each point on the figure corresponds to one rubber compound.

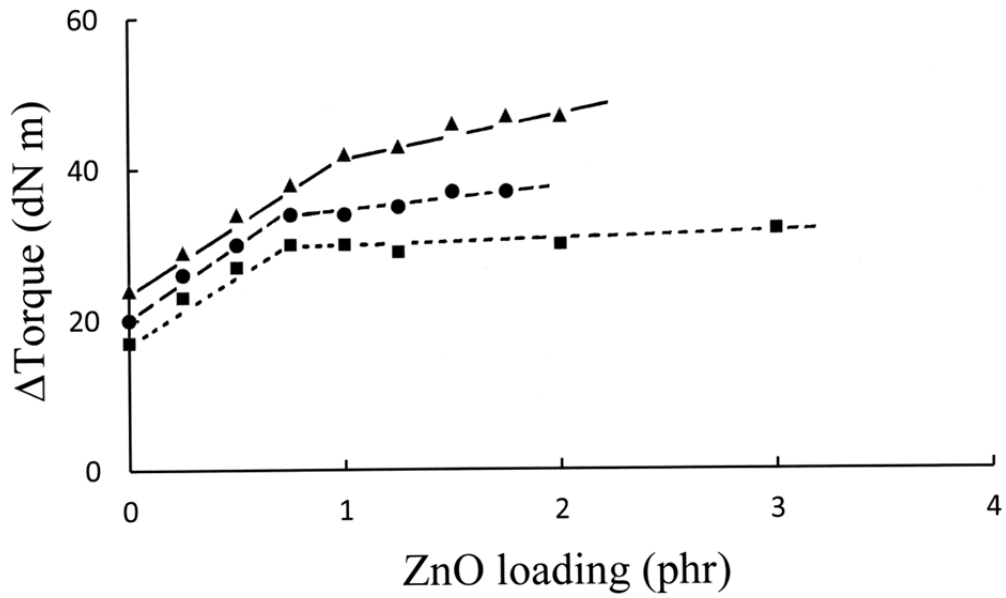


Figure 2 –  $\Delta$ Torque versus ZnO loading. (◆) rubber with 30 phr silanized silica and 2 phr TBBS, (●) rubber with 45 phr silanized silica and 4 phr TBBS, (▲) rubber with 60 phr silanized silica and 5 phr TBBS. Each point on the figure corresponds to one rubber compound.

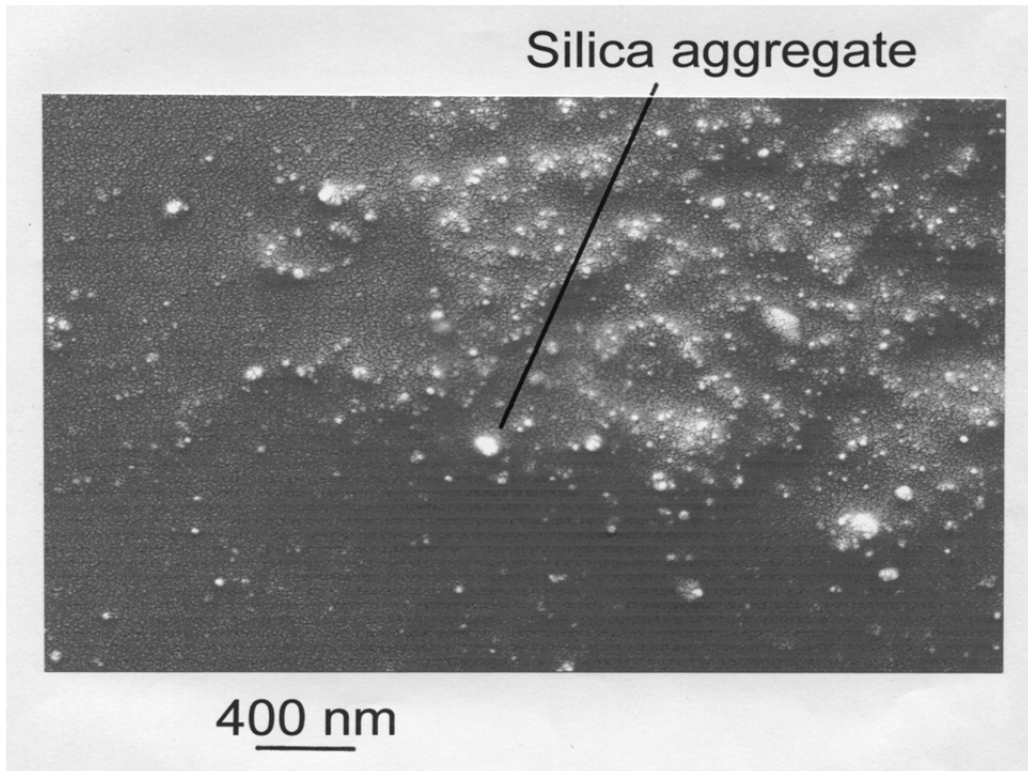


Figure 3 – SEM micrograph showing poor dispersion of silica in the rubber after 5 min mixing.

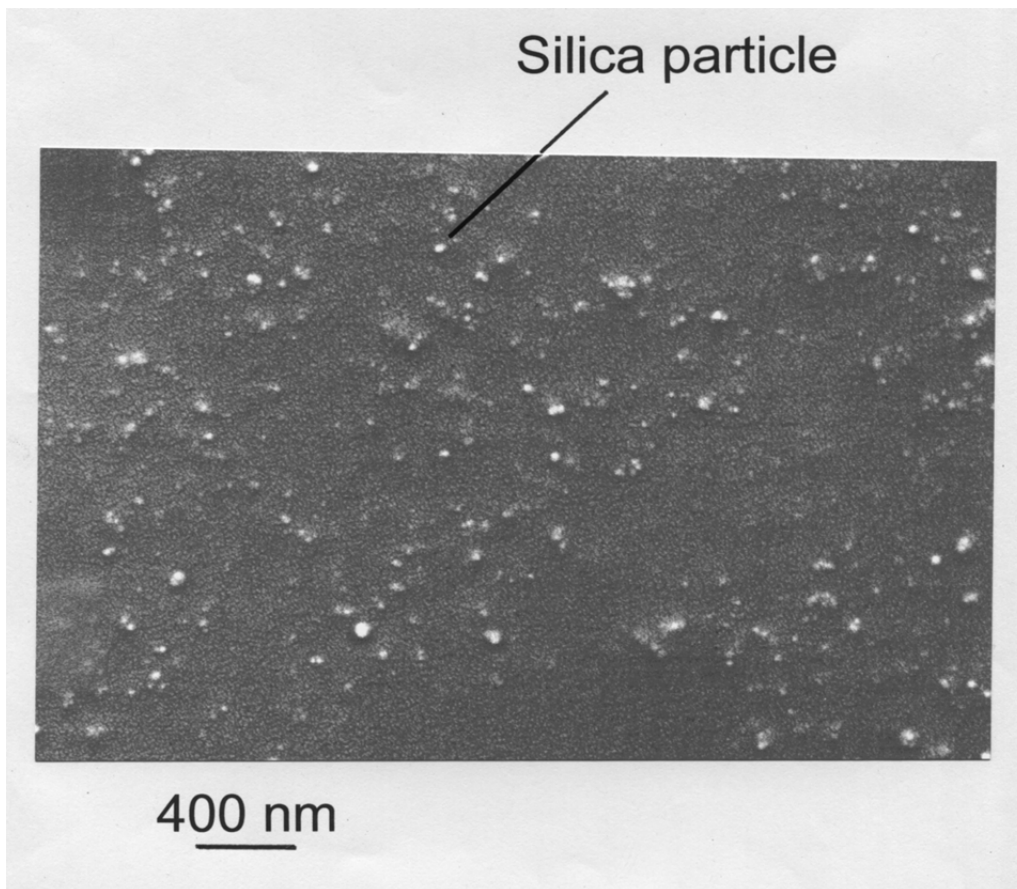


Figure 4 – SEM micrograph showing good dispersion of silica in the rubber after 14 min mixing.