# Using a Silanized Silica Nanofiller to Reduce Excessive Amount of Rubber Curatives in Styrene-Butadiene Rubber

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**ABSTRACT:** In recent years, the rubber industry has come under pressure to improve health and safety at work, minimize damage to the environment, reduce costs, and increase competitiveness. Rubber compounds contain additives including curing chemicals, which are hazardous and harmful. Reducing their use or eliminating them altogether will be beneficial to rubber compounders and manufacturers of rubber articles. A styrene-butadiene rubber (SBR) was cured and reinforced with a high loading of precipitated amorphous white silica nanofiller. The silica surfaces were pretreated with bis(3-triethoxysilylpropyl) tetrasulfide (TESPT), which is a sulfur-bearing bifunctional organosilane to chemically adhere silica to the rubber. The chemical bonding between the filler and rubber was optimized via the tetrasulfane groups of TESPT by adding accelerator and activator. The rubbers were subsequently cured and their hardness, tensile strength, elongation at break, stored energy density at break, tearing energy, tensile modulus, Young's modulus, and bound rubber content were measured. This study showed that using the filler in combination with a sulfur-donor accelerator was the most efficient method for curing and reinforcing the rubber. This led to a significant reduction in the use of the curing chemicals, a faster curing cycle, and very good mechanical properties for the rubber vulcanizate. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 922–928, 2011

**Key words:** elastomers; silicas; additives; crosslinking; mechanical properties

## INTRODUCTION

To enhance the mechanical properties of a rubber such as hardness, tear strength, tensile strength, and elongation at break, fillers with surface areas from 150 to 400 $m^2/g$ are added.[1] Among the fillers, short fibers, colloidal carbon blacks, metal oxides, and synthetic silicas are the most widely used materials in rubber reinforcement. In addition to filler, compounds used to manufacture industrial rubber articles such as passenger car tire tread contain up to eight classes of rubber chemicals. For instance, the cure system consists of up to five different chemicals; primary and secondary accelerators, primary and secondary activators, and elemental sulfur, which may add up to 11 parts per hundred rubber by weight (phr).[2] Antidegradants and processing aids are also included to protect rubber against environmental aging and improve processing properties, respectively. Excessive use of the curing chemicals is harmful to health, safety, and the environment and their use is restricted by the new European chemicals policy, Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) and various legislation for environment and safety. Reduction in the use of these chemicals in rubber compounds is now a priority.

Fillers and curing chemicals perform two distinct functions in rubber compounds. Fillers increase the mechanical properties[3,4] and curing chemicals produce crosslinks between the rubber chains at elevated temperatures, i.e., 140–240°C.[5,6] Synthetic precipitated amorphous white silica filler, which is replacing carbon blacks in some applications such as tire tread compound is acidic and moisture adsorbing.[7] This is caused by the presence of silanol or hydroxyl groups on the silica surfaces and is detrimental to the cure of rubber compounds. Moreover, it can also cause loss of crosslink density in sulfur-cured rubbers.[8] In addition, the viscosity increases significantly when a large amount of silica is added and processing becomes more difficult.[9] The availability of bifunctional organosilanes such as TESPT has provided an opportunity to combine silica and sulfur into one single product known as a "crosslinking filler."[10] One such filler is silanized silica, where the surfaces of precipitated silica are pretreated with TESPT to chemically adhere silica to rubber (Scheme 1) and to prevent the filler from interfering with the reaction mechanism of sulfur-cure in rubber.[7,8] TESPT is used to improve the reinforcing capability of the filler and also forms an

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Rubber chain segments

TESPT modified silica
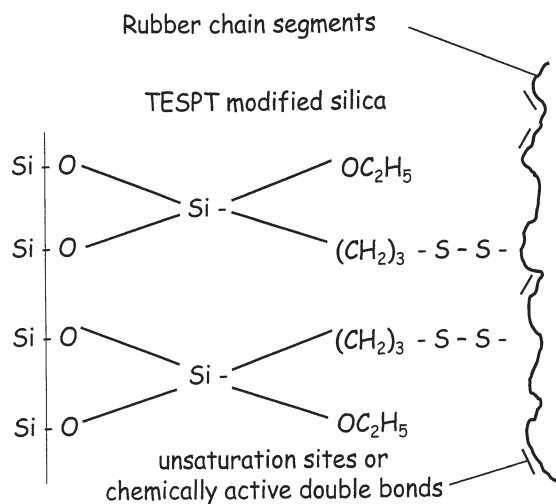


**Scheme 1** Silanized silica nanofiller pretreated with TESPT. Tetrasulfane groups react with rubber to form stable covalent sulfur bonds.

integral part of curing systems to improve crosslinking network properties.[7]

Using a precipitated silica filler pretreated with TESPT, the author and coworkers showed that a substantial reduction in the use of the curing chemicals was achieved in natural rubber (NR) without compromising the good mechanical properties of the rubber vulcanizate.[11] To crosslink the rubber and optimize the chemical bonding between the rubber and filler via TESPT, accelerator and activator were added. The mechanical properties of the cured rubber were improved significantly in spite of the reduction in the use of the curing chemicals.

The aim of this study was to use a high loading of a silanized silica nanofiller in a styrene-butadiene rubber (SBR) to crosslink and reinforce the rubber properties. Different accelerators and activators were added to optimize the reaction between the tetrasulfane groups of TESPT and rubber chains and cure the rubber. The hardness, tensile strength, elongation at break, stored energy density at break, tearing energy, tensile modulus, and Young's modulus were measured. The scorch and optimum cure times, cure rate index and bound rubber content of the rubber compounds were also determined.

## EXPERIMENTAL

### Materials: rubber, filler, curing chemicals, antidegradants, and processing oil

The raw elastomer used was a SBR (23.5 wt % styrene; Intol 1712, Polimeri Europa UK, Hythe, UK). SBR Intol 1712 is a cold emulsion copolymer, polymerized using a mixture of fatty acid and rosin acid soaps as emulsifiers. It is extended with 37.5 phr of highly aromatic oil and contains a styrenated phenol

as a nonstaining antioxidant. It has $\sim 4.8\%$ by weight organic acid and a viscosity of 32 Mooney units. The reinforcing filler was Coupsil 8113, which was supplied by Evonik Industries AG of Germany. Coupsil 8113 is a precipitated amorphous white silica-type Ultrasil VN3 surfaces of which had been pretreated with TESPT. It has 11.3% by weight silane, 2.5% by weight sulfur (included in TESPT), a 175 $m^2/g$ surface area (measured by $N_2$ adsorption), and a 20–54 nm particle size.

In addition to the raw rubber and filler, the other ingredients were N-tert-butyl-2-benzothiazole sulfenamide (a safe-processing delayed action non sulfur-donor accelerator with a melting point of 105°C) (Santocure TBBS, Flexsys, Dallas, TX; Scheme 2), Tetramethyl thiuram disulfide (a fast curing sulfur-donor accelerator with $\sim 13\%$ of the sulfur available to react with rubber and a melting point of 146°C) (Perkacit TMTD PDR D, Flexsys, Belgium, Europe; Scheme 2), zinc oxide (ZnO; an activator, Harcros Durham Chemicals, Durham, UK), N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (an antidegradant, Santoflex 13, Brussels, Belgium), stearic acid (an activator, Anchor Chemicals, Manchester, UK), and heavy paraffinic distillate solvent extract aromatic oil (a processing oil, Enerflex 74, Milton Keynes, UK). The oil was added to reduce the rubber viscosity. TBBS and TMTD are often used as primary and secondary accelerators, respectively, in industrial rubber compounds.[2] The cure system consisted of TBBS, TMTD, ZnO, and stearic acid, which were added to fully crosslink the rubber.

### Mixing

The compounds were prepared in a Haake Rheocord 90 (Berlin, Germany), a small size laboratory mixer with counter rotating rotors. In these experiments,

N-tert-butyl-2-benzothiazolesulphenamide (TBBS)



Tetramethylthiuramdisulphide (TMTD)
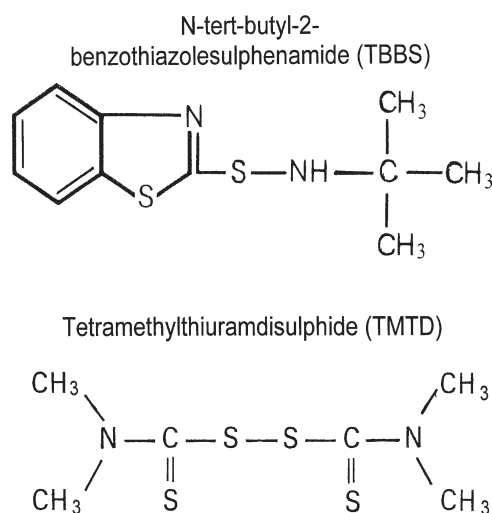


**Scheme 2** TBBS and TMTD accelerators.

the Banbury rotors and the mixing chamber were maintained at ambient temperature (23°C) during mixing, and the rotor speed was 45 rpm. The volume of the mixing chamber was 78 cm$^3$, and it was 55% full during mixing. Haake Software Version 1.9.1. was used for controlling the mixing condition and storing data.

### Assessment of the silica dispersion in the rubber

To select a suitable mixing time for incorporating the filler in the rubber, compounds containing 60 phr silica were prepared. Before mixing started, the filler was introduced into the mixing chamber and then the raw elastomer was added. The filler was added when the viscosity of the rubber was still relatively high, which lead to an improved dispersion.[12] The mixing time was increased to 10 min to determine the time needed to disperse the silica particles fully in the rubber.[13] Twenty four hours after mixing ended, the rubbers were examined in an scanning electron microscope (SEM) to assess the filler dispersion.

Dispersion of the silica particles in the rubber was assessed by a LEO 1530 VP Field emission gun scanning electron microscope (Carl Zeiss SMT, Cambridge, UK). Small pieces of the uncured rubber were placed in liquid nitrogen for 3 min. They were recovered and fractured into two pieces to create fresh surfaces. The samples, 40 mm$^2$ in area and 6 mm thick, were coated with gold and then examined and photographed in the SEM. The degree of dispersion of the silica particles in the rubber was subsequently studied from the SEM photographs.

For preparing the rubber compounds, a mixing time of 10 min was considered. TBBS, ZnO, TMTD, stearic acid, and antidegradant were added 4 min after the silica, rubber, and processing oil were mixed together. After these chemicals were added, mixing continued for an extra 6 min. The temperature of the compounds during mixing was 50–63°C.

Finally, when mixing ended, the rubber was recovered from the mixer and milled to a thickness of about 8 mm for further work. The compounds were kept at ambient temperature ($\sim$ 23°C) for at least 24 h before their cure properties were measured.

### Addition of TBBS and TMTD to the filled rubber

To activate the rubber reactive tetrasulfane groups of TESPT, TBBS, and TMTD were added. The loading of TBBS and TMTD in the rubber was increased progressively to 9 phr to measure the minimum amounts needed to optimize the chemical bonding between the rubber and TESPT and to increase the crosslink density in the rubber. The formation of crosslinks strengthened the rubber/filler interaction.[7]

### Addition of ZnO to the filled rubber with TBBS and TMTD

The loading of ZnO in the filled rubbers with TBBS and TMTD was raised to 2.5 phr to determine the amounts needed to maximize the efficiency of TBBS and TMTD and chemical bonding between the filler and rubber.

### Addition of stearic acid to the filled rubbers with TBBS, TMTD, and ZnO

Stearic acid is a fatty acid that is added to improve the solubility of ZnO in rubber. The loading of stearic acid in the filled rubbers with TBBS and ZnO and, TMTD, was increased to 2.5 phr to measure the amount needed to optimize the efficiency of the accelerators and cure.

### Viscosity and cure properties of the rubber compounds

The viscosity of the rubber compounds was measured at 100°C in a single-speed rotational Mooney viscometer (Wallace Instruments, Surrey, UK) according to a British Standard.[14] The results were expressed in Mooney Units (MU).

The 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 from the cure traces generated at 140 ± 2°C by an oscillating disk rheometer curemeter (ODR) (Monsanto, Swindon, UK).[15] The cure rate index, which is a measure of the rate of cure in the rubber, was calculated using the method described previously.[16] The rheometer tests ran for up to 2 h. Figure 1 shows typical cure traces produced for the rubbers with an increasing loading of TMTD. Δtorque, which is the difference between the maximum and minimum torque values on the cure trace of the rubber, is an indication of crosslink density changes and was calculated from these traces. Δtorque was subsequently plotted against the loading of TBBS, TMTD, ZnO, and stearic acid.

### Test pieces and test procedure

After these measurements were completed, the compounds were cured in a compression mold at 140°C with a pressure of 11 MPa. For measuring the mechanical properties of the rubbers, sheets 23 cm by 23 cm in dimensions by $\sim$ 2.7 mm thick were used from which various samples for further tests were cut.
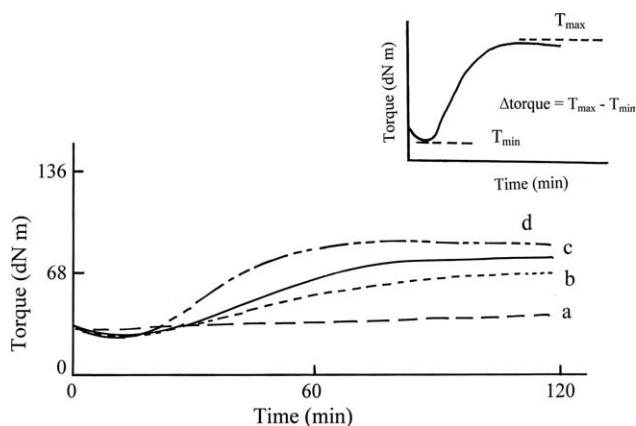
**Figure 1** Typical torque versus time traces by ODR for the filled rubber compound containing different amounts of TMTD. Formulations: 0.5 phr TMTD (a); 3.5 phr TMTD (b); 5 phr TMTD (c); 8.5 phr TMTD (d).

### Hardness

For determining the hardness of the rubber, cylindrical samples 12.5 mm thick and 28 mm in diameter, were cured. The samples were then placed in a Shore A Durometer hardness tester (The Shore Instrument and MFG, New York) and the hardness of the rubber was determined at 23.5°C after 15-s interval. This was repeated at three different positions on each sample and the medium of the three readings was subsequently indicated.[17]

### Tensile properties

The tensile stress, elongation at break, and stored energy density at break of the rubber vulcanizates were determined in uniaxial tension in a Lloyd mechanical testing machine (Hampshire, UK) with dumbbell test-pieces 3.6 mm wide and a central neck 25 mm long. These samples were die-stamped from sheets of the cured rubber. The tests were performed at 22.5°C and at a constant cross-head speed of 50 mm/min.[18] Lloyd DAPMAT computer software was used for storing and processing the data.

### Tear strength

The tear strength of the rubbers was measured using rectangular strips, 85 long and 30 mm wide, which were cut from the cured sheets of rubber. A sharp crack, ∼ 35 mm in length, was introduced into the strips half way along the width and parallel to the length of the strips to form the trouser test pieces for the tear experiments. Trouser tear tests were performed at an angle of 180° and a constant cross-head speed of 50 mm/min,[19] using a Lloyd mechanical testing machine. The test temperature was 22.5°C. The tear produced varied in length from ∼ 16 mm to 78 mm. In some cases, tearing produced

peaks on the trace where an average force was calculated and sometimes, tearing produced a single peak from which a force was measured. Five test pieces were used for each rubber. Tearing energies were calculated using eq. (1)[20]

$$T = 2F/t \qquad (1)$$

where $F$ is tearing force and $t$ is the thickness of the test piece.

### Young's modulus and tensile modulus at different strain amplitudes

The tensile modulus at 100, 200, and 300% strain amplitudes and the Young's modulus of the vulcanizates were measured in uniaxial tension, using dumbbell test-pieces. The tests were carried out at ambient temperature (22.5°C) at a cross head speed of 50 mm/min[18] in a HT Hounsfield mechanical testing machine (Hounsfield, Surrey, UK). QMAT-DONGLE version 2003 computer software was used to process the data.

### Bound rubber measurements

The solvent used for the bound rubber determination was toluene. For the determination, 10 g of the rubber compound was cured in a compression mold to produce cylindrical samples, 28 mm in diameter and 12 mm in height. The samples were then placed individually in 70 mL of the solvent in labeled bottles and allowed to swell at 21°C. It took up to 5 days for the samples to reach equilibrium. The weight of the samples was measured every day until it reached 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 reweighed. The bound rubber content was then calculated using the expression in Ref. [21].

## RESULTS AND DISCUSSION

### Effect of TBBS and TMTD accelerators on the Δtorque of the rubber compounds

As mentioned earlier, TBBS and TMTD are non sulfur-donor and sulfur-donor accelerators, respectively. Effects of an increasing loading of these accelerators on the Δtorque of the filled SBR rubber was investigated. Figure 2 shows Δtorque versus TMTD and TBBS loading. Δtorque increased from 8 to 22 dN m when 3 phr TBBS was added and thereafter, it rose at a much slower rate to 26 dN m when an extra 6 phr TBBS was included in the rubber. When the loading of TMTD was increased from 0.5 to 5.0
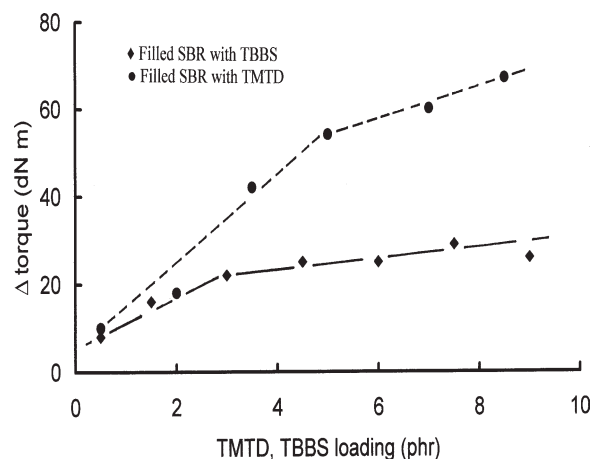
**Figure 2** Δtorque versus TMTD and TBBS loading for the filled SBR compound.

phr, Δtorque rose from 10 to 54 dN m and subsequently, it increased to 67 dN m when the loading of TMTD reached 8.5 phr. Evidently, the addition of 3 phr TBBS and 5 phr TMTD was sufficient to start the chemical bonding or crosslinking between the rubber reactive tetrasulfane groups of TESPT and the rubber.

### Effect of ZnO on the Δtorque of the rubber compounds with TMTD and TBBS

Figure 3 shows Δtorque as a function of ZnO loading for the filled SBR rubbers with TMTD and TBBS. For the filled rubber with 3 phr TBBS, Δtorque increased from 22 to 57 dN m when 0.5 phr ZnO was added and it continued rising slowly to 64 dN m when the loading of ZnO reached 2.5 phr. For the filled rubber with 5 phr TMTD, Δtorque rose rapidly from 54 to 111 dN m with 0.3 phr ZnO and thereafter, it reached 142 dN m when an extra 2.2 phr ZnO was included in the rubber.
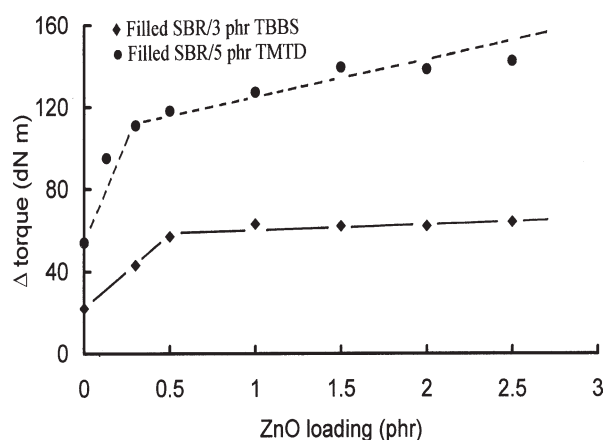


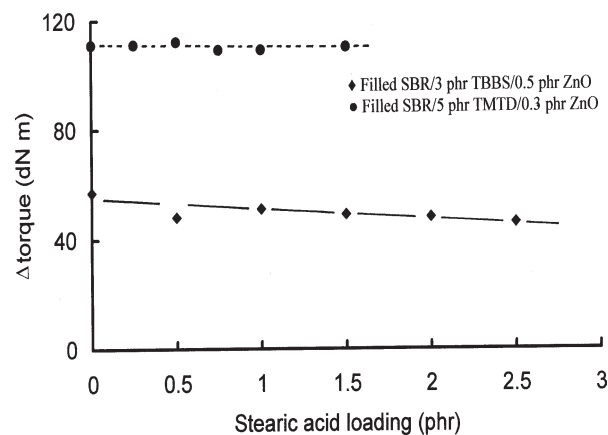**Figure 3** Δtorque versus zinc oxide loading for the filled SBR compounds with TMTD and TBBS.

**Figure 4** Δtorque versus stearic acid loading for the filled SBR compounds with TMTD, TBBS, and ZnO.

### Addition of stearic acid to the filled rubber compounds with TBBS, TMTD, and ZnO

To increase the efficiency of cure in the filled SBR rubbers with 3 phr TBBS and 0.5 phr ZnO, and 5 phr TMTD and 0.3 phr ZnO, an increasing loading of stearic acid was added (Fig. 4). For the rubber with TBBS and ZnO, Δtorque decreased from 57 to 46 dN m when the loading of stearic acid reached 2.5 phr. For the rubber with TMTD and ZnO, Δtorque hardly changed and remained at 111 dN m when 1.5 phr stearic acid was added. Clearly, adding stearic acid had no additional benefit for Δtorque at all and in fact it was detrimental to it. Note that no ZnO was subsequently included in the rubber with TMTD because it would have made the rubber too brittle. After the optimum loadings of TMTD, TBBS, and ZnO were measured, two compounds

**TABLE I**
**Recipe for the SBR Rubber Compounds**

| Formulation (phr) | Compound No. | |
| --- | --- | --- |
| | 1 | 2 |
| SBR Intol 1712 | 100 | 100 |
| Silanized silica | 60 | 60 |
| TBBS | 3 | – |
| TMTD | – | 5 |
| ZnO | 0.5 | – |
| Santoflex 13 | 1 | 1 |
| Enerflex 74 | 5 | 5 |
| | Mooney viscosity (MU) | |
| | 71 | 91 |
| | ODR results | |
| Minimum torque (dN m) | 18 | 22 |
| Maximum torque (dN m) | 56 | 71 |
| Δtorque (dN m) | 38 | 49 |
| Scorch time, $t_{s2}$ (min) | 16 | 11 |
| Optimum cure time, $t_{95}$ (min) | 80 | 58 |
| Cure rate index (min$^{-1}$) | 1.6 | 2.1 |

**TABLE II**
**Mechanical Properties of the Cured Rubbers**

| Property | Compound No. | |
|---|---|---|
| | 1 | 2 |
| Hardness (Shore A) | 62.5 | 65.5 |
| Tensile strength (MPa) | 26 | 18 |
| Elongation at break (%) | 1308 | 1112 |
| Stored energy density at break (mJ/m$^3$) | 140 | 94 |
| Tearing energy (kJ/m$^2$) | 75 | 87 |
| Range of values | 71–89 | 79–97 |
| Modulus at different strain amplitudes (MPa) | | |
| Strain amplitude (%) | | |
| 100 | 0.78 | 0.98 |
| 200 | 0.96 | 1.15 |
| 300 | 1.24 | 1.31 |
| Young's modulus (MPa) | 4.3 | 5.6 |
| Bound rubber content (%) | 64 | 63 |

were made (Table I), cured, and their mechanical properties were determined.

### Cure properties and viscosity of the filled rubbers

As shown in Table I, the filled rubber cured with TMTD had shorter scorch and optimum cure times, a faster cure rate and a higher Δtorque value. Since TMTD is a sulfur-donor accelerator and acts as a vulcanizing agent, this contributed to a higher Δtorque value and a shorter cure cycle. Note that TBBS is a non sulfur-donor substance. The rubber compound with TMTD had a higher viscosity in spite of both compounds having the same mixing time. This rubber had 43% by weight more curing powder (Table I), which contributed to its higher viscosity.

### Effect of the silanized silica nanofiller on the mechanical properties of the filled rubber vulcanizates with TBBS and ZnO, and TMTD

There were noticeable differences between the mechanical properties of the two rubbers (Table II). For example, the rubber cured with TMTD was harder and had higher Young's modulus, tensile modulus at 100–300% strain amplitudes and tearing energy but its tensile strength, elongation at break, and stored energy density at break were lower. Interestingly, these properties were similar or even better, in some cases, than those reported for the SBR compounds filled with a similar loading of silica and crosslinked with conventional sulfur-cure systems (two accelerators, two activators, and elemental sulfur).[3,22] This was in spite of reducing the curing chemicals in the compound by more than 60%. Clearly, a more efficient use of these selected chemi-

cals had no adverse effect on the mechanical properties of the rubber vulcanizates.

Mechanical properties of sulfur-cured silica-filled SBR rubber vulcanizates are affected by changes in crosslink density. For example, tensile modulus at 100% strain amplitude improved, whereas, elongation at break deteriorated as crosslink density was increased.[23] The Δtorque of the TMTD cured rubber was larger (Table I), which indicated a higher crosslink density. This explained the differences in the mechanical properties of the two rubbers for example the tensile modulus and elongation at break (Table II). Our results are in line with the previous findings.[23]

Using TMTD to cure the filled rubber eliminated the need for ZnO, elemental sulfur, and primary accelerator. Curing the filled rubber with TBBS required a small amount of ZnO, no elemental sulfur and no secondary accelerator. The presence of ZnO in tread compounds has come under growing scrutiny because of environmental concerns.[24] Since the tire industry is the largest single market for ZnO, the elimination or a more restricted use of ZnO in rubber compounds will help to reduce damage to the environment. Rubber reinforcement is mainly due to filler-rubber adhesion,[25] filler-filler interaction,[9] and formation of crosslinks in rubber.[5] The silica particles were fully dispersed in the rubber matrix (Fig. 5), and therefore, the filler–filler interaction was negligible. However, the mechanical properties benefited from the good dispersion of the silica particles in the rubber.[26,27] The bound rubber content was 63–64% (Table II), which indicated a very strong filler-rubber adhesion. Furthermore, the rubbers had Δtorque values of 38 dN m and 49 dN m, respectively, (Table I), which indicated
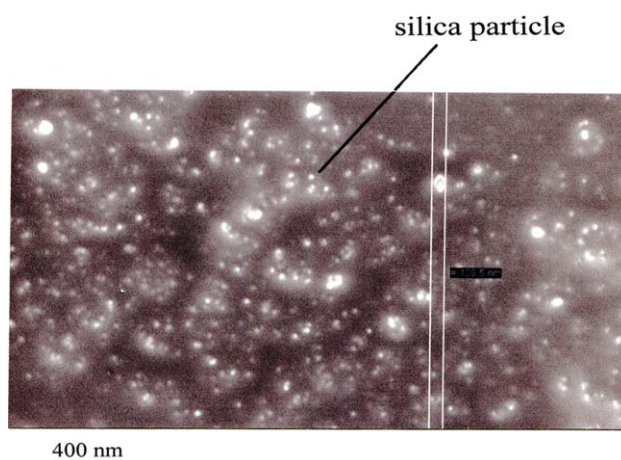


**Figure 5** SEM photograph showing good dispersion of the silica particles in the rubber. Mixing time = 10 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

contribution from crosslinks or chemical bonding between the rubber and filler to the rubber reinforcement.

## CONCLUSIONS

From this study, it is concluded that:

1. To start reaction between the rubber reactive tetrasulfane groups of TESPT and the rubber chains and to optimize cure 5 phr TMTD or 3 phr TBBS and 0.5 phr ZnO, were needed. There was no need to add stearic acid and elemental sulfur to the filled rubber, and in fact, stearic acid was detrimental to Δtorque.
2. The scorch and optimum cure times of the filled rubber cured with TMTD were shorter, its cure rate was faster, and it had a higher Δtorque value, which indicated a higher crosslink density.
3. For the rubber compound with TMTD, the Mooney viscosity was higher and the hardness, tearing energy, Young's modulus, and tensile modulus at strain amplitudes 100–300% were noticeably better. However, the tensile strength, elongation at break, and stored energy density at break were inferior.

In summary, when chemical bonding or crosslinking between the tetrasulfane groups of TESPT and the rubber chains were optimized with the sulfur-bearing TMTD accelerator, this provided a very efficient method for curing and reinforcing the SBR rubber. At the same time, a significant reduction in the use of the curing chemicals was achieved, which was beneficial to health, safety, and the environment.

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