

**Using a sulfur-bearing silane to improve rubber formulations for potential use
in industrial rubber articles**

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Sulfur-bearing silanes for green rubber formulation

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Abstract

The availability of the coupling agent bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT) has provided an opportunity for enhancing the reinforcing capabilities of precipitated amorphous white silicas in rubber. Styrene-butadiene rubber (SBR), synthetic polyisoprene rubber (IR), acrylonitrile-butadiene rubber (NBR), and natural rubber (NR) containing the same loading of a precipitated silica filler were prepared. The silica surfaces were pre-treated with TESPT, which is a sulfur-bearing silane to chemically bond silica to the rubber. The rubber compounds were subsequently cured by optimizing the chemical bonding between the tetrasulfane groups of TESPT and the rubber chains. This study showed that using TESPT with silica was a very efficient method for crosslinking and reinforcing the rubbers. It significantly reduced the use of the chemical curatives without compromising the good mechanical properties of the cured rubbers. Moreover, it improved health and safety at work and minimized damage to the environment because less chemicals were used. TESPT was classified as "green silane" for use in rubber formulations.

Key words: sulfur-bearing silane, silica, rubbers, chemical curatives, chemical bonding, reinforcement, environment

1. INTRODUCTION

Fillers and curing chemicals perform two distinct functions in rubbers. Fillers increase the mechanical properties, for example, hardness, tensile and fracture properties, abrasion resistance and modulus [1,2], and chemical curatives produce crosslinks between rubber chains at elevated temperatures [3,4]. Among the fillers, short fibres, colloidal carbon blacks, clay and synthetic silicas are the most widely used in rubber reinforcement and have surface areas from 150 to 400 m²/g [5-8].

Colloidal carbon blacks have been used extensively to reinforce mechanical properties of rubbers and are being replaced by synthetic silicas. Synthetic silicas are acidic [9] and moisture adsorbing [10] because they have silanol or hydroxyl groups on their surfaces, which are both detrimental to the cure of rubber compounds and can also cause loss of crosslink density in sulfur-cured rubbers [11]. For these reasons, use of silica in rubber products was hampered until bifunctional organosilanes were available. Bifunctional organosilanes are used as primers for treating silica surfaces to make the filler more suitable for use in rubber [12]. The silanization reaction of silica takes place in two different ways. Firstly, 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. Or, silanization is carried out *in situ*.

This is usually done in an internal mixer in the first stage of mixing, where the silane is added together with, or after the addition and dispersion of the silica. This process is carried out within the specified limits of temperature increases in the mixer and strict mixing times [13,14].

Bifunctional organosilanes, such as bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT), known also as Si69 coupling agent, have been used extensively with silica in rubber compounds. TESPT has a fast cure kinetics and ability to form disulfidic rubber-to-filler bonds [12,15]. This silane possesses tetrasulfane and ethoxy groups (Scheme 1). The tetrasulfane groups react with the rubber in the presence of accelerators at elevated temperatures, i.e., 140-240°C, with or without elemental sulfur being present, to form crosslinks in unsaturated rubbers such as natural rubber. The ethoxy groups react with the silanol groups on the surfaces of these fillers during compounding to form stable filler/TESPT bonds (Scheme 2). The TESPT reaction with silanol groups reduces their numbers, and the remaining groups become less accessible to the rubber because of steric hindrance. These changes reduce the viscosity of rubber compounds and improve their cure properties [12,16]. Moreover, this combines filler and sulfur into a single product known as “crosslinking filler”. One such filler is precipitated amorphous white silica the surface of which is pre-treated with TESPT to chemically bond silica to rubber. This also forms an integral part of curing systems to improve the crosslinking network properties [17].

KOENIC and Parker [18] measured effects of silane pre-treated silica, and silica and liquid silane mixture on the crosslink density of a sulphur-cured rubber and concluded that the rubber with silane pre-treated silica had a higher crosslink density and increased filler-rubber interaction both of which were beneficial to the mechanical properties of the cured rubber.

The aim of this study was to use a high loading of precipitated silica pre-treated with TESPT to crosslink and reinforce the mechanical properties of styrene-butadiene rubber (SBR), synthetic polyisoprene rubber (IR), acrylonitrile-butadiene rubber (NBR) and natural rubber (NR). A sulfenamide accelerator and two activators were added to optimize the chemical bonding between the silica and rubbers via the tetrasulfane groups of TESPT, and the mechanical properties of the cured rubbers were measured to assess the effect of the silane on the rubber properties.

2. EXPERIMENTAL

2.1. Materials

The raw rubbers used were standard Malaysian natural rubber (NR) grade L (98 wt % cis-1-4 content), styrene-butadiene rubber (SBR) (23.5 wt % styrene; Intol 1712, Polimeri Europa UK Ltd, Hythe, UK), synthetic polyisoprene (minimum 96 wt % cis- 1-4 content; Kraton IR-307,

Kraton Polymers, Houston, USA), and non-staining cold polymerized acrylonitrile-butadiene copolymer (NBR) (26% by weight acrylonitrile; Krynac 2645 F; LANXESS Europe GmbH, Germany). SBR 1712 is a cold emulsion co-polymer, polymerised 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 non-staining antioxidant. It has approximately 4.8% by weight organic acid.

The reinforcing filler was Coupsil 8113 (Evonik Industries AG, Germany). Coupsil 8113 is precipitated amorphous white silica-type Ultrasil VN3 surface of which had been pre-treated with TESPT. It has 11.3% by weight TESPT, 2.5% by weight sulfur (included in TESPT), 175 m²/g surface area (measured by N₂ adsorption), and a 20-54 nm particle size.

In addition to the raw rubbers 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 109°C) (Santocure TBBS, Flexsys, Dallas, TX), zinc oxide (ZnO; an activator, Harcros Durham Chemicals, Durham, UK), *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (6PPD, an antidegradant, Santoflex 13, Brussels, Belgium), stearic acid (an activator, Anchor Chemicals, Manchester, UK), and heavy paraffinic distillate solvent extract

containing aromatic oils (a processing oil, Enerflex 74, Milton Keynes, UK). The oil was added to reduce the rubber viscosity, and the antidegradant to protect the rubbers against environmental ageing. The cure system consisted of TBBS, ZnO and stearic acid, which were added to fully crosslink the rubbers (Table 2).

2.2. Mixing

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 SBR, IR and NBR compounds, and at 48°C for mixing the NR compound. The rotor speed was set at 45 r.p.m. The volume of the mixing chamber was 78 cm³, and it was 57% full during mixing. Polylab monitor 4.17 software was used for controlling the mixing condition and storing data.

2.3. Assessment of the silica dispersion in the rubber by SEM

In order to select a suitable mixing time for incorporating the filler in the rubbers, compounds containing 60 phr silanized silica (58.5 phr silica and TESPT and 1.5 phr tetrasulfane) were prepared. Before mixing started, the filler was introduced into the mixing chamber and then the raw rubber was added. The filler was added when the viscosity of the rubber was still relatively high, which led to an improved dispersion [19]. The mixing time was increased to 22 min to

measure the time needed to disperse the silica particles fully in the rubber. Twenty four hours after mixing ended, the rubbers were examined in a scanning electron microscope (SEM) to assess the filler dispersion.

Dispersion of the silica particles in the rubber was assessed by a Cambridge Instruments Stereoscan 360 Tungsten Filament SEM. 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, 58 mm² in area and 6 mm thick, were coated with gold, and then examined in the SEM. The degree of dispersion of the silica particles in the rubber was subsequently studied from the SEM micrographs. After the SEM micrographs were examined, suitable mixing times were used for adding the filler to the rubbers. For example, Figure 1 shows good dispersion of the silica particles in the NR after 13 min mixing.

2.4. Addition of TBBS to the silica-filled rubbers

To activate the rubber reactive tetrasulfane groups of TESPT (scheme 2), TBBS was added.

The loading of TBBS in the silica-filled rubbers was increased progressively to 10 phr to measure the amount 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 [9]. In total, 39 rubber compounds were made.

2.5. Addition of ZnO to the silica-filled rubbers with TBBS

The loading of ZnO in the silica-filled rubbers with TBBS was raised to 2.5 phr to determine the amount needed to maximize the efficiency of TBBS and to optimize the chemical bonding between the filler and rubber. In total, 30 rubber compounds were mixed.

2.6. Addition of stearic acid to the silica-filled rubbers with TBBS 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 silica-filled rubbers with TBBS and ZnO was increased to 2.5 phr to measure the amount needed to increase the solubility of ZnO and enhance the efficiency of the curing reaction in the rubber. In total, 21 rubber compounds were prepared.

After these measurements were completed, four rubber compounds were prepared for further tests. Full details of the mixing conditions are summarized in Table 1. Finally, when mixing ended, the rubbers were removed from the mixer and milled to a thickness of about 6-8 mm. 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.

2.7. Viscosity and cure properties of the rubber compounds

The viscosity of the raw rubbers 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 140 ± 2 °C by an oscillating disc rheometer (ODR) curemeter. 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). For instance, Figure 2 shows typical cure traces produced for the silica-filled NBR with different amounts of chemical curative.

Δ torque, which is the difference between the maximum and minimum torque values on the cure traces of the rubbers tested and is an indication of crosslink density changes in the rubber, was subsequently plotted against the loading of TBBS, ZnO and stearic acid for the four rubbers.

2.8. Test pieces and test procedure

After the viscosity and cure properties were measured (Table 2), the rubber compounds were cured in a compression mold at 140°C with a pressure of 11 MPa. Pieces of rubber, each ~ 140 g in weight, were cut from the milled sheets. Each piece was placed in the centre of the mold to enable it to flow in all the directions when pressure was applied. This prevented anisotropy from forming in the cured rubber. For determining the mechanical properties of the rubbers, sheets of

23 cm × 23 cm and approximately 2.5 mm thick were used, from which various samples for further tests were cut.

2.9. Measurement of the mechanical properties of the cured rubbers

To measure the mechanical properties of the cured rubbers, the following British Standards were used: • hardness: British Standard 903: Part A26, London, UK (1995). • tensile properties and tensile modulus at different strain amplitudes: British Standard 903: Part A2, London, UK (1995). • tear strength: British Standard 903: Part A3, London, UK (1995).

2.10. Bound rubber content of the cured rubbers

The solvent used for the bound rubber determination was toluene. For the determination, 2 g of the silica-filled NR, IR, NBR and SBR rubber compounds were cured in a compression mould to produce cylindrical samples of 28 mm in diameter and 12 mm in height. The samples were then placed individually in 200 ml of the solvent in labelled bottles and allowed to swell at 21°C for up to 21 days. The weight of the samples was measured every day until equilibrium was reached after 60 h. 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 expression [20]

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

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

3. RESULTS AND DISCUSSION

3.1. Comparing effects of TBBS, ZnO and stearic acid on the Δ torque of the silica-filled SBR,

NBR, IR and NR rubbers

Figure 3 shows Δ torque as a function of TBBS loading for the SBR, IR, and NBR rubbers. For

the SBR, Δ torque increased from 8 to 22 dN m when the loading of TBBS reached 3 phr.

Thereafter, Δ torque increased at a much slower rate to 26 dN m as the loading of TBBS was raised to 9 phr. Evidently, 3 phr TBBS was sufficient to start and optimize the reaction between the tetrasulfane groups of TESPT and the rubber. Similarly, for the IR and NBR, 7 phr and 4 phr TBBS, respectively were needed to maximize chemical bonding between the silica and rubber chains.

For the SBR with 3 phr TBBS, the addition of ZnO improved the efficiency of TBBS, and

Δ torque increased sharply from 22 to 57 dN m as the loading of ZnO was raised to 0.5 phr.

However, the rate of increase of Δ torque slowed down considerably with Δ torque rising from 57 to 64 dN m as the amount of ZnO reached 2.5 phr (Fig. 4). It was concluded that 0.5 phr ZnO was sufficient to optimize the efficiency of TBBS and increased the chemical bonding between the silica and rubber chains. Likewise, for the IR with 7 phr TBBS and NBR with 4 phr TBBS, 1 phr ZnO and 0.3 phr ZnO, respectively, enhanced the efficiency of cure and formation of covalent sulfur bonds between the silica and rubber.

The addition of stearic acid to the SBR, IR and NBR rubbers with TBBS and ZnO had no benefit for the Δ torque at all (Fig. 5). Normally, stearic acid has a plasticising effect on rubber at elevated curing temperatures. For the SBR with 3 phr TBBS and 0.5 phr ZnO, Δ torque decreased from 57 to 46 dN m as the loading of stearic acid reached 2.5 phr. A similar trend was also seen for the NBR with 4 phr TBBS and 0.3 phr ZnO. However, for the IR with 7 phr TBBS and 1 phr ZnO, Δ torque was unchanged and remained at about 110 dN m when up to 1 phr stearic acid was added. Therefore, stearic acid was not beneficial to the cure of the rubbers and could be removed from the formulation.

Synthetic polyisoprene rubber (IR) is the synthetic analogue of NR and is chemically and structurally similar to it. IR has been used in the same applications as NR such as in blends with

styrene-butadiene rubber and polybutadiene rubber to improve their processibility, and also mineral filled IR is used in footwear, sponge, and sporting goods [21]. Figure 6 shows Δ torque as a function of TBBS loading for the NR and IR. For the NR, Δ torque increased from 9 to 55 dN m as the loading of TBBS was raised to 6 phr, and it continued rising at a much slower rate to about 61 dN m when the loading of TBBS reached 10 phr. The NR required 1 phr less TBBS than the IR for reaction of the rubber reactive tetrasulfane groups of TESPT with the rubber chains to form chemical bonding between the two. When ZnO was added to improve the efficiency of TBBS, the NR with 6 phr TBBS required only 0.3 phr ZnO, whereas the IR with 7 phr TBBS needed 1 phr ZnO to achieve optimum cure (Fig. 7). The addition of up to 2 phr stearic acid to the NR with 6 phr TBBS and 0.3 phr ZnO was detrimental to the chemical bonding between the rubber and silica because Δ torque decreased by almost 9% (Fig. 8). Evidently, the TBBS and ZnO requirements for curing the NR were lower in spite of the rubber being chemically and structurally similar to its synthetic analogue IR. This was a useful finding.

As mentioned earlier, Coupsil 8113 has 2.5 wt% tetrasulfur, which is included in TESPT. This was equivalent to 1.5 phr sulfur in the formulation. This study showed that at a constant loading of sulfur, i.e. 1.5 phr, the amounts of TBBS and ZnO needed to fully cure the rubbers

depended on the rubber composition. This confirmed the previous findings [?]. The S/TBBS/ZnO requirement for the rubbers were: SBR (1.5/3/0.5); IR (1.5/7/1); NBR (1.5/4/0.3); NR (1.5/6/0.3). This information is vitally important to rubber formulation scientists who use chemical curatives to crosslink rubbers and came to light when TESPT pre-treated silica was used.

3.2. Effect of silanized silica nanofiller on the mechanical properties of the cured SBR, NBR, IR and NR rubbers

Table 3 shows the mechanical properties of the cured rubbers. The hardness of the cured SBR, IR, and NBR were 62, 80 and 70 Shore A, respectively. The tensile strength and elongation at break were 26, 17 and 28 MPa, and 1308, 404 and 973 %, respectively. The properties related to fracture, i.e. stored energy density at break and tear energy were, 140, 33 and 115 mJ/m³, and 75, 17 and 40 kJ/m², respectively. The tensile modulus of the three rubbers increased as a function of the strain amplitude. For example, for the SBR the modulus rose from 0.73 to 1.17 MPa, for the IR from 3.0 to 4.3 MPa, and for the NBR from 1.8 to 2.5 MPa, as the strain amplitude was raised from 100 to 300%. These properties were similar to those reported previously for sulfur-cured carbon black-filled SBR, IR, and NBR rubbers [22,24]. It appeared

that reducing the chemical curatives had no adverse effect on the rubber properties.

The results for the NR and IR rubbers were also interesting. The IR was harder and had a slightly higher modulus at different strain amplitudes but the other properties were inferior (Table 3). Rubber properties, for example, tensile strength, and stored energy density at break increase, reaching a maximum, and then deteriorate substantially as a function of crosslink density [3,4]. The Δ torque of the IR was 27% higher than that of the NR, which indicated a higher crosslink density (Table 2). The inferior properties of the IR were due to the excessive crosslinks in the rubber.

Rubber reinforcement is due to filler-rubber adhesion [11], filler-filler interaction [25], and formation of crosslinks in rubber [26,27]. The bound rubber content of the SBR, IR, NBR and NR rubbers were 64-98.5%, which indicated a very strong filler-rubber adhesion [20]. The Δ torque values of the SBR, IR, NBR and NR rubbers were 38-111 dN m (Table 2) and this confirmed contribution from the chemical bonding or crosslinks between the rubber and filler to the rubber properties [28]. The silica particles were dispersed well in the rubber matrix (Fig. 1), and this was beneficial to the mechanical properties of the cured rubber [29]. It was also evident from the results that when the chemical bonding between the rubber and tetrasulfane groups of TESPT was optimized, it reduced the amount of harmful TBBS and ZnO curatives and

eliminated stearic acid from the formulation.

3.3. Health, safety, and the environmental issues related to rubber compounds

Excessive use of the chemical curatives 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 legislations for environment

and safety. For example, formulations for liquid petroleum gas (LPG) resistant hoses contain

NBR, 100 phr; carbon black, 60 phr; wt % chemical curatives (two accelerators,

two activators, and elemental sulfur), and 24.5 wt% antidegradants and processing aids [30]. If

the carbon black and chemical curatives in the formulation were replaced with 60 phr silica, 4.0

phr TBBS and 0.3 phr ZnO, and the other additives retained, it would reduce the number of the

chemical curatives to two. On this basis, the total weight of the curatives in the rubber would be

reduced to about 2 wt%. In addition, a large decrease in the use of ZnO and removal of stearic

acid that is often used as a secondary activator with ZnO would ultimately lower cost and

minimize damage to the environment.

4. CONCLUSIONS

From this study, it is concluded that:

- Using TESPT pre-treated precipitated silica filler to crosslink and reinforce SBR, IR, NBR and NR rubbers reduces the use of TBBS and ZnO and eliminates stearic acid from the formulation altogether. This, in turn, improves health and safety at work-place, reduces cost and minimizes damage to the environment. Therefore, TESPT can be classified as “green silane” for use in rubber formulations.
- The use of TESPT pre-treated precipitated silica also helped to accurately determine the amounts of TBBS and ZnO needed to fully cure the SBR, IR, NBR and NR rubbers. At a constant loading of sulfur (in TESPT), the amounts of these chemical curatives required to produce optimum cure depended on the composition of the rubber, which confirmed the previous findings.

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Table 1.
Mixing conditions for the rubber compounds

Compound	Mixing cycle
1	SBR was mixed with processing oil for 2 min and then silica was added and mixed for another 2 min. Finally, the chemical curatives and antidegradant were added and mixed for another 6 min. The compound temperature reached 63°C during mixing.
2	IR was mixed with silica for 17 min and then the chemical curatives and antidegradant were added and mixed for another 3 min. The compound temperature reached 56°C during mixing.
3	NBR was mixed with silica for 17 min and then the chemical curatives and antidegradant were added and mixed for another 3 min. The compound temperature reached 80°C during mixing.
4	NR was mixed with silica for 13 min and then the chemical curatives and antidegradant were added and mixed for another 3 min. The compound temperature reached 85°C during mixing.

Chemical curatives: *N*-tert-butyl-2-benzothiazole sulfenamide (TBBS), zinc oxide (ZnO) and stearic

acid. Antidegradant: N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine. Note that the silica surface was pre-treated with TESPT by the supplier.

Table 2.

Recipe for the rubber compounds, Mooney viscosity at 100°C and cure properties at 140°C

Formulation (phr)	Compound			
	1	2	3	4
SBR	100	-	-	-
IR	-	100	-	-
NBR	-	-	100	-
NR	-	-	-	100
Silica+TESPT	58.5	58.5	58.5	58.5
Sulfur ^a	1.5	1.5	1.5	1.5
TBBS	3	7	4	6
ZnO	0.5	1	0.3	0.3
6PPD	1	1	1	1
Processing oil	5	-	-	-
		Cure system		
S/TBBS/ZnO	1.5/3/0.5	1.5/7/1	1.5/4/0.3	1.5/6/0.3
Double bond content (mole%)	19.1	21.0	27.0	25.0
		Mooney viscosity (MU)		
	71	105	107	106

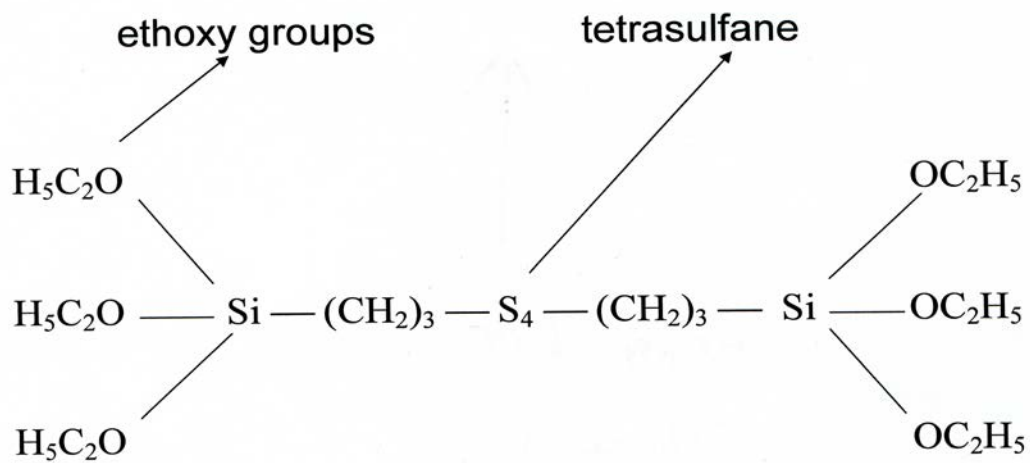
		ODR results		
Minimum torque (dN m)	18	26	26	26
Maximum torque (dN m)	56	137	101	107
Δ torque (dN m)	38	111	75	81
Scorch time, t_{S2} (min)	16	8	23	9
Optimum cure time, t_{95} (min)	80	34	80	27
Cure rate index (min^{-1})	1.6	3.9	1.7	5.6

^aSulfur is included in TESPT. Viscosity of raw rubbers: SBR, 52 MU; IR, 69 MU; NBR, 45 MU; NR, 97 MU.

Table 3.

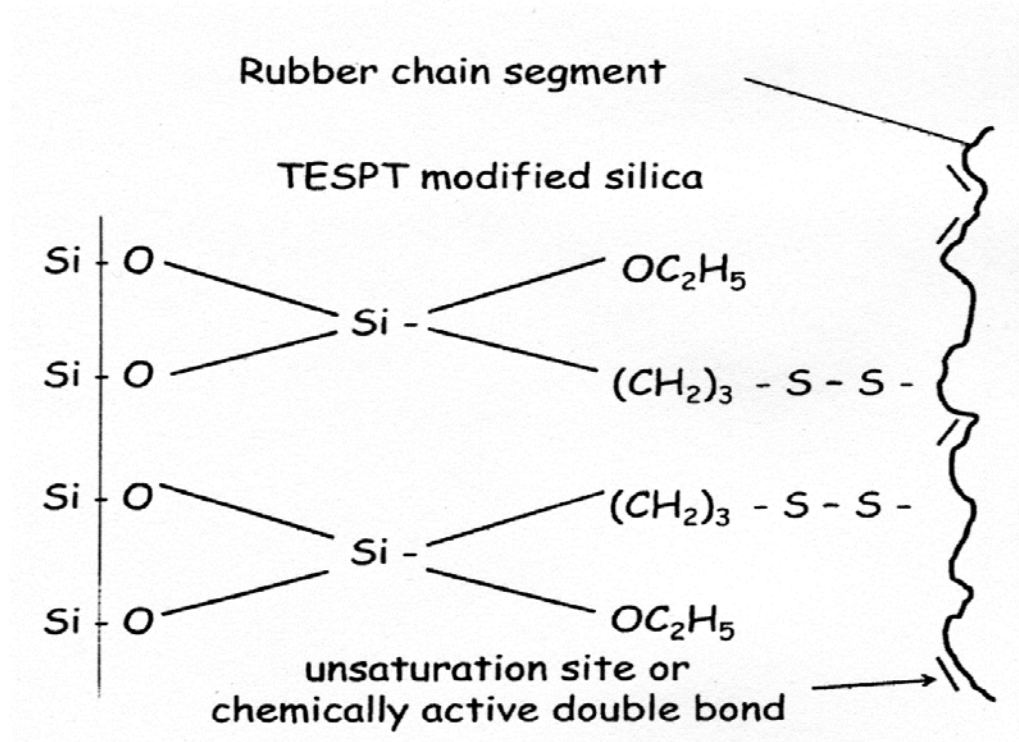
Mechanical properties of the cured rubbers shown in Table 2

Properties	Compound			
	1	2	3	4
Hardness (Shore A)	62	80	70	75
Tensile strength (MPa)	26	17	28	37
Elongation at break (%)	1308	404	973	837
Stored energy density at break (mJ/m^3)	140	33	115	137
Tear energy (kJ/m^2)	75	17	40	58
Range of values (kJ/m^2)	71-89	10-23	37-43	46-95
Modulus at different strain amplitudes (MPa)				
Strain amplitude (%)				
100	0.73	3.0	1.8	2.23
200	0.93	3.7	2.0	3.16
300	1.17	4.3	2.5	4.23



Bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT) or Si69
coupling agent

Scheme 1 – Chemical structure of bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT).



Scheme 2 – Silanized silica nanofiller pre-treated with TESPT. Tetrasulfane groups react with rubber chains to form stable covalent sulfur bonds.

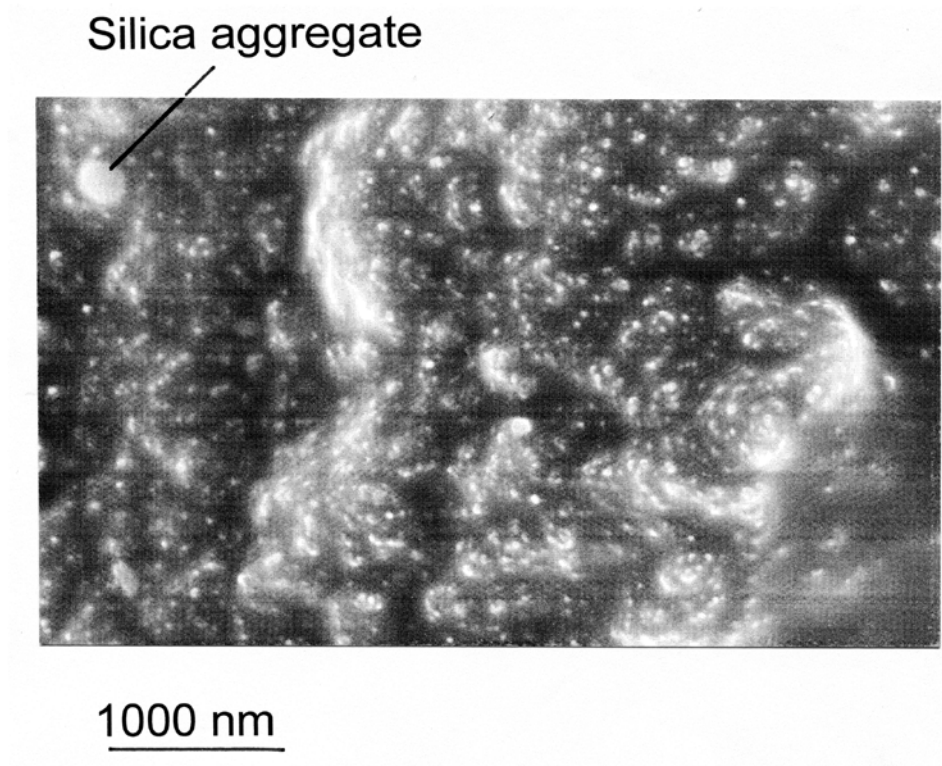


Figure 1a – SEM micrograph showing poor dispersion of silica particles in the rubber. Note the large silica aggregates in the rubber. Data for the SBR. Mixing time = 4 min.

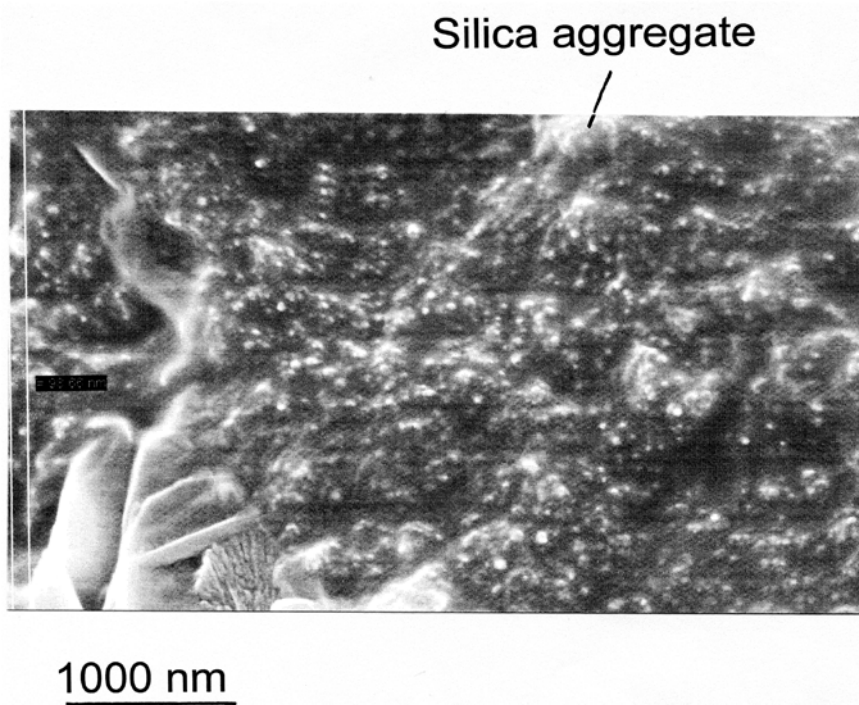


Figure 1b – SEM micrograph showing improved dispersion of silica particles in the rubber. Note small silica aggregates in the rubber. Data for the SBR. Mixing time = 7 min.

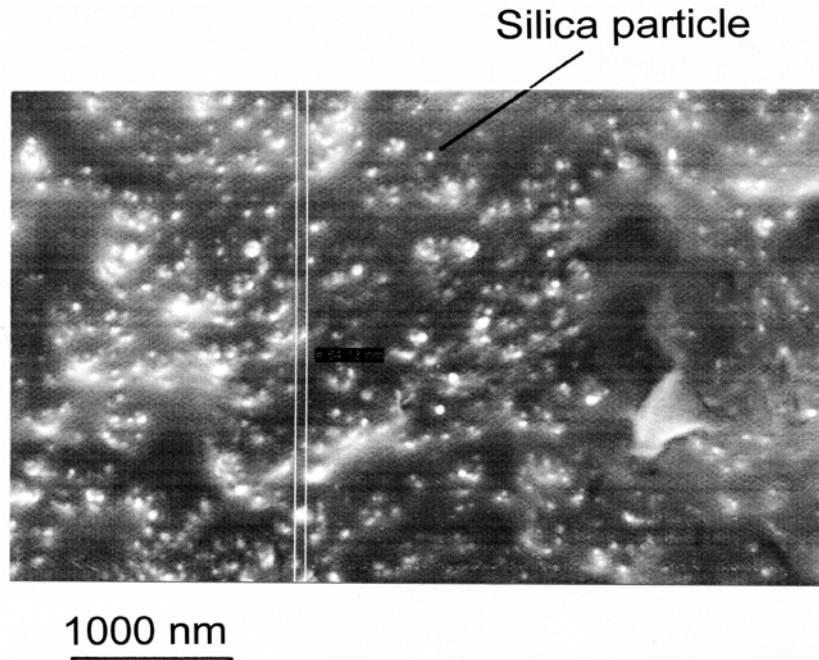


Figure 1c – SEM micrograph showing good dispersion of silica particles in the rubber. Data for the SBR. Mixing time = 10 min.

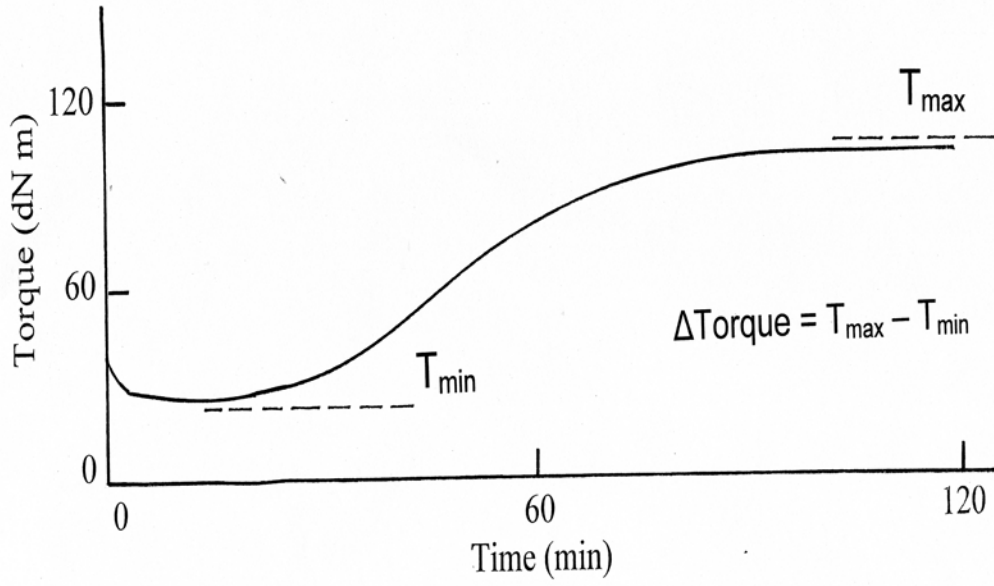


Figure 2 – A typical torque vs, time cure trace for the NBR produced at 140°C in the ODR.

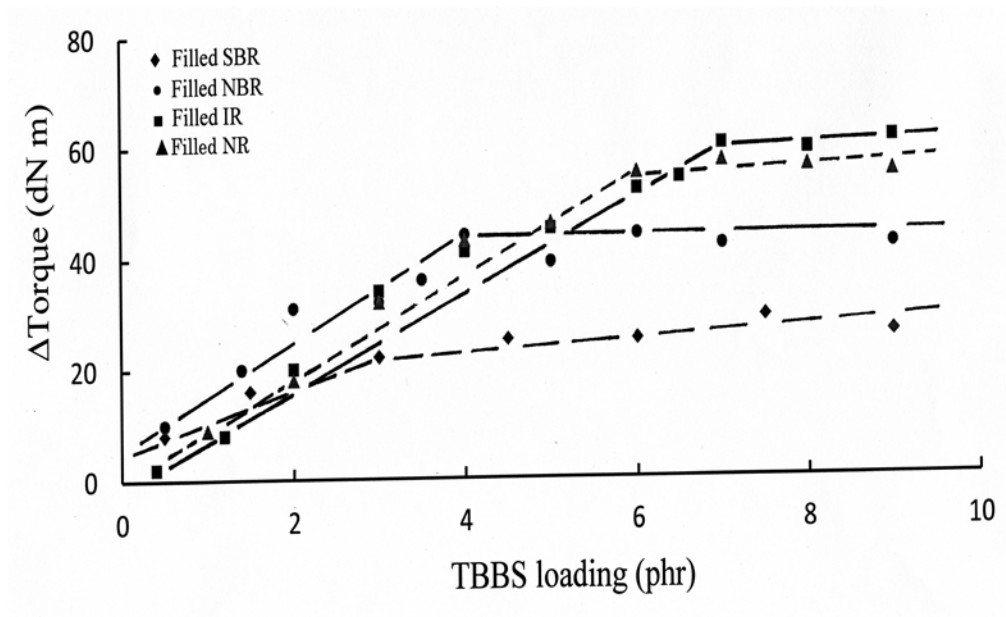


Figure 3 – Δ torque vs TBBS loading for the SBR, IR, NBR and NR rubber compounds. Each point on the figure corresponds to one compound.

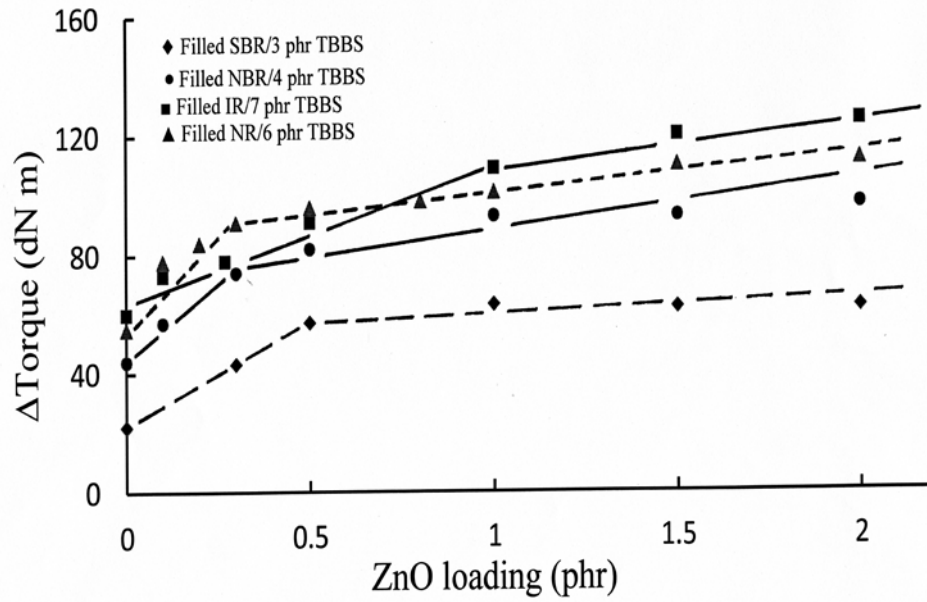


Figure 4 – Δ torque versus zinc oxide loading for the silica-filled SBR, IR, NBR and NR rubber compounds with TBBS.

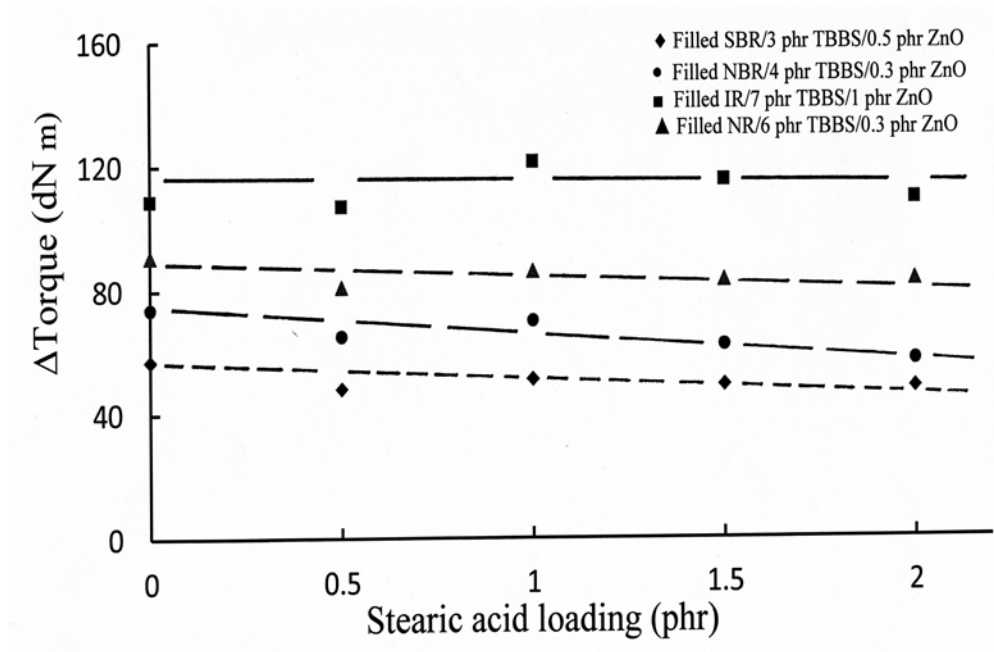


Figure 5 – Δ torque vs. stearic acid loading for the SBR, IR, NBR, and NR rubber compounds with TBBS and ZnO.