

# Comparing Effects of Silanized Silica Nanofiller on the Crosslinking and Mechanical Properties of Natural Rubber and Synthetic Polyisoprene

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**ABSTRACT:** The effect of the same amount of precipitated silica nanofiller on the curing and mechanical properties of natural rubber and synthetic polyisoprene was investigated. The silica surfaces were pretreated with bis(3-triethoxysilylpropyl) tetrasulfide (TESPT) to chemically bond silica to rubber. The rubbers were primarily cured by using sulfur in TESPT, and the cure was optimized by the addition of accelerator and activator, which helped to form sulfur chemical bonds between the rubber and filler. Different amounts of accelerator and activator were needed to fully crosslink the filled rubbers. The hardness, tensile

strength, elongation at break, stored energy density at break, tearing energy, and modulus of the vulcanizates improved substantially by the incorporation of the filler in the rubber. This was due to high level of rubber-filler adhesion and formation of chemical bonds between the rubber and TESPT. Interestingly, natural rubber benefited more from the filler than did synthetic polyisoprene. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 869–881, 2008

**Key words:** rubber; silicas; dispersions; crosslinking; mechanical properties

## INTRODUCTION

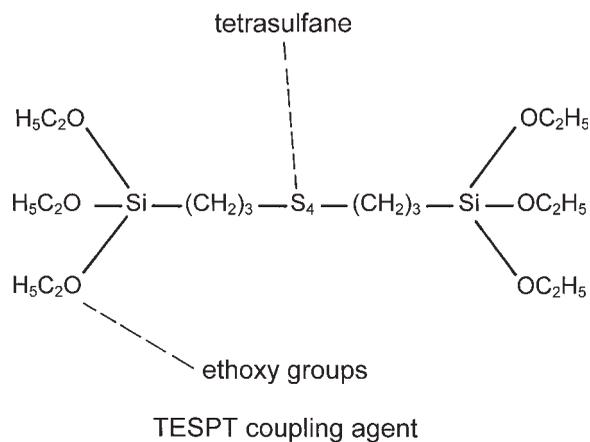
On tapping the *Hevea brasiliensis* tree, natural rubber latex exudes, which has a rubber content between 25 and 40% by weight. The solid rubber or *cis*-1-4 polyisoprene (NR) is extracted from the latex. The useful properties of NR include high gum and tear strength, high abrasion resistance, long flex life, and high resilience. Because of these excellent properties, NR is used in many industrial applications for example, tires, belting, antivibration mountings, and bridge bearings. Synthetic polyisoprene (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.<sup>1</sup>

Raw rubbers often possess weak mechanical properties and must be reinforced with fillers. Reinforcement increases properties for example hardness, abrasion resistance, and tensile strength. Carbon blacks, synthetic silicas, quartz, and metal oxides, which have large surface areas ranging from 150 to 400 m<sup>2</sup>/g are very effective in improving the rubber properties.<sup>2</sup> The major disadvantage of silicas is their acidity<sup>3</sup> and polarity,<sup>4</sup> which is caused by the presence of silanol groups on the silicas surfaces. This causes unacceptably long cure times and slow cure rates,<sup>5</sup> and also loss of crosslink density in sulfur-cured rubbers.<sup>6</sup> Moreover, processing becomes more difficult when a large amount of silica is added, because the viscosity increases significantly.<sup>7,8</sup> The availability of the coupling agent bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT) has provided a better opportunity for using synthetic silicas to crosslink and reinforce rubbers. TESPT possesses tetrasulfane and ethoxy reactive groups (Scheme 1). The tetrasulfane groups react with the rubber in the presence of accelerators at elevated temperatures, that is, 140–240°C, with or without elemental sulfur being present to form crosslinks in unsaturated rubbers. The ethoxy groups react with the silanol groups on the surfaces of silicas to form stable filler/TESPT bonds. Moreover, the number of silanol groups decreases after reaction with TESPT, and the remaining groups

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**Scheme 1** TESPT coupling agent.

become less accessible to the rubber because of steric hindrance.<sup>5</sup> This weakens the strong interaction between silica particles,<sup>5</sup> which reduces the viscosity of rubber compounds, and also improves cure properties by preventing acidic silicas from interfering with the curing reactions in sulfur-cured rubbers. It has been reported<sup>9</sup> that TESPT is a satisfactory property promoter in silica/NR composites through C—S bonding with rubber molecules.

Precipitated silica pretreated with TESPT is classified as a “crosslinking filler.” Parker and KOENIG<sup>10</sup> evaluated the effects of silane-pretreated silica, and silica and liquid silane mixture on the crosslink density of a sulfur-cured rubber and concluded that the rubber with silane pretreated silica had a higher crosslink density and increased filler-rubber adhesion. Ansarifard and coworkers<sup>11,12</sup> carried out a similar study and reached to the same conclusion. They also found that the mechanical properties of rubber improved more substantially with TESPT-pretreated silica.

The aim of this study was to crosslink and reinforce the mechanical properties of NR and IR rubbers with the same loading of TESPT pretreated silica and to determine whether IR could replace NR and retain the benefits of the filler for the properties. The bound rubber content and crosslink density of the rubbers were also measured to assess the extent of rubber-filler adhesion and chemical bonding between the rubber and filler, respectively.

## EXPERIMENTAL

### Materials-rubber, filler, and rubber chemicals

The raw rubbers used were standard Malaysian natural rubber grade L (98 wt % *cis*-1-4 content) and synthetic polyisoprene (minimum 96 wt % *cis*-1-4 content; Kraton IR-307, Kraton Polymers). The rein-

forcing filler was Coupsil 8113 (Degussa, Hanau, Germany). Coupsil 8113 is precipitated amorphous white silica-type Ultrasil VN3 surfaces of which had been pretreated with TESPT. 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.

### Curing chemicals, antidegradants, and processing oil

In addition to the raw rubbers and filler, the other ingredients were *N*-*t*-butyl-2-benzothiazole sulfenamide (Santocure TBBS, Woluwe, Belgium; a safe-processing delayed action accelerator), zinc oxide (Harcros Durham Chemicals, UK; activator), stearic acid (Anchor Chemical, UK; activator), elemental sulfur (Solvay Barium Strontium, Hannover, Germany; curing agent), *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (Santoflex 13, Brussels, Germany; antidegradant). The cure system consisted of TBBS, zinc oxide, stearic acid, and elemental sulfur. TBBS, zinc oxide, and stearic acid were added to optimize the chemical bonding or crosslinks between the rubber and filler. In total, 58 compounds were prepared for this study.

### Mixing

The compounds were prepared in a Haake Rheocord 90 (Berlin, Germany), a small size laboratory mixer with counter rotating rotors. In these experiments, the Banbury rotors and the mixing chamber were maintained at 24 and 48°C for making the IR and NR compounds, respectively, and the rotor speed was 45 rpm. The volume of the mixing chamber was 78 cm<sup>3</sup>, and it was half full. Haake Software Version 1.9.1. was used for controlling the mixing condition and storing data.

### Assessment of the silica dispersion in the rubbers

To select a suitable mixing time for incorporating the filler in the rubber, the rubber and filler were mixed together for different times. The filler was introduced first in the mixer, and then the raw rubber was added. The filler was added when the viscosity of the rubber was still relatively high, which lead to an improved dispersion.<sup>13</sup> Following the previous findings,<sup>14</sup> the mixing time was increased to 17 min to disperse the silica particles fully in the rubber. The temperature of the rubber compounds during mixing was 50–62°C. Twenty-four hours after mixing ended, the rubbers were examined in 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

**TABLE I**  
Formulations and ODR Test Results for the NR Compounds with an Increasing Loading of TBBS

	Compound										
	1	2	3	4	5	6	7	8	9	10	11
Formulation (phr) TBBS	1	2	3	4	5	6	7	7.5	8	9	10
ODR results											
Minimum torque (dN m)	27	29	28	26	26	26	24	21	21	21	18
Maximum torque (dN m)	36	47	60	69	72	81	81	77	76	77	79
$\Delta$ torque (dN m)	9	18	32	43	46	55	57	56	55	56	61

Formulation: 100 phr NR and 60 phr silica. The compound temperature rose to 48–85°C during mixing.

SEM. Small pieces of the uncured rubber were placed in liquid nitrogen for 3 min and then fractured to create two fresh surfaces. The samples, 60 mm<sup>2</sup> in area and 5 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 SEM photographs. After the SEM photos were examined, suitable mixing times were used for adding the filler to the rubbers.

#### Addition of TBBS to the filled NR and IR rubbers

To activate the rubber reactive tetrasulfane groups of TESPT, TBBS was added. The loading of TBBS in the rubber 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 rubbers (compounds 1–22; Tables I and II). The formation of crosslinks strengthened the rubber/TESPT interaction.<sup>5</sup>

#### Addition of zinc oxide to the filled NR and IR rubbers with TBBS

The loading of zinc oxide in the filled rubbers with TBBS was raised to 2 phr to determine the amount needed to maximize the efficiency of TBBS and cure (compounds 23–38; Tables III and IV).

#### Addition of stearic acid to improve the cure of the filled rubbers with TBBS and zinc oxide

Stearic acid is a fatty acid that is added to improve the solubility of zinc oxide in rubber. The loading of stearic acid in the filled rubbers with TBBS and zinc oxide was increased to 2 phr to measure the amount needed to optimize the efficiency of the accelerator and cure (compounds 39–48; Table V).

#### Addition of elemental sulfur to the filled NR rubber with TBBS and zinc oxide

To evaluate the effect of elemental sulfur on the cure properties of the filled NR compound with TBBS and zinc oxide, five compounds were prepared. The loading of sulfur in the rubber was increased to 2 phr (compounds 49–53; Table VI).

After these measurements were completed, three NR and two IR compounds were prepared for further tests (compounds 54–58; Table VII). The control compounds (compounds 54 and 57; Table VII) were made through the addition of 1.5 phr elemental sulfur, TBBS, zinc oxide, and Santoflex 13 to the rubbers. The amount of elemental sulfur in the control compounds was the same as the 2.5 wt % sulfur concentration in TESPT. A similar procedure was used for preparing the filled compounds, and before the mixing started, the filler was placed in the mixing chamber, and then the raw rubber was added. To prepare the NR compounds, TBBS, zinc oxide, ste-

**TABLE II**  
Formulations and ODR Test Results for the IR Compounds with an Increasing Loading of TBBS

	Compound										
	12	13	14	15	16	17	18	19	20	21	22
Formulation (phr) TBBS	0.4	1.2	2	3	4	5	6	6.5	7	8	9
ODR results											
Minimum torque (dN m)	29	36	31	28	27	24	22	22	19	21	19
Maximum torque (dN m)	31	44	51	62	68	69	74	76	79	80	80
$\Delta$ torque (dN m)	2	8	20	34	41	45	52	54	60	59	61

Formulation: 100 phr IR and 60 phr silica. The compound temperature rose to 24–56°C during mixing.

**TABLE III**  
Formulations and ODR Test Results for the NR Compounds with an Increasing Loading of Zinc Oxide

	Compound								
	23	24	25	26	27	28	29	30	31
Formulation (phr) Zinc oxide	0	0.1	0.2	0.3	0.5	0.8	1	1.5	2
ODR results									
Minimum torque (dN m)	26	24	23	23	24	22	24	24	24
Maximum torque (dN m)	81	102	107	114	120	120	125	134	136
$\Delta$ torque (dN m)	55	78	84	91	96	98	101	110	112

Formulation: 100 phr NR, 60 phr silica, and 6 phr TBBS. The Compound temperature rose to 48–74°C during mixing.

aric acid, sulfur, and Santoflex were added 13 min after the filler and rubber were mixed together, and mixing continued subsequently for an extra 3 min before the rubber compound was removed from the mixer. To prepare the IR compounds, the rubber and filler were mixed together for 17 min, and then the curing additives and Santoflex were added and mixed for an extra 3 min before the rubber compound was removed from the mixer. The temperature of the rubber compounds during mixing was 23–85°C.

Finally, when the mixing was ended, the rubber was recovered from the mixer and milled to a thickness of about 6 mm for further work. The compounds were stored at ambient temperature ( $\sim 23^\circ\text{C}$ ) for at least 24 h before their viscosity and cure properties were measured.

#### 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 the British Standard.<sup>15</sup> 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°C  $\pm 2^\circ\text{C}$  by an oscillating disc rheometer curemeter (Monsanto, Swindon, UK) at an angular displacement of  $\pm 3^\circ$  and a test frequency of 1.7 Hz.<sup>16</sup> The cure rate index, which is a measure of the

rate of cure in the rubber, was calculated using the method described in the British Standard.<sup>17</sup> The rheometer tests ran for up to 3 h. The cure traces of the compounds that were subsequently used in this study are shown in Figure 1. Results from these experiments were also summarized in Tables I–VII.  $\Delta$ 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<sup>6</sup> was subsequently plotted against the loading of TBBS, zinc oxide, stearic acid, and elemental sulfur.

#### Test pieces and test procedure

After these measurements were completed, the rubber compounds were cured in a compression mold at 140°C with a pressure of 11 MPa. Pieces of rubber, each  $\sim 140$  g in weight, were cut from the milled sheet. Each piece was placed in the center 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 23 cm  $\times$  23 cm by  $\sim 2.4$  mm thick were used, from which the various samples for further tests were cut.

#### Bound rubber and crosslink density measurement

The solvent used for the bound rubber and crosslink density determination was toluene. For the determi-

**TABLE IV**  
Formulations and ODR Test Results for the IR Compounds with an Increasing Loading of Zinc Oxide

	Compound						
	32	33	34	35	36	37	38
Formulation (phr) Zinc oxide	0	0.1	0.27	0.5	1	1.5	2
ODR results							
Minimum torque (dN m)	19	22	24	23	24	23	23
Maximum torque (dN m)	79	95	102	114	133	143	148
$\Delta$ torque (dN m)	60	73	78	91	109	120	125

Formulation: 100 phr IR, 60 phr silica, and 7 phr TBBS. The compound temperature rose to 23–55°C during mixing.

**TABLE V**  
**Formulations and ODR Test Results for the NR and IR Compounds with an Increasing Loading of Stearic Acid**

	Compound									
	39	40	41	42	43	44	45	46	47	48
Formulation (phr) Stearic acid	0	0.5	1	1.5	2	0	0.5	1	1.5	2
ODR results										
Minimum torque (dN m)	23	22	21	20	21	24	20	21	19	17
Maximum torque (dN m)	114	103	107	103	104	133	127	142	134	126
$\Delta$ torque (dN m)	91	81	86	83	83	109	107	121	115	109

Formulations: 100 phr NR, 60 phr silica, 6 phr TBBS, and 0.3 phr zinc oxide (compounds 39–43); 100 phr IR, 60 phr silica, 7 phr TBBS, and 1 phr zinc oxide (compounds 44–48). The NR compound temperature rose to 48–77°C during mixing. The IR compound temperature rose to 24–56°C during mixing.

nation, 1.7 g (control compound) and 2 g (filled compound) of the rubber compounds were cured in a compression mold to produce cylindrical samples, 15.6 mm in diameter and 9.5 mm in height. The samples were then placed individually in 70 mL of the solvent in labeled bottles and allowed to swell for 16 days at 21°C. The weight of the samples was measured every day until it reached an equilibrium. It took ~ 8 days for the control compound and 5 days for the filled compounds 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 reweighed. The bound rubber and crosslink density were then calculated using the expressions in refs. 18 and 19, respectively (Table VIII).

### Hardness

For measuring the hardness of the rubbers, cylindrical samples 12 mm thick and 28 mm in diameter, were used. 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 measured at 23.5°C over a 15-s interval after which a reading was taken. This was repeated at three different positions on the sample,

and the median of the three readings was calculated (Table VIII).<sup>20</sup>

### Cohesive tear strength

Rectangular strips, 100 mm long and 30 mm wide, were cut from the cured sheets of rubber and a sharp crack, ~ 30 mm in length, was introduced into the strips half way along the width and parallel to the length of the strip, to form the trouser test pieces for the tear experiments. The tear tests were performed at an angle of 180°, at ambient temperature (21°C) and at a constant cross-head speed of 50 mm/min<sup>21</sup> in a Lloyd mechanical testing machine (Hampshire, UK). The tears produced in the rubber after the test pieces were fractured were 14–79 mm in length. In each experiment, the tearing force was recorded to produce traces from which an average force was measured. The first peak corresponds to the onset of crack growth, where the tearing force was still rising, and the last peak corresponds to when test stopped or the sample broke. These were not considered. The remaining peaks on the trace were used for calculating an average tearing force for the rubber (Fig. 2). In some cases, the test produced only one peak from which a tearing force was calculated (Fig. 3). For each rubber, five test pieces were used. Details of the tear tests and tear behavior

**TABLE VI**  
**Formulations and ODR Test Results for the NR Compounds with an Increasing Loading of Elemental Sulfur**

	Compound				
	49	50	51	52	53
Formulation (phr) Elemental sulfur	0	0.5	1	1.5	2
ODR results					
Minimum torque (dN m)	23	26	26	25	25
Maximum torque (dN m)	114	119	124	134	130
$\Delta$ torque (dN m)	91	93	98	109	105

Formulation: 100 phr NR, 60 phr silica, 6 phr TBBS, and 0.3 phr zinc oxide. The compound temperature rose to 47–70°C during mixing.

**TABLE VII**  
Formulations, Mooney Viscosity, and Cure Properties of the NR and IR Compounds

	Compound				
	54*	55	56	57*	58
Formulation (phr)					
NR	100	100	100	–	–
IR	–	–	–	100	100
Silanized silica	–	60	60	–	60
TBBS	6	6	6	7	7
Zinc oxide	0.3	0.3	0.3	1	1
Elemental sulfur	1.5	1.5	0	1.5	0
Santoflex 13	1	1	1	1	1
Mooney viscosity ML(1 + 4) at 100°C	49	111	106	44	105
ODR results					
Minimum torque (dN m)	12	27	26	16	26
Maximum torque (dN m)	71	135	107	78	137
$\Delta$ torque (dN m)	59	108	81	62	111
$t_{s2}$ (min)	24	6	9	27	8
$t_{95}$ (min)	34	9	27	159	34
Cure rate index (min <sup>-1</sup> )	10	33	5.6	0.8	3.9

The NR compounds temperature rose to 44–77°C during mixing. The IR compounds temperature rose to 24–54°C during mixing. The control compounds are 54\* and 57\*. The viscosity of the raw NR and IR rubbers were 97 and 69 MU, respectively.

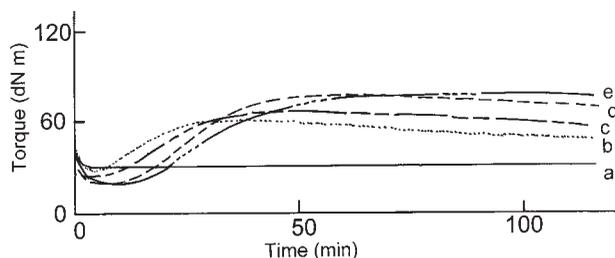
of the rubber are shown in Table IX. After these measurements were completed, and following the procedure described previously,<sup>22</sup> the force values were placed in eq. (1):

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

where  $F$  is the force and  $t$  the thickness of the test piece to calculate tearing energies,  $T$ , for the rubbers. The median values of the tearing energies were subsequently noted (Table VIII).

### Tensile properties

The tensile stress, elongation at break, and stored energy density at break of the rubbers were determined in uniaxial tension in a Lloyd mechanical testing machine, using dumbbell test pieces 75 mm long



**Figure 1** Typical torque versus time traces by ODR for the filled compounds. Data for the filled IR rubber compounds with (a) 0.4 phr TBBS, (b) 3 phr TBBS, (c) 5 phr TBBS, (d) 7 phr TBBS, and (e) 9 phr TBBS.

with a central neck 25 mm long and 3.6 mm wide. The test pieces were die stamped from the sheets of cured rubber. The tests were performed at 21°C and at a cross-head speed of 50 mm/min.<sup>23</sup> Lloyd DAP-MAT computer software was used for storing and processing the data (Table VIII).

### Loss tangent (tan $\delta$ )

Tan  $\delta$  is the ratio between loss modulus and elastic modulus. The loss modulus represents the viscous component of modulus and includes all the energy dissipation processes during dynamic strain. The tan  $\delta$  was measured in DMAQ800 model CFL-50 (TA Instruments), using Universal Analysis 2000 Software Version 4.3A. Test pieces 35 mm long, 13 mm wide, and  $\sim$  2.40 mm thick were used. The tests were performed at 1 and 20 Hz frequencies. The samples were deflected by 256  $\mu$ m (nominal peak to peak displacement) during the test, and the sample temperature was raised from  $-80$  to  $100^\circ\text{C}$  at  $3^\circ\text{C}/\text{min}$  steps.

### Modulus at different strain amplitudes

The modulus of the vulcanizates was measured at 100, 200, and 300% strain amplitudes in uniaxial tension, using dumbbell test pieces. The tests were carried out at ambient temperature ( $\sim 28^\circ\text{C}$ ) at a cross head speed of 50 mm/min in a HT Hounsfield mechanical testing machine (Hounsfield, Surrey, UK). QMAT-DONGLE version 2003 computer software was used to process the data (Table VIII).

**TABLE VIII**  
**Crosslink Density, Bound Rubber, and Mechanical Properties of the NR and IR Rubber Vulcanizates**

	Compound				
	54*	55	56	57*	58
Hardness (Shore A)	52	77	75	42	80
Tensile strength (MPa)	18	34	37	1.2	17
Elongation at break (%)	1100	700	837	139	404
Stored energy density at break (MJ/m <sup>3</sup> )	59	109	137	0.95	33
<i>T</i> (kJ/m <sup>2</sup> )	15	57	58	0.7	17
Range of values	11–20	29–66	46–95	0.6–0.9	10–23
Bound rubber (%)	–	94	94	–	93
Crosslink density (mol/m <sup>3</sup> )	91	163	149	111	211
Modulus at different strain amplitudes (MPa)					
Strain amplitude (%)					
100	0.54	3.15	2.23	0.63	3.0
200	0.44	4.83	3.16	–	3.7
300	0.54	5.32	4.23	–	4.3

The control NR and IR compounds were 54\* and 57\*, respectively.

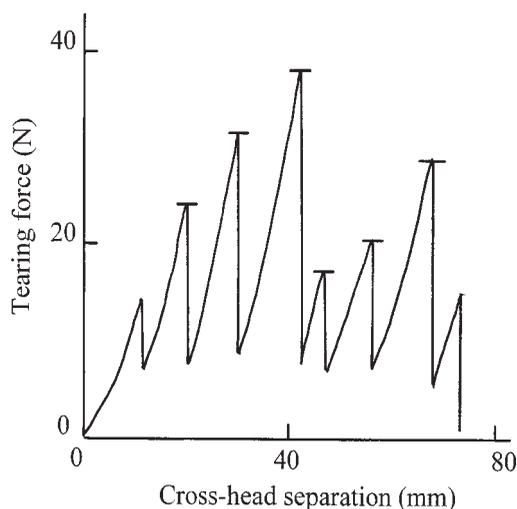
Definitions: mega pascal (MPa), millijoules/meter<sup>3</sup> (MJ/m<sup>3</sup>), killojoules/meter<sup>2</sup> (kJ/m<sup>2</sup>), mole/cubic meter (mol/m<sup>3</sup>), cubic millimeter/milligram (mm<sup>3</sup>/mg).

## RESULTS AND DISCUSSION

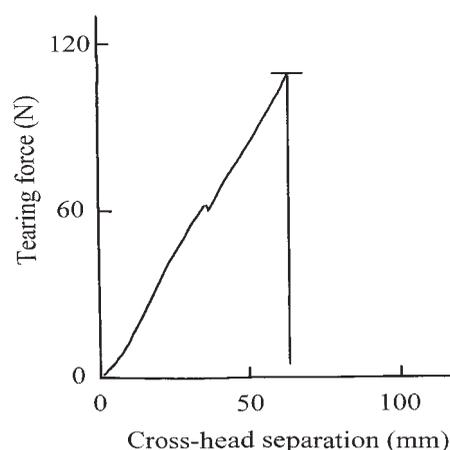
### Silica dispersion and effect of the filler on the rubber viscosity

As mentioned earlier, to disperse the silica particles fully in the rubbers, the mixing time was increased to 17 min. Large silica aggregates were seen in the rubber matrix after short mixing times, for example, 8 min (Fig. 4), and the filler dispersion improved as mixing time was increased to 17 min for the IR rubber (Fig. 5) and 13 min for the NR rubber (Fig. 6). There were also regions of high silica concentration in the IR rubber [Fig. 5(a)]. However, when these regions were examined at high magnifications [Fig. 5(b)], the silica particles were fully dispersed, and

the size of the particles was down to about 60 nm. This was similar to the actual particle size of the filler, 20–54 nm, before it was mixed with the rubber. It was concluded that minimum mixing times of 13 and 17 min were sufficient to fully disperse the silica particles in the NR and IR rubbers, respectively. The full dispersion of the silica particles in the rubber helped to maximize the reinforcing effect of the filler on the mechanical properties of the vulcanizates.<sup>24</sup> Long mixing time breaks down the rubber and causes a reduction in its molecular weight and viscosity.<sup>13,25</sup> The reduction is due to chain scission<sup>26,27</sup> 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. The viscosity of the NR rubber increased from 97 (raw rubber) to 106



**Figure 2** Typical record of the tearing force as a function of crosshead separation. Data for compound 58 in Table VIII;  $T = 20$  kJ/m<sup>2</sup>.



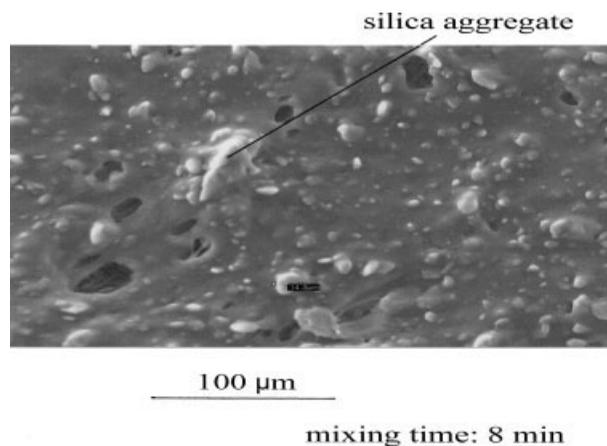
**Figure 3** Typical record of the tearing force as a function of crosshead separation. Data for compound 56 in Table VIII;  $T = 95$  kJ/m<sup>2</sup>.

**TABLE IX**  
**Details of the Tear Tests and Tear Behavior of the NR and IR Rubber Vulcanizates**

Rubber	$T$ (kJ/m <sup>2</sup> )	Tear path	Tear length after test piece was fractured (mm)
Compound 54*			
Test piece			
1	11	—*	—*
2	14	A	79
3	15	A	40
4	15	A	77
5	20	A	53
Compound 55			
Test piece			
1	29	B	18
2	46	B	17
3	59	B	15
4	67	C	15
5	71	B	16
Compound 56			
Test piece			
1	46	B	35
2	49	B	30
3	53	B	28
4	72	B	18
5	95	B	19
Compound 57*			
Test piece			
1	0.6	A	27
2	0.6	A	35
3	0.7	A	38
4	0.8	A	28
5	0.9	A	35
Compound 58			
Test piece			
1	10	A	18
2	12	B	14
3	17	A	35
4	20	A	33
5	23	D	35

Definitions for the tear path: A = crack turned slowly to the edge of the test piece as it propagated ( $\int$ ); B = crack turned sharply to the edge of the test piece immediately after growth started ( $\int$ ); C = crack turned in a semi circular path as soon as it started to grow, forming knotty tearing ( $\int$ ); D = crack grew linearly parallel to the edges of the test piece all the way ( $\int$ ). Compounds 54\* and 57\* were the control NR and IR compounds, respectively.

MU when the filler and curing chemicals were added (compound 56; Table VII). The inclusion of 1.5 phr elemental sulfur into the filled NR compound increased the viscosity from 106 to 111 MU (cf. compounds 56 with compound 55; Table VII). The control NR compound had a viscosity of 49 MU (compound 54; Table VII). Viscosity increases when additives such as fillers, elemental sulfur, and activators are mixed with NR.<sup>13</sup> When the filler and curing additives were incorporated in the IR rubber, the viscosity increased from 69 (raw rubber) to 105 MU (compounds 58; Table VII). The control IR compound had a viscosity of 44 MU (compound 57;

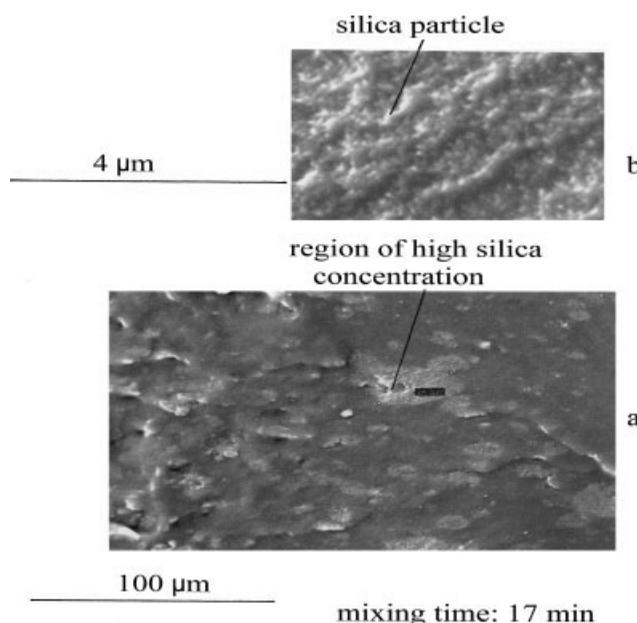


**Figure 4** SEM photograph showing the dispersion of the silica in the rubber. Data for the IR rubber. Mixing time = 8 min with poor dispersion.

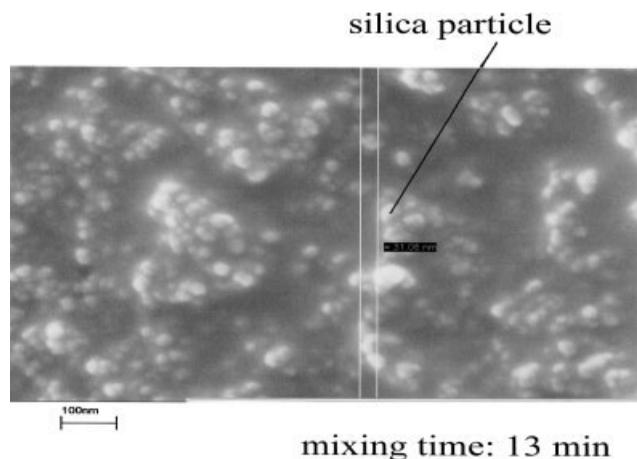
Table VII). At low shear rates, which occur during the determination of Mooney viscosity, differences in macrostructure between the IR and NR rubbers play a major role.<sup>28</sup> In addition, if the viscometer measures values well above 80 MU, it can be somewhat insensitive to subtle differences among raw rubbers or mixed compounds.<sup>29</sup> Therefore, the results must be treated with caution.

#### Effect of TBBS on the $\Delta$ torque of the filled rubbers

Figure 7 shows  $\Delta$ torque as a function of TBBS loading for the filled NR and IR compounds. For the filled NR compound,  $\Delta$ torque increased from 9 to



**Figure 5** SEM photograph showing the dispersion of the silica particles in the rubber. Data for the IR rubber. Mixing time = 17 min with good dispersion.

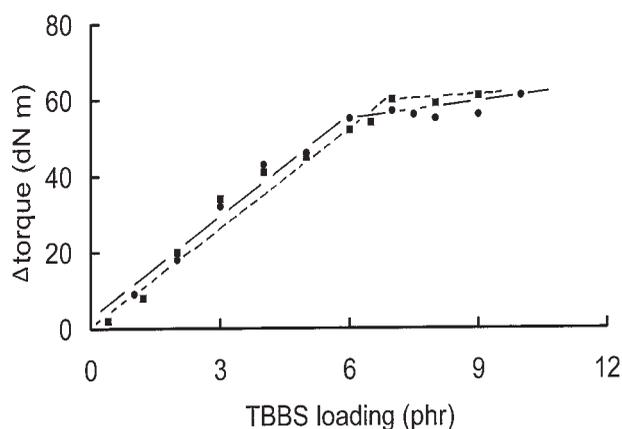


**Figure 6** SEM photograph showing the dispersion of the silica particles in the rubber. Data for the NR rubber. Mixing time = 13 min with good dispersion.

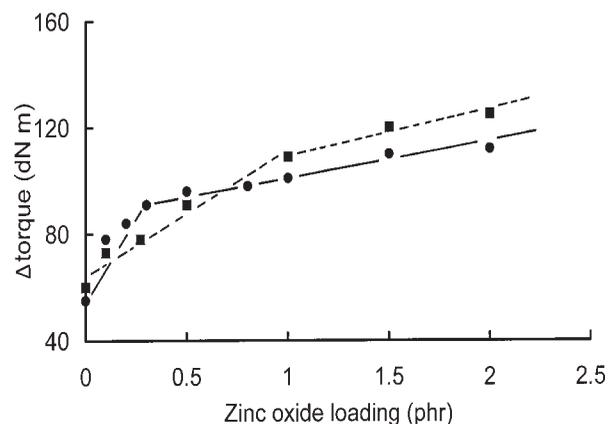
55 dN m as the loading of TBBS was raised to 6 phr, and it continued rising at a much slower rate to about 61 dN m when the loading of TBBS reached 10 phr. For the filled IR compound,  $\Delta$ torque increased to about 60 dN m as the loading of TBBS reached 7 phr and remained at this level thereafter, when the amount of TBBS was raised to 9 phr. Evidently, the addition of 6 phr and 7 phr TBBS to the filled NR and IR compounds, respectively, was sufficient to react the rubber reactive tetrasulfane groups of TESPT with the rubbers to form crosslinks and to optimize the chemical bonding between the two.

#### Effect of zinc oxide and stearic acid on the efficiency of TBBS and cure of the filled rubbers

Zinc oxide was added to improve the efficiency of TBBS in the filled rubbers.  $\Delta$ torque for the filled NR with 6 phr TBBS increased sharply to 91 dN m



**Figure 7**  $\Delta$ torque versus TBBS loading for the filled NR and IR compounds: (●) NR, (■) IR.

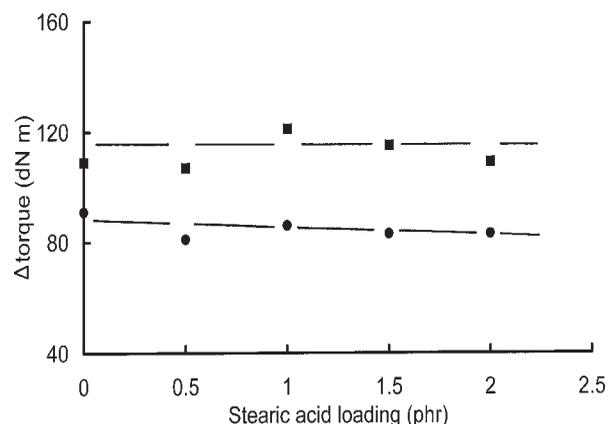


**Figure 8**  $\Delta$ torque versus zinc oxide loading for the filled NR with 6 phr TBBS and filled IR with 7 phr TBBS: (●) NR, (■) IR.

when 0.3 phr zinc oxide was included, and it continued rising at a much slower rate to 112 dN m when the loading of zinc oxide reached 2 phr (Fig. 8). For the filled IR compound with 7 phr TBBS (Fig. 8),  $\Delta$ torque increased slowly to 109 dN m when the amount of zinc oxide was raised to 1 phr. Further increases in the loading of zinc oxide had little effect on  $\Delta$ torque, which rose to 125 dN m.

It emerged that the addition of 0.3 phr and 1 phr zinc oxide was sufficient to maximize the efficiency of TBBS in the filled NR and IR rubbers with TBBS, respectively, and to optimize further the chemical bonding between TESPT and the rubber.

When up to 2 phr stearic acid was incorporated in the filled NR with 6 phr TBBS and 0.3 phr zinc oxide,  $\Delta$ torque decreased from 91 to about 83 dN m (Fig. 9). A similar trend was also seen for the filled IR with 7 phr TBBS and 1 phr zinc oxide (Fig. 9). For this rubber,  $\Delta$ torque remained almost constant at about 110 dN m, when the full loading of stearic



**Figure 9**  $\Delta$ torque versus stearic acid loading for the filled NR with 6 phr TBBS and 0.3 phr zinc oxide and filled IR with 7 phr TBBS and 1 phr zinc oxide: (●) NR, (■) IR.

acid was added. It was concluded that the addition of stearic acid had no potential benefit to  $\Delta$ torque and the chemical bonding between the filler and rubber.

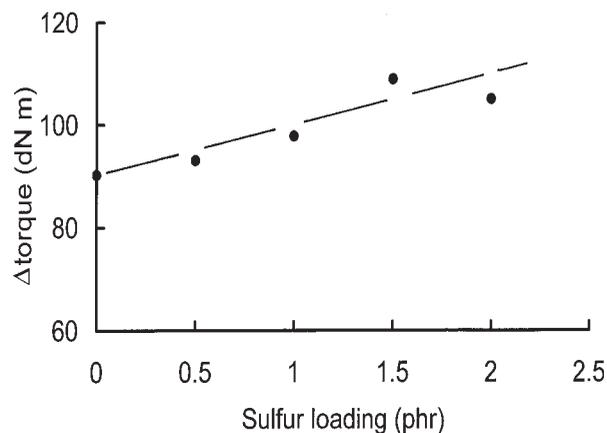
#### Effect of silanized silica on the curing behavior of the rubbers

When silanized silica was added to the NR compound (cf. compounds 54 and 56; Table VII), the optimum cure time,  $t_{95}$ , decreased from 34 to 27 min, and the rate of cure slowed down, with the cure rate index decreasing from 10 to  $5.6 \text{ min}^{-1}$ . In addition, the scorch time,  $t_{s2}$ , shortened from 24 to 9 min, and  $\Delta$ torque rose from 59 to 81 dN m. As shown in Table VIII, the crosslink density increased from 91 to  $149 \text{ mol/m}^3$  for compounds 54 and 56, respectively, which was consistent with the increases in  $\Delta$ torque. Similarly, the inclusion of silanized silica in the IR compound reduced the scorch and optimum cure times from 27 to 8 min, and 159 to 34 min, respectively, (cf. compound 57 and compound 58; Table VII). The cure rate index also increased from 0.8 to  $3.9 \text{ min}^{-1}$  and  $\Delta$ torque from 62 to 111 dN m. The crosslink density rose from 111 to  $211 \text{ mol/m}^3$  for these two compounds, which was in line with the increases recorded for  $\Delta$ torque. The benefits to the cure properties were due to the 2.5 wt % sulfur content of TESPT.<sup>5,30</sup> The longer scorch and optimum cure times and slow cure rate of the IR compounds were due to the absence of proteins, which are normally present in NR and are beneficial to cure.<sup>1</sup> (cf. compound 57 with compound 54, and compound 58 with compound 56; Table VII).

Please note, the cure rate index was calculated using  $100/(t_{95} - t_{s2})$ .<sup>16,17</sup> For compounds 54 and 56, the difference between the optimum cure and scorch times were 10 and 18 min, and this produced a reduction in the cure rate index from 10 to  $5.6 \text{ min}^{-1}$ , respectively. However, for compounds 57 and 58, the difference between the optimum cure and scorch times was 132 and 26 min, which caused the cure rate index to increase from 0.8 to  $3.9 \text{ min}^{-1}$ , respectively. The filler was more beneficial to the cure properties of the filled IR rubber.

#### Effect of elemental sulfur on the curing behavior of the filled NR rubber

The addition of elemental sulfur to the filled NR compound affected its cure characteristics (cf. compound 56 with compound 55; Table VII).  $t_{s2}$  and  $t_{95}$  decreased from 9 to 6 min and 27 to 9 min, respectively. The rate of cure increased, with the cure rate index rising from  $5.6$  to  $33 \text{ min}^{-1}$ , and  $\Delta$ torque rose from 81 to 108 dN m. The latter indicated a significant increase in the crosslink density of the rubber,



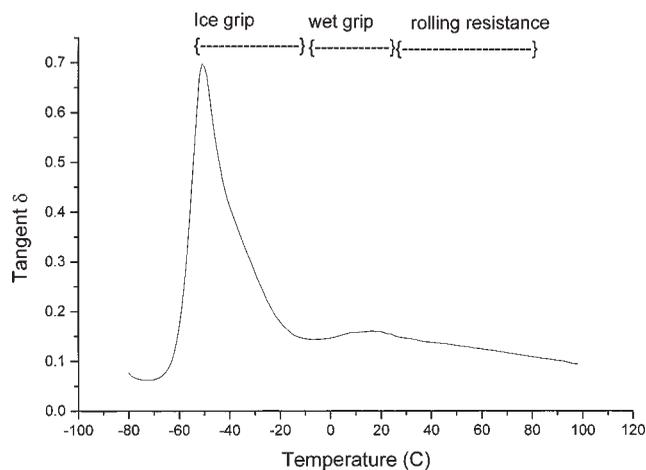
**Figure 10**  $\Delta$ torque versus sulfur loading for the filled NR with 6 phr TBBS and 0.3 phr zinc oxide.

and as shown in Table VIII, the crosslink density did increase from 149 to  $163 \text{ mol/m}^3$ .  $\Delta$ torque also increased as a function of sulfur loading (Fig. 10). When elemental sulfur is added to rubber filled with silanized silica, scorch, and optimum cure times decrease and rate of cure and crosslink density increase.<sup>31</sup> Our results confirmed the previous findings.

#### Effect of silica on the mechanical properties of the cured rubbers

The addition of the filler influenced the mechanical properties of the NR vulcanizates (cf. compound 54 with compound 56; Table VIII). The hardness and tensile strength increased from 52 to 75 Shore A and from 18 to 37 MPa, respectively. The modulus increased by a factor of four at 100% strain and approximately by a factor of eight at 200–300% strain amplitudes. This indicated a much stiffer rubber because of the filler. Similarly,  $T$  and stored energy density at break were also up from 15 to  $58 \text{ kJ/m}^2$  and from 59 to  $137 \text{ MJ/m}^3$ , respectively, but elongation at break decreased from 1100% to 837% when the filler was added.

For the IR rubber, a similar behavior was also observed. The hardness and tensile strength increased from 42 to 80 Shore A and from 1.2 to 17 MPa, respectively, (cf. compound 57 with compound 58; Table VIII). The modulus rose approximately by a factor of five at 100% strain, but it was not possible to measure the increase at higher strain amplitudes because the control compound (compound 57) fractured at less than 200% strain amplitude. The elongation at break increased from 139 to 404%, and properties related to fracture such as  $T$  and stored energy density at break were also up from 0.7 to  $17 \text{ kJ/m}^2$  and from 0.95 to  $33 \text{ MJ/m}^3$ , respectively.



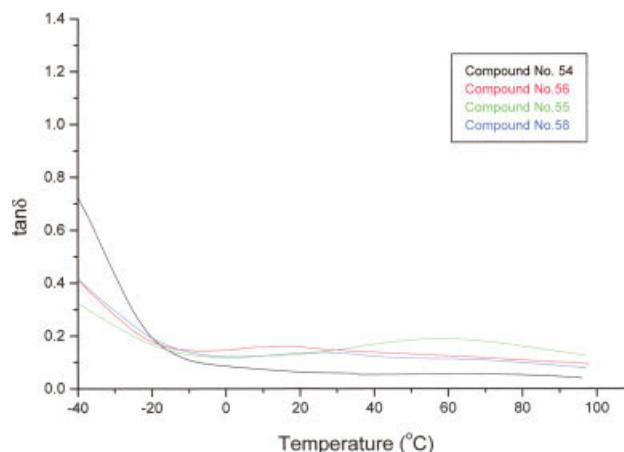
**Figure 11**  $\tan \delta$  versus temperature at 1 Hz for compound 56 in Table VIII.

#### Effect of elemental sulfur on the mechanical properties of the filled NR rubber

The addition of elemental sulfur affected the mechanical properties of the filled NR compound, although there was no overall advantage, as some properties improved and others deteriorated (cf. compound 56 with compound 55; Table VIII). The hardness increased from 75 to 77 Shore A, and the modulus rose by up to 50% over a 300% increase in the strain amplitude.  $T$  remained almost unchanged at 57 kJ/m<sup>2</sup>. However, the remaining properties were adversely affected. For example, the tensile strength decreased from 37 to 34 MPa, elongation at break from 837 to 700%, and stored energy density at break from 137 to 109 MJ/m<sup>3</sup>.

#### Effect of elemental sulfur on the $\tan \delta$ of the rubbers

$\tan \delta$  was affected by the test temperature, test frequency, sulfur loading, and rubber composition. At 1 Hz, the  $\tan \delta$  for the filled NR compound (compound 56; Table VIII) increased sharply from 0.07 to 0.7 as the temperature was raised from  $-70$  to  $-50^\circ\text{C}$ .  $\tan \delta$  subsequently decreased to about 0.15 when the temperature reached  $-10^\circ\text{C}$  (Fig. 11), and it continued decreasing though at a much slower rate, to about 0.09 when the temperature was raised to  $100^\circ\text{C}$ . For high performance tires, a high  $\tan \delta$  value (high hysteresis) at low temperatures for example,  $-50$  to  $-30^\circ\text{C}$ , to obtain high-skid resistance and ice- and wet grip is essential.<sup>32</sup> A low  $\tan \delta$  value (low hysteresis) at high temperatures, that is,  $50$ – $80^\circ\text{C}$  to reduce rolling resistance and save energy and fuel is also required.<sup>32</sup> Compound 56 satisfied both of these requirements.



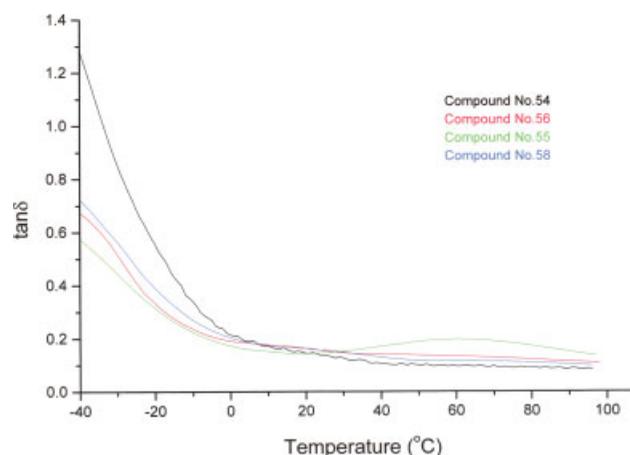
**Figure 12**  $\tan \delta$  versus temperature at 1 Hz for compounds 54–56 and 58 in Table VIII. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

#### Comparing the $\tan \delta$ of the filled NR and IR rubbers

At 1 Hz, the  $\tan \delta$  for the filled NR and IR compounds (cf. compound 56 with compound 58; Table VIII) decreased approximately from 0.40 to 0.10 as the temperature was increased from  $-40$  to  $100^\circ\text{C}$  (Fig. 12). A similar trend was also observed at 20 Hz, with  $\tan \delta$  decreasing from  $\sim 0.7$  to 0.16 as the temperature was raised from  $-40$  to  $30^\circ\text{C}$ .  $\tan \delta$  then dropped to 0.11 when the temperature was increased to  $100^\circ\text{C}$  (Fig. 13). At both frequencies, the  $\tan \delta$  values were almost the same for both compounds, irrespective whether NR or IR was used.

#### Effect of elemental sulfur on the $\tan \delta$ of the filled NR rubber

At 1 Hz, the  $\tan \delta$  for the filled NR compound with 1.5 phr elemental sulfur was 25% lower at  $-40^\circ\text{C}$



**Figure 13**  $\tan \delta$  versus temperature at 20 Hz for compounds 54–56 and 58 in Table VIII. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

than that of the filled NR compound (cf. compound 55 with compound 56; Table VIII). However, the difference between the  $\tan \delta$  values of the two compounds diminished as temperature was increased to 30°C. Thereafter, the filled NR compound with elemental sulfur showed a higher  $\tan \delta$  (Fig. 12). Interestingly, a similar trend was also seen at 20 Hz. At the lowest temperature, the addition of elemental sulfur to the filled NR compound reduced  $\tan \delta$  by 20%, but as the temperature was raised to 30°C, the difference disappeared (Fig. 13). However, as the temperature reached 100°C, the filled NR compound with elemental sulfur had a higher  $\tan \delta$  (Fig. 13). The addition of elemental sulfur reduced the  $\tan \delta$  and energy dissipation processes at low temperatures, but increased them at high temperatures. As mentioned earlier,<sup>32</sup> for high performance tires, a high  $\tan \delta$  at low temperatures, and a low  $\tan \delta$  at high temperatures are needed. The addition of elemental sulfur to the filled NR forced  $\tan \delta$  in the wrong direction, and therefore it was not beneficial to this property.

At 1 Hz, the  $\tan \delta$  for the control compound was noticeably higher than the values measured for the filled rubbers at temperatures less than -20°C. However, as the temperature was increased to 100°C, the  $\tan \delta$  for the control compound had much lower values than the filled compounds (Fig. 12).

At 20 Hz, the  $\tan \delta$  for the control compound was much higher at temperatures less than 0°C, and fairly similar to the values measured for compounds 56 and 58 as the temperature reached 100°C (Fig. 13).

The addition of TBBS, zinc oxide, and elemental sulfur affected the  $\Delta$ torque and crosslink density of the rubbers in different ways. IR required more TBBS and zinc oxide to fully crosslink and possessed a much higher crosslink density than NR (Tables VII and VIII). The effect of curing agents including TBBS, sulfur and zinc oxide, and carbon black filler on the crosslink density and mechanical properties of IR and NR was investigated.<sup>33</sup> The crosslink density of the IR vulcanizate was found to be higher than that of the NR at a given curative content for both control and black-filled rubbers. It is interesting that we observed a similar behavior. The crosslink densities of the control NR and IR vulcanizates were 91 and 111 mol/m<sup>3</sup>, respectively (compounds 54 and 57; Table VIII). Similarly, the filled NR and IR vulcanizates had very different crosslink densities, that is, 149 and 211 mol/m<sup>3</sup>, respectively, (cf. compound 56 with compound 58; Table VIII). Although, IR needed an extra 1 phr TBBS and 0.7 phr zinc oxide to fully crosslink, this did not explain the high crosslink densities measured for the control and filled IR rubbers. The reason for the high crosslink density of the IR vulcanizates was not immediately clear, although it has been suggested that it might be due

to some additives incorporated in the IR during manufacturing.<sup>33</sup>

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.<sup>34,35</sup> The inferior properties of the control IR vulcanizate was due to excessive crosslinks. The crosslink density increased even more in the filled IR vulcanizate when sulfur chemical bonds were formed between the rubber and TESPT. In addition, it is reported that NR crystallizes much faster than IR although their chemical constitution is similar, which might have also contributed to the superior properties of the NR vulcanizates.<sup>36</sup> The strength of NR and IR depends on their crystallizability during deformation. However, ability to crystallize on stretching will be severely hampered if there are too many crosslinks in the rubber.<sup>37</sup> The much larger crosslink density of the filled IR indicated that the rubber did not benefit from crystallization as much as the filled NR did.

The bound rubber content of the filled NR and IR rubbers were 94%–93%, respectively, (Table VIII), which indicated strong rubber-filler adhesion.<sup>38</sup> The silica particles were fully dispersed in the rubber matrix (Figs. 5 and 6), and therefore, filler-filler interaction was negligible.<sup>7</sup> The crosslink density of the filled NR and IR vulcanizates were 149 and 211 mol/m<sup>3</sup>, respectively (Table VIII), which indicated significant contribution from crosslinks to the rubber properties.<sup>34</sup> The surfaces of silica were pretreated with rubber reactive TESPT, and the surface area of the filler particles was less than 400 m<sup>2</sup>/g, which also contributed to the improvement in the mechanical properties of the rubbers.<sup>2,6</sup> It is evident from the results that when the chemical bonding between the rubber and filler was optimized, this led to a substantial reinforcement of the rubber properties. The two major contributions to the reinforcement were from strong rubber-filler interaction, and high crosslink density in the rubber vulcanizates.

## CONCLUSIONS

From this study, it can be concluded that

1. The filled NR and IR rubbers needed 6 phr TBBS and 0.3 phr zinc oxide, and 7 phr TBBS and 1 phr zinc oxide, respectively, to optimize the reaction between the rubber reactive tetrasulfane groups of TESPT and the rubbers. The incorporation of stearic acid in the filled rubbers with TBBS and zinc oxide offered no benefit to  $\Delta$ torque and the chemical bonding between the rubber and filler.
2. The addition of elemental sulfur to the filled NR rubber with 6 phr TBBS and 0.3 phr zinc oxide increased the  $\Delta$ torque value, which indicated benefit

for the crosslink density of the rubber. However, there was no overall advantage for the mechanical properties as some properties improved and others deteriorated.

3. The hardness, tensile strength, elongation at break, stored energy density at break,  $T$ , and modulus of the rubber vulcanizates increased substantially when the filler was added. The improvement in the mechanical properties of the rubbers was mainly due to high level of rubber-filler adhesion and high-crosslink density that was produced by the chemical bonding between the rubber and TESPT. The bound rubber measurements also confirmed a strong rubber-filler adhesion.

In summary, it is abundantly clear from the results that replacing NR with IR when the same loading of silanized silica nanofiller was used in the rubber offered no benefit because more TBBS and zinc oxide were needed to fully crosslink the filled IR rubber. Moreover, with the exception of the hardness and modulus which increased, the remaining mechanical properties deteriorated when IR replaced NR.

This was due to excessive crosslinks in the IR vulcanizate, which might also have hindered the ability of the rubber to crystallize on stretching.

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