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Influence of Chemical Curatives on the Reaction Between Sulphur in Silane and Rubber Phases in Natural Rubber/Polybutadiene Blend Reinforced with a Silanised Silica Nanofiller

ZAINUDIN UMAR*# AND ALI ANSARIFAR*#

This study prepared a natural rubber/polybutadiene (NR/BR: 50/50 wt%) blend using precipitated amorphous white silica filler the surface of which had been pre-treated with bis-(3-triethoxysilylpropyl)-tetrasulphane (TESPT). TESPT is a sulphur-bearing bifunctional organosilane, which chemically bonds silica to rubber via the sulphur to form strong rubber-silica interaction. The rubbers were primarily cured by using sulphur in TESPT, and the cure was optimised by adding sulphenamide accelerator, zinc oxide activator and elemental sulphur. The chemical bonding between the sulphur in TESPT and the rubbers was affected mainly by the addition of the chemical curatives. In the absence of full chemical bonding between the sulphur in TESPT and the rubbers, most of the mechanical properties of the blend were inferior. But when chemical bonds or crosslinks fully formed between the sulphur in TESPT and the rubbers, the tensile strength, elongation at break, stored energy density at break, tear energy, cyclic fatigue life and abrasion resistance were enhanced. For example, the cyclic fatigue life of the blend increased by almost 50,000 times, which was a major improvement.

Keywords: Rubber blend; silica; coupling agent; chemical bonding; crosslinking; reinforcement; mechanical properties

Blending dissimilar rubbers combines outstanding properties of different existing rubbers and is often used to improve the durability and performance of rubber products in service. For instance, natural rubber (NR), styrene-butadiene rubber (SBR), polybutadiene rubber (BR) and acrylonitrile-butadiene rubber (NBR) are mixed together to produce NR/BR, SBR/NR, NBR/SBR and NBR/BR blends for use in articles such as truck and passenger car tyres, general purpose hydraulic hoses and shoe soles.

Raw rubbers have poor properties and must be reinforced with solid fillers such as carbon black (CB), synthetic silica, carbon nanotube, quartz, metal oxides, and calcium carbonate. Effect of CB on the mechanical...
and dynamic properties of some NR/BR blends was investigated and major improvement in both properties was reported\textsuperscript{12-14}. Among the fillers, synthetic silica offers major benefits to rubber reinforcement in industrial blends such as passenger car tyres\textsuperscript{9-11}. However, the surface of silicas possesses siloxane and silanol groups\textsuperscript{15}. The silanol groups are acidic\textsuperscript{16} and interact with basic accelerators causing detrimental effects such as long cure times and slow cure rates and also loss of crosslink density in sulphur-cured rubbers\textsuperscript{15,17}. Moreover, the surfaces of silica are polar and hydrophilic and there is a strong tendency to adsorb moisture\textsuperscript{18}, which adversely influence cure and hence properties of the cured rubber.

Bifunctional organosilanes such as bis-(3-triethoxysilylpropyl)-tetrasulphane (TESPT), known also as the Si69 coupling agent, are used to treat the silicas surfaces to make the filler more suitable for use in rubber compounds\textsuperscript{15,17}. TESPT is used to improve the reinforcing capability of precipitated silica and also forms an integral part of curing systems to improve crosslinking network. The silanisation of silica can be carried out in two different ways. Firstly, silica and silane are mixed together in a preliminary mixing stage at an optimum temperature and reaction time. Alternatively, silanisation is carried out \textit{in situ}\textsuperscript{19,20} during mixing the silane is added to the rubber together with, or after the silica. TESPT possesses tetrasulphane and ethoxy reactive groups. The tetrasulphane groups are rubber reactive\textsuperscript{15} and react in the presence of accelerators at elevated temperature, \textit{i.e.} 140-210°C, with or without elemental sulphur being present, to form crosslinks in rubbers containing carbon-carbon double bonds. Silanisation reduces the rubber viscosity\textsuperscript{17,21,22}, disperses the silica particles a lot more efficiently in rubber\textsuperscript{23}, and improves cure characteristics by preventing acidic silicas from interfering with the reaction mechanism of sulphur-cured rubber\textsuperscript{15,17}.

Precipitated silica pre-treated with TESPT is classified as crosslinking filler\textsuperscript{24}. TESPT strengthens the filler-rubber interaction by forming crosslinks between the two. Effects of TESPT pre-treated silica, and silica and liquid TESPT mixture on the crosslink density of a sulphur-cured rubber was investigated. It was concluded that the rubber with TESPT pre-treated silica had a higher crosslink density and increased rubber-filler interaction\textsuperscript{25}.

A number of studies have shown major improvement in the mechanical and dynamic properties of NR\textsuperscript{26,27}, BR\textsuperscript{28}, ethylene-propylene diene rubber (EPDM)\textsuperscript{29}, and SBR\textsuperscript{30} when TESPT pre-treated precipitated silica was used. For instance, in some work, 60 phr of TESPT pre-treated precipitated silica was mixed with NR and BR rubbers. The rubber was cured primarily with sulphur in TESPT, and the cure was optimised by adding sulphenamide accelerator and zinc oxide, which helped to form sulphur chemical bonds between the rubber and filler. The mechanical properties of the rubber vulcanisates, \textit{e.g.} hardness, tear strength, abrasion resistance, stored energy density at break, Young’s modulus, and cyclic fatigue life improved substantially\textsuperscript{25-29}. High level of rubber-filler interaction and formation of chemical bonds or crosslinks between the rubber chains and TESPT improved the mechanical properties of the rubber vulcanisates.

More interestingly was the influence of TESPT pre-treated precipitated silica on the mechanical and dynamic properties of some SBR/BR blends\textsuperscript{22}. Not only the mechanical properties were significantly better compared with the control compounds, also optimising the chemical bonding between TESPT and the SBR and BR phases in the blend, reduced the
amount of the chemical curatives by almost 58 wt% when the blend was considered for possible use in passenger car tyre tread. Reduction in the chemical curatives helped to improve health and safety at work and minimised damage to the environment. Byers reviewed work on the use of TESPT/silica filler systems in SBR/BR blends for passenger car tyre tread and reported a significant reduction in rolling resistance compared with CB-filled blends.

This study prepared a natural rubber/polybutadiene (NR/BR: 50/50 wt%) blend, using precipitated amorphous white silica filler the surface of which had been pre-treated with TESPT. The sulphur in TESPT was reacted with the rubbers by adding an accelerator and an activator, and then elemental sulphur was incorporated to cure the rubbers at elevated temperature. In one blend, reaction between the sulphur in TESPT and the rubbers was incomplete, producing weak rubber-silica interaction, and in another it was complete, producing strong rubber-silica interaction.

The cure properties, hardness, tensile properties, tear strength, abrasion resistance, heat build-up, cyclic fatigue life, density, and glass transition temperature ($T_g$) of the blends were measured.

EXPERIMENTAL

Materials

The raw rubbers used were standard Malaysian natural rubber (NR) grade L (98 wt% 1, 4-cis content; SMRL) and high-cis polybutadiene rubber BR (96 wt% 1, 4-cis content; Buna CB 24, Bayer, Newbury, UK; not oil extended). The reinforcing filler was Coupsil 8113. Coupsil 8113 is a 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 sulphur (included in TESPT), a 175 m$^2$/g surface area (measured by N2 adsorption) and a 20-54 nm particle size. Evonik Industries AG of Germany supplied the Coupsil.

In addition to the raw rubbers and silica, the other ingredients were (a) N-cyclohexyl-2-benzothiazole sulphenamide (fast curing delayed action accelerator with a melting point of 105ºC) (Santocure CBS, Flexsys, Dallas, TX), (b) Zinc oxide (ZnO; an activator, Harcros Durham Chemicals, Durham, UK), (c) Elemental sulphur (curing agent: Solvay Barium Strontium, Hannover, Germany), (d) N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene diamine (6PPD) (an antidegradant with a melting point of 45-51ºC, Santoflex 13, Brussels, Belgium), (e) Polymerised 1,2-dihydro-2,2,4-trimethyl-quinoline (TMQ) (an antidegradant with a melting point of 83-93ºC, Sovereign Chemicals, USA), (f) Microcrystalline wax with a melting point of 76-82ºC (ProChemical & Dye, USA) and (g) Hydro-treated heavy Naphthenic oil (plasticiser with a flash point greater than 212ºC, CrossTrans 206, USA). These chemicals are used extensively in industrial rubber blends.

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 initially set at ambient temperature (25ºC) and the rotor speed was set at 45 rpm. The volume of the mixing chamber was 78 cm$^3$, and it was 74% full during mixing. Polylab monitor 4.17 software was used for controlling the mixing condition and storing data.
Assessment of the Dispersion of Silica Filler in the NR and BR Rubbers and NR/BR Blends

Dispersion of the silica filler and chemical curatives in the rubber was assessed by a Carl Zeiss Leo 1530VP field emission gun scanning electron microscope (FEGSEM) (Carl Zeiss NTS GmbH, Oberkochen, Germany). Small pieces of the cured rubber were placed in liquid nitrogen for 5 min, and then fractured to create two fresh surfaces. The samples, 30 mm$^2$ 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 filler and chemical curatives in the NR and BR rubbers and NR/BR blends was subsequently studied from SEM micrographs. Energy dispersive X-ray spectroscopy (EDS) was also performed to identify and determine the composition of the additives in the rubber.

Addition of CBS to the Silica-filled NR and BR Rubbers

Accelerators are added to control the onset and rate of cure as well as crosslink density of rubber. To activate the rubber reactive tetrasulphane groups of TESPT, CBS was added. The loading of CBS in the silica-filled BR and NR rubbers was increased progressively to 1.75 phr to measure the amount needed to optimise $\Delta$torque and the chemical bonding or crosslinking between the rubber and silica via the sulphur in TESPT. The difference between the maximum and minimum torque values on the cure trace of the rubber ($\Delta$torque), is an indication of crosslink density changes in the rubber (Figure 1). The formation of crosslinks strengthened the rubber/silica interaction$^{14,15}$. In total, three compounds were made.

Addition of Zinc Oxide to the Silica-Filled NR and BR Rubbers with CBS

Zinc oxide was used as an activator to improve the effectiveness of CBS during curing of the rubbers. The loading of ZnO in the silica-filled BR and NR rubbers with CBS was raised to 3 phr to determine the amounts required to increase efficiency of CBS and chemical bonding or crosslinking between the sulphur in TESPT and the rubber. In total, twenty five compounds were made.

Stearic acid was not included in the cure system of the rubbers and blends because previous studies showed that the addition of up to 2.5 phr stearic acid as a secondary activator to NR and BR rubbers filled with a high loading of silanised silica containing sulphenamide accelerator and ZnO curatives, had no effect on the $\Delta$torque. The $\Delta$torque for these rubbers stayed unchanged as a function of the loading of stearic acid$^{26,28}$.

Addition of Elemental Sulphur to the Silica-Filled NR and BR Rubbers with CBS and ZnO

To evaluate effect of elemental sulphur on the cure properties of the silica-filled BR and NR rubbers with CBS and ZnO, 15 compounds were prepared. The loading of elemental sulphur was raised gradually to 3 phr to determine the amounts required to fully crosslink the rubbers. This was in addition to the crosslinks that formed between the sulphur in TESPT and the rubbers.

Mixing of the NR and BR Rubbers

To prepare the NR and BR compounds, the raw rubbers were introduced first in the mixer, and then the silanised silica was added and
mixed for 10 minutes. Santocure CBS, ZnO, and elemental sulphur were subsequently mixed for another 6 min before the compound was removed from the mixer. The temperature of compounds during mixing was 45-53ºC. Note that at this stage, the remaining chemical ingredients were not added.

Preparation of the NR/BR Blends

The NR and BR rubbers were mixed together to produce the blends. The total mixing time was 13 min, and the following procedure was used for making the blends.

(a) The raw NR and BR rubbers at a weight ratio of 50/50 were placed in the mixing chamber and mixed together for 2 minutes;
(b) The silica, which was already pre-treated with TESPT by the supplier, was added and mixed for 6 minutes;
(c) CBS, ZnO, and elemental sulphur were added and mixed for 2 minutes;
(d) The naphthenic oil was added and mixed for 1 minute.
(e) Mixing stopped and the chamber temperature was raised to 93ºC. Then TMQ, microcrystalline wax and 6PPD were added and mixed for 2 minutes. The chamber temperature was increased to above the melting points of the microcrystalline wax, TMQ and 6PPD to facilitate full dispersion of these chemicals in the rubber.

Finally, when the mixing ended, the blend was removed from the mixer and left at ambient temperature to cool down. It was subsequently milled to a thickness of about 7 mm for further work. The blends were stored at 24ºC for at least 24 h before their cure properties were measured.

Cure Properties of the Silica-Filled NR and BR Compounds and NR/BR Blends

The cure properties of the silica-filled NR and BR compounds and NR/BR blends were measured at 160 ± 2ºC in an oscillating disc rheometer curemeter (ODR, Monsanto,
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Swindon, UK) at an angular displacement of ± 3° and a test frequency of 1.7 Hz according to the BS1673-10:1977. From the cure traces, scorch time, \( t_s \), which is the time for the onset of cure, and the optimum cure time, \( t_{95} \), which is the time for the completion of cure, were determined. The cure rate index, which is a measure of the rate of cure in the rubber was calculated using the method described in BS903-A60:1996. Results from these experiments were also summarised in Table 1. Delta torque was subsequently plotted against the loading of CBS, zinc oxide, and elemental sulphur.

**Test Pieces and Test Procedure**

After the cure properties were determined, the blends were cured in a compression mould at 160°C for 10 and 57 min with an actual pressure of 7.5 tonnes/ m². The cure tests for the NR and BR rubber compounds ran for up to 2 hours. Pieces of rubber, each approximately 130 g in weight, were cut from the milled sheet. Each piece was placed in the centre of the mould 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 and glass transition temperatures of the blends, sheets 23 by 23 cm by approximately 2.8 mm thick were used, from which various samples for further tests were cut. The dimensions of the samples cured for measuring the hardness, abrasion resistance, and heat build-up are given in the section on the test methods.


The density, mechanical properties and cyclic fatigue life of the blends were measured according to the procedures described in the BS903 and ISO standards as follow.

- **Density:** the density was determined in accordance with ISO 2781, using samples 16 mm in diameter and 6 mm thick.
- **Hardness:** BS 903-A26:1995, using cylindrical samples 12 mm thick and 28 mm in diameter, in a Shore A Durometer hardness tester (The Shore Instrument & MFG, Co., New York). The test temperature was 23.5°C.
- **Tensile stress-strain properties (tensile strength, elongation at break, stored energy at break, Young’s modulus, and modulus at 100, 200 and 300% strain amplitudes): BS 903-A2:1995, in a LR50K plus materials testing machine (Lloyd Instrument, UK), using standard dumbbell test pieces. Lloyd Nexygen 4.5.1 was used to process and store the data. The test temperature was 28°C and the crosshead speed was set at 100 mm/ min.
- **Tear energy:** BS 903-A3:1995, in a LR50K plus materials testing machine (Lloyd Instruments, UK), using trouser test pieces. The test temperature was ambient (21°C), tear angle 180°, and crosshead speed was set at 100 mm/min.
- **For determining the abrasion resistance of the blends, tests were performed in accordance with ISO 4649:2010, using rotating test pieces. The mass loss of rubber due to abrasion was calculated from the volume loss recorded and density of the test material. For these tests, samples 16 mm in diameter and 6 mm thick were used.
- **The heat build-up of the blends was determined in duplicate based on ISO 46666-3:2010. The temperature rise of each sample was subsequently recorded over the duration of the test. The samples used for these tests were 18 mm in diameter and 25 mm in height.**

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The cyclic fatigue life \( N \) (number of cycles to failure) of the blends was measured using standard dumbbell test pieces in uniaxial tension in a Hampden dynamic testing machine (Northampton, UK). The tests were performed at a constant maximum deflections of 100% and test frequency of 3.72 Hz. The strain on each test piece was relaxed to zero at the end of each cycle. For each blend, eight test pieces were used and the test temperature was 23 ± 3ºC.

### RESULTS AND DISCUSSION

#### Loss Tangent (\( \tan \delta \)) of the Blends

Loss tangent 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, USA), using Universal Analysis 2000 Software Version 4.3A. Test pieces 35 mm long, 12 mm wide and approximately 2.40 mm thick were used. The tests were performed at 10 Hz frequency. The sample was deflected 256 µm (nominal peak to peak displacement) during the test, and the sample temperature was raised from -140ºC to 100ºC at 3ºC/min steps.

**Effect of CBS and ZnO on the Reaction of Sulphur in TESPT with Rubber in the Silica-filled BR**

To react the sulphur in TESPT with rubber, 1 phr CBS was added to the silica-filled BR. The cure trace of the rubber

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| TABLE 1. FORMULATIONS AND CURE PROPERTIES OF THE BR AND NR RUBBER COMPOUNDS AND NR/BR BLENDS |
|---|---|---|---|
| **Formulation (phr)** | **Compound no.** | | **Blend no.** |
|  | 1 | 2 | 1 | 2* |
| BR | - | 100 | 50 | 50 |
| NR (SMRL) | 100 | - | 50 | 50 |
| Silanised silica | 50 | 50 | 50 | 50 |
| CBS | 1 | 1.75 | 1 | 1.75 |
| ZnO | 1.25 | 0 | 1.25 | 1.25 |
| Sulphur | 1.25 | 2 | 1.25 | 2 |
| Naphthenic Oil | 0 | 0 | 6 | 6 |
| TMQ | 0 | 0 | 1.5 | 1.5 |
| 6PPD | 0 | 0 | 2.5 | 2.5 |
| Microcrystalline wax | 0 | 0 | 2 | 2 |
| ODR test results at 160ºC | | | | |
| Minimum torque (dN m) | 24 | 35 | 30 | 23 |
| Maximum torque (dN m) | 57 | 124 | 59 | 95 |
| \( \Delta \)Torque (dN m) | 33 | 89 | 29 | 72 |
| \( t_{52} \) (min) | 2 | 2 | 1.8 | 2.1 |
| \( t_{95} \) (min) | 10 | 8 | 10 | 6.7 |
| Cure rate index (min\(^{-1}\)) | 12.5 | 16.7 | 12.2 | 21.7 |

*Blend 1 was cured for 10 min and blend 2 for 57 minutes.
showed a marching cure over a 60 min test time (Figure 2), which indicated incomplete reaction between sulphur in TESPT and the rubber. Although the cure might have reached equilibrium at a much longer test time, this would have been of no practical benefit to the present work. As mentioned earlier\(^{14,15}\), formation of chemical bonds or crosslinks between rubber and silica via sulphur in TESPT is essential for strong rubber/silica interaction and ultimately high level of rubber reinforcement. The loading of CBS in the rubber was then raised progressively until an equilibrium cure was produced with 1.75 phr CBS, which was sufficient to optimise reaction between sulphur in TESPT and the rubber (Figure 2).

To increase the efficiency of CBS, ZnO was added. Figure 3 shows $\Delta$torque vs ZnO loading for the silica-filled BR with 1 phr CBS. Delta torque remained essentially unchanged at about 17 dN m as the loading of ZnO was increased to 1.25 phr. The rubber did not require any ZnO. A similar behaviour was also observed for the silica-filled BR with 1.75 phr CBS. Delta torque remained constant at about 34 dN m, when the loading of ZnO was raised from 0 to 1.5 phr (Figure 4). The addition of ZnO had no additional benefit for the $\Delta$torque and the chemical bonding between the sulphur in TESPT and the rubber. Hence, only 1.75 phr CBS was needed to fully react the sulphur in TESPT with the rubber.

**Effect of Added Elemental Sulphur on the $\Delta$torque of the Silica-filled BR with CBS**

To cure the rubber in addition to the crosslinks formed between the sulphur in TESPT and the rubber, elemental sulphur was added to the silica-filled BR with 1.75 phr CBS. The loading of elemental sulphur was raised to 3 phr to determine the amount necessary to fully cure the rubber. The $\Delta$torque rose from 35 to 89 dN m when 2 phr elemental sulphur was incorporated in the rubber (Figure 5). Afterwards, there was no obvious increase in the value of $\Delta$torque. When CBS was added, it dispersed though out the rubber. Some of the CBS reacted with the sulphur in TESPT to produce chemical bonds between the rubber and silica, and the remaining CBS, reacted with elemental sulphur to form crosslinks in the rubber phase. This, in turn, increased the $\Delta$torque of the rubber as shown in Figure 5. However, above 2 phr elemental sulphur, the $\Delta$torque remained fundamentally unchanged because there was no more CBS left in the rubber to react with elemental sulphur to produce more crosslinks. Evidently, to fully cure the rubber, 2 phr elemental sulphur was sufficient. So, the cure system for the silica-filled BR consisted of 1.75 phr CBS and 2 phr elemental sulphur.

**Effect of CBS and ZnO on the Reaction of Sulphur in TESPT with the Rubber in the Silica-filled NR**

To react the sulphur in TESPT with the rubber, 1 phr CBS was added to the silica-filled NR. This gave an equilibrium cure (inset in Figure 2), which indicated complete reaction between the sulphur in TESPT and the rubber. To improve the efficiency of CBS, ZnO was incorporated. Figure 6 shows $\Delta$torque as a function of ZnO loading. Delta torque increased from 5.4 to 9.8 dN m as the loading of ZnO was raised to 1.25 phr. Thereafter, $\Delta$torque gradually decreased to about 7.7 dN m when the amount of ZnO was raised to 3 phr. It was interesting that the addition of ZnO was beneficial to the crosslink density of the rubber as indicated by increases in the $\Delta$torque in the absence of stearic acid (Figure 6). In conventional, semi-efficient and efficient sulphur cure systems, stearic acid is frequently used with ZnO as a secondary activator\(^{1–8}\). Clearly, adding CBS and then
Figure 2. Typical torque vs time cure traces by ODR at 160°C for the silica-filled BR with different loadings of CBS over a 60 min test time: 1 phr CBS (●), 1.75 phr CBS (■). The insert is the cure trace of the silica-filled NR with 1 phr CBS.

Figure 3. ΔTorque vs ZnO loading for the silica-filled BR with 1 phr CBS. Each point on the figure corresponds to one compound.
ZnO loading (phr)

Figure 4. \(\Delta\text{Torque}\) vs ZnO loading for the silica-filled BR with 1.75 phr CBS. Each point on the figure corresponds to one compound.

Sulphur loading (phr)

Figure 5. \(\Delta\text{Torque}\) vs elemental sulphur loading for the silica-filled BR with 1.75 phr CBS. Each point on the figure corresponds to one compound.
ZnO to react the sulphur in TESPT with the rubber, removed the need to use stearic acid, which was a major advantage.

The addition of 1.25 phr ZnO was enough to improve the efficiency of CBS and optimise bonding between the sulphur in TESPT and the rubber. When the loading of ZnO exceeded 1.25 phr, e.g. 2.5 phr, aggregates formed in the rubber matrix (Figure 7). EDS analysis indicated the aggregates to be ZnO and silica (Figure 8). When too much was added, ZnO particles aggregated together and could no longer react with CBS. This explained the reduction in Δtorque at higher loading of ZnO. At low loading of ZnO, there was no aggregate in the rubber matrix (Figure 9), suggesting that most of the additive reacted during curing.

**Effect of Added Elemental Sulphur on the Cure Properties of Silica-filled NR with CBS and ZnO**

The loading of elemental sulphur in the silica-filled NR with 1 phr CBS and 1.25 phr ZnO was increased progressively from 0 to 1.75 phr. Delta torque rose from 9.8 to 32.4 dNm when the loading of elemental sulphur reached 1.25 phr. Further increases in the loading of elemental sulphur had little effect on Δtorque, which increased slightly to about 34 dNm (Figure 10). In fact, 1.25 phr elemental sulphur was enough to fully cure the rubber. Therefore, the cure system for the silica-filled NR was made of 1 phr CBS, 1.25 phr ZnO, and 1.25 phr elemental sulphur.

**Assessing Effect of CBS, ZnO and Elemental Sulphur on Cure Properties of the Silica-filled NR/BR Blend**

The raw NR and BR rubbers were mixed together with the silanised silica and chemical additives to produce two NR/BR blends (blends 1 and 2; Table 1). The blends were cured at 160°C and their mechanical properties and glass transition temperatures were then measured. It is worth mentioning that a blend of NR with a high cis-1,4 BR was examined to determine the distribution of crosslinks between the two rubbers in the blend. The blend was vulcanised using a semi-efficient
Figure 7. SEM micrograph showing ZnO aggregates (white bright) in the rubber after freeze-fracture. Data for the silica-filled NR with 1 phr CBS and 2.5 phr ZnO.

Figure 8. EDS analysis of the composition of the aggregates seen in Figure 7.
Figure 9. SEM micrograph showing the internal structure of the rubber after freeze-fracture. Data for the silica-filled NR with 1 phr CBS and 0.5 phr ZnO.

Figure 10. $\Delta$Torque vs elemental sulphur loading for the silica-filled NR with 1 phr CBS and 1.25 phr ZnO. Each point on the figure corresponds to one compound.
vulcanisation system consisting of sulphur, accelerator and ZnO. There was no significant diffusion of the crosslinking agents between the two phases and both phases achieved similar crosslink levels to those expected in single polymer vulcanisates of equivalent curative loading.

The cure system in blend 1 consisted of 1 phr CBS, 1.25 phr ZnO, and 1.25 phr elemental sulphur. In this blend, which was cured for 10 min (Table 1), reaction between the sulphur in TESPT and the BR did not complete during curing. As stated before, the BR with 1 phr CBS showed a marching cure over a 60 min test time (Figure 2). Note that the rate of reaction of elemental sulphur with rubber is significantly higher than that of the sulphur in TESPT with rubber at a given temperature. Therefore, a longer cure time of 57 min had to be used for blend 2 to react the two types of sulphur with the rubbers.

The NR phase in the blend had an optimum cure time of 57 min (Figure 11). This was the time needed for reaction between the sulphur in TESPT and the rubber to complete. In the same figure, the optimum cure time of the blend was 10 min when elemental sulphur was added (Table 1). This time was too short for the reaction between the sulphur in TESPT and the NR to complete during curing to produce chemical bonds or crosslinks, which were essential for high level of rubber/silica interaction. The disulphane and tetrasulphane groups in TESPT have higher dissociation energy than added elemental sulphur and consequently, are more thermally stable. The superior thermal stability of the disulphane and tetrasulphane groups of TESPT meant that they took longer to react with the NR, i.e. 57 min, than elemental sulphur did, i.e. 10 minutes.

In blend 2, the cure system was made of 1.75 phr CBS, 1.25 phr ZnO, and 2 phr elemental sulphur. The BR phase in the blend had 1.75 phr CBS, which was sufficient to fully react the sulphur in TESPT with the rubber. Besides, the blend was cured for 57 min to ensure that the sulphur in TESPT wholly reacted with the NR during curing. Blend 2 had an optimum cure time of approximately 7 min, which was far too short to allow the sulphur in TESPT to react fully with the rubber (Table 1), hence, the 57 min cure time was considered.

In blend 1, reaction between the sulphur in TESPT and the rubbers was incomplete, resulting in weak rubber-silica interaction, whereas in blend 2, reaction between the sulphur in TESPT and the rubbers was complete, giving rise to strong rubber-silica interaction. Extensive studies in the past showed that NR, BR, and SBR rubbers filled with a high loading of the silanised silica nanofiller were cured fully with a sulphenamide accelerator and ZnO in the absence of elemental sulphur. This was also the case for some SBR/BR blends. In all the cases studied, links were formed between the sulphur in TESPT and the rubbers. It is envisaged that a similar process also occurred in the rubbers prepared for this study.

**Mechanical Properties of the Silica-filled NR/BR Blends**

The mechanical properties of blends 1 and 2 were summarised in Table 2. Some of the properties of blend 2 were better than those of blend 1. The only exceptions were the hardness, Young's modulus, M100, M200 and M300, which were inferior. The heat build-up was 29% higher for blend 2. The tensile strength, elongation at break, stored energy density at break and tear energy were 7%, 24%, 8%, and 171% higher, respectively for blend 2. Moreover for blend 2, the average weight loss in the abrasion test was 41% lower and the cyclic fatigue life 50,000 times
longer, reaching almost 8 million cycles. To understand the reason for the inferior properties of blend 1, the internal structure of the rubbers were examined in the SEM.

**SEM Analysis of Internal Structure of the NR/BR Blends**

For blend 1, the silica particles dispersed well in the rubber matrix and there was no evidence of any damage to the rubber structure prior to mechanical testing (Figure 12). However, when the rubber was re-examined after the tensile test, large cavities were present because the solid aggregates separated from the rubber matrix (Figure 13). In some parts of the sample, the rubber was extensively damaged because of the cavities (Figure 14). These cavities were so numerous that could only have been formed when silica separated from the rubber matrix, noting also that the silica was the largest amount of additive in the rubber, *i.e.* 50 phr. This indicated poor bonding between the rubber and silica, which contributed to the inferior properties of the blend. This was in line with what was expected, since in blend 1, which was cured for 10 min, the sulphur in TESPT did not have enough time to fully react with the rubber to produce chemical bonds or crosslinks, which were essential for strong rubber-silica interaction. There was also evidence that the silica particles did not disperse well in the

<table>
<thead>
<tr>
<th>TABLE 2. MECHANICAL PROPERTIES OF THE NR/BR RUBBER BLENDS</th>
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<tr>
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</tr>
<tr>
<td>Hardness (IRHD)</td>
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</tr>
<tr>
<td>Tensile strength (MPa)</td>
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<tr>
<td>Range of values (MPa)</td>
<td>11-15</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
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<tr>
<td>Range of values (%)</td>
<td>517-639</td>
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<tr>
<td>Stored energy density at break (MJ/m³)</td>
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<tr>
<td>Range of values (MJ/m³)</td>
<td>27-44</td>
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<tr>
<td>T (kJ/m²)</td>
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<tr>
<td>Range of values (kJ/m²)</td>
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</tr>
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<td>Young’s modulus (MPa)</td>
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</tr>
<tr>
<td>Range of values (MPa)</td>
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<tr>
<td>Modulus at different strain amplitudes (MPa)</td>
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</tr>
<tr>
<td>Strain amplitudes (%)</td>
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</tr>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>300</td>
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<tr>
<td>Cyclic fatigue life at 1.4 Hz (kc)</td>
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<tr>
<td>Range of values (kc)</td>
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<tr>
<td>Heat build-up and mass loss in the abrasion tests</td>
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<td>Heat build-up (°C)</td>
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<tr>
<td>Average weight loss (mg)</td>
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<tr>
<td>Standard deviation</td>
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<tr>
<td>Density (Mg/m³)</td>
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<tr>
<td>Tg (°C)</td>
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Figure 11. Typical torque vs time traces by ODR for the silica-filled NR with 1 phr CBS and 1.25 phr ZnO (●), and blend 1 in Table 2 (■).

Figure 12. SEM micrograph showing dispersion of silica in the rubber after freeze-fracture for blend 1 in Table 2.
Figure 13. SEM micrograph showing ZnO and cavities in the rubber after silica was de-bonded and pulled out of the rubber in the tensile test. Data for blend 1 in Table 2.

Figure 14. SEM micrograph showing extensive cavitation in some parts of the rubber after silica was separated and pulled out of the rubber in the tensile test. Data for blend 1 in Table 2.
blend and cavities up to 7 µm in size were seen (Figure 14). The particle size of the silica is 35-50 nm, which is considerably less than the cavity size.

The SEM results for blend 2 showed good dispersion of the silica particles in the rubber matrix (Figure 15). After it was fractured in the tensile test and re-examined in the SEM, the internal structure of the rubber remained perfectly intact and there was no sign of cavities (Figure 16). Therefore, the improvement seen in most properties of blend 2 was primarily due to the formation of chemical bonds or crosslinks between the rubber and silica via the sulphur in TESPT (compare Figure 14 and Figure 16), which increased the rubber-silica interaction and enhanced the mechanical properties of the blend as shown in Table 2.

As mentioned earlier, the hardness and modulus of blend 2 were inferior to those of blend 1. When the cure trace of blend 2 was examined, it was evident that the rubber had undergone reversion during curing whilst crosslinks between the sulphur in TESPT and the rubber chains were being formed. The blend became softer because the optimum torque decreased by almost 20% after 57 min cure due to reversion (Figure 17). Recall that in blend 1, the crosslinks formed mainly in the rubber phases with little links developing between the sulphur in TESPT and the rubber chains. The Δtorque for blend 2 (torque value at 57 min cure – minimum torque) was approximately 50% higher than that of blend 1 (Table 1), in spite of the blend being softer. It may be that in blend 2, most of the crosslinks were formed between the sulphur in TESPT and the rubber, and less in the rubber phases. The Δtorque measurements did not differentiate between the effects of the two types of crosslinks on the cure of the blend. It was concluded that the Δtorque did not accurately indicate the true crosslink density of the rubber phases, which were softer than the Δtorque indicated. The softening effect resulted in the hardness and modulus to decrease, and elongation at break, tear energy, cyclic fatigue life and abrasion resistance to improve (Table 2).

Glass Transition Temperatures of the NR/BR Blends

Glass transition temperature (Tg) is governed by the extend of chain mobility within the rubber network. When chain mobility is inhibited, e.g. by the presence of crosslinks between the rubber chains and/or strong rubber/filler interaction, Tg rises. The Tg of blend 1 and blend 2 were -44.7°C and -41.1°C, respectively due to the NR phase (Figure 18). On the same Figure, the glass transition temperature of BR was about -95°C for blend 1 and -83°C for blend 2. The increases recorded in the Tg of the BR and NR rubbers were in line with the rise in the Δtorque of blend 2. The higher Tg value of blend 2 was attributed partly to the crosslinks between the sulphur in TESPT and the rubber, and partly due to the crosslinks in the rubber phases. But the exact contribution from these two types of crosslinks to the Tg remained uncertain. This increased the rubber/silica interaction and subdued chain mobility within the rubber network, raising the Tg. The higher Tg made blend 2 less resilient, since resilience of rubber depends on the value of Tg. Importance of good interfacial bonding between the rubber and filler was self-evident.

Rubber reinforcement is, to a large extent, due to filler particle size and dispersion, activity or surface chemistry of filler, filler-rubber interaction, filler-filler interaction, and crosslink density. As mentioned earlier, precipitated silica has a surface area of 175 m²/g and an average particle size of 20-54 nm, which made it highly reinforcing. Large differences in the mechanical properties of the two blends were observed. For blend 2, the rubber-silica chemical bonding was strong.
Figure 15. SEM micrograph showing dispersion of silica in blend 2 in Table 2. Note absence of cavities in the rubber.

Figure 16. SEM micrograph showing dispersion of silica in the rubber after tensile test. Data for blend 2 in Table 2. Note absence of cavities in the rubber.
Figure 17. Typical torque vs time cure traces by ODR at 160°C for blend 1 (■), and blend 2 (○). Note the cure for blend 2 underwent reversion after 57 minutes.

Figure 18. Tanδ vs temperature traces at 10 Hz test frequency for blend 1 and blend 2.
(compare Figure 14 and Figure 16). Rubber properties, for example, tensile strength and tear energy increase, reaching a maximum, and then deteriorate substantially as a function of crosslink density\(^{40,41}\). It was concluded that the inferior mechanical properties of blend 1 were mainly caused by the weak rubber-silica interaction and lesser crosslinks in the rubber.

CONCLUSIONS

From this study, the following conclusions were drawn. Blend 1, which had 1 phr CBS, 1.25 phr ZnO and 1.25 phr elemental sulphur and was cured for 10 min with poor reaction between the sulphur in TESPT and the rubber, had higher Young’s modulus and moduli at 100, 200 and 300% strain amplitudes and was harder with a much lower heat build-up. Blend 2, with 1.75 phr CBS, 1.25 phr ZnO and 2 phr elemental sulphur cured for 57 min with strong reaction between the sulphur in TESPT and the rubber. It had slightly better tensile strength and stored energy density at break and much higher elongation at break as well as tear energy. Blend 2 also possessed much lower average weight loss in the abrasion tests. Probably, the most interesting feature of the results was the fact that the cyclic fatigue life of blend 2 was approximately 50,000 times longer than that of blend 1.

This study has shown some positive effects of CBS and ZnO chemical curatives on the reaction between the sulphur in TESPT and the rubber in the NR/BR blend. Evidently, most of the mechanical properties benefited from a strong interaction between the rubber and silica but the reaction time between the sulphur in TESPT and the rubber remained unacceptably too long. This still remains a major drawback with the use of sulphur-bearing bifunctional organosilanes such as TESPT in rubber.

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REFERENCES


