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Two Advanced Styrene-butadiene/Polybutadiene Rubber Blends Filled with a Silanized Silica Nanofiller for Potential Use in Passenger Car Tire Tread Compound

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ABSTRACT

Styrene-butadiene rubber (SBR) and polybutadiene rubber (BR) were mixed together (75:25 by mass) to produce two SBR/BR blends. The blends were reinforced with a precipitated amorphous white silica nanofiller the surfaces of which were pre-treated with bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT). TESPT is a sulfur-bearing bifunctional organosilane that chemically bonds silica to rubber. The rubbers were primarily cured by using sulfur in TESPT and the cure was optimized by adding non-sulfur donor and sulfur donor accelerators and zinc oxide. The hardness, Young’s modulus, modulus at different strain amplitudes, tensile strength, elongation at break, stored energy density at break, tear strength, cyclic fatigue life, heat build-up, abrasion resistance, glass transition temperature, bound rubber and tan δ of the cured blends were measured. The blend which was cured with the non-sulfur donor accelerator and zinc oxide had superior tensile strength, elongation at break, stored energy density at break and modulus at different strain amplitudes. It also

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possessed a lower heat build-up, a higher abrasion resistance and a higher \( \tan \delta \) at low

temperatures to obtain high-skid resistance and ice-and wet-grip. Optimizing the chemical

bonding between the rubber and filler reduced the amount of the chemical curatives by

approximately 58% by weight for passenger car tire tread. This helped to improve health and

safety at work and reduce damage to the environment.

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

**INTRODUCTION**

The invention of wheel almost fifty five hundred years ago has been one of the greatest

achievements of mankind. The wheel is used on cars, planes and farm equipment. The

first air filled, pneumatic tire was patented in 1888 with a specific aim to replace hard

rubber tires and provide a smooth and high speed ride for cyclists. Eventually, car tires

were invented but the early ones lasted up to 40 miles on average before repair or

replacement was needed. Indeed, car tires have come a long way and this was mainly

due to the brilliance of rubber scientists and technologists who used chemical ingredients

such as processing aids, accelerators, activators, fillers, and antidegradants to improve the

processing and mechanical properties of rubber compounds for tire applications. A great deal

is also owed to tire manufacturers who developed more efficient and refined tire testing
To improve the mechanical properties of a rubber for example hardness, tear strength, tensile strength and elongation at break, fillers with surface areas from 150 to 400 m²/g such as colloidal carbon blacks, synthetic silicas, organoclays, and metal oxides are added. In addition to filler, compounds used to manufacture industrial rubber articles such as passenger car tire tread contain up to eight classes of rubber chemicals. For instance, the cure system consists of up to five different chemicals; primary and secondary accelerators, primary and secondary activators and elemental sulfur, which may add up to 11 parts per hundred rubber by weight (phr). Antidegradants and processing aids are also included to protect rubber against environmental ageing and to improve processing properties, respectively.

Fillers and curing chemicals perform two distinct functions in rubber compounds. Fillers increase the mechanical properties and curing chemicals produce crosslinks between the rubber chains at elevated temperatures, i.e. 140-240°C. Synthetic precipitated amorphous white silica filler is replacing carbon blacks in some applications such as tire tread compound. This filler has silanol or hydroxyl groups on its surfaces which make it acidic and moisture adsorbing. Acidity and moisture are both detrimental to the
cure of rubber compounds\textsuperscript{14} and can also cause loss of crosslink density in sulfur-cured rubbers.\textsuperscript{4} Furthermore, when a large amount of silica is added, processing becomes more difficult because the rubber viscosity increases significantly.\textsuperscript{15} Bifunctional organosilanes such as bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT) are used to enhance the reinforcing capability of fillers with silanol groups on their surfaces, such as precipitated silicas, and also forms an integral part of curing systems to improve the cross-linking network properties\textsuperscript{14}.

TESPT combines silica and sulfur into one single product known as a “crosslinking filler”.\textsuperscript{16} One such filler is silanized silica where the surfaces of precipitated silica are pre-treated with TESPT to chemically bond silica to rubber (Scheme 1) and to prevent the filler from interfering with the reaction mechanism of sulfur-cure in rubber.\textsuperscript{4}

Using a precipitated silica filler pre-treated with TESPT, a substantial reduction in the use of the curing chemicals was achieved in natural rubber (NR),\textsuperscript{17} styrene-butadiene rubber (SBR),\textsuperscript{18} polybutadiene rubber (BR),\textsuperscript{19} and nitrile rubber (NBR)\textsuperscript{20} without compromising the good mechanical properties of the rubber vulcanizates. To crosslink the rubber and optimize the chemical bonding between the rubber and filler via TESPT, accelerators and activators were added. The mechanical properties of the cured rubbers were improved significantly in spite of reducing the amount of the curing chemicals.
The aim of this study was to develop two styrene-butadiene/polybutadiene rubber blends (75:25 by mass) for potential use in passenger car tire tread formulations. The mass fraction of SBR with respect to BR in some passenger tire-tread compounds is 75:25.

The blends were reinforced and crosslinked with a high loading of a silanized silica nanofiller, and the chemical bonding between the rubber and filler was optimized by adding sulfenamide and thiuram accelerators and zinc oxide activator. The hardness, tensile strength, elongation at break, stored energy density at break, tear strength, Young’s modulus, modulus at different strain amplitudes, bound rubber, cyclic fatigue life, heat build-up, abrasion resistance, glass transition temperature, and tan δ of the blends were measured.

**EXPERIMENTAL**

**Materials: Rubber and nanofiller**

The raw elastomers used were styrene-butadiene rubber (SBR) (23.5 wt % styrene; Intol 1712, Polimeri Europa UK Ltd., Hythe, UK) and high-cis polybutadiene rubber BR (96% 1,4-cis; Buna CB 24, Bayer, Newbury, UK; not oil extended). SBR Intol 1712 is a cold emulsion co-polymer, polymerized using a mixture of fatty acid and rosin acid soaps as emulsifiers. It is extended with 37.5 phr of highly aromatic oil and contains a styrenated phenol as a non-staining anti-oxidant. It has approximately 4.8% by weight organic acid.
The reinforcing filler was Coupsil 8113, which was supplied by Evonik Industries AG of Germany. Coupsil 8113 is a precipitated amorphous white silica-type Ultrasil VN3 surfaces of which had been pre-treated with TESPT. It has 11.3% by weight silane, 2.5% by weight sulfur (included in TESPT), a 175 m²/g surface area (measured by N₂ 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-tert-butyl-2-benzothiazole sulffenamide (a safe-processing delayed action non sulfur-donor accelerator with a melting point of 105°C) (Santocure TBBS, Flexsys, Dallas, TX), Tetramethyl thiuram disulfide (a fast curing sulfur-donor accelerator with ~13% of the sulfur available to react with rubber and a melting point of 146°C) (Perkacit TMTD PDR D, Flexsys, Belgium, Europe), zinc oxide (ZnO; an activator, Harcros Durham Chemicals, Durham, UK), N-(1,3-dimethylbutyl)-N’-phenyl-p-phenylenediamine (an antidegradant, Santoflex 13, Brussels, Belgium), 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 rubber against environmental ageing. The cure system consisted of TBBS, TMTD, and ZnO, which were added to fully crosslink the rubber.
Mixing equipment

The compounds were prepared 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 ambient temperature (23°C) and 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.

Assessment of the silica dispersion in the rubber

To select a suitable mixing time for incorporating the silica in the rubbers, the mixing time was increased to 22 min to disperse the silica particles fully in the rubber. Twenty-four hours after the 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 scanning electron microscope. Small pieces of the uncured rubber were placed in liquid nitrogen for 3 min and then fractured to create two fresh surfaces. The samples, 65 mm² in area and 7 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 then studied from SEM photographs. For example, Figure 1 shows a typical good dispersion
of the silica particles in the rubber. After the photos were examined, a total mixing time of 10 min for the SBR rubber and 16 min for the BR rubber, respectively, were found to be sufficient to fully disperse the silica particles in the rubbers. These mixing times were subsequently used to make rubber compounds for this study.

**Mixing procedure**

To prepare the SBR compounds, TBBS, TMTD and ZnO were added 4 min after the filler and rubber were mixed together, and mixing continued subsequently for another 6 min before the compounds were removed from the mixer. The SBR compounds with the processing oil were made in the same way and the processing oil was added to the rubber at the start of mixing. For making the BR compounds, the filler and rubber were mixed together for 10 min and then TBBS, TMTD and ZnO were added and mixed for another 6 min. In total, 45 SBR and BR rubber compounds were made.

To make the SBR/BR rubber blends, SBR was mixed with the processing oil for 2 min and then BR was added and mixed for 1 min. Silica was subsequently added and mixed for 3 min after which, TBBS, ZnO, TMTD, and antidegradant were incorporated and mixed for another 6 min before the compounds were removed from the mixer. Temperature of the rubber compounds reached 53°C during mixing. Before the curing chemicals were added, the
rotors were stopped and the rubber compounds were cooled down to below 50°C to avoid pre-scorch during the subsequent mixing.

Finally, when mixing ended, the rubber compounds were removed from the mixer and milled to a thickness of 6-8 mm for further work. The compounds were stored at 21±2°C for at least 24 h before their viscosity and cure properties were measured.

**Addition of TBBS to the silanized silica-filled SBR and BR rubbers**

Accelerators were added to control the onset and rate of cure as well as crosslink density of the rubbers. To activate the rubber reactive tetrasulfane groups of TESPT, TBBS was added. The loading of TBBS in the silica-filled SBR rubber was increased progressively to 9 phr to measure the minimum amount needed to optimize \( \Delta \text{torque} \) and the chemical bonding or crosslinking between the rubber and filler via TESPT. The minimum amount of TBBS measured for the silica-filled SBR rubber was subsequently added to the silica-filled BR rubber. Note that \( \Delta \text{torque} \) is an indication of crosslink density changes in the rubber. The formation of crosslinks strengthened the rubber/TESPT interaction. In total, 7 compounds were made (compounds 1-7; Table I).

**Addition of zinc oxide to the silanized silica-filled SBR and BR rubbers with TBBS**

Zinc oxide was added to enhance the effectiveness of TBBS during the curing reaction in the
rubbers. The loading of ZnO in the silica-filled SBR and BR rubbers with TBBS was raised to
2.5 phr to determine the minimum amount needed to maximize ∆torque and the efficiency of
TBBS and cure. In total, 18 compounds were mixed (compounds 8-14; Tables II and
compounds 15-25; Table III).

**Addition of TMTD to the silanized silica-filled SBR and BR rubbers**

To activate the rubber reactive tetrasulfane groups of TESPT, TMTD was added. The
loading of TMTD in the silica-filled SBR rubber was increased progressively to 8.5 phr to
measure the minimum amount needed to optimize ∆torque and the chemical bonding between
the rubber and TESPT. The minimum amount of TMTD measured for the silica-filled SBR
rubber was then included in the silica-filled BR rubber. In total, 6 compounds were made
(compounds 26-31; Table IV)

**Addition of zinc oxide to the silanized silica-filled SBR and BR rubbers with TMTD**

The loading of zinc oxide in the silica-filled SBR and silica-filled BR rubbers with TMTD
was raised to 2.5 phr to determine the minimum amount needed to maximize ∆torque and the
efficiency of TMTD and cure. In total, 10 compounds were made (compounds 32-41;
Table V).

**Effect of the processing oil on the cure properties of the silica-filled SBR rubber with 5**
To assess effect of the processing oil on the cure properties of the silanized silica-filled SBR with TMTD, 4 compounds were made. The loading of the processing oil was increased from 0 phr to 15 phr (compounds 42-45; Table VI).

Mooney viscosity and cure properties of the rubber compounds and the blends

The viscosity of the rubber compounds was measured at 100°C in a single-speed rotational Mooney viscometer (Wallace Instruments, Surrey, UK) according to a British Standard. 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 and 170±2°C by an oscillating disc rheometer curemeter (ODR, Monsanto, Swindon, UK) at an angular displacement of ±3° and a test frequency of 1.7 Hz. The cure rate index, which is a measure of the rate of cure in the rubber, was calculated using a British Standard. The rheometer tests ran for up to 2 h. Figure 2 shows typical cure traces produced for the rubber compounds. Δtorque, is the difference between the maximum and minimum torque values on the cure trace of the rubber, and as mentioned earlier, indicates changes in the crosslink density and was calculated from these traces. Δtorque was subsequently plotted against the loading of TBBS, ZnO and TMTD. Results from these
experiments are also summarized in Tables I-VIII.

**Preparation of test pieces and testing of rubber compounds**

The rubber compounds were cured in a compression mould with a pressure of 11 MPa. Pieces of rubber, each approximately 140 g in weight, were cut from the milled sheet 6 mm thick. Each piece was placed in the centre of the mould to enable it to flow in all the directions when pressure was applied and prevent anisotropy from forming in the cured rubbers.

For determining the tensile properties, tear strength, Young’s modulus, modulus at different strain amplitudes, cyclic fatigue life and $\tan \delta$ of the rubbers, sheets 23 cm by 23 cm by approximately 2.7 mm thick were cured at $170\pm2^\circ$C, from which various samples for further tests were cut. For measuring the abrasion resistance and bound rubber content, cylindrical samples 16 mm in diameter and 8 mm in height were cured at $170\pm2^\circ$C. For the hardness determination, cylindrical samples 29 mm in diameter and 13 mm in height, and for the heat buildup, samples 17 mm in diameter and 25 mm in height were cured at $140\pm2^\circ$C. The bigger samples were cured at a lower temperature to ensure full cure in the centre of the rubber.

**Bound rubber content of the rubber vulcanizates**
The solvent used for the swelling tests and bound rubber determination was toluene.

For the determination, the samples were placed individually in 100 ml of the solvent in labeled bottles and allowed to swell for up to 18 days at ambient temperature (21±2°C). The weight of the samples was measured every day until it reached equilibrium. It took up to 4 days for the rubber samples to reach equilibrium. The solvent was removed after this time elapsed, and the samples were dried in air for 9 h. The samples were subsequently dried in an oven at 85°C for 24 h and allowed to stand for an extra 24 h at ambient temperature before they were re-weighed. The bound rubber was then calculated using the following expression:

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

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.

**Hardness, cohesive tear strength, tensile properties and cyclic fatigue life of the rubber vulcanizates**

The hardness of the rubber vulcanizates was measured in a Shore A Durometer hardness tester (The Shore Instrument & MFG, Co., New York) at ambient temperature (20°C) over a
15-second interval after which a reading was taken. This was repeated at four different positions on each sample and the median of the four readings was calculated.\textsuperscript{25} The tear tests were performed at an angle of 180\degree, at ambient temperature (20\degree C) and at a constant cross-head speed of 50 mm/min\textsuperscript{26}. For each rubber, five test pieces were fractured and the average tearing force was used to calculate tearing energy, $T$, for the rubbers.\textsuperscript{27} The median values of the tearing energies were subsequently noted.

The tensile stress, elongation at break, and stored energy density at break of the rubbers were determined in uniaxial tension using standard dumbbell test pieces. The tests were performed at 20\degree C and at a cross-head speed of 50 mm/min.\textsuperscript{28} The median of the three values were subsequently noted. Lloyd Nexygen 4.5.1. computer software was used for storing and processing the data.

The cyclic fatigue life of the rubbers (number of cycles to failure) was measured in uniaxial tension in a Hampden dynamic testing machine (Northampton, UK) with standard dumbbell test pieces. The test pieces were die-stamped from the sheets of cured rubber. The tests were performed at a constant maximum deflection of 100\% and a test frequency of 1.4 Hz.\textsuperscript{29} The test temperature was 21±2\degree C, and the strain on each test piece was relaxed to zero at the end of each cycle. For each rubber, eight test pieces were cycled to failure, and the tests
were stopped whenever the number of cycles exceeded 1000 kilocycles (kc).

**Modulus at different strain amplitudes, abrasion resistance and heat build-up of the rubber vulcanizates**

The modulus of the vulcanizates at 50%, 100%, 200% and 300% strain amplitudes and Young’s modulus were measured in uniaxial tension, using standard dumbbell test-pieces. The tests were carried out at ambient temperature (20°C) at a cross-head speed of 50 mm/min\(^2\). Nexygen 4.5.1 computer software was used to store and process the data. The tear strength, tensile properties and modulus of the rubber vulcanizates were measured in a Lloyd testing machine LR50K (Hampshire, UK).

The abrasion resistance of the cured rubbers was measured according to a British Standard\(^30\) and was expressed as abrasion resistance index (ARI). An index value of greater than 100% indicated that the test compound was more resistance to abrasion than the standard rubber under the conditions of the test. The heat build-up of the rubber compounds was determined using cylindrical test pieces and the temperature rises on the inside and on the surface of the test pieces were measured.\(^31\)

**Glass transition temperature and loss tangent (tan δ) of the raw SBR and BR rubbers and SBR/BR rubber blends**
A modulated-temperature differential scanning calorimeter (model 2920, TA Instruments, New Castle, DE) was used to measure the glass transition temperature, Tg, of the pure BR and SBR rubbers and the SBR/BR rubber blends. An oscillation amplitude of 1°C and a period of 60 s were used throughout the investigations, which were conducted at a heating rate of 3°C/min. TA Instruments Graphware software was used to measure the heat flow and heat capacity. The calorimeter was calibrated with indium standards. Both temperature and baseline were calibrated as for conventional DSC. A standard aluminum pan and lid were used and samples of rubber approximately 9-10 mg in weight were placed in the pan at ambient temperature and the lid was subsequently closed under some nominal pressure. The assembly was placed in the chamber of the calorimeter and the temperature was lowered to -140°C with the flow of liquid nitrogen. Nitrogen gas was also used with a flow rate of 35 ml/min as a medium.

Tan δ 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 δ was measured in DMAQ800 model CFL-50 (TA Instruments, USA), using Universal Analysis 2000 Software Version 4.3A. Test pieces 35 mm long, 10 mm wide and approximately 2.70 mm thick were used.
The tests were performed at 1, 10 and 100 Hz frequencies. The samples were deflected by 256 µm (nominal peak to peak displacement) during the test, and the sample temperature was raised from -140°C to 120°C at 3°C/min steps.

RESULTS AND DISCUSSION

Effect of TBBS and ZnO on the $\Delta$torque of the silica-filled SBR and BR rubber compounds

Figure 3 shows $\Delta$torque as a function of TBBS loading for the silica-filled SBR. $\Delta$torque increased to 22 dN m as the loading of TBBS was raised to 3 phr. Further increases to 9 phr had a lesser effect on the $\Delta$torque value, which rose to 26 dN m. Evidently, 3 phr was sufficient to activate the rubber reactive tetrasulfane groups of TESPT and form crosslinks between the rubber and filler. 3 phr TBBS was subsequently added to the silica-filled BR rubber compound.

To enhance the crosslink density of the silica-filled SBR rubber compound with 3 phr TBBS, ZnO was added. $\Delta$torque increased to 57 dN m when 0.5 phr ZnO was incorporated in the rubber and showed only a slight improvement to 64 dN m thereafter when an extra 2 phr ZnO was added (Fig. 4). Similarly, for the silica-filled BR compound with 3 phr TBBS, $\Delta$torque increased to 80 dN m with 0.2 phr ZnO and showed no further
improvement when another 1.8 phr ZnO was included in the rubber. An SBR/BR rubber blend was made by adding 60 phr silanized silica, 3 phr TBBS, 0.5 phr ZnO, 7.5 phr processing oil, and 1 phr antidegradant to the SBR and BR rubbers (compound 46; Table VIII).

Effect of TMTD and ZnO on the $\Delta$torque of the silanized silica-filled SBR and BR rubber compounds

Figure 5 shows $\Delta$torque against the loading of TMTD for the silica-filled SBR compound. $\Delta$torque increased sharply to 53 dN m when 5 phr TMTD was added and then, it continued rising at a much slower rate to 67 dN m when the loading of TMTD reached 8.5 phr. Apparently, 5 phr TMTD was sufficient to activate the rubber reactive tetrasulfane groups of TESPT and cure the rubber. 5 phr TMTD was subsequently mixed with the silica-filled BR rubber compound.

To improve the efficiency of TMTD, ZnO was mixed with the silica-filled SBR and BR rubber compounds. $\Delta$torque of the silica-filled SBR compound with 5 phr TMTD increased rapidly to 111 dN m after 0.3 phr ZnO was added, and it continued rising to 142 dN m as the loading of ZnO was raised to 2.5 phr. Similarly, the $\Delta$torque of the silica-filled BR compound with 5 phr TMTD rose from 82 dN m to to 131 dN m with 0.1 phr
ZnO, and no more ZnO was added because it would have made the rubber too brittle (Fig. 6). An SBR/BR rubber blend was prepared by adding 60 phr silanized silica, 5 phr TMTD, 7.5 phr processing oil, and 1 phr antidegradant to the SBR and BR rubbers (compound 47; Table VIII).

**Effect of the processing oil on the cure properties of the silica-filled SBR rubber with 5 phr TMTD**

Aromatic oils are often added as processing aid to reduce viscosity and increase processibility of rubber compounds. Passenger car tire tread compounds can contain up to 37 phr processing oil. Previous studies showed that adding up to 10 phr processing oil had no adverse effect on the scorch and optimum cure times of a sulfur-cured SBR rubber but 

To assess effect of the processing oil on the cure properties of the silica-filled SBR rubber compound with 5 phr TMTD, the loading of the oil was raised to 15 phr. The scorch and optimum cure times increased by approximately 60% and 54%, respectively, and the cure rate index decreased by 35%. This was in contrast to what was reported previously. However, the addition of the oil did have a detrimental effect on 

43%. This indicated a significant reduction in the crosslink density of the rubber (Table VI).
Viscosity and cure properties of the SBR/BR rubber blends

To optimize the reinforcing effect of the filler on the mechanical properties of the vulcanizates, it was essential to disperse the filler particles well in the rubber. The BR and SBR compounds were mixed for 16 and 10 min, respectively, to achieve good dispersion of the silica particles. However, long mixing times, for example 10 min, breaks down the rubber and causes reduction in its molecular weight and viscosity. The reduction is due to chain scission, 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 addition of silica, TBBS, TMTD, ZnO, antidegradant and processing oil increased the viscosity of the raw SBR/BR rubber blend from 40 MU to 98 MU for compound 46 and 84 MU for compound 47 (Table VII). Note that both compounds had similar glass transition temperatures around - 80°C (Table VII). Fillers increase rubber viscosity because of the formation of bound rubber. The bound rubber content of compounds 46 and 47 was 69 % (Table IX), and this indicated a high level of rubber-filler interaction. It is known that bound rubber forms during mixing while filler dispersion occurs and increases as a function of mixing temperature, mixing time, and storage time. Since the mixing time was 12 min
for compounds 46 and 47, and the temperature rose to 53°C during mixing, bound rubber formed. Furthermore, the rubber blends were stored at ambient temperature (21±2°C) for 3-4 days before and one week after they were cured. This also helped to increase the bound rubber, which reinforced the mechanical properties of the rubber blends. Compound 47 had shorter scorch and optimum cure times and a faster cure rate (cf, compound 46 and compound 47; Table VIII). TMTD is a fast curing accelerator, which explained the shorter cure cycle of compound 47.

**Mechanical properties of the cured SBR/BR rubber blends**

The mechanical properties of the SBR/BR rubber blends are summarized in Table IX. With the exception of the hardness and tearing energy, the remaining properties of compound 46 were noticeably better than those of compound 47. For example, tensile strength, elongation at break, and stored energy density at break were higher by approximately 46%, 6% and 45%, respectively. The Young’s modulus was the same for both compounds at 4 MPa. The modulus of compound 46 was 13-25% higher as the strain amplitude on the rubber was increased from 50 to 300%, respectively (cf, compound 46 with compound 47; Table IX). The properties which are of significant importance to tire tread performance were also superior for compound 46. For instance, the heat buildup tests
measured internal and surface temperatures of 148.7°C and 85.7°C, respectively, for compound 46, which were almost 8% lower than those measured for compound 47. Probably, the most interesting result was for the abrasion resistance index of compound 46. It was 34% higher than that of compound 47 and this indicated a much better resistance to abrasion. The cyclic fatigue life of both compounds exceeded 1000 kc.

Rubber reinforcement is to a great extent due to filler-rubber adhesion, filler-filler interaction, and crosslink density. The filler-filler interaction was negligible because the silica particles were dispersed well in the rubbers. The chemical bonding between the rubber and filler was optimized and the bound rubber was 69%. This indicated strong filler-rubber adhesion. The ∆torque of the two compounds were 52 and 47 dN m, at 170°C, respectively (Table VIII), which also indicated contribution from crosslinks to the rubber properties. The surfaces of silica had been pre-treated with rubber reactive TESPT, and the surface area of the filler particles was less than 400 m²/g, which also contributed to the improvement in the mechanical properties of the rubber blends. In addition, when the SBR and BR rubbers were mixed together for 12 min to produce compounds 46 and 47 and then cured at 170°C for up to 13 min, a strong interphase was formed between the two rubbers. The development of a strong interphase between dissimilar rubbers is an important factor in
the durability and performance of rubber blends in service.

**Tan δ of the cured SBR/BR rubber blends at different test frequencies**

The energy loss in car tires during dynamic strain affects their service performance such as rolling resistance. Rolling resistance is related to the movement of the whole tire corresponding to deformation at a frequency 10-100 Hz and a temperature ranging from 50 to 80°C. To meet the requirements of high-performance tires, a low tan δ value at a temperature of 50-80°C to reduce rolling resistance and save energy and fuel is often required. A high tan δ value (high hysteresis) at low temperatures for example, -50 to -30°C, to obtain high-skid resistance and ice-and wet-grip is also essential.

Figures 7-9 show tan δ as a function of the test temperature at 1, 10 and 100 Hz test frequencies, respectively for compounds 46 and 47. The peak tan δ values were also summarized in Table X. At 1 Hz, the peak tan δ of compound 46 and compound 47 were 0.47 at -36.6°C and 0.49 at -35.5°C, respectively (Fig. 7). At 10 Hz, the peak tan δ of compound 46 increased to 0.53 at – 31.7°C and that of compound 47 to 0.50 at -30.7°C, respectively (Fig. 8). At 100 Hz, the peak tan δ for compound 46 and compound 47 were 0.72 at -24.0°C and 0.55 at -32.4°C, respectively (Fig. 9). Clearly, compound 46 possessed a better skid resistance and ice-and wet-grip at 10 and 100 Hz because it had higher tan δ values at
low temperatures. However, at above 50°C, which is important to reduce the rolling resistance and save energy, the tan δ of both compounds were fairly similar at 1 Hz but that of compound 47 was slightly lower at 10 Hz. Notably, increases in the test frequency had a significant effect on the peak tan δ of these compounds. For example, the peak tan δ of compound 46 rose by more than 50% and that of compound 47 by approximately 12% when the test frequency was increased to 100 Hz (Figs. 10 and 11, respectively). It was concluded that compound 46, which also had a much higher abrasion resistance index and a lower heat build-up, could potentially replace the passenger car tire treads currently in use.

Health, safety, and the environmental issues related to passenger car tires

Excessive use of the curing chemicals is harmful to health, safety and the environment and their use is restricted by the new European chemicals policy, Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) and various legislations for environment and safety. The presence of ZnO in tread compounds has also come under growing scrutiny because of environmental concerns. The tire industry is the largest single market for ZnO. The elimination or a more restricted use of ZnO in rubber compounds will help to reduce damage to the environment.

The average weight of a new radial passenger car tire is approximately 12.5 kg.
The tread weight is 32.6% of the total weight of a tire and is roughly 4.1 kg. As mentioned earlier, formulations for passenger car tire tread compound can contain up to 11 phr chemical curatives that is 4.8% of the total weight of all the ingredients in the formulation. On this basis, the total amount of the chemical curatives in a tire tread compound can be as high as 197 g. As shown in Table VIII, compound 46 was fully cured with 3 phr TBBS and 0.5 phr ZnO. The chemical curatives in this compound were 2% of the total weight of all the ingredients in the formulation. If this compound was to replace the current tire tread compounds, it would reduce the loading of the chemical curatives by approximately 58% to 82 g. Moreover, a large reduction in the use of ZnO will be greatly beneficial to tire manufacturers and will ultimately reduce costs and minimize damage to the environment.

CONCLUSIONS

From this study, it was concluded that:

1 - The SBR/BR blend which was cured with the non-sulfur donor accelerator and zinc oxide had superior tensile strength, elongation at break, stored energy density at break and modulus at different strain amplitudes. It also possessed a lower heat build-up, a higher abrasion resistance, a higher tan δ value at low temperatures to obtain high-skid resistance and ice- and wet-grip.
2 - Optimizing the chemical bonding between the rubber and filler via the tetrasulfane groups of TESPT reduced excessive use of the chemical curatives significantly. This improved health and safety at workplace and reduced damage to the environment.

3 - The addition of the processing oil had a detrimental effect on the scorch and optimum cure times, rate of cure and Δtorque of the silanized silica-filled SBR rubber cured with TMTD.

ACKNOWLEDGEMENT

The authors thank Evonik Industries AG of Germany for supplying the silica filler. The scanning electron microscopy of the samples was carried out at the Loughborough Materials Characterization Centre, UK. We are also grateful to DTR VMS Limited of UK (formerly Avon Automotive VMS) for supporting this project. The abrasion resistance index and heat build-up measurements were carried out at the Korea Institute of Footwear and Leather Technology in Busan, Korea.
REFERENCES


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30. Br Standards Institution. Rubber, vulcanized or thermoplastic – Determination of


47. Rubber Manufacturers Association website at

   http://rma.org/scrap_tires/scrap_tires_markets/scrap_tire_characteristics/
TABLE I

Formulation and ODR Test Results for the Silica-filled SBR Rubber with an Increasing Loading of TBBS

<table>
<thead>
<tr>
<th>Compound no</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBBS(phr)</td>
<td>0.5</td>
<td>1.5</td>
<td>3.0</td>
<td>4.5</td>
<td>6.0</td>
<td>7.5</td>
<td>9.0</td>
</tr>
<tr>
<td>Minimum torque (dN m)</td>
<td>26</td>
<td>27</td>
<td>22</td>
<td>21</td>
<td>18</td>
<td>18</td>
<td>17</td>
</tr>
<tr>
<td>Maximum torque (dN m)</td>
<td>34</td>
<td>43</td>
<td>44</td>
<td>46</td>
<td>43</td>
<td>47</td>
<td>43</td>
</tr>
<tr>
<td>∆torque (dN m)</td>
<td>8</td>
<td>16</td>
<td>22</td>
<td>25</td>
<td>25</td>
<td>29</td>
<td>26</td>
</tr>
</tbody>
</table>

Formulation: 100 phr styrene-butadiene rubber and 60 phr silica.
TABLE II
Formulation and ODR Test Results for the Silica-filled SBR Rubber with an Increasing Loading of zinc oxide

<table>
<thead>
<tr>
<th>Compound no</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO(phr)</td>
<td>0</td>
<td>0.3</td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Minimum torque (dN m)</td>
<td>22</td>
<td>26</td>
<td>24</td>
<td>22</td>
<td>20</td>
<td>18</td>
<td>19</td>
</tr>
<tr>
<td>Maximum torque (dN m)</td>
<td>44</td>
<td>69</td>
<td>81</td>
<td>85</td>
<td>82</td>
<td>80</td>
<td>83</td>
</tr>
<tr>
<td>Δtorque (dN m)</td>
<td>22</td>
<td>43</td>
<td>57</td>
<td>63</td>
<td>62</td>
<td>62</td>
<td>64</td>
</tr>
</tbody>
</table>

Formulation: 100 phr styrene-butadiene rubber, 60 phr silica, and 3 phr TBBS.
TABLE III

Formulation and ODR Test Results for the Silica-filled BR Rubber with an Increasing Loading of zinc oxide

<table>
<thead>
<tr>
<th>Compound no</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
<th>21</th>
<th>22</th>
<th>23</th>
<th>24</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO(phr)</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.8</td>
<td>1</td>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td>Minimum torque (dN m)</td>
<td>53</td>
<td>52</td>
<td>49</td>
<td>53</td>
<td>50</td>
<td>61</td>
<td>58</td>
<td>55</td>
<td>51</td>
<td>52</td>
<td>50</td>
</tr>
<tr>
<td>Maximum torque (dN m)</td>
<td>106</td>
<td>125</td>
<td>129</td>
<td>131</td>
<td>138</td>
<td>138</td>
<td>133</td>
<td>140</td>
<td>131</td>
<td>129</td>
<td></td>
</tr>
<tr>
<td>∆torque (dN m)</td>
<td>52</td>
<td>73</td>
<td>80</td>
<td>78</td>
<td>81</td>
<td>77</td>
<td>80</td>
<td>78</td>
<td>89</td>
<td>79</td>
<td>79</td>
</tr>
</tbody>
</table>

Formulation: 100 phr polybutadiene rubber, 60 phr silica, and 3 phr TBBS.
TABLE IV

Formulation and ODR Test Results for the Silica-filled SBR Rubber with an Increasing Loading of TMTD

<table>
<thead>
<tr>
<th>Compound no</th>
<th>26</th>
<th>27</th>
<th>28</th>
<th>29</th>
<th>30</th>
<th>31</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMTD (phr)</td>
<td>0.5</td>
<td>2.0</td>
<td>3.5</td>
<td>5.0</td>
<td>7.0</td>
<td>8.5</td>
</tr>
<tr>
<td>Minimum torque (dN m)</td>
<td>29</td>
<td>27</td>
<td>25</td>
<td>24</td>
<td>23</td>
<td>22</td>
</tr>
<tr>
<td>Maximum torque (dN m)</td>
<td>39</td>
<td>45</td>
<td>67</td>
<td>78</td>
<td>83</td>
<td>89</td>
</tr>
<tr>
<td>Δtorque (dN m)</td>
<td>10</td>
<td>18</td>
<td>42</td>
<td>54</td>
<td>60</td>
<td>67</td>
</tr>
</tbody>
</table>

Formulation: 100 phr styrene-butadiene rubber, 60 phr silica.
TABLE V
Formulation and ODR Test Results for the Silica-filled SBR and BR Rubbers with an Increasing Loading of zinc oxide

<table>
<thead>
<tr>
<th>Compound no</th>
<th>32</th>
<th>33</th>
<th>34</th>
<th>35</th>
<th>36</th>
<th>37</th>
<th>38</th>
<th>39</th>
<th>40*</th>
<th>41*</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO (phr)</td>
<td>0</td>
<td>0.13</td>
<td>0.3</td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>Minimum torque (dN m)</td>
<td>24</td>
<td>29</td>
<td>31</td>
<td>32</td>
<td>30</td>
<td>28</td>
<td>29</td>
<td>23</td>
<td>51</td>
<td>66</td>
</tr>
<tr>
<td>Maximum torque (dN m)</td>
<td>78</td>
<td>124</td>
<td>142</td>
<td>150</td>
<td>157</td>
<td>167</td>
<td>167</td>
<td>165</td>
<td>133</td>
<td>197</td>
</tr>
<tr>
<td>Δtorque (dN m)</td>
<td>54</td>
<td>95</td>
<td>111</td>
<td>118</td>
<td>127</td>
<td>139</td>
<td>138</td>
<td>142</td>
<td>92</td>
<td>131</td>
</tr>
</tbody>
</table>

Formulations:

Compounds 32-39: 100 phr styrene-butadiene rubber, 60 phr silica, 5 phr TMTD.

Compound 40: 100 phr polybutadiene, 60 phr silica, 5 phr TMTD, 0 phr ZnO.

Compound 41: 100 phr polybutadiene, 60 phr silica, 5 phr TMTD, 0.1 phr ZnO.
TABLE VI
Formulation and ODR Test Results for the Silica-filled SBR Rubber with an Increasing Loading of Processing Oil

<table>
<thead>
<tr>
<th></th>
<th>Compound no</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>42</td>
<td>43</td>
<td>44</td>
<td>45</td>
</tr>
<tr>
<td>Enerflex 74 (phr)</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Minimum torque (dN m)</td>
<td>29</td>
<td>27</td>
<td>23</td>
<td>18</td>
</tr>
<tr>
<td>Maximum torque (dN m)</td>
<td>78</td>
<td>76</td>
<td>58</td>
<td>46</td>
</tr>
<tr>
<td>Δtorque (dN m)</td>
<td>49</td>
<td>49</td>
<td>35</td>
<td>28</td>
</tr>
<tr>
<td>Scorch time, ( t_{s2} ) (min)</td>
<td>10</td>
<td>10</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>Optimum cure time, ( t_{95} ) (min)</td>
<td>61</td>
<td>58</td>
<td>83</td>
<td>94</td>
</tr>
<tr>
<td>Cure rate index (min(^{-1}))</td>
<td>2.0</td>
<td>2.1</td>
<td>1.5</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Formulation: 100 phr styrene-butadiene rubber, 60 phr silica, 5 phr TMTD.
TABLE VII
Mooney Viscosity and Glass-Transition Temperature Values of the Pure Rubbers, Pure SBR/BR Rubber Blend and Compounds 46 and 47

<table>
<thead>
<tr>
<th>Rubber</th>
<th>Mooney viscosity (MU)</th>
<th>Glass-transition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>52</td>
<td>-50</td>
</tr>
<tr>
<td>BR</td>
<td>49</td>
<td>-107</td>
</tr>
<tr>
<td>Pure SBR/BR blend</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td>Compound 46</td>
<td>98</td>
<td>-79</td>
</tr>
<tr>
<td>Compound 47</td>
<td>84</td>
<td>-80</td>
</tr>
</tbody>
</table>

Compound 46: SBR/BR rubber blend cured with TBBS and ZnO.
Compound 47: SBR/BR rubber blend cured with TMTD.
<table>
<thead>
<tr>
<th>Compound no</th>
<th>46</th>
<th>47</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>BR</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Silanized silica</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>TBBS</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>TMTD</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Santoflex 13</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Enerflex 74</td>
<td>7.5</td>
<td>7.5</td>
</tr>
</tbody>
</table>

ODR results at 170°C

<table>
<thead>
<tr>
<th></th>
<th>46</th>
<th>47</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum torque (dN m)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Maximum torque (dN m)</td>
<td>72</td>
<td>67</td>
</tr>
<tr>
<td>Δtorque (dN m)</td>
<td>52</td>
<td>47</td>
</tr>
<tr>
<td>$t_{52}$ (min)</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>$t_{95}$ (min)</td>
<td>13</td>
<td>9</td>
</tr>
<tr>
<td>Cure rate index (min⁻¹)</td>
<td>11</td>
<td>14.3</td>
</tr>
</tbody>
</table>

ODR results at 140°C

<table>
<thead>
<tr>
<th></th>
<th>46</th>
<th>47</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum torque (dN m)</td>
<td>22</td>
<td>24</td>
</tr>
<tr>
<td>Maximum torque (dN m)</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>Δtorque (dN m)</td>
<td>58</td>
<td>66</td>
</tr>
<tr>
<td>$t_{52}$ (min)</td>
<td>19</td>
<td>7</td>
</tr>
<tr>
<td>$t_{95}$ (min)</td>
<td>65</td>
<td>55</td>
</tr>
<tr>
<td>Cure rate index (min⁻¹)</td>
<td>2.2</td>
<td>2.1</td>
</tr>
</tbody>
</table>
### TABLE IX
Bound Rubber and Mechanical Properties of the SBR/BR Rubber Blends

<table>
<thead>
<tr>
<th>Compound no</th>
<th>46</th>
<th>47</th>
</tr>
</thead>
</table>

#### Swelling tests data
- **Bound rubber content (%)**  
  - Compound 46: 69  
  - Compound 47: 69

#### Mechanical properties
- **Hardness (Shore A)**  
  - Compound 46: 66  
  - Compound 47: 69
- **Young’s modulus (MPa)**  
  - Compound 46: 4  
  - Compound 47: 4
- **Modulus at different strain amplitudes (MPa)**
  - **Strain amplitude (%)**  
    - 50: 1.6  
    - 100: 1.7  
    - 200: 1.9  
    - 300: 2.0
- **Tensile strength (MPa)**  
  - Compound 46: 26  
  - Compound 47: 14
- **Elongation at break (%)**  
  - Compound 46: 1030  
  - Compound 47: 968
- **Stored energy density at break (MJ/m³)**  
  - Compound 46: 121  
  - Compound 47: 67
- **T (kJ/m²)**  
  - Compound 46: 36.5  
  - Compound 47: 86
- **Range of values**  
  - Compound 46: 32-38  
  - Compound 47: 58-103
- **Cyclic fatigue life (kc)**  
  - Compound 46: >1000  
  - Compound 47: >1000

#### Heat buildup and abrasion resistance index
- **Internal temperature (°C)**  
  - Compound 46: 148.7  
  - Compound 47: 161
- **Surface temperature (°C)**  
  - Compound 46: 85.7  
  - Compound 47: 92.3
- **Abrasion resistance index (%)**  
  - Compound 46: 230  
  - Compound 47: 151
TABLE X

Peak Tan δ and Test Temperature Data for the two SBR/BR Rubber Blends Tested at Different Test Frequencies.

<table>
<thead>
<tr>
<th></th>
<th>Compound</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>46</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>Peak tan δ</td>
<td>1 Hz</td>
<td>0.47</td>
<td>0.49</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>-36.6</td>
<td>-35.5</td>
<td></td>
</tr>
<tr>
<td>Peak tan δ</td>
<td>10 Hz</td>
<td>0.53</td>
<td>0.50</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>-31.7</td>
<td>-30.7</td>
<td></td>
</tr>
<tr>
<td>Peak tan δ</td>
<td>100 Hz</td>
<td>0.72</td>
<td>0.55</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>-24.0</td>
<td>-32.4</td>
<td></td>
</tr>
</tbody>
</table>
Scheme 1 – Chemical structure of bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT) or Si69 coupling agent
Figure 1 – SEM photograph showing good dispersion of the silica particles in the rubber. Data for the SBR rubber with mixing time = 10 min.
Figure 2 – Torque versus time traces by ODR for the SBR/BR rubber blends at 170°C. (- - - - - ) compound 46, (____) compound 47.
Figure 3 – $\Delta$Torque versus TBBS loading for the silica-filled SBR rubber.
Figure 4 - Δtorque versus ZnO loading. (●), silica-filled SBR rubber with 3 phr TBBS; (○), silica-filled BR rubber with 3 phr TBBS.
Figure 5 – ΔTorque versus TMTD loading for the silica-filled SBR rubber.
Figure 6 – ΔTorque versus ZnO loading. (●), silica-filled SBR rubber with 5 phr TMTD; (♦), silica-filled BR rubber with 5 phr TMTD.
Figure 7 – Tan δ versus the temperature at 1 Hz. (---) compound 46, (-----) compound 47.
Figure 8 – Tan δ versus the temperature at 10 Hz. (---) compound 46, (---) compound 47.
Figure 9 – Tan δ versus the temperature at 100 Hz. (- - -) compound 46, (——) compound 47.
Figure 10 – Tan δ versus the temperature at 1, 10, and 100 Hz for compound 46.
Figure 11 – Tan δ versus the temperature at 1, 10, and 100 Hz for compound 47.