Comparing the dynamic behaviour of several rubbers filled with silanized silica nanofiller
Saeed Ostad Movahed,* Ali Ansarifar and Mo Song

Abstract
BACKGROUND: The effect of the same amount of precipitated silica nanofiller on the curing and dynamic properties of different rubbers, including natural rubber (NR) without and with the addition of elemental sulfur (NR with S), synthetic polyisoprene (IR), polybutadiene (BR) and poly(styrene-co-butadiene) copolymer (SBR), was investigated. The silica surfaces were pre-treated with bis(3-triethoxysilylpropyl)tetrasulfane (TESPT) to chemically bond the silica to the rubber. The rubbers were primarily cured by using sulfur in TESPT with the addition of optimum accelerator (TBBS) and activator (ZnO), which helped to form sulfur chemical bonds between the rubber and filler.

RESULTS: Cure properties, Mooney viscosity, glass transition temperature, bound rubber and crosslink density along with dynamic properties of the filled rubbers, including tan δ, loss modulus (G") and storage modulus (G'), were measured as a function of double oscillation amplitude (DSA) from 15 to 1000 µm, temperature from −130 to 100 °C and frequency from 1 to 100 Hz. The results with emphasis on potential for tyre tread applications are discussed. It emerged that SBR along with BR filled rubbers had the highest rolling resistance while IR filled rubber had the least. Moreover, it was found that SBR filled rubber had the best skid resistance and BR filled rubber the worst.

CONCLUSION: Interestingly, the variation of G' with DSA showed a complicated behaviour for different filled rubbers. It emerged that in some DSA ranges the Payne effect was observed, and in the remaining ranges increments of G' with DSA were seen. Because the bound rubber of most of the filled rubbers was more than 92%, there should be another predominant mechanism in the systems studied rather than simply de-agglomeration or filler network breakdown, which is proposed by the Payne model. In addition, the nanoscale of the filler may be effective for this behaviour.

INTRODUCTION
Although static mechanical properties have a significant role in the service life of tyre treads, considerable attention should be paid to the dynamic properties. Wearing of the tyre tread and tyre performance are two sides of the same coin. Fillers, when added to polymer systems, are known to cause a change in dynamic properties. This includes both the viscous (loss) modulus and the elastic (storage) modulus, along with their ratio (tan δ), which is related to the portion of energy dissipated during dynamic deformation.1 In practice, the energy loss in rubber products during dynamic strain is of great importance, as, for example, in vibration mounts and automotive tyres where it affects the service performance of these products with regard to heat generation and fatigue life for the former, and rolling resistance, traction and skid resistance for the latter. In fact, with regard to tyre applications, it has been well established that repeated straining of the rubber compound due to rotation and braking can be approximated as a process of constant energy input involving different temperatures and frequencies.2–4 Rolling resistance, for example, is related to the movement of the whole tyre corresponding to deformation at a frequency of 10–100 Hz and a temperature of 50–80 °C.1 In the case of skid or wet grip, the stress is generated by resistance from the road surface and movement of the rubber at the surface, or near the surface, of the tyre tread. The frequency is around 10^4–10^7 Hz at room temperature.3,4 It is therefore obvious that any change in dynamic hysteresis of the rubber compounds at different frequencies and temperature will alter the performance of the tyre.

Since certain tyre properties involve frequencies that are too high to be measured, these frequencies are reduced to a measurable level (1 Hz) at lower temperatures by applying the time–temperature equivalence principle, even though in the case of filled vulcanizates the shift factors for building the elastic (storage) modulus master curve are not exactly the same as those for the master curve of viscous (loss) modulus,5 and hence tan δ. However, the master curve for each property can be constructed experimentally according to the temperature–frequency principle.

Ansarifar et al.6–12 studied the effect of silanized pre-treated silica nanofilmer as a rubber reinforcement agent on the properties of filled rubber. In accordance with those works, silanized (here bis(3-triethoxysilylpropyl)tetrasulfane (TESPT)), pre-treated precipitated silica nanofilmer (Schemes 1 and 2) was a strong...
reinforcement agent, which improved the physical properties as well as the dynamic performance of filled rubber compared with other reinforcement agents, including carbon black. This silane (TESPT) possesses tetrasulfane and ethoxy reactive groups. The tetrasulfane groups are rubber reactive and react in the presence of accelerators at elevated temperatures, i.e. 140–240 °C, with or without elemental sulfur being present, to form crosslinks in elastomers containing carbon–carbon double bonds. The ethoxy groups react with the silanol groups on the surface of silica during compounding and this leads to the formation of stable silica/TESPT bonds.10 Pre-treated silanized precipitated silica nanofiller displays many advantages when compared to a separate employment of a liquid coupling agent and silica in rubber compounding.13 There are many reports on the effect of different fillers on the oscillation amplitude dependency of dynamic characteristics of filled rubbers1 but we could not find any report on silanized pre-treated silica nanofiller. Therefore, in this study, the dynamic behaviours of different rubbers filled (reinforced) with silanized pre-treated silica nanofiller, with emphasis on tyre tread applications, were compared and the results discussed.

**EXPERIMENTAL**

**Rubbers and filler**

The raw rubbers used were standard Malaysian natural rubber grade L (98 wt% cis-1,4 content, denoted NR and obtained from SMRL), synthetic polyisoprene (minimum 96 wt% cis-1,4 content, denoted IR and obtained as Kraton IR-307 from Kraton Polymers, USA), cis-butadiene rubber (denoted BR and obtained as BUNA CB 24 from Bayer, UK) and poly(styrene-co-butadiene) polymer (denoted SBR and obtained as SBR-1712 from Polimeri Europa–UK Ltd). Table 1 lists the specifications. The reinforcing filler was Coupsil 8113 obtained from Degussa Ltd, Hanau, Germany. Coupsil 8113 is a precipitated amorphous white silica, type Ultrasil VN3, the surfaces of which had been pre-treated with TESPT. It has 11.3% by weight TESPT, 2.5% by weight sulfur (included in TESPT), 175 m² g⁻¹ surface area (measured by nitrogen adsorption) and a 20–54 nm particle size.

Authors have previously suggested 14,15 that the optimum amount of accelerator (TBBS) and activator (ZnO) for an SBR rubber filled with 60 parts per hundred rubber (phr) silanized silica (Coupsil 8113) was 3 and 0.5 phr, respectively. Similarly, the optimum amount of accelerator for BR rubber filled with 60 phr silanized silica was 7.5 phr with no need for activator. With the addition of 0.3 phr elemental sulfur to the above BR filled rubber, two compounds, SBR and BR filled rubbers, became well mixed and were suitable for blending. This meant that their optimum cure time ($t_{90}$) was the same (Tables 2 and 3, compounds 1 and 2). Accordingly, the optimum amount of accelerator and activator for NR filled with 60 phr silanized silica was 6 and 0.3 phr, respectively (Table 2, compound 3). For IR filled rubber, the same materials were used in a different respective ratio of 7 and 1 phr (Table 2, compound 5). Unlike IR, NR contains a few percent of other materials such as proteins, fatty acids, resins and inorganic materials that alter its properties. To evaluate the effect of elemental sulfur on the dynamic properties of SBR filled rubber, one more compound with 0.2 phr elemental sulfur was prepared (Table 2, compound 6).

The glass transition temperature ($T_g$) of the raw rubbers was measured using the modulated temperature differential scanning calorimetry (MDSC) technique (TA Instruments, model 2920) with an oscillation amplitude of 1 °C and an oscillation period of 60 s.
The heating rate and temperature range were 3 °C min⁻¹ and −140 to 20 °C, respectively.

Curing chemicals, antidegradants and processing oil
In addition to the raw rubbers and filler, the other ingredients were N-1-butyl-2-benzothiazole sulfenamide (Santocure TBBS, Woluwe, Belgium; safe-processing delayed-action accelerator), zinc oxide (Harcros Durham Chemicals, UK; activator), elemental sulfur (Solvay Barium Strontium, Hannover, Germany; curing agent), N-(1,3-dimethylbutyl)-N’-phenyl-p-phenylenediamine (Santoflex 13; antidegradant) and Enterflex 74 (processing oil). The curing system consisted of TBBS, zinc oxide and elemental sulfur. TBBS and zinc oxide were added to optimize the chemical bonding or crosslinks between the rubber and filler. Accelerators are ingredients used to control the onset and rate of cure and the crosslink density in rubber. Activators are chemicals used to enhance the effectiveness of the accelerators during the curing reaction in rubber. Elemental sulfur is a curing agent used to crosslink rubbers with unsaturated sites or chemically active double bonds such as in natural rubber.

Mixing
The compounds were prepared using a Haake Rheocord 90 (Berlin, Germany), a small laboratory mixer with counter-rotating rotors. In these experiments, the Banbury rotor speed was 45 rpm and the mixing chamber was maintained at 50 °C for BR and NR compounds and at ambient temperature for SBR and IR compounds. The first temperature mentioned was nominal and the exact temperature and at ambient temperature for SBR and IR compounds. The first stage, 6 min was chosen. For SBR, the compounding for the time of the first stage was 4 min, and after 2 min process oil was added to the compound with continuation of mixing. For the second stage, the same as BR, an extra 6 min was chosen. For NR and IR compounding, 13 and 16 min were chosen for the first stage, respectively, and an extra 3 min for the second stage.

After finishing the first stage, the ram of the mixing chamber was elevated, the mixture was allowed to cool to 50 °C and then all curing chemicals were added. After finishing the second mixing stage, the compound was removed from the mixing chamber and allowed to cool and reach a steady-state condition for at least 24 h, based on the advice of a relevant British standard.

Curing procedure and physical testing methods
Viscosity measurement
The viscosity of the rubber compounds was measured as Mooney units for a large rotor (ML₁₈₄₃₆₁₇) at 100 °C in a single-speed rotational Mooney viscometer supplied by Wallace Instruments, Surrey, UK, according to the relevant British standard.

Cure properties measurement
An oscillating disc rheometer curemeter (ODR; Monsanto, Swindon, UK) was employed to measure the cure properties, namely the scorch times t₁ and t₂ (which are, respectively, the time for cure onset and the time for a cure of one unit greater), and the t₉₅ and t₉₀ times (which are, respectively, the times to reach 95 and 90% of the completed cure). The ODR was also used to measure the minimum, maximum and delta torque (ΔT). An angular displacement of ±3° and a test frequency of 1.7 Hz at 140 ± 2 °C were employed. The total run time was 2 h and ΔT, which is an indication of crosslink density changes in rubber, was monitored.

Bound rubber and crosslink density measurement
The bound rubber is a measurement of the percentage of polymer bound by filler. The solvent used for bound rubber determination was toluene (Merck, Germany). Cylindrical-shaped samples with a diameter of 15 mm and height of 9 mm were employed. The

Table 3. ODR results and physical properties of filled rubbers

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min. torque (dN m)</td>
<td>22.7</td>
<td>39.25</td>
<td>25.8</td>
<td>26.8</td>
<td>26</td>
<td>21.15</td>
</tr>
<tr>
<td>Max. torque (dN m)</td>
<td>65.9</td>
<td>123.8</td>
<td>106.9</td>
<td>135.1</td>
<td>137</td>
<td>70.44</td>
</tr>
<tr>
<td>ΔT (dN m)</td>
<td>43.2</td>
<td>84.6</td>
<td>81.1</td>
<td>108.3</td>
<td>111</td>
<td>49.29</td>
</tr>
<tr>
<td>t₁ (min)</td>
<td>12.22</td>
<td>5.21</td>
<td>8.11</td>
<td>5.53</td>
<td>-</td>
<td>10.54</td>
</tr>
<tr>
<td>t₂ (min)</td>
<td>13.48</td>
<td>6.01</td>
<td>9.00</td>
<td>6.00</td>
<td>8.00</td>
<td>12.05</td>
</tr>
<tr>
<td>t₉₀ (min)</td>
<td>49.20</td>
<td>49.32</td>
<td>23.46</td>
<td>9.06</td>
<td>-</td>
<td>37.23</td>
</tr>
<tr>
<td>t₉₅ (min)</td>
<td>57.15</td>
<td>57.31</td>
<td>26.56</td>
<td>9.20</td>
<td>34.00</td>
<td>43.50</td>
</tr>
<tr>
<td>CRI</td>
<td>2.70</td>
<td>2.26</td>
<td>5.6</td>
<td>33</td>
<td>3.9</td>
<td>3.75</td>
</tr>
<tr>
<td>Mooney viscosity at 100 °C (ML₁₈₄₃₆₁₇)</td>
<td>124</td>
<td>149</td>
<td>178</td>
<td>249</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bound rubber (%)</td>
<td>65.7</td>
<td>93</td>
<td>94</td>
<td>94</td>
<td>93</td>
<td>-</td>
</tr>
<tr>
<td>Crosslink density (mol m⁻³)</td>
<td>124</td>
<td>220</td>
<td>149</td>
<td>178</td>
<td>249</td>
<td>-</td>
</tr>
</tbody>
</table>

The compounds were prepared using a Haake Rheocord 90 (Berlin, Germany), a small laboratory mixer with counter-rotating rotors. In these experiments, the Banbury rotor speed was 45 rpm and the mixing chamber was maintained at 50 °C for BR and NR compounds and at ambient temperature for SBR and IR compounds. The first temperature mentioned was nominal and the exact temperature and at ambient temperature for SBR) and the second for the addition of other curing chemicals. The time for the first stage, for BR compounding, was chosen as 10 min, as recommended by Ansarifar et al. For the second stage, 6 min was chosen. For SBR, the compounding for the time of the first stage was 4 min, and after 2 min process oil was added to the compound with continuation of mixing. For the second stage, the same as BR, an extra 6 min was chosen. For NR and IR compounding, 13 and 16 min were chosen for the first stage, respectively, and an extra 3 min for the second stage.

After finishing the first stage, the ram of the mixing chamber was elevated, the mixture was allowed to cool to 50 °C and then all curing chemicals were added. After finishing the second mixing stage, the compound was removed from the mixing chamber and allowed to cool and reach a steady-state condition for at least 24 h, based on the advice of a relevant British standard.
test temperature was ambient or 23 °C. The samples were then placed individually in 90 mL of the solvent in labelled bottles, and allowed to swell. The weight of the samples was measured each day until equilibrium. After this stage, the solvent was removed and samples were dried in air for 9 h. Subsequently, the samples were dried in a vacuum 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 and crosslink density were calculated using equations recommended by Hamed and Rattanasom20 and Wolff.21

Dynamic properties measurement
Tan δ is the ratio of the loss modulus, \( G'' \), and storage modulus, \( G' \). The loss modulus represents the viscous component of the modulus and includes all the energy dissipation processes during dynamic strain. Tan δ was measured using a dynamic mechanical thermal analyser (DMA-800). TA analysis software was used to store and analyse the data. Rectangular samples of 35 mm × 13 mm × 2.5 mm (thickness) were chosen as test pieces. The samples were deflected by 15, 256, 500 and 1000 µm (nominal peak-to-peak displacement) at several frequencies of 1, 20 and 100 Hz (only for SBR filled rubber). The sample temperature was raised from −130 to 100 °C with a ramp step of 5 °C min⁻¹. In addition to tan δ, the loss modulus and storage modulus of samples were measured using the instrument mentioned above under the same conditions.

RESULTS AND DISCUSSION
Table 3 gives the ODR results (cure properties) along with bound rubber, crosslink density and Mooney viscosities of compounds 1–6. Addition of silanized silica nanofiller increased the Mooney viscosities of NR, SBR, BR and IR from Mooney unit 96.7, 51.3, 49 and 69 to Mooney unit 106, 109, 162 and 105, respectively (Tables 1 and 3). Filler loading and subsequent Mooney viscosity increment may be considered an important indication of a substantial difference between the dynamic behaviour of raw rubbers and filled rubbers.1 All filled rubbers (except SBR) had extremely high bound rubber (more than 90%; Table 3). This fact indicates strong filler–polymer networking in the studied systems.1,21 For better filler–filler (if any) and filler–polymer networking evaluation, dynamic characteristics, i.e. tan δ, \( G'' \) and \( G' \), were swept with double oscillation amplitudes (DSAs) in the glass transition zone (here −35 °C) and the rubbery state (here 25 and 65 °C) of the filled rubbers. The dynamic behaviour of the filled rubbers is governed by in situ polymer (i.e. polymer that is not bound to filler particles) in the glass transition zone, and by filler–filler or filler–polymer networks in the rubbery state.1

Oscillation amplitude dependency of dynamic characteristics at low temperatures near the glass transition zone
Figures 1–3 show tan δ, loss modulus and storage modulus versus oscillation amplitude at 1 Hz and −35 °C for compounds 1–5. It is clearly observed, for all compounds, that tan δ increases with oscillation amplitude (Fig. 1), owing to more heat dissipation as the oscillation amplitude increases. At this temperature, the tan δ values for BR are substantially lower than those for the other rubbers; values for SBR and IR are the highest. This is because BR is far from its glass transition temperature and consequently polymer segments display a higher Brownian motion and lower viscosity, which reduces resistance to imposed strains, resulting in lower heat dissipation and lower tan δ. In contrast, SBR and IR are near to their glass transition temperatures with higher viscosity and more resistance to imposed strains, resulting in higher heat dissipation and higher tan δ.

At moderate oscillation amplitudes (256–500 µm), the rate of increase of tan δ with oscillation amplitude for SBR is the highest. At low temperatures, polymer–polymer interactions are more responsible for heat dissipation than polymer–filler or filler–filler interactions.

Figure 1. Tan δ versus oscillation amplitude at 1 Hz and −35 °C for compounds 1–5.

Figure 2. Loss modulus (\( G'' \)) versus oscillation amplitude at 1 Hz and −35 °C for compounds 1–5.

Figure 3. Storage modulus (\( G' \)) versus oscillation amplitude at 1 Hz and −35 °C for compounds 1–5.
network breakdowns and re-formation. SBR has the least bound rubber and crosslink density among the filled rubbers with values of 65.7% and 124 mol m\(^{-3}\), respectively (Table 3). Consequently, it has more free polymer, which is not trapped in the filler matrix, resulting in more heat dissipation and a greater dependency of \(\tan \delta\) on increases in the oscillation amplitude. This characteristic is clearer in loss and storage moduli variation with oscillation amplitude (Figs 2 and 3). The values of these parameters for SBR filled rubber are higher in comparison with the other filled rubbers, especially at low oscillation amplitudes.

The increase in \(\tan \delta\) for all of the other filled rubbers (except IR) shows small slopes or even a plateau (NR with S for DSA at 1 Hz and ambient temperature (25°C), SBR shows the highest \(\tan \delta\) values, followed by BR and finally NR in that order (Fig. 1). It seems that IR is an exception. Although its strongest filler–polymer networks followed by BR and finally NR and filler–filler networks with oscillation amplitude. The absolute values of \(\tan \delta\) at this temperature are less than 50% of those values in the glass transition zone (−35°C) because here in the rubbery state (25°C) the polymer matrix including polymer chains and polymer–filler networks are more rubbery and they resisted less against imposed strains and move in the same direction as the strain resulting in lower heat dissipation and lower \(\tan \delta\). In the rubbery state (25°C), SBR shows the highest \(\tan \delta\) values, followed by BR, NR, NR with S and IR in that order. In fact, at ambient temperature, the dominant mechanism of heat dissipation is filler–filler network breakdown and re-formation. Hence, SBR with the lowest bound rubber and crosslink density (hence the highest filler–filler and lowest filler–polymer networks) has the highest level of heat dissipation resulting in the highest \(\tan \delta\) among all the filled rubbers. The trend of \(\tan \delta\) decrease with crosslink density increase holds true, except for BR, with the sequence SBR, NR, NR with S and IR (Fig. 4 and Table 3).

The value of \(G''\) for the filled rubbers against oscillation amplitude at ambient temperatures passes through a maximum except for IR, which increases, and SBR, which is approximately independent of oscillation amplitude (Fig. 5). Figure 6 shows storage modulus for the filled rubbers versus oscillation amplitude at the same temperature (25°C). As in the case of loss modulus, the storage modulus passes through a maximum, except for IR, which increases, and SBR, which decreases (Payne effect). The absolute values of loss and storage moduli of all filled rubbers are lower as they were recorded far from the glass transition temperature zone (cf. Figures 2, 3, 5 and 6).

Figures 7–9 show tan \(\delta\), loss modulus and storage modulus versus oscillation amplitude at 1 Hz and 65°C for compounds 1–5. This temperature is a good criterion for rolling resistance assessment of tyre treads.1 From the viscoelastic property point
the highest values for the former and lowest for the latter. Tan \( \delta \) with oscillation amplitude for SBR, NR and IR filled rubbers with a lower rolling resistance. Figure 7 shows a slight increase of tan \( \delta \) for compounds 1–5.

BR filled rubber decreases sharply up to an oscillation amplitude of 500 \( \mu \text{m} \) with a subsequent slight increase up to 1000 \( \mu \text{m} \).

For NR with S filled rubber, a sharp increase in tan \( \delta \) is observed for oscillation amplitude greater than 500 \( \mu \text{m} \) (Fig. 7). At a lower oscillation amplitude (256 \( \mu \text{m} \)), both SBR and BR filled rubbers have a maximum tan \( \delta \). At the highest oscillation amplitude (1000 \( \mu \text{m} \)), NR with S has the highest tan \( \delta \). For all oscillation amplitudes, IR filled rubber has the lowest tan \( \delta \). The values of tan \( \delta \) at different oscillation amplitudes for SBR, NR and IR filled rubbers are sustained with minimum variation, which represents the least variation in polymer–filler and/or filler–filler networks (Fig. 7). Generally, the values of tan \( \delta \) at this temperature (65 \( ^\circ \text{C} \)) are lower than those at \(-35\) and 25 \( ^\circ \text{C} \), due to the more rubbery state of the filled rubbers (cf. Figures 1, 4 and 7).

The loss modulus of all filled rubbers, except IR and SBR, passes through a maximum at an oscillation amplitude of 500 \( \mu \text{m} \). For SBR, this parameter decreases for all studied oscillation amplitudes, and for BR it increases (Fig. 8). At low oscillation amplitudes (256 \( \mu \text{m} \)), SBR filled rubber has the highest loss modulus and BR filled rubber the lowest; at high oscillation amplitude (1000 \( \mu \text{m} \)), NR filled rubber has the maximum and NR with S the minimum loss modulus values (Fig. 8). Except for SBR and IR filled rubbers, the storage moduli of the filled rubbers pass through a maximum at an oscillation amplitude of 500 \( \mu \text{m} \). The value for SBR decreases and shows a Payne effect, while for IR it increases (Fig. 9). The storage modulus values for NR filled rubber at all oscillation amplitudes are the highest among the filled rubbers. For low oscillation amplitude, BR filled rubber has the lowest value and for high oscillation amplitude, NR with S has the lowest value of storage modulus (Fig. 9). The values of loss and storage moduli for all filled rubbers at this temperature (65 \( ^\circ \text{C} \)) were more or less the same as those at ambient temperature (25 \( ^\circ \text{C} \)) but substantially lower than at the glass transition temperature (\(-35\) \( ^\circ \text{C} \)).

Temperature dependency of tan \( \delta \)

Figures 10 and 11 show tan \( \delta \) versus temperature at frequencies of 1 and 20 Hz for compounds 1–5. From the viscoelastic property point of view, an ideal material that is able to meet the requirements of a high-performance tyre tread should have a low tan \( \delta \) value at temperatures of 50–80 \( ^\circ \text{C} \) to reduce rolling resistance and save energy.\(^1\) The ideal material should also demonstrate high hysteresis at lower temperatures, e.g., \(-30\) to 0 \( ^\circ \text{C} \), to give good skid resistance and wet grip. However, the factors involved in skid resistance have been recognized to be more complex than a single compound property.\(^2\) Hence, for skid and rolling resistance assessment, two temperature ranges, \(-30\) to 0 \( ^\circ \text{C} \) and 50 to 80 \( ^\circ \text{C} \), were employed, respectively. Figures 10 and 11 clearly show that in the temperature range \(-30\) to 0 \( ^\circ \text{C} \), the values of tan \( \delta \) for SBR filled rubber are the highest and for BR the lowest. After SBR, the ordering is IR followed by NR and finally NR with S. It may be concluded that the skid resistance of SBR filled rubber is the best and BR the worst. The other filled rubbers lie between these two with the sequence of IR, NR and NR with S. For the second temperature range, 50–80 \( ^\circ \text{C} \), the lowest tan \( \delta \) is shown by IR filled rubber and then NR and NR with S. The tan \( \delta \) values for SBR and BR filled rubbers in this range are more than those for the other filled rubbers, but for temperatures of 50–65 \( ^\circ \text{C} \), the value for BR filled rubber is greater than that for SBR filled rubber; for temperatures of 65–80 \( ^\circ \text{C} \), the situation is reversed (Figs 10 and 11). As a conclusion, the rolling resistance of BR and SBR filled rubbers is greater than that of NR, IR and NR with S filled rubbers. The sequence is NR with S being the highest

![Figure 7. Tan \( \delta \) versus oscillation amplitude at 1 Hz and 65 \( ^\circ \text{C} \) for compounds 1–5.](image1)

![Figure 8. Loss modulus (\( G'' \)) versus oscillation amplitude at 1 Hz and 65 \( ^\circ \text{C} \) for compounds 1–5.](image2)

![Figure 9. Storage modulus (\( G' \)) versus oscillation amplitude at 1 Hz and 65 \( ^\circ \text{C} \) for compounds 1–5.](image3)
increase. The glass transition temperatures (and NR with S filled rubbers decrease and those of NR, BR and IR and carbon black fillers. A widely held view is that filler agglomeration of dynamic characteristics compared with traditional silica silica nanofiller show a complicated oscillation amplitude dependence. This is attributed to the strain amplitude dependency of filler–filler linkages which are broken down by strain. Because the storage modulus of pure gum polymers is independent of strain amplitude and the lower bound rubber of the SBR filled rubber under investigation (Table 3) resulting in higher filler–filler agglomeration, the Payne effect is clearly observed for this compound (Figs 3, 6 and 9). In contrast, more complicated behaviours were observed for the other filled rubbers (Figs 3, 6 and 9). This means that, whereas in some strain ranges storage modulus increases with strain amplitude, in other ranges it decreases (Payne effect). Drawing attention to the high bound rubber (rubber bound by filler particles) and covalent chemical bonds between filler particles and polymer chains (via TESPT) in the filled rubbers under study, it may be concluded that there is a different predominant filler–filler interaction mechanism than simply de-agglomeration and filler–filler network breakdown, as was suggested by the Payne model. Maier and Gortiz have proposed an alternative mechanism to filler structure breakdown, suggesting that the Payne effect is due to the stress induced by de-bonding of polymer chains from the filler surface. Sternstein and Zhu proposed a new mechanism underlying the reinforcement and nonlinear behaviour of storage modulus with strain in nanofilled polymers. They believed that filler–matrix interactions, and not filler agglomeration or de-agglomeration, are responsible for such nonlinearity. They also believed that the polymeric matrix (entanglements) and the manner in which the filler–matrix interface alters matrix behaviour in the presence of an applied stress share a fundamental mechanism regarding the origin of the nonlinear viscoelastic behaviour. The present authors more or less agree with them and believe that the polymeric matrix (entanglements) along with structure and type of polymer (here rubber) in the interface of filler–filler networks (particles) alter the viscoelastic behaviour of the whole polymeric system. For example, it can be observed in Figs. 3, 6 and 9 that, whereas storage modulus versus strain amplitude for IR filled rubber increases for all strains, it passes a maximum or a minimum for other rubbers. Alternatively, there is a tendency for fillers to form some sort of ‘weak structure’ when filler size becomes very small (nanoscale). In the systems studied here, the amount of filler loading is relatively high (60 phr) at the nanoscale. This high loading increases the chance of filler particles existing in the system without chemical interaction (bonds) with polymer chains and simultaneously reduced filler particle distances. Incorporating strain with the above phenomena may facilitate the filler particles making aggregates and subsequently agglomerates, resulting in storage modulus increasing with strain. However, the nature of these new mechanisms is not very clear and will require further study.

Effect of elemental sulfur on ODR results and dynamic properties of SBR filled rubbers

Tables 2 and 3 clearly show that with the addition of 0.2 phr elemental sulfur to the curing recipe, $t_{1,3}$ and $t_{90}$ were reduced by 2 and 12 min, respectively. In addition, $\Delta T$ and cure rate index (CRI) were increased by 6 dN m and 1.05 units, respectively. As a conclusion, the addition of a small amount of elemental sulfur to the SBR formulation improves the ODR properties substantially.

Figures 12–14 show $\tan \delta$ against temperature for compounds 1 and 6 at frequencies of 1, 20 and 100 Hz with a displacement amplitude of 256 $\mu$m. Comparison of the values of $\tan \delta$ for

**Additional discussion of nonlinear viscoelastic behaviour of filled rubbers**

As has been observed, rubbers filled with silanized pre-treated silica nanofiller show a complicated oscillation amplitude dependency of dynamic characteristics compared with traditional silica and carbon black fillers. A widely held view is that filler agglomeration and network formation are responsible for the high levels of reinforcement and that de-agglomeration and network breakdown are responsible for the nonlinearity with strain. A normally defined Payne effect in filled elastomers refers to the reduction of dynamic storage modulus with increasing strain amplitude. This is attributed to the strain amplitude dependency of filler–filler linkages which are broken down by strain. Because the storage modulus of pure gum polymers is independent of strain amplitude and the lower bound rubber of the SBR filled rubber under investigation (Table 3) resulting in higher filler–filler agglomeration, the Payne effect is clearly observed for this compound (Figs 3, 6 and 9). In contrast, more complicated behaviours were observed for the other filled rubbers (Figs 3, 6 and 9). This means that, whereas in some strain ranges storage modulus increases with strain amplitude, in other ranges it decreases (Payne effect). Drawing attention to the high bound rubber (rubber bound by filler particles) and covalent chemical bonds between filler particles and polymer chains (via TESPT) in the filled rubbers under study, it may be concluded that there is a different predominant filler–filler interaction mechanism than simply de-agglomeration and filler–filler network breakdown, as was suggested by the Payne model. Maier and Gortiz have proposed an alternative mechanism to filler structure breakdown, suggesting that the Payne effect is due to the stress induced by de-bonding of polymer chains from the filler surface. Sternstein and Zhu proposed a new mechanism underlying the reinforcement and nonlinear behaviour of storage modulus with strain in nanofilled polymers. They believed that filler–matrix interactions, and not filler agglomeration or de-agglomeration, are responsible for such nonlinearity. They also believed that the polymeric matrix (entanglements) and the manner in which the filler–matrix interface alters matrix behaviour in the presence of an applied stress share a fundamental mechanism regarding the origin of the nonlinear viscoelastic behaviour. The present authors more or less agree with them and believe that the polymeric matrix (entanglements) along with structure and type of polymer (here rubber) in the interface of filler–filler networks (particles) alter the viscoelastic behaviour of the whole polymeric system. For example, it can be observed in Figs. 3, 6 and 9 that, whereas storage modulus versus strain amplitude for IR filled rubber increases for all strains, it passes a maximum or a minimum for other rubbers. Alternatively, there is a tendency for fillers to form some sort of ‘weak structure’ when filler size becomes very small (nanoscale). In the systems studied here, the amount of filler loading is relatively high (60 phr) at the nanoscale. This high loading increases the chance of filler particles existing in the system without chemical interaction (bonds) with polymer chains and simultaneously reduced filler particle distances. Incorporating strain with the above phenomena may facilitate the filler particles making aggregates and subsequently agglomerates, resulting in storage modulus increasing with strain. However, the nature of these new mechanisms is not very clear and will require further study.

**Effect of elemental sulfur on ODR results and dynamic properties of SBR filled rubbers**

Tables 2 and 3 clearly show that with the addition of 0.2 phr elemental sulfur to the curing recipe, $t_{1,3}$ and $t_{90}$ were reduced by 2 and 12 min, respectively. In addition, $\Delta T$ and cure rate index (CRI) were increased by 6 dN m and 1.05 units, respectively. As a conclusion, the addition of a small amount of elemental sulfur to the SBR formulation improves the ODR properties substantially.

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<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>tan δ at 1 Hz</th>
<th>tan δ at 20 Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>-100</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>-50</td>
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<tr>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>50</td>
<td>0.0</td>
<td>0.0</td>
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Figures 12–14 show $\tan \delta$ against temperature for compounds 1 and 6 at frequencies of 1, 20 and 100 Hz with a displacement amplitude of 256 $\mu$m. Comparison of the values of $\tan \delta$ for
these two compounds at different temperatures suggests that the addition of elemental sulfur has no benefit at least from the viewpoint of dynamic behaviour. This is clearer in Fig. 14 (frequency of 100 Hz) where compound 1 (without elemental sulfur) shows a lower tan δ at high temperatures and a lower rolling resistance.

A temperature of 65 °C is suitable for rolling resistance assessment. A slight increase of tan δ at all oscillation amplitudes for all filled rubbers was a distinction of this temperature with the exception of NR with S filled rubber, which showed a sharp tan δ increase at higher oscillation amplitudes (greater than 500 µm). Generally, the values of tan δ were lower than those at the two other temperatures studied, −35 and 25 °C. The loss modulus of SBR filled rubber was constant, more or less, for all oscillation amplitudes at this temperature.

Addition of elemental sulfur for SBR compounding improved ODR (curing) properties, but simultaneously worsened the dynamic behaviour of this compound. Owing to high bound rubber of the most filled rubbers and covalent chemical bonds between filler particles and polymer chains, there should be another mechanism predominant for nonlinear viscoelastic behaviour of filled rubbers rather than that proposed by the Payne model for filler–filler interactions. In addition, the nanoscale of the studied filler may be effective for this behaviour.

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