Measuring dynamic behavior of several rubbers filled with silanized silica nanofiller

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ABSTRACT

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 elemental sulfur addition (NR with S), synthetic polyisoprene (IR), poly Butadiene (BR) and poly Styrene-Butadiene co-polymer (SBR) was investigated. The silica surfaces were pre-treated with bis (3-triethoxysilylpropyl) tetrasulfane (TESPT) to chemically bond silica to rubber. The rubbers were primarily cured by using sulfur in TESPT with addition of optimum accelerator (TBBS) and activator (ZnO), which helped to form sulfur chemical bonds between the rubber and filler.

Cure properties, Mooney viscosity, glass transition temperature (Tg), Bound rubber and crosslink density along with dynamic properties of 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 and results with emphasis on potential for tire tread application, were discussed. It emerged that, SBR along with BR filled rubbers had the highest rolling resistance while IR filled rubber had the least. Moreover, it seemed SBR filled rubber had the best skid resistance and BR filled rubber, the worst.

Interestingly, G′ variation versus DSA showed complicate behavior for different filled rubbers. It emerged that while in some DSA ranges, Payne effect was observed, in the remaining ranges, incremental of G″ with DSA was seen. Due to bound rubber of most filled rubbers were more than %92, there should be another predominant mechanism in studied systems rather than simply de agglomeration or filler network break down which proposed by Payne model. In addition nano scale of filler may be effective on this behavior.

Keywords: Dynamic behavior, filled rubber, tan δ, loss modulus (G″), Storage modulus (G′), Silanized silica nanofiller

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INTRODUCTION

Although static mechanical properties have a great role in service life of tire tread, enough attention should be made on dynamic properties. In fact, wearing of the tire tread along with its performance, are two sides of the same coin.

Filler when added to polymer systems are known to cause a considerable change in dynamic properties, not only the dynamic modulus, both viscous (loss) modulus and elastic (storage) modulus but also their ratio (tan δ) which is related to the portion of the 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 tires 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 tire applications, it has been well established that repeated straining of the compound due to rotation and braking can be approximated as a process of constant energy input involving different temperature and frequencies[2,3,4].

Rolling resistance, for example, is related to the movement of the whole tire. Corresponding to deformation at a frequency of 10-100Hz 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 tire tread. The frequency of around $10^4$ to $10^7$ Hz at room temperature[3,4]. It is therefore obvious that any change in dynamic hysteresis of the compounds at different frequency and temperature will alter the performance of the tire.

Since certain tire properties involve frequencies which are too high to be measured, these frequencies are reduced to a measurable level (1Hz) at lower temperature 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)[5], hence of tan δ. However, the master curve for each property can be constructed experimentally according to the temperature-frequency principle.

Ansarifar and his co-workers[6-12] had a hard study on silanized pre-treated precipitated silica nano fillers. According with his works silanized (here bis[3-triethoxy silylpropyl]-tetrasulfane, TESPT) pre-treated precipitated silica nanofiller (Scheme I and II), was a strong reinforcement agent which improved the physical properties as well as dynamic performance of filled rubber
better than other reinforcement agents including carbon black. This silane (TESPT) possesses
tetrasulfane and ethoxy reactive groups. The tetrasulphane 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[10]. 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].
In addition pre treated silanized precipitated silica nanofiller had so much advantages comparing
with separate employment of liquid coupling agent and silica in rubber compounding[13].
In current study, dynamic behaviors of different rubbers filled (reinforced) with silanized pre
treated silica nanofiller with emphasis on their capability for tire tread application, were
compared and results were discussed.

Materials

Rubbers and filler

The used raw rubbers were standard Malaysian natural rubber grade L (98 wt % cis-1-4 content;
SMRL), synthetic polyisoprene (minimum 96 wt % cis-1-4 content; Kraton IR-307), Kraton
Polymers-USA, cis-butadiene rubber, BUNA CB 24, Bayer–UK and styrene-butadiene
copolymer, SBR-1712, Polimeri Europa-UK Ltd. (Table I).
The reinforcing filler was Coupsil 8113, Degussa Ltd., Hanau-Germany. Coupsil 8113 is
precipitated amorphous white silica, type Ultrasil VN3, 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 surface area (measured by N₂ adsorption), and a 20-54 nm particle size.

\( T_g \) (°C) (glass transition temperature) of raw rubbers measured by modulated temperature
differential scanning calorimetry (MTDSC) technique.

Curing chemicals, antidegradants and processing oil

In addition to the raw rubbers and filler, the other ingredients were \( N \)-t-butyl-2-benzothiazole
sulfenamide (Santocure TBBS), Woluwe-Belgium, a safe-processing delayed action accelerator,
Zinc oxide, Harcros Durham Chemicals-UK (activator), 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 unsaturation sites or chemically active double bonds such as natural rubber.

**Mixing**

The compounds were prepared in a Haake Rheocord 90 (Berlin, Germany), a small laboratory mixer with counter rotating rotors. In these experiments, the Banbury rotors speed was 45 rpm and the mixing chamber were maintained at 50°C for BR and NR compounds and ambient temperature for SBR and IR compounds.

The above temperature was nominal and the exact temperature of mixing in some cases rose to 72°C due to heat generation by friction forces during mixing.

The mixer chamber first fed with Coupsil 8113 (about 50%), then all rubber added and rotor started. The remaining amount of filler added within next 30 seconds before the viscosity of component reduces. This is due to small size of mixer chamber which make difficult to add all components in single stage. During mixing the ram of chamber should be down to retain the component at high tension. The volume of chamber was 78 cm³ and filled about 60%.

Haake software version 1.9.1 was used to control the mixing conditions and data storage. Mixing did in two stages. The first stage was for rubber plus filler (and process oil in SBR case) and the second one for other curing agents addition. The time for first stage, for BR compounding was chosen 10 minutes as recommended by Ansarifar and his co-workers[14]. For second stage 6 minutes was chosen.

In SBR compounding, the time of first stage was chosen 4 minutes[15] and after two minutes, process oil added to compound with mixing continuation. For second stage, the same of BR, extra 6 minutes was chosen. For NR and IR compounding, 13 and 16 minutes were chosen for stage one respectively and an extra 3 minutes for second stage[10].

After finishing the first stage, ram of chamber rose up and allowed to mixture temperature cool down to about 50°C before proceeding to second stage.

Subsequently, compound removed from mixing chamber and was allowed to cool and reach to steady state condition for at least 24 hours based upon advice of British standard[16].

**Curing procedure and physical testing methods**

**Viscosity measurement**
The viscosity of the rubber compounds was measured ML (1+4 min) at 100°C in a single-speed rotational Mooney viscometer supplied by Wallace Instruments, Surrey, UK according with British standard advice[17].

**Cure properties measurement**

An oscillating disc rheometer curemeter (ODR), Monsanto supplied by Swindon, U.K, employed to measure cure properties like $t_{s1}$ & $t_{s2}$, scorch times which are the time for the onset of cure and one unit more than that respectively and optimum cure times $t_{95}$ & $t_{90}$, which are the times to reach %95 and %90 completion of cure respectively.

ODR measures minimum, maximum and delta torque ($\Delta Torque$) as well. An angular displacement of $\pm 3^\circ$ and a test frequency of 1.7 Hz at 140°C $\pm 2^\circ$C was employed[18].

Total run time was 2 hours and the $\Delta Torque$, which is an indication of crosslink density changes in rubber[19] was monitored.

**Compound curing**

Curing of the final compounds took place in an electrical press with nominal 110 atmosphere pressure (40000 kg. on a 8 inch diameter disc).

The curing temperature adjusted to 140 °C with optimum cure time, $t_{90}$ (Table III for ODR results).

**Bound rubber and crosslink density measurement**

The bound rubber is a measurement of the percentage of polymer, bounded by filler. The solvent used for bound rubber determination was Toluene (Merck-Germany). Cylindrical shaped samples with diameter 15-mm and height 9 mm were employed. Test temperature was ambient or 23°C.

The samples were then placed individually in 90 ml of the solvent in labeled bottles, and allowed to swell. The weight of the samples was measured every day until it reached an equilibrium. After this stage, the solvent was removed and samples were dried in air for 9 hours. Subsequently the samples were dried in an vacuum oven at 85 °C for 24 hours, and allowed to stand for an extra 24 hours at ambient temperature before they were re-weighed. The bound rubber and crosslink density were calculated using equations recommended by Hamed and Wolff[20,21] respectively.

**Dynamic properties measurement**

The tan $\delta$ is the ratio between 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. \(\tan \delta\) was measured in a dynamic mechanical thermal analyzer (DMA-800). TA-analysis software used to store and analysis the data.

The rectangular samples 35mm X 13mm X 2.5mm (thickness) were chosen as test pieces. The samples were deflected by 15, 256, 500 and 1000 \(\mu m\) (nominal peak to peak displacement) in several frequencies 1 and 20 and 100 Hz (only for SBR filled rubber).

Sample temperature raised from -130°C to 100°C with ramp step 5°C /min.

In addition to \(\tan \delta\), loss modulus and storage modulus of samples measured by mentioned instrument in the same conditions.

**RESULTS AND DISCUSSION**

Six filled rubbers were prepared based upon following considerations (Table II).

Authors previously suggested[14,15], the optimum amount of accelerator (TBBS) and activator (ZnO) for a SBR filled rubber with 60 phr silanized silica (Coupsil-8113) was 3 and 0.5 phr respectively. Similarly the optimum amount of accelerator for BR filled rubber with 60 phr silanized silica is 7.5 phr with no need for activator addition. With addition of 0.3 phr elemental sulfur to above BR filled rubber, two compounds, SBR and BR filled rubbers, became harmonized with each other and were suitable for blending. It means, their optimum cure time, \(t_{90}\) of them were the same(Table II-III for compounds 1 and 2).

Accordingly, the optimum amount of accelerator and activator for NR filled rubber with 60 phr silanized silica was 6 and 0.3 phr (compounds 3 and 4 in Table II) and for IR filled rubber, 7 and 1 phr respectively (compound No. 5 in Table II). To evaluate the effect of elemental sulfur on dynamic properties of SBR filled rubber, one more compound with 0.2 phr elemental sulfur was prepared(compound 6 in Table II).

Table III represents ODR results (cure properties) along with bound rubber, crosslink density and Mooney viscosity of compounds 1-6.

Addition of silanized silica nanofiller increased Mooney viscosities of NR, SBR, BR and IR rubbers from Mooney unit 96.7, 51.3, 49 and 69 to 106, 109, 162 and 105 respectively (Table I and III).

Mooney viscosity increment may consider an important signal for substantial difference between dynamic behavior of raw rubbers and of filled rubbers.

All filled rubbers (except SBR) had extremely high bound rubber (more than %90- Table III). This fact represents strong filler-polymer networking in studied systems.
For better filler-filler (if any) and filler-polymer networking evaluation, dynamic characteristics including, tan δ, \( G'' \) and \( G' \) were swept with double oscillation amplitudes (DSA) in two glass transition zone (here -35 °C) and rubbery state (here 25 °C and 65 °C) of filled rubbers. It was stated[22] that when in glass transition zone, polymer in situ would be responsible for the high portion of energy dissipation and dynamic behavior of filled rubbers, in rubbery state, filler networking was the predominant phenomenon.

**Oscillation amplitude dependency of dynamic characteristics in glass transition zone**

Figures I-III represent tan δ, loss modulus (\( G'' \)) and storage modulus (\( G' \)) versus different oscillation amplitudes at 1 Hz frequency and temperature, -35 °C for compounds 1-5.

As it was clearly observed, for all compounds, tan δ increased with oscillation amplitude (Fig. I), due to more heat dissipation with oscillation amplitude enhancement. In this temperature, the tan δ values of BR is substantially lower than of other rubbers and for SBR and IR the highest. This was due to, BR was far enough of its glass transition temperature and consequently polymer segments have higher Brownian motion and lower viscosity which cause less resistance to imposed strains, resulting in lower heat dissipation and tan δ.

In the other hand SBR and IR were near to their glass transition temperature with higher viscosity and more resistance to imposed strains, consequently high heat dissipation and higher tan δ.

In moderate oscillation amplitudes, 256-500 \( \mu m \), the rate of tan δ increment with oscillation amplitude for SBR is the highest. In low temperatures, the polymer in situ is more responsible than polymer-filler and or filler-filler networks break down and re-formation for heat dissipation. SBR had the least bound rubber and crosslink density among of all other filled rubbers with the values, %65.7 and 124 mol/m³ respectively (Table III). Consequently, it had more free polymer which has not trapped in filler matrix, resulting more heat dissipation and tan δ dependency with oscillation amplitude increment.

This fact was more clear in loss and storage modulus variation versus oscillation amplitude (Figures II-III). The values of these parameters for SBR filled rubber, were absolutely higher in comparison with other filled rubbers, specially in low oscillation amplitudes.

Tan δ increment of all rest filled rubbers (except IR), showed low slopes or even plateau (NR with S for DSA greater than 256 \( \mu m \)) in different oscillation amplitudes. Drawing attention to this point that bound rubbers of all of them were more than %93 resulting strong filler –polymer networking, we may conclude that here, in absence of enough polymer in situ, break down and re-formation of these networks with strain, dissipate energies. Hence more strong filler-polymer
networking, less strain dependency of \( \tan \delta \). Sequence lied down on NR with elemental Sulfur, BR and finally NR (Figure I).

It seemed, IR was an exception. Although it’s bound rubber and crosslink density was high (93\% and 249 mol/m\(^3\) respectively -Table III), It had the sharpest \( \tan \delta \) increment. Previous finding of author suggested that IR had weak tensile properties which directly refers to polymer-filler networking strength. It means in spite of high crosslink density of IR filled rubber, it had still weak polymer-filler networks due to intrinsic weakness of IR polymer chains.

**Oscillation amplitude dependency of dynamic characteristics in rubbery state**

Figures IV-VI represent \( \tan \delta \), loss modulus \( (G') \) and storage modulus \( (G'') \) versus different oscillation amplitudes at 1 Hz frequency and ambient temperature, 25\(^\circ\)C for compounds 1-5.

At ambient temperature, 25\(^\circ\)C, \( \tan \delta \) versus oscillation amplitude of all filled rubbers were incremental with low slopes (Fig. IV) which was the result of more heat dissipation by polymer-filler and or filler-filler networks with oscillation amplitude.

The absolute values of \( \tan \delta \) in this temperature were less than half of their values in glass transition zone, -35\(^\circ\)C due to here, polymer matrix was more rubbery and polymer chains resist less against imposed strains and move in the same direction of strain and consequently lower heat dissipation and \( \tan \delta \).

The highest values of \( \tan \delta \) belonged to SBR and subsequently BR, NR, NR with S and finally IR. In fact in ambient temperature, dominant mechanism of heat dissipation was filler-filler networks break down and reformation. Hence SBR with the least bound rubber and crosslink density, had the most heat dissipation resulting the highest \( \tan \delta \) among of other filled rubbers.

The rule of \( \tan \delta \) reduction with crosslink density enhancement, was true except for BR with the sequence of SBR, NR, NR with S and IR (Fig. IV and Table III).

Loss modulus, \( G' \) of all filled rubbers versus oscillation amplitude in ambient temperature, passed through a maximum except for IR which was incremental and SBR which was approximately independent of oscillation amplitude (Fig. V). Figure VI showed storage modulus of all filled rubbers versus oscillation amplitude in the same temperature (25\(^\circ\)C). Like loss modulus, storage modulus passed through a maximum, except for IR filled rubber which was completely incremental and SBR filled rubber which decreased (Payne effect).

The absolute values of loss and storage modulus of all filled rubbers were lower due to far enough from glass transition temperature zone (compare Figures II, III, V and VI).
Figures VII-IX represent \( \tan \delta \), loss modulus \( (G') \) and storage modulus \( (G'') \) versus different oscillation amplitudes at 1 Hz frequency and temperature, 65\(^\circ\)C for compounds 1-5.

This temperature was a good criteria for rolling resistance assessment of tire tread. The lower \( \tan \delta \) means the less rolling resistance. Figure VII showed slight increment of \( \tan \delta \) with oscillation amplitude for SBR, NR and IR filled rubber with the highest values for the former and lowest for the latter. \( \tan \delta \) of BR filled rubber reduced sharply up to oscillation amplitude, 500 \( \mu \)m with subsequent enhancement with lower slope up to 1000 \( \mu \)m.

For NR with S filled rubber, it was observed sharp \( \tan \delta \) enhancement for oscillation amplitude more than 500 \( \mu \)m (Fig. VII). In lower oscillation amplitude (256 \( \mu \)m), both SBR and BR filled rubbers had the most \( \tan \delta \) and for high oscillation amplitude (1000 \( \mu \)m), NR with S had the highest \( \tan \delta \). In all oscillation amplitudes, IR filled rubber had the least \( \tan \delta \). The values of \( \tan \delta \) in different oscillation amplitudes for SBR, NR and IR filled rubbers, were sustained the minimum variation which represented the least variation in polymer-filler and or filler-filler networks (Fig. VII).

Generally the values of \( \tan \delta \) in this temperature (65\(^\circ\)C) were lower than other two temperatures, -35 and 25 \( ^\circ\)C due to more rubbery state of filled rubbers (compare Figures I, IV and VII).

Loss modulus of all filled rubbers, except IR and SBR, passed through a maximum at 500 \( \mu \)m oscillation amplitude. For SBR, this parameter reduced in all studied oscillation amplitudes and for BR increased (Fig. VIII).

In low oscillation amplitudes (256 \( \mu \)m), SBR filled rubber had the most loss modulus and BR filled rubber the least, whereas in high oscillation amplitude (1000 \( \mu \)m), NR filled rubber had the maximum and NR with S, had the minimum loss modulus values (Fig. VIII).

Except SBR and IR filled rubbers, all storage modulus of filled rubbers passed through a maximum at 500 \( \mu \)m oscillation amplitude. These values for SBR decreased and showed Payne effect while for IR was incremental (Fig. IX).

The storage modulus values of NR filled rubber in all oscillation amplitudes were the highest among of all other filled rubbers, while for low oscillation amplitude, BR filled rubber and in high oscillation amplitude, NR with S had the minimum values of storage modulus (Fig. IX).

The values of loss and storage modulus of all filled rubbers in this temperature (65\(^\circ\)C), were more or less the same of ambient temperature, 25\(^\circ\)C but substantially lower than of glass transition temperature, -35\(^\circ\)C.
Temperature dependency of \( \tan \delta \)

Figures X and XI show \( \tan \delta \) versus temperature at both frequencies 1 and 20 Hz for compounds 1-5.

From the viscoelastic property point of view, an ideal material which is able to meet the requirements of a high performance tire tread should give a low \( \tan \delta \) value at a temperature of 50-80°C in order to reduce rolling resistance and save energy[1].

The ideal material should also demonstrate high hysteresis at lower temperatures, for example -30-0°C, in order to obtain high skid resistance and wet grip. However, the factors involved in skid resistance were recognized to be more complex than a single compound property[1].

Hence for skid and rolling resistance assessment, two temperature ranges, -30-0°C and 50-80°C were employed respectively.

Figures X and XI clearly showed in temperature region -30-0°C, the values of \( \tan \delta \) of SBR filled rubber were the highest and for BR, the least. After SBR, the sequence lied on IR, NR and finally NR with S.

It may be concluded that the skid resistance of SBR filled rubber was the best and of BR the worst. Other filled rubbers lied between these two with the sequence of IR, NR and NR with S.

For the second temperature region, 50-80°C, the least \( \tan \delta \) belonged to IR filled rubber and then NR and NR with S. The \( \tan \delta \) values of SBR and BR filled rubbers in this region were more than \( \tan \delta \) values of the rest filled rubbers, but in temperature 50-65°C, these values for BR filled rubber were greater than SBR filled rubber and in temperature 65-80°C, the situation was vice versa(Figures X–XI).

As a conclusion, the rolling resistance of BR and SBR filled rubber were more than NR, IR and NR with S filled rubber.

The sequence lied on NR with S, NR and finally IR with the least rolling resistance.

Interestingly, It was observed a hump around temperature 50°C for BR filled rubber, which showed sharp heat dissipation in this temperature.

Comparison between two figures X and XI, showed with frequency enhancement from 1 to 20 Hz, the maximum \( \tan \delta \) values of SBR and NR with S filled rubbers reduced and of NR, BR and IR, increased.

Glass transition temperatures (\( T_g \)) of raw rubbers, NR, SBR and BR were -64, -50 and -107°C respectively. Comparing these values with values of filled rubbers (-45, -24 and -85°C) showed substantial shift of this parameter to higher temperatures due to reinforcement effect of silanized pre treated silica nanofiller (Table I and Figure X).
Complementary discussion on non linear viscoelastic behavior of filled rubbers

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 break down are responsible for the non linearity with strain[23,24]. A normally defined, the Payne effect in filled elastomers refers to the reduction of dynamic storage modulus with increasing strain amplitude. This fact attributed to the strain amplitude dependency of filler-filler linkages of a physical nature which are broken down by straining[25,26].

Due to storage modulus of pure gum polymers is independent of strain amplitude[26] and lower bound rubber of studied SBR filled rubber (Table III), resulting higher filler-filler agglomeration, Payne effect clearly was observed for this compound(Figures III, VI and IX).

On the other hand, It was observed more complicate behaviors for the rest filled rubbers (the same figures).

It means whereas in some strain ranges, storage modulus was increased with strain amplitude, in the other ranges, it was decreased (Payne effect).

Drawing attention on high bond rubber (rubber bounded by filler particles) and covalent chemical bonds between filler particles and polymer chains (via TESPT) in studied filled rubbers, may be concluded to different filler-filler interaction predominant mechanism than simply de agglomeration and filler-filler network break down as was suggested by Payne model[26].

Marier and Goritz[27] have proposed an alternative mechanism to filler structure break down suggesting Payne effect is due to the stress induced de bonding of polymer chains from filler surface.

Sternstein and Zhu[28] proposed a new mechanism underlying for reinforcement and non linear behavior of storage modulus with straining in nano filled polymers. They believed filler matrix interactions, but not filler agglomeration and or de agglomeration were responsible for such non linearity. They also believed polymeric matrix (entanglements) and the manner in which the filler matrix interface alters matrix behavior in the presence of an applied stress, share a fundamental mechanism regarding the origin of the non linear viscoelasticity behavior.

The author more or less agree with them and believe polymeric matrix (entanglements) along with structure and kind of polymer (here rubber) in the interface of filler-filler networks (particles), alters the viscoelastic behavior of the whole polymeric system.

For example, It can be observed (Figures III, VI and IX), whereas storage modulus versus strain amplitude for IR filled rubber, were totally incremental in all strains, It passes a maximum and or minimum for others.
Alternatively there is a tendency for fillers to form some sort of “weak structure” when filler size becomes very small (nano scale)[28]. Here in studied systems the amount of filler loading is relatively high (60phr) with nano scale. This high loading, increased the chance of those filler particles which exist in system without chemical interaction (bonds) with polymer chains and simultaneously reduced filler particles distances. Strain incorporation with above phenomena, may facilitate mentioned filler particles to make aggregates and subsequently agglomeration, resulting storage modulus enhancement with straining.

However the nature of these new mechanisms are not very clear and need more work in future.

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

Tables II and III clearly showed , with addition of 0.2 phr elemental sulfur to curing recipe, scorch time ($t_{st}$) reduced about two minutes and optimum cure time ($t_{90}$) gained a benefit of 12 minutes. Simultaneously $\Delta$Torque(dN.M) and cure rate index (CRI) improved 6 and 1.05 units respectively. As a conclusion, addition of small amount of elemental sulfur to SBR formulation, improved ODR properties substantially.

Figures XII to XIV compare $\tan \delta$ versus temperature of compounds 1 and 6 for frequencies 1, 20 and 100 Hz with 256 $\mu$m displacement amplitude.

Comparison the values of $\tan \delta$ for these two compounds in different temperatures, suggested elemental sulfur addition, had no benefit at least from dynamic behavior view point.

This is more clear in Figure XIV for frequency 100 Hz when compound No. 1 (without elemental sulfur) showed less $\tan \delta$ in high temperatures and consequently less rolling resistance.
CONCLUSION

We may conclude the gains of this study as below:

1) Dynamic properties of all rubbers, highly affected by Silanized Silica Nanofiller addition to raw rubbers. This fact was be observed more clearly when we compared glass transition temperatures ($T_g$) of raw rubbers, SBR, BR and NR with the values of $-50$, $-107$ and $-64 \degree C$ with filled rubbers with the values $-24$, $-85$ and $-45 \degree C$ respectively.

2) IR filled rubber showed the least rolling resistance with tan $\delta$ values $0.1$-$0.12$ in $50$-$80 \degree C$ and SBR and BR filled rubbers the highest rolling resistance with tan $\delta$ values $0.12$-$0.24$ and $0.17$-$0.20$ in the same temperature range respectively.

3) SBR filled rubber showed the best skid resistance with tan $\delta$ values $0.58$-$0.29$ in $-30$-$0 \degree C$ and BR filled rubber, the worst skid resistance with tan $\delta$ values $0.1$-$0.13$ in the same temperature range.

4) Temperature $65 \degree C$ is a suitable temperature for rolling resistance assessment. Slight increment of tan $\delta$ in all oscillation amplitudes for all filled rubbers, was a distinction of this temperature with exception of NR with S filled rubber which showed sharp tan $\delta$ increase in higher oscillation amplitudes (greater than $500 \mu m$). Generally the values of tan $\delta$ were lower than of values in two other temperatures, $-35 \degree C$ and $25 \degree C$.

Loss modulus of SBR filled rubber, more or less was constant in all oscillation amplitudes in this temperature.

5) Addition of elemental sulfur for SBR compounding, improves ODR (curing) properties but simultaneously deteriorates dynamic behavior of this compound.

6) Due 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 on non-linear viscoelastic behavior of filled rubbers rather than those which was proposed by Payne model for filler-filler interaction. In addition nano scale of studied filler may be effective on this behavior.

ACKNOWLEDGEMENT

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### TABLE I : RAW RUBBERS SPECIFICATIONS

<table>
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<tr>
<th>Rubber</th>
<th>Specific gravity</th>
<th>Mooney viscosity ,ML(1+4) at 100 °C</th>
<th>$T_s$ (°C)</th>
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<tr>
<td>NR (SMRL)</td>
<td>0.92</td>
<td>96.71</td>
<td>-64</td>
</tr>
<tr>
<td>SBR-1712</td>
<td>0.94</td>
<td>51.30</td>
<td>-50</td>
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<tr>
<td>High cis-BR</td>
<td>0.91</td>
<td>49.00</td>
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<tr>
<td>IR</td>
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<td>69.00</td>
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### TABLE II : FILLED RUBBERS RECIPE

<table>
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<th>Compound No.</th>
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<th>3</th>
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<td>100</td>
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<tr>
<td>BR (phr)</td>
<td>---</td>
<td>100</td>
<td>---</td>
<td>---</td>
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<td>NR (phr)</td>
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<td>100</td>
<td>100</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>IR (phr)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>100</td>
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<td>---</td>
</tr>
<tr>
<td>Si (phr)</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
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<td>60</td>
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<tr>
<td>TBBS(phr)</td>
<td>3</td>
<td>7.5</td>
<td>6</td>
<td>6</td>
<td>7</td>
<td>3</td>
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<tr>
<td>ZnO (phr)</td>
<td>0.5</td>
<td>---</td>
<td>0.3</td>
<td>0.3</td>
<td>1</td>
<td>0.5</td>
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<tr>
<td>Elemental sulphur(phr)</td>
<td>---</td>
<td>0.3</td>
<td>---</td>
<td>1.5</td>
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<td>0.2</td>
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<tr>
<td>Enterflex 74 (phr)</td>
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<td>---</td>
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<td>5</td>
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<tr>
<td>Santoflex 13 (phr)</td>
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<td>1</td>
<td>1</td>
<td>1</td>
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### TABLE III: ODR RESULTS AND PHYSICAL PROPERTIES OF FILLED RUBBERS

<table>
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<tr>
<th>Compound No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<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>
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<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>
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<tr>
<td>$\Delta$Torque(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>
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<tr>
<td>$t_{s1}$ (min.)</td>
<td>12.22</td>
<td>5.21</td>
<td>8.11</td>
<td>5.53</td>
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<td>10.54</td>
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<tr>
<td>$t_{s2}$ (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>
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<td>$t_{90}$ (min.)</td>
<td>49.20</td>
<td>49.32</td>
<td>23.46</td>
<td>9.06</td>
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<td>37.23</td>
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<tr>
<td>$t_{95}$ (min.)</td>
<td>57.15</td>
<td>57.31</td>
<td>26.56</td>
<td>9.20</td>
<td>34..00</td>
<td>43.5</td>
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<td>CRI</td>
<td>2.70</td>
<td>2.26</td>
<td>5.6</td>
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<td>3.9</td>
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<td>Mooney viscosity ML</td>
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<tr>
<td>(1+4) at 100 °C</td>
<td>109</td>
<td>162</td>
<td>106</td>
<td>111</td>
<td>105</td>
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<tr>
<td>Bound rubber (%)</td>
<td>65.7</td>
<td>93</td>
<td>94</td>
<td>94</td>
<td>93</td>
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<tr>
<td>Crosslink density (mol/m$^3$)</td>
<td>124</td>
<td>220</td>
<td>149</td>
<td>178</td>
<td>249</td>
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</table>
FIGURE CAPTIONS

Figure I: tan $\delta$ versus oscillation amplitudes at 1 Hz frequency and temperature, $-35^\circ C$ for compounds 1-5.
Figure II: Loss modulus ($G''$) versus oscillation amplitudes at 1 Hz frequency and temperature, $-35^\circ C$ for compounds 1-5.
Figure III: Storage modulus ($G'$) versus oscillation amplitudes at 1 Hz frequency and temperature, $-35^\circ C$ for compounds 1-5.
Figure IV: tan $\delta$ versus oscillation amplitudes at 1 Hz frequency and temperature, $25^\circ C$ for compounds 1-5.
Figure V: Loss modulus ($G''$) versus oscillation amplitudes at 1 Hz frequency and temperature, $25^\circ C$ for compounds 1-5.
Figure VI: Storage modulus ($G'$) versus oscillation amplitudes at 1 Hz frequency and temperature, $25^\circ C$ for compounds 1-5.
Figure VII: tan $\delta$ versus oscillation amplitudes at 1 Hz frequency and temperature, $65^\circ C$ for compounds 1-5.
Figure VIII: Loss modulus ($G''$) versus oscillation amplitudes at 1 Hz frequency and temperature, $65^\circ C$ for compounds 1-5.
Figure IX: Storage modulus ($G'$) versus oscillation amplitudes at 1 Hz frequency and temperature, $65^\circ C$ for compounds 1-5.
Figure X: tan $\delta$ versus temperature at 1 Hz frequency and oscillation amplitude, $256 \mu m$ for compounds 1-5.
Figure XI: tan $\delta$ versus temperature at 20 Hz frequency and oscillation amplitude, $256 \mu m$ for compounds 1-5.
Figure XII: tan $\delta$ versus temperature at 1 Hz frequency and oscillation amplitude, $256 \mu m$ for compounds 1 and 6.
Figure XIII: tan $\delta$ versus temperature at 20 Hz frequency and oscillation amplitude, $256 \mu m$ for compounds 1 and 6.
Figure XIV: tan $\delta$ versus temperature at 100 Hz frequency and oscillation amplitude, $256 \mu m$ for compounds 1 and 6.
Figure I

Figure II
Figure III
Figure IV

Figure V
Figure VI

Figure VII
Figure X

Figure XI
Figure XII

Figure XIII
Figure XIV

Scheme I: TESPT

Scheme II: Silica surface