



## Bifunctional Silane (TESPD) Effects on Silica Containing Elastomer Compound

### Part II: Styrene-co-Butadiene Rubber (SBR)

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(Received February 24, 2009, Revised & Accepted March 11, 2009)

## 양기능성실란(TESPD)이 실리카 함유 복합 소재에 미치는 영향 Part II: Styrene-co-Butadiene Rubber (SBR)

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(2009년 2월 24일 접수, 2009년 3월 11일 수정 및 채택)

**ABSTRACT** : Bifunctional silane (TESPD) is added into silica filled SBR compound and its effects with respect to the vulcanization properties, the processability, and the physical properties are investigated. The addition of the TESPD into silica filled SBR compound increases the degree of crosslinking by formation of a strong 3-dimensional network structure with silica surface via coupling reaction, which results in an improved mechanical property. It also improves the processabilities compared to the Control compound.

**요약** : 양기능성실란(TESPD)이 실리카가 함유된 SBR 복합 소재에 첨가되었을 시 그에 따른 가교특성, 가공정도, 물리적 특성들에 미치는 영향을 조사하였다. TESPD를 첨가한 SBR 복합 소재는 TESPD가 실리카와 고무를 화학적으로 결합하여 3차원적인 구조를 형성함으로써 가교밀도가 증가하였고, 이에 따라 기계적 강도가 증가하였다. 이는 또한 TESPD를 첨가하지 않은 소재와 비교했을 시 가공성이 증가하였다.

**Keywords** : SBR, TESPD, silica, processability, mechanical property

## I. Introduction

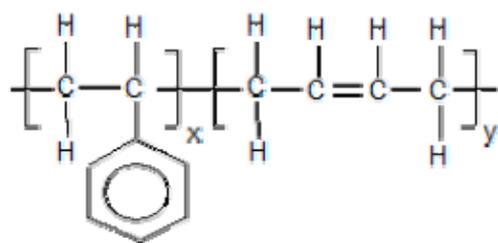
We introduced the mechanism and the application of bifunctional silanes (bis (triethoxysilyl propyl) tetrasulfide (TESPT) and bis (triethoxysilyl propyl) disulfide (TESPD)) in Part I.<sup>1-15</sup>

Styrene-butadiene rubber (SBR) is one of the most common elastomers used in rubber industry.<sup>16,17</sup> SBR is a synthetic rubber. SBRs are consumed about one-half of all rubber, natural and synthetic, used in the U.S. The requirement for SBR has been liable for the building of a massive production capability for this material. More than half of SBR production goes into passenger-car tires in the U.S. SBR/BR compounds have been used in 'green tire' compounds, which exhibits low rolling resistance, good wet and snow traction. The styrene content of most styrene-butadiene rubber varies from 0% to 50%. The

styrene content of most commercially available grades of emulsion polymerized styrene-butadiene rubber is 23.5%. In the cold polymerized E-SBR, the butadiene component has, on average, about 9% cis-1,4, 54.5% trans-1,4, and 13% of vinyl-1,2 structure. At a 23.5% bound styrene level, the glass transition temperature,  $T_g$ , of SBR is about -50 °C. As the styrene content in the SBR increases, the glass transition temperature also increases. It is a general trend that rubbers with very low  $T_g$  (i.e. low styrene content) values show a high resilience and good abrasion resistance, but show poor wet traction. By contrast, those rubbers with high  $T_g$ , (i.e. high styrene content) exhibit a low resilience, low dynamic property and poor abrasion resistance with an excellent wet traction. The chemical structure of SBR is shown in Scheme 1.

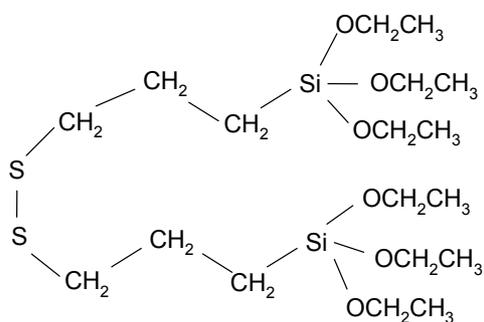
There have been many researches on SBR compounds,<sup>6,8,16-23</sup> however, there have been few published researches on application of TESPD in silica containing SBR compound. There seems very few published studies of the TESPD effect

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styrene-butadiene rubber (SBR)

(a)



(b) TESPD (bis(triethoxysilylpropyl)disulfide)

**Scheme 1.** Chemical structure of (a) SBR, (b) TESPD

in silica filled SBR compound in practical tire tread application.

In this research, we investigate the effects of TESPD in silica filled SBR tread compound, which consists with many different additives using in the tire manufacturing industry, with respect to the processability and the mechanical properties.

## II. Experimental

### 1. Materials

The elastomer used in this study was solution styrene-butadiene rubber (S-SBR), which was a Firestone product by the brand name of Duradene 750 (18% styrene, 37.5% aromatic oil).

Various additives including activator (zinc oxide), processing aid/activator (stearic acid), silica surface modifier/UV absorber (titanium dioxide), antioxidant (TMQ), antiozonant/inhibitor (Sunolite 240), homogenizer (60NS Flakes), plasticizer (Stanplas 2000), curing agent (Sulphur), and accelerators (TBBS, DPG) were used.

The silane used in this study was TESPD (bis (triethoxysilylpropyl) disulfide), which is a product of Struktol Co. (America brand name of SCA985) The main chemical structure of the TESPD is shown in Scheme 1. The silica used in the study was Hi-Sil 243, which is precipitated silica with BET area 150 (m<sup>2</sup>/g) and primary particle diameter 19 nm supplied by PPG. The information of the materials used in this study is summarized in Table 1.

### 2. Mixing

Banbury internal mixer (BR 1600) was used for masterbatch mixings (MB1 and MB2) of rubber and additives (batch: the product of one mixing operation). All the materials with the same ingredients in each elastomer compound were added in masterbatch 1 (MB1) and discharged (dropped) at 300sec mixing. After drop out of MB1, real temperature of each compound was measured by probing. At second pass mixing

**Table 1. Materials used in this Study**

Usage	Trade name	Supplier	cf
Rubber	Duradene 750 <sup>1</sup>	Firestone	S SBR
Filler	Hi-Sil 243	PPG	150 (m <sup>2</sup> /g)
Activator	ZOCO	Zochem	Zinc Oxide
Activator/processing aid	Stearic acid	Harwick Standard	
Silica surface modifier/UV absorber	TiO <sub>2</sub>	Malvern Minerals	Titanium dioxide
Antioxidant	TMQ <sup>2</sup>	R. T. Vanderbilt	
Homogenizer	60NS	Struktol	
Antiozonant/inhibitor	Sunolite 240	Sovereign Chemical Co.	Blended wax
Plasticizer/softener	Stanplas 2000	Harwick	Naphthenic oil
Silane	SCA985	Struktol	S2 (TESPD)
Accelerator	TBBS <sup>3</sup> DPG <sup>4</sup>	Flexsys America L.P. Harwick	
Vulcanizer	Sulfur	C. P. Hall	

1 Styrene-butadiene rubber: solution & block copolymer

2 1,2-dihydro-2,2,4-trimethylquinoline

3 N-t-butylbenzothiazole-2-sulfenamide

4 Diphenylguanidine

**Table 2. Formulation and Mixing Procedure of SBR Compound**

2.1 Formulation (phr)		
1st Stage Material	SBR B4	SBR-S2 B5
Duradene 740	100.0	100.0
Hi-Sil 243	60.00	60.00
Zinc Oxide	4.00	4.00
Stearic Acid	2.00	2.00
TiO <sub>2</sub>	5.00	5.00
TMQ	1.00	1.00
Sunolite 240	1.25	1.25
60 NS Flakes	3.50	3.50
Stanplas 2000	4.00	4.00
2nd Stage Material	SBR B4	SBR-S2 B5
Sulfur	2.00	2.00
TBBS	2.00	2.00
DPG	0.50	0.50

## 2.2 Mixing Procedure (70 RPM, 30 PSI, Fill Factor 0.7, Starting Temp 65°C)

### 1st stage (MB1)

- Add rubber.
- Mix for 30 sec.
- Add rest additives.
- Mix for 1 min and sweep
- Mix for 2 min and sweep.
- Mix for 5 min and dump.

### 2nd stage (MB2) (70 RPM, 30PSI)

- Add 1/2 MB1
- Mix for 30 sec
- Add cures and 1/2 MB1.
- Drop at 90 sec.

(MB2), each compound was further mixed with curatives for 90sec. The total mixing time of the compounds was the same, 6.5 min each. The fill factor, RAM pressure, and rotor speed was fixed at 70%, 30PSI, and 70RPM, respectively. The mixing formulations and procedures are shown in Table 2.

## 3. Mooney viscosity measurement

Mooney viscosities were measured as a function of apparent shear rate at 2RPM and ML1+4 at 100 °C according to ASTM D1646. The rotor diameter of the shearing disc rheometer was 38.1 mm and the thickness of the rotor was 5.5 mm. The machine we used for measuring Mooney viscosity was brand name of Mooney Viscometer 2000 (MV 2000) manufactured from Alpha Technology. The shear rate at the outer radius of the shearing disc could be expressed as follows:<sup>24,25</sup>

$$\dot{\gamma}(R) = \frac{R\Omega}{H} \quad (1)$$

where  $R$  is the radius of rotating disc,  $\Omega$ , the rotor rotation rate,  $H$ , the distance between the disc surface and the stationary housing.

## 4. Cure rheometer test

Oscillating disc cure rheometer (Model Rheotec) manufactured from Tech Pro Inc. was used for measuring vulcanization and reversion resistance property of the compounds in a pressurized rotational rheometer with a biconical rotor following ASTM D 2084 at 160 °C. The oscillation frequency was 100 cycles/min (1.66 Hz) with amplitude of 3°. Minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), torque rise ( $M_H - M_L$ ), scorch (premature vulcanization of a rubber compound) time ( $T_s-2$ ), cure time ( $T_c-90$ ), and reversion (deterioration of vulcanizate properties that may occur when vulcanization time is extended beyond the optimum) resistance time ( $T-2$ ) were measured.

## 5. Viscoelastic property ( $\tan \delta$ ) measurement

Vulcanized specimens were characterized using Mechanical Energy Resolver (MER-1100B) manufactured by Instrumentors, Inc. This instrument measures the oscillatory input of axial compression and tension response of the cylindrical specimen. Oscillatory signal response depending on material was measured and recorded as the elastic and the viscous property as follows:<sup>24,25</sup>

$$\tan \delta = G''/G' \quad (2)$$

$$G'(\omega) = G^* \cos \delta \quad (3)$$

$$G''(\omega) = G^* \sin \delta \quad (4)$$

$$\eta'(\omega) = \frac{G''}{\omega} = \frac{G^*}{\omega} \sin \delta \quad (5)$$

where  $\omega$  represents oscillation frequency;  $G^*$ , the complex modulus;  $\delta$ , the phase angle;  $G'(\omega)$ , the storage modulus;  $G''(\omega)$ , the loss modulus; and  $\eta'(\omega)$ , the dynamic viscosity. Depending on each sample group condition (23 °C or 100 °C) the static servo position (signal acceptor position) was adjusted.

## 6. Screw extrusion

Single Screw Lab Extruder (SSE) manufactured by C. W. Brabender Instruments Inc. (CWB) attached with a roll feeder (Model 1513) was used and data were obtained from a PC attached to CWB at the time of extrusion of the compounds. The drive type of the extruder for SSE was Plasti-Corder PL2100 manufactured by CWB. The length/diameter (L/D) ra-

ratio of the barrel was 15:1 (barrel diameter 19 mm) with compression ratio of three-to-one (3:1). The processing temperature and screw speed were set to 100 °C and 30 RPM, respectively. Garvey type ASTM Extrusion Die (see ASTM D 2230-88) was attached at the exit of the screw. The pressure buildup (PSI) of each compound at the exit of the die was measured.

## 7. Tensile test

An Instron tensile tester (Model 4201) with data acquisition system was used to obtain tensile test data of dumbbell specimen. The average of three specimens was obtained following the ASTM D 412-87 method. This instrument meets the ASTM E4 and measures mechanical properties of the materials, which was a table mounted units consisting of loading frame and control console as separate assemblies. The modulus (Pa) of each compound was measured at 300% elongation. The average thickness and width of the specimens were 2.2 mm and 6.3 mm, respectively.

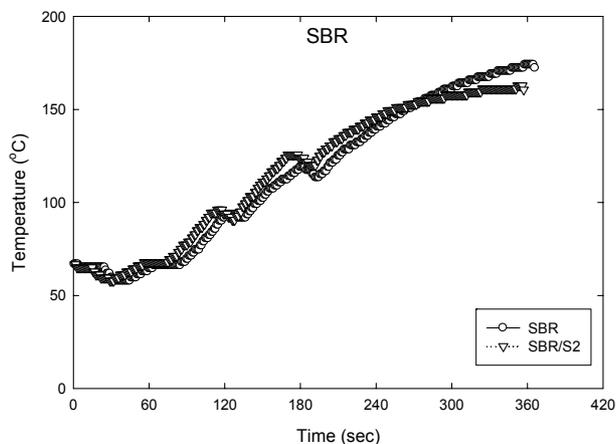
## III. Results

### 1. MB1 mixing temperature changes

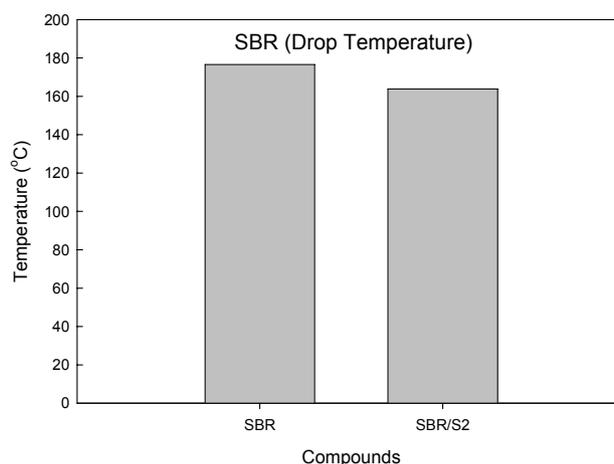
Figure 1 represents the mixing temperature changes (MB1) of SBR compound in a Banbury internal mixer. Addition of S2 lowered the rate of mixing temperature rise compare to the SBR compound.

### 2. Drop temperature

Figure 2 shows the drop/probe temperatures of each compound from MB1. The SBR/S2 compound showed a lower drop temperature than the SBR compound



**Figure 1.** The mixing temperature changes (MB1) of the SBR compounds in a Banbury internal mixer.



**Figure 2.** The drop/probe temperatures of the SBR compounds from MB1.

### 3. Vulcanization curve

Figure 3(a) shows the vulcanization curve changes of the SBR compound for 30 min at 160 °C. S2 added compound showed a higher  $M_H$ , lower  $M_L$ , higher torque rise ( $M_H - M_L$ ), delayed scorch ( $T_s-2$ ) time, and longer cure ( $T_c-90$ ) than the SBR compound as shown in Figure 3(b) and 3(c). This is an implication that addition of silane (S2) improves the processability and the degree of cross-linking of SBR compound.

Figure 4 shows the torque rise ( $M_H - M_L$ ) of each compound. Silanes added compound (SBR/S2) showed a higher torque rise than the SBR compound.

Figure 5 shows the maximum torque ( $M_H$ ) and the minimum torque ( $M_L$ ) of each compound. Silane added compound (SBR/S2) showed a higher torque maximum ( $M_H$ ) and lower minimum torque ( $M_L$ ) than the SBR compound.

### 4. Viscoelastic property ( $\tan \delta$ )

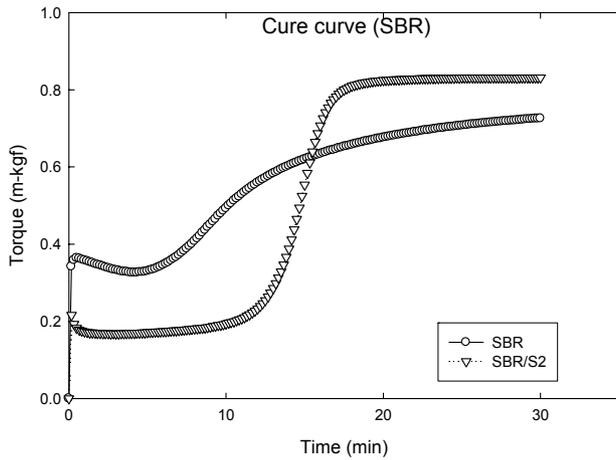
Figure 6 shows the  $\tan \delta$  values of each compound. At room temperature, the  $\tan \delta$  of the SBR/S2 compound showed equal or higher than that of the SBR one. At 100 °C, the  $\tan \delta$  of the SBR/S2 compound showed lower than that of the SBR one.

### 5. Mooney viscosity

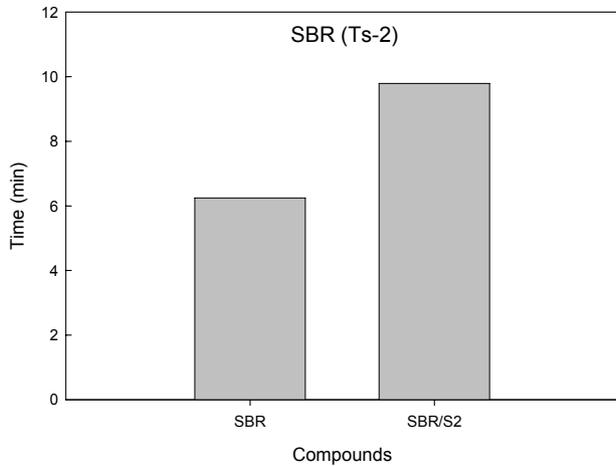
Figure 7 shows the Mooney viscosity of each compound. The SBR/S2 compound showed a lower Mooney viscosity than the SBR compound.

### 6. Extrusion torque

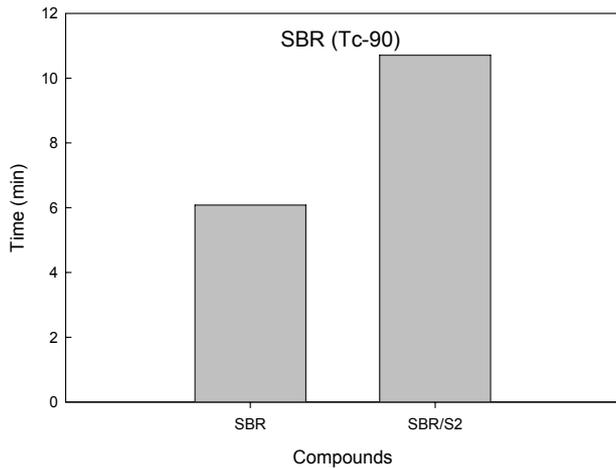
Figure 8 shows the (a) extrusion torque and (b) pressure



(a)

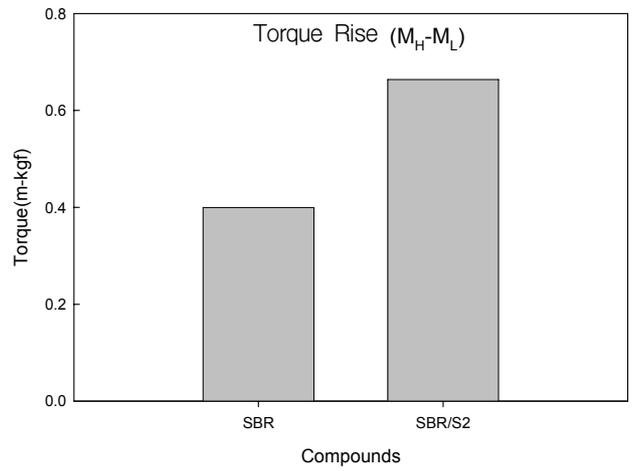


(b)

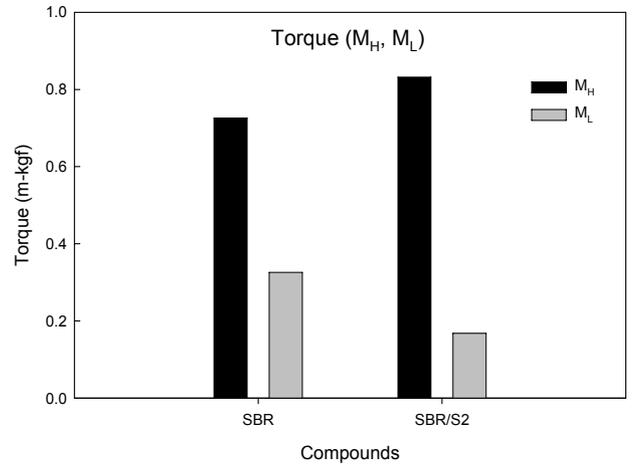


(c)

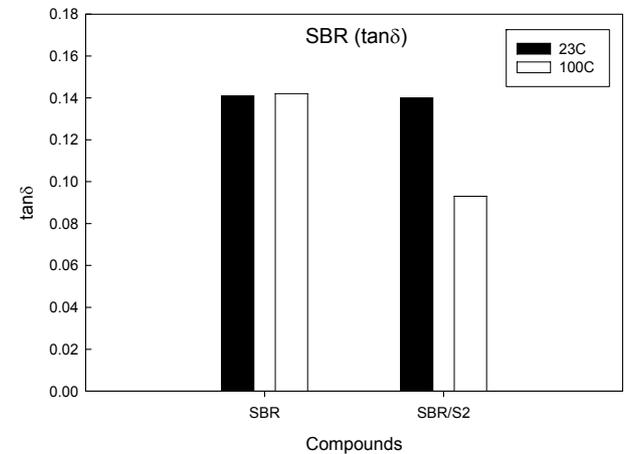
**Figure 3.** (a) vulcanization curve changes for 30 min at 160 °C, (b) scorch (Ts-2), (c) Cure (Tc-90) of the SBR compounds



**Figure 4.** The torque rise ( $M_H - M_L$ ) of the SBR compounds.



**Figure 5.** The maximum torque ( $M_H$ ) and the minimum torque ( $M_L$ ) of the SBR compounds.



**Figure 6.** The  $\tan \delta$  values of the SBR compounds.

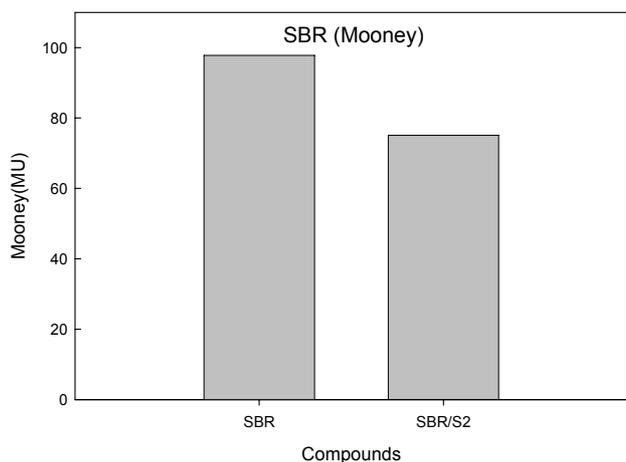


Figure 7. The Mooney viscosity of the SBR compounds.

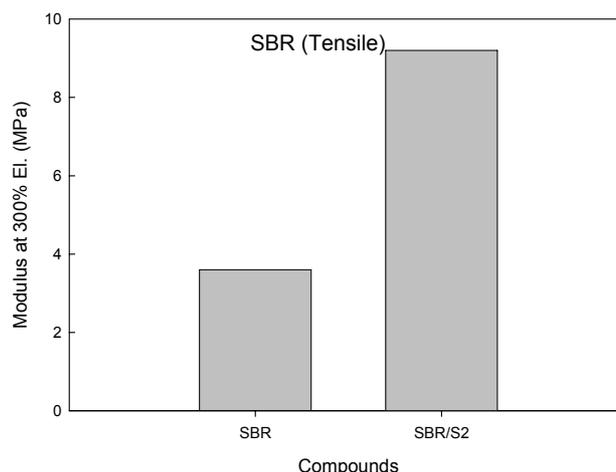


Figure 9. The elongational modulus of the SBR compounds at 300% elongation.

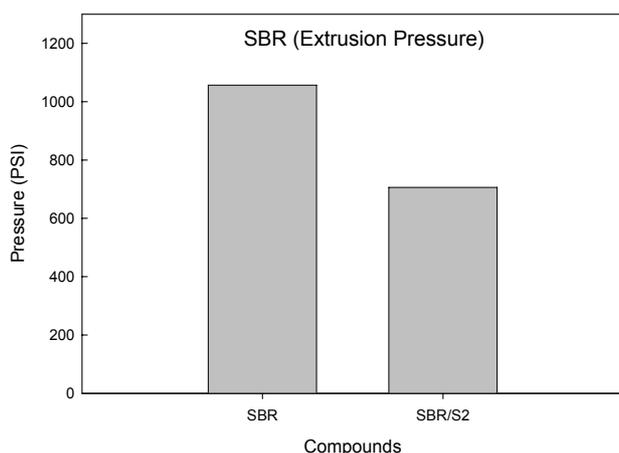
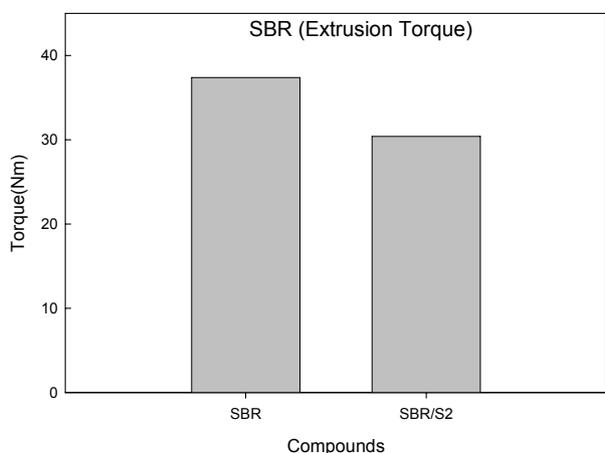


Figure 8. (a) extrusion torque and (b) pressure build up of the SBR compounds in an extruder.

build up of each compound in an extruder. Silanes added compound (SBR/S2) showed a lower torque and pressure build up than the SBR one.

### 7. Tensile test

Figure 9 shows the modulus of each compound at 300% elongation. Silane added compound (SBR/S2) showed a higher elongation modulus than the SBR one.

## IV. Discussion

When the ethoxy groups attached on one side of the TESPD chemically react with silanol groups on silica surface at mixing stage via hydrolysis mechanism,<sup>9-12</sup> the processability of the silica compound increases.<sup>4,26-32</sup> After then the sulfur groups attached on the other side of the TESPD reacts with double bonds in rubber chains<sup>4,33</sup> at vulcanization stage, the mechanical property of the compound increases<sup>5,32</sup> due to formation of a stable silica-silane-rubber network. Author showed the application of the bifunctional organosilanes such as TESPT and TESPD for reinforcing of silica filled elastomer compounds<sup>5,6,16,17,34-36</sup> In our various additive filled silica/SBR tread system, addition of a bifunctional silane (TESPD) showed a reduced heat generation during mixing, low  $M_L$ , low drop temperature, and low extrusion torque and pressure build up inside the extruder, which represent an improved processability. It also showed a high vulcanization torque, torque rise ( $M_H - M_L$ ), torque maximum ( $M_H$ ) and high elongational modulus, which implicates an improved mechanical properties. This is due to lubrication effects of the silane, interfaces between polymer-polymer, polymer-silica, and silica-silica during mixing, and then after vulcanization, formation a strong 3-dimensional

network structure interface between silica and EPDM via coupling reaction as described by author previously.<sup>5</sup> Previously other researchers observed a similar trend as we shown above,<sup>26-32</sup> however, their system did not include various additives as we did in this research, which corresponds to a practical tread compound.

## V. Conclusions

Comparing the SBR/TESPD and the SBR (Control) compound, the SBR/TESPD one showed a better processability, better processing safety, higher degree of crosslinking, higher torque rise than the Control one. This showed the same trend as we observed in the NR matrix system in Part I.

Addition of the TESPD into silica filled SBR compound formed a strong 3-dimensional network structure with a silica surface via coupling reaction, results in increased mechanical properties and processability of the compound.

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