



Bifunctional Silane (TESPD) Effects on Silica Containing Elastomer Compound

Part I: Natural Rubber (NR)

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양기능성실란(TESPD)이 실리카함유 복합소재에 미치는 영향

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ABSTRACT : Organo bifunctional silane (TESPD) is added into silica containing NR and its effects are investigated with respect to the vulcanization properties, the processability, and the physical properties. The addition of the TESPD into silica filled NR 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 NR복합소재에 첨가되었을시 그에따른 가교특성, 가공정도, 물리적 특성들에 미치는 영향을 조사하였다. TESPD를 첨가한 NR복합소재는 TESPD가 실리카표면과 고무의표면을 화학적으로 결합하여 3차원적인 구조를 형성함으로써 가교도가 증가하였고, 이에따라 기계적강도가 증가하였다. 이 복합소재는 또한 TESPD를 첨가하지않은 소재와 비교했을시 가공성이 증가하는것을 보여주었다.

Keywords : NR, TESPD, silica, processability, mechanical property

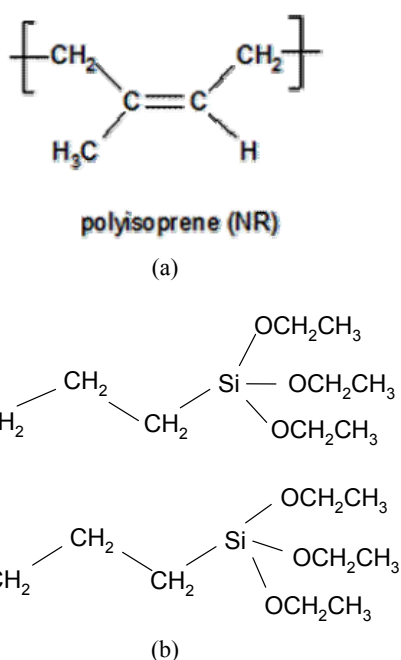
I. Introduction

General silane chemistry is widely used in various industries. Silanes are used for automotives (e.g. engine mount, door sealing), military vehicles (e.g. air, ground (heavy duty tires, tank innerliner), and underwater), military goods (e.g. gas masks, boots, protective gloves, hose, rubber gasket), aerospace vehicles (e.g. hose, wire products), tires (e.g. airplane, heavy-duty, high performance (racing etc.)), belts (e.g. automotives, conveyer), general rubber goods, construction (e.g. building vibration absorption), medical (e.g. artificial teeth), recycling of end-of-life polymers, biodegradable fibers coupling with polymers (cf. bio-resin: poly(lactic acid), poly(trimethylene terephthalate), etc.

Use of bifunctional silanes such as TESPT and TESPD with silica particle in natural rubber (NR) and styrene-co-butadiene rubber (SBR) or SBR/BR has been known to improve several tire properties such as gas mileage,¹ wet and snow traction due to improved rolling resistance² and degree of cross-linking via improved silica-silane coupling.³⁻⁸ One end of silane chemically bond on silica surface via hydrolysis reaction⁹⁻¹² and

the other end of silane bond on rubber chain via sulfur cross-linking.¹³⁻¹⁵

NRs have been used in the area of heavy-duty tires and building vibration absorption against earthquakes.¹⁶ NR is non-polar and has more double bonds than SBR. Each rubber has different levels of double bonds and different types of residues. The unit cell of crystalline form NR has a density of 1.0 g/cm³ and that of amorphous unfilled rubber is 0.9 g/cm³, respectively.¹⁷ The NR is mainly based on isoprene and has many other ingredients such as sugars, fats and proteins, which influence the vulcanizate properties. The residue such as fatty acids, amino acids, and proteins will also react with the initial zinc oxide. These acids should present in the final vulcanizate as their zinc soaps. Wunderlich¹⁸ theoretically described the nucleation rate based on absolute rate reaction theory. Avrami¹⁹⁻²¹ describe rate relationships for crystals growing uniformly in metals in one, two or three dimensions. The state of equilibrium is a function of the rubber crosslink density,²² the temperature²³ and the strain.²⁴ Flory has made use of thermodynamic arguments to derive theoretical expressions for relaxation of stress due to crystallization for the



Scheme 1. Chemical Structure of (a) NR, (b) TESPD (Bis(triethoxysilylpropyl)disulfide).

equilibrium degree of crystallinity. After Flory's²⁴ proposed model 'fringed micelle', Andrews^{25,26} discovered 'chain fold' structure in electron microscopy studies of strained ultra thin rubber films. More refined versions of chain fold have developed by Keller²⁷ and later authors.²⁸⁻³⁰ The crystallization is

accompanied by an increase in density (i.e. decrease in volume) and volume changes.^{31,32} Nucleation may occur spontaneously and homogeneously throughout the amorphous phase at lower temperature or be 'seeded' by foreign surfaces or structure discontinuities. The crystal growth²⁶ is influenced by the type and density of nucleation. Embryo nuclei grow to a critical size and distribution before any macroscopic effect such as elastic modulus increase is observed.

The chemical structure of NR is shown in Scheme 1. There have been many researches on NR compounds,^{8, 33-37} however, there have been few published researches on application of TESPD in silica containing NR⁸ compound. Furthermore, there were very few published studies effects of the TESPD in practical tire compound.

In this research, we investigate the effects of TESPD in a silica filled NR compound, which consists with many different ingredients used in practical tire industry, with respect to the processability and the mechanical properties.

II. Experimental

1. Materials

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 was Hi-Sil 243, which is precipitated silica with BET area 150 (m²/g) and primary particle diameter 19 nm supplied by PPG.

Table 1. Materials Used in This Study

Usage	Trade name	Supplier	Remark
Rubber	SMR20 ¹	Goodyear	NR
Filler	Hi-Sil 243	PPG	150 (m ² /g)
Peptizer	A 86	Struktol	
Activator	ZOCO	Zochem	Zinc Oxide
Activator/processing aid	Stearic acid	Harwick Standard	
Silica surface modifier/UV absorber	TiO ₂	Malvern Minerals	Titanium dioxide
Antioxidant	TMQ ²	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
Accelerator	TBBS ³ DPG ⁴	Flexsys America L.P. Harwick	
Vulcanizer	Sulfur	C. P. Hall	

¹ Natural rubber

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

³ N-t-butylbenzothiazole-2-sulfenamide

⁴ Diphenylguanidine

The elastomer used was natural rubber (polyisoprene rubber), which was a Goodyear product by the brand name of SMR-20. Various additives including activator (zinc oxide), processing aid/activator (stearic acid), peptizer (A 86), silica surface modifier/UV absorber (titanium dioxide), anti oxidants (TMQ), anti antiozonant/inhibitor (Sunolite 240), homogenizer (60NS Flakes), plasticizer (Stanplas 2000), curing agent (Sulphur), and accelerators (TBBS, DPG) were used. The information on the materials used in this study was 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). The silane level in the NR

Table 2. Formulation and Mixing Procedure for NR Compound

2.1 Formulation

1st Stage Material	NR	NR/S2
SMR20	100.00	100.00
A 86	0.25	0.25
Hi-Sil 243	60.00	60.00
Zinc Oxide	4.00	4.00
Stearic Acid	2.00	2.00
TiO ₂	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
ZS	0.00	0.00
2nd Stage Material	NR	NR-S2
Sulfur	2.00	2.00
TBBS	1.00	1.00
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 and A86.
- 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 curatives and 1/2 MB1.
- Drop at 90 sec.

compounds was 3 phr. All the materials with the same ingredients in each elastomer compounds were added in masterbatch 1 (MB1) and discharged (dropped) at 300 sec mixing. After drop out of MB1, real temperature of each compound was measured by probing. At second pass mixing (MB2), each compound was further mixed with curatives for 90 sec. The total mixing times of the compounds were the same for 6.5 min each. The fill factor, RAM pressure, and rotor speed was fixed at 70%, 30 PSI, and 70 RPM, respectively. The mixing formulations and procedures are included 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 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:^{38,39}

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

where R is the radius of rotating disc, Ω , 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:^{38,39}

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

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

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

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

where ω represents oscillation frequency; G^* , the complex modulus; δ , 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 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) 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 NR compounds in a Banbury internal mixer. The addition of the S2 lowered the rate of mixing temperature rise than

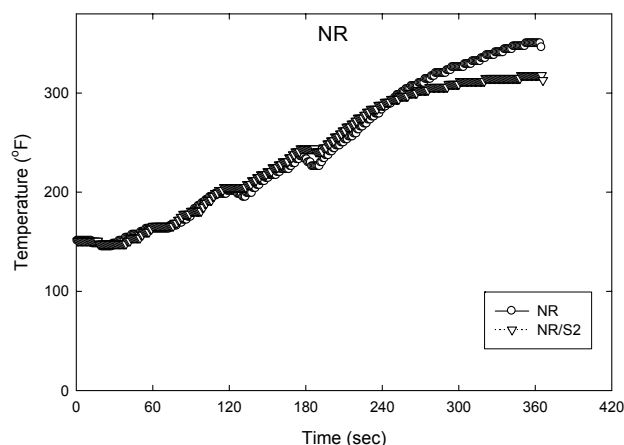


Figure 1. Mixing temperature changes (MB1) of NR compounds in a Banbury internal mixer.

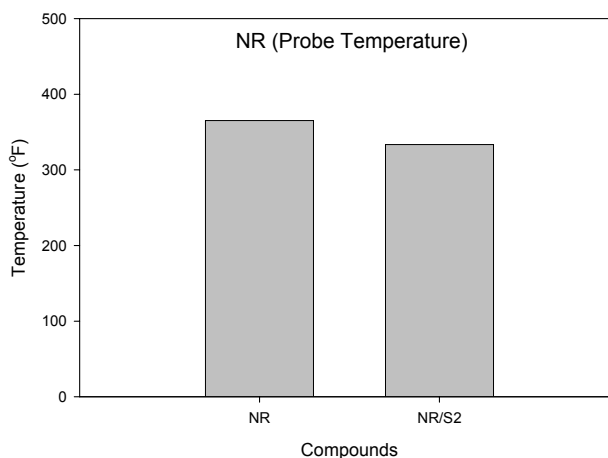


Figure 2. Probe temperatures of each compound measured from MB1.

the NR compound.

2. Drop temperature

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

3. Vulcanization curve

Figure 3 shows the vulcanization curve changes of the NR compounds for 30 min at 160 °C. The S2 added compounds showed a higher M_H , lower M_L , higher torque rise ($M_H - M_L$), and delayed scorch (T_s-2) time than the NR one. This is an implication that addition of silane (S2) improves the processability and the degree of cross-linking of the NR compound.

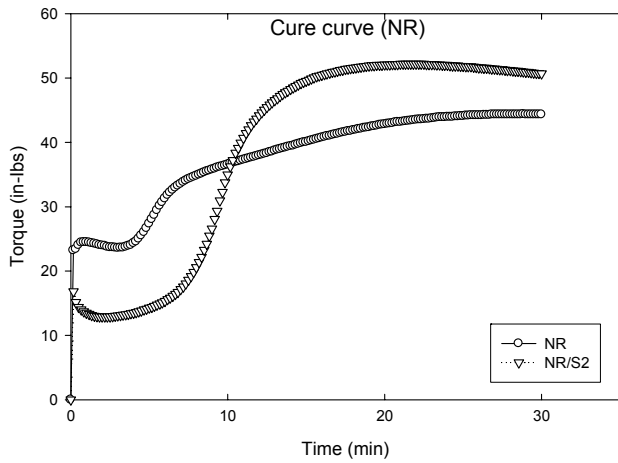


Figure 3. Vulcanization curve changes of NR compounds for 30 min at 160 °C.

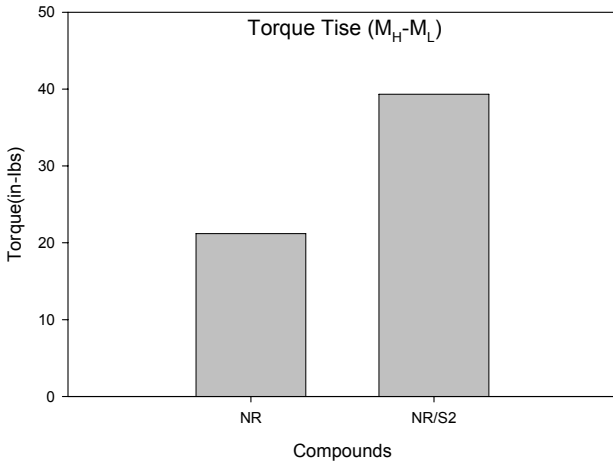


Figure 4. The torque rise ($M_H - M_L$) of the NR compounds.

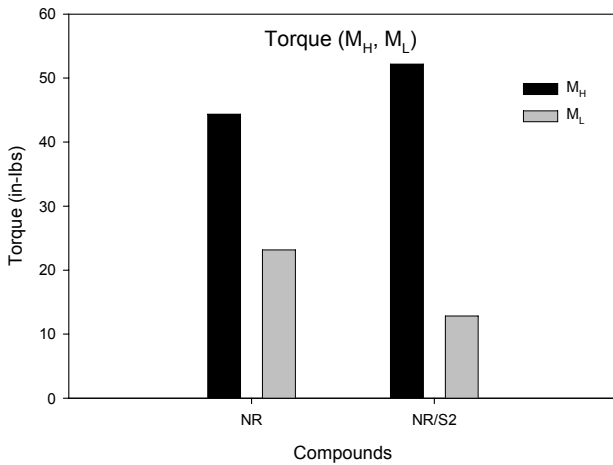


Figure 5. The torque maximum (M_H) and the torque minimum (M_L) of the NR compounds.

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

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

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

Figure 6 shows the $\tan \delta$ values of each compound. At room temperature, the $\tan \delta$ of NR/S2 compound showed a lower value than that of the Control one.

5. Mooney viscosity

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

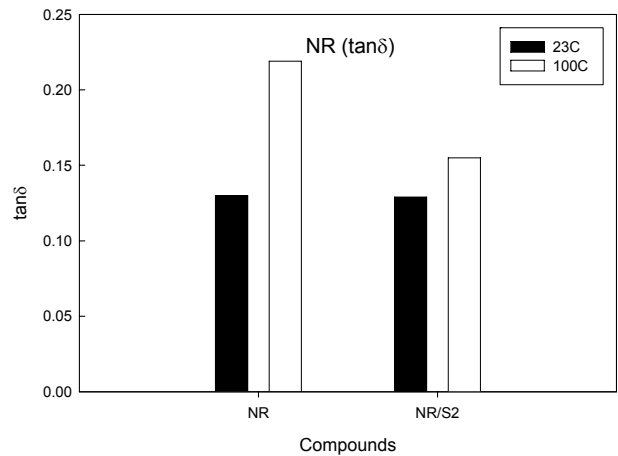


Figure 6. The $\tan \delta$ values of the NR compounds.

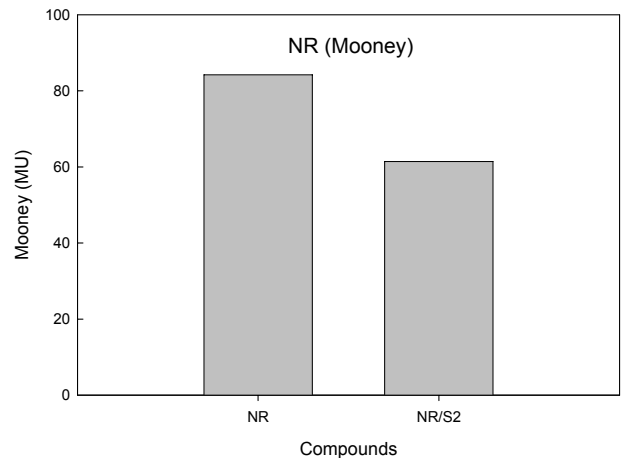
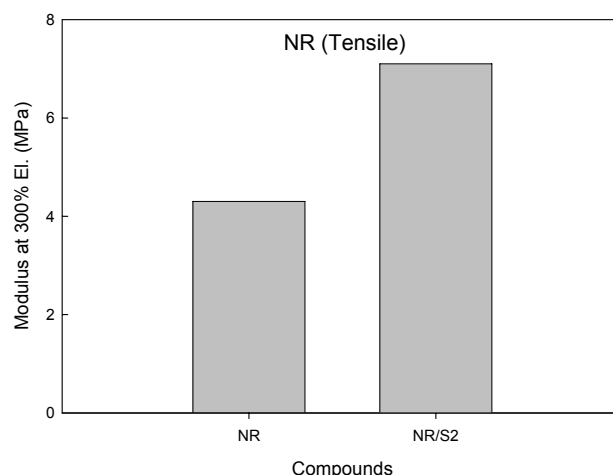
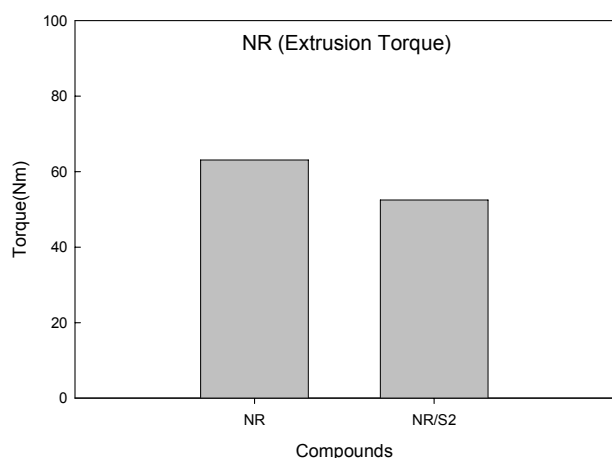
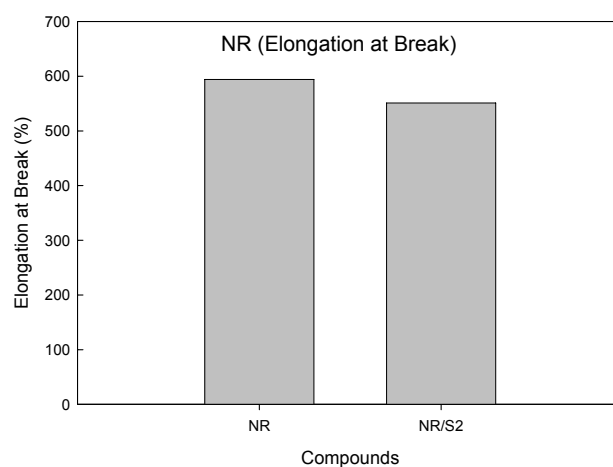
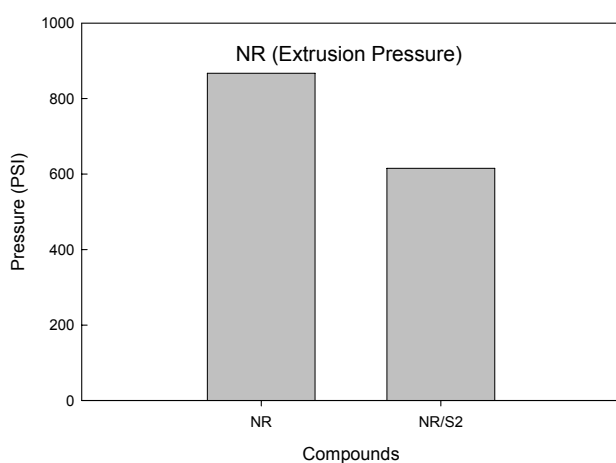


Figure 7. The mooney viscosity of the NR compounds.



(a)



(b)

Figure 8. The extrusion torque and the pressure build up of each compound processed through a single screw extruder.

Figure 9. (a) the modulus at 300% elongation (b) the elongation% at break of the NR compounds.

6. Extrusion torque

Figure 8 shows the extrusion torque and the pressure build up of each compound processed through a single screw extruder. Silane added compound (NR/S2) showed a lower torque and pressure build up than the NR one.

7. Tensile test

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

Figure 9(b) shows the elongation% at break of each compound.

IV. Discussion

Surface treatment of silica with bifunctional organosilanes improves the processability of silica compounds^{4,40-47} as well as their mechanical properties.^{5,47} This is due to the function of ethoxy groups and sulfur groups. The ethoxy groups attached on silane chemically react with silanol groups on silica surface at the mixing stage via hydrolysis mechanism,⁹⁻¹² and then the sulfur groups react with double bonds on rubber chains^{4,48} at vulcanization stage. Those lead to a formation of a stable silica-silane-rubber network. Bifunctional organosilanes such as bis (triethoxysilyl propyl) tetrasulfide (TESPT) and bis (triethoxysilyl propyl) disulfide (TESPD) have been widely used for reinforcing silica filled elastomer systems.^{5,6,49-53}

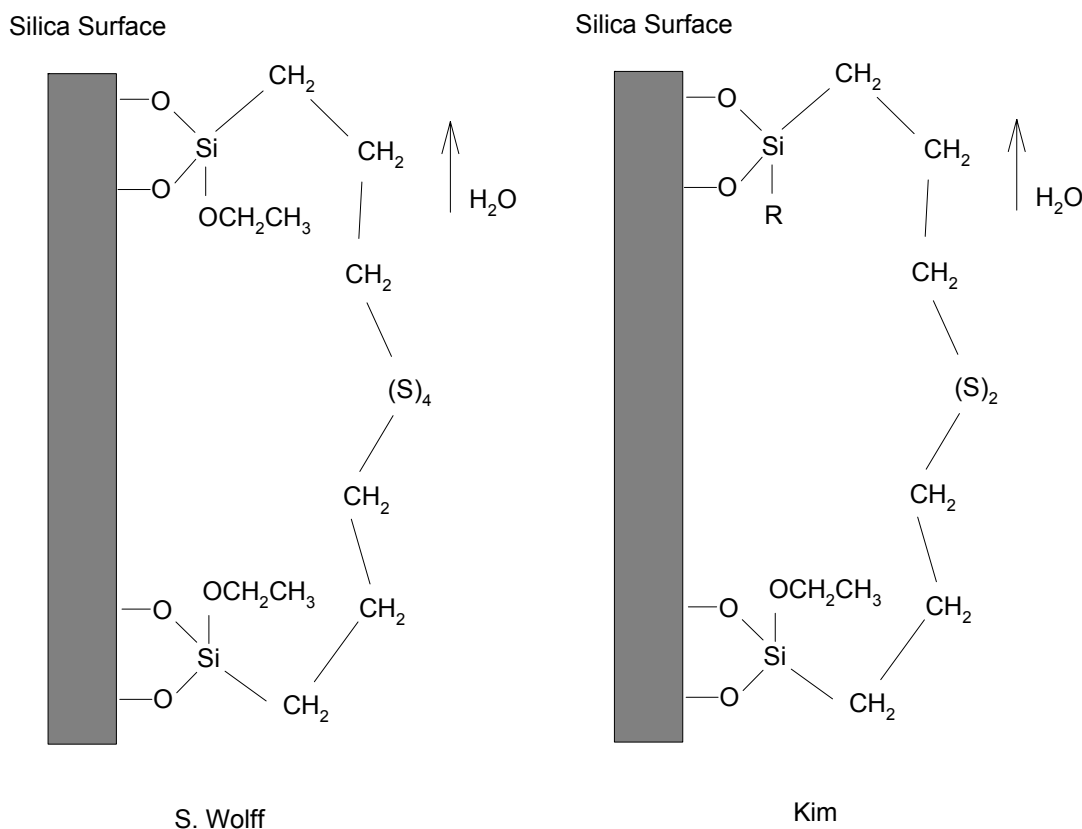


Figure 10. Schematic presentation of the proposed improved hydrolyzation of the alkoxy group remained in a silane.

The hydrolysis reaction mechanism of Wolff as described in 1979,^{54,55} which had been accepted in the silane hydrolysis process as a mechanism. This is a steric hindrance theory, which a third alkoxy group in a trialkoxysilane does not hydrolyze (67% hydrolysis) due to steric hindrance. Recently, Kim proposed a water molecule treated silica systems, which shows additional hydrolyzation of the alkoxy group remained in a silane (81% hydrolysis) and produces fewer alcohols in the silane compound and it improves mechanical properties in 2005 with moisture treated silica filled system.⁴⁹ This is further increased to 89% hydrolysis.⁵⁶ Thus the hydrolyzation of the alkoxy group remained in a silane should be represented as shown in Figure 10, i.e. about alkoxy group out of six alkoxy groups in a silane should be remained.

In this various additive filled silica/NR system, addition of bifunctional silane (TESPD) showed an improved processability and mechanical properties, which is a similar trend as observed from other researchers previously.^{40-45,47}

V. Conclusions

Comparing the NR/S2 and the Control compound, the NR/S2 one showed a better processability, better processing safety,

higher degree of crosslinking, higher torque rise than the Control one.

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

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