

## Zinc Surfactant Effects on Nr/Tespd/Silica and SBR/Tespd/Silica Compounds

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**ABSTRACT** : The effects of zinc surfactant (ZB) on the bis(triethoxysilylpropyl)disulfide (TESPD)-silica mixture in natural rubber (NR) and solution butadiene-*co*-styrene rubber (S-SBR) were compared with respect to their rheological property, processability, physical properties, and silica dispersion. In the NR compound, addition of the ZB increased the reversion resistance time (T-2), the tensile modulus, and the BO time; however, lowered the viscosity, the HBU, and  $\tan\delta$  values. In the S-SBR copound, addition of the ZB increased the  $\tan\delta$  values while lowered the T-2, the tensile modulus, the BO time, the viscosity, and the HBU of the compound. In the NR compounds, addition of the ZB significantly increased the processability and mechanical property. However, in the S-SBR compounds, it improved the processability the mechanical property was not improved.

*Keywords* : zinc surfactant, precipitated silica, TESP bis(triethoxysilylpropyl)disulfide, rheology, NR and S-SBR.

### I. Introduction

Organo bifunctional silane, which containing sulfur, bis(triethoxysilylpropyl)tetrasulfide (TESPT), have been studied since 1970's to improve the processability and chemical bonding between silica and rubber chain,<sup>1,2</sup> and they were utilized in the 'green tire' tread compound.<sup>3-5</sup> However TESPT exhibit less stable during mixing due to their low dissociation energy than the bis(triethoxysilylpropyl)disulfide (TESPD).<sup>6</sup>

Silane has been used to improve processability of the silica compounds.<sup>7-13</sup> Bifunctional silane into silica compounds improves the processability<sup>7,9,11,13</sup> and the mechanical property<sup>17,18</sup> of the compounds. The porous and polar characteristics of the silica surface<sup>8,10</sup> make the compound process harder than other particle filled compounds such as carbon black, zinc oxide, calcite etc.<sup>16</sup>

Zinc-ion containing surfactants such as zinc stearate, zinc tallowate, zinc naphthenate, and zinc 2-ethylhexanoate acts as an intermolecular lubricant and activator because they are rubber soluble and zinc-ion acts as an activator. Depending on their structure such as carbon chain length, chain length distribution, polarity, and branching, their final product property varies. Large amount of additives are used in the industry now, however, there were few systematic theory or researches<sup>17,18</sup> on the zinc surfactant illustrated above. Addition of zinc surfactant in the silica/TESPD/NR compound exhibited significant improvement on processability and mechanical property,<sup>17-19</sup> however there were no researches on zinc surfactant application in the silica/TESPD/SBR compounds.

The NR compounds have been used in the area of truck tire industries and building's vibration absorption against earthquake etc.<sup>20</sup> The NR is non-polar and has more double bonds than the SBR.<sup>20</sup>

The SBR/BR compounds have been used in the

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'green tire' compounds, which exhibits low rolling resistance, good wet and snow traction.<sup>3-5</sup>

We present the effects of the zinc surfactant (a class of zinc soap), which developed in our lab, on TESP treated silica compounds in the NR and the SBR compounds during mixing and after vulcanization. Processability, silica agglomerate dispersion, vulcanization characteristics, and mechanical properties of each compound were compared.

## II. Experimental

### 1. Materials

The silanes used in this study were the TESP

trade name SCA985, which was a product of Struktol. The zinc surfactant used in this study was ZB47 (ZB), which was a product of Struktol.

The elastomer used were NR, which was a Goodyear product by the brand name of SIR-20, and S-SBR (SBR), which was a Firestone product by the brand name of Duradene 740 (17% styrene).

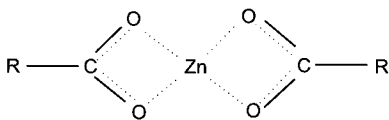
The silica used was Ultrasil VN3, which was precipitated silica with BET area 175 (m<sup>2</sup>/g) supplied by Degussa.

Various additives including activator, processing aids, anti oxidant, homogenizer, curing agent, and accelerators were used. The information of the materials used in this study is summarized on Table 1.

**Table 1. Materials Used In This Study**

	Trade name (Code)	Supplier
Rubber	SIR 20 (NR) Duradene 740 (S-SBR)	Goodyear Firestone
Peptizer	A86	Struktol
Filler	Ultrasil VN3 (Silica)	Degussa
Activator	Zinc Oxide [ZnO], Stearic acid	
Processing aid	Titanium dioxide [TiO <sub>2</sub> ]	DuPont
Antioxidant	TMQ [poly(trimethyl dihydroquinilin)]	Vanderbilt
Antioxidant, Antiozonant, Inhibitor	Sunolite 240	
Lubricant, Activator	Carbowax 3350 [polyethylene glycol]	Harwick
Homogenizer	60 NS Flakes	Struktol
Processing aid, Dispersing agent	WB 222	Struktol
Plasticizer, Softener	Stanplas 2000	Harwick
Bonding agent	SCA 985[bis(triethoxysilylpropyl)disulfide]	Struktol
Activator	ZB47*(ZB)	Struktol
Vulcanizer	Sulfur (S)	
Accelerator	MOR** Vanax A (4,4'-dithiodimorpholine) DPG (Diphenylguanidine)	**Harwick

\*



R=C<sub>6</sub>-C<sub>20</sub>

## 2. Mixing

A Banbury internal mixer (BR 1600) was used for mixing rubber and additives and a data acquisition computer was attached to this to obtain the data at the time of mastification. The fill factor was fixed at 0.7 and the starting operation temperature of mixer was set to 65.5°C. The rotor speed was set to 77 RPM.

The mixing formulations and procedures are included in Table 2.

**Table 2. Mixing Formulations (phr) and Procedure**

① Formulation

⊖ 1st Stage

Material	S2	S2Z2	S2S5	S2	S2Z2	S2S5
NR	100.0	100.0	100.0	0.0	0.0	0.0
S-SBR	0.0	0.0	0.0	100.0	100.0	100.0
A 86	0.25	0.25	0.25	0.25	0.25	0.25
Silica	57.0	57.0	57.0	57.0	57.0	57.0
Zinc Oxide	4.0	4.0	4.0	4.0	4.0	4.0
Stearic Acid	2.0	2.0	2.0	2.0	2.0	2.0
TiO <sub>2</sub>	5.0	5.0	5.0	5.0	5.0	5.0
TMQ	1.0	1.0	1.0	1.0	1.0	1.0
Sunolite 240	1.25	1.25	1.25	1.25	1.25	1.25
PEG	1.0	1.0	1.0	1.0	1.0	1.0
60 NS Flakes	3.5	3.5	3.5	3.5	3.5	3.5
WB 222	2.0	2.0	2.0	2.0	2.0	2.0
Stanplas 2000	4.0	4.0	4.0	4.0	4.0	4.0
TESPD	2.5	2.5	2.5	2.5	2.5	2.5
ZB	0.0	2.0	5.0	0	2.0	5.0

⊖ 2nd Stage

Sulfur	2.0	2.0	2.0	2.0	2.0	2.0
MOR	2.0	2.0	2.0	2.0	2.0	2.0
Vanax A	0.5	0.5	0.5	0.5	0.5	0.5
DPG	0.5	0.5	0.5	0.5	0.5	0.5

② Mixing Procedure

1. Add rubber and A86
2. Mix to 30 sec
3. Add rest additives
4. Mix to 250°F and sweep
5. Mix to 5 min and dump.

## 3. Shear Viscosity Measurement

Shear viscosities were measured in a pressurized

rotational rheometer with a biconical rotor. This was the instrument described by Montes et al,<sup>21</sup> which measures the viscosity at various speeds. The shear rate and shear stress were given by

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

$$\sigma_{12} = \frac{3M}{4\pi R^3} \quad (1b)$$

where  $\Omega$  is the angular velocity,  $a$  is the cone angle,  $M$  is the torque and  $R$  is the cone radius.<sup>22</sup>

## 4. Reversion Test

An oscillating disc cure rheometer (ODR 2000) manufactured from Monsanto Co. was used measuring vulcanization property and reversion resistance time (T-2) of the compounds following ASTM D 2084 method at 160°C. T-2 is length of the time that takes two Mooney unit drop from the Mooney maximum torque  $M_H$ . The oscillation frequency was 100 cycles/min (1.66 Hz) with amplitude of 3°.

## 5. Viscoelastic Property ( $\tan\delta$ )

The vulcanized materials were characterized using Mechanical Energy Resolver (MER-1100B) manufactured by Instrumentors, Inc. Oscillatory tension/compression signal responses from test specimens were measured as follow<sup>23</sup>:

$$E'(\omega) = E^* \cos\delta \quad (2a)$$

$$E''(\omega) = E^* \sin\delta \quad (2b)$$

$$E^* = (E'^2 + E''^2)^{1/2} = E'[1 + (\tan\delta)^2]^{1/2} \quad (2c)$$

$$\omega\eta_{el} = E'' \quad (2d)$$

where  $\omega$  represents oscillation frequency,  $E^*$  is the complex dynamic modulus,  $\delta$  is the phase angle,  $E'(\omega)$  is the real dynamic modulus,  $E''(\omega)$  is the imaginary dynamic modulus, and  $\eta_{el}(\omega)$  is the tensile viscosity.

## 6. Tensile Test

The tensile test results were obtained from the dumbbell shaped specimens measured following ASTM D 412-87 method. The tensile modulus at 100% elongation (Pa) of each compound was measured. The thickness and the width of the specimens were average 2.2 mm and 6.3 mm, respectively.

## 7. Blowout (BO) Time and Heat Build Up (HBU)

The "Firestone Flexometer"<sup>24</sup> was used measuring BO time and HBU temperature of each sample as of ASTM D 623. This is a testing apparatus for applying a uniform circulatory oscillating action under compression. The bottom moving part is circulatory oscillating at constant speed of 13.1 Hz. The amplitude of the lower moving part was 7.6 mm. The test specimen was in the shape of a frustum of a rectangular pyramid with dimensions; base, 54 by 28.6 mm; top, 50.8 by 25.4 mm; and altitude, 38.1 mm.

## 8. Scanning Electron Microscope Observation

A Hitachi S-2150 scanning electron microscope (SEM) was used to characterize the order of silica agglomerate particle size. The prepared compounds were fractured in liquid nitrogen and coated with silver using a sputter coater. Each specimen was observed at 5,000 magnification.

## III. Results and Discussion

### 1. Temperature Changes During Mixing

Figure 1 represents the stock temperature changes during internal mixer mixing. Addition of the ZB into the TESPd-silica compounds, S2 (NR, SBR), lower the stock temperature rise of both the NR and the SBR compounds. As the concentration of the ZB increased from 0 to 2 parts by hundred rubber

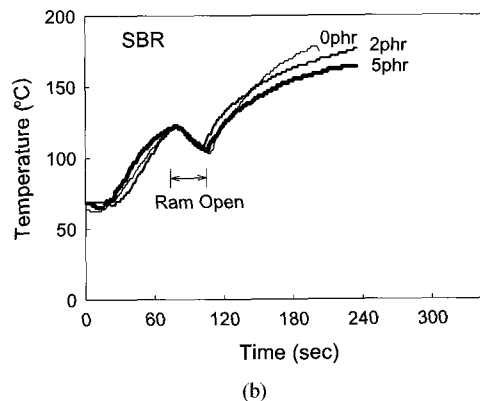
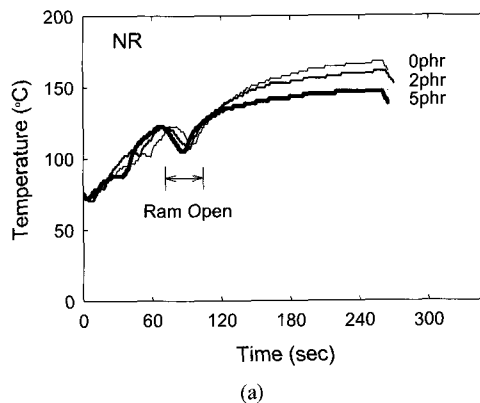


Figure 1. ZB concentration effects on the stock temperature changes (a) the NR compounds, (b) the SBR compounds during first stage mixing.

(phr) and to 5 phr, the temperature rises in the mixer further decreased on both compounds during mixing. Comparing the NR and the SBR compounds at 200s mixing time, the stock temperature of the (S2) SBR compound rapidly increased to 177°C (350°F) while other compounds Z2S2 (SBR) and S2Z5 (SBR) increased to 170°C and 160°C, respectively. At the same mixing time at 200s, the SBR compounds exhibited higher temperature rise than the NR compounds i.e. SBR(S2) > NR(S2), SBR(S2Z2) > NR(S2Z2), and SBR(S2Z5) > NR(S2Z5), respectively.

### 2. Steady Shear Viscosity

Figure 2 represents the steady shear viscosity of each compound. As the slope of the viscosity is

closer to vertical or viscosity shows at a high stress, it tends to show yield values or hard to process, respectively. Addition of the ZB in the NR and the SBR compounds lowered the viscosity of each compound and the order of viscosity was proportional to the concentration of the ZB, i.e. the viscosity of each compound decreased as the concentration of the ZB increased i.e.  $S2(NR) > S2Z2(NR) > S2Z5(NR)$ , and  $S2(SBR) > S2Z2(SBR) > S2Z5(SBR)$ . Similar trend, the viscosity reduction of the TESPT treated silica compounds depending on the ZB concentration, was reported previously.<sup>18</sup>

The ZB clearly reduced the viscosity of silane treated silica compounds in the NR and the SBR.

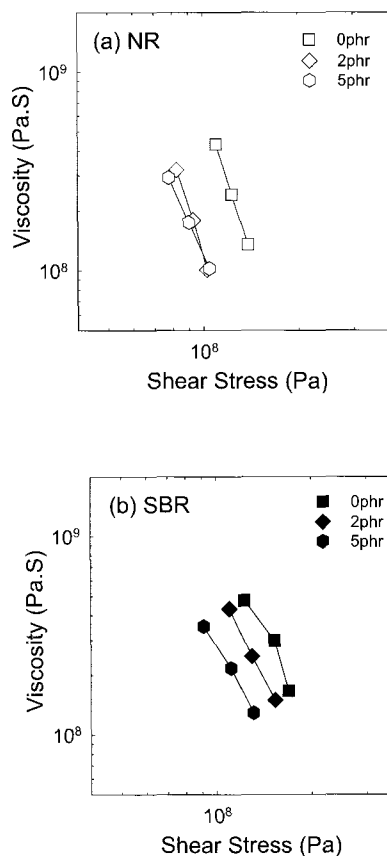
### 3. Mooney Viscosity

Figure 3 represents the dynamic viscosity, Mooney viscosity, of each compound measured at 0.2 rad/sec and 100°C. As the concentration of the ZB increased, the viscosity of the NR and the SBR compounds decreased, which exhibited the same trend measured from the steady shear viscosity data as shown above i.e.  $(S2(NR) > S2Z2(NR) > S2Z5(NR))$ , and  $(S2(SBR) > S2Z2(SBR) > S2Z5(SBR))$ .

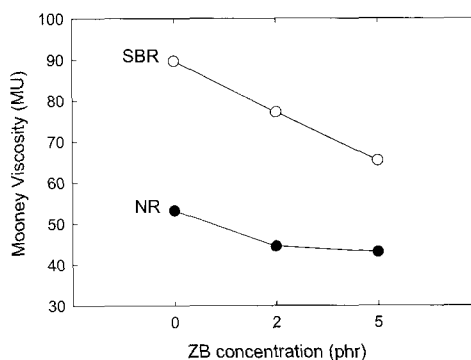
It is clear that the ZB acted as a lubricant on both the NR and the SBR compounds.

### 4. Viscoelasticity ( $\tan\delta$ )

Figure 4 represents the  $\tan\delta$  values ( $E''/E'$ ) depending on the ZB concentration of each compound after vulcanization at 23°C and 100°C, respectively. As the test temperature increased from 23°C to 100°C the  $\tan\delta$  value of each compound decreased, which was the typical trend on that system on vulcanized systems. At 23°C, as the concentration of the ZB increased the  $\tan\delta$  values of both compounds NR and SBR decreased i.e.  $\tan\delta (NR, SBR)[S2 > S2Z2 > S2Z5]$ . The viscoelasticity at 100°C, as the concentration of the ZB increased, while the  $\tan\delta$  values of the NR decreased i.e.  $\tan\delta [S2(NR) > S2Z2(NR) > S2Z5(NR)]$ , that of the SBR ones increased i.e.  $\tan\delta [S2(SBR) < S2Z2(SBR) < S2Z5(SBR)]$ .



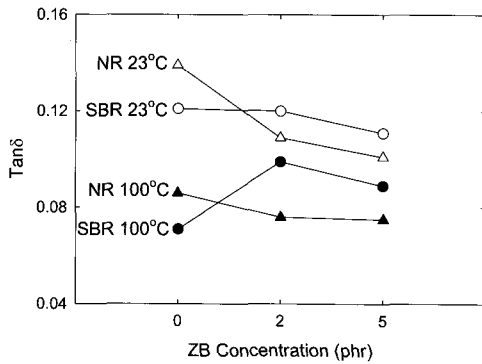
**Figure 2.** ZB concentration effects on the shear viscosity (a) the NR compounds, (b) the SBR compounds at 100°C.



**Figure 3.** ZB concentration effects on the Mooney viscosity of the NR and the SBR compounds.

$S2Z5(SBR)]$ .

Addition of the ZB clearly lowered the  $\tan\delta$  values

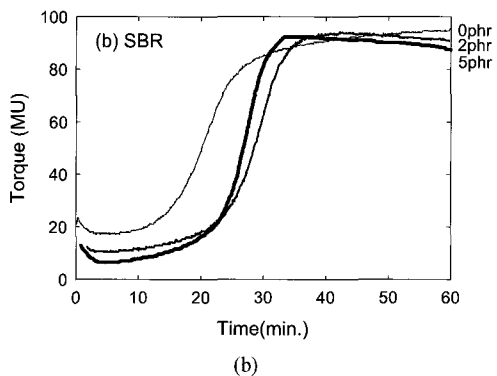
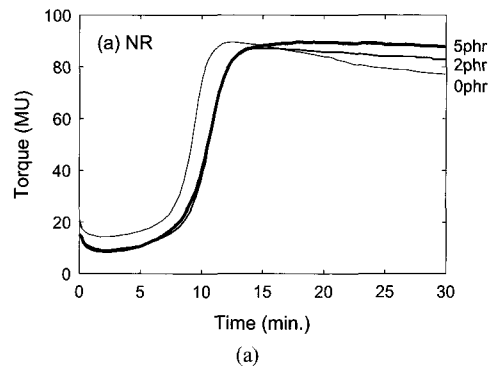


**Figure 4.** ZB concentration effects on the viscoelastic property ( $\tan\delta$ ) of the NR and SBR compounds at 1 Hz, 23°C and 100°C.

of the NR compounds at both 23°C and 100°C; however in the SBR compounds it was not effective lowering the  $\tan\delta$  values, which was the same trend observed from the TESPT treated silica compound.<sup>18</sup>

**5. Reversion Test**

Figure 5 shows the vulcanization curves of the NR and the SBR compounds at 160°C for 30 min. While the S2(NR) compound exhibit the reversion behavior, the S2(SBR) compound did not exhibit reversion behavior, rather this exhibited a marching behavior. While addition of the ZB increased the T-2 in the NR compounds, it decreased the T-2 in the SBR compounds. The higher minimum torque ( $M_L$ ) of both the S2(NR) and the S2(SBR) compound matches with the shear viscosity data and the Mooney viscosity as shown previously. Addition of the ZB in the NR compounds increased the T-2 of each compound and it increased proportionally as the ZB concentration increased; however, it decreased the T-2 in the SBR ones. The S2Z5(NR) and S2(SBR) compounds exhibited no reversion behavior. Addition of ZB in the NR systems seems increased the degree of cross-linking; however it decreased the degree of cross-linking in the SBR systems due to their different matrix characteristics. This will be discussed in section 3.10.



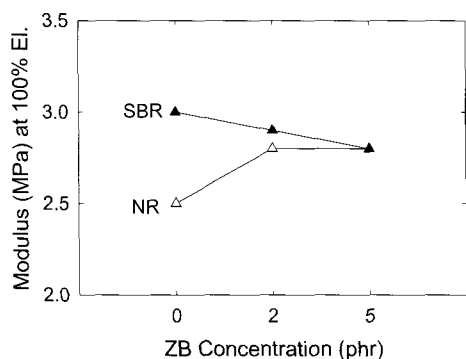
**Figure 5.** ZB concentration effects on the vulcanization curves (a) the NR compounds, (b) the SBR compounds.

**6. Tensile Test**

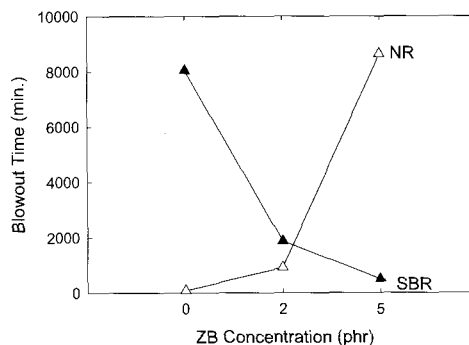
Figure 6 represents the modulus changes at 100% elongation as a function of the ZB concentration, which measured from the dumbbell shaped specimens. As the ZB concentration increased from 0 to 2 and to 5 phr, in the S2(NR) compounds, the modulus of each compound increased; however, in the S2(SBR) compounds it decreased.

**7. Blowout (BO) and Heat Build Up (HBU)**

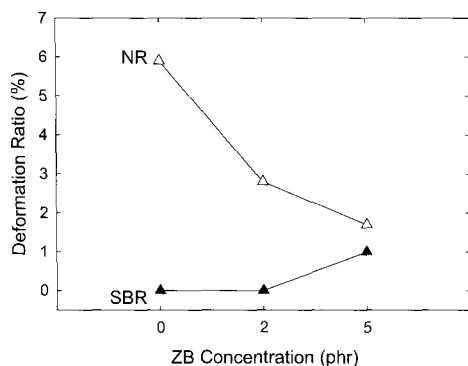
Figure 7 represents the order of deformation after the BO test measured from the Firestone Flexometer. Addition of the ZB into the S2(NR) compounds lowered the deformation ratio from 5.9% to 1.7%; however, in the SBR compounds, it increased



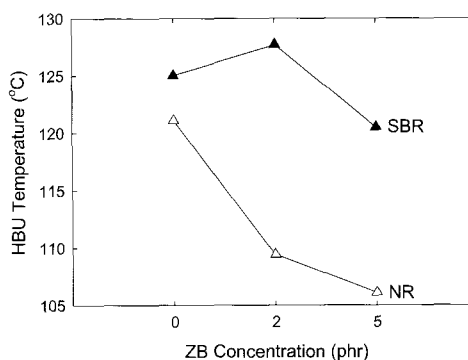
**Figure 6.** ZB concentration effects on the tensile modulus at 100% elongation of the NR and the SBR compounds.



**Figure 8.** ZB concentration effects on the BO time of the NR and the SBR compounds.



**Figure 7.** ZB concentration effects on the BO deformation ratio (d/D) of the NR and the SBR compounds.



**Figure 9.** ZB concentration effects on the HBU temperature of the NR and the SBR compounds.

the deformation ratio from 0.01% to 1.0%.

Figure 8 represents the BO time of each compound measured from the Firestone Flexometer. Addition of the ZB(5phr) into the S2(NR) compounds increased the BO time considerably from 80min.(S2(NR)) to 8640min.(S2Z5(NR)); however, it lowered the BO time in the S2(SBR) compounds from 8040min.(S2(SBR)) to 500min.(S2Z5(SBR)), respectively.

Figure 9 represents the HBU temperature of each compound measured from the Firestone Flexometer. Addition of the ZB(5phr) into the S2(NR) compound decreased the HBU temperature from 121°C (S2(NR)) to 109°C(S2Z5(NR)), and into the S2(SBR) compound decreased it from 125°C(S2(SBR)) to 120°C(S2Z5(SBR)), respectively. In the

NR system, this trend is consistent with the  $\tan\delta$  values as showed in Figure 4. However, in SBR system, as the temperature in the compound increases, S2Z2 compound showed higher temperature than S2 compound, which matches with the  $\tan\delta$  values showed in Figure 4. The S2Z5(SBR) compound showed lower temperature rise than the control, but higher  $\tan$ ( than the S2(SBR)). This may come from the differences from the rubber matrix, which represents some of the ZB in the SBR might play a lubricant role in the compound.

Stiffer compounds generate less heat and smaller temperature rise due to the smaller amplitude of oscillation at constant load amplitude.<sup>23</sup>

Addition of the ZB into the S2(NR) compounds seems formed a stronger 3-dimension network than

the S2(SBR) compounds.

### 8. SEM Observation

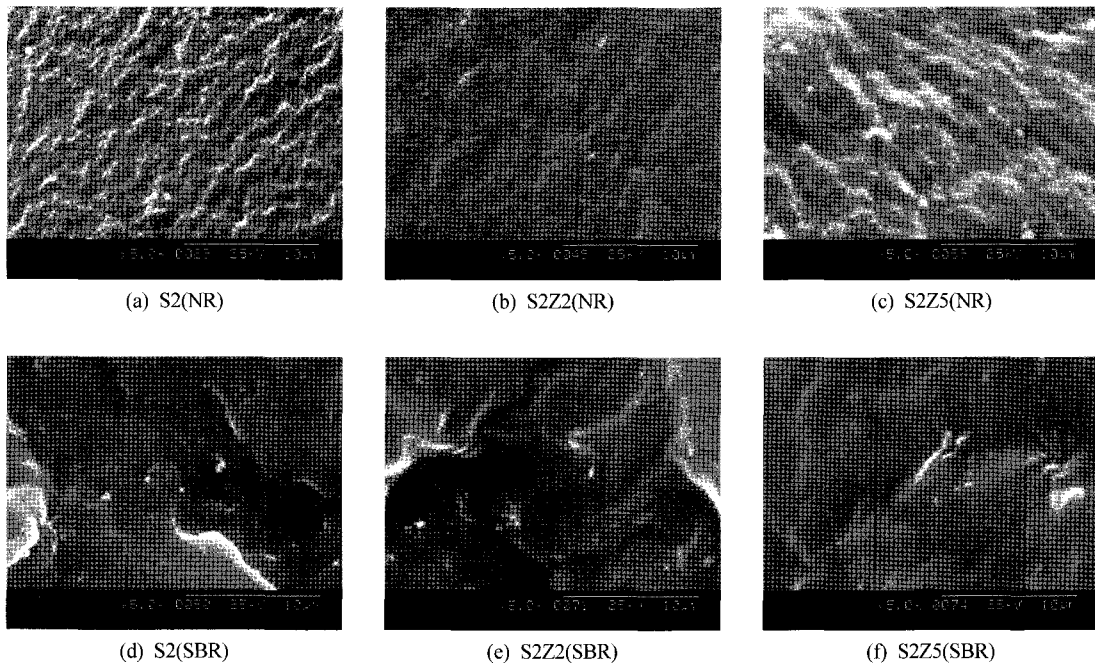
Figure 10 represents typical SEM photographs of the NR and the SBR compounds after vulcanization. In the S2(NR) compounds, the silica agglomerates were well dispersed; however, in the S2(SBR) compounds, several big agglomerates exist. In the NR compounds, addition of the ZB exhibited several big agglomerates; however, in the SBR compounds, smaller agglomerates disappeared significantly. We will discuss about the mechanism at section III-9.

The zinc ion seems to help the re-agglomeration of silica particles in the presence of silane, which is rubber-(silane-silica)<sub>x</sub>-silane-rubber network. The role of zinc ion on silica re-agglomeration mechanism is not clear at this stage.

### 9. Discussion

#### 9-1 Silica dispersion

Silica agglomerates disperse in two different mechanisms. First, the coupling of silane (silane-rubber,<sup>25-30</sup> silica-silane<sup>28,30</sup>) reduces the filler-filler interactions due to increased filler-polymer interactions.<sup>31</sup> Polar silica particles interact with polar rubber results in smaller silica agglomerates in the SBR compound than relatively non-polar NR compound due to increased filler-polymer interactions; however, the silane treated silica compounds, the S2(NR) exhibited smaller silica agglomerate size than the S2(SBR) compound. In the coated particle filled system, when organic acids coat on inorganic fillers, the interaction between the filler and polymer decreases.<sup>32,33</sup> This<sup>32,33</sup> represents the polarity of the silane coated silica particles are lower than untreated silica particles. Second, self agglomeration of the silica agglomerates, which are silica(A)-silane(S)-



**Figure 10.** SEM photographs of the vulcanized compounds (a) S2(NR), (b) S2Z2(NR), (c) S2Z5(NR), (d) S2(SBR), (e) S2Z2(SBR), and (f) S2Z5(SBR) at 5,000 magnifications.



silica(A) (ASA) and silica(A)-silane(S)-silica(B) (ASB).<sup>13,30,34</sup> In the ASA agglomeration type, the silica agglomerates are easily break down due to lowered polarity between silica agglomerates; however, in the ASB agglomeration type, even the big silica agglomerates remain constant, the 3D-network between particles is stronger than without silane coated system as shown in the SBR compounds. The role of the silica source, grape shape or branched shape, seems play a role as well as the level of the moisture in the silica.<sup>3,18,30,35-36</sup>

#### 9-2 NR vs. SBR

Each rubber has different levels of double bonds and different types of residues. The NR has more double bonds than the SBR. The unit cell of crystalline form NR has a density  $1.0 \text{ g/cm}^3$  and that of amorphous unfilled rubber is  $0.9 \text{ g/cm}^3$ , respectively.<sup>37</sup> The NR is mainly based on isoprene and has many other ingredients such as sugars, fats and proteins, which influence the vulcanizate properties.<sup>18</sup> 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. There were many researches focused on the nucleation rate,<sup>38</sup> crystals growth,<sup>39-41</sup> rubber crosslink density,<sup>42</sup> the temperature<sup>43</sup> and the strain<sup>44</sup>; models such as Flory's 'fringed micelle' model,<sup>44</sup> Andrews' 'chain fold' model,<sup>45,46</sup> and later authors.<sup>48-50</sup> The crystallization is accompanied by an increase in density (i.e. decrease in volume) and volume changes.<sup>50,51</sup> Nucleation may occur spontaneously and homogeneously throughout the amorphous phase at lower temperature or is 'seeded' by foreign surfaces or structure discontinuities. The crystal growth<sup>45</sup> 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. We observed improvement of the reversion and elongational modulus with the addition of the ZB in the NR compounds; however, we could not observe im-

**Table 3. Density and Abrasion Loss of Vulcanized NR and SBR Compounds**

	NR			SBR		
	S2	S2Z2	S2Z5	S2	S2Z2	S2Z5
Density ( $\text{g/cm}^3$ )	1.17	1.18	1.19	1.19	1.19	1.19
Abrasion loss ( $\text{mm}^3$ )	133	136	131	122	134	135

provement in the SBR compounds as shown in Figure 5 and Figure 6, respectively. We presented that the addition of ZB into NR compounds increased the density of compound ( $\text{g/cm}^3$ ) and lowered the abrasion loss ( $\text{mm}^3$ ).<sup>52</sup> In SBR compound system, the addition of ZB did not effect the density changes of the compound, but increased the abrasion loss. They are summarized on Table 3. This confirms the ZB effectively increased the cross-linking of NR compounds.<sup>18</sup> In the SBR compounds, it decreased the cross-linking in this system. This system is under further investigation.

## IV. Conclusions

Addition of the ZB increase the strong 3-dimensional network structure in the TESPD treated silica filled NR compound; however, it was not effective in the SBR compounds. The zinc ion in the ZB seemed reacting differently in different matrix systems and seemed relate to the vulcanization mechanism, which related to the degree of cross-linking of the compounds. Thus affecting the processability and properties of the final compounds.

We conclude here that the role of the zinc ion on sulfur reaction mechanism was effective in the NR compounds; however it was not effective in the SBR compounds.

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## References

1. F. Thurn and S. Wolff, "Neue Organosilane für die Reifenindustrie", *Kautsch. Gummi Kunstst.*, **28**, 733 (1975).
2. S. Wolff, "A New Development for Reversible Sulfur-Cured NR Compounds", *Kautsch. Gummi Kunstst.*, **32**, 760 (1979).
3. A. Hunsche, U. Görl, A. Müller, M. Knaack, Th. Göbel, and Hurth, "Investigations Concerning the Reaction Silica/Organosilane and Organosilane/Polymer", *Kautsch. Gummi Kunstst.*, **50**, 881 (1997).
4. R. Rauline (Michelin), Europe Patent EP0501 227, (1991).
5. R. Rauline (Michelin), U.S. Patent (filed Feb. 20, 1992) 5,227,425 (1993).
6. Anonymous, "Rubber Industry Manual", Bayer A. G., 1993.
7. J. H. Bachmann, J. W. Sellers, and M. P. Wagner, "Fine Particle Reinforcing Silicas and Silicates in Elastomers", *Rubber Chem. Technol.*, **32**, 1286 (1959).
8. E. M. Dannenberg, "The Effects of Surface Chemical Interactions on the Properties of Filler-Reinforced Rubbers", *Rubber Chem. Technol.*, **48**, 410 (1975); "Reinforcement of Silicone Rubber by Particulate Silica", *Rubber Chem. Technol.*, **48**, 558 (1975).
9. M. P. Wagner, "Reinforcing Silicas and Silicates", *Rubber Chem. Technol.*, **49**, 703 (1976).
10. P. Vondracek, M. Hradec, V. Chvalovsky, and H. D. Khanh, "The Effect of the Structure of Sulfur-Containing Silane Coupling Agents on Their Activity in Silica-Filled SBR", *Rubber Chem. Technol.*, **57**, 675 (1984).
11. A. Krysztakiewicz, "Modified Silica Precipitated in the Medium of Organic Solvents-an Active Rubber Filler", *Colloid Polym. Sci.*, **267**, 399 (1989).
12. S. Kohjiya and Y. Ikeda, "Reinforcement of General-Purpose Grade Rubbers by Silica Generated In Situ", *Rubber Chem. Technol.*, **73**, 534 (2000).
13. K. J. Kim and J. L. White, "TESPT and Different Aliphatic Silane Treated Silica Compounds Effects on Silica Agglomerate Dispersion and on Processability During Mixing in EPDM", *J. Ind. Eng. Chem.*, **7**, 50 (2001).
14. J. A. Hockley, and B. A. Pethica, "Surface Hydration of Silicas", *Faraday Soc. Trans.*, **57**, 2247 (1961).
15. D. R. Bassett, E. A. Boucher, and A. C. Zettlemoyer, "Adsorption on Hydrated and Dehydrated Silicas", *J. Colloid Interface Sci.*, **27**, 649 (1968).
16. K. J. Kim, and J. L. White, "Silica Agglomerate Breakdown in Three-Stage Mix Including A Continuous Ultrasonic Extruder", *J. Ind. Eng. Chem.*, **6**(4), 262 (2000).
17. K. J. Kim, and J. VanderKooi, "TESPT and TESP treated Silica Compounds on Rheological Property and Silica Break Down in Natural Rubber", *Kautsch. Gummi Kunstst.*, **55**(10), 518 (2002).
18. K. J. Kim and J. VanderKooi, "Rheological Effects of Zinc Surfactant on the TESPT-Silica Mixture in NR and S-SBR Compounds", *Int. Polym. Process.*, **17**, 192 (2002).
19. K. J. Kim and J. VanderKooi, "Effects of Zinc Ion Containing Surfactant on Bifunctional Silane Treated Silica Compounds in Natural Rubber", *J. Ind. Eng. Chem.*, **8**(4), 334 (2002).
20. A. D. Roberts Ed., "Natural Rubber Science and Technology", Oxford Science Publications, New York, 1988.
21. S. Montes, J. L. White, and N. Nakajima, "Rheological Behavior of Rubber Carbon Black Compounds in Various Shear Flow Histories", *J. Non-Newtonian Fluid Mech.*, **28**, 183 (1988).
22. J. L. White, "Rubber Processing: Technology, Materials, and Principles", Hanser Publishers, Cincinnati, 1995.
23. A. N. Gent, "Engineering with Rubber: How to Design Rubber Components", Hanser Publishers, New York, 1992.
24. R. W. Allen (Firestone Tire & Rubber Co.), U.S. Patent (filed June 9, 1931) 02,048,314 (1936).
25. E. P. Plueddemann, "Silane Coupling Agents", Plenum Press, New York, 1982.
26. S. Wolff, "Vernetzung von 1,5-Dien-Kautschuken

- mittels Bis-(3-triathoxysilylpropyl)-tetrasulfid", *Kautsch. Gummi Kunstst.*, **30**, 516 (1977).
27. S. Wolff, "Fullstoffentwicklung Heute und Morgen", *Kautsch. Gummi Kunstst.*, **32**, 312 (1979).
  28. S. Wolff, "Reinforcing and Vulcanization Effects of Silane Si69 in Silica-Filled Compounds", *Kautsch. Gummi Kunstst.*, **34**, 280 (1981).
  29. S. Wolff, "Optimization of Silane-Silica OTR Compounds. Part I: Variations of Mixing Temperature and Time During The Modification of Silica with Bis-(3-triethoxysilylpropyl)-tetrasulfide", *Rubber Chem. Technol.*, **55**, 967 (1982).
  30. C. Lin, W. L. Hergenrother, and A. S. Hilton, "Mooney Viscosity Stability and Polymer Filler Interactions in Silica Filled Rubbers", *Rubber Chem. Technol.*, **75**, 215 (2002).
  31. E. H. Tan, S. Wolff, M. Haddeman, H. P. Grewatta, and M. J. Wang, "Filler-Elastomer Interactions. Part IX. Performance of Silicas in Polar Elastomers", *Rubber Chem. Technol.*, **66**, 594 (1993).
  32. E. Sheng and I. Sutherland, "A Quantitative XPS Study of Spherically Shaped Powders Coated with an Overlayer", *Surface Sci.*, **314**, 325 (1994).
  33. B. Haworth, C. L. Raymond, and I. Sutherland, "Polyethylene Compounds Containing Mineral Fillers Modified by Acid Coatings. 1: Characterization and Processing", *Polym. Eng. Sci.*, **40**, 1953 (2000).
  34. K. J. Kim and J. L. White, "Silica Surface Modification Using Different Aliphatic Chain Length Silane Coupling Agents and Their Effects on Silica Agglomerate Size and Processability", *Composite Interfaces*, **9**(6), 541 (2002).
  35. U. Goerl, A. Hunsche, A. Mueller, and H. G. Koban, "Investigations into the Silica/Silane Reaction System", *Rubber Chem. Technol.*, **70**, 608 (1997).
  36. K. J. Kim and J. VanderKooi, "Improved Polymer Processing for Critical Extrusions", ITEC 2002 Akron OH (No. 7A).
  37. C. W. Bunn, "Molecular Structure and Rubber-Like Elasticity: I. The Crystal Structure of  $\beta$  Gutta-Percha, Rubber and Polychloroprene", *Proc. Roy. Soc. A*, **180**, 40 (1942).
  38. B. Wunderlich, "Macromolecular Physics, Vol 2", Academic Press, New York, (1978).
  39. M. Avrami, "Kinetics of Phase Change. I", *J. Chem. Phys.*, **7**, 1103 (1939).
  40. M. Avrami, "Kinetics of Phase Change. II Transformation-Time Relaxation for Random Distribution of Nuclei", *J. Chem. Phys.*, **8**, 212 (1940).
  41. M. Avrami, "Kinetics of Phase Change. III Granulation, Phase Change, and Microstructure", *J. Chem. Phys.*, **9**, 177 (1941).
  42. A. N. Gent, "Crystallization and the Relaxation of Stress in Stretched Natural Rubber Vulcanizates", *Faraday Soc. Trans.*, **50**, 521 (1954).
  43. A. N. Gent, "Crystallization in Natural Rubber. IV. Temperature Dependence", *J. Polym. Sci.*, **18**, 321 (1955).
  44. P. J. Flory, "Thermodynamics of Crystallization in High Polymers: I. Crystallization Induced by Stretching", *J. Chem. Phys.*, **15**, 397 (1947).
  45. E. H. Andrews, "Crystalline Morphology in Thin Films of Natural Rubber: II. Crystallization Under Strain", *Proc. Roy. Soc. A*, **277**, 562 (1964).
  46. E. H. Andrews, "Spherulite Morphology in Thin Films of Natural Rubber", *Proc. Roy. Soc. A*, **270**, 232 (1962).
  47. A. Keller, and M. J. Machin, "Oriented Crystallization in Polymers", *J. Macromol. Sci.*, **B1**, 41 (1967).
  48. J. D. Hoffmann, J. I. Lauritzen, E. Passaglia, G. S. Ross, L. J. Frolen, and J. J. Weeks, "Kinetics of Polymer Crystallization from Solution and the Melt", *Koll. Z. Polym.*, **231**, 564 (1969).
  49. P. D. Calvert, and D. R. Uhlmann, "Theory of Polymer Crystallization Chain Folding", *J. Appl. Phys.*, **43**, 944 (1972).
  50. K. J. Smith, "Crystallization of Networks under Stress", *Polym. Eng. Sci.*, **16**, 168 (1976).
  51. N. Bekkedahl, and L. A. Wood, "Crystallization of Vulcanized Rubber", *Ind. Eng. Chem.*, **33**, 381 (1941).
  52. K. J. Kim and J. VanderKooi, "Zinc Soap Effects on TESPT and TESPDP Treated Silica Compounds on Processing and Silica Dispersion During Mixing in Natural Rubber", Paper presented at ACS: Rubber Division, Oct. 2001, Cleveland, OH (Paper No.79).