

Influence of Silane Coupling Agent Content on Crosslink Type and Density of Silica-Filled Natural Rubber Vulcanizates

Sung-Seen Choi^{*} and Seok-Ju Choi[†]

*Department of Chemistry, Sejong University, Seoul 143-747, Korea. *E-mail: sschoi@sejong.ac.kr*

[†]Kumho Tire R&D Center, Gwangju 506-711, Korea

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Crosslink type and degree of crosslink density of a rubber vulcanizate determine the physical properties such as modulus, hardness, resilience, elongation at break, heat build-up, and so forth.¹ By increasing the crosslink density, the modulus, hardness, resilience, and abrasion resistance increase, whereas the elongation at break, heat build-up, and stress relaxation decrease. The stress relaxation, tensile strength, and resilience increase in proportion to the content of polysulfides, whereas the fatigue and thermal aging resistance decrease.

Silica and carbon black have been used as the main reinforcing agents in rubber compounds but their surface chemistries are very different.^{2,4} Silica has a number of hydroxyl groups on the surface, which results in strong filler-filler interactions and adsorption of polar materials by hydrogen bonds.^{2,5,6} Since intermolecular hydrogen bonds between hydroxyl groups on the silica surface are very strong, it can aggregate tightly.^{2,7} Its property can cause a poor dispersion of silica in a rubber compound. The adsorption of curatives by silica results in delay of the scorch time and reduction of the delta torque of a silica-filled rubber compound. The polar surface of silica makes hydrogen bonds with polar materials in rubber compounds. Since the silica surface is acidic, especially it forms a strong hydrogen bond with basic materials. *N-tert-Butyl-2-benzothiazole sulfenamide* (TBBS) and *N-cyclohexyl benzothiazole sulfenamide* (CBS) are generally used as cure accelerators for rubbers. Since they have basic functional groups such as amide, they are adsorbed well on the acidic silica surface. The adsorption of curatives to silica results in delay of the scorch time and reduction of the crosslink density in silica-filled rubber compounds. In general, silane coupling agent such as bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) is used to improve the silica dispersion as well as to prevent adsorption of curatives on the silica surface.⁸⁻¹⁰ The silane coupling agent reacts with silanol on the silica surface and then a siloxane bond is formed. The silane molecule is bound to the silica surface.

In the present work, we studied the influence of silane coupling agent content on the crosslink type and level of crosslink density using silica-filled natural rubber (NR) compounds with different TESP contents. Variation of the crosslink density and type after the thermal aging was also investigated. Sulfur linkages are composed of monosulfide,

disulfide, and polysulfides. Polysulfides of the total sulfur crosslinks are enhanced by increasing the elemental sulfur content in a rubber compound. Cure accelerators such as TBBS, CBS, 2-mercaptobenzothiazole (MBT), and tetramethyl thiuramdisulfide (TMTD) make the cure rate of a rubber compound faster. Sulfur linkages, especially polysulfides, can be dissociated by heating and this brings about decrease of the crosslink density.¹¹⁻¹³ Curatives, especially sulfur, remained in a rubber vulcanizate make new crosslinks¹⁴ and this results in increase of the crosslink density.

Figure 1 shows the variations of the crosslink densities with the silane coupling agent content. The crosslink densities of the mono- and disulfides, polysulfides, and total sulfur linkages were investigated. All the crosslink densities are enhanced by increasing the silane coupling agent

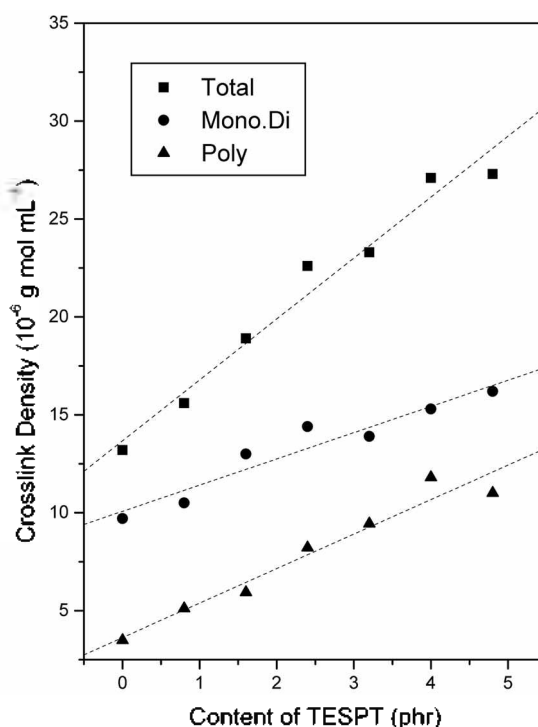


Figure 1. Variation of the crosslink density of the NR vulcanizate before the thermal aging as a function of the TESPT content. Squares, circles, and triangles indicate the total crosslink density, the crosslink density for mono- and disulfides, and the crosslink density for polysulfides, respectively.

content. The crosslink density of the mono- and disulfides is higher than that of the polysulfides. The crosslink densities for the mono- and disulfides, polysulfides, and total sulfur linkages increase 1.34×10^{-6} , 1.76×10^{-6} , and 3.11×10^{-6} g mol mL⁻¹ every 1.0 phr of the silane coupling agent content, respectively. The increased crosslink densities are due to the increased silane coupling agent. The silane coupling agent has about four sulfur atoms every one molecule of TESPT. Elemental sulfur can be isolated from the silane coupling agent by heating.⁹ Thus, the total sulfur content is increased by increasing the TESPT content and amount of the sulfur crosslinks is also enhanced.

In general, by increasing the elemental sulfur content in a rubber compound the crosslink density increases and especially the content of the polysulfides increase notably. Figure 1 shows the enhanced crosslink densities by increasing the TESPT content. The increasing rate of the crosslink density of the polysulfides is larger than that of the mono- and disulfides. This is because the silane coupling agent prevents the adsorption of the curatives on the silica surface by modifying the silica surface and makes crosslinks between the silica and rubber chain. The prevention of the curative adsorption leads to enhancement of the crosslink density. Ethoxy groups of the TESPT can react with silanol groups of the silica to form siloxane bond ($\sim\text{Si-O-Si}\sim$). Polysulfide linkage of the TESPT can be dissociated by heating and react with the rubber chain to form a sulfur linkage. Thus, a crosslink between the silica and rubber can be formed by the silane coupling agent.

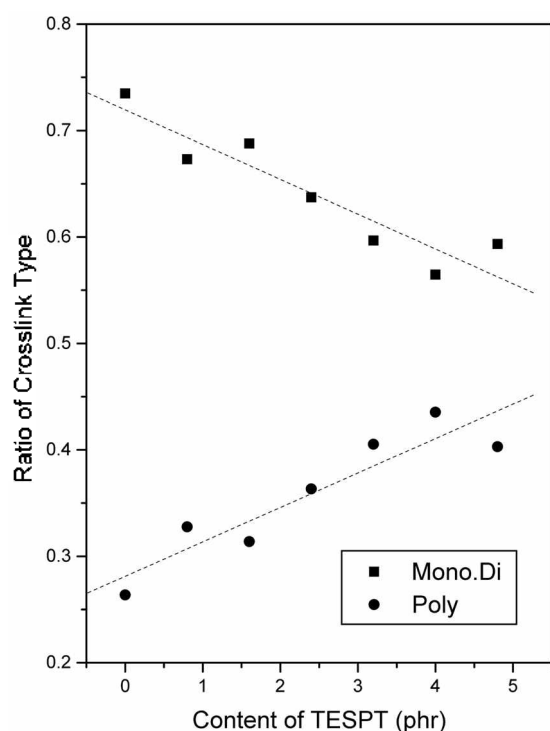


Figure 2. Variation of the crosslink type ratio of the NR vulcanizate before the thermal aging as a function of the TESPT content. Squares and circles indicate the mono- and disulfides and the polysulfides, respectively.

Figure 2 shows the variations of the crosslink type ratios of the total crosslinks with the TESPT content. The ratio of the mono- and disulfides decreases with increase of the TESPT content whereas that of the polysulfides increases. The ratio of the mono- and disulfides decreases 3.27×10^{-2} every 1.0 phr of the TESPT content whereas that of the polysulfides increases 3.24×10^{-2} every 1.0 phr of the TESPT content. The absolute values of the decreasing and increasing rates of the ratios for the mono- and disulfides and polysulfides are nearly the same. The reduced ratio of the mono- and disulfides and the enhanced ratio of the polysulfides are also explained with the increased sulfur content and the prevention of the adsorption of curatives by modification of the silica surface as discussed previously. The acidic silica surface makes a strong hydrogen bond with basic materials, especially cure accelerators. The adsorbed cure accelerators can not participate in crosslinking reactions. The cure accelerators released from the silica surface for the thermal aging can participate in crosslinking reactions to form sulfur crosslinks.

Chemical and physical properties of rubber composites are varied by thermal aging. The samples were aged at 80 °C for 1 day and the types and densities of crosslinks of the aged samples were measured. Figure 3 shows the variations of the crosslink densities of the NR vulcanizates after the thermal aging as a function of the TESPT content. All the crosslink densities are also enhanced by increasing the silane coupling agent content. The crosslink densities for the mono- and

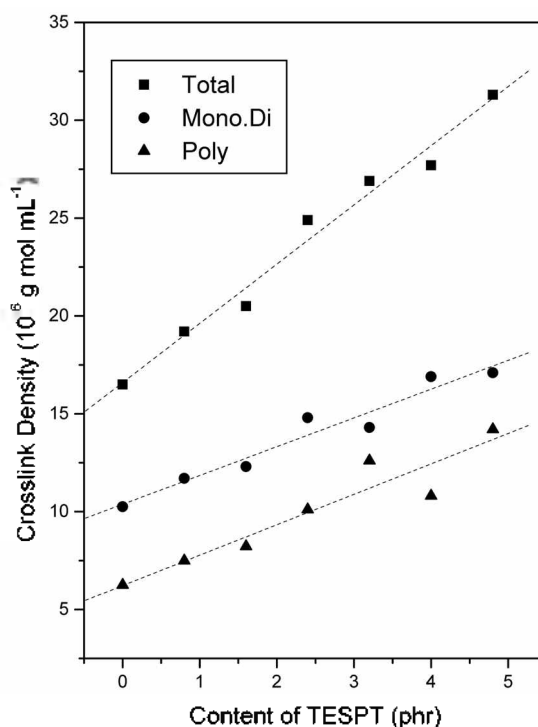


Figure 3. Variation of the crosslink density of the NR vulcanizate after the thermal aging at 80 °C for 1 day as a function of the TESPT content. Squares, circles, and triangles indicate the total crosslink density, the crosslink density for mono- and disulfides, and the crosslink density for polysulfides, respectively.

disulfides, polysulfides, total sulfur linkages increase 1.47×10^{-6} , 1.56×10^{-6} , and 3.03×10^{-6} g mol mL⁻¹ every 1.0 phr of the TESPT content, respectively. The crosslink densities of the NR vulcanizates after the thermal aging are higher than those before the thermal aging. The increasing rates of the mono- and disulfides and polysulfides are nearly the same. The difference between the increasing rates of the mono- and disulfides and polysulfides is reduced compared to the results before the thermal aging. The experimental results for the thermally aged samples say that concentration of the mono- and disulfides is increased by the thermal aging. Polysulfides are less stable than mono- and disulfides and the polysulfide linkages can be easily dissociated by heating.¹⁵ The increased crosslink densities by the thermal aging are due to the formation of new crosslinks by crosslinking reactions of the residual curatives. Some curatives are remained in the rubber vulcanizates and react with rubber chains to form new crosslinks. The curatives adsorbed on the silica surface can be released during the thermal aging and the desorbed curatives also participate in the crosslinking reactions.

Figure 4 shows the variations of the crosslink type ratios after the thermal aging as a function of the silane coupling agent. The ratio of the mono- and disulfides also decreases with increase of the TESPT content whereas that of the polysulfides increases. The mono- and disulfides ratio decreases 1.3×10^{-2} every 1.0 phr of the TESPT content whereas the polysulfides ratio increases 1.3×10^{-2} every 1.0 phr of the TESPT content. The absolute values of the

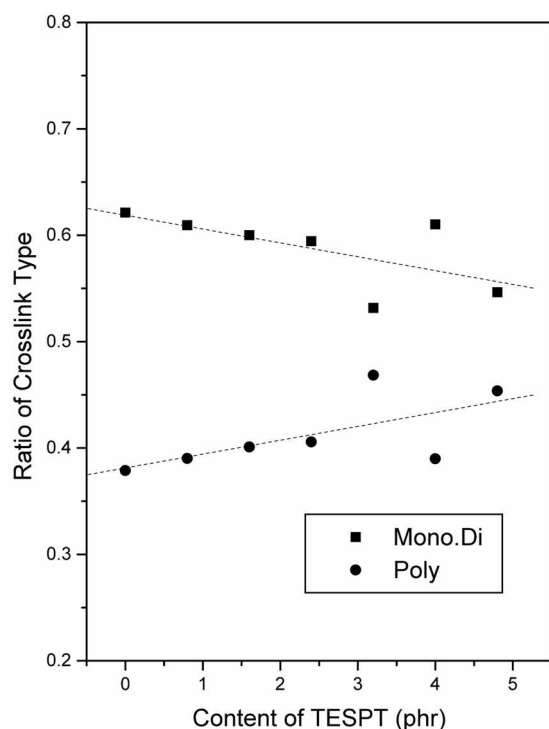


Figure 4. Variation of the crosslink type ratio of the NR vulcanizate after the thermal aging at 80 °C for 1 day as a function of the TESPT content. Squares and circles indicate the mono- and disulfides and the polysulfides, respectively.

increasing and decreasing rates of the ratios for the mono- and disulfides and polysulfides are the same. The difference in the absolute values of the increasing and decreasing rates of the ratios is much reduced compared to the experimental results before the thermal aging. The varying rates of the ratios after the thermal aging are much smaller than those before the thermal aging. This implies that the concentration of the mono- and disulfides is relatively more enhanced by the thermal aging.

Experimental Section

Seven silica-filled natural rubber (NR) compounds with different contents of silane coupling agent were prepared. The compounds were made of NR, silica, silane coupling agent, cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS and sulfur). Si69, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT), supplied from Degussa Co. was employed as silane coupling agent. Contents of the silane coupling agent were 0.0, 0.8, 1.6, 2.4, 3.2, 4.0, and 4.8 phr. The formulations were given in Table 1.

Mixing was performed in a Banbury type mixer at a rotor speed of 40 and 30 rpm for master batch (MB) and final mixing (FM) stages, respectively. The initial temperatures of the mixer were 110 and 80 °C for the MB and FM stages, respectively. The MB compounds were prepared as follow. (1) The rubber was loaded into the mixer and premixed for 0.5 min. (2) The silica and Si69 (TESPT) were compounded into the rubber for 2.0 min. (3) The cure activators and antidegradants were mixed for 1.5 min and the compounds were discharged. The FM compounds were prepared by mixing the curatives with the MB compounds for 2.0 min.

The vulcanizates were prepared by curing at 180 °C. The crosslink densities of the samples were measured by the swelling method.^{16,17} The procedure to measure the crosslink density was as follows: initially the samples were cut to about 10 × 10 mm; then, organic additives in the samples were removed by extraction with THF and *n*-hexane for 2 days each and were dried for 2 days at room temperature; the

Table 1. Formulations (phr)

Compound No.	1	2	3	4	5	6	7
SMR CV60	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Z175	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Si69	0.0	0.8	1.6	2.4	3.2	4.0	4.8
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0
ZnO	4.0	4.0	4.0	4.0	4.0	4.0	4.0
HPPD	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Wax	2.0	2.0	2.0	2.0	2.0	2.0	2.0
TBBS	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Sulfur	1.4	1.4	1.4	1.4	1.4	1.4	1.4

SMR CV60: Malaysian standard rubber (natural rubber) with Mooney viscosity of 60. Z175: silica. Si69: silane coupling agent, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT). HPPD: *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine. TBBS: *N*-*tert*-butyl-2-benzothiazole sulfenamide

weights of the organic material-extracted samples were then measured; following that they were soaked in *n*-decane for 1 day and the weights of the swollen samples were measured; finally, the crosslink density was calculated. The χ (interaction parameter between the rubber network and the swelling agent, *i.e.*, *n*-decane) of 0.43,¹⁶ the density of the rubber network of 0.93, and the molar volume of *n*-decane of 194.9 mL mol⁻¹ were employed. Experiments were carried out on three occasions (with three different sets of samples) and averaged. The concentrations of mono-, di-, and polysulfidic crosslinks were determined after the selective scission with the thiol-amine agents.^{18,19}

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