Influence of TESPT Content on Crosslink Types and Rheological Behaviors of Natural Rubber Compounds Reinforced with Silica

Sung-Seen Choi,[1] Ik-Sik Kim,[2] Chang-Su Woo[3]

[1]*Department of Applied Chemistry, Sejong University, Seoul 143-747, South Korea*
[2]*Aerospace Technology Research Institute, Daegu 701-799, South Korea*
[3]*Korea Institute of Machinery and Materials, Daejeon 305-600, South Korea*

ABSTRACT: Rheological behaviors in the rheographs and crosslink types of silica-filled natural rubber compounds with differing contents of silane coupling agent were investigated. Bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) was used as a silane coupling agent. In the rheographs of the silica-filled compounds containing TESPT, the local minimum torque regions after the maximum torque were observed, and the time to reach the local minimum torque was found to become faster with increase of the TESPT content. The reversion ratio, on the whole, was decreased by increasing the TESPT content. By increasing the TESPT content, the crosslink densities of the mono-, di-, and poly-sulfides were increased. Ratio of the polysulfides of the total crosslink density increased, while those of the mono- and disulfides decreased with increase of the TESPT content. Changes of the crosslink densities after thermal aging were also investigated. The experimental results were explained with the reduction of curatives adsorbed on the silica, increase of sulfur content, and crosslink formation between the silica and rubber by adding TESPT. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2753–2758, 2007

Key words: crosslink type; reversion; TESPT; silica-filled NR compound

INTRODUCTION

Cure characteristics of filled rubber compounds having an accelerated sulfur cure system are affected by all the materials that constitute the compounds. Content of sulfur is critical. The more the sulfur content, the faster the cure time and the higher the crosslink density. In general, cure accelerators make the crosslinking reactions fast and the crosslink density high. Types and contents of cure accelerators and sulfur content determine the cure characteristics, such as scorch time, cure rate, optimum cure time, and crosslink density.[1–6] Rubbers have different cure characteristics according to their chemical properties.[7,8] Types and contents of fillers also affect the cure characteristics.[9–12]

Silica-filled rubber compounds have slower cure characteristics than carbon black-filled ones since silica adsorbs curatives.[13–16] Silica and carbon black have been used as the main reinforcing agents in rubber compounds,[17–19] but their surface chemistries are very different. 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.[17,20] The polar surface of silica makes hydrogen bonds with polar materials in a rubber compound. Since the silica surface is acidic, especially it forms a strong hydrogen bond with basic materials. Sulfenamides such as *N-tert*-butyl-2-benzothiazole sulfenamide (TBBS) and *N*-cyclohexyl benzothiazole sulfenamide are generally used as cure accelerators for rubber compounds. Since they have basic functional groups, such as amide (=NH), they are adsorbed well on the silica surface. The adsorption of curatives on the silica results in delay of the scorch time and reduction of the crosslink density of a silica-filled rubber compound. In general, silane coupling agent such as bis(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) is used to improve the filler dispersion as well as to prevent adsorption of curatives on the silica surface.[15,16,21] The silane coupling agent reacts with silanol on the silica surface and a siloxane bond is then formed. The silane molecule is bound to the silica surface.

In the present work, influence of the TESPT content on rheological behaviors, crosslink types, and densities of silica-filled natural rubber (NR) compounds was studied. Rheological behaviors in the rheographs, especially reversion and variation, after the maximum torque, were focused. Variation of the crosslink type and density after thermal aging was also investigated.

EXPERIMENTAL

Seven silica-filled NR compounds with different contents of silane coupling agent were prepared. The

	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.

compounds were made of NR, silica, silane coupling agent, cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS and sulfur). Z175 (Brunauer–Emmett–Teller, N_2 adsorption isotherm = 175 m^2/g) supplied from Kofran Co. (Incheon, Korea) was employed as silica. Si69, bis(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT), supplied from Degussa Co. (Bitterfeld, Germany) was employed as a silane coupling agent. TESPT contents were 0.0, 0.8, 1.6, 2.4, 3.2, 4.0, and 4.8 phr. The formulations were given in Table I.

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 follows.[1] The rubber was loaded into the mixer and premixed for 0.5 min.[2] The silica and 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.

Cure characteristics were obtained using a Flexsys rheometer (MDR 2000) at 180°C. The vulcanizates were prepared by curing at 180°C for 10 min. Physical properties of the vulcanizates were measured with the universal testing machine (Instron 6021). Samples were thermally aged at 80°C for 2 days in a convection oven to investigate the influence of thermal aging on the physical properties, the type, and density of sulfur crosslinks.

The crosslink densities of the samples were measured by the swelling method.[22,23] The procedure to measure the crosslink density was as follows: initially, the samples were cut to about 10 × 10 mm^2; organic additives in the samples were removed by extraction with THF and *n*-hexane for 2 days each and were dried for 2 days
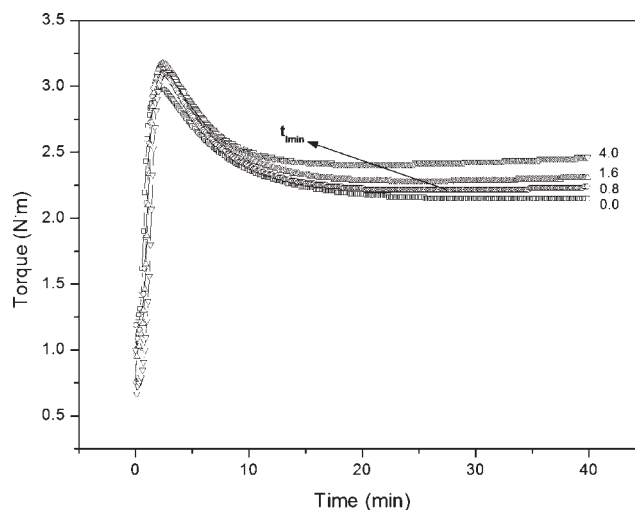
Figure 1 Rheographs of the silica-filled NR compounds. The test temperature was 160°C. Rectangles, circles, up-triangles, and down-triangles indicate the compounds containing TESPT of 0.0, 0.8, 1.6, and 4.0 phr, respectively. The $t_{1\,min}$ means the time to reach a local minimum torque after the maximum torque.

at room temperature; the weights of the organic material-extracted samples were then measured; they were soaked in *n*-decane for 2 days and the weights of the swollen samples were measured; finally, the crosslink density was calculated. The mono-, di-, and polysulfides were determined by cleavage of the sulfides, using mixture solvents of *n*-hexanethiol/piperidine and propane-2-thiol/piperidine.[22] Experiments were carried out on three occasions (with three different sets of samples) and averaged.

RESULTS AND DISCUSSION

Figure 1 shows variation of the rheological behaviors in rheocurve at 180°C with the TESPT content. The
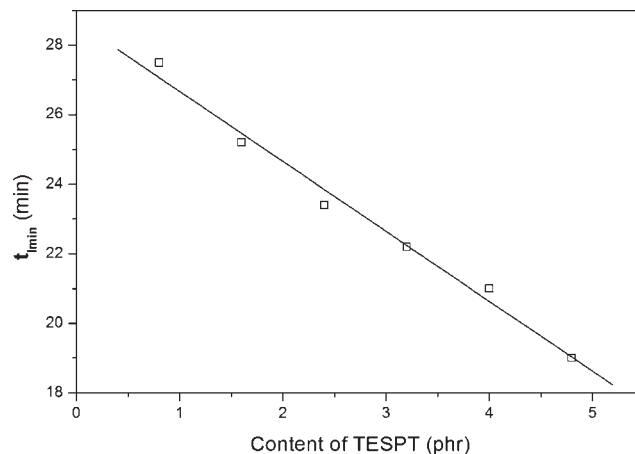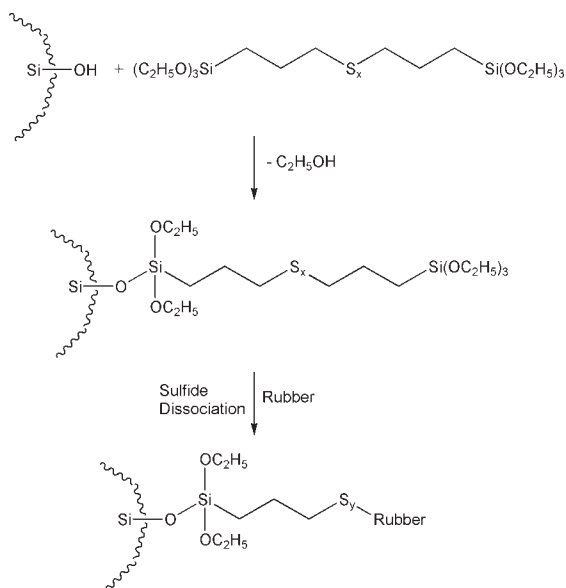

Figure 2 Variation of the local minimum torque $t_{1\,min}$ with the TESPT content. The curve-fitted equation is $y = -2.01x + 28.7$ ($r = -0.994$).

Scheme 1 Mechanism for the chemical bond formation between silica and rubber.

minimum torque (T_{min}) increases with increase of the TESPT content. This implies that the viscosity decreases with increase of the TESPT content. This is due to the improved filler dispersion by the silane coupling agent.[14,24] The delta torque (ΔT) also increases with increase of the TESPT content. The delta torque is the difference between the maximum and minimum torques ($\Delta T = T_{max} - T_{min}$), which reflects the crosslink density. This is due to the increased sulfur content and the reduction of adsorbed cure accelerator on the silica.[14]

For the rheograph of the compound without TESPT, the torque increases steeply after the T_{min} until the T_{max} and then decreases. For the rheographs of the compounds containing TESPT, the torques also increase steeply after the T_{min} until the T_{max} and then decreases
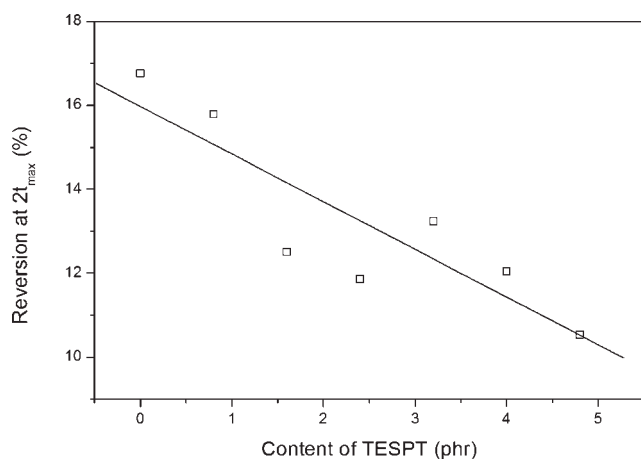
to a local minimum region. But the torques increase again after the local minimum point. This cannot be observed in the rheograph of the compound without TESPT, as shown in Figure 1. The time to reach the local minimum point ($t_{1\,min}$) becomes faster with increase of the TESPT content. Figure 2 shows variation of the $t_{1\,min}$ with the TESPT content. The $t_{1\,min}$ value decreases linearly with increase of the TESPT content. The $t_{1\,min}$ value decreases by 2 min/1 phr of TESPT.

Three possible causes about the increased torque after the $t_{1\,min}$ can be considered: (1) filler–filler interactions of silica, (2) sulfur generated from TESPT, and (3) crosslink formation between the silica and rubber. For silica-filled rubber compounds, the filler–filler interactions of silica are very strong because of hydrogen bonds of silanol groups of the silica surface. If the $t_{1\,min}$ is due to the filler–filler interactions, the $t_{1\,min}$ should be observed more clearly in the compound without TESPT since TESPT modifies the silica surface. Thus, it can lead to a conclusion that the filler–filler interactions of silica are not a reason of the $t_{1\,min}$.

The silane coupling agent has a sulfidic linkage of di- to octa-sulfides and the average number of —S_x— is about 3.8.[15] Elemental sulfur (S_8) is formed by heat-
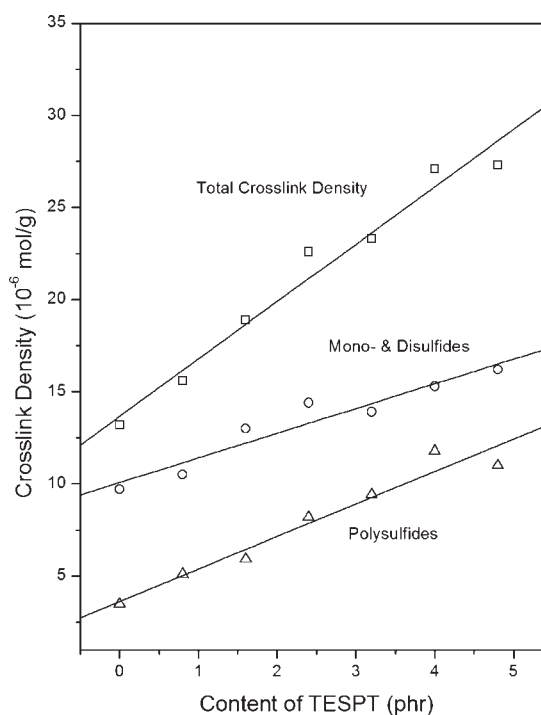

Figure 4 Variation of the crosslink density of the vulcanizates before the thermal aging with the TESPT content. Rectangles, circles, and triangles indicate the total crosslink densities, crosslink densities of mono- and disulfides, and crosslink densities of polysulfides, respectively. The curve-fitted equations are $y = (3.11 \times 10^{-6})x + (13.7 \times 10^{-6})$ ($r = 0.984$) for the total crosslink densities, $y = (1.34 \times 10^{-6})x + (10.1 \times 10^{-6})$ ($r = 0.960$) for the mono- and disulfides, and $y = (1.76 \times 10^{-6})x + (3.63 \times 10^{-6})$ ($r = 0.975$) for the polysulfides.
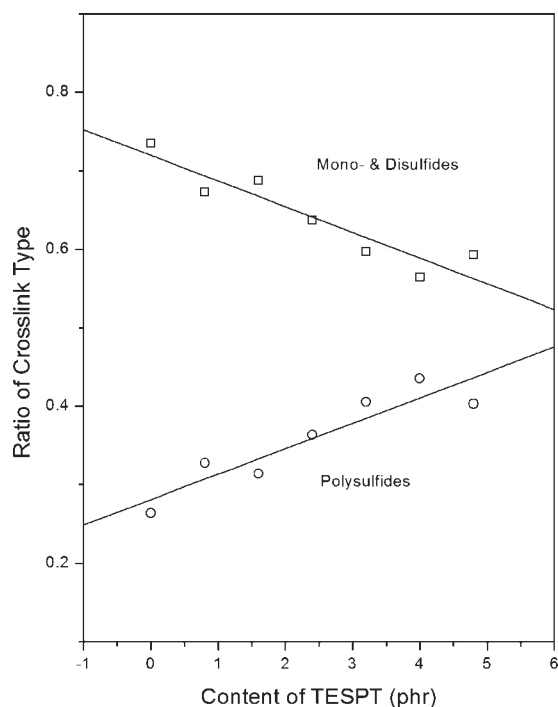

Figure 3 Variation of the reversion ratio at $2t_{max}$ with the TESPT content. The curve-fitted equation is $y = -1.14x + 16.0$ ($r = -0.876$).

Figure 5 Variation of the ratio of crosslink type of the vulcanizates before the thermal aging with the TESPT content. Rectangles and circles indicate the mono- and disulfides and the polysulfides, respectively. The curve-fitted equations are $y = (-3.27 \times 10^{-2})x + 0.720$ $(r = -0.931)$ for the mono- and disulfides, and $y = (3.24 \times 10^{-2})x + 0.281$ $(r = 0.923)$ for the polysulfides.

ing.[25] Sulfur and cure accelerator in the compound can make new crosslinks.[26,27] The elemental sulfur generated from TESPT is increased by increasing the TESPT content, and the torque after the $t_{1 \text{ min}}$ will be increased more and more as the TESPT content increases. Chemical bonds between the silica and rubber can be formed by TESPT (Scheme 1). Ethoxy group (CH_3CH_2O—) of TESPT reacts with silanol group of silica to form a siloxane bond. Sulfide linkage of TESPT bonded to silica is dissociated and reacts with rubber chain to form crosslink between the silica and rubber. These new crosslinks between the silica and rubber make the torque higher. Thus, it can lead to a conclusion that the torque increase after the $t_{1 \text{ min}}$ is due to the sulfur generated from TESPT and the chemical bond formation between the silica and rubber by TESPT.

In the rheocurve of vulcanization time versus torque, the torque increases after the minimum torque by crosslinking reaction to the maximum one and then decreases if reversion occurs. Reversion is observed when the desulfurization reaction is faster than the crosslinking reaction during vulcanization. The vulcanization reactions produce different crosslink structures including mono-, di-, and polysulfidic linkages. Polysulfidic linkages can be changed into mono- or disulfi-

dic linkage, as the vulcanization proceeds. The reversion ratio was determined by dividing the difference between the maximum torque and the torque at $2t_{\text{max}}$ by the delta torque; t_{max} means the time at the maximum torque. Figure 3 shows variation of the reversion ratio at $2t_{\text{max}}$ with the TESPT content. The reversion ratio decreases by about 1.14%/1 phr of TESPT with increase of the TESPT content. In general, reversion is more severe for a compound with higher sulfur cure system than for a compound with lower sulfur cure system. But, Figure 3 cannot be explained simply with the amount of polysulfides because contents of the total sulfur and the free cure accelerator (not be adsorbed on the silica) increase by increasing the TESPT content. The increased sulfur content leads to the increment of polysulfides, while the increased cure accelerator leads to the increment of mono- and disulfides.

Figure 4 shows variation of the crosslink types with the TESPT content. All of the crosslink types increase as well as the total crosslink density with the TESPT content. The increased total crosslink density can be explained with the increased total sulfur content and the reduction of cure accelerator adsorbed on silica.
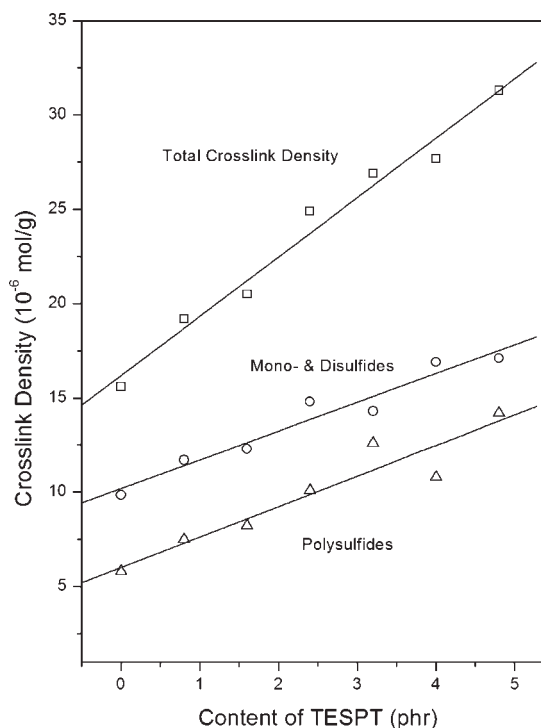

Figure 6 Variation of the crosslink density of the vulcanizates after the thermal aging at 80°C for 2 days with the TESPT content. Rectangles, circles, and triangles indicate the total crosslink densities, crosslink densities of mono- and disulfides, and crosslink densities of polysulfides, respectively. The curve-fitted equations are $y = (3.15 \times 10^{-6})x + (16.2 \times 10^{-6})$ $(r = 0.989)$ for the total crosslink densities, $y = (1.53 \times 10^{-6})x + (10.2 \times 10^{-6})$ $(r = 0.973)$ for the mono- and disulfides, and $y = (1.62 \times 10^{-6})x + (6.01 \times 10^{-6})$ $(r = 0.948)$ for the polysulfides.
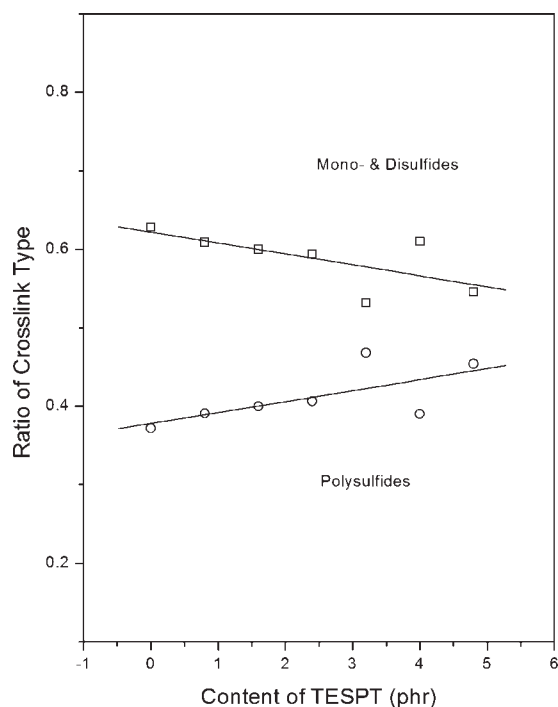
Figure 7 Variation of the ratio of crosslink type of the vulcanizates after the thermal aging at 80°C for 2 days with the TESPT content. Rectangles and circles indicate the mono- and disulfides and the polysulfides, respectively. The curve-fitted equations are $y = (-1.39 \times 10^{-2})x + 0.622$ ($r = -0.676$) for the mono- and disulfides and $y = (1.39 \times 10^{-2})x + 0.378$ ($r = 0.676$) for the polysulfides.

Elemental sulfur can be formed from TESPT by heating[25] and will participate in crosslinking reactions to increase the crosslink density. TESPT molecules react with silica to form siloxane bonds and the silica surface is modified to reduce the polarity. The polar cure accelerator molecules are less adsorbed on the modified silica surface than on the unmodified one, which leads to increase the content of free cure accelerator.

Ratio of polysulfides of the total sulfur crosslinks increases with increase of the TESPT content, while that of mono- and disulfides decreases (Fig. 5). This may be due to the increased total sulfur content in the compound as discussed previously. The decreased reversion ratio with increase of the TESPT content (Fig. 3) cannot be explained with the ratio of polysulfides. One possible reason about the decreased reversion ratio is types of polysulfides. Polysulfides include trisulfide ($RS-S_2R'$), tetrasulfide (RS_2-S_2R'), and so forth. Bond strength of polysulfide becomes weaker as the length of sulfide increases. Bond strengths of trisulfide ($RS-S_2R'$) and tetrasulfide (RS_2-S_2R') are 218–232 and 177–202 kJ/mol, respectively.[28] If the ratio of trisulfide of polysulfides increases with increase of the TESPT, the compound having higher content of TESPT can have a lower reversion property than that having lower content of TESPT. This assumption is reasonable to some extent, since content of the

free cure accelerator will increase with increase of the TESPT content as discussed previously.

Change of type and density of crosslink by thermal aging was investigated. Figure 6 shows variation of the total crosslink density and the crosslink types of the thermally aged samples with the TESPT content. The total crosslink density also increases with increase of the TESPT content. Ratios of the mono-, di-, and polysulfides also increase with increase of the TESPT content. For the aged vulcanizates, ratio of polysulfides of the total sulfur crosslinks increases with increase of the TESPT content, while that of mono- and disulfides decreases as similar to the unaged samples (Fig. 7). The slopes for the aged vulcanizates are smoother than those for the unaged ones. For the ratio of mono- and disulfides, the slopes are −0.0327 and −0.0139 for the vulcanizates before and after the thermal aging, respectively. For the ratio of polysulfides, the slopes are +0.0324 and +0.0139 for the vulcanizates before and after the thermal aging, respectively. The difference in the ratios between the two crosslink types is decreased notably by the thermal aging (Figs. 5 and 7). This may be due to the dissociation of longer polysulfides and the formation of new crosslinks.
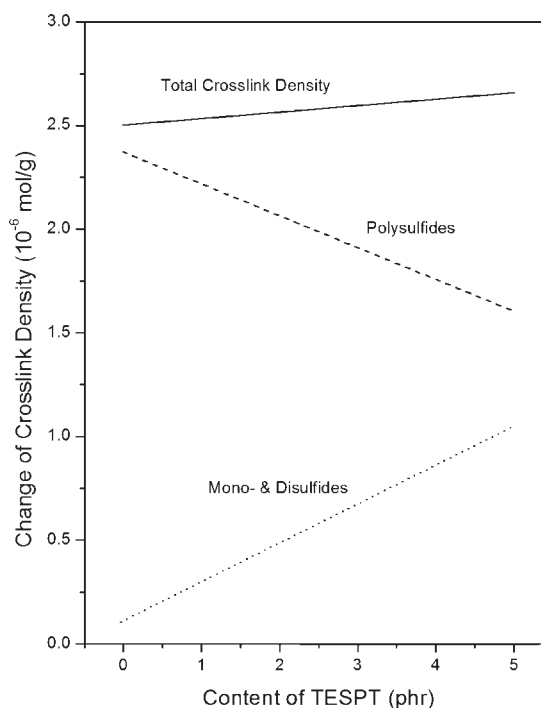

Figure 8 Variation of the crosslink density change of the vulcanizates after and before the thermal aging with the TESPT content. The change of crosslink density was the difference between the curve-fitted equations after and before the thermal aging. Solid [$y = (0.036 \times 10^{-6})x + (2.50 \times 10^{-6})$], dot [$y = (0.186 \times 10^{-6})x + (0.12 \times 10^{-6})$], and dash [$y = (-0.145 \times 10^{-6})x + (2.38 \times 10^{-6})$] lines indicate the total crosslink densities, crosslink densities of mono- and disulfides, and crosslink densities of polysulfides, respectively.

Crosslink density values before and after the thermal aging were compared. Figure 8 shows variation of the crosslink density changes after the thermal aging with the TESPT content. The lines in Figure 8 were the differences between the curve-fitted equations after and before the thermal aging. All the values in Figure 8 are "positive," which means that all the crosslink densities are increased by the thermal aging. The change of the total crosslink density slightly increases as the TESPT content increases. The change of the polysulfide crosslink density decreases, while that of the mono/disulfide one increases with increase of the TESPT content. This can be explained with the modification of silica surface and total sulfur content. Amount of the free cure accelerator increases with increase of the TESPT content, since the cure accelerator is adsorbed on the polar silica surface and TESPT modifies the silica surface to reduce the adsorption of cure accelerator as discussed previously. By decreasing the cure accelerator content in a rubber compound, amount of the free sulfur remaining in a vulcanizate increases.[27] The free sulfur remaining in a vulcanizate makes new sulfur crosslinks by thermal aging.[27,29] The polysulfides can dissociate to form new crosslinks during the thermal aging. If the vulcanizate with lower content of TESPT has longer polysulfides than that with higher one, sulfur crosslinks of the former will be changed more severely than those of the latter.

CONCLUSIONS

The rheographs of the silica-filled NR compounds containing TESPT showed the local minimum torque region after the maximum torque. The time to reach the local minimum point became faster with increase of the TESPT content. The reversion ratio decreased with increase of the TESPT content. All the crosslink types increased by increasing the TESPT content. Ratio of the polysulfides of the total crosslink density increased by increasing the TESPT content, while that of the mono- and disulfides decreased. All the crosslink types were increased after the thermal aging.

After the thermal aging, change of the polysulfide crosslink density became smaller, while that of the mono/disulfide one became larger as the TESPT content increased.

References

1. Hann, C. J.; Sullivan, A. B.; Host, B. C.; Kuhls, G. H., Jr. Rubber Chem Technol 1994, 67, 76.
2. Krejsa, M. R.; Koenig, J. L. Rubber Chem Technol 1993, 66, 376.
3. Datta, R. N. J Appl Polym Sci 1989, 37, 443.
4. Morita, E. Rubber Chem Technol 1984, 57, 744.
5. Campbell, D. S. Rubber Chem Technol 1972, 45, 1366.
6. Feldshtein, M. S.; Chernomorskaya, I. G.; Guryanova, E. N.; Eitingon, I. I. Rubber Chem Technol 1962, 35, 562.
7. Choi, S.-S. Elastomer 2000, 35, 215.
8. Chough, S.-H.; Chang, D.-H. J Appl Polym Sci 1996, 61, 449.
9. Cotton, C. R. Rubber Chem Technol 1972, 45, 129.
10. Chen, C. H.; Koenig, J. L.; Shelton, J. R.; Collins, E. A. Rubber Chem Technol 1982, 55, 103.
11. Devlin, E. F. Rubber Chem Technol 1986, 59, 666.
12. Wanpler, W. A.; Gerspacher, M.; Yang, H. H. In 143rd Meeting of the Rubber Division, American Chemical Society, Denver, CO, 1993; Paper No. 26.
13. Choi, S.-S. Elastomer 2001, 36, 37.
14. Choi, S.-S. Korea Polym J 2000, 8, 285.
15. Görl, U.; Hunsche, A. In 151st Meeting of the Rubber Division, American Chemical Society, Anaheim: CA, 1997; Paper No. 38.
16. Hashim, A. S.; Azahari, B.; Ikeda, Y.; Kohjiya, S. Rubber Chem Technol 1998, 71, 289.
17. Wolff, S.; Wang, M.-J. Rubber Chem Technol 1992, 65, 329.
18. Boonstra, B. B.; Cochrane, H.; Dannenberg, E. M. Rubber Chem Technol 1975, 48, 558.
19. Voet, A.; Morawski, J. C.; Donnet, J. B. Rubber Chem Technol 1977, 50, 342.
20. Ou, Y.-C.; Yu, Z.-Z.; Vidal, A.; Donnet, J. B. Rubber Chem Technol 1994, 67, 834.
21. Görl, U.; Hunsche, A. In 150th Meeting of the Rubber Division, American Chemical Society, Louisville, KY, 1996; Paper No. 76.
22. Cunneen, J. I.; Russell, R. M. Rubber Chem Technol 1970, 43, 1215.
23. Kramer, O.; Good, W. R. J Appl Polym Sci 1972, 16, 2677.
24. Choi, S.-S. J Polym Sci Part B: Polym Phys 2001, 39, 439.
25. Luginsland, H.-D. Kautsch Gummi Kunstst 2000, 53, 10.
26. Choi, S.-S. J Appl Polym Sci 2000, 75, 1378.
27. Choi, S.-S. Bull Korean Chem Soc 2000, 21, 628.
28. Choi, S.-S. Korea Polym J 1997, 5, 39.
29. Layer, R. W. Rubber Chem Technol 1992, 65, 211.