

# Influence of Cure Accelerator Content on Change of Crosslink Density by Thermal Aging in Natural Rubber Vulcanizates Filled with Silica

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## 실리카로 보강된 천연고무 가황물의 가교 밀도 변화에 가황촉진제 함량이 미치는 영향

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### 요 약

실리카로 보강된 천연고무 가황물에서 가황촉진제의 양이 열노화에 의한 가교밀도의 변화에 미치는 영향에 대해 연구하였다. 또한 실란커플링제의 영향도 조사하였다. 가황촉진제로는 *N-tert-butyl-2-benzothiazole sulfenamide* (TBBS)를 실란 커플링제로는 bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT)를 사용하였다. 가황물을 열노화 시키면 가교밀도는 증가하였고 노화 온도가 높을수록 그 변화 정도는 컸다. 실란 커플링제가 포함되지 않은 가황물의 가교밀도 변화가 실란 커플링제를 포함한 것에 비해 더 크게 나타났다. 실란 커플링제가 포함되지 않은 가황물의 경우에는 가교밀도의 변화에 대한 활성화 에너지가 가황촉진제의 함량이 증가할수록 순차적으로 낮아지는 경향을 보였다.

### ABSTRACT

The effect of cure accelerator content on the change in crosslink density by thermal aging was studied for silica-filled natural rubber (NR) vulcanizates. Influence of silane coupling agent was also investigated. *N-tert-Butyl-2-benzothiazole sulfenamide* (TBBS) and bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) were used as a cure accelerator and a silane coupling agent, respectively. The crosslink density increased by thermal aging and the increasing level became larger as the aging temperature increased. The degree of crosslink density change of the vulcanizates without the silane coupling agent was larger than that of the vulcanizates containing the silane coupling agent. For the vulcanizates silane coupling agent, the activation energy for the crosslink density change decreased with increase

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of the cure accelerator content in the vulcanizate.

**KEYWORDS : CROSSLINK DENSITY, THERMAL AGING, SILICA-FILLED NATURAL RUBBER VULCANIZATE, CURE ACCELERATOR, SILANE COUPLING AGENT**

## INTRODUCTION

The crosslink type and degree of crosslink density of a rubber vulcanizate determine physical properties of the vulcanizate such as modulus, hardness, resilience, elongation at break, heat build-up, and so forth.<sup>[1]</sup> By increasing crosslink density, modulus, hardness, resilience, and abrasion resistance increase, while elongation at break, heat build-up, and stress relaxation decrease. Stress relaxation, tensile strength, and resilience increase in proportion to the content of di- and polysulfides, while fatigue and thermal aging resistance decrease. Sulfide linkages, especially polysulfides, are dissociated by heating<sup>[2,3]</sup> and this brings about a decrease in crosslink density. Curatives, especially sulfur, in rubber vulcanizates make new sulfur-crosslinks<sup>[4]</sup> and this results in increase of the crosslink density.

Silica has been used as an important reinforcing filler in a rubber compound together with carbon black.<sup>[5-7]</sup> Since silica has the strong filler-filler interactions, filler dispersion of a silica-filled rubber compound is worse than that of a carbon black-filled one. The polar surface of silica tends to make hydrogen bonds with polar materials in the rubber compound. Since the silica surface is acidic, it forms a strong hydrogen bond with basic materials especially. *N-tert*-Butyl-2-benzothiazole sulfenamide (TBBS) and *N*-cyclohexyl benzothiazole sulfenamide (CBS) are the typical cure accelerators for rubbers. Since they have basic functional groups

such as amide (=NH), they are adsorbed well on the silica surface. The adsorption of curatives by 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 in order not only to improve the filler dispersion but also to prevent the adsorption of curatives on the silica surface.<sup>[8-10]</sup> The silane coupling agent reacts with silanol on the surface of silica and a siloxane bond is formed. The silane molecule is bound to the silica surface.

In this study, the influence of cure accelerator content on change of the crosslink density of natural rubber (NR) vulcanizates filled with silica, TBBS was used as a cure accelerator. Influence of TESPT on the change of crosslink density was also investigated.

## EXPERIMENTAL

Three silica-filled NR vulcanizates without silane coupling agent and three silica-filled NR vulcanizates containing silane coupling agent were prepared. *N-tert*-Butyl-2-benzothiazole sulfenamide (TBBS) was employed as a cure accelerator and its contents were 1.0, 1.8, and 2.6 phr. Si69 (bis-(3-(triethoxysilyl)propyl)-tetrasulfide, TESPT) of Degussa Co. was used as a silane coupling agent. Table 1 gives formulations of the compounds.

Mixing of the compounds was performed

**Table 1. Formulations (phr) and Chemical Analysis**

Compound No.	1	2	3	4	5	6
SMR CV60 <sup>a)</sup>	100.0	100.0	100.0	100.0	100.0	100.0
Z175 <sup>b)</sup>	40.0	40.0	40.0	40.0	40.0	40.0
Si69 <sup>c)</sup>	0.0	0.0	0.0	3.2	3.2	3.2
Stearic acid	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
HPPD <sup>d)</sup>	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
TBBS <sup>e)</sup>	1.0	1.8	2.6	1.0	1.8	2.6
Sulfur	1.4	1.4	1.4	1.4	1.4	1.4
Initial crosslink density (1/Q) of the vulcanizate	0.44	0.48	0.64	0.72	0.85	1.02
Content of free sulfur in the vulcanizate (w%)	0.02	0.10	0.16	0.05	0.10	0.12

a) standard malaysian rubber with constant viscosity of 60 MU, b) silica, c) bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT), d) *N*-phenyl-*N*-(1,3-dimethylbutyl)-*p*-phenylenediamine, e) *N*-*tert*-butyl-2-benzothiazole sulfenamide

in a Banbury type mixer at a rotor speed of 40 and 30 rpm for the 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. MB compounds were prepared as follow. (1) The rubber was loaded into the mixer and premixed for 0.5 min. (2) Silica (and silane coupling agent) were compounded into the rubbers for 3.0 min. (3) Ingredients (cure activators and antidegradants) were mixed for 1.0 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 160°C for 30 min. Organic materials-extracted samples were prepared by extraction of unbound organic materials in the vulcanizates with tetrahydrofuran (THF) for 3 days, acetone for 3 days, and *n*-hexane for 2 days and drying.

Experiments for thermal aging were carried out at 40, 50, 60, 70, and 80°C for 7 days in a convection oven. Crosslink densities of the samples before and after

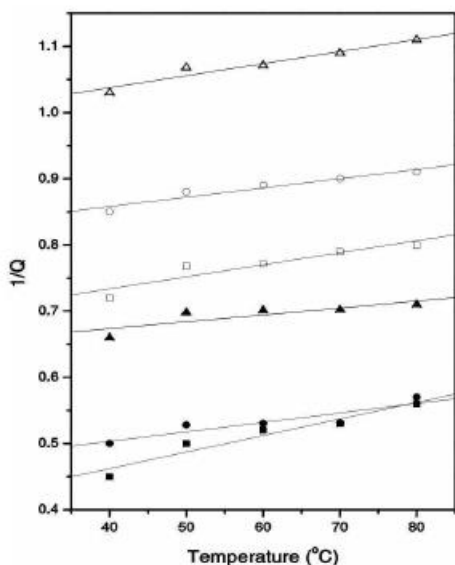
the thermal aging were measured by swelling method. Organic additives in the samples were removed by extracting with THF and *n*-hexane for each 2 days and they were dried for 2 days at room temperature. The weights of the organic material-extracted samples were measured. They were soaked in *n*-decane for 1 day and the weights of the swollen samples were measured. The swelling ratio (Q) was calculated by equation (1).

$$Q = (W_s - W_u) / W_u \quad (1)$$

where  $W_s$  and  $W_u$  are weights of the swollen and unswollen samples. The reciprocal swelling value,  $1/Q$ , was used as the apparent crosslink density.<sup>[11]</sup> Experiments were carried out three times and they were averaged.

## RESULTS AND DISCUSSION

Figure 1 gives the variation of  $1/Q$  for the unextracted vulcanizates after the

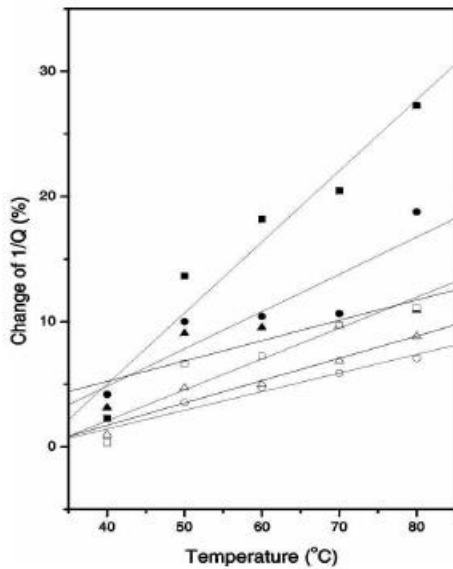


**Figure 1.** Variation of the crosslink density (inverse swelling ratio,  $1/Q$ ) with the aging temperature for the silica-filled NR vulcanizates before the extraction. Thermal aging was performed for 7 days in a convectin oven. The squares, circles, and triangles indicate the TBBS contents of 1.0, 1.8, and 2.6 phr, respectively. Solid and open symbols stand for the vulcanizates without and containing TESPT, respectively.

thermal aging as a function of the aging temperature. The  $1/Q$  increases with increase of the aging temperature. This implies that new crosslinks are formed by the thermal aging. For the vulcanizates without the silane coupling agent (TESPT), the increased crosslink density is larger for the vulcanizate containing lower content of TBBS than for the vulcanizate containing higher one. The slopes in Figure 1, for the vulcanizates without TESPT, are 0.0025, 0.00143, and 0.00104 for the vulcanizates containing TBBS of 1.0, 1.8, and 2.4 phr, respectively. For the vulcanizates containing TESPT, however, any specific trend depending on the TBBS content does not appear.

In order to investigate the degree of crosslink density change compared to the initial crosslink density, degree of the  $1/Q$  change compared to the initial state was calculated by dividing the difference in the  $1/Q$  of the vulcanizate after and before the thermal aging by the initial  $1/Q$ . Figure 2 shows the variation of the  $1/Q$  change with the aging temperature. Degree of the  $1/Q$  change linearly increases with increase of the aging temperature. Curve fitting equations for Figure 2 were summarized in Table 2. For the vulcanizates without TESPT, the degree of the  $1/Q$  change decreases with increase of TBBS. The ratios of the increased  $1/Q$  are about 5.7, 3.0, and 1.6% per  $10^\circ\text{C}$  of the aging temperature for the vulcanizates with TBBS of 1.0, 1.8, and 2.6 phr, respectively. This trend, however, was not observed in the vulcanizates containing TESPT.

Major cause to increase the crosslink density by thermal aging is free sulfur in a vulcanizate. Crosslink densities of the vulcanizates containing a high content of free sulfur after the thermal aging increase larger than those containing a low content of free sulfur.<sup>[4,12]</sup> Free sulfur contents in the vulcanizates were listed in Table 1. Contents of free sulfur components in the vulcanizates were determined by difference in the sulfur contents of the samples before and after extraction of unbound materials. Sulfur and organic additives in the NR vulcanizates were removed by extraction with acetone/THF (1:1) and acetone for each 3 days. Sulfur contents in the NR vulcanizates were obtained with sulfur determinator (LECO SC-132). The free sulfur content increases as the TBBS content increases as listed in Table 1. The experimental results (Figures 1 and 2) indicate that the crosslink density change in the vulcanizate with higher free sulfur content is lower than



**Figure 2.** Variation of the change of the crosslink density (inverse swelling ratio,  $1/Q$ ) with the aging temperature for the silica-filled NR vulcanizates before the extraction. The degree of the change was calculated by dividing the difference in the crosslink density after and before the thermal aging by the initial crosslink density. Thermal aging was performed for 7 days in a convectin oven. The squares, circles, and triangles indicate the TBBS contents of 1.0, 1.8, and 2.6 phr, respectively. Solid and open symbols stand for the vulcanizates without and containing TESPT, respectively.

that of the vulcanizate with lower one. The experimental results of Figures 1 and 2 can not be explained with the free sulfur content. Thus it seems that other factors as well as the free sulfur content affect the crosslink density change.

One major cause to change the crosslink density is dissociation of the existing sulfur crosslinks by thermal aging. The dissociation of the existing crosslinks results in decrease of the crosslink density. The polar organic additives such as HPPD and vulcanizing products in the vulcanizates accelerate the dissociation of the existing sulfur crosslinks.<sup>[12]</sup> The major vulcanizing products are zinc complex and mercaptobenzothiazole (MBT) formed by reactions of zinc oxide, fatty acids, sulfur, and TBBS.<sup>[13-15]</sup> The polar organic materials in the vulcanizate form a hydrogen bond with sulfur crosslinks since they have a good hydrogen-bond site of  $-SH$  or  $-NH-$  ( $-N=$ ). Thus, the  $S-S$  bond of the sulfur crosslink will be weakened by the hydrogen bond with the polar chemicals. The polysulfide bridges can be dissociated by reaction with a nucleophile. The reactions of polysulfide with the nucleophile were studied by several groups.<sup>[16-19]</sup> The nucleophiles such as HPPD, MBT, and stearic acid attack the sulfide bridge so that the sulfide bridge can be dissociated.

**Table 2.** Curve Fitting Equations for the Crosslink Density Change of the Vulcanizates Before the Extraction\*

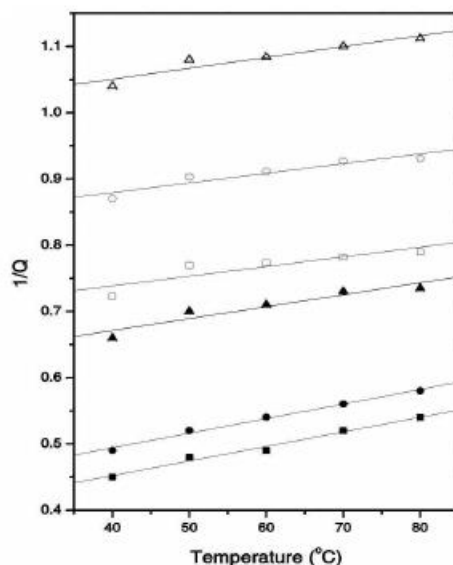
Content of TBBS(phr)	Curve fitting equation	Correlation coefficient
Vulcanizates without silane coupling agent		
1.0	$y = 0.568x - 17.73$	0.967
1.8	$y = 0.298x - 7.08$	0.906
2.6	$y = 0.163x - 1.28$	0.838
Vulcanizates containing silane coupling agent		
1.0	$y = 0.247x - 7.80$	0.937
1.8	$y = 0.149x - 4.53$	0.979
2.6	$y = 0.178x - 5.43$	0.968

\*Curve fitting for Figure 2

The vulcanizate with higher TBBS content has the more vulcanization products than that with lower one.

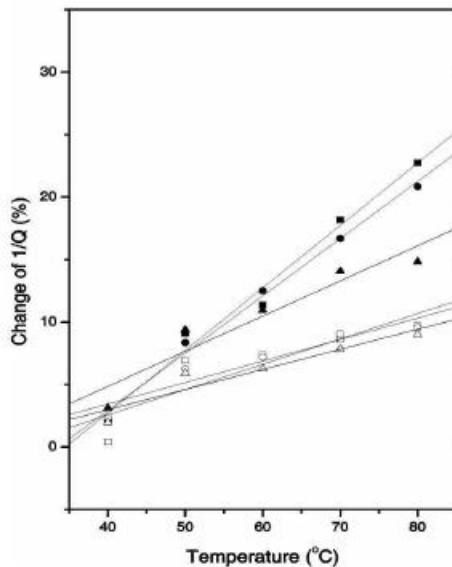
In order to investigate the crosslink density change by thermal aging to the exclusion of influence of the free sulfur and organic materials in the vulcanizate, organic materials-extracted samples were prepared. The experimental results after the extraction were demonstrated in Figures 3 and 4. The  $1/Q$  is also increased by the thermal aging and the degree of the  $1/Q$  change also increase with increase of the aging temperature. For the vulcanizates without TESPT, degree of the increased crosslink density becomes larger as the TBBS content decreases. The increased crosslink density in the organic materials-extracted vulcanizate after the thermal aging is due to the combination reactions between the pendent groups terminated by the curative residues and formation of new crosslinks by sulfide radical formed by dissociation of polysulfides.<sup>[12,20]</sup> Some of the MBT and *t*-butylamine radicals formed from TBBS at the beginning of vulcanization become pendent groups by pending to a rubber chain.<sup>[1,21,22]</sup> The pendent sulfide groups terminated by a cure accelerator residue were studied by several groups.<sup>[23-25]</sup> The pendent group reacts with another pendent group of the neighboring rubber chains and a new crosslink can be formed.<sup>[12,20-22]</sup>

Figure 4 shows variation of the  $1/Q$  change with the aging temperature. Degree of the  $1/Q$  change linearly increases with increase of the aging temperature. Curve fitting equations for Figure 4 were summarized in Table 3. For the vulcanizates without TESPT, the ratios of the increased  $1/Q$  are about 5.0, 4.6, and 2.8% per 10°C of the aging temperature for the vulcanizates with TBBS of 1.0, 1.8, and 2.6 phr, respec-



**Figure 3.** Variation of the crosslink density (inverse swelling ratio,  $1/Q$ ) with the aging temperature for the silica-filled NR vulcanizates after the extraction. Thermal aging was performed for 7 days in a convect oven. The squares, circles, and triangles indicate the TBBS contents of 1.0, 1.8, and 2.6 phr, respectively. Solid and open symbols stand for the vulcanizates without and containing TESPT, respectively.

tively. This trend was also observed in the vulcanizates containing TESPT. For the vulcanizates without TESPT, the ratios of the increased  $1/Q$  are about 2.0, 1.7, and 1.6% per 10°C, respectively. Degree of the  $1/Q$  change is larger for the vulcanizate without TESPT than for the vulcanizate containing TESPT. This may be due to adsorption of TBBS on the silica surface. Since TESPT prevents adsorption of curatives on the silica surface,<sup>[8-10]</sup> actual content of TBBS participating in vulcanizing reaction in the compound without TESPT is much lower than that in the compound containing TESPT. The number of polysulfide crosslinks in the vulcanizate increases as the relative sulfur content



**Figure 4.** Variation of the change of the crosslink density (inverse swelling ratio,  $1/Q$ ) with the aging temperature for the silica-filled NR vulcanizates after the extraction. The degree of the change was calculated by dividing the difference in the crosslink density after and before the thermal aging by the initial crosslink density. Thermal aging was performed for 7 days in a convectin oven. The squares, circles, and triangles indicate the TBBS contents of 1.0, 1.8, and 2.6 phr, respectively. Solid and open symbols stand for the vulcanizates without and containing TESPT, respectively.

increases. Thus, the vulcanizate without TESPT will have polysulfide crosslinks more than the vulcanizate containing TESPT and polysulfides increase as the TBBS content decreases. The polysulfide crosslinks can be dissociated with ease by heating.<sup>(3,12)</sup>

In order to obtain the activation energy for the crosslink density change by thermal aging, the experimental results were fitted to the Arrhenius plot of  $\ln k$  vs.  $1/T$ , where  $k$  is the reaction rate and  $T$  is the Kelvin temperature. In this study, the increment of crosslink density (%) by the thermal aging was employed as the reaction rate,  $k$ . Figure 5 gives the Arrhenius plot for the vulcanizates before the extraction. The data at 40°C was largely deviated from other data. This may be because 40°C is not enough thermal energy to form new crosslinks. In an attempt to get a linear fitting, the 40°C data were eliminated from the Arrhenius plot and it was replotted in Figure 6. Results for the curve fitting equations of Figure 6 were summarized in Table 4. For the vulcanizates without TESPT, the activation energy decreases as the TBBS content increases. For the vulcanizates containing TESPT, however, this trend was not observed. The organic materials-extracted vulcanizates also show similar trends to

**Table 3.** Curve Fitting Equations for the Crosslink Density Change of the Vulcanizates After the Extraction\*

Content of TBBS(phr)	Curve fitting equation	Correlation coefficient
Vulcanizates without silane coupling agent		
1.0	$y = 0.500x - 17.27$	0.992
1.8	$y = 0.458x - 15.42$	0.996
2.6	$y = 0.281x - 6.41$	0.951
Vulcanizates containing silane coupling agent		
1.0	$y = 0.203x - 5.56$	0.883
1.8	$y = 0.172x - 3.44$	0.949
2.6	$y = 0.161x - 3.45$	0.949

\*Curve fitting for Figure 4

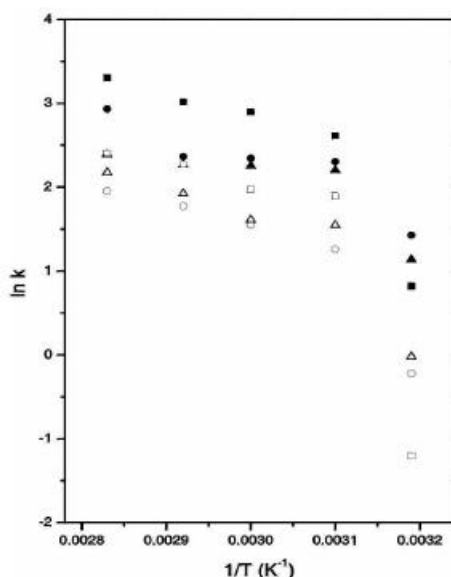


Figure 5. Plot of  $1/T$  vs.  $\ln k$  for the silica-filled NR vulcanizates before the extraction.  $k$  is the degree of the crosslink density change.

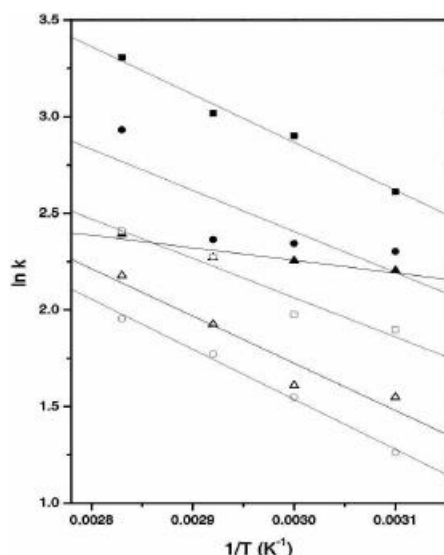


Figure 6. Arrhenius plot for the crosslink density change of the silica-filled NR vulcanizates before the extraction.  $k$  is the degree of the crosslink density change.

the vulcanizates before the extraction (Figures 7 and 8). The data at  $40^\circ\text{C}$  was

Table 4. Activation Energies Obtained from the Arrhenius Equations for the Vulcanizates Before the Extraction\*

Content of TBBS (phr)	Activation energy (kJ/mol)
Vulcanizates without silane coupling agent	
1.0	20.596
1.8	17.673
2.6	5.419
Vulcanizates containing silane coupling agent	
1.0	16.915
1.8	21.534
2.6	20.338

\*Data obtained from curve fitting for Figure 6

also largely deviated from other data. The activation energies for the organic materials-extracted vulcanizates were also obtained from the Arrhenius plot except the data at  $40^\circ\text{C}$  (Figure 8). The results were summarized in Table 5. For the vulcanizates without TESPT, the activation energy also decreases as the TBBS content increases. The vulcanizates containing TESPT also do not show a specific trend depending on the TBBS content. This may be because both of the participation of TESPT in the formation of new crosslinks and the dissociation of the existing crosslinks. The role of TESPT in crosslink density change of the sulfur-cured vulcanizate will be further studied.

## CONCLUSION

Crosslink densities of the silica-filled NR vulcanizates prepared by accelerated sulfur cure system increase by the thermal aging and the degree of the crosslink density change linearly increases with increase of the aging temperature. The degree of crosslink density change for the vulcanizates without TESPT is higher



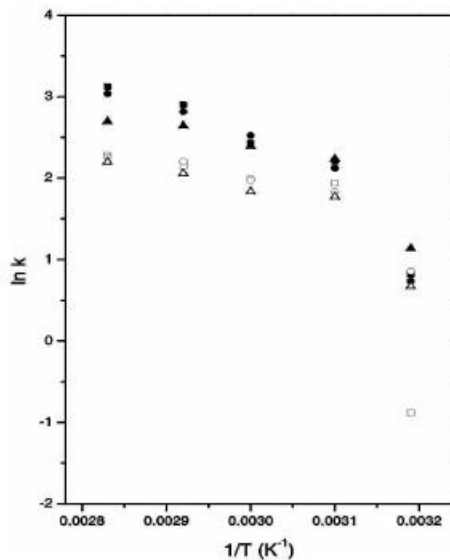


Figure 7. Plot of  $1/T$  vs.  $\ln k$  for the silica-filled NR vulcanizates after the extraction.  $k$  is the degree of the crosslink density change.

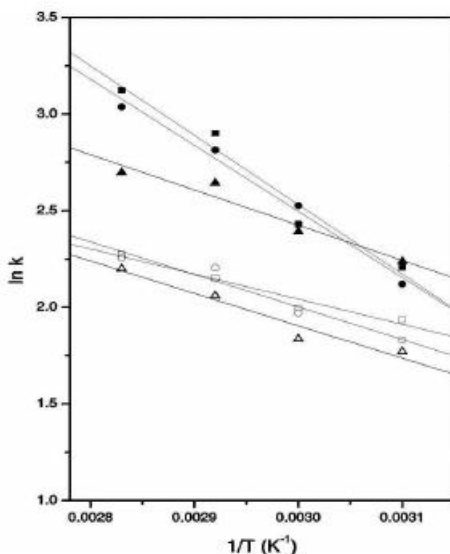


Figure 8. Arrhenius plot for the crosslink density change of the silica-filled NR vulcanizates after the extraction.  $k$  is the degree of the crosslink density change.

than for the vulcanizates containing TESPT. The crosslink density change at 40 °C is much smaller than at relatively

Table 5. Activation Energies Obtained from the Arrhenius Equations for the Vulcanizates After the Extraction\*

Content of TBBS (phr)	Activation energy (kJ/mol)
Vulcanizates without silane coupling agent	
1.0	29.861
1.8	28.428
2.6	15.159
Vulcanizates containing silane coupling agent	
1.0	10.800
1.8	13.999
2.6	13.923

\*Data obtained from curve fitting for Figure 8

higher temperatures (above 40°C). For the vulcanizates without TESPT, activation energy for the crosslink density change becomes smaller as the TBBS content increases.

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