



## Influence of Reinforcing Systems on Thermal Aging Behaviors of NR Composites

Sung-Seen Choi<sup>†</sup> and Jong-Chul Kim

Department of Chemistry, Sejong University, 98 Gunja-dong, Gwangjin-gu, Seoul 143-747, Korea

(Received May 16, 2011, Revised May 25, 2011, June 3, Accepted June 8, 2011)

### 충전 시스템이 NR 복합체의 열노화 거동에 미치는 영향

최성신<sup>†</sup> · 김종철

세종대학교 화학과

접수일(2011년 5월 16일), 수정일(2011년 5월 25일), 게재확정일(2011년 6월 8일)

**ABSTRACT** : Five natural rubber (NR) composites with different reinforcing systems of unfilled, carbon black, carbon black with silane coupling agent, silica, and silica with silane coupling agent were thermally aged and change of the crosslink densities by the accelerated thermal aging was investigated. The crosslink densities on the whole increased as the aging time elapsed irrespective of the reinforcing systems. The crosslink density changes became noticeable by increasing the aging temperature. For carbon black-filled composites, the silane coupling agent made the crosslink density change to be increased. For silica-filled composites, however, the silane coupling agent made the crosslink density increment reduced at 60 and 70°C and it hardly affect the degree of the crosslink density change at 80 and 90°C. The activation energies for the crosslink density changes of the carbon black-filled samples increased continuously in a logarithmic fashion, whereas that of the silica-filled one showed a quasi-steady state ranges at aging times of 30-150 days. The activation energy of the unfilled sample increased exponentially with the aging time. The experimental results were explained with sulfur donation from the silane coupling agent, surface modification of the filler by the silane coupling agent, adsorption of curative residues on the silica surface, and release of the adsorbed curative residues.

**요약** : 비보강, 카본블랙, 카본블랙과 실란커플링제, 실리카, 실리카와 실란커플링제 등 5가지의 다른 충전 시스템을 갖는 NR 복합체를 열노화시켰으며, 가속 열노화에 의한 가교밀도 변화를 연구하였다. 가교밀도는 충전 시스템과 관계없이 노화 시간이 경과함에 따라 증가하였다. 노화 온도가 높아질수록 가교밀도는 눈에 띄게 변화하였다. 카본블랙으로 보강된 NR 복합체의 경우, 실란커플링제는 가교밀도를 증가시켰다. 하지만 실리카로 보강된 NR 복합체의 경우에는 60°C와 70°C 노화에서는 가교밀도 증가분이 감소하였으며, 80°C와 90°C에서는 거의 영향을 주지 않았다. 카본블랙으로 보강된 NR 복합체의 가교밀도 변화에 대한 활성화 에너지는 로그 함수 형태로 지속적으로 증가한 반면, 실리카로 보강된 NR 복합체의 경우에는 노화 시간 30-150일 구간에서는 거의 변화가 없었다. 비보강 시험편의 활성화 에너지는 노화 시간에 따라 지수 함수 형태로 증가하였다. 실험 결과는 실란커플링제로부터의 황 제공, 실란커플링제에 의한 충전제의 표면 개질, 실리카 표면에서의 가교제 잔류물의 흡착, 그리고 흡착된 가교제 잔류물의 방출 등으로 설명하였다.

**Keywords** : NR composite, thermal aging, reinforcing system, crosslink density change

## I. Introduction

Physical properties of rubber composites are improved by reinforcing with fillers and the most popular reinforcing fillers used in rubber compounds are carbon black and silica.<sup>1-10</sup> Types and contents of fillers also affect the cure characteristics and the cure rate of a filled rubber compound is faster than that of an unfilled one.<sup>11,12</sup> Silica-filled rubber compounds have

slower cure characteristics relative to carbon black-filled ones since silica adsorbs curatives.<sup>13-15</sup> The crosslink density of a carbon black-filled rubber composite is influenced by the structure and surface chemistry of carbon black.<sup>11</sup> The carbon black leads to higher crosslink density and better reversion resistance.<sup>11,16</sup>

Silica has a number of hydroxyl groups (silanol, ~Si-OH), which results in strong filler-filler interactions and adsorption of polar materials by hydrogen bonds.<sup>6,17</sup> Since intermolecular hydrogen bonds between silanol groups on the silica surface are very strong, it can aggregate tightly.<sup>7,18</sup> Its property can

<sup>†</sup> Corresponding Author. E-mail: [sschoi@sejong.ac.kr](mailto:sschoi@sejong.ac.kr)

cause a poor dispersion of silica in a rubber compound. In general, a silane coupling agent such as bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) is used to improve the filler dispersion and to prevent adsorption of curatives on the silica surface.<sup>15</sup> TESPT reacts with silanol on the silica surface and a siloxane bond is formed. The silane molecule bound to the silica surface can react with a rubber chain to form a crosslink between silica and rubber.

Brown and coworkers reported physical property changes of rubber composites after natural aging for 40 years and compared with the accelerated heat aging results.<sup>19,20</sup> Relative deviations for the physical property changes of natural aging results for long time were very big but the data are valuable. The big deviation of the physical property might be due to the difference in the initial state of the samples. Lots of samples are needed to measure physical properties and to perform thermal aging for long time. Physical properties of a rubber composite depend on its crosslink density.<sup>21</sup> The crosslink density of a rubber vulcanizate varies with the vulcanization temperature as well as with the cure time even for the same formulation. The size of sample should be small enough to minimize the experimental errors, but relatively large sample size should be required for the measurement of physical properties. Sample dimension for measurement of the crosslink density is less than  $1 \times 1 \text{ cm}^2$ . Thus, experimental errors to examine thermal aging behaviors can be reduced by measuring the crosslink density changes not the physical property changes because lots of samples with the same initial conditions can be obtained from one press mold to measure the crosslink density changes.

In the present work, we studied thermal aging behaviors of natural rubber (NR) composites reinforced with different reinforcing systems via tracing the changes in crosslink densities. Unfilled, carbon black, carbon black with silane coupling agent, silica, and silica with silane coupling agent were employed as the reinforcing systems. Thermal aging was carried out for 2 to 185 days in a convection oven and the thermal aging behaviors were compared for two cases: short-term and long-term aging periods. Activation energy for the crosslink density change by thermal aging was obtained from the Arrhenius plot and the variation with the aging time was also investigated to characterize the thermal aging behaviors.

## II. Experimental

Five NR compounds were made of rubber, filler (carbon black or silica), silane coupling agent (TESPT), antidegradants (HPPD and wax), cure activators (ZnO and stearic acid), cure accelerator (TBBS), and sulfur. Si69, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT), supplied from Degussa Co. was employed as a silane coupling agent. The formulations were given in Table 1. Mixing was performed in a Banbury type

**Table 1. Formulations** (phr)

Compound No.	1	2	3	4	5
SMR CV60	100.0	100.0	100.0	100.0	100.0
N220	-	50.0	50.0	-	-
Z175	-	-	-	50.0	50.0
Si69	-	-	3.0	-	3.0
Wax	2.0	2.0	2.0	2.0	2.0
HPPD	2.0	2.0	2.0	2.0	2.0
ZnO	2.0	2.0	2.0	2.0	2.0
Stearic acid	2.0	2.0	2.0	2.0	2.0
TBBS	1.4	1.4	1.4	1.4	1.4
Sulfur	1.4	1.4	1.4	1.4	1.4

N220: carbon black

Z175: silica

Si69: Si69: bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT)

HPPD: *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine

TBBS: *N*-*tert*-butyl-2-benzothiazole sulfenamide

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 filler and silane coupling agent were compounded into the rubber for 2.5 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 sheet-shaped vulcanizates were prepared by curing at 160 °C for 20.0 min in a press mold.

The sample dimension for accelerated thermal aging was  $3.0 \times 6.0 \text{ cm}^2$  with 2.0 mm thickness. Thermal aging was performed at 60, 70, 80, and 90 °C for 2, 4, 6, 8, 10, 15, 20, 25, 30, 35, 45, 55, 65, 75, 85, 105, 125, 145, 165, and 185 days in a convection oven. Crosslink densities of the samples were measured by a swelling method. Organic additives in the samples were removed by extracting with THF and *n*-hexane for 3 and 2 days, respectively, and they were dried for 2 days at room temperature. The weights of the organic materials-extracted samples were measured. They were soaked in *n*-decane for 2 days and the weights of the swollen samples were measured. The swelling ratio (*Q*) was calculated by the equation,  $Q = (W_s - W_u) / W_u$ , where  $W_s$  and  $W_u$  are weights of the swollen and unswollen samples. In general, the reciprocal swelling ratio ( $1/Q$ ) was used as the apparent crosslink density. Experiments were carried out three times and the obtained values were averaged.

Organic materials in the aged samples were extracted with

THF and analyzed with GC/MS. GC/MS chromatograms and mass spectra of the extracted materials were acquired with 6890N/5987 GC/MS of Agilent Co. DP-5MS capillary column (length 30 m) was used. Injector temperature of the GC was 250 °C. The GC oven temperature program was as follows: (1) The initial temperature was 70 °C and kept for 3 min. (2) The temperature was then increased from 70 to 300 °C at a rate of 10 °C/min.

### III. Results and discussion

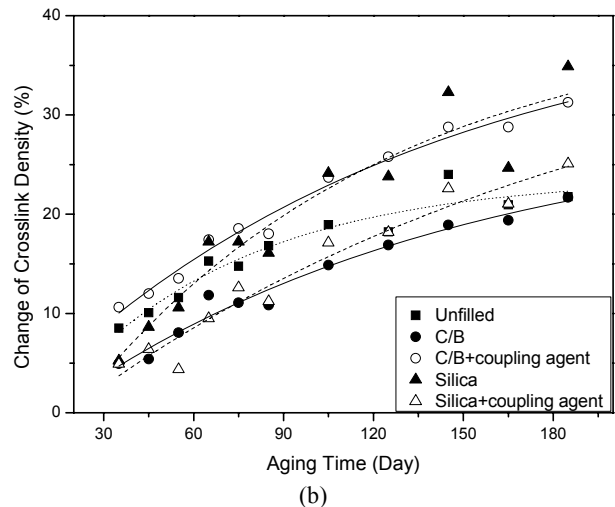
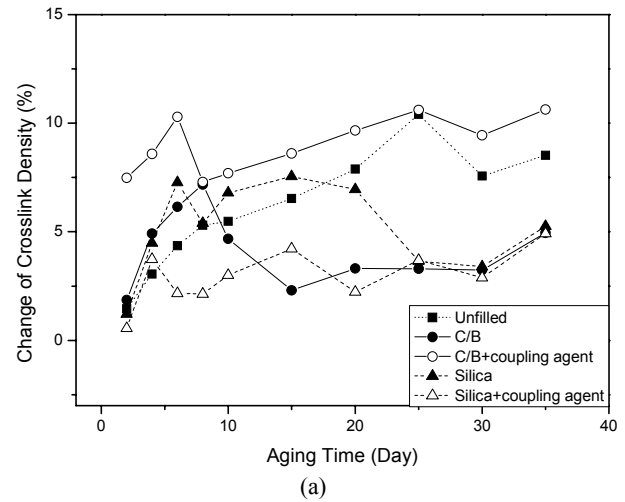
Bound rubber contents of the filled samples were measured to compare the degree of reinforcement. In general, the bound rubber content depends on characteristics of filler such as surface area, structure or morphology, and surface activity. Bound rubber contents of the carbon black-filled compounds without and containing TESPT were 20.0 and 22.1 %, respectively, while those of the silica-filled ones were 10.9 and 21.2 %, respectively. Difference in the bound rubber contents of carbon black-filled compounds without and containing TESPT was not significant, but for the silica-filled ones the difference was noticeably big. This indicates that TESPT strikingly enhances the bound rubber content of the silica-filled compound.

Crosslink density change ( $\Delta X_c$ ) was calculated by the equation (1)

$$\Delta X_c = 100 \times \{(1/Q_f) - (1/Q_i)\} / (1/Q_i) \quad (1)$$

where  $(1/Q_i)$  and  $(1/Q_f)$  are the apparent crosslink densities of the specimens before and after the thermal aging. The experimental results were plotted by two aging times of short-term and long-term agings as shown in Figures 1 - 4. The  $\Delta X_c$ s for the short-term aging of 2 - 35 days generally increase with increasing the aging time, but the increasing pattern is somewhat fluctuated. The degree of  $\Delta X_c$  is governed by the competition reactions between the formation of new crosslinks and the dissociation of existing crosslinks. The newly formed crosslinks give rise to the increase of total crosslink density, whereas the dissociation of existing crosslinks reduces the total crosslink density. Curatives and their residues such as sulfur, zinc complex, cure accelerator residues, and pendent sulfide groups remained in a rubber vulcanizates can lead to new crosslinks,<sup>22</sup> whereas the polysulfides are easily dissociated by heating.<sup>23,24</sup> The enhancement of crosslink density by thermal aging implies that the formation of new crosslinks dominates over the dissociation of existing crosslinks.

For the thermal aging at 60 °C within 35 days (Figure 1(a)), the crosslink density ( $X_c$ ) increased after the thermal aging and the degree of  $\Delta X_c$  varied up and down with the aging time except the unfilled sample. This indicates that there exists a local minimum region where the dissociation of existing



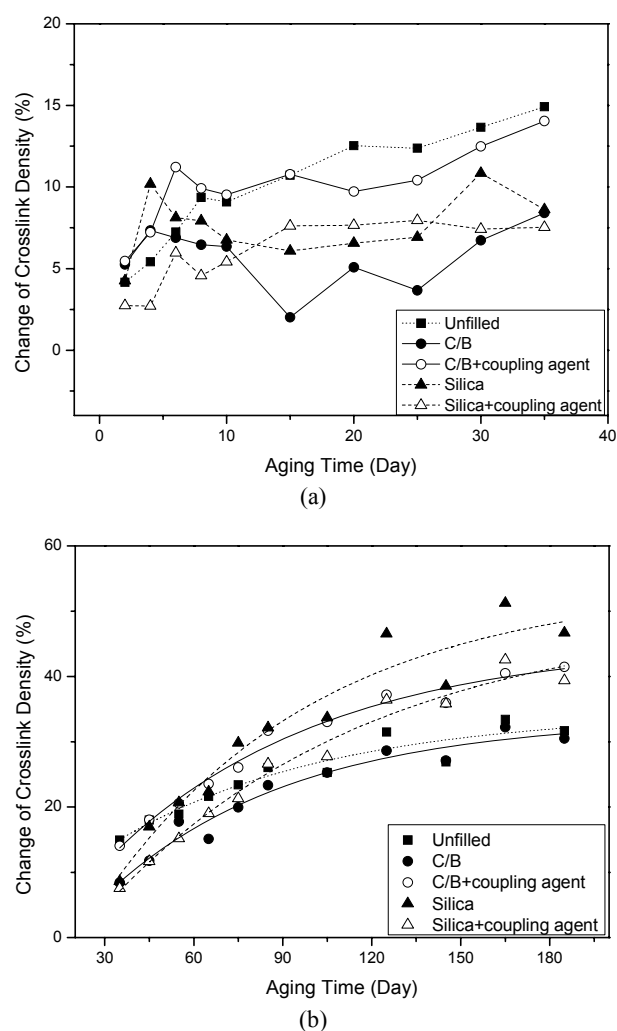
**Figure 1.** Variations of the crosslink density changes with the aging time for NR composites: (a) short-term and (b) long-term thermal aging at 60 °C. The squares, circles, and triangles indicate the unfilled, carbon black-filled, and silica-filled specimens, respectively. The solid and open symbols stand for the specimens without and containing the coupling agent, respectively.

crosslinks exceeds the amounts of newly formed crosslinks. For the short-term aging, the  $\Delta X_c$ s of the carbon black-filled composite containing TESPT are larger than those of the others. Considering the long-term aging for 185 days at 60 °C (Figure 1(b)), the  $\Delta X_c$ s continuously increased with the aging time elapsed irrespective of the reinforcing systems. For the carbon black-filled composites, the  $\Delta X_c$ s of the sample containing TESPT were much larger than those of the sample without TESPT, whereas for the silica-filled composites the  $\Delta X_c$ s of the sample containing TESPT were much smaller than those of the sample without TESPT. This indicates that TESPT plays a role to increase  $\Delta X$  of the carbon black-filled composite, whereas it does not play an increasing role of  $\Delta X$

in the silica-filled ones. This can be explained by the preferential role of TESPT either preventing the adsorption of the curatives on the silica surface or acting as a sulfur donor. Silica has a number of silanol groups, polar materials such as cure accelerator and antiozonant in a rubber compound can be easily adsorbed on the silica surface. Ethoxy groups of TESPT,  $(\text{CH}_3\text{CH}_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{-S}_4\text{-CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$ , can react with silanol groups of the silica to form siloxane bond ( $\sim\text{Si-O-Si}\sim$ ). The TESPT molecules bonded to the silica surface prevent the curatives from adsorption. Since TESPT has about four sulfur atoms every one molecule, elemental sulfur can be isolated from it by heating.<sup>18</sup> Thus, the total sulfur content becomes higher in a rubber compounds by adding TESPT. However, TESPT in the carbon black-filled compound rarely react with carbon black because the number of functional groups on the carbon black surfaces is quite limited. Thus, most of TESPT in the carbon black-filled compound will remain. The sulfur donation of TESPT increases the crosslink density of the carbon black-filled composite during thermal aging. On the contrary, for the silica-filled compounds, TESPT can react with silanol groups of silica and also make a crosslink between silica and rubber by formation of siloxane bond with silica and sulfur bond with a rubber chain. For the silica-filled composite without TESPT, some curatives will be adsorbed on the silica surface. The adsorbed curatives can be released during thermal aging and participate in crosslinking reactions leading to an increase of the crosslink density.

The  $\Delta X_{cs}$  of the unfilled sample are smaller than those of the carbon black-filled composite containing TESPT and silica-filled composite without TESPT, while they are larger than those of the carbon black-filled composite without TESPT and silica-filled composite containing TESPT. The  $\Delta X_{cs}$  of the carbon black-filled composite without TESPT are lower than those of the others. This means that the carbon black-filled composite without TESPT has a good thermal resistance at 60 °C.

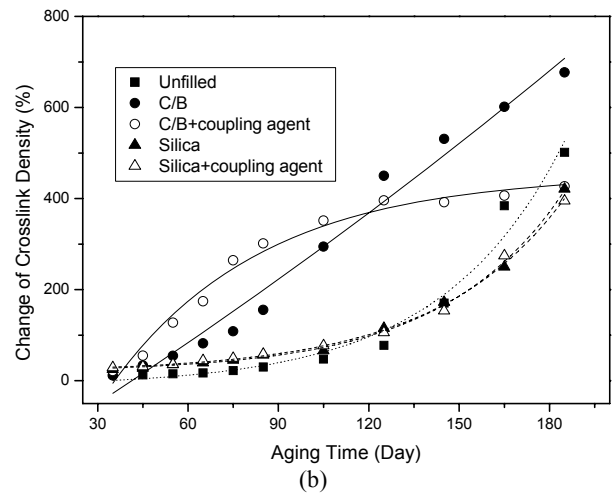
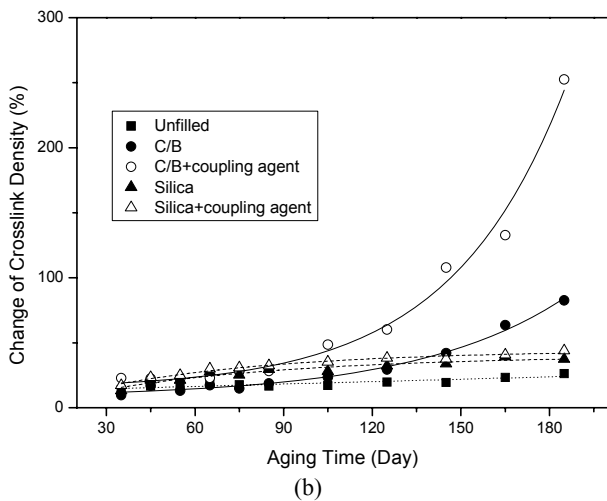
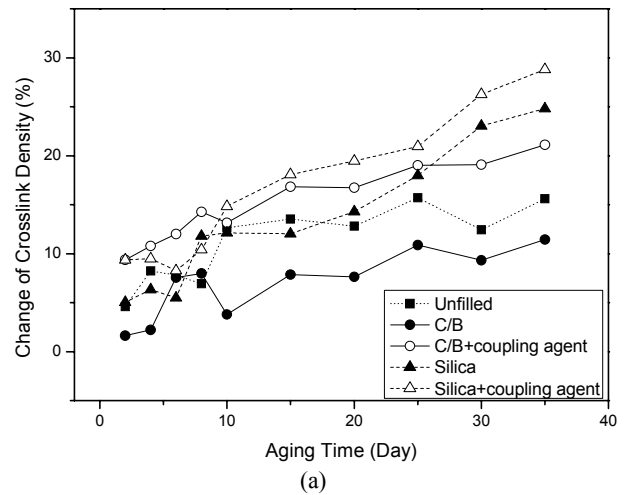
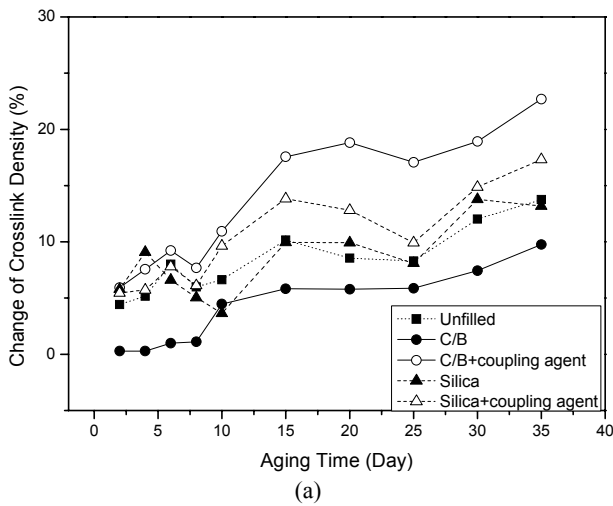
The  $\Delta X_{cs}$  notably increased as the aging temperature became higher as shown in Figures 1-4. The  $\Delta X_{cs}$  at 70 °C aging are higher than those at 60 °C aging (Figures 1 and 2). Some experimental results at 70 °C aging showed similar trends to those at 60 °C aging. The  $\Delta X_{cs}$  of the carbon black-filled composite without TESPT are lower than those of the others. For long-term aging, the  $\Delta X_{cs}$  of the unfilled sample are smaller than those of the carbon black-filled sample containing TESPT and silica-filled sample without TESPT, while they are larger than those of the carbon black-filled sample without TESPT and silica-filled sample containing TESPT. For the short-term aging within 35 days, the  $\Delta X_{cs}$  of the unfilled sample are relatively higher than those of the others. For thermal aging longer than 85 days, the  $\Delta X_{cs}$  of the silica-filled sample without TESPT are larger than those of the



**Figure 2.** Variations of the crosslink density changes with the aging time for NR composites: (a) short-term and (b) long-term thermal aging at 70 °C. The squares, circles, and triangles indicate the unfilled, carbon black-filled, and silica-filled specimens, respectively. The solid and open symbols stand for the specimens without and containing the coupling agent, respectively.

carbon black-filled sample containing TESPT. This may be due to the activation of release of adsorbed curatives and implies that release of the adsorbed curatives is strikingly activated at 70 °C.

Variation of the  $\Delta X_{cs}$  at 80 °C with the aging time shows different trends from those at 60 and 70 °C as shown in Figure 3. For the short-term aging as shown in Figure 3(a), the fluctuation of the  $\Delta X_{cs}$  values at 80 °C was considerably smaller compared with those at 60 and 70 °C aging. The  $\Delta X_{cs}$  of the carbon black-filled sample containing TESPT are larger than those of the others. The decreasing order of the  $\Delta X_{cs}$  was carbon black-filled sample containing TESPT > silica-filled sample containing TESPT > unfilled sample  $\cong$  silica-filled sample without TESPT > carbon black-filled sample



**Figure 3.** Variations of the crosslink density changes with the aging time for NR composites: (a) short-term and (b) long-term thermal aging at 80 °C. The squares, circles, and triangles indicate the unfilled, carbon black-filled, and silica-filled specimens, respectively. The solid and open symbols stand for the specimens without and containing the coupling agent, respectively.

**Figure 4.** Variations of the crosslink density changes with the aging time for NR composites: (a) short-term and (b) long-term thermal aging at 90 °C. The squares, circles, and triangles indicate the unfilled, carbon black-filled, and silica-filled specimens, respectively. The solid and open symbols stand for the specimens without and containing the coupling agent, respectively.

without TESPT. For the long-term aging as shown in Figure 3(b), the  $\Delta X_{c,s}$  of the carbon black-filled samples exponentially increase as the aging time elapses. This may be due to the fast consumption of antidegradants in the sample at high temperature. In general, migration rates of antidegradants in a carbon black-filled rubber vulcanizate are relatively faster than those in a silica-filled one.<sup>25,26</sup> If antidegradants do not exist in a rubber vulcanizate, carbon-carbon double bonds (C=C) of rubber chains are degraded by ozone and oxygen and then new chemical bonds between rubber chains can be formed by a radical process. A direct bond formation between rubber chains results in increase of the crosslink density. The  $\Delta X_{c,s}$  of the unfilled sample are higher than

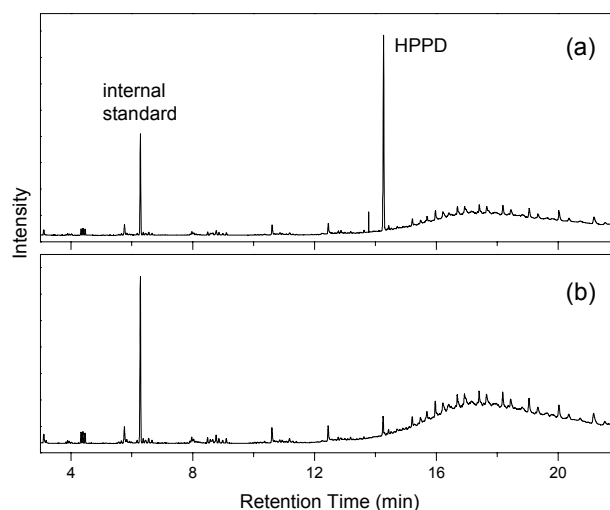
those of the carbon black-filled sample without TESPT for the thermal aging at 80 °C during 75 days. However, after 75 days of thermal aging, the  $\Delta X_{c,s}$  of the unfilled sample are lower than those of the carbon black-filled sample without TESPT.

The  $\Delta X_{c,s}$  of the rubber composites after thermal aging at 90 °C notably increase irrespective of the reinforcing systems as shown in Figure 4. The  $\Delta X_{c,s}$  of the carbon black-filled sample containing TESPT are larger than those of the others within 8 days at 90 °C aging as shown in Figure 4(a) and the  $\Delta X_{c,s}$  of the carbon black-filled sample containing TESPT are smaller than those of the silica-filled sample containing TESPT until 35 days. For the long-term aging as shown in

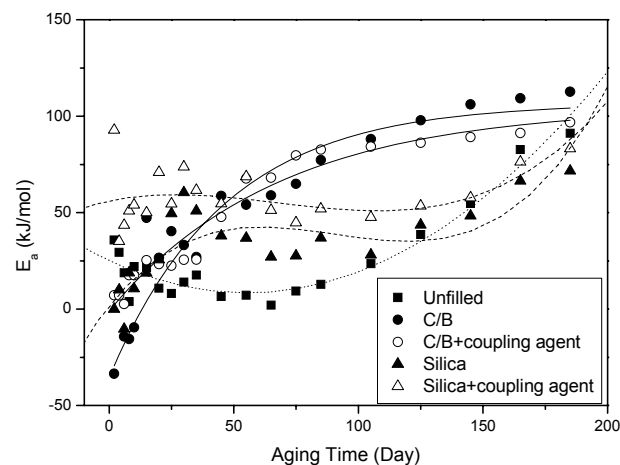
Figure 4(b), the  $\Delta X_{c,s}$  of the unfilled and silica-filled samples increase exponentially as the aging time elapses. The  $\Delta X_{c,s}$  of the carbon black-filled samples are larger than those of the unfilled and silica-filled samples. The  $\Delta X_{c,s}$  of the silica-filled samples containing and without TESPT are nearly the same. The  $\Delta X_{c,s}$  of the unfilled sample are larger than those of the silica-filled samples after 145 days. The  $\Delta X_{c,s}$  of the carbon black-filled samples without TESPT are larger than those of the carbon black-filled samples containing TESPT after 130 days. The amazing increase of the crosslink density by the long-term thermal aging at 90 °C may be due to the lack of antidegradants remained in the aged samples. Antidegradants protect degradation of rubber chain. As discussed above, new chemical bonds between rubber chains can be formed when antidegradants do not exist in a rubber vulcanizate. Consumption rates of antidegradants rapidly increase as the aging temperature increases. Figure 5 shows notable decrease of HPPD in the silica-filled sample by thermal aging at 90 °C for 5 and 35 days.

Activation energies for the  $\Delta X_{c,s}$  by thermal aging were obtained from the Arrhenius plot of  $\ln k$  vs  $1/T$ , where  $k$  is the  $\Delta X_c$  and  $T$  is the aging temperature, to characterize the thermal aging behaviors according to the reinforcing systems. The activation energies vary with the aging time as shown in Figure 6. This implies that states of the vulcanizates depend on the aging time. Density and type of crosslinks are changed hourly because new crosslinks are formed and the existing crosslinks are dissociated by thermal aging. And kinds and amounts of curative residues remained in the sample are also hourly changed. The activation energies of the carbon black-filled composites continuously increase with increase in the aging time. This is natural because amounts of curative residues remained in the sample decrease as the aging time elapses. For the thermal aging for a long time, activation energies of the carbon black-filled composites are higher than those of the silica-filled ones. This may be due to the release of curative residues adsorbed on silica. Values of the activation energies of the silica-filled composites are very fluctuating up and down at the initial period and do not show a significant change during 45 - 145 days and then increase. The quasi-plateau values of activation energies of the silica-filled composites at 45 - 145 days imply that kinds and amounts of curative residues remained in the sample are significantly not changed due to release of the adsorbed curatives.

The activation energy of the unfilled sample decreases until 65 days and then increases. This trend was reported for NBR.<sup>27</sup> This can be explained with the reactivity of rubber chain and migration behaviors of crosslinking-related chemicals such as zinc complexes, curative residues, sulfur, and so on. In general, sulfur crosslinks are made between allylic carbons.<sup>24</sup> As the aging time elapses, the crosslinking-related chemicals will



**Figure 5.** GC/MS TIC chromatograms of the extracted organic materials from the silica-filled NR composite containing TESPT thermally aged for 5 (a) and 35 (b) days at 90 °C.



**Figure 6.** Variations of the activation energies for the crosslink density changes by thermal aging as a function of the aging time. The squares, circles, and triangles indicate the unfilled, carbon black-filled, and silica-filled specimens, respectively. The solid and open symbols stand for the specimens without and containing the coupling agent, respectively.

gather around the C=C double bonds. The gathered chemicals react with rubber chains to make new crosslinks. The remained crosslinking-related chemicals will be consumed very rapidly by crosslinking reactions and then the activation energy will be increased as the aging time elapses because of lack of the remained crosslinking-related chemicals.

#### IV. Conclusions

Crosslink density changes ( $\Delta X_{c,s}$ ) of the rubber composites

continuously increased as the aging temperature and time increased irrespective of the reinforcing systems. Variation of the  $\Delta X_c$ s at the initial period of thermal aging showed a considerable fluctuation up and down, however the fluctuation notably reduced at high temperatures. For the carbon black-filled composites, the  $\Delta X_c$ s of the sample containing TESPT were much larger than those of the sample without TESPT except for the long-term aging longer than 125 days. This was due to the sulfur donation of TESPT. For the silica-filled composites, the  $\Delta X_c$ s of the sample containing TESPT were much lower than those of the sample without TESPT for the thermal aging at 60 and 70 °C, whereas the formers were on the whole higher than the latters for the thermal aging at 80 and 90 °C. The  $\Delta X_c$ s of the unfilled sample for the thermal aging at 60 °C were higher than those of the carbon black-filled sample without TESPT and silica-filled sample containing TESPT. However, the degree of  $\Delta X_c$ s of the unfilled sample was relatively smaller than those of the others at high temperatures. For the long-term aging, the activation energies of the carbon black-filled composites were higher than those of the silica-filled ones. This was explained with the release of curative residues adsorbed on silica. The activation energies of the carbon black-filled composites continuously increased with increase in the aging time, while those of the silica-filled ones showed a quasi-plateau state period. The activation energy of the unfilled sample decreased until 65 days and then increased. Variation of the activation energy with the aging time was due to the gathering and consumption of the crosslinking-related chemicals remained in the samples.

### Acknowledgements

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

### References

- G. R. Cotton, "Mixing of carbon black with rubber - I. Measurement of dispersion rate by changes in mixing torque", *Rubber Chem. Technol.*, **57**, 118 (1984).
- J. S. Kim, J. H. Lee, W. S. Jung, J. W. Bae, H. C. Park, and D. P. Kang, "Effects of reinforcing fillers on far-infrared vulcanization characteristics of EPDM", *Elast. Compos.*, **44**, 47 (2009).
- T. C. Gruber and C. R. Herd, "Anisometry measurements in carbon black aggregate populations", *Rubber Chem. Technol.*, **70**, 727 (1997).
- S.-S. Choi and S.-H. Ha, "Influence of the swelling temperature and acrylonitrile content of NBR on the water swelling behaviors of silica-filled NBR vulcanizates", *J. Ind. Eng. Chem.*, **15**, 167 (2009).
- H. Raab, J. Fröhlich, and D. Göritz, "Surface topography and its influence on the activity of carbon black", *Kautsch. Gummi Kunstst.*, **53**, 137 (2000).
- K. J. Kim, "Bifunctional silane (TESPD) effects on silica containing elastomer compound Part I: Natural rubber (NR)", *Elast. Compos.*, **44**, 134 (2009).
- S. Wolff and M.-J. Wang, "Filler-elastomer interactions. Part IV. The effect of the surface energies of fillers on elastomer reinforcement", *Rubber Chem. Technol.*, **65**, 329 (1992).
- A. I. Medalia, "Effect of carbon black on dynamic properties of rubber vulcanizates", *Rubber Chem. Technol.*, **51**, 437 (1978).
- W. M. Hess and V. E. Chirico, "Elastomer blend properties EM dash influence of carbon black type and location", *Rubber Chem. Technol.*, **50**, 301 (1977).
- Y. Bomal, S. Touzet, R. Barruel, Ph. Cochet, and B. Dejean, "Developments in silica usage for decreased tyre rolling resistance", *Kautsch. Gummi Kunstst.*, **50**, 434 (1997).
- C. H. Chen, J. L. Koenig, J. R. Shelton, and E. A. Collins, "The influence of carbon black on the reversion process in sulfur-accelerated vulcanization of natural rubber", *Rubber Chem. Technol.*, **55**, 103 (1982).
- E. F. Devlin, "Effect of cure variables on cis/trans isomerization in carbon black-reinforced cis-1,4-polybutadiene", *Rubber Chem. Technol.*, **59**, 666 (1986).
- S.-S. Choi, "Influence of filler composition ratio on properties of both silica and carbon black-filled styrene-butadiene rubber compounds", *Elastomer*, **36**, 37 (2001).
- S.-S. Choi, "Influence of silane coupling agent on properties of filled styrene-butadiene rubber compounds", *Kor. Polym. J.*, **8**, 285 (2000).
- A. S. Hashim, B. Azahari, Y. Ikeda, and S. Kohjiya, "Effect of bis(3-triethoxysilyl propyl)tetrasulfide on silica reinforcement of styrene-butadiene rubber", *Rubber Chem. Technol.*, **71**, 289 (1998).
- S.-S. Choi, K.-J. Hwang, and B.-T. Kim, "Influence of bound polymer on cure characteristics of natural rubber compounds reinforced with different types of carbon blacks", *J. Appl. Polym. Sci.*, **98**, 2282 (2005).
- Y.-C. Ou, Z.-Z. Yu, A. Vidal, and J. B. Donnet, "Effects of alkylation of silica filler on rubber reinforcement", *Rubber Chem. Technol.*, **67**, 834 (1994).
- Y. Li, M. J. Wang, T. Zhang, F. Zhang, and X. Fu, "Study on dispersion morphology of silica in rubber", *Rubber Chem. Technol.*, **67**, 693 (1994).
- R. P. Brown and T. Butler, *Natural ageing of rubber. Changes in physical properties over 40 years*, RAPRA Technology Ltd. (2000).
- R. P. Brown, T. Butler, and S. W. Hawley, *Ageing of rubber. Accelerated heat ageing test results*, RAPRA Technology Ltd. (2001).
- N. J. Morrison and M. Porter, "Temperature effects on the stability of intermediates and crosslinks in sulfur vulcan-

- ization”, *Rubber Chem. Technol.*, **57**, 63 (1984).
22. C. H. Chen, J. L. Koenig, J. R. Shelton, and E. A. Collins, “Characterization of the reversion process in accelerated sulfur curing of natural rubber”, *Rubber Chem. Technol.*, **54**, 734 (1981).
  23. S.-S. Choi, “Bond dissociation of sulfur crosslinks in IR and BR vulcanizates using semi-empirical calculations”, *Kor. Polym. J.*, **5**, 39 (1997).
  24. R. W. Layer, “Recurring vulcanizates. I. A novel way to study the mechanism of vulcanization”, *Rubber Chem. Technol.*, **65**, 211 (1992).
  25. S.-S. Choi, “Influence of silica content on migration of anti-degradants to the surface in NR vulcanizates”, *J. Appl. Poly. Sci.*, **68**, 1821 (1998).
  26. S.-S. Choi, “Migration of antidegradants to the surface in NR vulcanizates containing both silica and carbon black”, *Kor. Polym. J.*, **6**, 256 (1998).
  27. S.-S. Choi, J.-C. Kim, and C.-S. Woo, “Accelerated thermal aging behaviors of EPDM and NBR vulcanizates”, *Bull. Kor. Chem. Soc.*, **27**, 936 (2006).