

Influence of the Cure Systems on Long Time Thermal Aging Behaviors of NR Composites

Sung-Seen Choi* and Jong-Chul Kim

Department of Chemistry, Sejong University, Seoul 143-747, Korea

Seung Goo Lee*

BK21 FTIT, Department of Advanced Organic Materials & Textile System Engineering, Chungnam National University, Daejeon 305-764, Korea

Yong L. Joo

School of Chemical & Biomolecular Engineering, Cornell University, Ithaca, NY 14850, U.S.A.

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Abstract: NR composites with different curing systems were aged thermally at 60, 70, 80, and 90 °C for 2-185 days in a convection oven, and the changes in the crosslink density were investigated as a function of the accelerated thermal aging. The overall crosslink densities increased with increasing aging time irrespective of the aging temperatures and curing systems. The changes in crosslink density were enhanced by increasing the aging temperature. The degree of the increased crosslink density was in the following order: “the conventional cure system > the semi-EV system > the EV system”. For short term thermal aging, the change in crosslink density with the aging time was complicated, particularly for low temperature aging. The activation energies of the change in crosslink density with thermal aging using the conventional and semi-EV cure systems increased and then remained relatively constant with increasing aging time, whereas that of the specimen with an EV cure system tended to increase linearly. The experimental results were explained by the dissociation of the existing polysulfidic linkages and the formation of new crosslinks through the crosslinking-related chemicals remaining in the sample.

Keywords: thermal aging, NR composites, cure systems, crosslink density change, activation energy change.

Introduction

Mechanical properties of rubber materials are improved by formation of crosslinks. In general, rubber compounds are crosslinked by sulfur vulcanization,¹⁻³ peroxide curing,⁴ or resole curing.⁵ Sulfur vulcanization is the most popular. In the case of sulfur curing of unsaturated rubbers, crosslinking and reversion as competing reactions depend on the curing time and temperature. Since sulfide crosslinks of S-S and C-S bonds are relatively unstable, the sulfur curing at high temperatures deteriorates the mechanical properties of rubbers due to reversion. Crosslink type and degree of crosslink density of a rubber vulcanizate determine the physical properties such as modulus, hardness, resilience, elongation at breaking, heat build-up, and so forth.⁶ By increasing crosslink density, modulus, hardness, resilience,

and abrasion resistance increase, whereas breaking elongation, heat buildup, and stress relaxation decrease. Stress relaxation, tensile strength, and resilience increase in proportion to the content of di- and polysulfides, whereas fatigue and thermal aging resistances decrease. Sulfide linkages, especially polysulfides, are dissociated by heating^{7,8} and this brings about decrease of the crosslink density. Curatives, especially sulfur, in rubber vulcanizates make new crosslinks⁹ and this result in increase of the crosslink density.

Crosslink type and degree of crosslink density of a rubber vulcanizate are affected by type and content of a cure accelerator.¹⁰⁻¹² There are three types of sulfur cure system in the conventional cure system, semi-efficient vulcanization (semi-EV) system, and efficient vulcanization (EV) system. The conventional cure system has high sulfur content and low cure accelerator content whereas the EV cure system has low sulfur content and high cure accelerator content. The semi-EV cure system is that difference in contents of sulfur and cure accelerator is not big. In general, an EV cure

*Corresponding Authors. E-mails: sschoi@sejong.ac.kr or lsgoo@cnu.ac.kr

system has faster scorch time and cure rate than a conventional one. Scorch time and cure rate of a rubber compound become faster as content of a cure accelerator increases and the crosslink density also increases.¹³

Brown and coworkers reported physical property changes of rubber composites after natural aging for 40 years and compared with the accelerated heat aging results.^{14,15} 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 may be due to the difference in the initial states 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.⁶ Crosslink density of a rubber vulcanizate varies with vulcanization temperature and time though having the same formulation. Sample size should be small to minimize the experimental error, but relatively large sample size for measurement of the physical properties should be required. Sample dimension for measurement of the crosslink density is less than $1 \times 1 \text{ cm}^2$. Thus, experimental error for thermal aging behaviors of a rubber article can be reduced by measuring the crosslink density changes not the physical property changes.

In the present work, we studied thermal aging behaviors of natural rubber (NR) composites with different cure systems by measuring crosslink density changes. Thermal aging was performed for 2 to 180 days in a convection oven and the thermal aging behaviors were investigated by dividing into short and long time aging. Activation energy for the crosslink density change by thermal aging was obtained from Arrhenius plot and the variation with the aging time was also investigated to characterize the thermal aging behaviors.

Experimental

Carbon black-reinforced NR compounds with different cure systems were made of NR (SMR CV60 100.0 phr), carbon black (N220 50.0 phr), antidegradants (*N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD) 2.0 phr and wax 2.0 phr), cure activators (stearic acid 2.0 phr and ZnO 2.0 phr), sulfur (variable), and cure accelerator (*N*-*tert*-butyl-2-benzothiazole sulfenamide (TBBS), variable). Contents of sulfur/TBBS of the compounds with conventional, semi-EV, and EV cure systems are 2.0/0.8, 1.4/1.4, and 0.8/2.0 phr, respectively. Mixing was performed in a Banbury type mixer at a rotor speed of 45 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 MB and FM stages, respectively. The MB compounds were prepared as follow. (1) The rubber was loaded into the mixer and pre-heated for 0.5 min. (2) The carbon black was compounded into the rubber for 2.0 min. (3) The antidegradants and cure activators were mixed for 2.0 min and the compounds were

discharged. The FM compounds were prepared by mixing the sulfur and TBBS with the MB compounds for 2.0 min. The vulcanizates were prepared by curing at 160 °C for 20 min in a compression mold ($140 \times 140 \times 2 \text{ mm}^3$).

The sample dimension for the thermal aging experiment was $3 \times 6 \text{ cm}^2$. Thermal aging was performed at 60, 70, 80, and 90 °C for 2-185 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 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 toluene for 2 days and the weights of the swollen samples were measured. The swelling ratio (Q) was calculated by the equation of $Q = (W_s - W_u) / W_u$, 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 they were averaged.

Organic materials in the aged samples were extracted with THF and analyzed with GC. GC chromatograms were acquired with 6890N GC of Agilent Co. DP-1MS capillary column (length 30m) was used. Injector (FID) and detector temperatures of the GC were 250 and 300 °C. The GC oven temperature program was as follows. (1) The initial temperature was 150 °C and kept for 2 min. (2) The temperature was then increased to 300 °C at a rate of 10 °C/min and kept for 5 min at 300 °C.

Results and Discussion

Crosslink density change (ΔX_c) was calculated by the equation of $\Delta X_c = 100 \times \{(1/Q_f) - (1/Q_i)\} / (1/Q_i)$, 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 arranged by dividing the results with short and long aging times as shown in Figures 1-4. ΔX_c for the short aging time of 2-35 days on the whole tends to increase as the aging time goes on but the variation is very complex. The crosslink density is increased by increasing the thermal aging but level of the increment is up and down with the aging time. Degree of the ΔX_c is determined by the competition reactions of formation of new crosslinks and dissociation of the existing crosslinks. Formation of new crosslinks brings about increase of the crosslink density whereas dissociation of the existing crosslinks reduces the crosslink density. Curatives and their residues such as sulfur, zinc complex, cure accelerator residues, and pendent sulfide groups remaining in rubber vulcanizates make new crosslinks⁹ whereas polysulfides are easily dissociated by heating.^{7,8} Enhancement of the crosslink density by the thermal aging implies that formation of new crosslinks dominates over dissociation of the existing crosslinks.

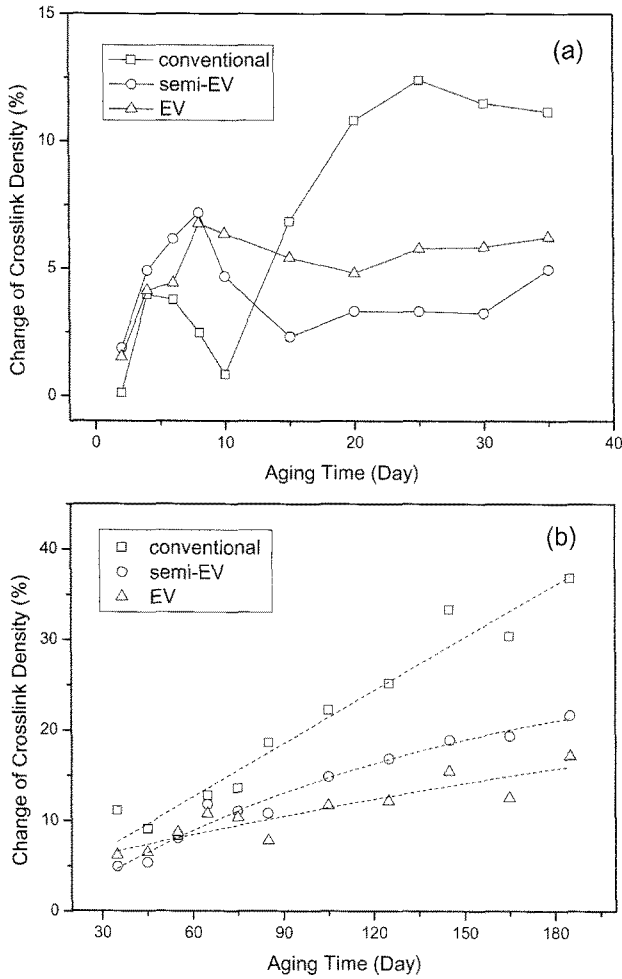


Figure 1. Variations of the crosslink density change of the NR composites by short time (a) and long time (b) thermal aging at 60 °C with the aging time. The squares, circles, and triangles indicate the conventional, semi-EV, and EV cure systems, respectively.

For the thermal aging at 60 °C, the crosslink density increases and decreases around 10-20 days of the aging time and then increases again. This means that the variation shows a local minimum and dissociation of the existing crosslinks exceeds over formation of new crosslinks around the local minimum point. The local minimum time varies with the cure system. The local minimum time of the specimen with the conventional cure system is shorter than the others and the specimen with the EV cure system has longer local minimum time than the others. This can be explained with the difference in the crosslink types. In general, a rubber vulcanizate with conventional cure system has polysulfide crosslinks more than those with semi-EV and EV cure systems and that with semi-EV cure system has higher polysulfides than that with EV one. Thus, reduction of the crosslink density due to dissociation of the existing polysulfide crosslinks can be occurred well in a rubber vulcanizate with conventional cure system. Decrease of the crosslink

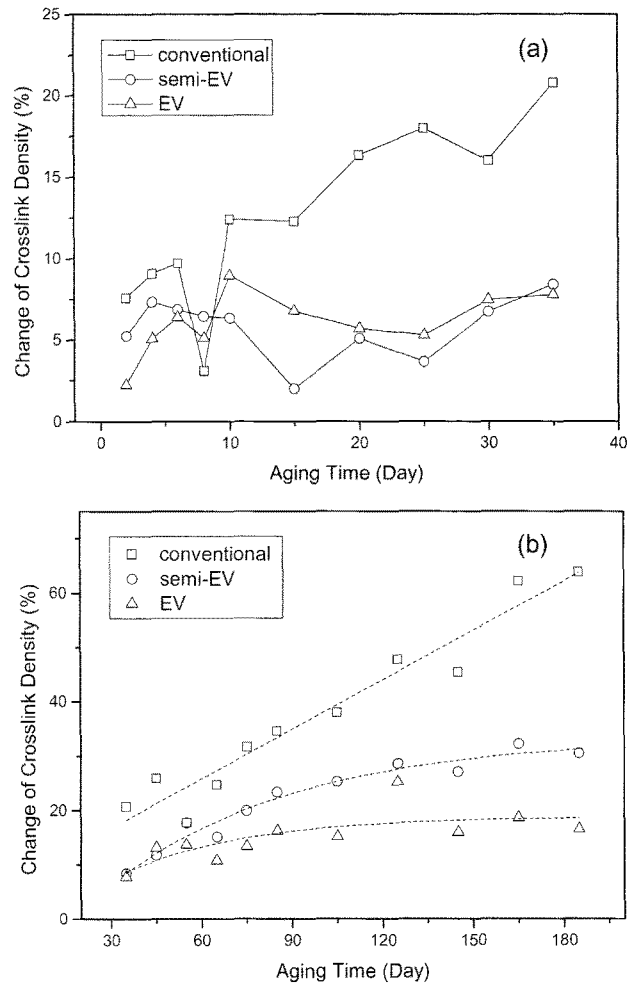


Figure 2. Variations of the crosslink density change of the NR composites by short time (a) and long time (b) thermal aging at 70 °C with the aging time. The squares, circles, and triangles indicate the conventional, semi-EV, and EV cure systems, respectively.

density by dissociation of the existing crosslinks in NR vulcanizates was reported even at 40 °C and nucleophiles in a rubber vulcanizate such as antidegradants, fatty acids, and cure accelerators activate dissociation of the existing polysulfides.¹⁶ ΔX_c of the specimen with the conventional cure system is smaller than the others for the short aging time less than 15 days but for the long aging time it is larger than the others as shown in Figure 1. The specimen with the conventional cure system has higher crosslink density change than the others. This is because the specimen with the conventional cure system contains higher level of sulfur than the others. Some curatives such as free sulfur, cure accelerators, and their residues are remained in cured rubber composites.¹⁶ In general, rubber vulcanizate with conventional cure system has higher free elemental sulfur than those with semi-EV and EV cure systems whereas that with an EV cure system has more cure accelerator and its resi-

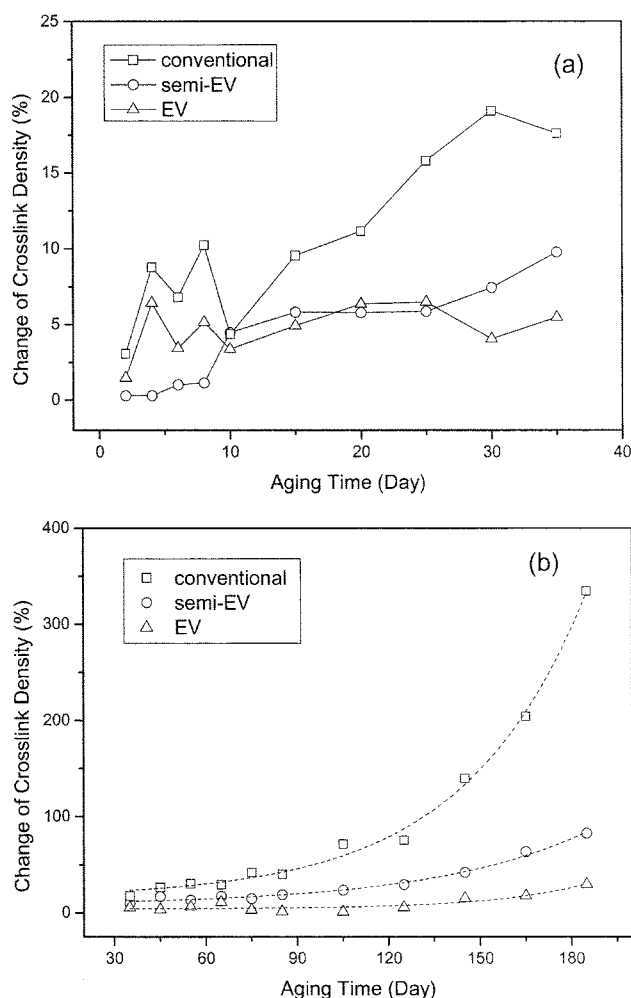


Figure 3. Variations of the crosslink density change of the NR composites by short time (a) and long time (b) thermal aging at 80 °C with the aging time. The squares, circles, and triangles indicate the conventional, semi-EV, and EV cure systems, respectively.

due. From the experimental results, it can lead to a conclusion that free sulfur is more effective to increase the crosslink density by thermal aging than cure accelerators and their residues.

ΔX_c of the specimen with the conventional cure system for the thermal aging at 60 °C within 10 days is lower than those with the semi-EV and EV ones but it is notably increased after 10 days as the aging time goes on. The relatively lower ΔX_c of the specimen with the conventional cure system for the short time aging was clearly observed only at the 60 °C thermal aging. This indicates that polysulfidic linkages can be easily dissociated at relatively low temperatures because the specimen with the conventional cure system has more polysulfidic crosslinks. ΔX_c variations of the specimen with the semi-EV and EV cure systems show relatively similar trends compared to those with the conventional cure system. But, ΔX_c of the specimen with the semi-

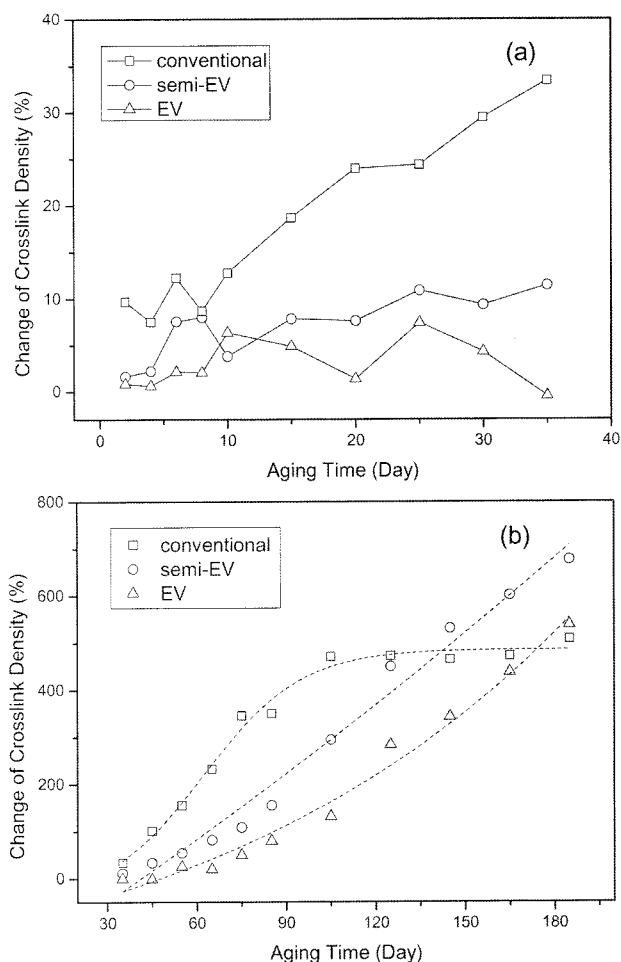


Figure 4. Variations of the crosslink density change of the NR composites by short time (a) and long time (b) thermal aging at 90 °C with the aging time. The squares, circles, and triangles indicate the conventional, semi-EV, and EV cure systems, respectively.

EV and EV cure systems within 50 days are competitive. For the thermal aging at 60 °C, ΔX_c of the specimen with the semi-EV cure system is little larger than that with the EV cure system within 8 days but is smaller after then until 55 days. ΔX_c of the specimen with the semi-EV cure system is again larger than that with the EV cure system after 55 days (Figure 1). The smaller ΔX_c of the specimen with the semi-EV cure system compared to the specimen with the EV cure system was also observed in the thermal aging at 70 and 80 °C (Figures 2 and 3). ΔX_c s of the specimen with the semi-EV cure system are larger than those with the EV cure system after 35 and 30 days for the thermal aging at 70 and 80 °C, respectively. Reversion of ΔX_c s of the specimens with the semi-EV and EV cure systems for the short time aging can be explained with the curative complex and pendent sulfide groups remaining in the sample. Formation of new crosslinks in rubber vulcanizate by the thermal aging comes from curative complex and pendent sulfide groups

terminated with cure accelerator residues as well as the free sulfur.¹⁶ The specimen with the EV cure system may contain the curative complex and pendent sulfide groups more than that with the semi-EV one because cure accelerator generates the curative complex and pendent sulfide groups.

For the long time aging, ΔX_c s of the specimen with the conventional cure system are much larger than those with the semi-EV and EV ones except the thermal aging at 90 °C (Figure 4). Difference in the ΔX_c s is getting bigger as the aging time goes on and the aging temperature increases. The big ΔX_c of the specimen with the conventional cure system is due to the free elemental sulfur remaining in the sample as discussed above. Difference in the ΔX_c s of the specimens with the semi-EV and EV cure systems is also due to the free elemental sulfur remaining in the sample as discussed above. The specimen with the semi-EV cure system has relatively higher content of sulfur than that with the EV one.

For the thermal aging at 90 °C of the specimen with the conventional cure system, the ΔX_c continuously increases from the start without the minimum point but the increment is halted at 105 days and then shows plateau state (Figure 4). ΔX_c of the specimen with the conventional cure system is lower than those with the semi-EV and EV cure systems after the aging time of 145 and 185 days, respectively. This implies that most of the remained curatives including the pendent sulfide groups are exhausted within 105 days at 90 °C. Continuous increases of the ΔX_c s of the specimens with the semi-EV and EV cure systems can be explained with the abundant pendent sulfide groups remaining in the samples. Free organic materials can be evaporated during the thermal aging, especially at high temperatures. Free curatives remaining in the sample are consumed by evaporating at high temperatures as well as by participating in crosslinking reactions. Since the specimen with the conventional cure system contains the cure accelerator much less than those with the semi-EV and EV cure systems, the specimen aged at high temperatures for long time will have organic materials by trace. Figure 5 shows the organic materials extracted from the specimen with the conventional cure system aged at 90 °C for 5 and 35 days. The peak at 6.28 min is 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) used as the internal standard. HPPD and stearic acid in the formulation are detected at 14.26 and 9.32 min, respectively. The several peaks at 15–22 min are assigned to wax. The specimen aged at 90 °C for 5 days contains some organic materials such as HPPD, stearic acid, and wax but that for 35 days does not have HPPD and stearic acid.

Activation energies for the crosslink density changes by the thermal aging were obtained from the Arrhenius plot of $\ln k$ vs $1/T$, where k is the crosslink density change and T is the aging temperature, to characterize the thermal aging behaviors depending on the cure system and aging time. Figure 6 shows variation of the activation energy with the

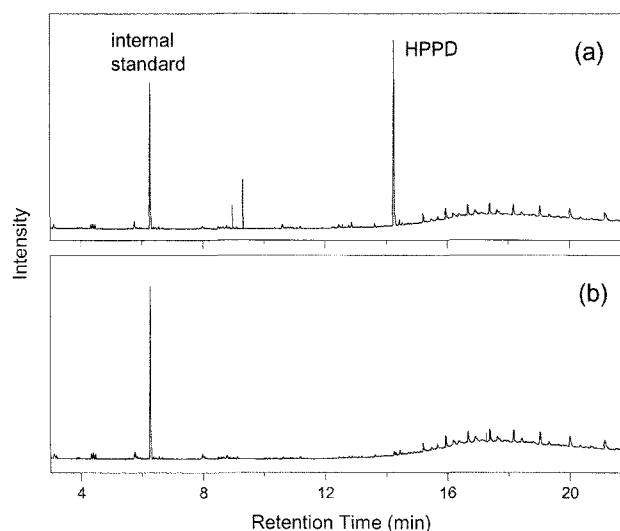


Figure 5. GC chromatogram of the organic materials extracted with THF from the NR composite with the conventional cure system thermally aged for 5 (a) and 35 (b) days at 90 °C.

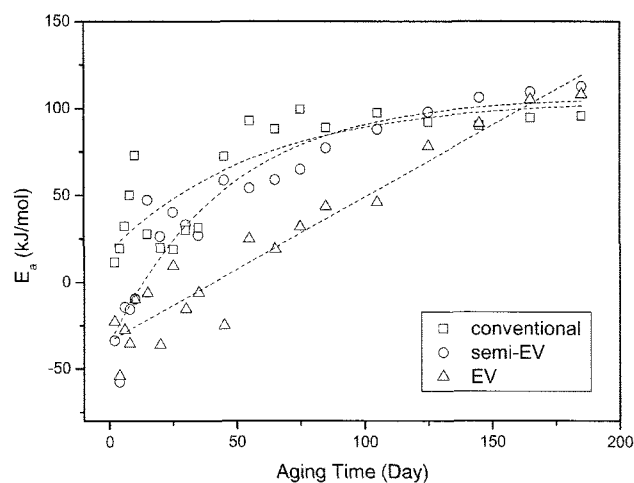


Figure 6. Variations of the activation energy for the crosslink density changes by thermal aging as a function of the aging time. The squares, circles, and triangles indicate the conventional, semi-EV, and EV cure systems, respectively.

aging time. The activation energies vary with the aging time. 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. The activation energy on the whole tends to increase with increasing the aging time but the curves show local minima. The local minimum in the activation energy variation was reported in the previous work.¹⁷ Activation energies of the specimens with the conventional and semi-EV cure systems increase until 105 days and then reach to plateau state whereas that with the EV cure system linearly increases until 165 days. The activation energy of specimen with the EV cure system

was lower than those with the conventional and semi-EV cure systems.

Conclusions

Crosslink densities of the NR composites with different cure systems increased as the aging time elapsed irrespective of the aging temperatures and cure systems. Variations of the crosslink density changes of the specimens aged at relatively low temperatures for short time within 30 days showed a local minimum. This implied that dissociation of the existing crosslinks exceeded over formation of new crosslinks around the local minimum point. Crosslink density change of the specimen with the conventional cure system was larger than those with the semi-EV and EV ones except the thermal aging at 90 °C for over 145 days and that with the semi-EV cure system was larger than that with the EV one. For the thermal aging at high temperature for long time, the crosslink density did not enhance any more since most of free organic materials including the curatives and their residues were evaporated. The activation energy of specimen with the EV cure system was lower than those with the conventional and semi-EV ones. Difference in the crosslink density changes of the NR composites with the different cure systems were explained with the crosslinking-related chemicals such as zinc complexes, curative residues, sulfur, and so on remaining in the sample and their evaporation by heating.

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