Influence of Thermal Aging on Change of Crosslink Density and Deformation of Natural Rubber Vulcanizates

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Crosslink is the most important chemistry in a rubber vulcanizate. Degree and type of crosslinks of the vulcanizate determine its physical properties. Change of crosslink density and deformation of a rubber vulcanizate by thermal aging were studied using natural rubber (NR) vulcanizates with various cure systems (conventional, semi-EV, and EV) and different cure times (under-, optimum-, and overcure). All the NR vulcanizates were deformed by the thermal aging at 60-100 °C. The higher the aging temperature is, the more degree of the deformation is. The undercured NR vulcanizates after the thermal aging were deformed more than the optimum- and overcured ones. The NR vulcanizates with the EV cure system were less deformed than those with the conventional and semi-EV cure systems. The deformation of the NR vulcanizates was found to be due to change of the crosslink density of the vulcanizates. The crosslink densities of all the vulcanizates after the extraction of organic materials were also changed by the thermal aging. The sources to change the crosslink densities of the vulcanizates by the thermal aging were found to be dissociation of the existing sulfur crosslink and the formation of new crosslinks by free sulfur, reaction products of curing agents, and pendent sulfide groups.

Introduction

Tires loaded by a vehicles for long periods of time in high temperature (for example, hot summer) have *flatspots* that do not come out with driving. Ohta and coworkers studied the influence of tire deformation on ride comfort of a truck.[1] They reported that the vibration of the vehicle with flatspotted tires is caused mainly by the 2nd-order and the 3rd-order deformations. While these problems are sometimes associated with nylon capped speed rated tires, it has been shown that the nylon is not the only source of the flatspots. Another source is permanent set or compression in the tread rubber.[2]

In general, rubber compounds are crosslinked by sulfur vulcanization,[3-5] peroxide curing,[6] or resole curing.[7] The sulfur vulcanization is the most popular. The mechanical properties of rubber materials are improved by vulcanization. S-S and C-S bonds made by sulfur curing are relatively unstable. Especially, polysulfides are more unstable than mono- and disulfides.[8] Thus, the sulfur curing at high temperatures deteriorates the mechanical properties of rubbers due to reversion. Physical properties of sulfur-cured rubber vulcanizates are dependent on their crosslink densities.[3]

In the present work, change of crosslink density and deformation of sulfur-cured NR vulcanizates by thermal aging depending on their initial crosslink conditions were studied. The deformation experiments were performed by changing a linear sample to a circular form to show degree of the deformation. Thermal aging experiments of the vulcanizates before and after extraction of the organic materials from the vulcanizates were performed to investigate the sources to cause the deformation in detail. There are various organic materials such as curatives, antidegradants, and vulcanizing products in a rubber vulcanizate. It can be considered that these materials affect the change of the crosslink density. Behaviors of the vulcanizing products remaining in the vulcani-

zates were also calculated by the molecular mechanics and molecular dymanics to explain the crosslink density change by the thermal aging.

Experimental Section

Sample preparation. Nine carbon black-filled NR vulcanizates with three cure systems (conventional, semi-EV, and efficient vulcanization (EV)) and three cure times (3, 6, and 20 min) were prepared. Table 1 gives formulations of the NR compounds with the conventional, semi-EV, and EV cure systems. The conventional cure system is a vulcanizing system with very low accelerator ratio while the EV cure system is one with very high ratio of accelerator. The semi-EV cure system is a vulcanizing system with the nearly same ratios of sulfur and accelerator. Wax and *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD) were added to the compounds as antidegradants. *N-tert*-Butyl-2-benzothia-

Table 1. Formulations (phr) and cure characteristics

Compound	Conventional	Semi-EV	EV
SMR 20	100.0	100.0	100.0
N330	50.0	50.0	50.0
ZnO	5.0	5.0	5.0
Stearic acid	3.0	3.0	3.0
Wax	3.0	3.0	3.0
HPPD	3.0	3.0	3.0
TBBS	0.6	1.2	2.5
Sulfur	2.8	1.2	0.6
Cure Characteristics at 160 °C			
Delta Torque (N · m)	3.09	2.27	2.29
t_5 (min)	1.10	1.55	1.53
t_{40} (min)	1.57	3.02	3.42
t_{95} (min)	6.17	5.40	6.95

zole sulfenamide (TBBS) was used as a cure accelerator. Cure characteristics of the compounds were obtained using a Flexsys rheometer (MDR 2000) at a frequency of 100 cycles/min and ±1.5 arc at 160 °C. Cure characteristics of the NR compounds were also listed in Table 1.

Vulcanization was carried out at 160 °C for 3, 6, and 20 min. The cure time of 6 min is close to optimum cure condition. The cure times of 3 and 20 min correspond to under- and overcure conditions, respectively. The cure time of 3 min for the conventional, semi-EV, and EV cure systems corresponds to t_{45}, t_{40}, and t_{30}, respectively. Reversion ratios at 20 min of cure time for the conventional, semi-EV, and EV cure systems are about 17, 4, and 3%, respectively.

Deformation experiment. The deformation experiments were carried out as follow (Figure 1): First, samples were cut with dimension of 5 × 100 mm with 2 mm thickness. Second, the linear sample was changed to a circular form by fixing the both ends with a pin. Third, the samples with the circular form were thermally aged at 60, 80, and 100 °C for 5 days in a convection oven. Finally, removing the pin and the gap-distance between both ends of the sample was measured after 2 days. Crosslink densities of the samples before and after the thermal aging were measured.

Thermal aging of the extracted samples. Extracted vulcanizates were prepared by extraction of organic materials from the vulcanizates with THF/acetone (1 : 1) and acetone for each 3 days and drying for 3 days at room temperature. Dimensions of the samples were 50 × 10 mm with 2 mm thickness. Experiments were carried out at 40 and 80 °C for 5 days in a convection oven. Crosslink densities of the samples before and after the thermal aging were measured.

Chemical analysis. The procedure to measure the crosslink density as follow. First, the samples were cut with about 5 × 10 mm. Second, 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. Third, the weights of the organic material-extracted samples were measured. Fourth, they were soaked in *n*-decane for 1 day and the weights of the swollen samples were measured. Finally, the crosslink density was calculated. The χ (interaction parameter between the natural rubber network and the swelling agent, *n*-decane) of 0.43[9], the density of the rubber network of 0.93, and the molar volume of n-decane of 194.9 ml/mol were employed.

Contents of free sulfur components in the NR 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[10] for each 3 days. Sulfur contents in the NR vulcanizates were obtained with sulfur determinator (LECO SC-132). Contents of TBBS and mercaptobenzothiazole (MBT) remaining in the vulcanizates were analyzed with gas chromatography. MBT is produced by dissociation of TBBS.[11]

Molecular simulation. Intermolecular interactions between polyisoprene network crosslinked by disulfide and MBT were calculated by molecular mechanics and molecu-

lar dynamics. Intermolecular interactions between two polyisoprenes having the pendent sulfide group terminated by MBT were also calculated. The initial structures of those molecules were generated by the *Insight II* package and molecular dynamics and molecular mechanics were performed using the *Discover* of MSI. We used one of the parameter sets, CFF91 force field. Potential cutoff distance of 10.0 Å and dielectric constant of 2.94 (vulcanized Hevea) were employed. The model rubber (*cis*-1,4-polyisoprene) was composed of 30 repeat units.

The interactive structure of polyisoprene network crosslinked by a disulfide and MBT was calculated as follows. First, two model rubbers were linked with disulfide at the center of the molecules. Second, the crosslinked rubber and MBT were assembled into one system under constrained conditions to prevent MBT from separating from the rubber chain. The constraint condition was artificial bonding potential possesing 1,000 N/cm of force constant and 5 Å of equilibrium distance between -SH of MBT and the disulfide linkage. Third, the system with constrained conditions was calculated by minimization after molecular dynamics at 900 K for 10 ps and this process was performed by 30 times. The most stable system was obtained from the 30 conformers. Finally, the most stable system was reminimized without constrained conditions.

The interactive structure of two polyisoprenes having the pendent sulfide group terminated by MBT was calculated as follows. First, the pendent groups (-S-MBT) was linked to the model rubber at the center of the rubber and two polyisoprenes having the pendent group were assembled into one system under constrained conditions to prevent separating from each other. The constrained conditions applied between both the pendent groups were 5 Å of distance and 1,000 N/cm of force constant. Second, the system with constrained conditions was calculated by minimization after molecular dynamics at 900 K for 10 ps and this process was performed by 30 times. The most stable system was obtained from the 30 conformers. Finally, the most stable system was reminimized without constrained conditions.

Results and Discussion

Degree of deformation. Usually rubber vulcanizates under small deformation at ambient temperature can return to the original position with ease. If the vulcanizate is deformed permanently, it is hard to return to the original position. The experiments were performed 1 month after the vulcanization to stabilize the vulcanizates. In this study, experiments were carried out by changing the shape of a sample from a linear form to a circular one as shown in Figure 1. After the thermal aging and unfixing, the circularly deformed sample did not return to the linear shape irrespective of the cure conditions. The deformed samples were stretched in order to return to the linear form but never returned to the original condition. Figure 2 shows the permanently deformed vulcanizates with the EV cure system after the thermal aging at 80 °C. The gap-distances between both ends of the deformed
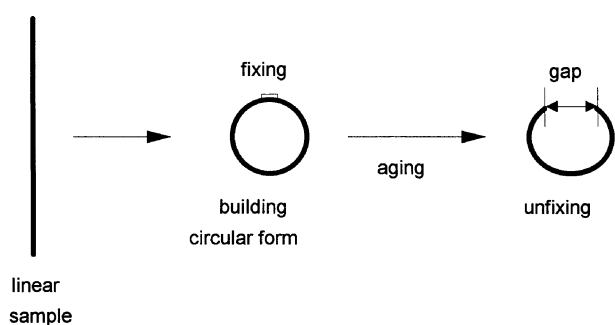
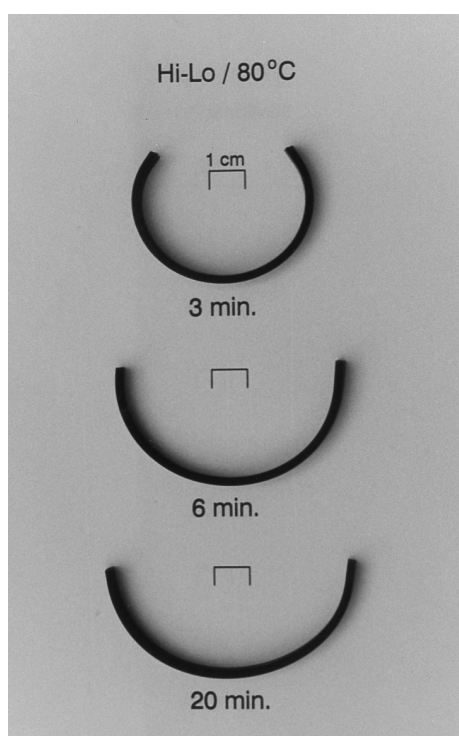**Figure 1**. Process of the deformation experiment.

Figure 2. Shapes of the deformed NR vulcanizates with the EV cure system after the thermal aging at 80 °C for 5 days.

samples were measured to investigate degree of the deformation. The gap-distances of the NR vulcanizates after the thermal aging at 60, 80, and 100 °C for 5 days were summarized in Table 2. The gap-distances reflect degree of the deformation. That is, the deformed sample with a short gap-distance is more deformed than that with a long one. The gap-distances of the undercured vulcanizates are much shorter than those of the optimum- and overcured ones. This means that the undercured vulcanizates are more deformed than the optimum- and overcured ones.

The gap-distances become shorter notably by increasing the temperature from 60 to 100 °C. The gap-distances of the vulcanizates with the conventional cure system are slightly longer than those with the semi-EV or EV cure system when the aging temperature is 60 °C. At 80 and 100 °C, the gap-distances of the vulcanizates with the conventional cure system are shorter than those with the semi-EV or EV one. The gap-distances of the vulcanizates with the semi-EV cure sys-

Table 2. Gap-distances of the deformed samples after the thermal aging for 5 days (mm)

Cure system/time	60 °C	80 °C	100 °C
Conventional/undercured	68	32	10
Conventional/optimum-cured	83	50	11
Conventional/overcured	83	53	14
Semi-EV/undercured	66	35	16
Semi-EV/optimum-cured	80	52	21
Semi-EV/overcured	83	56	23
EV/undercured	67	36	16
EV/optimum-cured	79	60	34
EV/overcured	80	66	42

tem are shorter than those with the EV one. The optimum- and overcured NR vulcanizates with EV cure system are much less deformed than the others at the high temperatures.

In order to investigate the source to cause the permanent deformation of the NR vulcanizates by the thermal aging, variation of crosslink densities (X_c) of the NR vulcanizates before and after the thermal aging were measured. The results were summarized in Table 3. The X_c of the optimum-cured vulcanizates before and after the thermal aging are, on the whole, higher than those of the under- and overcured ones. The X_c of the vulcanizates with the conventional cure system after the thermal aging increase under the experimental conditions, irrespective of cure times. The X_c of the vulcanizates with the conventional cure system after the thermal aging become higher by increasing the aging temperature. The X_c of the undercured vulcanizates with the semi-EV and EV cure systems after the thermal aging also increase as similar to the vulcanizates with the conventional cure system. But the X_c of the optimum- and overcured vulcanizates with the semi-EV and EV cure systems decrease after the thermal aging. This may be due to the low content of free sulfur in the optimum- and overcured vulcanizates with the semi-EV and EV cure systems.

Influence of curing agents that remained in the vulcanizates. In order to investigate the sources to change the crosslink density by the thermal aging, contents of free curing agents that remained in the vulcanizate were analyzed. Table 4 gives contents of free sulfur components, TBBS, and MBT in the vulcanizates. The free sulfur components include

Table 3. Crosslink densities, X_c, of the NR vulcanizates after the thermal aging for 5 days (10^{-3} g · mol /mL)

Cure system/time	non-aging	60 °C	80 °C	100 °C
Conventional/undercured	1.763	3.278	3.505	4.347
Conventional/optimun-cured	4.168	5.034	5.244	6.009
Conventional/overcured	3.416	4.094	4.136	5.654
Semi-EV/undercured	1.783	2.987	3.219	3.991
Semi-EV/optimun-cured	4.215	3.673	3.695	3.561
Semi-EV/overcured	3.455	2.988	3.076	2.876
EV/undercured	1.777	2.500	2.749	3.064
EV/optimun-cured	4.199	3.477	3.391	3.700
EV/overcured	3.442	3.297	3.225	3.276

free sulfur and sulfur-containing chemicals such as TBBS and MBT. Amount of the extracted sulfur from the under-cured vulcanizates are more than those from the optimum- and overcured ones. The free sulfur component in the vulca-nizates with the conventional cure system is more abundant than those in the vulcanizates with the semi-EV and EV cure systems.

The free TBBS was also detected in the vulcanizates by 0.02-0.19 wt%. Content of the free TBBS in the vulcanizate which has a high initial content of TBBS is more than that in the vulcanizate which has a low initial content of TBBS. The free TBBS contents in the optimum- and overcured vulcani-zates with the EV cure system are 0.18 and 0.19 wt%, respectively, which correspond to more than 10% of the ini-tial TBBS content. Since cure accelerators are very reactive and thermally unstable, it was interesting that there were some TBBS in the vulcanizate after curing. In general, cure accelerators having a chemical structure of benzothiazolyl-sulfenamide are so reactive that most of them are changed into reaction products such as zinc complex, MBT, the counter amine, and so forth.[3,11,12] Thus, the free TBBS in the vulcanizates is not an unreacted TBBS but may be a recom-bined product of benzothiazole and amine groups. Hann and coworkers[13] analyzed contents of TBBS in a polyisoprene vulcanizate at 140 °C depending on time and reported that content of the free TBBS in it increased until cure time of 30 min and then decreased. Contents of the free sulfur in the vulcanizates decrease as the cure time increases. Degree of the deformation of the NR vulcanizates and the increase of the crosslink density by the thermal aging can be well explained by the free sulfur in the vulcanizates. 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. Layer[4] studied cure characteristics of rubber vulcanizates which a curative (sul-fur, cure accelerator, or zinc complex) is added by swelling and reported that the delta-torque (crosslink density) of the vulcanizates after adding a curative increased.

For the vulcanizates with the semi-EV and EV cure sys-tems, the X_c of the undercured vulcanizates after the thermal aging increase while those of the optimum- and overcured ones decrease. On the other hand, the X_c of the vulcanizates with the conventional cure system after the thermal aging increase irrespective of cure times. This may be because the free sulfur is rich in the vulcanizates with the conventional cure system. The optimum- and overcured vulcanizates with the semi-EV and EV cure systems have few free sulfur by less than 0.1 wt% as listed in Table 4. Sulfur portion of TBBS and MBT was included in the total sulfur contents. Thus, pure contents of free sulfur in the optimum- and over-cured vulcanizates with the semi-EV and EV cure systems are less than 0.05 wt%. Although the optimum- and over-cured vulcanizates with the EV cure system have a few TBBS by about 0.2 wt%, the X_c decrease after the thermal aging. Thus, the experimental results can lead to a conclu-sion that a principal source to increase the X_c by the thermal aging is the free sulfur not TBBS.

Table 4. Contents of free curing agents that remained in the NR vulcanizates (wt%)

Cure system/time	extracted sulfur[a]	TBBS[b]	MBT[b]
Conventional/undercured	1.26	0.03	0.03
Conventional/optimum-cured	0.16	0.02	0.02
Conventional/overcured	0.08	0.02	0.01
Semi-EV/undercured	0.42	0.05	0.09
Semi-EV/optimum-cured	0.06	0.09	0.04
Semi-EV/overcured	0.06	0.08	0.03
EV/undercured	0.19	0.13	0.08
EV/optimum-cured	0.06	0.18	0.07
EV/overcured	0.06	0.19	0.06

[a]Data were obtained by analysis with sulfur determinator. [b]Data were obtained by analysis with gas chromatography.

Comparison of extracted and unextracted vulcani-zates. In order to investigate the influence of the organic materials and the pendent sulfide groups in the vulcanizates on change of the X_c by thermal aging, the thermal aging of the vulcanizates before and after the extraction was per-formed at 40 and 80 °C and the results were compared. This experiment was performed after about 6 months from the curing. Tables 5 and 6 give the experimental results for the thermal aging at 40 and 80 °C, respectively. The results show that the X_c of all the NR vulcanizates are changed by the thermal aging even at 40 °C. The initial X_c measured after 6 months from the vulcanization are different those measured after 1 month as shown in Tables 3 and 5. It is interesting that the X_c of the vulcanizates are changed during the storage at room temperature.

The experimental results for the thermal aging at 40 °C of the vulcanizates before and after extraction are very different as shown in Table 5. The X_c of the unextracted vulcanizates after the thermal aging at 40 °C decrease by about 1-10% except the undercured vulcanizate with the conventional cure system. The increase of the X_c of the undercured vulca-nizate with the conventional cure system may be due to the rich free sulfur in the vulcanizate as discussed previously. The change of the X_c by the thermal aging at the low temper-ature of 40 °C is a very interesting fact because the thermal energy of 40 °C is not enough to dissociate the existing S-S

Table 5. Crosslink densities, X_c, $(10^{-3}$ g · mol/mL) of the extracted and unextracted NR vulcanizates before and after thermal aging at 40 °C for 5 days

Cure system/time	Initial	Unextracted	Extracted
Conventional/undercured	2.297	2.405	2.369
Conventional/optimum-cured	3.951	3.890	4.256
Conventional/overcured	3.584	3.501	3.851
Semi-EV/undercured	2.434	2.238	2.680
Semi-EV/optimum-cured	2.814	2.789	3.058
Semi-EV/overcured	2.706	2.614	2.931
EV/undercured	1.401	1.345	1.689
EV/optimum-cured	2.864	2.749	3.009
EV/overcured	2.882	2.762	3.026

Table 6. Crosslink densities, X_c, (10^{-3} g · mol/mL) of the extracted and unextracted NR vulcanizates before and after thermal aging at 80 °C for 5 days

Cure system/time	Initial	Unextracted	Extracted
Conventional/undercured	2.297	2.757	2.464
Conventional/optimum-cured	3.951	4.845	5.363
Conventional/overcured	3.584	4.276	4.384
Semi-EV/undercured	2.434	3.329	2.916
Semi-EV/optimum-cured	2.814	3.298	3.243
Semi-EV/overcured	2.706	2.822	2.953
EV/undercured	1.401	1.974	2.697
EV/optimum-cured	2.864	3.214	3.332
EV/overcured	2.882	2.957	3.042

bond in the vulcanizates or form new crosslinks. The bond dissociation energy of S-S bond of polysulfides in a NR vulcanizate is higher than 170 kJ/mol.[8] The decrease of the X_c by the thermal aging at 40 °C may result from the dissociation of the existing S-S crosslinks in the vulcanizate. Thus, it can be considered that the organic additives and vulcanizing products in the vulcanizates accelerate the dissociation of the existing sulfur crosslinks so that the X_c of the vulcanizates decrease even at the low temperature of 40 °C. The vulcanizing products are formed by reactions of zinc oxide, fatty acids, sulfur, and cure accelerator. The major vulcanizing products are zinc complex and MBT.[12,14,15] The vulcanization products and HPPD may make 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 weaken by the hydrogen bond with the polar chemicals. The polysulfide bridges can be dissociated by reaction with a nucleophile. The reactions of polysulfide with nucleophile were studied by several groups.[16-19] Amines[16,17] and phosphines[18,19] react with polysulfides so that amine (or phosphine)-sulfur complexes are formed. The nucleophiles such as HPPD, MBT, and stearic acid attack the sulfide bridge so that the sulfide bridge can be dissociated (Scheme 1).
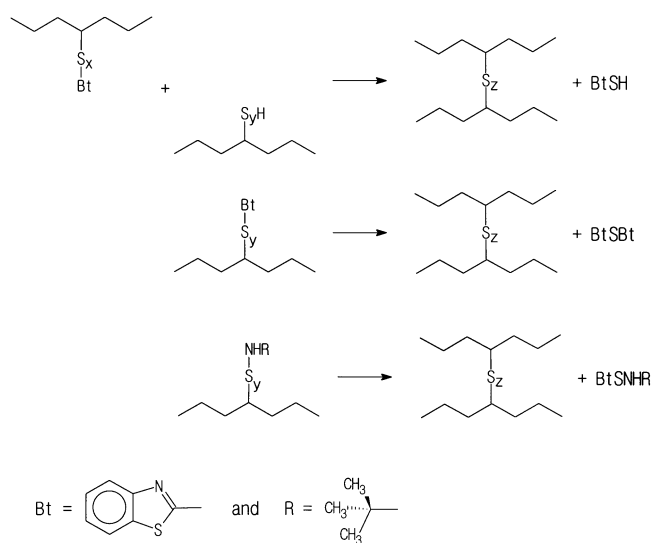
Figure 3 shows the interactive structure between MBT and

Nu: =

$CH_3(CH_2)_{16}CO_2H$

Zinc Complex
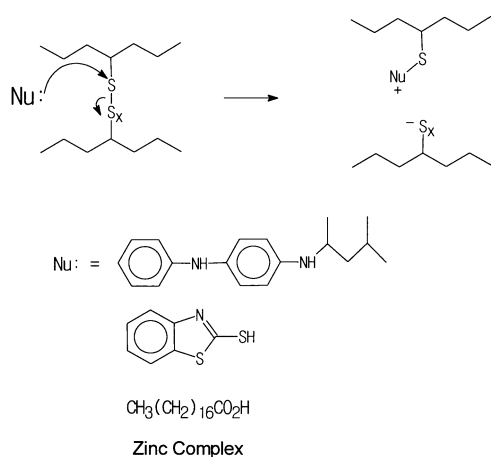
Scheme 1
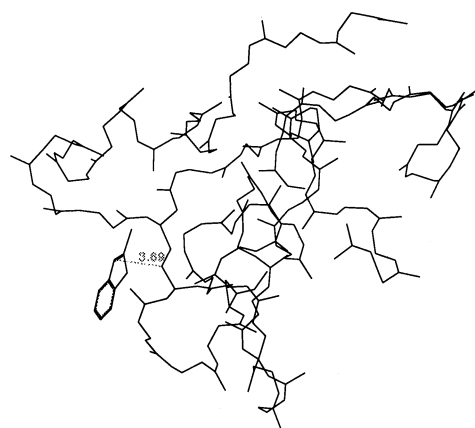
Figure 3. The interactive structure between MBT and disulfide crosslink of NR vulcanizate, which was obtained by the molecular simulation. Nitrogen atom of MBT forms hydrogen bond with the disulfide linkage. The distance of the hydrogen bond is 3.69 Å.

disulfide crosslink of NR vulcanizate, which was obtained by the molecular simulation. Nitrogen atom of the MBT forms a hydrogen bond with the disulfide linkage. The distance of the hydrogen bond is 3.69 Å. The partial charge of nitrogen atom of the MBT is -0.499 and those of sulfur atoms of the disulfide linkage are 0.050. The S-S bond of the disulfide linkage may weaken by the hydrogen bond with MBT and the dissociation of the S-S bond will be accelerated.

Though there are no organic materials, especially sulfur, in the extracted vulcanizates, the X_c of the extracted vulcanizates after the thermal aging at 40 °C increase by 1-20%, irrespective of the cure conditions, as shown in Table 5. This suggests that the source to increase the X_c of the vulcanizates by the thermal aging at 40 °C is not only organic chemicals in the vulcanizates. The increase of the X_c of the extracted vulcanizates by the thermal aging can be expalined by the combination reactions between the pendent groups terminated by the curative residues. TBBS is dissociated into MBT and t-butylamine radicals by heating at the beginning of vulcanization.[20] The [MBT-H] radical will become the neutral MBT by abstraction of a hydrogen atom from a rubber chain, a zinc complex by bonding with zinc ion,[4,21] or a pendent group by pending to a rubber chain.[22-24] The t-butylamine radical will become the neutral amine by abstraction of a hydrogen atom from a rubber chain or a pendent group formed by pending to a rubber chain.[23] The pendent sulfide groups terminated by an accelerator residue were studied by several groups.[25-27] The pendent MBT reacts with another pendent group of the neighboring rubber chains so a new crosslink will be formed as shown in Scheme 2.[22,23] The pendent amine also can react with the pendent MBT to form a new crosslink.[22] Thus, it can lead to a conclusion that the principal source to increase the X_c of the extracted vulcanizates by the thermal aging at 40 °C is the combination reaction of the pendent groups.

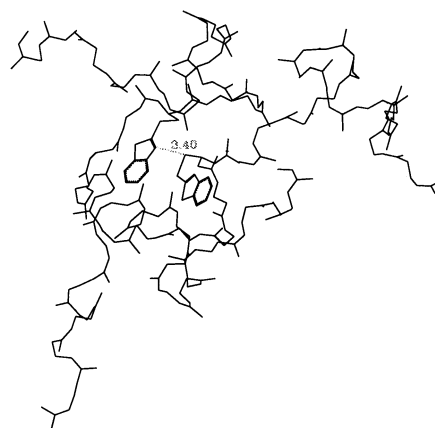One pendent sulfide group terminated by the accelerator residue should be close to the other one to occur the combi-

Scheme 2

Figure 4. The interactive structure between two polyisoprene rubber chains having the sulfide pendent group terminated by MBT, which was obtained by the molecular simulation. Hydrogen bonds are formed between nitrogen atom of the pendent MBT and disulfide of the pendent sulfide groups. The distance of the hydrogen bond is 3.40 Å.

nation reaction. In order to investigate intermolecular interactions between the pendent groups, the interactive structure between two polyisoprene rubber chains having the pendent sulfide group terminated by MBT was calculated. Figure 4 gives the interactive structure obtained by the molecular simulation. Hydrogen bonds between the pendent groups are formed. The partial charge of nitrogen atom of the pendent MBT is -0.499 while those of sulfur atoms linked to rubber chain and the pendent MBT are 0.050 and -0.028, respectively. Nitrogen atom of the pendent MBT of one rubber chain forms hydrogen bond with sulfide linkage of the other rubber chain. The distance of the hydrogen bond is 3.40 Å. Thus, the new crosslink can be formed by the combination reaction of the pendent groups since the distance between the pendent groups become close by the hydrogen bond.

It may be hard that the combination reactions of the pendent sulfide groups occur in the unextracted vulcanizate because of hindrance by the polar materials. Since, in the unextracted vulcanizates, the pendent sulfide groups terminated by an accelerator residue (MBT or *t*-butylamine) are binding with the polar unbound materials by intermolecular interactions such as a hydrogen bond, the pendent groups will be surrounded with the polar materials. Thus, a pendent group can not meet another pendent group by inhibition of the polar chamicals so the combination reactions can not occur in the unextracted vulcanizates.

The whole trend about the experimental results for the thermal aging at 80 °C of the vulcanizates before and after extraction are similar. The X_c of all the vulcanizates, both the extracted and unextracted ones, after the thermal aging at 80 °C increase by 3-99%. For the thermal aging at 80 °C of the unextracted vulcanizates with the conventional cure system, degree of the X_c change of the three vulcanizates by the thermal aging at 80 °C is nearly same, irrespective of the cure times, as listed in Table 6 (20-30% increase), although the contents of free sulfur in the vulcanizates are very different. This means that the other factors as well as free sulfur content and organic materials in the vulcanizate affect an increase

of the X_c by the thermal aging at 80 °C. The another factor may be considered to be polysulfide crosslinks which is easily dissociated by heating. The dissociated sulfur radicals will make new crosslinks. The vulcanizate with the conventional cure system has a high ratio of polysulfide crosslinks.

For the thermal aging at 80 °C of the extracted vulcanizates with the conventional cure system, the X_c of the optimum- (about 36-37%) and overcured vulcanizates (about 22-28%) after the thermal aging increase much larger than those of the undercured one (about 7%). This can be explained by the pendent sulfide groups terminated by an accelerator residue and cyclic sulfides. By increasing the cure time until the optimum cure (about t_{95}), amounts of the pendent sulfide groups and cyclic sulfides increase in the vulcanizate. The major sources to increase the X_c of the extracted vulcanizates by the thermal aging are the pendent sulfide groups and cyclic sulfides. Thus, the increments of the X_c of the optimum- and overcured vulcanizates with high contents of the pendent sulfide groups and cyclic sulfides are larger than those of the undercured vulcanizate with low contents of them.

For the optimum- and overcured vulcanizates, the X_c of the extracted vulcanizates after the thermal aging at 80 °C are higher than those of the unextracted ones except the optimum-cured vulcanizates with the semi-EV cure system. This means that some organic materials of HPPD, MBT, stearic acid, and TBBS remaining in the vulcanizate inhibit the formation of new crosslinks or activate the dissociation of the existing crosslinks as discussed previously. For the undercured vulcanizates, the X_c of the extracted vulcanizates with the conventional and semi-EV cure systems after the thermal aging at 80 °C are lower than those of the unextracted ones, while the X_c of the extracted vulcanizate with the EV cure system is lower than that of the unextracted one. This can be explained by the free sulfur content. The initial sulfur contents of the vulcanizates with the conventional and semi-EV cure systems are much higher than that of the vul-

canizate with the EV cure system by over two times.

Conclusion

Degree of the deformation increases with an increase of the aging temperature. The vulcanizates with the high monosulfide crosslinks (the EV cure system) were less deformed than the low ones (the conventional and semi-EV cure systems). The permanent deformation of the vulcanizate is due to the change of the crosslink density. The sources to cause the change of the crosslink density are the dissociation of the existing sulfur crosslinks and the formation of new crosslinks. The new crosslinks are formed by the reaction of curing agents remaining in the vulcanizates and the combination reaction of the pendent sulfide groups. The crosslink densities of all the extracted vulcanizates after the thermal aging at 40 °C increase but those of the unextracted ones decrease except the undercured vulcanizate with the conventional cure system. Polar chemicals in the vulcanizate inhibit the formation of new crosslinks or activate the dissociation of the existing crosslinks. The crosslink densities of all the extracted and unextracted vulcanizates after the thermal aging at 80 °C increase. The principal source to increase the crosslink densities in the extracted vulcanizates by the thermal aging is the combination reaction of the pendent sulfide groups terminated by an accelerator residue.

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