Influence of Rubber Composition on Change of Crosslink Density of Rubber Vulcanizates with EV Cure System by Thermal Aging

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ABSTRACT: Variation of the crosslink density of a rubber vulcanizate depending on the rubber composition after the thermal aging was studied with single rubber, biblend, and triblend vulcanizates of natural rubber (NR), butadiene rubber (BR), and styrene-butadiene rubber (SBR). The efficient vulcanization (EV) system was employed to minimize the influence of free sulfur in the vulcanizate on the change of the crosslink density. Thermal aging was performed at 40, 60, and 80°C for 20 days with 5-day intervals. The crosslink densities of the vulcanizates after the thermal aging increase. For the single rubber vulcanizates, variation of the crosslink density by the thermal aging has the order: SBR > BR > NR. For the biblend vulcanizates, variations of the crosslink densities of the NR/SBR and SBR/BR blends are larger than that of NR/BR blend. Variation of the crosslink density of the vulcanizate increases by increasing the SBR content in the vulcanizate. Variation of the crosslink density of the rubber vulcanizate depending on the rubber composition was explained by miscibility of the blends, combination reaction of the pendent groups, and mobility of the pendent group. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1378–1384, 2000

Key words: crosslink density; rubber vulcanizate; rubber composition; pendent group

INTRODUCTION

In general, rubber compounds are crosslinked by sulfur vulcanization,[1–3] peroxide curing,[4] or resole curing.[4] The sulfur vulcanization is the most popular method in a tyre industry. 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 buildup, and so forth.[1] 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 resistance decrease.[1]

Sulfide linkages, especially polysulfides, are dissociated by heating[5,6] and this brings about decrease of the crosslink density. Curatives, especially sulfur, in rubber vulcanizates make new crosslinks[7] and this result in increase of the crosslink density. Blends of elastomers[8–12] are employed in rubber products for a variety of reasons that include improved physical properties, increased service life, easier processing, and reduced product cost. In this study, the influence of rubber composition on change of the crosslink density of rubber vulcanizates of natural rubber (NR), styrene–butadiene rubber (SBR), and butadiene rubber (BR), including single rubber, biblend, and triblend vulcanizates, was investi-

Table I   Formulations (phr)

Compound No.	1	2	3	4	5	6	7	8	9
SMR 20 (NR)	100.0	0.0	0.0	50.0	50.0	0.0	40.0	40.0	20.0
SBR 1500	0.0	100.0	0.0	50.0	0.0	50.0	40.0	20.0	40.0
BR 01	0.0	0.0	100.0	0.0	50.0	50.0	20.0	40.0	40.0
N330 carbon black	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Wax	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
IPPD[a]	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
HPPD[a]	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
ZnO	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
TBBS[a]	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
Sulfur	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6

[a] IPPD: *N*-phenyl-*N'*-isopropyl-*p*-phenylenediamine;   HPPD: *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine;   TBBS: *N*-*tert*-Butyl-2-benzothiazole sulfenamide.

gated. The efficient vulcanization (EV) system was employed as a cure system to minimize the influence of free sulfur in the vulcanizate on the change of the crosslink density and to investigate the other source, except the free sulfur and polysulfide crosslinks, to change the crosslink density. In order to explain the variation of the crosslink density of the vulcanizates depending on the rubber composition, mobility of the sulfide pendent group terminated by an accelerator residues was calculated using molecular simulation.

EXPERIMENTAL

Nine vulcanizates including three single rubber vulcanizates, three biblend ones, and three triblend ones of NR, SBR, and BR were prepared. Rubber compositions of the biblends are 50/50 NR/SBR, NR/BR, and SBR/BR and those of the triblends are 40/40/20, 40/20/40, and 20/40/40 NR/SBR/BR. These compounds had the EV cure system, which is a vulcanizing system with a low sulfur and a high accelerator content. The vulcanizate cured by the EV cure system has a low polysulfide and high mono- and disulfides. Table I gives formulations of the compounds. Vulcanization was carried out at 160°C for 20 min.

Experiments were carried out at 40, 60, and 80°C for 5, 10, 15, and 20 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 was calculated: $Q = 100 \times (W_s - W_u)/W_u$, where W_s and W_u are weights of the swollen and unswollen samples. The reciprocal swelling value, $1/Q$, was used as crosslink density.[13] Experiments were carried out three times and averaged. Sulfur contents in the vulcanizates were obtained with a sulfur determinator (LECO SC-132).

In order to investigate the mobility of the sulfide pendent group terminated by the accelerator residue, rubber chains having the pendent group were calculated by molecular mechanics and molecular dynamics. 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)[14] were employed.

The model BR, *cis*-1,4-polybutadiene, was composed of 30 repeat units. The model SBR was composed of 26 butadienes (*cis*-1,4-polybutadiene) and 4 styrenes that were located between (butadiene)$_5$ to meet 23 wt % styrene content of emulsion SBR. The model SBR had the sequence of B_5-S-B_5-S-B_5-S-B_5-S-B_6, where B and S indicate butadiene and styrene units, respectively. The sulfide pendent group was located at the center of the model rubber.

The energy-minimized structures of the rubber chains having the pendent group were obtained by conformational search. The conformational

search was done by the annealing technique consisting of 300 ps molecular dynamics at 900 K and 30 times sampling for further minimizations. With the lowest energetic conformation among 30 conformers, molecular dynamic simulations were performed at 333 K for 1000 ps to investigate the mobility of the pendent in the rubber chain. Average geometry of the each molecule was obtained by averaging the 1000 ps dynamic fluctuation.

RESULTS AND DISCUSSION

Single Rubber Vulcanizates

Figure 1 gives variation of the $1/Q$ of the NR, SBR, BR vulcanizates as a function of the aging time. The variation of the $1/Q$ was calculated by dividing the difference of the $1/Q$ of the vulcanizate after and before the thermal aging by the $1/Q$ before the thermal aging. The $1/Q$ of the NR and BR vulcanizates after the thermal aging at 40°C within 20 days keep the initial condition (the variation is less than 1%). Variation of the $1/Q$ of the SBR vulcanizate after the thermal aging at 40°C for 20 days is about 2.5%. The $1/Q$ of the BR and SBR vulcanizates by the thermal aging at 60°C
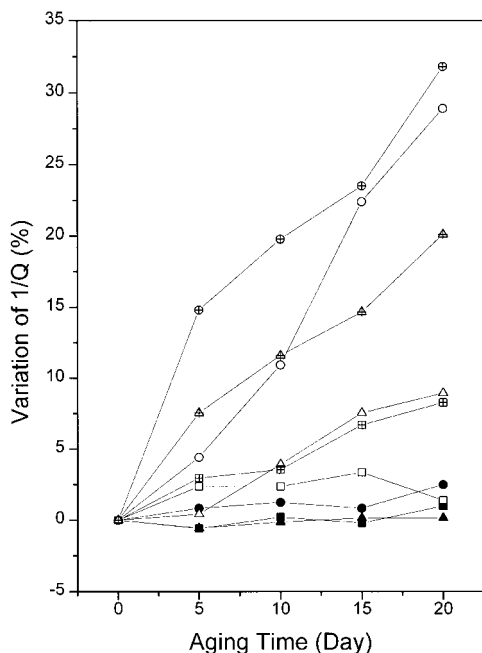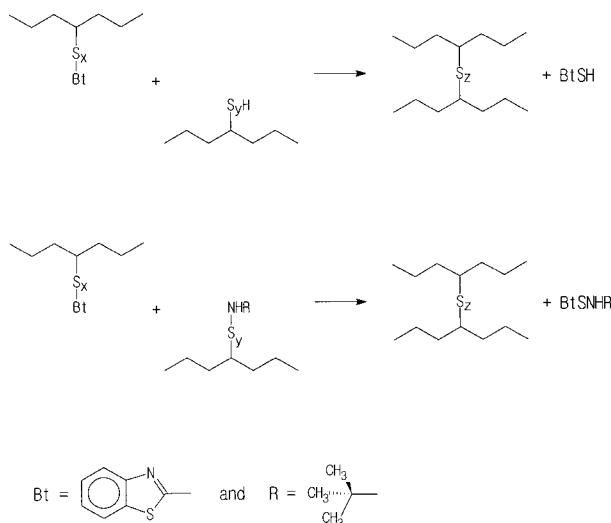

Figure 1 Variation of the crosslink density of the single vulcanizates after the thermal aging. Squares, circles, and triangles stand for the NR, SBR, and BR vulcanizates, respectively. Solid, open, and crossed symbols indicate 40, 60, and 80°C, respectively.

Table II   Sulfur Contents in the Rubber Vulcanizates (wt %)

Compound No.	Before Extraction	After Extraction	Free Sulfur
1	0.939	0.713	0.226
2	0.954	0.769	0.185
3	1.020	0.755	0.265
4	0.986	0.734	0.252
5	0.950	0.735	0.215
6	0.984	0.763	0.221
7	0.977	0.743	0.234
8	0.957	0.750	0.207
9	0.964	0.746	0.218

increase continuously as the aging time elapses. The $1/Q$ of the NR vulcanizate by the thermal aging at 60°C increases at the beginning of 5 days by about 2% and then increases or decreases slightly. For the thermal aging at 80°C, the $1/Q$ of all the NR, BR, and SBR vulcanizates by the thermal aging increase continuously with an increase of the aging time.

Variation of the $1/Q$ of the SBR vulcanizate by the thermal aging is larger than those of the NR and BR ones. The $1/Q$ of the BR vulcanizate by the thermal aging is changed more than that of the NR one. The larger variation of the $1/Q$ of the BR vulcanizate than the NR vulcanizate can be explained by the free sulfur content. Curatives, especially sulfur, remaining in the vulcanizate react with rubber chains and make new crosslinks.[7] The free sulfur content remaining in the BR vulcanizate is more than that in the NR one by about 15%. Table II gives the free sulfur contents in the vulcanizates. The content of the free sulfur include the free N-tert-butyl-2-benzothiazole sulfenamide (TBBS) and its residue (mercaptobenzothiazole [MBI]) as well as pure sulfur. However, the big increase of the crosslink density of the SBR vulcanizate by the thermal aging can not be explained by the free sulfur remaining in the vulcanizate. If the $1/Q$ variation of the vulcanizate by the thermal aging primarily depends on the free sulfur content remaining in the vulcanizate, the $1/Q$ variation of the SBR vulcanizate should be smaller than those of the NR and BR ones because the free sulfur content in the SBR vulcanizate is less than those in the NR and BR ones by about 20–40%. This means that besides the free curatives the other sources to change the crosslink density of the vulcanizate are there. The vulcanizates cured by the EV cure

Scheme 1

system do not contain abundantly the free sulfur due to the low initial sulfur content. Thus, the free sulfur may be not a major factor to change the crosslink density.

The difference of the $1/Q$ variation due to the rubber kind may be explained by the combination reaction between the pendent groups not the free sulfur content in the vulcanizate. An important source to increase the crosslink density of a rubber vulcanizate by thermal aging is combination of pendent groups binding to the rubber chains.[15] TBBS is dissociated into MBT and *t*-butylamine radicals by heating at the beginning of vulcanization.[16] The MBT radical will become the neutral MBT formed by abstraction of a hydrogen atom from a rubber chain, a zinc complex formed by bonding with zinc ion,[7,17] or a pendent group formed by pending to a rubber chain.[18–20] The *t*-butylamine radical will become the neutral amine formed by abstraction of a hydrogen atom from a rubber chain or a pendent group formed by pending to a rubber chain.[19] The pendent sulfide groups terminated by an accelerator residue were studied by several groups.[21–23] The pendent MBT reacts with another pendent group of the neighboring rubber chains so a new crosslink will be formed as shown in Scheme I.[15,18,19]

In order to react between the pendent groups, they should be close to meet and keep the close distance for enough time to combine. The contact time between the pendent groups may be dependent upon the mobility of the pendent groups. That is, the contact time is shorter when the pendent group moves fast than when moving

slow. It can be considered that the predominant variation of the $1/Q$ of the SBR vulcanizate is due to the slow mobility of the pendent group by the interaction between the pendent group and the styrene unit. In order to investigate the influence of the styrene units on the mobility of the pendent group, the mobilities of the sulfide pendent group terminated by MBT in the BR and SBR vulcanizates having the pendent group were calculated using molecular simulation. Figures 2 and 3 gives the energy-minimized structures of the BR and SBR having the sulfide pendent group obtained from the conformational search. The dihedral angles of C-S-S-C of the pendent group were measured (Scheme II). Range of the dihedral angle was obtained from the dynamic fluctuation at 333 K for 1000 ps. The average dihedral angles of the BR and SBR are $-92.33°$ (range: -115.00 to $-67.86°$, standard deviation [SD]: 10.45) and $-91.38°$ (range: -114.30 to $-70.24°$, SD: 9.05), respectively. The width of the range of the dihedral angle in the SBR is narrower than that in the BR. This may be due to the interactions between phenyl ring of the styrene unit and the pendent group. The distances between the pendent group
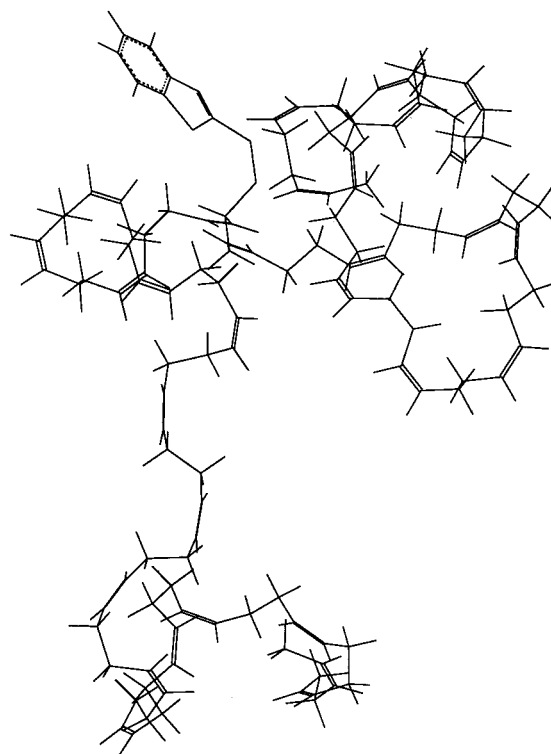
Figure 2   Energy-minimized structure of the *cis*-1,4-polybutadiene (BR) having the sulfide pendent group terminated by the MBT.
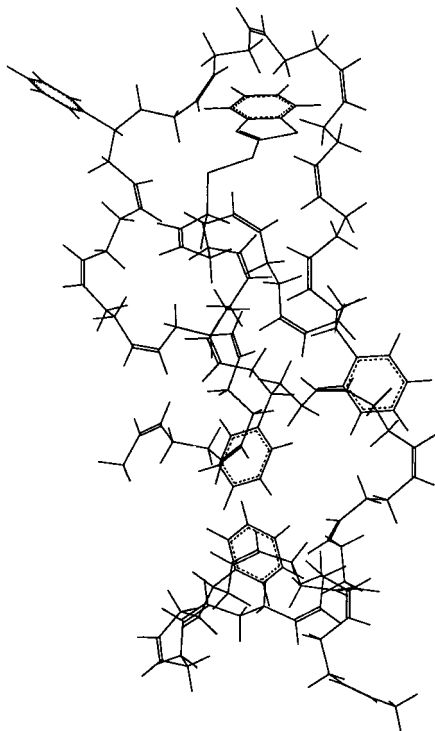
Figure 3 Energy-minimized structure of the SBR with 23 wt % styrene content having the sulfide pendent group terminated by the MBT.

and the second (r_2)/third (r_3) repeat unit in the BR and SBR were measured (Scheme II). The distances between the pendent group and the styrene unit (r_{S2} and r_{S3}) in the SBR were also measured (Scheme II). The r_2 and r_3 in the BR are 8.60 (4.28–15.94) and 10.66 Å (6.32–14.99 Å), respectively, whereas those in the SBR are 8.08 (4.82–14.65) and 10.24 Å (4.04–16.27 Å), respectively. The r_{S2} and r_{S3} in the SBR are 7.88 (3.98–13.45) and 9.75 Å (3.82–15.13 Å), respectively. The r_2 and r_3 in the SBR are shorter than those in the BR. In the SBR, the r_{S2} and r_{S3} are shorter than the r_2 and r_3. Thus, it can lead to a conclusion that the motion of the pendent group in the SBR is restricted by the styrene unit so the combination reaction between the pendent groups in the SBR is more favorable than that in the BR.

Biblend Vulcanizates

Figure 4 gives variation of the 1/Q of the 50/50 NR/SBR, NR/BR, and SBR/BR vulcanizates as a function of the aging time. The 1/Q of the biblend vulcanizates after the thermal aging increase, irrespective of the rubber composition. The 1/Q of the NR/SBR and SBR/BR vulcanizates after the

thermal aging at 40°C increase within about 3% whereas that of the NR/BR vulcanizate increases within in about 1%. The 1/Q of all the biblend vulcanizates by the thermal aging at 60 and 80°C increase continuously with an increase of the aging time.

The variation of the 1/Q of the SBR/BR vulcanizate by the thermal aging is larger than those of the NR/SBR and NR/BR ones. The variation of the 1/Q of the NR/SBR vulcanizate by the thermal aging is larger than that of the NR/BR one. This can be explained by the difference of the mobility of the pendent group in the vulcanizate depending upon the rubber composition. As discussed above, the combination reaction between the pendent groups is the principal source to increase the 1/Q the vulcanizate by the thermal aging for the vulcanizates with the EV cure system and it is dependent on the mobility of the pendent group. Because the pendent group in SBR moves slower than in BR, the motion of the pendent group in the biblend vulcanizates containing SBR (NR/SBR and SBR/BR) is slower than that in the biblend vulcanizate not containing SBR (NR/BR).

For the biblend vulcanizates containing SBR (NR/SBR and SBR/BR), the variation of the 1/Q of the SBR/BR vulcanizate by the thermal aging is larger than that of the NR/SBR. For example, the variations of the 1/Q of the SBR/BR, NR/SBR, and NR/BR vulcanizates after the thermal aging
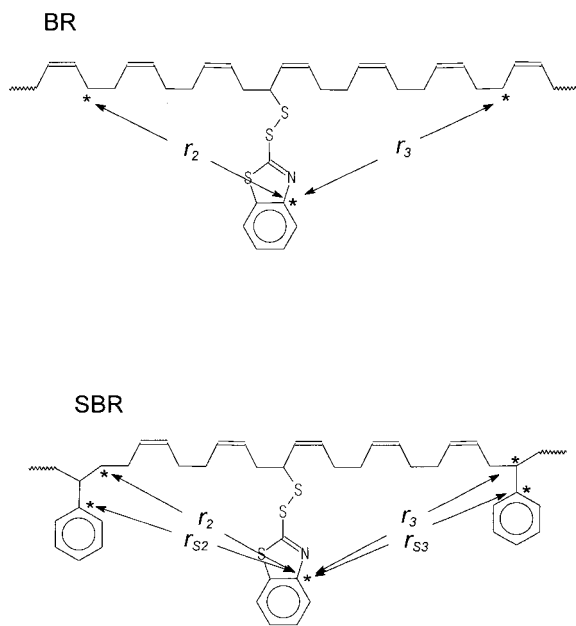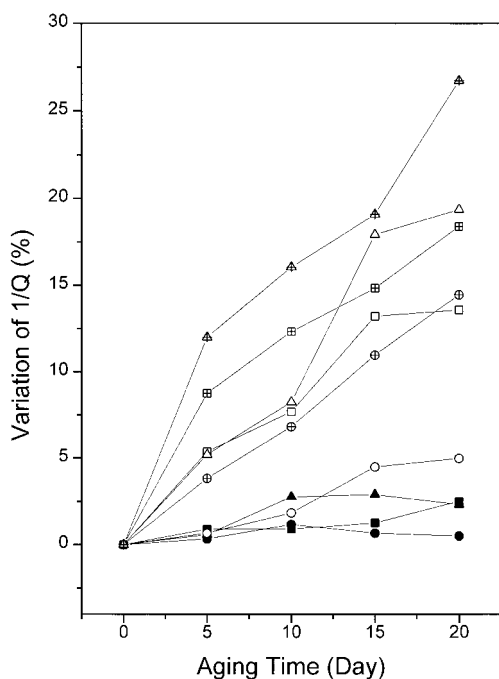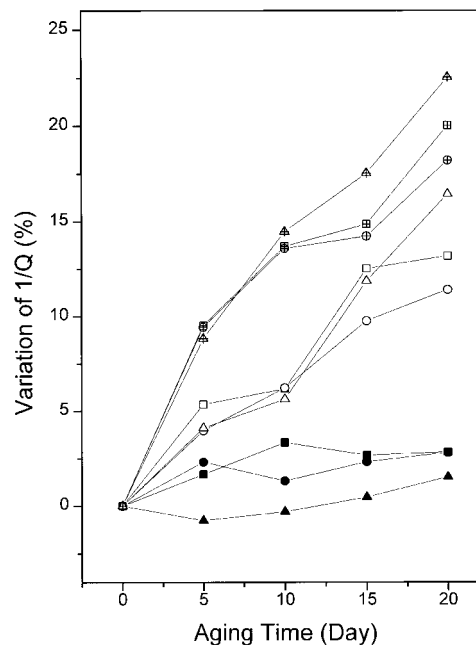

Scheme 2

at 80°C for 20 days are about 27, 18, and 14%, respectively. This may be due to the miscibility of the biblends. Callan and coworkers[24] measured average areas of disperse phase in 75/25 rubber blends and reported that the size of the disperse phase in SBR/BR blend was smaller than those in NR/BR and NR/SBR blends. This means that SBR/BR blends are more compatible than NR/BR and NR/SBR blends. Distances between the dissimilar rubbers will be closer when the blend is more compatible than when it is less compatible. There is interface formed between the dissimilar rubbers in elastomer blends. Thus, the crosslink density in the interface of the SBR/BR vulcanizate by the thermal aging increases more than that of the NR/SBR one since the former is more compatible than the latter.

Triblend Vulcanizates

Figure 5 gives variation of the $1/Q$ of the 40/40/20, 40/20/40, and 20/40/40 NR/SBR/BR vulcanizates as a function of the aging time. The $1/Q$ of the 40/40/20 and 40/20/40 NR/SBR/BR vulcanizates after the thermal aging at 40°C increase

Figure 5 Variation of the crosslink density of the triblend vulcanizates after the thermal aging. Squares, circles, and triangles stand for the 40/40/20, 40/20/40, and 20/40/40 NR/SBR/BR triblends, respectively. Solid, open, and crossed symbols indicate 40, 60, and 80°C, respectively.

Figure 4 Variation of the crosslink density of the biblend vulcanizates after the thermal aging. Squares, circles, and triangles stand for the 50/50 NR/SBR, NR/BR, and SBR/BR biblends, respectively. Solid, open, and crossed symbols indicate 40, 60, and 80°C, respectively.

within about 3%. The $1/Q$ of the 20/40/40 NR/SBR/BR vulcanizate after the thermal aging at 40°C decreases at the beginning of 10 days and then increases within about 1%. The $1/Q$ of all the triblend vulcanizates by the thermal aging at 60 and 80°C increase continuously with an increase of the aging time, irrespective of the rubber composition.

The variation of the $1/Q$ of the triblend vulcanizate by the thermal aging depending on the rubber composition does not show a specific trend. Only the variations of the $1/Q$ of the triblend vulcanizates containing the SBR 40 phr (40/40/20 and 20/40/40 NR/SBR/BR) are slightly larger than that of the triblend vulcanizate containing the SBR 20 phr (40/20/40 NR/SBR/BR).

The variation of the $1/Q$ of the vulcanizates containing SBR by the thermal aging become smaller as the SBR content in the vulcanizate decreases. The variations of the $1/Q$ of the SBR single rubber, SBR/BR biblend, and 20/40/40 and 40/20/40 NR/SBR/BR triblend vulcanizates after the thermal aging at 60°C for 20 days are about 29, 19, 16, and 11%, respectively, and those at 80°C are about 32, 27, 23, and 18%, respectively. This can be also explained by the slow mobility of

the pendent group in SBR as discussed previously.

CONCLUSIONS

The crosslink densities of the vulcanizates after the thermal aging increase continuously with an increase of the aging time. Variation of the crosslink density of the SBR vulcanizate by the thermal aging is larger than those of the NR and BR ones. This is because the mobility of the pendent group in SBR becomes slower by the strong interaction between the pendent group and the styrene unit. For the vulcanizates containing SBR, the variation of the crosslink density of the vulcanizate containing a high SBR content is larger than that of the vulcanizate containing a low one. The predominant source to increase the crosslink density of the vulcanizate with the EV cure system by the thermal aging was found to be the combination reaction between the pendent groups and not the free sulfur content because the free sulfur content is not rich in the vulcanizate with the EV cure system.

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