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Thermal Aging Properties of NR Vulcanizates with Different Cure Systems

Sung-Seen Choi† and Byung-Ho Park*
Department of Applied Chemistry, Sejong University, 98 Koonja-dong, Kwangjin-gu, Seoul 143-747, Korea
**Kumho Research and Development Center, 555 Sochon-dong, Kwangsan-gu Kwangju 506-711, Korea*
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가교 시스템이 다른 NR 가황물의 열노화 특성

최 성 신†·박 병 호*
세종대학교, *금호타이어
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ABSTRACT : Changes of physical properties of NR vulcanizates with different cure systems by thermal aging were investigated. Two sulfur cure systems and one resole cure system were employed, and total contents of the curatives were varied. For the NR vulcanizates with sulfur cure systems, hardness and modulus after the thermal aging at 90 ℃ for 3 days were increased, but elongation at break and tensile strength were decreased. For the NR vulcanizates with resloe cure system, the physical properties after the thermal aging were decreased. The change of physical properties by the thermal aging was explained with the crosslink density change. The crosslink densities of the NR vulcanizates with sulfur cure systems were increased after the thermal aging, but those with resole cure system were decreased. Influence of the migration of antidegradant on the changes of physical properties was also investigated. However, the changes of physical properties by the thermal aging were not explained sufficiently with the migration of antigradant.

요 약 : 가교 시스템이 다른 NR 가황물의 열노화에 의한 물성 변화를 연구하였다. 두 가지 황 가교 시스템과 한 가지 레졸 가교 시스템을 도입하였으며, 가교제 함량을 변화시켰다. 황 가교 시스템으로 만든 NR 가황물의 경우, 90 ℃에서 3일간 노화 후 경도와 모듈러스는 증가한 반면 신율과 인장강도는 감소하였다. 레졸 가교 시스템으로 만든 NR 가황물의 경우에는 노화 후 전반적으로 물성이 하락하였다. 열노화에 의한 물성 변화를 가교밀도의 변화로 설명하였다. 노화 후, 황 가교 시스템으로 만든 NR 가황물의 가교밀도는 증가한 반면, 레졸 가교 시스템으로 만든 NR 가황물의 가교밀도는 감소하였다. 노화방지제의 이동이 물성에 미치는 영향에 대해서도 조사하였다. 그러나 노화방지제의 이동으로는 노화에 의한 물성의 변화를 충분히 설명할 수 없었다.

Keywords : thermal aging, NR vulcanizate, crosslink density, migration of antidegradant, physical property

† 대표저자(*e-mail : sschoi@sejong.ac.kr*)

Ⅰ. Introduction

In general, rubber compounds are crosslinked by sulfur,[1-3] peroxide,[4] or resole cure system.[5] The sulfur vulcanization is the most popular method. Types and contents of curatives affect the cure characteristics and crosslink density.[6-12] Crosslink type and degree of crosslink density of a rubber vulcanizate determine the physical properties such as modulus, hardness, resilience, elongation at break, heat build-up, and so forth.[1] By increasing the crosslink density, the modulus, hardness, resilience, and abrasion resistance increase, whereas the elongation at break, heat build-up, and stress relaxation decrease. The stress relaxation, tensile strength, and resilience increase in proportion to the content of di- and polysulfides, whereas the fatigue and thermal aging resistance decrease.

Sulfide linkages, especially polysulfides, are dissociated by heating[13,14] and this brings about decrease of the crosslink density. Curatives, especially sulfur, in rubber vulcanizates make new crosslinks[2] and this results in increase of the crosslink density. In the present work, we studied influence of the cure system on changes of physical properties by thermal aging. NR vulcanizates with sulfur or resole cure system were prepared. Two sulfur-accelerated cure systems (single and binary cure systems) were employed. The single cure system had one cure accelerator of *N-tert*-butyl-2-benzothiazole sulfenamide (TBBS) and binary one had two cure accelerators of TBBS and 1,6-bis(*N,N'*-dibenzylthiocarbamoyldithio)-hexane (DBTH). The binary cure system had faster cure rate and better reversion resistance than the single cure system.[15] Changes of the physical properties by thermal aging were explained with the crosslink density change and migration of antidegradant.

Ⅱ. Experimental

The NR compounds were made of NR (SMR 20), carbon black (N330), cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS, DBTH, sulfur, and resole). The formulations were given in Table 1. The compounds S1, S2, and S3 have single accelerator cure systems of TBBS, the compounds B1, B2, and B3 have binary accelerator cure systems of TBBS and DBTH, and the compounds R1, R2, and R3 have

Table 1. Formulations (phr)

Compound No.	S1	S2	S3	B1	B2	B3	R1	R2	R3
SMR20	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
N330	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
ZnO	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
HPPD	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Wax	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sulfur	1.0	1.4	1.8	0.8	1.0	1.2	0.0	0.0	0.0
TBBS	1.0	1.4	1.8	0.5	0.5	0.5	0.0	0.0	0.0
DBTH	0.0	0.0	0.0	0.5	0.9	1.3	0.0	0.0	0.0
SP1045	0.0	0.0	0.0	0.0	0.0	0.0	5.0	10.0	15.0

HPPD: *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine
TBBS: *N-tert*-butyl-2-benzothiazole sulfenamide
DBTH: 1,6-bis(*N,N'*-dibenzylthiocarbamoyldithio)-hexane
SP1045: *p-tert*-octylphenol formaldehyde resole resin

resole cure systems of SP1045. Contents of the curatives were varied to prepare samples with different crosslink densities.

Vulcanizates were prepared by curing at 160 ℃ for 20 min (for the sulfur cure systems) and at 190 ℃ for 30 min (for the resole cure systems). Thermal aging was performed at 90 ℃ for 3 days in a convection oven. Physical properties of the vulcanizates were measured with universal testing machine (Instron 6021). Crosslink densities of the samples 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. Weights of the organic materials-extracted samples were measured. They were soaked in *n*-decane for 2 days and weights of the swollen samples were measured. Amount of antidegradants migrated to the surface was determined by the measurements of the amounts of antidegradants that remained in the rubber vulcanizates before and after the thermal aging. The amount of antidegradants that remained in the rubber vulcanizates was analyzed by gas chromatography after the extraction of the antidegradants with THF.

Ⅲ. Results and Discussion

Physical properties of the vulcanizates before the thermal aging were summarized in Table 2. The hardness and modulus increase with increase of the curatives contents while the elongation at break decreases. This is due to the increased crosslink density. Physical properties of a vulcanizate such as modulus, tensile strength, elongation at break, and so on depend on degree of crosslink density. Modulus is a proportional property to degree of crosslink density, while elongation at break is an inversely proportional property to degree of crosslink density. For the vulcanizates with the sulfur cure systems, tensile strength decreases with increase of the curatives contents due to the decreased elongation at break. But for the vulcanizates with the resole cure systems, the tensile strength increases with increase of the curatives contents. This result can be explained with the big increase of modulus and the small decrease of elongation at break. Tensile strength is proportional to modulus but is inversely proportional to elongation at break. The tensile strength will be increased when increment of the modulus is larger than the decrement of elongation at break.

Physical properties of the vulcanizates after the thermal aging at 90 ℃ for 3 days were summarized in Table 3. Variations of the physical properties of vulcanizates after the thermal aging with the curatives contents show the same trends with the physical properties of vulcanizates before the thermal aging. The moduli are largely increased by the thermal aging. Change percentages of the physical properties and crosslink density by the thermal aging were calculated. Figure 1 shows variation of the crosslink density (1/Q) change with the curatives contents. The swelling ratio was calculated as $Q = (W_s-W_u)/W_u$, where W_s and W_u are weights of the swollen and unswollen samples. The reciprocal

Table 2. Physical properties before thermal aging

Compound No.	S1	S2	S3	B1	B2	B3	R1	R2	R3
Hardness (Shore A)	63	66	70	65	69	75	57	65	69
100% Modulus (kg/cm^2)	22.7	30.2	39.4	26.7	35.0	53.2	12.1	22.2	32.8
300% Modulus (kg/cm^2)	116.8	146.6	174.4	129.9	159.1	207.0	54.9	103.6	148.6
Elongation at break (%)	565.3	495.5	426.8	549.1	467.9	316.3	487.6	438	410.1
Tensile strength (kg/cm^2)	277.7	274.9	259.5	291.8	273.9	218.6	117.9	173.1	220.2

Table 3. Physical properties and HPPD migration after thermal aging for 3 days at 90 ℃

Compound No.	S1	S2	S3	B1	B2	B3	R1	R2	R3
Hardness (Shore A)	64	70	74	66	70	78	54	66	70
100% Modulus (kg/cm^2)	28.6	40.3	55.4	31.4	42.2	65.7	10.7	23.2	35.6
300% Modulus (kg/cm^2)	141.2	174.9	216.7	143.7	179.5	-	39.7	96.1	143.5
Elongation at break (%)	441.5	396.1	294.2	510.8	418.4	190.5	405.1	335.8	308.1
Tensile strength (kg/cm^2)	221.3	232.3	211.3	264.8	255.6	143.5	55.3	109.6	148.6
Migration of HPPD (%)	37.5	48.6	45.4	52.0	56.7	65.9	44.0	33.3	31.0

value of the swelling ratio, 1/Q, is used as crosslink density.[16] For the vulcanizates with the sulfur cure systems (Compounds S1-S3 and B1-B3), the crosslink densities increase after the thermal aging and the crosslink density change also increases with increase of the curatives contents. This is due to the formation of new crosslinks by the curatives and their derivatives remained in the vulcanizates. But for the vulcanizates with the resole cure systems (Compounds R1-R3), the crosslink densities are decreased after the thermal aging and the change rate decreases with increase of the resole contents. The decreased crosslink density is due to the dissociation of the existing crosslinks. In general, resole linkages are thermally more stable than sulfur ones, but the ether linkages in a resole molecule is not stable. The ether linkage can be dissociated by thermal aging and the crosslink density will be decreased.[17-19]

For the vulcanizates with the sulfur cure systems, the hardness and modulus changes increase with increase of the curatives contents as shown in Figures 2 and 3. This is due to the increased crosslink density change. For the vulcanizates with the resole cure systems, the hardness and 100% modulus changes of the vulcanizates R2 and R3 increase although the crosslink densities are decreased after the thermal aging. This may be due to the stabilization of the vulcanizates having rigid resole crosslinks. The resole linkages in the initial vulcanizates will be deformed because the vulcanizates are prepared in a high pressure mold. The

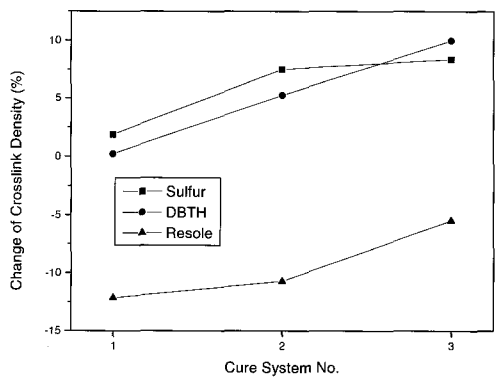

Figure 1. Variation of the crosslink density change with the cure system. The squares, circles, and triangles indicate the vulcanizates prepared with the single cure system, binary cure system, and resole cure system, respectively. The cure system numbers of x-axis are the numbers of formulations as listed in Table 1.

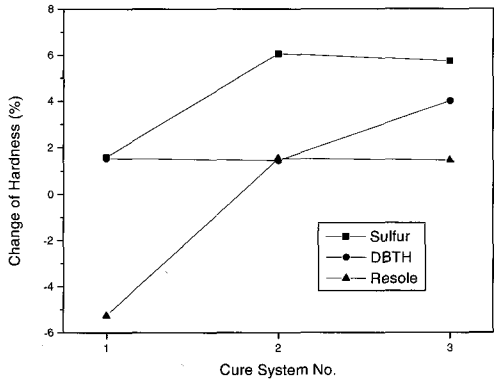

Figure 2. Variation of the hardness change with the cure system. The squares, circles, and triangles indicate the vulcanizates prepared with the single cure system, binary cure system, and resole cure system, respectively. The cure system numbers of x-axis are the numbers of formulations as listed in Table 1.

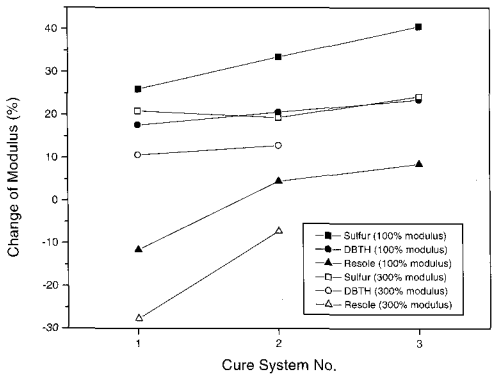

Figure 3. Variation of the modulus change with the cure system. The squares, circles, and triangles indicate the vulcanizates prepared with the single cure system, binary cure system, and resole cure system, respectively. Solid and open symbols stand for the 100% and 300% moduli, respectively. The cure system numbers of x-axis are the numbers of formulations as listed in Table 1.

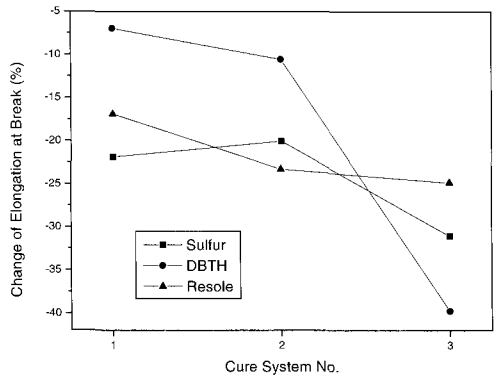

Figure 4. Variation of the elongation at break change with the cure system. The squares, circles, and triangles indicate the vulcanizates prepared with the single cure system, binary cure system, and resole cure system, respectively. The cure system numbers of x-axis are the numbers of formulations as listed in Table 1.

thermal aging can help the deformed structures stabilize. Figure 4 shows variation of the elongation change with the curatives contents. For the vulcanizates with the sulfur cure systems, the change rate of the elongation at break increases with increase of the curatives contents. This is also due to the increased crosslink density change. The elongation at break is a proportional property to the crosslink

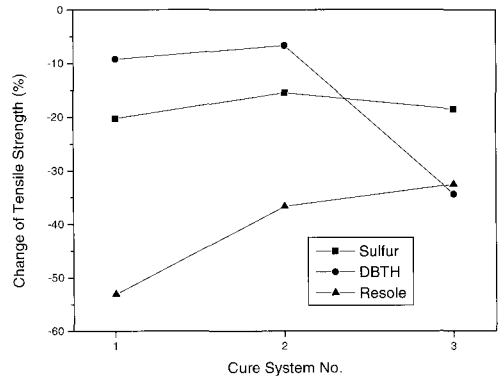

Figure 5. Variation of the tensile strength change with the cure system. The squares, circles, and triangles indicate the vulcanizates prepared with the single cure system, binary cure system, and resole cure system, respectively. The cure system numbers of x-axis are the numbers of formulations as listed in Table 1.

density. For the vulcanizates with the resole cure systems, the change rate also increases with increase of the curatives contents. Figure 5 shows variations of the tensile strength change with the curatives contents. The tensile strength changes do not show a specific trend. This can be explained with the correlation of tensile strength with crosslink density. The tensile strength of a rubber vulcanizate increases and then decreases with increase of the crosslink density.

As discussed previously, crosslink density directly affects the physical properties. Polar organic materials influences dissociation of the existing crosslinks and formation of new crosslinks.[20,21] A representative polar organic material in a rubber vulcanizate is an antidegradant, especially diamine derivatives. In this study, we used HPPD as a chemical antidegradant. We measured change of the amounts of HPPD before and after the thermal aging. The amounts of HPPD consumed by migration and evaporation were summarized in Table 3. Variations of the migration of HPPD do not show a specific trend. For the vulcanizates with the single sulfur-accelerated cure systems (Compounds S1-S3), the migration of HPPD increases and then decreases as the sulfur and TBBS contents increase.

For the vulcanizates with the binary sulfur-accelerated cure systems (Compounds B1-B3), the migration of HPPD increases with increase of the DBTH content, while for the vulcanizates with the resole cure systems (Compounds B1-B3), the migration of HPPD increases with decrease of the resole content. Thus, we can say that the changes of the crosslink densities or the changes of the physical properties by the thermal aging cannot be explained sufficiently with the results of antidegradant migration.

Ⅳ. Conclusions

Physical properties of the NR vulcanizates were changed by the thermal aging. The physical property changes were explained with the crosslink density changes. The crosslink densities of the vulcanizates with the sulfur cure systems increased after the thermal aging, while those with the resole ones decreased. For the vulcanizates with the sulfur cure systems, the change rates of physical properties were explained with the change rates of crosslink densities.

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