

Characterization of NR Vulcanizates Cured by Both Sulfur and Resole

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황과 레졸로 가교된 천연고무 가교물의 특성

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ABSTRACT: Physical properties of NR vulcanizates cured by both sulfur and resole were studied. Cure characteristics of the compounds were also investigated. Two types of resoles with different molecular weight distributions were employed. The scorch time of the NR compound containing the resole with a low molecular weight distribution was shorter than that of the compound containing the resole with a high one. Crosslink densities of the NR vulcanizates with a high resole content after the thermal aging at 95°C decreased, while that of the vulcanizate without resole after the thermal aging at 95°C increased. Though crosslink densities of the NR vulcanizates with a high resole content decreased with increasing the aging time, the moduli increased while the tensile strength and tear strength decreased.

요약: 황과 레졸로 가교된 천연고무 배합물의 가황 특성과 가교물의 물리적 특성을 연구하였다. 분자량 분포가 다른 2가지 레졸을 사용하였다. 분자량 분포도가 낮은 레졸이 포함된 배합물의 스코치 시간은 분자량 분포도가 높은 레졸이 포함된 배합물에 비해 빠르다. 레졸 함량이 높은 가교물의 가교 밀도는 95°C 열노화 후 감소한 반면, 레졸이 없는 가교물의 경우에는 열노화 후 가교 밀도가 증가하였다. 레졸 함량이 높은 가교물의 가교 밀도는 노화 시간이 길어질수록 감소하지만 모듈러스는 증가하고 인장 강도와 인열 강도는 감소한다.

Keywords : NR vulcanizate, sulfur, resole

I. Introduction

In general, rubber compounds are cross-linked by sulfur,¹⁻³ peroxide,⁴ or resole.⁵ The sulfur vulcanization is the most popular method in a tire industry. Degree and type of

crosslink of a rubber vulcanizate have an effect on the physical properties such as modulus, hardness, resilience, breaking elongation, heat build-up, and so forth. By increasing degree of crosslinking, modulus, hardness, resilience, and abrasion resistance are increased while elongation at break, heat

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build-up, and stress relaxation are decreased. By increasing in proportion of di- and polysulfides, stress relaxation, tensile strength, and resilience are increased while fatigue failure is decreased.

The vulcanization process produces several different crosslink structures including mono-, di-, and polysulfidic linkages. It is well established that the network structure varies with the time and temperature of vulcanization. Polysulfidic linkages are changed into mono- or disulfidic linkage as the vulcanization is proceeded. In the case of the sulfur curing of unsaturated rubbers, crosslinking and reversion as competing reactions depend on cure time and temperature. S-S and C-S bonds are relatively unstable. Thus, the sulfur curing at high temperatures deteriorates the mechanical properties of rubbers due to reversion. Reversion is speculated to occur when the desulfurization reaction is faster than the crosslinking reaction. Reversion occurs well in NR compounds.^{6,7}

Vulcanization using a *p*-alkylphenol formaldehyde resole makes C-C bonds more stable than S-S and C-S bonds. Therefore, a resole-cured rubber vulcanizate has a good resistance to reversion at high temperatures. Curing of natural rubber (NR) and butyl rubber (isobutylene-isoprene rubber, IIR) using a phenolic resole resin has been investigated since the end of the 1930s.⁸ The crosslinking between an unsaturated elastomer and a phenolic resole resin was proposed by the chroman mechanism, based on the study of low molecular weight model compounds.⁹⁻¹³ A phenolic resole is changed to an *o*-methylene quinone intermediate by dehydration at high

temperatures.^{14,15} This intermediate reacts with double bonds of olefins and forms chroman structures by 1,4-cycloaddition.

The traditional curing system for rubber compounds consisting of sulfur and cure accelerator provides a good balance of mechanical properties and cost compared to other curing systems. However, the system has disadvantages such as relatively low stability of sulfur crosslinks¹⁶ between rubber chains and environmental concerns related to nitrosamines (suspected carcinogens) formation associated with many cure accelerators during rubber mixing and cure operation¹⁷. In order to improve the accelerated sulfur cure system, mixed cure system such as accelerated sulfur and peroxide cure system^{18,19} has been studied. In this work, cure characteristics of NR compounds containing both sulfur and resole and physical properties of the NR vulcanizates before and after thermal aging were studied in order to investigate roles of the resole as a curing agent and reinforcing material. Two types of resoles with different molecular weight distribution were used.

II. Experimental

Two types of *p-t*-octylphenol formaldehyde resoles with different molecular weight distribution and linkage type were used in this study. The one is SP 1045 (commercial product) and the other one is LM-Resole (synthetic resole with low molecular weight distribution). The SP 1045 is a mixture of *p-t*-octylphenol formaldehyde resoles with both methylene (-CH₂-) and dimethylene ether (-CH₂OCH₂-) linkages. The LM-Resole is a *p*

-*t*-octylphenol formaldehyde resole with the methylene linkage and low molecular weight distribution.

The LM-Resole was synthesized by slightly modifying the published procedures^{20,21} for the synthesis of analogs of *p-t*-butylphenol. *p-t*-Octylphenol (20.6 g, 0.1 mol), NaOH(4.0 g in 40 mL of H₂O), and formaldehyde (15 mL, 35% aqueous solution) were stirred under N₂ for 5 days at 40°C and the precipitated sodium salt was collected by filtration, washed with brine (40 mL), dissolved in H₂O and then acidified with 1N HCl. The resulting yellow oil was extracted with CH₂Cl₂ (70 mL) and organic layer was separated, washed with H₂O and dried (MgSO₄). Evaporation of solvent afforded 22.9 g (86%) of slightly waxy solid. Analytical sample was further purified by column chromatography (eluent; acetone : hexane = 3 : 7).

¹H NMR(CDCl₃) δ 8.10 (br s, 1H, phenolic OH), 7.02 (s, 2H, ArH), 4.75 (s, 4H, -CH₂O-), 3.04 (br s, 2H, OH), 1.67, 1.31, and 0.71 (three s, 17H, octyl protons). ¹³C NMR(CDCl₃) δ 152.22, 141.64, 125.61, and 125.13 (Ar), 63.89 (-OCH₂-), 56.85, 37.88, 32.32, 31.78, and 31.57 (octyl carbons).

Seven carbon black-filled NR compounds were prepared. The formulations are given in Table 1. Compound 1 does not contain any resoles. Compounds 2-4 contain the LM-Resole while Compounds 5-7 contain the SP 1045. The resole contents in the Compounds 2-7 were twice of the reduction of sulfur and TBBS in the Compound 1. The seven NR vulcanizates

were prepared by curing at 160°C for 20 min.

FT-IR spectra of the resoles were acquired with Bruker IFS 85. The molecular weight distributions of the resoles were measured with GPC. The analyzing temperature was 40°C. THF was eluted at 1 mL/min flow rate. Cure characteristics were obtained using a Flexsys rheometer (MDR 2000) at a frequency of 100 cycles/min and 1.5 arc for 140, 160, and 180°C. The vulcanizates were aged in a convection oven at 95°C for 3 and 6 days. Crosslink densities of the vulcanizates before and after the thermal aging were measured by a swelling method²². Organic additives in the samples were removed by extracting with THF and *n*-hexane for each 3 days before swelling. Physical properties of the vulcanizates before and after the thermal

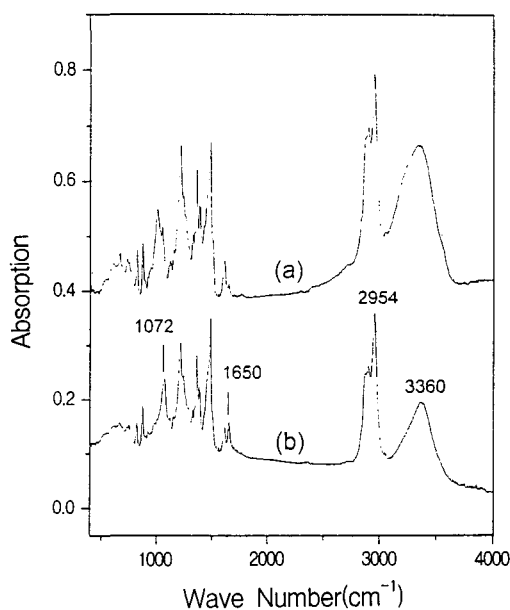


Fig. 1. FT-IR spectra of the LM-Resole (a) and the SP 1045 (b).

Table 1. Formulations (phr) and Cure Characteristics

Compound No.	1	2	3	4	5	6	7
SMR 20	100.00	100.00	100.00	100.00	100.00	100.00	100.00
N330	50.00	50.00	50.00	50.00	50.00	50.00	50.00
Stearic acid	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Zinc oxide	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Wax	2.00	2.00	2.00	2.00	2.00	2.00	2.00
HPPD	2.00	2.00	2.00	2.00	2.00	2.00	2.00
TMDQ	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Sulfur	1.20	1.02	0.84	0.66	1.02	0.84	0.66
TBBS	2.00	1.70	1.40	1.10	1.70	1.40	1.10
LM-Resole	0.00	0.96	1.92	2.88	0.00	0.00	0.00
SP 1045	0.00	0.00	0.00	0.00	0.96	1.92	2.88
Cure characteristics at 140°C							
t ₅ (min)	6.03	6.35	6.67	6.83	6.95	7.25	7.52
t ₉₅ (min)	23.70	21.02	21.90	35.60	22.22	23.47	33.68
Delta torque (Nm)	2.93	2.40	1.90	1.47	2.37	1.89	1.50
Cure characteristics at 160°C							
t ₅ (min)	1.95	2.08	2.13	2.12	2.13	2.12	2.15
t ₉₅ (min)	7.90	6.72	7.83	10.78	6.80	7.60	11.25
Delta torque (Nm)	2.45	1.98	1.57	1.16	1.96	1.55	1.23
Cure characteristics at 180°C							
t ₅ (min)	0.53	0.57	0.62	0.72	0.60	0.63	0.68
t ₉₅ (min)	2.22	2.20	2.37	3.32	2.28	2.45	3.07
Delta torque (Nm)	2.29	1.88	1.49	1.09	1.85	1.46	1.14

aging were measured by the Universal Testing Machine (Instron 6021).

III. Results and Discussion

1. Characterization of the resoles

Figure 1 shows IR spectra of the LM-Resole and SP 1045. In the previous work²³, the IR analysis of a resole was described in detail. The 2954 cm⁻¹ was assigned to alkyl group. The typical IR peaks of the resole are 3360 and 1072 cm⁻¹ corresponding to hydroxyl group and dimethylene ether-linkage (or methylo), respectively. There is little or no

peak at 1072 cm⁻¹ in the spectrum of the LM-Resole. There is one important peak in the IR spectrum. It is 1650 cm⁻¹, assigned to conjugated C=O double bond, which indicates o-methylene quinone intermediate.

Figure 2 shows GPC chromatograms of the LM-Resole and SP 1045. The Mw of the LM-Resole and SP 1045 were 4.73 × 10² and 19.5 × 10², respectively. Peaks at 41.3 and 39.8 min correspond to 2,6-bis(hydroxymethyl)-p-octylphenol (monomer diol of the p-t-octylphenol formaldehyde resole) and 2-hydroxy-3-(3-hydroxymethyl-5-octylsalicyl)-5-octylbenzyl alcohol (dimer diol of the p-t-octylphenol for-

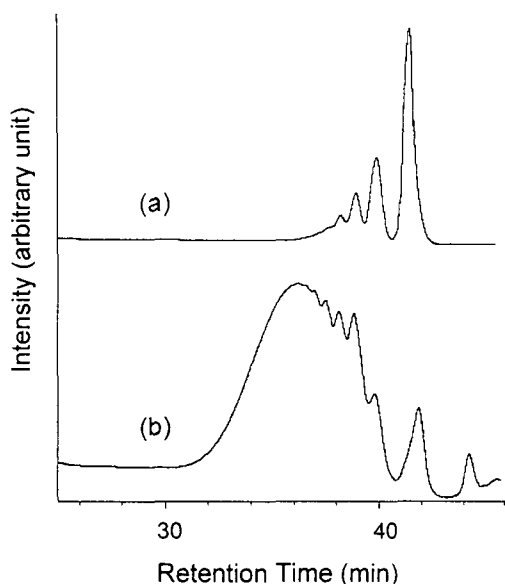


Fig. 2. GPC chromatograms of the LM-Resole (a) and the SP 1045 (b).

maldehyde resole), respectively.

2. Cure characteristics

Cure characteristics of the NR compounds were measured using a Flexsys rheometer (MDR 2000) at 140, 160, and 180°C. The scorch time (t_s), optimum cure time (t_{95}), and delta torque were listed in Table 1. The scorch and optimum cure times of the compounds decrease remarkably by increasing the temperature. The delta-torques of the compounds decrease with an increase of the temperature. The scorch time of the compound without the resoles is shorter than those of the compounds containing the resoles. This may be due to the low content of sulfur and TBBS and inhibition of radical or ionic reaction to form crosslinks. For the accelerated sulfur cure system, zinc complexes should be formed to make sulfur crosslinks. The zinc complexes

were formed through the radical or ionic reaction of zinc oxide with fatty acid, accelerator, and sulfur.^{24,25} Since the resoles have many hydroxyl groups, they may react with the intermediate radicals or ions formed by the reactions of the curing agents. The optimum cure times at 140 and 160°C of the compound without the resoles are longer than those of the compounds containing the resoles of 0.96 and 1.92 phr, while they are shorter than those of the compounds containing the resoles of 2.88 phr.

Scorch and optimum cure times of the compounds containing the resoles become longer as the resole content increases. This can be also explained by the low content of sulfur and TBBS and inhibition of radical or ionic reaction to form crosslinks as discussed above. Scorch times of the compounds containing the LM-Resole (Compounds 2 - 4) are shorter than those of the compounds containing the SP 1045 (Compounds 5 - 7). This may be due to the dimethylene ether linkage of the SP 1045. Optimum cure time of the Compound 2 (containing the LM-Resole of 0.96 phr) is also shorter than that of the Compound 5 (containing the SP 1045 of 0.96 phr). The delta-torques of the compounds containing the resoles are lower than that of the compound without the resoles. Delta torques of the compounds containing the resoles decrease with an increase of the resole content. This means that crosslinks are hardly formed by the resoles even at 180°C.

Table 2. Crosslink Densities Before and After the Thermal Aging at 95°C (10^{-3} g·mol/ml)

Compound No.	1	2	3	4	5	6	7
Before Aging	3.31	2.69	2.13	1.54	2.71	2.11	1.68
After Aging at 95°C							
(for 3 days)	3.84	2.93	2.04	1.38	3.10	2.17	1.48
(for 6 days)	3.96	2.92	1.97	1.23	2.94	2.05	1.38

3. Change of the crosslink density by the thermal aging

The NR vulcanizates were thermally aged at 95°C for 3 and 6 days in order to investigate the thermal stability. Crosslink densities of the vulcanizates before and after the thermal aging are summarized in Table 2. The crosslink densities of the NR vulcanizate without the resoles (Compound 1) increase after the thermal aging. The increment of the crosslink density by the thermal aging increases from 16 to 20% with an increase of the aging time from 3 to 6 days. The crosslink densities of the NR vulcanizates containing the resoles of 0.96 phr (Compounds 2 and 5) after the thermal aging are also higher than before the thermal aging. But, for the Compound 5, the increments of the crosslink density of the NR vulcanizate by the thermal aging decrease from 14 to 8% with an increase of the aging time from 3 to 6 days. The crosslink density of the NR vulcanizates with the resoles of 2.88 phr (Compounds 4 and 7) after the thermal aging are lower than before the thermal aging. The decrements of the crosslink density by the

thermal aging increase from 10 to 20% and from 12 to 18% for the Compounds 4 and 7, respectively, with an increase of the aging time from 3 to 6 days.

In general, crosslink density of a sulfur-cured NR vulcanizate increases after thermal aging.²⁶ However, the crosslink densities of the NR vulcanizates containing the resoles of 2.88 phr decreased after the thermal aging. This can be explained by inhibition of new sulfur crosslinks by the resoles. Polysulfides in the vulcanizates are dissociated into sulfide radicals at the high temperature. The dissociated sulfide radicals recombine each other, change into thiols by abstraction of a hydrogen atom from a rubber chain, or form new sulfur crosslinks with another rubber chain. When the resoles exist in the vulcanizates by excess, they can be around the polar sulfide radicals since the resoles have many hydroxyl groups. Thus, the resoles may prevent the sulfide radicals from the recombination and the formation of new sulfur crosslinks.

4. Physical properties

Modulus of a rubber vulcanizate is a proportional property to the degree of crosslink density. Figures 3, 4, 5, and 6 show variations of moduli at 50, 100, 200, and 300% strain, respectively, of the vulcanizates with the aging time. The moduli of the vulcanizates show the same trends depending on the aging time irrespective of strain ratio. The moduli of the vulcanizates increase by increasing the aging time. Since the crosslink density of the vulcanizate without the resoles is higher than those of the vulcanizate contain-

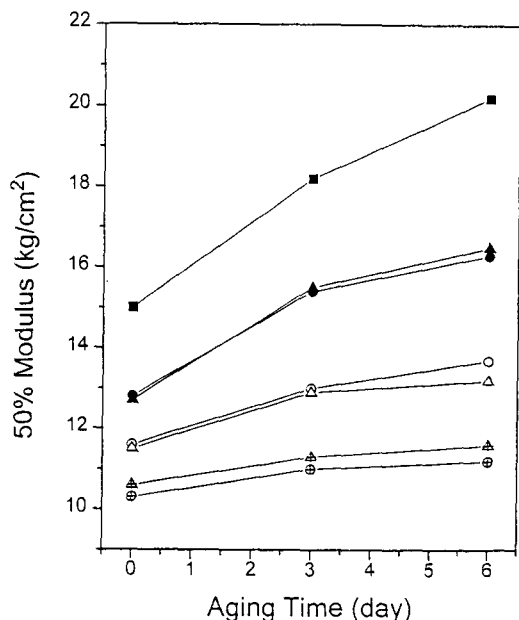


Fig. 3. Variations of modulus at 50% strain of the NR vulcanizates as a function of the aging time at 95°C. Rectangles, circles, and triangles stand for the NR vulcanizates without the resoles, with the LM-Resole, and with the SP 1045, respectively. Solid, open, and crossed symbols indicate the NR vulcanizates containing the resole of 0.96, 1.92, and 2.88 phr, respectively.

ning the resoles, the moduli of the vulcanizate without the resoles are higher than those of the vulcanizates containing the resoles. The moduli of the vulcanizates with the high resole content are lower than those of the vulcanizates with the low one.

The moduli of the vulcanizates without and with the resoles increase by increasing the aging time. The increase of the moduli of the vulcanizate without the resoles after the thermal aging is explained by the increase of the crosslink density with an increase of the

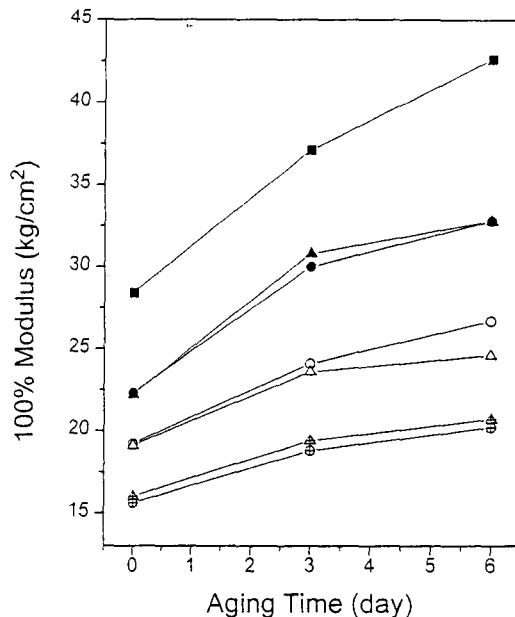


Fig. 4. Variations of modulus at 100% strain of the NR vulcanizates as a function of the aging time at 95°C. Rectangles, circles, and triangles stand for the NR vulcanizates without the resoles, with the LM-Resole, and with the SP 1045, respectively. Solid, open, and crossed symbols indicate the NR vulcanizates containing the resole of 0.96, 1.92, and 2.88 phr, respectively.

aging time. However, for the vulcanizates with the resoles, the moduli are lower after the thermal aging for 3 days than after the thermal aging for 6 days although the crosslink density decreases as the aging time increases. This can be explained by the role of the resole as a reinforcing agent²⁷. The resoles have many methylol and *o*-methylene quinone terminals which react with other resoles so that three dimensional networks of resole are formed by the autocondensation between the resoles²⁸. The resole networks

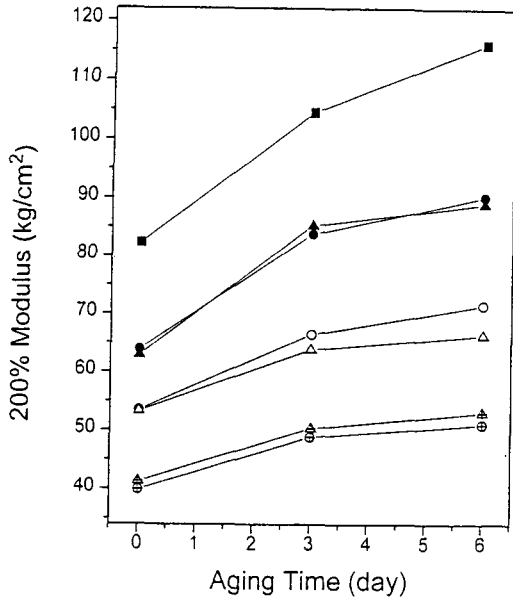


Fig. 5. Variations of modulus at 200% strain of the NR vulcanizates as a function of the aging time at 95°C. Rectangles, circles, and triangles stand for the NR vulcanizates without the resoles, with the LM-Resole, and with the SP 1045, respectively. Solid, open, and crossed symbols indicate the NR vulcanizates containing the resole of 0.96, 1.92, and 2.88 phr, respectively.

will reinforce the vulcanizate.

Tensile strength of a rubber vulcanizate increases and then decreases by increasing the crosslink density. Figure 7 shows the variations of tensile strength of the vulcanizates as a function of the aging time. The variations of all the NR vulcanizates show the same trend. The tensile strength decreases with an increase of the aging time.

The tensile strength of the vulcanizate without the resoles is lower than that of the vulcanizate containing the SP 1045 of 0.96

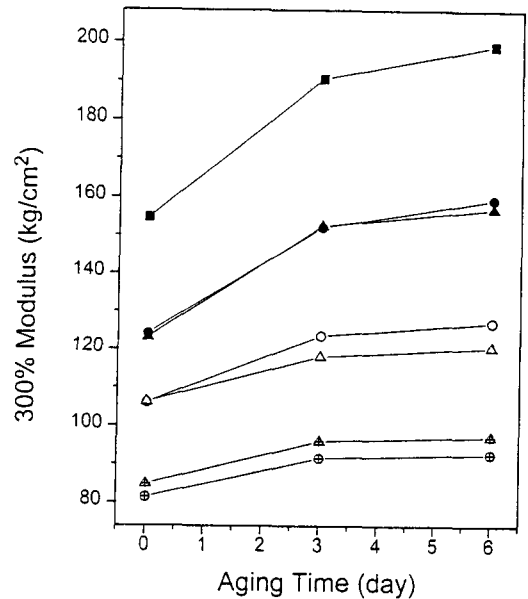


Fig. 6. Variations of modulus at 300% strain of the NR vulcanizates as a function of the aging time at 95°C. Rectangles, circles, and triangles stand for the NR vulcanizates without the resoles, with the LM-Resole, and with the SP 1045, respectively. Solid, open, and crossed symbols indicate the NR vulcanizates containing the resole of 0.96, 1.92, and 2.88 phr, respectively.

phr although the crosslink density of the vulcanizate without the resoles is much higher than that of the vulcanizate containing the SP 1045 of 0.96 phr. Even after the thermal aging, the tensile strength of the vulcanizate without the resoles is lower than that of the vulcanizate containing the LM-Resole of 0.96 phr. This may be also due to the formation of the three dimensional network of the resoles as discussed previously.

Elongation at break of a rubber vulcanizate is an inversely proportional property to

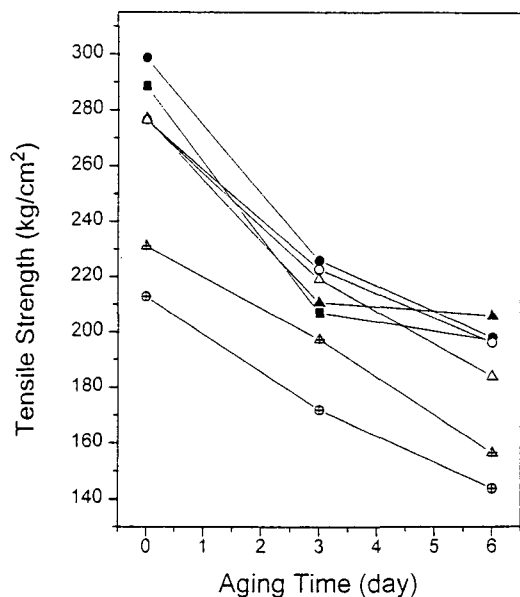


Fig. 7. Variations of tensile strength of the NR vulcanizates as a function of the aging time at 95°C. Rectangles, circles, and triangles stand for the NR vulcanizates without the resoles, with the LM-Resole, and with the SP 1045, respectively. Solid, open, and crossed symbols indicate the NR vulcanizates containing the resole of 0.96, 1.92, and 2.88 phr, respectively.

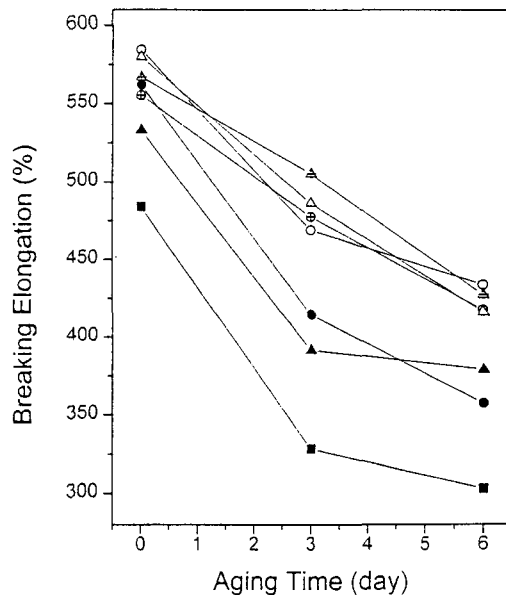


Fig. 8. Variations of elongation at break of the NR vulcanizates as a function of the aging time at 95°C. Rectangles, circles, and triangles stand for the NR vulcanizates without the resoles, with the LM-Resole, and with the SP 1045, respectively. Solid, open, and crossed symbols indicate the NR vulcanizates containing the resole of 0.96, 1.92, and 2.88 phr, respectively.

the degree of crosslink density. Breaking elongation of a rubber vulcanizate with a high crosslink density is shorter than that of a rubber vulcanizate with a low one. Figure 8 shows the variations of breaking elongation of the vulcanizates as a function of the aging time. The breaking elongations of all the NR vulcanizates show the same trend that the breaking elongation decreases with an increase of the aging time. The breaking elongation of the vulcanizate without the resoles is shorter than for the vulcanizates with the

resoles. This is because the crosslink density of the vulcanizate without the resoles is higher than that of the vulcanizates containing the resoles. The breaking elongations of the vulcanizates containing the resoles of 2.88 phr are shorter than those of the vulcanizates containing the resoles of 1.92 phr although the crosslink densities of the formers are lower than those of the latters. This may be due to the high networks of the resoles in the vulcanizate with the high content of the resoles.

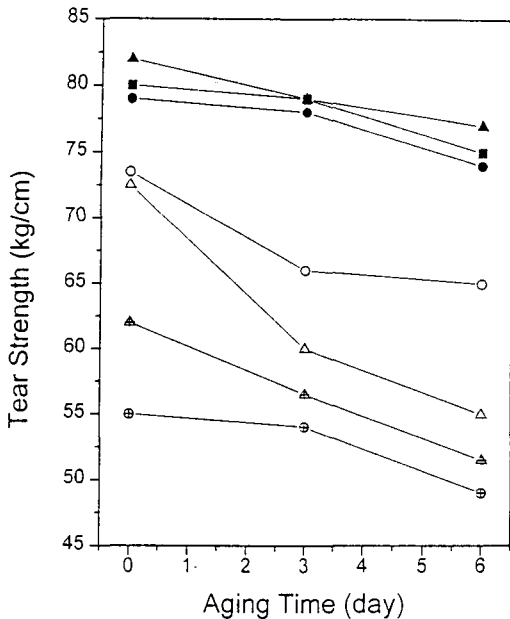


Fig. 9. Variations of tear strength of the NR vulcanizates as a function of the aging time at 95°C. Rectangles, circles, and triangles stand for the NR vulcanizates without the resoles, with the LM-Resole, and with the SP 1045, respectively. Solid, open, and crossed symbols indicate the NR vulcanizates containing the resole of 0.96, 1.92, and 2.88 phr, respectively.

Tear strength of a sulfur-cured vulcanizate passes through the maximum with increasing the crosslink density. The tear strengths of all the NR vulcanizates before the aging are higher than after the thermal aging. (Figure 9) For the vulcanizates containing the resoles, the tear strengths of the vulcanizates with a high resole content are lower than those of the vulcanizates with a low one. The tear strength of the vulcanizate containing the SP 1045 of 0.96 phr is higher than that of the vulcanizate without the resoles although the

crosslink density of the former is lower than that of the latter. This may be also due to the formation of the resole networks as discussed previously.

IV. Conclusions

The scorch time of the NR compound containing the resole with a low molecular weight distribution is shorter than that of the compound containing the resole with a high one. Crosslink densities of the NR vulcanizates with a high resole content after the thermal aging at 95°C decrease, while that of the vulcanizate without resole after the thermal aging at 95°C increases. Moduli of the vulcanizates with a high resole content increase as the aging time increases though the crosslink density decreases after the thermal aging. For the vulcanizates with high resole contents, modulus, tensile strength, and tear strength of the vulcanizate containing SP 1025 are higher than those of the vulcanizate containing LM-Resole though crosslink density of the former is lower than for the latter. This is due to the reinforcing effect by formation of the resole networks.

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