

Resole-Cured NR Vulcanizates with Thermally Reacted *p*-*t*-Octylphenol Formaldehyde Resole

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ABSTRACT: Crosslink dissociation of resole-cured NR vulcanizates was studied using steam aging. Four carbon black-filled NR vulcanizates were prepared to investigate the influence of heated *p*-*t*-octylphenol formaldehyde resole (at 160°C for 0.0, 1.5, 3.0, and 6.0 h) on the cure characteristics and stability of the crosslinks. By increasing the heating time of the resole, dimethylene ether linkages of the resole decrease while *o*-methylene quinone intermediates increase. The cure rate of the NR vulcanizates with the heated resole for 1.5 h is faster but those for 3.0 and 6.0 h are slower than that with the unheated resole. In comparison with the vulcanizates containing the non-heated resole, the delta torque of the NR vulcanizate with the heated resole for 1.5 h increases, while those for 3.0 and 6.0 h decrease. The swelling ratios of the four NR vulcanizates decrease after steam aging at 95°C for 7 days. The differences of the swelling ratios before and after steam aging decrease with increase of the heating time of the resole. The decrease of the swelling ratio after the steaming is due to the dissociation of the dimethylene ether linkage in the vulcanizates. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1811–1819, 1998

Key words: resole; dissociation; dimethylene ether linkage; steam aging

INTRODUCTION

In general, rubber compounds are crosslinked by sulfur vulcanization,^{1–3} peroxide curing,⁴ or resole curing.⁵ Sulfur vulcanization is the most popular. The mechanical properties of rubber materials are improved by vulcanization. In the case of sulfur curing of unsaturated rubbers, crosslinking and reversion as competing reactions depend on the curing time and temperature. S—S and C—S bonds are relatively unstable. Thus, sulfur curing at high temperatures deteriorates the mechanical properties of rubbers due to reversion. Tire bladders were initially manufactured by sulfur curing. Tire bladder compounds are usually made of butyl rubber (IIR) with, typically, 1–5% of isoprene.

Reversion of the IIR bladders dominated at the high temperatures (over 140°C) used in tire curing. Thus, the service life of these bladders became shorter. To increase the service life of the bladders, it was necessary to develop a new vulcanizing technique. *p*-Alkylphenolic resole vulcanization makes C—C bonds more stable than S—S and C—S bonds. Therefore, a resin-cured IIR has a good resistance to reversion at high temperatures.

Curing of NR and IIR using a phenolic resole resin has been investigated since the end of the 1930s.⁶ Crosslinking between unsaturated elastomers and phenolic resole resins was proposed by the chroman mechanism, based on the study of low molecular weight model compounds.^{7–11} A phenolic resole is changed to an *o*-methylene quinone intermediate by dehydration at high temperatures. This intermediate reacts with the double bonds of olefins and forms chroman structures by a 1,4-cycloaddition.

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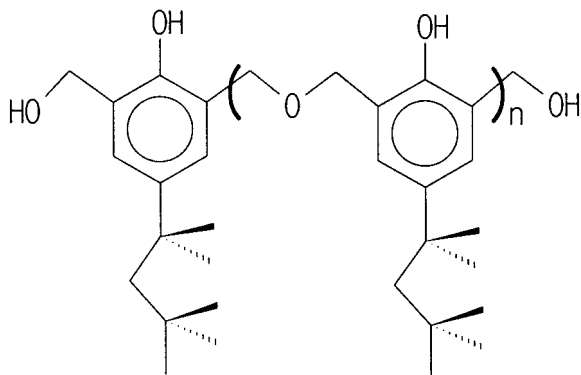


Figure 1 General formula of *p-t*-octylphenol formaldehyde resole.

In the tire industry, SP 1045 is employed as a resin curing agent for bladder curing. SP 1045 is one of the alkylphenolic resoles and its general structure, *p-t*-octylphenol formaldehyde resole, is shown in Figure 1. The SP 1045 has two types of linkages between two *p-t*-octylphenols. The major linkage is dimethylene ether ($-\text{CH}_2\text{OCH}_2-$) and the minor one is methylene ($-\text{CH}_2-$). Only the resoles with both terminals of methylol ($-\text{CH}_2\text{OH}$) can participate in the crosslinking. Most end groups of SP 1045 are methylol and there are also some terminals with hydrogen and *o*-methylene quinone. In the previous work,¹² we studied thermal reactions of SP 1045. We reported that the *o*-methylene quinone intermediates increase and the dimethylene ether linkages decrease with increase of the reaction time. The resin curing agent is changed during storage, especially under high temperature and high humid conditions, but the reason for this has not been elucidated clearly.

In this work, crosslink dissociation of resole-cured NR vulcanizate was studied with steam aging to investigate the presence of dimethylene ether linkage in the vulcanizates. Thermal reactions of dilute solutions of SP 1045 and 2,6-dihydroxymethyl-*p-t*-octylphenol, the monomer of *p-t*-octylphenol formaldehyde resole, were also studied to investigate the dissociation of dimethylene ether linkage of *p-t*-octylphenol formaldehyde resole, formation of *o*-methylene quinone intermediate, and condensation between resoles in detail.

EXPERIMENTAL

2,6-Dihydroxymethyl-*p-t*-octylphenol was synthesized as follows^{13–15}: A mixture of *p-t*-octylphenol

(50 g, 242.3 mmol), NaOH (10 g in 100 mL of H_2O), and formaldehyde (38 mL, 37% aqueous solution) were stirred at 40–45°C for 4 days. The mixture was cooled, poured into 200 mL of water, acidified with dilute HCl, and extracted into CH_2Cl_2 of 200 mL. Evaporation of the solvent afforded 60 g (93%) of a brownish waxy oil. The crude product was purified by column chromatography (eluent, acetone/*n*-hexane = 1/10) to give a white solid of 2,6-dihydroxymethyl-*p-t*-octylphenol.

¹H-NMR (CDCl_3): δ 8.08 (br s, 1H, OH), 7.02 (s, 2H, ArH), 4.75 (s, 4H, $-\text{CH}_2-$ from benzyl), 3.04 (br s, 2H, OH), 1.67 (s, 2H, $-\text{CH}_2-$ from *t*-octyl). ¹³C-NMR (CDCl_3): δ 152.22, 141.64, 125.61, and 125.13 (Ar), 63.88 and 56.85 ($-\text{CH}_2\text{Ar}$), and 37.88, 32.32, 31.78, and 31.57 (*t*-octyl).

SP 1045 was employed as the *p-t*-octylphenol formaldehyde resole.

Thermal reactions of SP 1045 and 2,6-dihydroxy-*p-t*-octylphenol dilute solutions with *n*-decane were carried out at 160°C for 1 h. SP 1045, 4.0 g, was diluted with *n*-decane, 400 mL, and 2,6-dihydroxy-*p-t*-octylphenol, 200 mg, was also diluted with *n*-decane, 200 mL. To prevent SP 1045 or 2,6-dihydroxy-*p-t*-octylphenol from reacting with the solvent, *n*-decane was used as a dilute solvent. SP 1045 was also heated under the melt condition in a convection oven at 160°C for 1.5, 3.0, and 6.0 h.

Carbon black-filled NR compounds containing 7.0 phr SP 1045 heated for 0.0, 1.5, 3.0, and 6.0 h were prepared. The formulations are given in Table I. The four NR compounds are hereafter referred to as Compounds 1, 2, 3, and 4, respectively. The four NR vulcanizates were prepared by curing at 180°C for 40 min.

The contents of total organic compounds in the NR vulcanizates were measured by extraction with boiling THF for 7 h. Steam aging was carried out at 95°C for 7 days. The swelling ratios of the NR vulcanizates before and after steam aging were measured by swelling with *n*-decane for 2 days. Before swelling, free organic additives in the vulcanizates were extracted with acetone/THF (= 1/1) and acetone each for 3 days.

IR spectra were acquired on a Bruker IFS 85. GPC was performed with a Tosoh system. One Tosoh (GRCL3K 0001) and two Waters (T32991A 02 and T33441A 03) columns were coupled in se-

Table I Formulations and Cure Characteristics

Formulations and Characteristics	Compound No.			
	1	2	3	4
SMR 20	93.0	93.0	93.0	93.0
Neoprene W	7.0	7.0	7.0	7.0
N220	50.0	50.0	50.0	50.0
ZnO	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0
Aromatic oil	3.0	3.0	3.0	3.0
SP 1045	7.0 (0.0 h) ^a	7.0 (1.5 h) ^a	7.0 (3.0 h) ^a	7.0 (6.0 h) ^a
<u>Rheometer (MDR 2000) at 180°C</u>				
ΔT (dN m)	3.06	3.26	2.80	1.83
t_5 (min)	0.70	0.73	0.70	0.72
t_{40} (min)	3.17	3.27	3.18	3.40
t_{95} (min)	25.00	25.02	25.92	27.72
Cure rate ^b (dN m/min)	0.54	0.55	0.51	0.28
<u>At 200°C</u>				
ΔT (dN m)	2.99	3.07	2.68	1.70
t_5 (min)	0.42	0.42	0.40	0.38
t_{40} (min)	1.15	1.15	1.10	1.12
t_{95} (min)	7.22	7.27	6.82	6.65
Cure rate ^b (dN m/min)	1.67	1.73	1.55	0.93

^a Heating time of SP 1045 at 160°C.

^b Slope at t_{10} was employed.

ries. The analyzing temperature was 40°C. THF was eluted at a 1 mL/min flow rate. HPLC was performed with a Waters 510. The column used was a Zorbox SV-C18 of 4.6 mm \times 25 cm. A gradient program was employed with solvent A (20 methanol/80 water) and B (methanol). Torque–time curves were obtained using a Flexsys rheometer (MDR 2000) at a frequency of 100 cycles/min and a ± 1.5 arc for vulcanizing temperatures of 160, 180, and 200°C.

RESULTS AND DISCUSSION

Thermal Reactions of Resole

Thermal reactions under melt and dilute conditions of SP 1045 and a dilute condition of 2,6-dihydroxymethyl-*p*-*t*-octylphenol were carried out. The thermal reactions of melt SP 1045 were performed to investigate the influence of the resole with different species on the cure characteristics. SP 1045 (*p*-*t*-octylphenol formaldehyde resole) was heated at 160°C for 0.0, 1.5, 3.0, and 6.0 h under the melt condition. The variation of termi-

nal and linkage types depending on the heating time was investigated with IR spectroscopy. In the previous work,¹² the IR analysis was described in detail. The typical IR peaks of the resole are 3379 and 1072 cm^{-1} , corresponding to the hydroxyl group and dimethylene ether linkage (or methylol), respectively. There is one important peak in the IR spectrum. It is 1655 cm^{-1} , assigned to the conjugated C=O double bond, which indicates the *o*-methylene quinone intermediate. Table II shows the normalized intensities of the dimethylene ether linkage (1072 cm^{-1}), the *o*-methylene quinone intermediate (1655 cm^{-1}), and the

Table II Normalized Intensities of Major Peaks in FTIR Spectrum of the Heated SP 1045

Heating Time (h)	1072 cm^{-1}	1655 cm^{-1}	3379 cm^{-1}
0.0	0.47	0.11	0.44
1.5	0.46	0.10	0.43
3.0	0.43	0.19	0.38
6.0	0.39	0.39	0.28

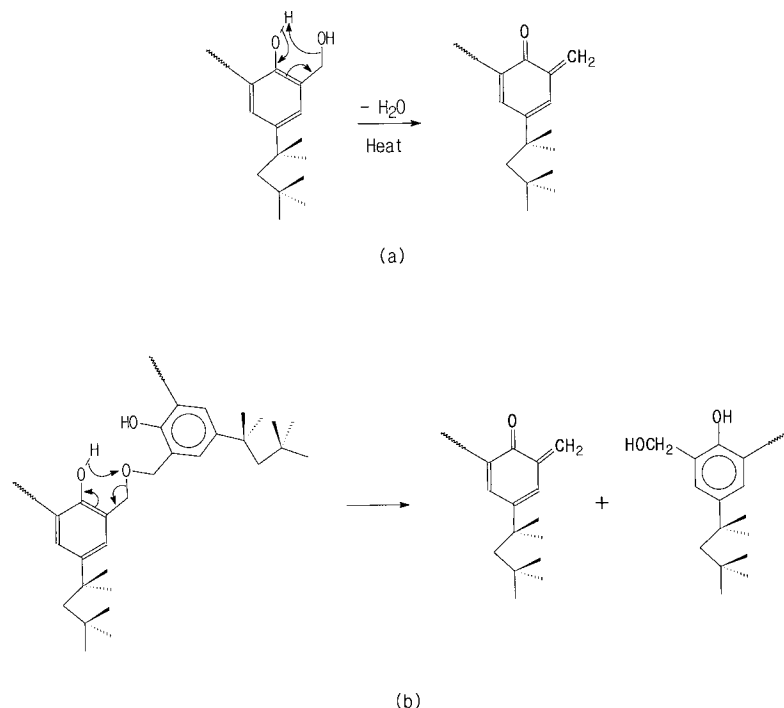


Figure 2 Production mechanism of *o*-methylene quinone intermediate from (a) methylol terminal and (b) dimethylene ether linkage.

hydroxyl group (3379 cm^{-1}). Normalization of the peaks was performed with the highest peak of 2954 cm^{-1} , assigned to the alkyl group. The intensity of 2954 cm^{-1} cannot be changed since the *t*-octyl group is not changed into the other form by the thermal reaction. From Table II, it was found that the intensity of the *o*-methylene quinone intermediate increases remarkably while those of the dimethylene ether linkage and the hydroxyl group decrease as the heating time increases from 1.5 to 6.0 h.

The *o*-methylene quinone intermediate can be produced by dehydration from the methylol terminal as shown in Figure 2(a). To make clear the production of the *o*-methylene quinone intermediate from the methylol terminal, the thermal reaction of 2,6-dihydroxymethyl-*p*-*t*-octylphenol, corresponding to the monomer of *p*-*t*-octylphenol formaldehyde resole, was carried out at 160°C for 1 h under the dilute condition. Figure 3 shows HPLC chromatograms of the 2,6-dihydroxymethyl-*p*-*t*-octylphenol and heated 2,6-dihydroxymethyl-*p*-*t*-octylphenol. Figure 3(b) shows that most of the monomer is changed into other species by the thermal reaction. The peak before the monomer peak in Figure 3(b), which is assigned to the *o*-methylene quinone intermediate of the monomer, 1-methylene-3-*t*-octyl-6-hydroxymethylbenzoqui-

none, can be formed by dehydration. Reaction products with molecular weight more than that of the monomer were also detected. They may be dimer and trimer species formed by condensation.

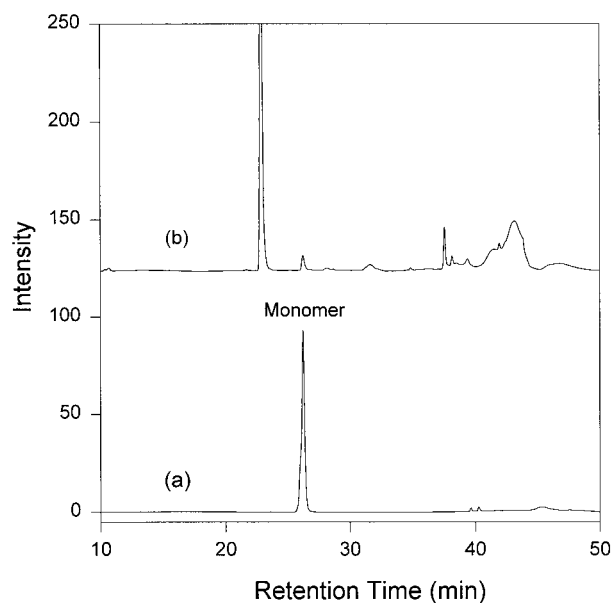


Figure 3 HPLC chromatograms of (a) unreacted 2,6-dihydroxymethyl-*p*-*t*-octylphenol and (b) reaction products after thermal reaction at 160°C for 1.0 h.

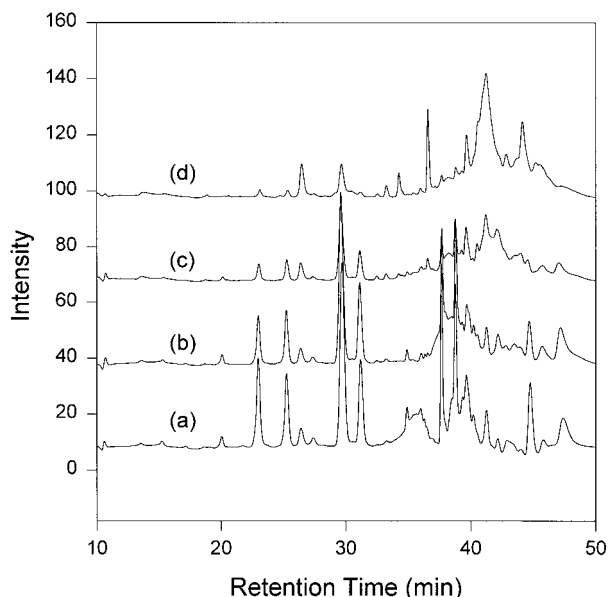


Figure 4 HPLC chromatograms of the heated SP 1045 at 160°C for (a) 0.0, (b) 1.5, (c) 3.0, and (d) 6.0 h under the melt condition.

Thus, one can expect that the condensation occurs in the thermal reaction of the resole.

In the previous work,¹² we analyzed the reaction products of heated SP 1045 by GPC. To investigate precisely the variation of the monomer, dimer, and trimer species, HPLC analysis was performed in the present study. Figure 4 shows the variation of the reaction products of heated SP 1045. The peaks at retention times of 24.9 and 22.4 min correspond to the monomer and its *o*-methylene quinone intermediate. Peaks from 32 to 49 min correspond to the dimer and trimer species. The monomer species decrease while the dimer and trimer species increase with an increase of the heating time from 0.0 to 6.0 h. The ratio of the peak area from 32 to 49 min is 1 : 1.02 : 1.03 : 1.18 for the heating times of 0.0, 1.5, 3.0, and 6.0 h, respectively. The HPLC analysis shows that there are many species of the dimer and trimer in the resole. For example, the number of possible species of the dimer are 18 ($= 2 \times 3 \times 3$) since the dimer can have two linkage types (dimethylene ether and methylene) and three terminal types (hydrogen, methylol, and *o*-methylene quinone).

A thermal reaction of the dilute SP 1045 solution was carried out to investigate a source of an increase of the dimer and trimer species by heating the melt SP 1045. The SP 1045 was diluted with *n*-decane to condensation. Figure 5 shows

the variation of the molecular weight distributions before and after the thermal reaction of the dilute SP 1045 solution. The molecular weight distribution of SP 1045 after the thermal reaction under the dilute condition was shifted from $M_w = 2.42 \times 10^3$ to 1.39×10^3 . HPLC analysis of the dilute SP 1045 was also performed to investigate the reaction products with the monomer, dimer, and trimer species in detail. Figure 6 shows HPLC chromatograms of the dilute SP 1045 solution before and after the thermal reaction. All the monomer, dimer, and trimer species increased after the thermal reaction. From the GPC and HPLC analyses of the reaction products of the dilute SP 1045, it was clear that dissociation of the dimethylene ether linkage in the resole occurred before heating.

From the comparison between the thermal reactions under the melt and dilute conditions of SP 1045, it was found that the dilute condition gives reaction products with a lower molecular weight than that of the melt condition. This indicates that condensations of small species with the other species occur well under the melt condition. In Figure 6, monomer species with molecular weight less than that of 1-methylene-3-*t*-octyl-6-hydroxy-

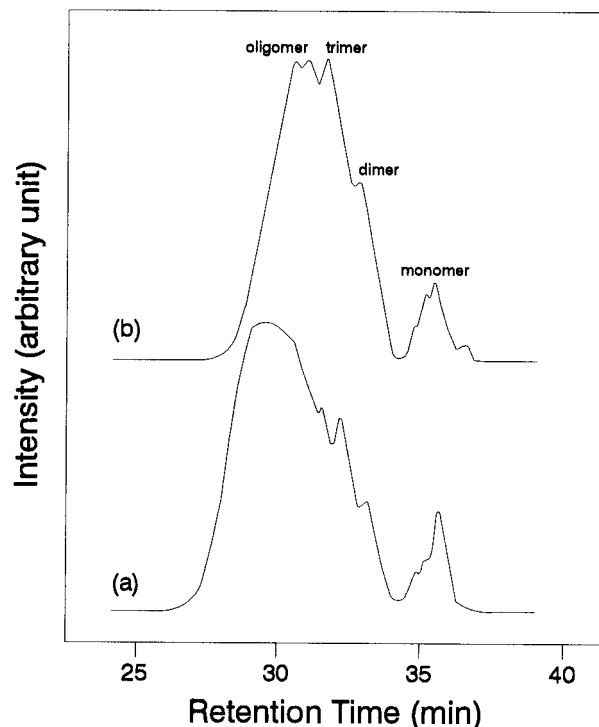


Figure 5 GPC chromatograms of (a) unreacted SP 1045 and (b) reaction products of the dilute solution after thermal reaction at 160°C for 1.0 h.

methylbenzoquinone (peak at 23.1 min) were observed and they increased after the thermal reaction. Since these species were not observed in the chromatogram of the resole monomer, 2,6-dihydroxymethyl-*p-t*-octylphenol (Fig. 3), they are supposed to be 2-hydroxymethyl-*p-t*-octylphenol, 1-methylene-3-*t*-octyl-benzoquinone, and *p-t*-octylphenol. 2-Hydroxymethyl-*p-t*-octylphenol and 1-methylene-3-*t*-octyl-benzoquinone can be produced by dissociation of the dimethylene ether linkage of the resoles with a hydrogen terminal.

The decrease of the monomer species means that condensation between resoles occur for heating. The condensation between resoles was elucidated by the result of the thermal reaction of 2,6-dihydroxymethyl-*p-t*-octylphenol. The increase of the dimer and trimer species indicates the dissociation of the dimethylene ether linkage of a big resole into one small resole and one *o*-methylene quinone intermediate as shown in Figure 2(b). Since the dimethylene ether linkage forms a hexagonal ring with hydroxyl groups of the alkylphenol by hydrogen bonding, the dimethylene ether linkage can be easily dissociated. The distances between the oxygen atoms of the hydroxyl group and the dimethylene ether linkage of the dimer to the decamer of *p*-alkylphenol formaldehyde resole, obtained from theoretical calculations, are $\sim 3 \text{ \AA}$.¹⁶ Another possibility is the condensation

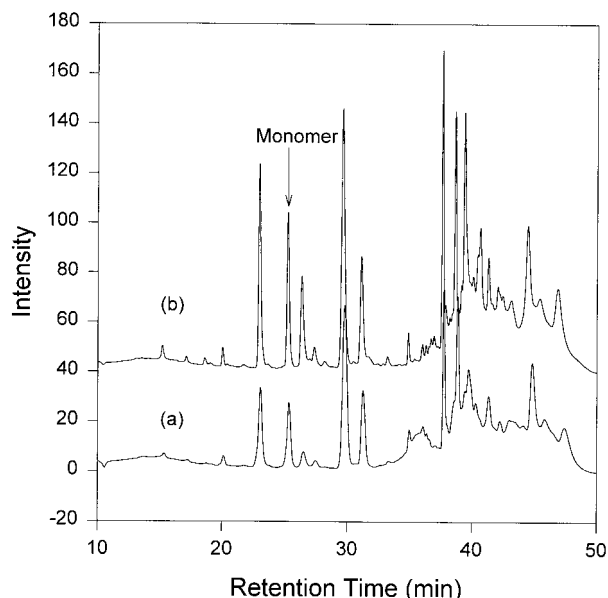


Figure 6 HPLC chromatograms of (a) unreacted SP 1045 and (b) reaction products of the dilute solution after thermal reaction at 160°C for 1.0 h.

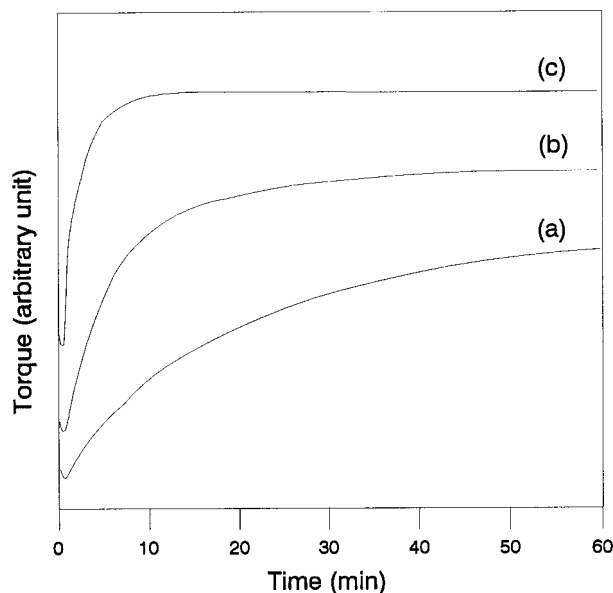


Figure 7 Rheographs of the NR compound 3 at (a) 160°C, (b) 180°C, and (c) 200°C.

of the monomer species with the other monomer or dimer species.

Cure Characteristics of the NR Vulcanizates

Rheographs are shown in Figure 7 for compound 3 at 160, 180, and 200°C. The rheographs of the other NR compounds show a similar trend. The processes of the manufacture and physical properties of rubber compounds are determined by scorch time (reaction starting point), cure rate, optimum cure time, and delta torque. Since the vulcanizing reaction between NR and SP 1045 did not reach an optimum cure at 160°C until 60 min, the cure properties are listed only for 180 and 200°C in Table I. The scorch time and cure rate became fast while the delta torque slightly decreased by increasing the temperature from 180 to 200°C. Rheographs are shown in Figure 8 for Compounds 1–4 at 180°C. The delta torque of Compound 2 at 180°C is higher than that of Compound 1 by about 0.2 dN m, while those of Compounds 3 and 4 are lower than that of Compound 1 by about 0.3 and 1.2 dN m, respectively. The scorch time at 180°C does not show a specific trend, but that at 200°C decreases with an increase of the heating time from 0.0 to 6.0 h. This may be because the vulcanization at 180°C for 60 min is not performed completely.

The decrease of scorch time can be considered due to the increase of the dimer and trimer spe-

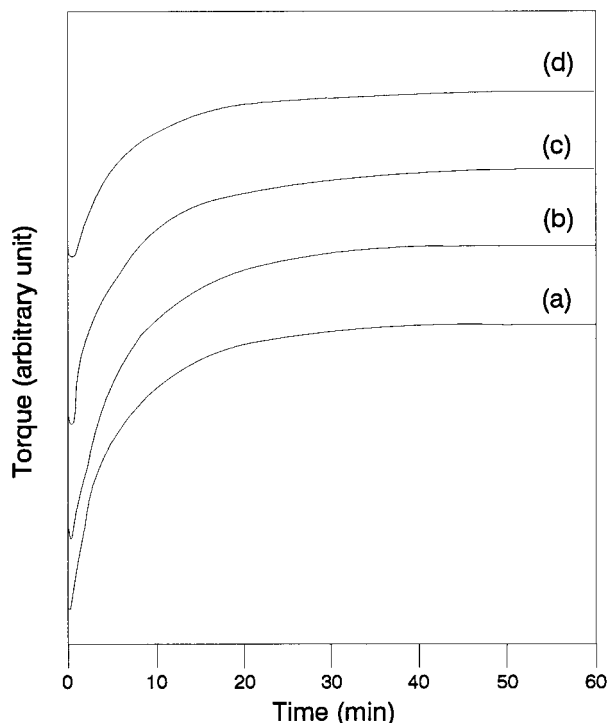


Figure 8 Rheographs of the NR compound (a) 1, (b) 2, (c) 3, and (d) 4 at 180°C.

cies. By the chroman mechanism, a resole crosslink between rubber chains is built when the resole size is equal to or more than the dimer. Since both terminals of a small resole is less hindered than are those of a big resole, a crosslinking reaction with a small resole can be faster than that with a big resole. Thus, the scorch time of the NR compounds containing the heated SP 1045 is faster than that containing the raw SP 1045. The decrease of the delta torque can be explained by the increase of the inactive species. The possible terminals of the resole are methylol ($-\text{CH}_2\text{OH}$), methylene ($=\text{CH}_2$), and hydrogen ($-\text{H}$). The methylene terminal is made by dehydration of methylol. The methylol and methylene terminals are active, so the resole with the methylol or the methylene terminal participates in the crosslinking reaction. But the resole with the hydrogen terminal can not participate in the crosslinking. Thus, an increase of the inactive terminals results in a decrease of the delta torque. New inactive resoles can be formed by condensation of one inactive resole and one active resole. Another source of the delta torque decrease can be the formation of cyclic compounds, calixarenes by condensation of both terminals. The formation of *p-t*-butyl-

calix[4,6,8]arenes, cyclic compounds of alkylphenolic resins, was reported.¹⁷⁻¹⁹

To compare the amounts of the inactive species, organic compounds in the four NR vulcanizates were extracted with THF. Since resoles with a hydrogen terminal or a cyclic form cannot participate in the crosslinking, they remained free in the vulcanizates. The results are summarized in Table III. The amounts of the extracted organic compounds is much more than the total content of SP 1045 (about 4.2 wt %) since stearic acid and aromatic oil (about 3.0 wt %) were also extracted. The contents of the extracted organic compounds increase with increase of the heating time. This can lead to the conclusion that the inactive species of the resoles increase with an increase of the heating time.

Steam Aging of the NR Vulcanizates

In general, resoles are used as a curing agent for the bladder. Tire is cured at a high temperature over 140°C. The heat is transferred through a bladder from hot steam for tire curing. Thus, a bladder should have resistance to steam aging to have a good service life. Steam aging of the four NR vulcanizates at 95°C for 7 days was carried out to investigate the influence of the heated SP 1045 on steam-aging resistance of the vulcanizates. The steam-aging resistance was studied by measurement of the swelling ratio before and after the aging. The swelling ratio reflects the crosslink density of rubber vulcanizates. When the formulations of rubber vulcanizates are similar, the lower the swelling ratio is, the higher the crosslink density.

Figure 9 shows the variation of the swelling ratio before and after steam aging. For the vulcanizates before steam aging, the swelling ratios are consistent with the delta torque. Compound 2, having the highest delta torque, has the lowest swelling ratio, while Compound 4, having the lowest delta torque, has the highest swelling ratio.

Table III Contents of Free Organic Additives in the NR Vulcanizates

Organic Compound	Compound			
	1	2	3	4
Extracted amount	5.24	5.28	5.44	6.57

Units are wt %.

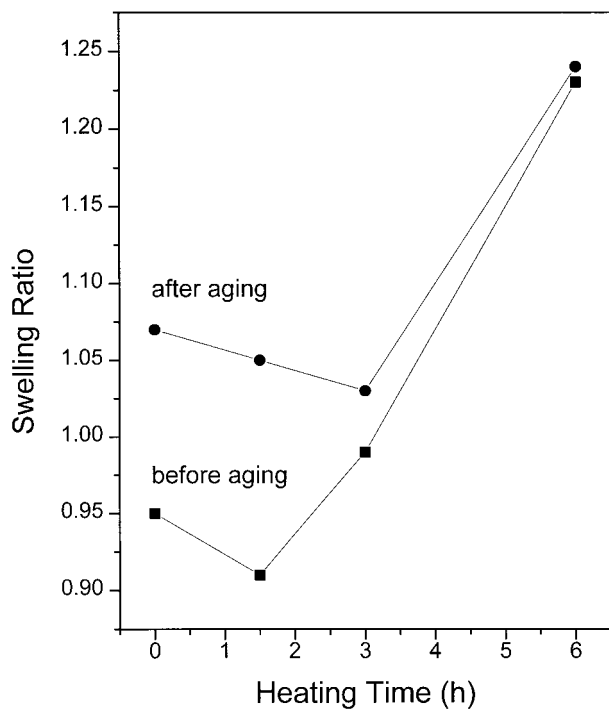


Figure 9 Variation of swelling ratio of the NR vulcanizates before and after steam aging. (Squares) before and (circles) after steam aging.

The swelling ratios were changed after the steam aging. The swelling ratios of Compounds 1, 2, 3, and 4 after steam aging decrease by 13, 15, 4, and 1%, respectively. This means that the crosslink densities decrease. The decrease of the crosslink density may result from dissociation of the crosslinks. The crosslink density of Compound 2 after steam aging decreases more than that of Compound 1. The steam-aging condition (95°C) employed in this study is much milder than the real condition of tire manufacture (over 140°C). Thus, we can expect that dissociation of the crosslink progresses during tire curing.

Decrease of the crosslink density of resolcured vulcanizates can occur by dissociation of the dimethylene ether linkage. As discussed previously, the dissociation of the dimethylene ether linkage was observed in the thermal reaction of SP 1045 at 160°C. The results of steam aging can lead to the conclusion that the dissociation of the dimethylene ether linkage occurs at 95°C and the dimethylene ether linkage survives even after heating at 160°C for 6.0 h and vulcanization at 180°C. The difference of the swelling ratios before and after steam aging decreases with increase of the heating time from 0.0 to 6.0 h. This indicates that the dimethylene ether linkage that remains

in the NR vulcanizates decreases with increase of the heating time of SP 1045. Variation of swelling ratios before and after steam aging of the NR compound 4 is negligible. This can lead to a conclusion that there are few dimethylene ether linkages in the heated SP 1045 for 6.0 h. Condensation between a resole with a hydrogen terminal and that with a methylol one gives a resole with a methylene linkage. Thus, when the heating time increases, the methylene linkage increases while the dimethylene ether linkage decreases.

CONCLUSIONS

In the thermal reaction of SP 1045 (*p-t*-octyphenol formaldehyde resole) at 160°C under the melt condition, the dimethylene ether linkage and methylol decrease and the *o*-methylene quinone intermediate increases by increasing the heating time. The condensation between resoles and the formation of the *o*-methylene quinone intermediate were elucidated by the thermal reaction of a dilute solution of 2,6-dihydroxymethyl-*p-t*-octylphenol. The dissociation of the dimethylene ether linkage was elucidated by the thermal reaction of the dilute solution of SP 1045. The types and molecular weight distribution of the resoles are changed for heating by condensation, dissociation of dimethylene ether linkage, and formation of *o*-methylene quinone intermediate. The delta torque of the NR compound containing the heated SP 1045 increases with increase of the heating time of SP 1045. The cure rate of the NR compound containing the heated SP 1045 for 1.5 h is faster than that for 0.0 h. The swelling ratios of the NR vulcanizates decreased after steam aging. The differences of the swelling ratios before and after steam aging decreased with increase of the heating time of SP 1045. This is due to the increase of the inactive species of the resoles by heating.

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