# Analysis of Unbound Materials in Carbon-Black-Filled NR Vulcanizates

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ABSTRACT: Extraction of unbound materials from carbon-black-filled natural rubber (NR) vulcanizates with different cure systems was studied using various solvents with different dielectric constants of *n*-hexane, toluene, THF, acetone, and acetonitrile. The extraction was performed at room temperature and 40°C for 2 days and in the boiling solvent for 8 h. Amounts of extracted materials from the NR vulcanizates increase by increasing the temperature. Amounts of extracted materials from the NR vulcanizates with *n*-hexane, toluene, and THF are more than those with acetone and acetonitrile. Amounts of extracted materials from the NR vulcanizates with *n*-hexane, toluene, and THF are more than those with a high crosslink density are less than those from the NR vulcanizate with a low one. Thermogravimetric analysis of the NR vulcanizates before and after the extraction were carried out to investigate components of the extracted materials. It was found that there were polymer components and metal complexes, as well as organic matters with a low molecular weight in the extracted materials. Abilities of the solvents to extract unbound materials from the NR vulcanizates were discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1995–2005, 1999

**Key words:** unbound materials; extraction; natural rubber vulcanizate; thermogravimetric analysis; swelling

# INTRODUCTION

In general, carbon-black-filled rubber compounds are composed of rubber, carbon black, antidegradants, curing agents, and processing aids. Ingredients in a rubber vulcanizate are extracted easily with proper organic solvents,<sup>1</sup> and unbound rubber molecules are also extractable.<sup>2</sup> For extraction of unbound materials, it is important to select a proper solvent to extract only target materials thoroughly.

Of compounding ingredients, the curing agents are chemically changed by vulcanization reaction. Zinc oxide reacts with stearic acid, sulfur, and cure accelerator so that zinc complexes are formed.<sup>3,4</sup> It is hard to extract the zinc complexes from a rubber vulcanizate since the zinc complex is big and has a poor solubility in organic solvents. The zinc dimethylenedithiocarbamate complex has a very poor solubility in toluene, but its pentacoordinated zinc complexes formed by involving one ligand have a good solubility in toluene.<sup>5</sup> There are some pendent groups terminated by a cure accelerator residue in a rubber vulcanizate.<sup>6,7</sup> These pendent groups are analyzed by treating with acid.<sup>8</sup>

In order to analyze a rubber vulcanizate, qualitative and quantitative analyses of extractable ingredients should be performed, and component ratios of organic matters, rubber, carbon black, and metal oxide should be also analyzed. In the present work, solvent effects on extraction of unbound materials from natural rubber (NR) vulcanizates cured by different cure systems were

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Compound No.	1	2	3	4	5	6
SMR20	100.0	100.0	100.0	100.0	100.0	100.0
N351	50.0	50.0	50.0	50.0	50.0	50.0
Wax	3.0	3.0	3.0	3.0	3.0	3.0
Stearic acid	0.0	0.0	0.0	3.0	3.0	3.0
ZnO	0.0	0.0	0.0	3.0	3.0	3.0
Sulfur	3.0	0.0	1.5	3.0	0.0	1.5
TBBS	0.0	4.0	2.0	0.0	4.0	2.0
Crosslink density						
$(10^{-3} \text{ g mol mL}^{-1})$	1.91	0.43	0.93	1.92	0.48	4.01
Reversion ratio (%)						
at 160°C at 20 min	<u> </u>	<u> </u>	58	5	b	3
Reversion ratio (%)						
at 160°C at 40 min	a	<u> </u>	72	9	b	8
Reversion ratio (%)						
at 160°C at 60 min	<u> </u>	a	75	18	1	11

#### Table I Formulations (phr)

 $t_{\max}$  is over 60 min.

<sup>b</sup>  $t_{\text{max}}$  is over 40 min.

studied. Extractability of solvents depending on carbon-black-filled NR vulcanizates with different cure systems were investigated. Components of unextracted materials were analyzed using a thermogravimetric analyzer.

## **EXPERIMENTAL**

In order to investigate solvent effects on extraction of unbound materials from a carbon-black-filled rubber vulcanizate, six carbon-black-filled NR vulcanizates with different cure systems were prepared. The formulations are given in Table I. Compounds 1-3 do not contain stearic acid and zinc oxide. Compounds 1 and 4 do not have TBBS (N-tert-butyl-2-benzothiazolyl sulfenamide), while compounds 2 and 5 do not have sulfur. The carbonblack-filled NR vulcanizates were prepared by curing at 160°C for 60 (compounds 1 and 2), 40 (compounds 4 and 5), and 20 min (compounds 3 and 6). Cure characteristics were obtained using Flexsys rheometer (MDR 2000) at a frequency of 100 cycles per min and  $\pm 1.5$  arc for the vulcanizing temperature of 160°C.

*n*-Hexane, toluene, THF, acetone, and acetonitrile were employed as extraction solvents. Organic materials in the vulcanizates were extracted at room temperature (about  $18^{\circ}$ C) and  $40^{\circ}$ C for 2 days and at boiling temperature of the solvents for 8 h with the solvents. The samples were dried at  $85^{\circ}$ C for 4 h. The amounts of extracted materials from the NR vulcanizates with the solvents were determined by the difference of the weight of the sample before and after the extraction.

The relative component ratios of organic matter, polymer, carbon black, and metal oxide in a carbon-black-filled rubber vulcanizate were determined using a TGA 2950 thermogravimetric analyzer of TA Instruments. The analysis conditions of thermogravimetric analysis (TGA) were as follows (the initial temperature is 100°C):



Figure 1 Rheocurves at  $160^{\circ}$ C of compounds (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, and (f) 6.

	Temperature						
Compound No.	(°C)	1	2	3	4	5	6
Extractable ingredie	$ents^{a}$	3.85	4.46	4.15	5.49	6.06	5.78
<i>n</i> -Hexane	$18^{\mathrm{b}}$	5.59	21.13	8.86	5.59	13.18	3.68
	$40^{\mathrm{b}}$	6.14	23.33	9.66	8.05	15.13	4.99
	$71^{\rm c}$	5.94	21.14	9.17	7.78	14.27	5.94
Toluene	$18^{\mathrm{b}}$	6.15	23.49	10.15	6.34	15.71	4.13
	$40^{ m b}$	6.56	26.55	11.24	10.56	19.27	6.10
	$115^{\rm c}$	8.98	27.90	12.91	13.56	18.87	6.64
THF	$18^{\mathrm{b}}$	5.89	26.70	10.38	8.54	17.92	6.10
	$40^{ m b}$	6.75	30.78	12.03	12.09	25.36	6.13
	$68^{c}$	5.93	27.54	9.46	8.50	17.15	6.15
Acetone	$18^{\mathrm{b}}$	3.12	4.06	3.51	2.65	3.79	2.98
	$40^{ m b}$	4.25	5.26	4.91	4.13	5.62	4.80
	$58^{\circ}$	4.36	5.47	5.18	4.62	6.60	5.50
Acetonitrile	$18^{\mathrm{b}}$	1.45	1.72	1.48	0.98	1.27	1.01
	$40^{ m b}$	2.45	3.43	2.91	2.13	3.31	2.31
	$85^{\circ}$	4.06	5.04	4.63	4.12	6.79	5.09

Table II Amounts of Extracted Materials (Wt %)

<sup>a</sup> Total amounts of extractable ingredients of wax, stearic acid, sulfur, and TBBS listed in the formulations.

<sup>b</sup> Extraction for 2 days.

<sup>c</sup> Extraction in boiling solvent for 8 h. Temperature of boiling solvent.

- 1. Increasing the temperature from 100 to 300°C with a rate of 40°C/min and then keeping at 300°C for 7 min.
- 2. increasing the temperature from 300 to 550°C with a rate of 100°C/min and then keeping at 550°C for 7 min.
- 3. increasing the temperature from 550 to 700°C with a rate of 100°C/min and then keeping at 700°C for 5 min.

TGA was performed under  $N_2$  for steps (1) and (2) and was performed under air for step (3). The amount decreased for the step (3) was determined as the content of carbon black in a carbon-blackfilled rubber vulcanizate. The amount that remained after steps (1)–(3) was determined as the content of ash (metal oxide). Crosslink densities of the samples were measured by a swelling method.<sup>9</sup>

### **RESULTS AND DISCUSSION**

Figure 1 gives cure characteristics of the compounds 1–6. The torques of the compounds 1 and 2 increase until 60 min. Reversion ratios at 60 min of compounds 3, 4, 5, and 6 are 75, 18, 1, and

11%, respectively. Reversion ratios at 20, 40, and 60 min of the NR compounds are listed in Table I. Reversion is speculated to occur when the desulfurization reaction is faster than the crosslinking reaction. Reversion occurs well in NR compounds.<sup>10,11</sup> The reversion ratio of compound 3 is higher than those of the others. It means that the NR vulcanizate 3 has more polysulfides than the others since polysulfides are weaker than monoand disulfides.<sup>12</sup> Delta-torques of the compounds containing zinc oxide and stearic acid are higher than those of the compounds without zinc oxide and stearic acid, as shown in Figure 1. Crosslink densities of the six NR vulcanizates are also listed in Table I.

There are zinc complexes in the NR vulcanizates 4-6 since compounds 4-6 contain zinc oxide and stearic acid. The kinds of zinc complexes in the NR vulcanizates are determined by the kinds of cure accelerators in the vulcanizates. Zinc benzothiazole-2-thiolate complexes do not exist in the NR vulcanizate 4 since compound 4 does not contain TBBS. There are cyclic sulfurs or pendent groups terminated by the TBBS residue.<sup>4,6,7</sup> It is hard to extract the cyclic sulfurs and pendent groups with organic solvent since they are bound to a rubber chain.



**Figure 2** TGA thermograms of the NR vulcanizate cured by zinc oxide, stearic acid, sulfur, and TBBS (compound 6) after extraction with acetone at (a) 58°C for 8 h, (b) 40°C for 2 days, and (c) 18°C for 2 days, and (d) before extraction. TGA conditions: 100°C (under N<sub>2</sub>)  $\rightarrow$  40°C/min  $\rightarrow$  300°C (keeping for 7 min)  $\rightarrow$  100°C/min  $\rightarrow$  550°C (keeping for 7 min)  $\rightarrow$  100°C/min  $\rightarrow$  100°C/min (under air)  $\rightarrow$  700°C (keeping for 5 min).

#### **Extraction of Unbound Materials**

Unbound materials in the NR vulcanizates were extracted with *n*-hexane, toluene, THF, acetone, and acetonitrile at 18 and 40°C for 2 days and in boiling solvent (71, 115, 68, 58, and 85°C, respectively) for 8 h. Polysulfides in the NR vulcanizates may be dissociated at high temperature. Thus, the extraction in boiling solvents was performed only for 8 h to minimize the dissociation of the existing sulfur crosslinks. The kinds of unbound materials may be mainly unreactive species and vulcanizing products of curing agents. Table II gives the amounts of the extracted materials with the organic solvents from the NR vulcanizates. The amounts of materials extracted with THF are larger than those of materials extracted with the other solvents. The amounts of materials extracted with n-hexane, toluene, and THF are much larger than those of materials extracted with acetone and acetonitrile. This may be due to interactions of the solvents with the unbound materials and the NR vulcanizates. Dielectric constants ( $\varepsilon$ ) of *n*-hexane, toluene, THF, acetone, and acetonitrile are 1.89, 2.38, 7.52, 21.01, and 36.64, respectively, while those of stearic acid, sulfur, 9-octylheptadecane ( $C_{25}H_{52}$ ), Balata (one of natural rubbers), and vulcanized Hevea (one of natural rubbers) are 2.31, 3.75, 2.11, 2.50, and 2.94, respectively.<sup>13</sup> The dielectric constant of toluene is closer to those of the components of the NR vulcanizates than to those of the other solvents. The dielectric constants of *n*-hexane, toluene, and THF are close to those of the components of the NR vulcanizates, while the dielectric constants of acetone and acetonitrile are very different from those of the components of the NR vulcanizates. The amounts of the extracted materials with toluene are less than those of the extracted materials with THF, although the dielectric constant of toluene is closer to those of the components of the NR vulcanizates than that of THF.

The amounts of the extracted materials increase by about 9-44, 7-67, 1-42, 30-61, and 69-161% for *n*-hexane, toluene, THF, acetone, and acetonitrile, respectively, as the temperature increases from 18 to 40°C. The increments of the amounts of the extracted materials with an increase of the temperature from 18 to 40°C for acetonitrile are larger than those for the other solvents. Thus, it may lead to a conclusion that the extraction of unbound materials from the NR vulcanizates with acetonitrile is more sensitive to the change of temperature than those with the other solvents. The increments of the amounts of the extracted materials by increasing the temperature for acetone and acetonitrile are larger than those for *n*-hexane, toluene, and THF. This may be due to the low solubility of the unbound materials in the polar solvents of acetone and acetonitrile. The increments of the amounts of the extracted materials from the NR vulcanizates containing stearic acid and zinc oxide (compounds 4-6) are larger than those from the NR vulcanizates without stearic acid and zinc oxide (compounds 4-6), except NR vulcanizate 6 for THF. The amounts of the extracted materials from the NR vulcanizates containing stearic acid and zinc oxide increase by about 15-44, 23-67, 41-42 (below 1% for the NR vulcanizate 6), 48-61, and 117–161% for *n*-hexane, toluene, THF, acetone, and acetonitrile, respectively, with an increase of the temperature from 18 to 40°C, while those from the NR vulcanizates without stearic acid and zinc oxide are about 9-10, 7-13, 15-16, 30-40, and 69-99%, respectively. This may be because the zinc complexes formed in the NR vulcanizates containing stearic acid and zinc oxide are not extracted well at the low temperature. For the NR vulcanizate 6, the amounts of the extracted materials with *n*-hexane, toluene, ace-



**Figure 3** TGA thermograms of the NR vulcanizate cured by zinc oxide, stearic acid, sulfur, and TBBS (compound 6) after extraction with (a) toluene, (b) THF, (c) acetone, (d) *n*-hexane, and (e) acetonitrile at 40°C for 2 days, and (f) before extraction. TGA condition; 100°C (under  $N_2$ )  $\rightarrow$  40°C/min  $\rightarrow$  300°C (keeping for 7 min)  $\rightarrow$  100°C/min  $\rightarrow$  550°C (keeping for 7 min)  $\rightarrow$  100°C/min (under air)  $\rightarrow$  700°C (keeping for 5 min).

tone, and acetonitrile increase remarkably by increasing the temperature, while that with THF is nearly the same, irrespective of the temperature.

For the NR vulcanizates without stearic acid and zinc oxide, the amounts of the extracted materials are more than total contents of extractable ingredients of wax, stearic acid, sulfur, and TBBS listed in the formulations, except the extraction with acetone and acetonitrile at 18 and 40°C. This means that some rubber molecules are extracted with the solvents from the NR vulcanizates without stearic acid and zinc oxide. This may be due to the low crosslink densities of the vulcanizates. The amounts of the extracted materials with nhexane, toluene, and THF from NR vulcanizates 4 and 5 are also more than the total contents of the extractable ingredients listed in the formulations. This phenomenon is not observed in the NR vulcanizate 6 because the crosslink density of the NR vulcanizate 6 is much higher than those of the other vulcanizates. The crosslink density of the NR vulcanizate 6 is  $4.01 \times 10^{-3}$  g mol mL<sup>-1</sup> while those of NR vulcanizates 1-5 are less than  $2.0 imes 10^{-3}$  g mol mL<sup>-1</sup>. If the crosslink density of a rubber vulcanizate is very low, some rubber chains will not be crosslinked. Thus, the uncrosslinked rubber chains can be extracted with the solvents from the vulcanizates. The amounts of the extracted materials from NR vulcanizates 2 and 5 with the crosslink densities of below 0.5  $\times$  10<sup>-3</sup> g mol mL<sup>-1</sup> are much more than those from NR vulcanizates 1 and 4 with the crosslink densities of about 2  $\times$  10<sup>-3</sup> g mol mL<sup>-1</sup>. This is evidence that the uncrosslinked rubber chains exist in the vulcanizates with a very low crosslink density and that they are extracted with the solvents.

In order to prove whether the zinc complexes are extracted from the NR vulcanizates or not, the unbound materials were extracted with THF for 7 days from the NR vulcanizates. After drying the extracted solution and then burning it at 700°C, some ash remained. The ash was analyzed with energy dispersive X-ray spectroscopy (EDS), and then zinc was detected. It can lead to the conclusion that some zinc complexes are extracted with organic solvents.

The amounts of the extracted materials from the NR vulcanizates with THF are more than those with n-hexane, although the dielectric constant of n-hexane is closer to the components of the vulcanizate than that of THF. This can be

	Temperature				
Component	(°C)	Organic Matter <sup>a</sup>	Polymer <sup>b</sup>	Carbon Black <sup>c</sup>	Ash <sup>d</sup>
Before extraction		14.4	223.6	100.0	3.1
After extraction					
<i>n</i> -Hexane	18	6.8	216.3	100.0	2.0
	40	6.6	212.4	100.0	2.2
	71	5.7	216.8	100.0	2.2
Toluene	18	6.6	215.3	100.0	2.5
	40	6.5	212.4	100.0	2.6
	115	6.0	205.2	100.0	2.5
THF	18	7.4	211.6	100.0	3.1
	40	8.0	209.5	100.0	3.0
	68	4.8	216.4	100.0	1.9
Acetone	18	8.6	223.5	100.0	2.6
	40	6.0	223.3	100.0	1.6
	58	5.6	221.1	100.0	2.9
Acetonitrile	18	11.8	223.5	100.0	1.6
	40	9.7	223.6	100.0	2.3
	85	6.3	223.9	100.0	1.9

 Table III
 Relative Component Ratio of the NR Vulcanizate 1 (%)

Data were obtained from TGA and normalized with carbon black.

<sup>a</sup> Components evaporated at below 300°C.

<sup>b</sup> Thermally decomposed components at 300-550°C under N<sub>2</sub>.

<sup>c</sup> Thermally decomposed components at 550–700°C under air.

<sup>d</sup> Components remained at over 700°C.

explained by the high swelling ratio of the vulcanizate with THF. The swelling ratios of the NR vulcanizate 6 are 75.7, 170.6, 169.0, 10.6, and 1.4 wt % for *n*-hexane, toluene, THF, acetone, and acetonitrile, respectively. The swelling ratios for acetone and acetonitrile are much lower than those for *n*-hexane, toluene, and THF. If a solvent swells the vulcanizate well, the solvent may extract unbound materials well from the vulcanizate. Thus, the swelling ratio of the vulcanizate depending on solvents may become one of factors influencing the extraction.

#### Thermogravimetric Analysis

In order to investigate extractabilities of the solvents from the NR vulcanizates, TG analyses of the NR vulcanizates before and after the extraction were performed. Organic matters (organic components with a low molecular weight) are evaporated or decomposed at below 300°C under N<sub>2</sub>, while polymers (organic components with a high molecular weight) are decomposed at 300–550°C under N<sub>2</sub>. Carbon black is burnt out at 550–700°C under air. Components remained after combustion are ash (metal oxide). Figure 2

gives TGA thermograms of the NR vulcanizate 6 before and after the extraction with acetone. Figure 2 shows that the amount of organic matter in the NR vulcanizate 6 after the extraction is less than that before the extraction, and the amount of organic matter decreases by increasing the extraction temperature. Figure 3 gives the variation of TGA thermograms of the NR vulcanizate 6 depending on the solvents. Tables III-VIII give relative component ratios of the NR vulcanizates before and after the extraction at 18 and 40°C and in the boiling solvents. Values in Tables III-VIII were obtained by normalizing with carbon black. We assumed that carbon black was not extracted with the solvents from the NR vulcanizates. Before the extraction, amounts of the organic matters in the vulcanizates obtained from TGA are 4.23, 5.65, 4.77, 5.38, 5.41, and 5.86 wt % for NR vulcanizates 1, 2, 3, 4, 5, and 6, respectively. For the NR vulcanizates without stearic acid and zinc oxide, the amounts of the organic matters obtained from TGA are more than those of the extractable ingredients listed in the formulations.

The organic components with a low molecular weight of the unbound materials are mostly extracted from the NR vulcanizates, as discussed

Component	Temperature (°C)	Organic Matter <sup>a</sup>	Polymer <sup>b</sup>	Carbon Black <sup>c</sup>	$\operatorname{Ash}^{\operatorname{d}}$
Before extraction		18.8	211.2	100.0	2.8
After extraction					
<i>n</i> -Hexane	18 40 71	7.8 6.5 6.9	$157.1 \\ 148.9 \\ 159.9$	100.0 100.0 100.0	$2.4 \\ 2.2 \\ 1.9$
Toluene	$18\\40\\115$	6.6 7.2 5.6	$146.1 \\ 140.4 \\ 135.2$	100.0 100.0 100.0	$2.1 \\ 2.7 \\ 1.8$
THF	18 40 68	6.3 6.2 5.6	$135.7 \\ 125.0 \\ 160.1$	100.0 100.0 100.0	$2.6 \\ 1.7 \\ 2.4$
Acetone	18     40     58	9.8 6.4 7.8	208.2 208.2 208.2	100.0 100.0 100.0	$1.7 \\ 1.7 \\ 2.6$
Acetonitrile	18 40 85	15.8 10.7 7.7	208.9 211.7 209.1	100.0 100.0 100.0	$2.6 \\ 1.4 \\ 1.7$

 Table IV
 Relative Component Ratio of the NR Vulcanizate 2 (%)

Data were obtained from TGA and normalized with carbon black.

<sup>a</sup> Components evaporated at below 300°C.

<sup>b</sup> Thermally decomposed components at 300-550°C under N<sub>2</sub>.

<sup>c</sup> Thermally decomposed components at 550–700°C under air.

<sup>d</sup> Components remained at over 700°C.

Component	Temperature (°C)	Organic Matter <sup>a</sup>	Polymer <sup>b</sup>	Carbon Black <sup>c</sup>	$\operatorname{Ash}^{\operatorname{d}}$
Before extraction		16.0	216.1	100.0	2.7
After extraction					
<i>n</i> -Hexane	18 40 71	7.2 6.7 6.9	198.7 197.1 198.2	100.0 100.0 100.0	$2.8 \\ 1.8 \\ 2.4$
Toluene	$18\\40\\115$	6.8 6.9 5.6	198.2 191.4 185.8	100.0 100.0 100.0	$2.6 \\ 2.1 \\ 2.3$
THF	18 40 68	7.8 7.6 5.5	$192.1 \\185.7 \\201.6$	100.0 100.0 100.0	$2.9 \\ 2.8 \\ 2.4$
Acetone	$18\\40\\58$	8.8 6.3 5.6	$213.2 \\ 211.3 \\ 210.6$	100.0 100.0 100.0	$1.8 \\ 1.6 \\ 1.6$
Acetonitrile	18 40 85	$13.1 \\ 10.0 \\ 6.7$	213.4 212.9 211.3	100.0 100.0 100.0	$1.4 \\ 2.2 \\ 2.1$

Table V Relative Component Ratio of the NR Vulcanizate 3 (%)

Data were obtained from TGA and normalized with carbon black.

<sup>a</sup> Components evaporated at below 300°C.

 $^{\rm b}$  Thermally decomposed components at 300–550°C under  $N_2.$ 

<sup>c</sup> Thermally decomposed components at 550-700°C under air.

<sup>d</sup> Components remained at over 700°C.

previously. However, the results of TGA shows that component of organic matter after the extraction is detected by about 2-5 wt %. The organic matters detected by the TGA may be organic components formed by dissociation of pendent groups bound to a rubber chain and isolated rubber chains by dissociation of the existing crosslinks at 100-300°C. Since some sulfur crosslinks in the NR vulcanizates can be dissociated for the extraction, some rubber chains will be crosslinked by only a few sulfur crosslinks. Thus, it is not hard that the rubber chains crosslinked with few sulfide linkages are isolated by thermal dissociation of the remaining sulfur crosslinks at 100-300°C for TGA. The relative component ratios of the organic matter in the vulcanizates after the extraction are less than those before the extraction by about 18-67, 16-70, 18-66, 1-64, 2-71, and 1-67% for NR vulcanizates 1, 2, 3, 4, 5, and 6, respectively. The relative component ratios of the polymer in the vulcanizates after the extraction are also less than those before the extraction by about below 9, 42, 15, 14, 34, and 6%, respectively. This means that the polymer components as well as organic matters were extracted from the vulcanizates with the solvents. The polymer components were isolated by dissociation of the existing crosslinks and were extracted with the solvents, as discussed previously. The relative component ratios of polymer in the NR vulcanizate with a low crosslink density are less than those in the NR vulcanizate with a high one. This is a positive evidence that some crosslinked rubber chains are isolated by dissociation of the existing sulfur crosslinks.

Components of metal oxide in the NR vulcanizates are mainly zinc oxide. Ash components were also detected in the NR vulcanizates without zinc oxide. Ash contents obtained from the TGA are 0.8-0.9 wt % in NR vulcanizates 1-3. The ash components in the NR vulcanizates without zinc oxide are originated from NR, carbon black, and organic additives. The relative component ratios of ash in the NR vulcanizates containing zinc oxide after the extraction are lower than those before the extraction by below 12, 24, and 21% for NR vulcanizates 4, 5, and 6, respectively. Zinc oxides were built zinc complexes with mainly cure accelerator and stearic acid, not sulfur.<sup>3,4</sup> There are only zinc stearates in NR vulcanizate 4, not zinc complexes, including residues of TBBS since compound 4 does not contain TBBS. Though NR

Component	Temperature (°C)	Organic Matter <sup>a</sup>	Polymer <sup>b</sup>	Carbon Black <sup>c</sup>	$\operatorname{Ash}^{\operatorname{d}}$
Before extraction		18.3	207.8	100.0	13.2
After extraction					
<i>n</i> -Hexane	$18\\40\\71$	14.5 12.2 10.6	195.9 190.4 196.1	100.0 100.0 100.0	12.6 13.2 11.6
Toluene	$18\\40\\115$	14.4 9.9 7.1	194.7 187.0 180.4	100.0 100.0 100.0	$12.9 \\ 12.7 \\ 11.7$
THF	18 40 68	8.1 9.6 6.6	191.7 180.3 196.2	100.0 100.0 100.0	$12.6 \\ 12.2 \\ 12.3$
Acetone	$18 \\ 40 \\ 58$	14.7 11.8 11.3	$207.1 \\ 205.5 \\ 207.8$	100.0 100.0 100.0	$13.1 \\ 12.2 \\ 12.8$
Acetonitrile	18 40 85	18.2 17.0 11.1	207.8 208.0 207.6	100.0 100.0 100.0	$12.4 \\ 13.1 \\ 12.0$

 Table VI
 Relative Component Ratio of the NR Vulcanizate 4 (%)

Data were obtained from TGA and normalized with carbon black. <sup>a</sup> Components evaporated at below 300°C. <sup>b</sup> Thermally decomposed components at 300–550°C under N<sub>2</sub>. <sup>c</sup> Thermally decomposed components at 550–700°C under air. <sup>d</sup> Components remained at over 700°C.

Component	Temperature (°C)	Organic Matter <sup>a</sup>	Polymer <sup>b</sup>	Carbon Black <sup>c</sup>	$\operatorname{Ash}^{\operatorname{d}}$
Before extraction		18.8	215.4	100.0	13.2
After extraction					
<i>n</i> -Hexane	$18\\40\\71$	12.9 8.9 7.0	182.5 179.9 187.2	100.0 100.0 100.0	$12.4 \\ 10.2 \\ 10.4$
Toluene	$18\\40\\115$	$12.6 \\ 6.9 \\ 5.9$	177.0 169.4 171.9	100.0 100.0 100.0	$12.0 \\ 10.3 \\ 10.6$
THF	18 40 68	7.0 7.8 5.4	$155.1 \\ 144.5 \\ 181.8$	100.0 100.0 100.0	$10.8 \\ 10.5 \\ 11.8$
Acetone	$18 \\ 40 \\ 58$	$14.5 \\ 10.3 \\ 8.1$	$215.0 \\ 214.9 \\ 215.7$	100.0 100.0 100.0	$11.2 \\ 11.8 \\ 10.7$
Acetonitrile	18 40 85	$18.5 \\ 15.0 \\ 6.8$	215.8 214.8 212.6	100.0 100.0 100.0	$13.1 \\ 11.7 \\ 10.1$

# Table VII Relative Component Ratio of the NR Vulcanizate 5 (%)

Data were obtained from TGA and normalized with carbon black.

<sup>a</sup> Components evaporated at below 300°C. <sup>b</sup> Thermally decomposed components at 300–550°C under  $N_2$ . <sup>c</sup> Thermally decomposed components at 550–700°C under air.

<sup>d</sup> Components remained at over 700°C.

	Temperature						
Component	(°C)	Organic Matter <sup>a</sup>	Polymer <sup>b</sup>	Carbon Black <sup>c</sup>	Ash <sup>d</sup>		
Before extraction		20.2	210.3	100.0	13.8		
After extraction							
<i>n</i> -Hexane	18	14.9	210.2	100.0	12.6		
	40	12.6	208.8	100.0	12.4		
	71	9.4	210.1	100.0	11.7		
Toluene	18	15.3	206.7	100.0	12.7		
	40	9.4	209.4	100.0	11.0		
	115	7.9	209.4	100.0	11.9		
THF	18	7.1	203.2	100.0	12.6		
	40	9.5	200.8	100.0	12.4		
	68	6.7	202.6	100.0	12.9		
Acetone	18	16.2	208.6	100.0	12.7		
	40	11.8	210.0	100.0	12.8		
	58	10.0	210.4	100.0	11.7		
Acetonitrile	18	20.1	211.2	100.0	12.7		
	40	17.8	210.7	100.0	13.2		
	85	10.5	210.7	100.0	11.5		

 Table VIII
 Relative Component Ratio of the NR Vulcanizate 6 (%)

Data were obtained from TGA and normalized with carbon black.

<sup>a</sup> Components evaporated at below 300°C.

 $^{\rm b}$  Thermally decomposed components at 300–550°C under  $N_2.$ 

<sup>c</sup> Thermally decomposed components at 550-700°C under air.

<sup>d</sup> Components remained at over 700°C.

vulcanizate 4 has many zinc stearates, the amount of extracted metal complexes from NR vulcanizate 4 is little. This can be explained by the big size of zinc stearate (m/z 348) and the poor solubility of zinc stearate in the organic solvents. Zinc stearate is a tetracoordinated zinc complex. A pentacoordinated zinc complex has good solubility in an organic solvent, but a tetracoordinated one does not.<sup>5</sup>

The relative component ratios of polymer in the vulcanizates after the extraction with *n*-hexane, toluene, and THF are lower than those after the extraction with acetone and acetonitrile, especially for NR vulcanizates 2 and 5. This can be explained by the hindrance of the dissociated sulfide radicals by solvation and the sulfur crosslinks strained by swelling. Sulfide radicals formed by dissociation of polysulfides in the NR vulcanizate become thiols by abstraction of a hydrogen atom, recombine with each other, or form new sulfur crosslinks. When the vulcanizates are swollen, recombination of the sulfide radicals and the formation of new crosslinks are inhibited since the solvents are solvated around the sulfide radicals. Since sulfur crosslinks in the swollen NR vulcanizates are strained, the dissociation of sulfur

crosslinks is activated. Thus, the existing sulfur crosslinks of the NR vulcanizates are dissociated more easily in the solvent with a high swelling ratio than in the solvent with a low one.

## **CONCLUSIONS**

Of *n*-hexane, toluene, THF, acetone, and acetonitrile, amounts of the extracted materials from the carbon-black-filled NR vulcanizates with THF are the highest, while those with acetonitrile are the lowest. The unbound materials in the vulcanizates are better extracted by *n*-hexane and toluene than by acetone. Amounts of the extracted materials with and toluene are more than those with n-hexane. Amounts of the extracted materials from the NR vulcanizates increase with an increase of the extraction temperature. Amounts of the extracted materials from the NR vulcanizate with a high crosslink density are less than those from the NR vulcanizate with a low one. The solvent with a high swelling ratio and a similar dielectric constant to the components of the vulcanizate extracts the unbound materials from the vulcanizate better than that with a low swelling ratio and a different dielectric constant to the components of the vulcanizate. Some zinc complexes, as well as organic components, are also extracted. Some crosslinked rubber chains are isolated by dissociation of the existing sulfur crosslinks, and the isolated rubber chains are extracted with the solvents.

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