Migration Behaviors of Antiozonants to the Surface in NR Vulcanizates, Depending on the Season: The Effect of Wax

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ABSTRACT: Influence of wax film on the surface of a rubber vulcanizate on migration of antiozonants was studied using NR vulcanizates containing various types of waxes. The waxes have different molecular weight distributions. *N*-phenyl-*N'*-isopropyl-*p*-phenyl-enediamine (IPPD), *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD), *N*,*N'*-di(*sec*-butyl)-*p*-phenylenediamine (SBPPD), and *N*,*N'*-di(1,4-dimethylpentyl)-*p*-phenylenediamine (DMPPD) were used as antiozonants. Migration experiments were performed outdoors for two months in the summer, fall, and winter. The migration rates of the antiozonants in the vulcanizate without wax are faster than those in the vulcanizates with waxes. The antiozonants migrate slower in the vulcanizate containing wax with a high-molecular-weight distribution than in the vulcanizate with a low one. In the summer, the migration rates of SBPPD and DMPPD are faster than those of IPPD and HPPD, respectively. But, in the fall, the migration rates of SBPPD and DMPPD are slower than those of IPPD and HPPD, respectively. The differences of migration behaviors of the antiozonants, depending on season and wax type, was discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1987–1993, 1999

Key words: antiozonants; migration; season; intermolecular interaction

INTRODUCTION

Migration behaviors of antidegradants in rubber vulcanizates are influenced by kinds of rubber and filler.¹⁻⁴ 2,6-Di-*t*-butyl-4-methyl phenol (BHT), *N*-phenyl-*N'*-isopropyl-*p*-phenylenediamine (IPPD), and *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD) migrate faster in SBR vulcanizates than in NR and BR vulcanizates.¹ Migration rates of BHT, IPPD, and HPPD in silica-filled rubber vulcanizates are slower than those in carbon-black-filled ones.²⁻⁴ Migration rates of the antidegradants become slower and slower by increasing the filler content in the vulcanizates. The principal sources to influence migration behaviors of antidegradants in rubber vulcanizates are intermolecular interactions between the antidegrants and matrices of rubber and filler.

It is generally agreed that waxes compounded into rubber are capable of migrating to the surface, thereby providing protection against ozone attack by formation of an impervious barrier. The ability of a wax to migrate to the surface depends upon the specific wax type, the rubber composition, and the time and temperature before and during exposure to ozone. These papameters influence the solubility/mobility characteristics of each specific wax.⁵ In general, substituted *para*phenylenediamine antiozonants were used with wax to protect against ozonation of rubber.⁶

In this study, the influence of wax film on migration of antiozonants to the surface in carbonblack-filled NR vulcanizates containing various types of waxes were studied. Experiments were performed outdoors during the summer, fall, and winter to investigate the influence of season on

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Figure 1 Formulae of antiozonants.

the migration. IPPD, HPPD, N,N'-di(sec-butyl)-pphenylenediamine (SBPPD), and N,N'-di(1,4dimethylpentyl)-p-phenylenediamine (DMPPD) were used as migrants. Their chemical structures were given in Figure 1. The influence of the content of wax in the vulcanizates on migration of the antiozonants was also investigated.

EXPERIMENTAL

In order to investigate the influence of wax barrier on migration of the antiozonants to the surface in a rubber vulcanizate, 16 carbon-blackfilled NR compounds containing three types of waxes were prepared. SMR 20 (one of Standard Malaysian Rubbers) was employed as an NR, and the grade of carbon black used is N330. The three waxes have a different molecular weight distributions, as shown in Figure 2. The molecular weight distributions of the waxes were obtained using gas chromatography. The waxes were a mixture of normal alkanes and their isomers. Peak areas in Figure 2 were percent ratios of the total peak area of the wax. The contents of the waxes in the compounds were from 0.0 to 5.0 phr. The antiozonants of IPPD, HPPD, SBPPD, and DMPPD of 2.0 phr were contained in the compounds each. Compounds 2-6, 7-11, and 12-16 contain the Wax-A, Wax-B, and Wax-C, respectively. The formulations are given in Table I. N-tert-Butyl-2benzothiazole sulfenamide (TBBS) was used as a curing agent. The NR vulcanizates were prepared by curing at 160°C for 15 min.

The migration experiments were performed outdoors for two months in the summer, fall, and winter. The weather conditions are summarized in Table II. The average low temperatures during the summer, fall, and winter are 22.3, 9.6, and -1.4° C, respectively, while the average high tem-



Figure 2 Molecular weight distributions of waxes. The peak areas are percent ratios to the total peak area.

Compound No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SMR 20	100.0	100.0	100.0	100.0	100.0	100.0	100.0	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	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Wax-A	0.0	1.0	2.0	3.0	4.0	5.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Wax-B	0.0	0.0	0.0	0.0	0.0	0.0	1.0	2.0	3.0	4.0	5.0	0.0	0.0	0.0	0.0	0.0
Wax-C	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	2.0	3.0	4.0	5.0
IPPD	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
HPPD	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
SBPPD	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
DMPPD	2.0	2.0	2.0	2.0	2.0	2.0	2.0	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	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
TBBS	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sulfur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

Table IFormulations (phr)

peratures are 30.8, 20.5, and 6.0°C, respectively. Amounts of the antiozonants that migrated to the surface in the NR vulcanizates were determined by the differences between the amounts of the antiozonants that remained in the vulcanizates before and after the migration. The amounts of the antiozonants remaining in the vulcanizates were analyzed using gas chromatography after extraction of the antiozonants with THF. Experiments were carried out three times and averaged.

RESULTS AND DISCUSSION

The molecular weight distribution of the Wax-C is higher than those of the Wax-A and Wax-B, as shown in Figure 2. The molecular weight distributions of the Wax-A and Wax-B have a similar shape but the highest peak position. The highest peaks of the Wax-A are $C_{24}H_{50}$ and $C_{25}H_{52}$, while those of the Wax-B are $C_{27}H_{56}$ and $C_{28}H_{58}$. The chemical structures^{7,8} and melting points⁹ of the

Table II Weather Conditions

Season	Summer	Fall	Winter		
Low temperature (°C)	22.3	9.6	-1.4		
(Range)	(19-25)	(2-16)	(-11-6)		
High temperature (°C)	30.8	20.5	6.0		
(Range)	(26 - 36)	(10-27)	(-6-14)		
Sunny (day)	33	49	33		
Cloudy (day)	6	4	14		
Rainy (day)	22	8	5		
Snowy (day)	0	0	9		

normal alkanes depend on the their size. The normal alkanes with a molecular weight heavier than n-C₃₅H₇₂ have a structure of end-chain bending and folding.⁸ The melting points of the normal alkanes increase by increasing their size. The melting points of the n-C₂₁H₄₄, n-C₂₄H₅₀, n-C₂₇H₅₆, n-C₃₀H₆₂, n-C₃₃H₆₈, n-C₃₆H₇₄, and n-C₄₀H₈₂ are 39, 51, 58, 63, 70, 75, and 79°C, respectively.⁹ It can be considered that composition of waxes affects formation of wax film since the alkanes have different structures and melting points, depending on their molecular weight.

Table II gives weather conditions during the migration experiments. The outdoor experiments were carried out by putting the samples in the sun for two months in summer, fall, and winter. The outdoor migration experiments have a merit (reflection of the real conditions) in comparison with the experiments performed in a convection oven, although the outdoor experiments need a long time. When the migration experiments are performed outdoors, the influences of weather conditions (sunlight, rain, snow, and wind), as well as temperature, on the migration can be observed.

Migration During the Summer

Experimental results for the migration during the summer are summarized in Table III. The IPPD and HPPD are derivatives of *N*-phenyl-*N'*-alkyl-*p*-phenylenediamine, while the SBPPD and DMPPD are derivatives of N,N'-dialkyl-*p*-phenylenediamine. The molecular weights of the IPPD, HPPD, SBPPD, and DMPPD are m/z 226, 268, 220, and 304, respectively. Though the molecular

Compound No.	IPPD	HPPD	SBPPD	DMPPD
1	30.7	15.4	54.9	23.6
2	28.4	13.4	54.2	16.4
3	26.5	9.8	52.0	16.9
4	24.2	8.8	48.1	13.0
5	25.0	12.3	46.2	14.2
6	26.6	12.9	51.0	16.7
7	23.1	9.8	44.4	14.1
8	23.1	10.8	49.1	9.9
9	21.2	9.7	40.4	13.8
10	20.2	11.1	41.2	15.2
11	26.7	10.9	43.4	13.2
12	20.4	9.7	40.7	10.7
13	22.2	9.7	38.5	13.5
14	19.6	10.3	44.0	11.8
15	21.4	9.9	42.0	15.1
16	23.3	11.0	45.3	14.5

Table III Amounts of Antiozonants That Migrated to the Surface in the NR Vulcanizates in the Summer for 2 Months (%)

weights of the IPPD and HPPD are smaller than those of the SBPPD and DMPPD, respectively, the migration rates of the IPPD and HPPD are slower than those of the SBPPD and DMPPD, respectively, as shown in Table III and Figure 3. The amount of the SBPPD that migrated to the surface in the NR vulcanizate without wax (54.9%) is much more than that of the IPPD (30.7%). The amount of the DMPPD that migrated to the surface in the NR vulcanizate without wax (23.6%) is also much more than that of the IPPD (15.4%). This may be due to intermolecular interactions of the antiozonants with carbon black. The carbon black has a graphite-like structure.¹⁰ The migration rates of the IPPD and HPPD in the carbon-black-filled NR vulcanizate become slower and slower by increasing the content of carbon black in the vulcanizate.³ The IPPD and HPPD have a phenyl ring as the N-substituent, but the SBPPD and DMPPD do not. The interaction of the phenyl group with carbon black is stronger than that of the alkyl group. Thus, the intermolecular interactions of the IPPD and HPPD with carbon black may be stronger than those of the SBPPD and DMPPD so that the migration rates of the IPPD and HPPD are slower than those of the SBPPD and DMPPD, respectively. The migration rate of the DMPPD is slower than that of the IPPD. This is because the DMPPD is much larger than the IPPD, although

the intermolecular interaction of the IPPD with carbon black is stronger than that of the DMPPD.

The amounts of the antiozonants that migrated in the vulcanizate without wax are more than those in the vulcanizate containing waxes by about 2–11%, 2–6%, 1–16%, and 7–14% for IPPD, HPPD, SBPPD, and DMPPD, respectively. This can be explained by the path length of the antiozonants and the interface between the wax film and the surface of the NR vulcanizate. The wax migrates to the surface in the NR vulcanizate and forms a protection film on the surface. The thickness of the wax film on the surface of a rubber vulcanizate containing paraffin wax of 1.6 phr after 30 days at 40°C was about 2 μ m.⁵ The path length of the antiozonants becomes longer by formation of the wax film. But, the increase of the path length due to the wax film hardly affects the migration of the antiozonants since the thickness of the wax film is much thinner than that of the vulcanizate (2 mm). Thus, the principal cause to decrease the amount of the antiozonants that migrated in the vulcanizates containing waxes may be the interface the wax film and the surface of the NR vulcanizate. The discontinuous interface is formed between the rubber vulcanizate and the



Figure 3 Average amounts of the antiozonants that migrated in the NR vulcanizates to the surface (%) depending on the wax type during the summer and fall. The values for the Wax-A, Wax-B, and Wax-C are average values obtained by averaging the amounts of the antiozonants that migrated in the vulcanizates containing the waxes from 1.0 to 5.0 phr.

wax film in the vulcanizates containing waxes. Gardiner studied the diffusion gradient of curatives in two rubbers.¹¹ In similar rubbers, the curative concentration showed a continuous gradient; but in dissimilar rubbers, the curative concentration showed a discontinuous gradient at the interface. The concentration at the interface was denser than that in the dissimilar rubbers. Thus, in the vulcanizates containing waxes, the antiozonants migrate to the surface in the NR vulcanizate and stay at the interface so that their migration rates will be slower.

The thickness of the paraffin wax film on the surface of the vulcanizate increases by increasing the content of wax in the vulcanizate.⁵ The thickness of the paraffin wax increases and then decreases with an increase of the melting point of the paraffin wax.⁵ The melting point of the paraffin wax is proportional to its molecular weight. Table III shows that the migration rates of the antiozonants in the vulcanizate containing wax with a high molecular weight distribution are slower than those in the vulcanizate containing wax with a low one. The amounts of the IPPD, HPPD, SBPPD, and DMPPD that migrated in the vulcanizates containing with the Wax-C are less than those in the vulcanizates containing with the Wax-A by about 18, 11, 16, and 15%, respectively. This cannot be explained by the path length but rather by interactions of the antiozonants with wax. If the path length affects the migration, the migration rates are slower and slower by increasing the content of wax in the vulcanizate. But, the experimental results do not show this trend (Table III). Thus, the migration behaviors of the antiozonants depending on the wax type in the vulcanizates is considered to be due to the intermolecular interactions of the antiozonants with wax. The intermolecular interactions between the antiozonants and wax with a high molecular weight will be stronger than those between the antiozonants and wax with a low one since the wax with a high molecular weight is less mobile than that with a low one.

For the vulcanizates containing Wax-B and Wax-C, the migration behaviors of the antiozonants, depending on the content of wax in the vulcanizate, do not show a specific trend. However, the migration behaviors of the antiozonants, depending on the content of wax in the vulcanizate containing the Wax-A, shows a specific trend. The migration rates of the antiozonants decrease by increasing the content of wax from 1.0 to 3.0 phr (4.0 phr for SBPPD) and then increase.

Table IVAmounts of Antiozonants ThatMigrated to the Surface in the NR Vulcanizatesin the Fall for 2 Months (%)

Compound No.	IPPD	HPPD	SBPPD	DMPPD
1	23.9	11.1	12.3	5.8
2	23.9	11.4	12.1	< 4.0
3	23.9	11.1	12.3	< 4.0
4	23.6	10.7	12.8	< 4.0
5	23.6	9.8	10.8	< 4.0
6	22.4	9.8	12.3	< 4.0
7	22.3	8.8	11.8	< 4.0
8	23.9	8.6	11.9	< 4.0
9	21.0	7.9	8.8	< 4.0
10	21.1	8.0	9.1	< 4.0
11	20.1	9.0	9.2	< 4.0
12	19.1	7.9	7.2	< 4.0
13	21.6	8.0	11.1	< 4.0
14	19.3	8.8	7.7	< 4.0
15	17.9	5.5	9.4	< 4.0
16	19.6	4.5	7.7	< 4.0

Migration During the Fall and Winter

Similar to the migration during the summer, the migration rates of the antiozonants in the vulcanizate without wax during the fall are also faster than those in the vulcanizates containing waxes, as demonstrated in Table IV. This can be also explained by the path length and the interface between the wax film and the surface of the vulcanizate, as discussed previously. The amounts of the DMPPD that migrated in the vulcanizates containing waxes during the fall less than 4%. During the winter, the amounts of the antiozonants that migrated in both of the vulcanizates with and without wax are less than 3%, except the IPPD, as listed in Table V. The amounts of the IPPD that migrated in the vulcanizates containing the Wax-B and Wax-C are less than 5%. The slow migration of the antiozonants during the winter may be due to the low temperature and low sunshine hours.

The migration behaviors of the antiozonants, depending on the wax type in the vulcanizates during the fall, show the same trends with those during the summer. The migration rates of the antiozonants in the vulcanizates containing wax with a low molecular weight are faster than those in the vulcanizates containing wax with a high one. During the fall, the average amounts of the IPPD that migrated in the vulcanizates containing the Wax-A, Wax-B, and Wax-C are 23.5, 21.7,

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4	< 2 0		
2 10.		< J.U	< 3.0	< 3.0
	8 .	< 3.0	< 3.0	< 3.0
3 13.	0	< 3.0	< 3.0	< 3.0
4 11.	1	< 3.0	< 3.0	< 3.0
5 4.	5	< 3.0	< 3.0	< 3.0
6 6	1	< 3.0	< 3.0	< 3.0
7 < 5.	0	< 3.0	< 3.0	< 3.0
8 < 5.	0	< 3.0	< 3.0	< 3.0
9 < 5.	0	< 3.0	< 3.0	< 3.0
10 < 5.	0	< 3.0	< 3.0	< 3.0
11 < 5.	0	< 3.0	< 3.0	< 3.0
12 < 5.	0	< 3.0	< 3.0	< 3.0
13 < 5.	0	< 3.0	< 3.0	< 3.0
14 < 5.	0	< 3.0	< 3.0	< 3.0
15 < 5.	0	< 3.0	< 3.0	< 3.0
16 < 5.	0	< 3.0	< 3.0	< 3.0

Table VAmounts of Antiozonants ThatMigrated to the Surface in the NR Vulcanizatesin the Winter for 2 Months (%)

and 19.5%, respectively, while those of the HPPD are 10.6, 8.5, and 6.9%, respectively, as shown in Figure 3. The average amounts of the antiozonants that migrated in the vulcanizates were obtained by averaging the amounts of the antiozonants that migrated in the vulcanizates containing the waxes from 1.0 to 5.0 phr. The average amounts of the IPPD that migrated in the vulcanizates containing wax during the fall decrease from 12.1 to 11.9 and 8.6% by increasing the wax size from the Wax-A to the Wax-B and Wax-C, respectively. During the fall, the migration behaviors depending on the content of wax in the vulcanizates do not show a specific trend. Only the migration rates of the IPPD and HPPD in the vulcanizates containing the Wax-A decrease by increasing the content of wax. During the winter, the migration rates of the IPPD in the vulcanizate with the Wax-A also decrease by increasing the content of wax.

The migration behaviors, depending on the antiozonant type, in the fall are different from those in the summer. In the summer and fall, the migration behaviors of the same chemical species show the same trend, but the trends of the different chemical species are reversed (Fig. 3). The IPPD and HPPD are the same species as N-phenyl-N'-alkyl-p-phenylenediamine, and the SBPPD and DMPPD are the same species as N,N'-dialkyl-p-phenylenediamine. The migration rates of the IPPD are faster than those of the HPPD, and those of the SBPPD are also faster than those of the DMPPD during the summer as well as during the fall. This is because the IPPD and SBPPD are smaller than the HPPD and DMPPD, respectively. But, the migration rates of the IPPD and HPPD during the fall are faster than those of the SBPPD and DMPPD, respectively, by about 45-60%, while the migration rates of the IPPD and HPPD during the summer are slower than those of the SBPPD and DMPPD, respectively, by about 20-50%. This may be due to intermolecular interactions of the antiozonants with rubber chains. The antiozonants interact with the NR chains and carbon black in the carbon-black-filled NR vulcanizates. The intermolecular interactions of phenyl ring of the IPPD and HPPD with carbon black are $\pi - \pi$ interactions, while those of alkyl groups of the antiozonants with NR chains are σ - σ interactions. The π - π interactions are stronger than the σ - σ interactions. Since the σ - σ interactions are relatively weak, at high temperatures, they hardly affect the migration of the antiozonants in the vulcanizates, but they affect the migration at low temperatures. Thus, during the fall and winter, the σ - σ interactions will become one of the principal factors influencing the migration. The SBPPD and DMPPD have two alkyl groups, while the IPPD and HPPD have only one alkyl group. If the σ - σ interactions between alkyl groups of the antiozonants and rubber chains are built at low temperatures, they become an important factor in influencing the migration since the content of NR in the carbon-black-filled NR vulcanizates is more than that of carbon black by twice. Since the temperature is low during the fall, the intermolecular interactions of alkyl groups of the antiozonants become stronger so that the interactions make the migration slow. Thus, the SBPPD and DMPPD migrate slower than the IPPD and HPPD, respectively, at low temperatures.

The amounts of the antiozonants that migrated in the vulcanizates during the summer are much more than those during the fall. During the summer and fall, the difference of the amounts of the antiozonants that migrated in the vulcanizates without wax is higher than that in the vulcanizates with the waxes. The differences of the IPPD, HPPD, SBPPD, and DMPPD in the vulcanizates without wax are about 22, 28, 78, and 75%, respectively, while those of the IPPD, HPPD, and SBPPD in the vulcanizates containing the waxes are about 9-13, 7-32, 75-80%, respectively. Of the four antiozonants, the differences of the IPPD is the lowest, while those of the SBPPD is the highest. This means that the migration of the IPPD is less affected by the season than those of the others. From the results, it can lead to a conclusion that the migrations of the *N*-phenyl-N'-alkyl-*p*-phenylenediamines (IPPD and HPPD) are less sensitive to change of season than those of the *N*,*N'*-dialkyl-*p*-phenylenediamines (SBPPD and DMPPD).

Comparison with Migration in a Convection Oven

In the previous work,¹² we studied the influence of wax on the migration of antiozonants in a rubber vulcanizate using a convection oven. The results of the outdoor experiments are different from the results obtained using a convection oven. The experimental results obtained using a convection oven¹² are as follows. The amounts of SBPPD and DMPPD that migrated in NR vulcanizates at 80°C for 30 days were more than 99%, and those of the SBPPD that migrated in NR vulcanizates at 60°C for 30 days were also more than 99%. The migration rates of the HPPD in NR vulcanizates at 60 and 80°C were slower than those of the IPPD and DMPPD. The migration rates of the IPPD in NR vulcanizates at 60 and 80°C were slower than those of the DMPPD as well the SBPPD. This is very different from the results of this work, as discussed previously, especially the results during the fall. The results obtained by performing outdoors and in a convection oven can lead to the conclusion that the interactions of matrices (rubber and carbon black) with the phenyl ring, as well as the alkyl group of the N, N'-disubstituted-*p*-phenylenediamines, are the principal factors influencing on the migration in a rubber vulcanizate at low temperatures but, at high temperatures, the interactions of the matrices with the alkyl group hardly affect the migration.

CONCLUSIONS

Migration rates of the N,N'-disubstituted-p-phenylenediamines (IPPD, HPPD, SBPPD, and DMPPD) in the vulcanizates containing waxes are slower than those in the vulcanizates without wax. This can be explained by the interface between the wax film and the surface of the vulcanizate. Migration rates of the antiozonants in the vulcanizates containing wax with a high-molecular-weight distribution are slower than those in the vulcanizates containing wax with a low one. Migration rates of the IPPD and HPPD in the summer are slower than those of the SBPPD and DMPPD, respectively, while those of the IPPD and HPPD in the fall are faster than those of the SBPPD and DMPPD, respectively. The migration behaviors of the N-phenyl-N'-alkyl-p-phenylenediamines (IPPD and HPPD) are less affected by change of season than those of the N,N'-dialkyl-p-phenylenediamines (SBPPD and DMPPD). The interactions of matrices (rubber and carbon black) with the phenyl ring, as well as the alkyl group of the antiozonants, are principal factors influencing on migration in a rubber vulcanizate at low temperatures but, at high temperatures, the interactions of the matrices with the alkyl group hardly affect the migration.

REFERENCES

- 1. Choi, S.-S. J Appl Polym Sci 1997, 65, 117.
- 2. Choi, S.-S. J Appl Polym Sci 1998, 68, 1821.
- 3. Choi, S.-S. Bull Kor Chem Soc 1998, 19, 170.
- 4. Choi, S.-S. Kor Polym J 1998, 6, 256.
- Dimauro, P. J.; Paris, H. L.; Fath, M. A. Rubber Chem Technol 1979, 52, 973.
- Lederer, D. A.; Fath, M. A. Rubber Chem Technol 1981, 54, 415.
- Maroncelli, M.; Qi, S. P.; Strauss, H. L.; Synder, R. G. J Am Chem Soc 1982, 104, 6237.
- Hastie, G. P.; Roberts, K. J. J Mater Sci 1994, 29, 1915.
- Heyding, R. D.; Russell, K. E.; Varty, T. L.; St-Cyr, D. Power Diffrac 1990, 5, 93.
- Ayala, J. A.; Hess, M. W.; Dotson, A. O.; Joyce, G. A. in Proceedings of the Rubber Division 135th Meeting, American Chemical Society, Mexico City, Mexico, May 9–12, 1989; American Chemical Society: Washington, DC; Paper No. 30.
- 11. Gardiner, J. B. Rubb Chem Technol 1968, 41, 1312.
- 12. Choi, S.-S. Bull Kor Chem Soc to appear.