

Influence of Rubber Composition on Migration Behaviors of Antiozonants in Carbon Black-Filled Rubber Vulcanizates Composed of NR, SBR, and BR

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ABSTRACT: Migration behaviors of antiozonants in carbon black-filled rubber vulcanizates with different rubber compositions of natural rubber (NR), styrene–butadiene rubber (SBR), and butadiene rubber (BR) were studied at constant temperatures of 40–100°C and outdoors. Three single rubber-based vulcanizates, three biblends, and three triblends were used. *N*-Phenyl-*N'*-isopropyl-*p*-phenylenediamine (IPPD) and *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD) were employed as antiozonants. Migration rates of the antiozonants became faster with increasing the temperature. The order of the migration rates in the single rubber-based vulcanizates was BR > NR > SBR. The migration rates in the vulcanizates containing SBR, on the whole, increased with decreasing the SBR content, while those in the vulcanizates containing BR decreased with decreasing the BR content. Difference in the migration behaviors of the antiozonants depending on the rubber composition was explained both by the intermolecular interactions of the antiozonants with the matrix and by interface formed between dissimilar rubbers in the blends. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 237–242, 2001

Key words: antiozonants; migration; rubber composition; NR; SBR; BR

INTRODUCTION

Migration behaviors of antidegradants in rubber vulcanizates are influenced by matrices 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 slower in SBR vulcanizates than in NR and BR ones.¹ Migration rates of antidegradants 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 in-

creasing the filler content in the vulcanizates. Intermolecular interactions between the antidegradants and the matrices in rubber vulcanizates affect the migration behaviors of the antidegradants.^{1–4} That is, the stronger the intermolecular interactions of antidegradants with the matrices, the slower the migration rates.

Given the economic and technical uncertainties associated with synthesizing new polymeric materials, the utilization of polymer mixtures to achieve a desired combination of properties has obvious attraction. Blends of elastomers^{5–9} are employed in rubber products for a variety of reasons, which include improved physical properties, increased service life, easier processing, and reduced product cost. In this study, the influence of rubber composition on migration behaviors of an-

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Table I Formulations (phr)

Compound No.	1	2	3	4	5	6	7	8	9
SMR 20	100.0	0.0	0.0	50.0	50.0	0.0	40.0	40.0	20.0
SBR 1500	0.0	100.0	0.0	50.0	0.0	50.0	40.0	20.0	40.0
BR 01	0.0	0.0	100.0	0.0	50.0	50.0	20.0	40.0	40.0
N330	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Wax	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
IPPD	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
ZnO	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic Acid	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
TBBS	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
Sulfur	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6

antiozonants to the surface in rubber vulcanizates containing natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR) was investigated. Experiments were performed not only outdoors but also in a convection oven. IPPD and HPPD were used as antiozonants. *N,N'*-Disubstituted-*p*-phenylenediamines, in which at least one of the side groups is alkyl (preferably *sec*-alkyl) are the most effective antiozonants.^{10,11} Migration behaviors of the antiozonants in single rubber, biblend, and triblend vulcanizates were compared.

EXPERIMENTAL

To investigate the influence of the rubber composition on migration behaviors of antiozonants to the surface in rubber vulcanizates, nine carbon black-filled rubber compounds of three single rubber vulcanizates (NR, SBR, and BR), three biblends (50/50 NR/SBR, NR/BR, and SBR/BR), and three triblends (NR/SBR/BR = 40/40/20, 40/20/40, and 20/40/40) were prepared. The formulations were given in Table I. *N-tert*-Butyl-2-benzothiazole sulfenamide (TBBS) was used as a cure accelerator. The rubber vulcanizates were prepared by curing at 160°C for 20 min.

The migration experiments were performed at 40, 60, 80, and 100°C for 14 days in a convection oven. The experiments were also performed outdoors for 80 days. During the outdoor experiment, the average low and high temperatures were 16.84°C (range: 8–24°C) and 26.08°C (range: 18–32°C), respectively. Of the 80 days, the rainy days were 12 days. Sample size was 2 × 5 cm with 2 mm thickness.

Amounts of the antiozonants that migrated to the surface in the vulcanizates were determined by the difference between 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 a gas chromatography after extraction of the antiozonants from the sample with THF. HP 5890 gas chromatograph was used. Temperatures of the injector and detector (FID) were 250 and 260°C, respectively. The initial oven temperature was 150°C (holding for 2 min) and the temperature was raised at rate of 8°C/min. Ultra 1 (10 m × 0.2 mm) capillary column was used. Experiments were carried out three times and averaged.

RESULTS AND DISCUSSION

Tables II and III are the results for IPPD and HPPD, respectively. The amounts of IPPD and

Table II Amounts of IPPD That Migrated in the Rubber Vulcanizates (%)

Compound No.	60°C	80°C	100°C	Outdoor
1	32.2	80.0	>99.0	31.1
2	22.2	67.8	>99.0	24.6
3	33.8	82.5	>99.0	45.6
4	25.6	76.8	>99.0	29.4
5	29.9	80.5	>99.0	33.3
6	24.7	72.9	>99.0	26.8
7	28.7	75.9	>99.0	27.6
8	32.5	80.7	>99.0	33.7
9	27.6	74.7	>99.0	25.1

Table III Amounts of HPPD That Migrated in the Rubber Vulcanizates (%)

Compound No.	60°C	80°C	100°C	Outdoor
1	4.3	50.5	97.4	15.2
2	1.9	38.5	93.3	11.5
3	4.6	50.6	> 99.0	26.7
4	3.0	48.0	96.0	14.6
5	4.4	52.7	98.3	16.3
6	2.1	40.6	95.9	14.0
7	4.0	45.5	97.0	14.1
8	4.2	47.4	97.2	17.9
9	2.1	44.2	95.2	11.6

HPPD that migrated in the vulcanizates at 40°C for 14 days are less than 1% for all the samples. IPPD in all the vulcanizates after the migration at 100°C for 14 days was detected by trace. The migration rates of IPPD and HPPD in the vulcanizates increase steeply with increasing the temperature. The migration behaviors of the antiozonants in the vulcanizates show different trends with the rubber composition. For the single rubber vulcanizates (Compounds 1–3), migration rates of the antiozonants in the SBR vulcanizate are slower than those in the NRs and BRs, while those in the BR vulcanizate are faster than those in the NRs. This is because the order of the intermolecular interaction energies of the rubbers with the antiozonants is SBR > NR > BR.¹ The migration rate of a migrant becomes slower with increasing its intermolecular interaction with the matrices in a rubber vulcanizate.

For the biblends (Compounds 4–6), migration rates of the antiozonants in the NR/BR vulcanizate are faster than those in the NR/SBR and SBR/BR. This can be explained both by the intermolecular interactions of the antiozonants with the rubbers, and by compatibility of dissimilar rubbers in the biblends. Because the intermolecular interactions of SBR with the antiozonants are stronger than those of NR and BR, the migration rates in the vulcanizates containing SBR, the NR/SBR and SBR/BR biblends, are slower than those in the vulcanizate without SBR, the NR/BR.

The migration rate in the SBR/BR biblend is slower than in the NR/SBR. This cannot be explained by the intermolecular interactions because the intermolecular molecular interactions of NR is stronger than that of BR.¹ This can be explained by immiscibility of dissimilar rubbers in the biblends and interface formed between the dissimilar rubbers. Most rubber blends are im-

miscible because the mixing is endothermic and the entropic contribution is small because of the high molecular weights.¹² The discontinuous interface is formed between dissimilar rubbers in rubber blends due to the incompatibilities. Gardiner studied diffusion gradient of curatives in blends of two rubbers.¹³ In blends of similar rubbers, curative concentration showed a continuous gradient, but, in blends of dissimilar rubbers, curative concentration showed a discontinuous gradient at the interface. SBR/BR blends are less incompatible than NR/BR and NR/SBR blends.¹⁴ Thus, the interface formed between the two rubbers in the NR/SBR biblend can be more developed than in the SBR/BR. The antiozonants can migrate along the interface as well as through the matrices of rubber and filler.

To investigate degree of miscibility of the biblends and triblends, glass transition temperatures (T_g) of the vulcanizates were measured using differential scanning calorimeter (DSC) after extraction of organic materials from the vulcanizates with THF and *n*-hexane. Table IV gives the T_g of the vulcanizates. Degree of the T_g shift of the SBR/BR vulcanizate from the each single rubber vulcanizates is larger than for the NR/SBR and NR/BR. The T_g shift of the SBR/BR biblend is about 7 and 16°C from the SBR and BR vulcanizates, respectively, while those of the NR/SBR and NR/BR biblends are less than 2°C from the respective single rubbers. This implies that the SBR/BR vulcanizate is more miscible than the NR/SBR and NR/BR. It can be considered that migration of the antiozonants along the interface formed between the dissimilar rubbers determines the migration behaviors of the antiozonants in the biblends. The antiozonants will migrate along the interface faster than through the matrices when the vulcanizate has the developed

Table IV Glass Transition Temperatures (T_g) of the Vulcanizates

Compound No.	T_g (°C)
1	-53.27
2	-40.68
3	-92.64
4	-52.40, -40.13
5	-92.14, -54.93
6	-85.86, -56.43
7	-87.20, -56.14
8	-88.70, -57.45
9	-90.28, -55.87

interface. Thus, because the interfaces between dissimilar rubbers in the NR/BR and NR/SBR vulcanizates are more developed than in the SBR/BR vulcanizate, the migration rates in the formers are faster than those in the latter.

For the triblends (Compounds 7–9), the migration rates of the antiozonants in the 40/20/40 NR/SBR/BR vulcanizate are faster than those in the 40/40/20 and 20/40/40 ones. This is because the migration rate in the SBR vulcanizate is slower than in the NR and BR ones, as discussed previously. The migration rates in the 20/40/40 NR/SBR/BR vulcanizate are slower than those in the 40/40/20 and 40/20/40 NR/SBR/BRs. This can be explained both by the intermolecular interactions and by the miscibility of dissimilar rubbers in the triblends. The 20/40/40 NR/SBR/BR vulcanizate will be more miscible than the 40/40/20 and 40/20/40 NR/SBR/BR triblends because the total content of BR and SBR in the former is larger than in the latter. SBR and BR are miscible, while NR and BR (or SBR) are immiscible. Thus, it can lead to a conclusion that the migration rates of the antiozonants in the more miscible triblend (NR/SBR/BR = 20/40/40) are slower than in the less miscible ones (NR/SBR/BR = 40/40/20 and 40/20/40).

The migration rates of the antiozonants in the vulcanizates containing NR, on the whole, become faster by increasing the BR content while those become slower with an increase of the SBR content, as shown in Tables II and III. This cannot be explained by the interface formed between dissimilar rubbers because all the blends containing NR will have the interface between NR and the other rubber(s) because of the immiscibility between NR and SBR (or BR). This can be explained by the intermolecular interaction. The intermolecular interactions of SBR with the antiozonants are much stronger than those of BR.¹ For the migration behaviors in the vulcanizates containing SBR, the migration rates become faster by decreasing the SBR content. The amounts of IPPD that migrated in the SBR 100, SBR/NR 50/50 (SBR/BR 50/50), SBR/NR/BR 40/40/20 (40/20/40), and SBR/NR/BR 20/40/40 vulcanizates (decrease of the SBR content from 100 to 20 phr) at 60°C for 14 days are about 22, 26 (25), 29 (28), and 33%, respectively. The migration rates in the SBR blends are slower when the BR content is high than when the NR content is high. This is because SBR/BR blends are miscible but SBR/NR blends are immiscible, so that the interface in the SBR blends having a high NR content is more

developed than for the SBR blends having a high BR content. For the migration behaviors in the vulcanizates containing BR, the migration rates become slower by increasing the NR and SBR contents, especially by increasing the SBR content. The amounts of IPPD that migrated in the BR 100, BR/NR/SBR 40/40/20, BR/NR/SBR 40/20/40, and BR/SBR 50/50 vulcanizates (increase of the SBR content from 0 to 50 phr) at 60°C are about 34, 33, 28, and 25%, respectively. This is because the intermolecular interactions of SBR with the antiozonants are strong, and BR is miscible with SBR.

The results of the outdoor experiment will give more useful information than the oven experiment, especially when rubber products are used outdoors, for example, tires. The outdoor experimental results show similar trends with the oven experimental results except the 50/50 SBR/BR biblend and the 20/40/40 NR/SBR/BR triblend. For the outdoor experiment, the migration rates of the antiozonants in the 50/50 SBR/BR biblend are faster than in the 20/40/40 NR/SBR/BR triblend. This can be explained by the intermolecular interactions of the antiozonants with the matrix. Because the migration rates in BR is faster than in SBR and NR, the migration rates of the antiozonants in a vulcanizate with a high BR content will be faster than in a vulcanizate with a low BR content. For the oven experiment, however, the migration rates in the 50/50 SBR/BR biblend are slower than in the 20/40/40 NR/SBR/BR triblend, as discussed previously. This may be due to the activation of the interface formed in the 20/40/40 NR/SBR/BR triblend at high temperature. The interface formed in the 20/40/40 NR/SBR/BR triblend is activated more and more by increasing the temperature so that the migration rates become faster. Due to this, the migration rates in the 50/50 SBR/BR biblend are faster than in the 20/40/40 NR/SBR/BR triblend outdoors (at low temperature) but, at high temperature, those in the former are slower than in the latter.

To investigate variation of the migration rates with the rubber composition in detail, variation of the migration rates was plotted as a function of the rubber content for the outdoor experimental results (Figs. 1–6). When the SBR content is higher than the BR one in the blends, the migration rate in the vulcanizate containing NR becomes slower by decreasing the NR content even though the BR content is higher than the NR content (Fig. 1). This may be because the migra-

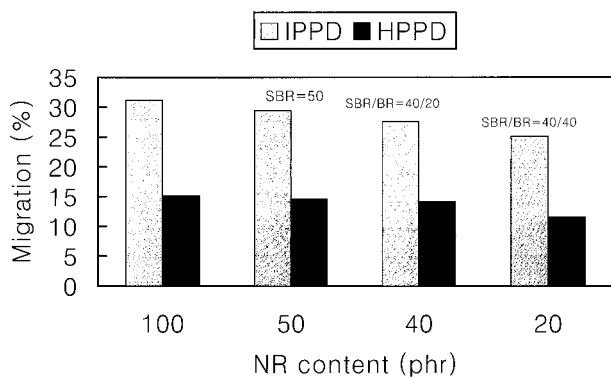


Figure 1 Variation of amounts of the antiozonants migrated in the vulcanizates containing NR after the migration outdoors for 80 days as a function of the NR content. The SBR content is not less than the BR one.

tion rate in SBR is much slower than that in BR, and miscibility of SBR and BR is good. When the BR content is higher than the SBRs in the blends, however, the migration rate increases slightly until the NR content is 40 phr, and then decreases notably at the NR content of 20 phr (Fig. 2). This may be because the migration rate in BR is faster than in NR.

For the vulcanizates containing SBR, the migration rates in the SBR vulcanizate are slower than in the SBR biblends and triblends (Figs. 3 and 4). This is because the migration rates in SBR is much slower than in NR and BR. The migration rates, on the whole, become faster with decreasing the SBR content. The migration rates in the 50/50 NR/SBR and 50/50 SBR/BR biblends (the SBR content is 50 phr) are slower than in the 40/20/40 NR/SBR/BR triblend (the SBR content is

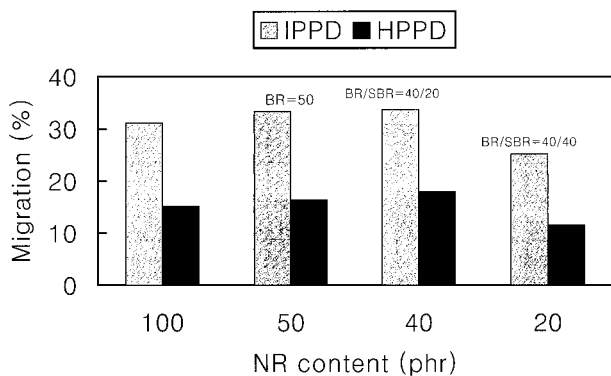


Figure 2 Variation of amounts of the antiozonants migrated in the vulcanizates containing NR after the migration outdoors for 80 days as a function of the NR content. The BR content is not less than the SBR one.

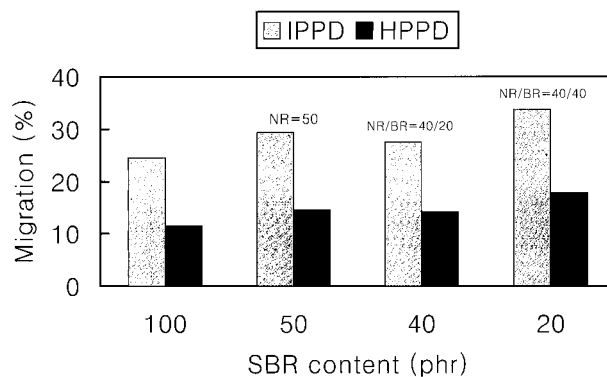


Figure 3 Variation of amounts of the antiozonants migrated in the vulcanizates containing SBR after the migration outdoors for 80 days as a function of the SBR content. The NR content is not less than the BR one.

20 phr). However, the migration rates in the 50/50 NR/SBR biblend are faster than in the 40/40/20 NR/SBR/BR triblend (the SBR content is 40 phr). This may be due to the more developed interface in the former than in the latter. The migration rates in the 50/50 SBR/BR biblend are also faster than in the 20/40/40 NR/SBR/BR triblend (the SBR content is 40 phr). This may be due to the low NR content. Because SBR and BR are miscible and the NR content is very low in the 50/50 SBR/BR and 20/40/40 NR/SBR/BR blends, the interface will not be developed sufficiently. Thus, the BR content in the vulcanizate containing SBR will largely affect the migration rates because the migration rates in BR are much faster than in SBR and NR. The migration rates in the vulcanizate with a high BR content are faster than in the vulcanizate with a low BR content.

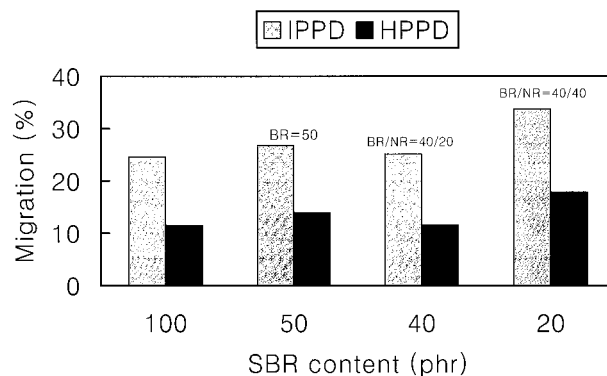


Figure 4 Variation of amounts of the antiozonants migrated in the vulcanizates containing SBR after the migration outdoors for 80 days as a function of the SBR content. The BR content is not less than the NR one.

For the vulcanizates containing BR, because the migration rates in BR are much faster than in SBR and NR, the migration rates in the BR vulcanizate are faster than in the BR blends and triblend (Figs. 5 and 6). The migration rates, on the whole, become slower by decreasing the BR content in the vulcanizate. When the SBR content is not lower than the NR content in the blends (Fig. 6), however, the migration rates in the 20/40/40 NR/SBR/BR triblend (the BR content is 40 phr) are slower than in the 40/40/20 one (the BR content is 20 phr). This may be due to the more developed interface in the 40/40/20 NR/SBR/BR triblend. The interface is developed more and more by increasing the NR content in the blend, because NR is not miscible with SBR or BR.

CONCLUSION

The migration rates of the antiozonants in the vulcanizates containing NR become faster by increasing the BR content, while those become slower with an increase of the SBR content. For the migration behaviors in the vulcanizates containing SBR, the migration rates, on the whole, become faster by decreasing the SBR content. For the migration behaviors in the vulcanizates containing BR, the migration rates become slower with decreasing the BR content. Variation of the migration behaviors of the antiozonants with the

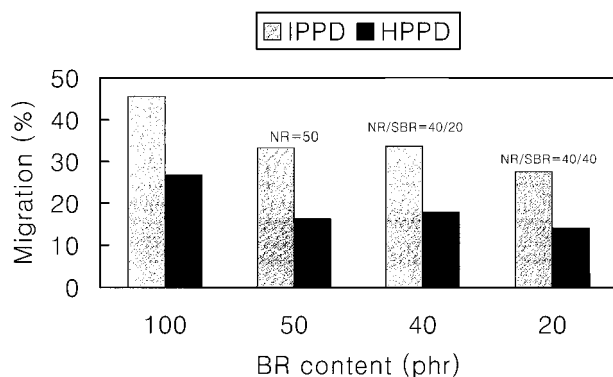


Figure 5 Variation of amounts of the antiozonants migrated in the vulcanizates containing BR after the migration outdoors for 80 days as a function of the BR content. The NR content is not less than the SBR one.

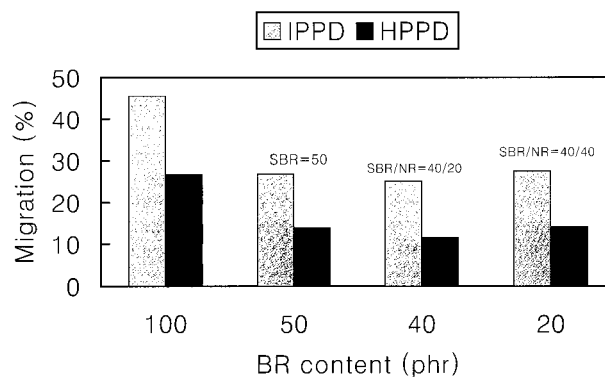


Figure 6 Variation of amounts of the antiozonants migrated in the vulcanizates containing BR after the migration outdoors for 80 days as a function of the BR content. The SBR content is not less than the NR one.

rubber composition was explained by the interface formed between dissimilar rubbers and by the intermolecular interactions of the antiozonants with the matrix.

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