

Migration Behaviors of Antiozonants in Binary Rubber-Based Vulcanizates of NR, SBR, and BR

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ABSTRACT: Influence of rubber composition on migration of *N*-phenyl-*N'*-isopropyl-*p*-phenylenediamine (IPPD), and *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD) to the surface in binary rubber-based vulcanizates of natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR) was studied. Migration experiments were performed at 60 and 80°C for 21 days and outdoors for 4 months. Migration rates of IPPD and HPPD in the vulcanizates of SBR/NR and BR/NR blends outdoors increased by decreasing the content of NR, and those in the vulcanizates of BR/SBR blends decreased with an increase of the content of BR. Migration behaviors of the antiozonants in the vulcanizates of SBR/NR and BR/NR blends at 60 and 80°C, on the whole, showed trends similar to the outdoor results. Migration rates of the antiozonants in the vulcanizates of BR/SBR blends at 60 and 80°C showed some differences. Variation of migration behaviors of the antiozonants in the binary rubber-based vulcanizates depending on rubber composition was explained by the interface between dissimilar rubbers and the intermolecular interactions between the matrices and the antiozonants. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3130–3136, 1999

Key words: antiozonants; migration; binary rubber-based vulcanizates; interface

INTRODUCTION

Migration behaviors of antidegradants in rubber vulcanizates are influenced by matrices, including rubber and filler, composed of the vulcanizates.^{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 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 increasing the filler content in the vulcanizates. One of the principal sources influencing migration behaviors of antidegradants in rubber vulcanizates are inter-

molecular interactions between the antidegradants and the matrices of rubber and filler.

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 that include improved physical properties, increased service life, easier processing, and reduced product cost. In this study, the influence of rubber composition on migration of antiozonants to the surface in binary rubber-based vulcanizates of 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

Table I Formulations (phr)

Compound No.	1	2	3	4	5	6	7	8	9	10	11	12
SMR 20	80.0	60.0	40.0	20.0	80.0	60.0	40.0	20.0	0.0	0.0	0.0	0.0
SBR 1500	20.0	40.0	60.0	80.0	0.0	0.0	0.0	0.0	80.0	60.0	40.0	20.0
BR 01	0.0	0.0	0.0	0.0	20.0	40.0	60.0	80.0	20.0	40.0	60.0	80.0
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
Wax	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
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
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
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
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
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
Sulfur	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2

(preferably *sec*-alkyl) are the most effective antiozonants.^{10,11}

EXPERIMENTAL

In order to investigate the influence of rubber composition on migration of antiozonants to the surface in binary rubber-based vulcanizates, 12 carbon black-filled rubber compounds containing two rubbers of NR, SBR, and BR were prepared. The rubber content ratios of the 12 compounds were SBR/NR, BR/NR, and BR/SBR = 20/80, 40/60, 60/40, 80/20 phr. The formulations are given in Table I. SMR 20 (standard Malaysian rubber) and N330 were employed as an NR and a carbon black. *N-tert*-Butyl-2-benzothiazole sulfenamide (TBBS) was used as a curing accelerator. The compounds were prepared in a Banbury mixer at a rotor speed of 40 and 30 rpm for the carbon master batch (MB) and final mixing (FM). The initial and dump temperatures of the MB were 110 and 160°C, respectively, while those of the FM were 80 and 100°C. The binary rubber-based vulcanizates were prepared by curing at 160°C for 20 minutes.

The migration experiments were performed at 60 and 80°C for 21 days using a convection oven and were performed outdoors for 4 months. During the outdoor experiment (120 days), the average low and high temperatures were 11.44°C (range: 1–23°C) and 21.88°C (range: 6–30°C), respectively. Of the 120 days, there were 32 rainy days.

Amounts of the antiozonants that migrated to the surface in the vulcanizates were determined by the differences between amounts of the anti-

ozonants 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 from the sample with THF. Experiments were carried out three times and averaged.

RESULTS AND DISCUSSION

The experimental results were plotted as a function of the rubber composition in the binary rubber-based vulcanizates, as shown in Figures 1–6. Migration behaviors of a migrant in a rubber vulcanizate are largely affected by the intermolecular interactions of the migrant with matrices including rubbers and fillers.^{1–4} Migration rate of a migrant in a rubber vulcanizate becomes slower by increasing the intermolecular interactions. Thus, one can expect that rubber composition of the binary rubber-based vulcanizates also has a great influence on the migration behaviors of the antiozonants. Figures 1–6 show the difference of the migration behaviors of the antiozonants in the binary rubber-based vulcanizates depending on the rubber composition. However, the variation of migration behaviors in the blends was not consistent with the order of the intermolecular interaction of rubber with the antiozonants, SBR > NR > BR. For single rubber-based vulcanizates, the migration rates of IPPD and HPPD in an SBR vulcanizate were slower than those in NR and BR ones, while those in an NR one were slower than those in a BR one.¹ For the binary rubber-based vulcanizates (Figs. 1–6), however, the migration rates of IPPD and HPPD in the

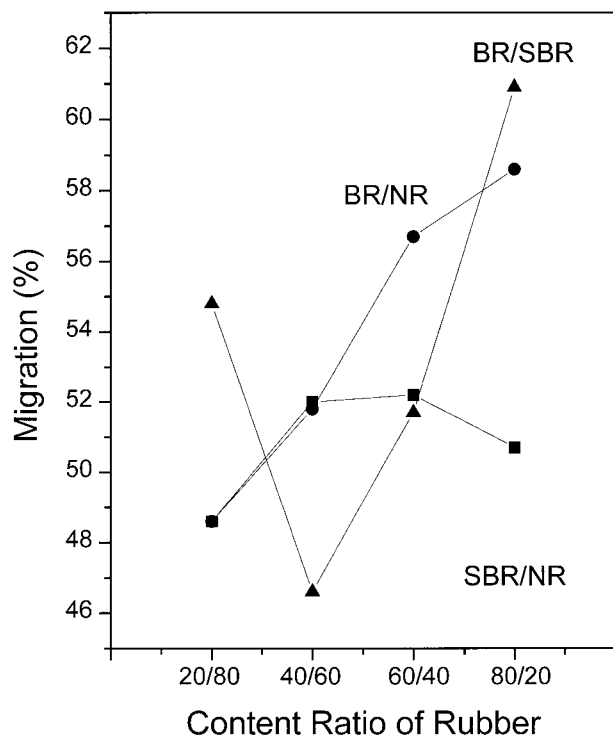


Figure 1 Variation of amounts of IPPD that migrated at 60°C for 21 days as a function of the content ratio of rubber. Squares, circles, and triangles represent the SBR/NR, BR/NR, and BR/SBR blends, respectively.

SBR/NR vulcanizates become faster by increasing the SBR content, although the intermolecular interactions of SBR with the antiozonants are stronger than those of NR.¹ Thus, the migration behaviors of the antiozonants in the binary rubber-based vulcanizates can not be explained by only the intermolecular interactions between the matrices and the antiozonants.

Migration Behaviors at 60°C

Migration behaviors of IPPD and HPPD at 60°C show similar trends, depending on rubber composition of SBR/NR, BR/NR, and BR/SBR (Figs. 1 and 2). Migration rates of the antiozonants in the BR/NR vulcanizates at 60°C become faster as the BR content increases. This may be due to the intermolecular interactions of the antiozonants with the rubbers. Since the intermolecular interactions of the antiozonants with NR are stronger than those with BR,¹ migration rates of the antiozonants in the BR/NR vulcanizates increase by increasing the BR content in the vulcanizates.

Migration behaviors of IPPD and HPPD in the BR/SBR vulcanizates at 60°C are similar to those in the BR/NR vulcanizates, except for the migration in the BR/SBR (20/80 phr) vulcanizates. Migration rates of the antiozonants in the BR/SBR vulcanizates increase by increasing the BR contents from 40 to 80 phr. This can be also explained by the intermolecular interactions. Since the intermolecular interactions of the antiozonants with SBR are stronger than those with BR,¹ migration rates of the antiozonants in the BR/SBR vulcanizates increase by increasing the BR content in the vulcanizates. However, migration rates of IPPD and HPPD in the BR/SBR vulcanizates with the content ratio of 20/80 phr at 60°C are faster than those in the BR/SBR ones with the content ratios 40/60 and 60/40 phr. This can not be explained by the intermolecular interactions.

Migration behaviors of IPPD and HPPD in the SBR/NR vulcanizates at 60°C, on the whole, show the trends similar to those in the BR/NR ones. The migration rates of the antiozonants in the SBR/NR vulcanizates become faster with a de-

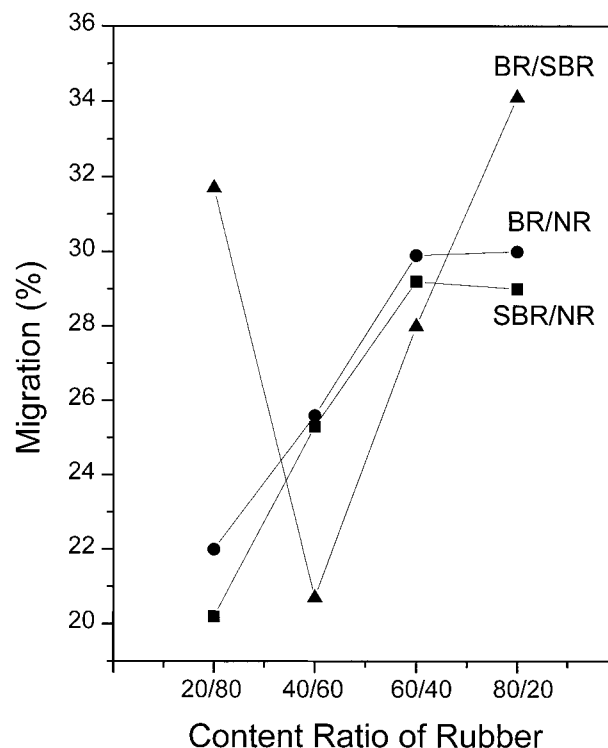


Figure 2 Variation of amounts of HPPD that migrated at 60°C for 21 days as a function of the content ratio of rubber. Squares, circles, and triangles represent the SBR/NR, BR/NR, and BR/SBR blends, respectively.

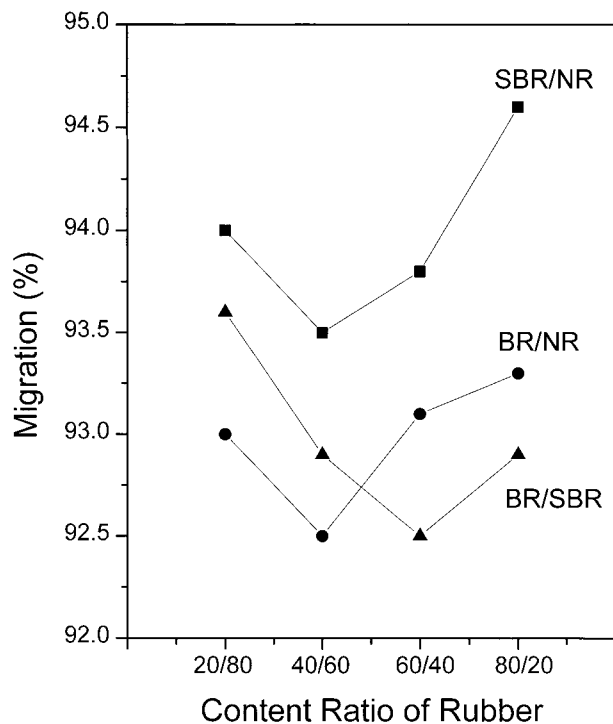


Figure 3 Variation of amounts of IPPD that migrated at 80°C for 21 days as a function of the content ratio of rubber. Squares, circles, and triangles represent the SBR/NR, BR/NR, and BR/SBR blends, respectively.

crease of the NR content. This can not be explained by only the intermolecular interactions, as discussed previously. Migration rates of IPPD and HPPD in the SBR/NR vulcanizates are slower than those in the BR/NR ones when the NR content is the same in both the SBR/NR and BR/NR blends. This is because the intermolecular interactions of the antiozonants with SBR are stronger than those with BR.¹

Migration Behaviors at 80°C

Migration behaviors of IPPD and HPPD at 80°C are to some extent different from those at 60°C, as shown in Figures 3 and 4. Migration rates of IPPD in the SBR/NR and BR/NR vulcanizates become faster as the NR content decreases from 60 to 20 phr. Migration behaviors of IPPD in the BR/NR vulcanizates can be explained by the intermolecular interactions, but those in SBR/NR ones cannot be explained by the intermolecular interactions. Migration rates of IPPD in the BR/SBR vulcanizates become slower as the BR content increases from 20 to 60 phr. This also cannot

be explained by the intermolecular interactions. Migration rates of IPPD in the SBR/NR vulcanizates are faster than those in BR/NR vulcanizates irrespective of rubber composition. This is an interesting result and also cannot be explained by the intermolecular interactions, because the intermolecular interaction of IPPD with SBR is stronger than that with BR.¹

The migration behaviors of HPPD at 80°C are very similar to those of IPPD except the migration in the 20/80 SBR/NR and BR/NR vulcanizates. Migration rates of HPPD in the SBR/NR and BR/NR vulcanizates become faster as the NR content decreases from 80 to 20 phr. The migration behaviors of HPPD in the BR/NR vulcanizates can be explained by the intermolecular interactions, but those in the SBR/NR ones cannot be explained by the intermolecular interactions. Migration rates of IPPD and HPPD in the SBR/NR vulcanizates are faster than those in the BR/NR ones when the NR content ratio is the same in both the SBR/NR and BR/NR blends. The migration rates of the antiozonants in the 40/60 and 60/40 BR/SBR vulcanizates are slightly slower

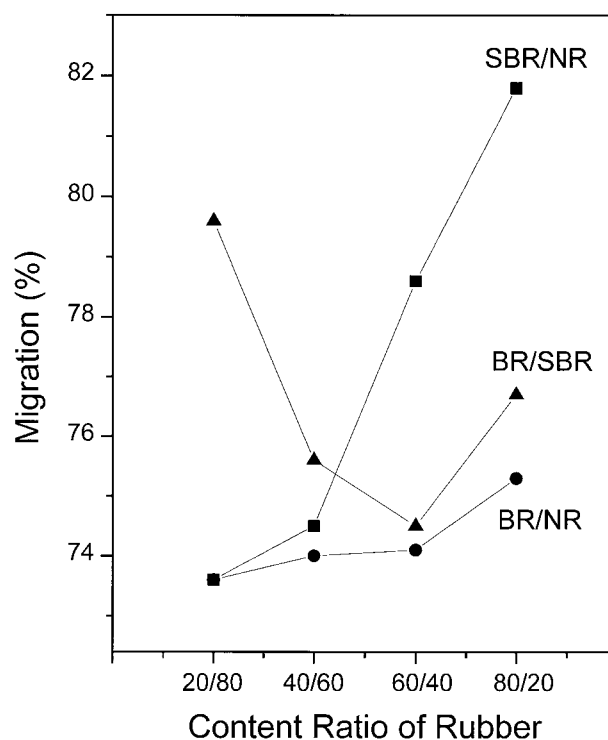


Figure 4 Variation of amounts of HPPD that migrated at 80°C for 21 days as a function of the content ratio of rubber. Squares, circles, and triangles represent the SBR/NR, BR/NR, and BR/SBR blends, respectively.

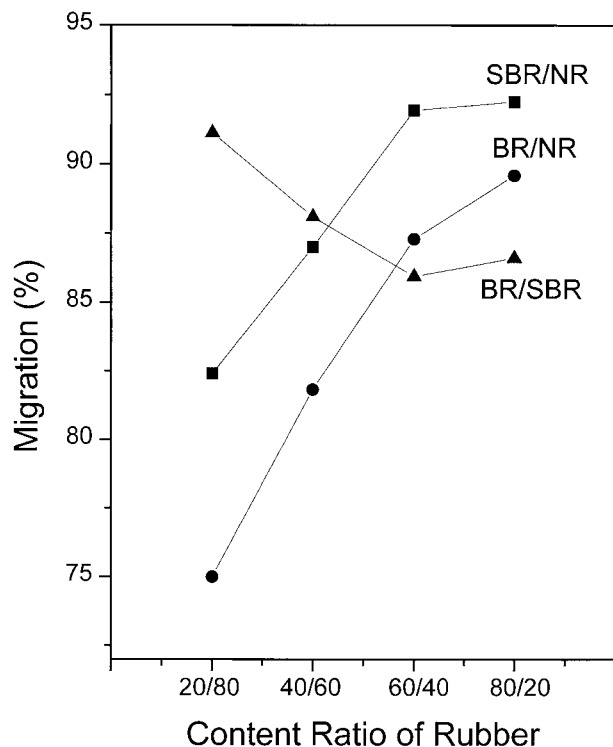


Figure 5 Variation of amounts of IPPD that migrated outdoors for 4 months as a function of the content ratio of rubber. Squares, circles, and triangles represent the SBR/NR, BR/NR, and BR/SBR blends, respectively.

than those in the 20/80 and 80/20 ones and similar to those at 60°C.

Migration Behaviors Outdoors

The outdoor experiments were carried out by putting the samples in the sun for 4 months from spring to summer. The outdoor migration experiments have a merit (reflection of the real conditions) in comparison with the experiments performed in a convection oven, although they need a long time. When the migration experiments are performed outdoors, the influences of weather conditions (sunlight, rain, and wind) as well as temperature on the migration can be observed.

Migration behaviors of HPPD and IPPD in the SBR/NR and BR/NR vulcanizates outdoors show some trends similar to those at 60°C, whereas those in BR/SBR vulcanizates outdoors are rather similar to those at 80°C (Figs. 5 and 6). Migration rates of the antiozonants in the SBR/NR and BR/NR vulcanizates outdoors increase as the NR content decreases. Migration rates of the antiozo-

nants in the BR/SBR vulcanizates outdoors become slower by increasing the BR content. The outdoor experiments are similar to the results at 80°C, with migration rates of IPPD and HPPD in the SBR/NR vulcanizates being faster than those in the BR/NR ones when the NR content is the same in both the SBR/NR and BR/NR blends.

Factors Determining the Migration Behaviors

Of the experimental results, only the migration behaviors of IPPD and HPPD in the BR/NR vulcanizates can be explained by the intermolecular interactions of the antiozonants with the matrices. What are the principal factors influencing the migration behaviors of the antiozonants in the binary rubber-based vulcanizates?

Most blends of elastomers are immiscible, because mixing is endothermic, and the entropic contribution is small because of the high molecular weights.¹² Three types of incompatibility have generally been noted: incompatibility due to viscosity mismatch, thermodynamic incompatibility, and incompatibility due to cure rate mismatch.¹³

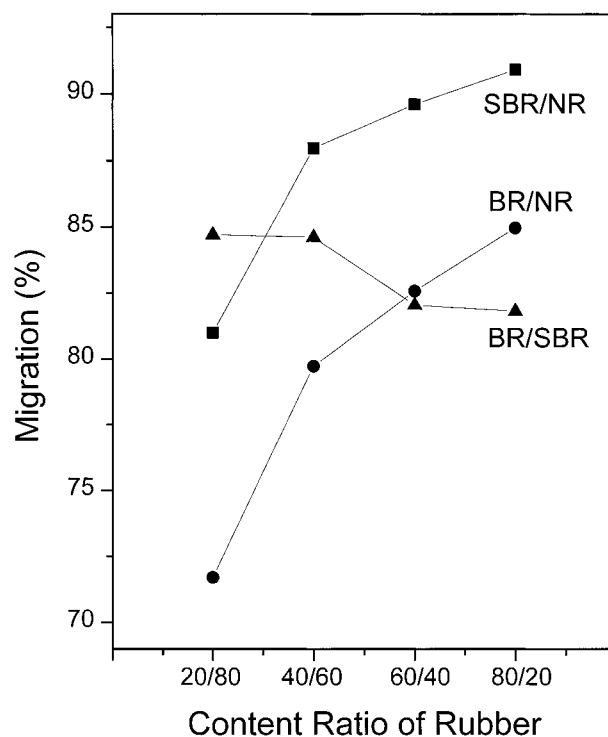


Figure 6 Variation of amounts of IPPD that migrated outdoors for 4 months as a function of the content ratio of rubber. Squares, circles, and triangles represent the SBR/NR, BR/NR, and BR/SBR blends, respectively.

Table II Glass Transition Temperatures (T_g) of the Binary Rubber-Based Vulcanizates

Compound No.	T_g (°C)
1	-51.51, -40.83
2	-52.91, -41.33
3	-53.42, -40.50
4	-52.02, -39.36
5	-93.75, -51.92
6	-92.79, -52.97
7	-91.38, -77.59, -51.48
8	-92.46, -72.23
9	-82.36, -46.87
10	-87.22, -65.34
11	-85.84
12	-91.92, -63.47
NR = 100	-53.27
SBR = 100	-40.66
BR = 100	-92.64

Because of these incompatibilities, the discontinuous interface is formed between dissimilar rubbers in rubber blends. Gardiner¹⁴ studied diffusion gradient of curatives in blends of two rubbers. 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. Callan and coworkers¹⁵ measured average areas of disperse phase in 75/25 rubber blends and reported that the size of the disperse phase in BR/SBR blend was smaller than that in BR/NR and SBR/NR blends. BR/SBR blends are more compatible than BR/NR and SBR/NR blends. The average disperse phase sizes in 25/75 BR/NR and SBR/NR blends (about 0.7 and 0.5 μm^2 , respectively) are smaller than those in 25/75 NR/BR and NR/SBR blends (about 1.5 and 1.2 μm^2 , respectively).

To investigate degree of miscibility of the binary rubber-based vulcanizates, 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 II gives the T_g s of the 12 binary rubber-based vulcanizates and pure NR, SBR, and BR vulcanizates. Most blend vulcanizates have two T_g s. The T_g of the BR/SBR vulcanizates shifted more than those of the SBR/NR and BR/NR ones. This means that the BR/SBR blends are more compatible than the SBR/NR and BR/NR ones.

The migration behaviors of the antiozonants in SBR/NR and BR/NR vulcanizates can be explained by the interface formed between the dissimilar rubbers and the disperse phase sizes. The disperse phase sizes in SBR/NR and BR/NR blends are larger when the NR is disperse phase than when the NR is continuous phase.¹⁵ In the vulcanizates with the interface, the antiozonants will migrate to the surface along the interface or through the matrices. The migration along the interface may be more favorable than that through the matrices. Because the interface between the dissimilar rubbers in the blends is more and more developed by increasing the disperse phase size, the migration rates of IPPD and HPPD become faster with a decrease of the NR content in the SBR/NR vulcanizates as well as the BR/NR ones.

The migration rates of IPPD and HPPD in the 40/60 and 60/40 BR/SBR vulcanizates at 60 and 80°C are slower than those in the 20/80 and 80/20 ones, as discussed previously. This can be explained by the compatibility of the BR/SBR blends. The T_g of the 60/40 BR/SBR vulcanizate is only one. This means that 60/40 BR/SBR vulcanizate is completely miscible. The degree of the T_g shift of the 40/60 BR/SBR vulcanizate is larger than those of the 20/80 and 80/20 ones. This means that the 40/60 BR/SBR vulcanizate is more miscible than the 20/80 and 80/20 ones. Thus, the migration rates of the antiozonants in the BR/SBR vulcanizates with good mixing conditions are slower than those with bad ones.

As discussed above, the migration behaviors of the antiozonants in the binary rubber-based vulcanizates were to some extent explained with the interface formed between dissimilar rubbers and the intermolecular interactions. Another one of factors affecting migration behaviors of antiozonants in rubber vulcanizates is the cross-link density of the vulcanizate. Their migration rates increase by increasing the cross-link density.¹⁶ Inverse swelling ratios (1/Q) of the vulcanizates were measured to investigate correlation between the 1/Q and the migration behaviors. *n*-Decane was employed as a swelling solvent. The degree of solvent-swelling depends on the polymer-solvent interaction parameter. The polymer-solvent interaction parameters of NR, SBR, and BR with *n*-decane are 0.444, >0.671 (28.5% styrene), and <0.57, respectively.¹⁷ Figure 7 gives variation of the 1/Q of the vulcanizates, depending on the rubber composition. The 1/Q of the SBR/NR and BR/NR vulcanizates increases by decreasing the

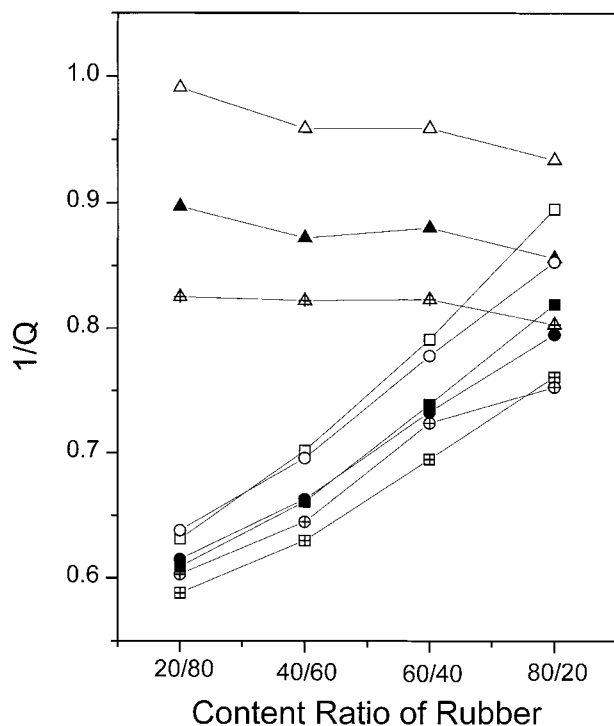


Figure 7 Variation of inverse swelling ratio ($1/Q$) of the binary rubber-based vulcanizates as a function of the content ratio of rubber. Squares, circles, and triangles represent the SBR/NR, BR/NR, and BR/SBR blends, respectively; solid, open, and cross-centered symbols indicate 60°C (for 21 days), 80°C (for 21 days), and outdoor (for 4 months), respectively.

NR content ratio, whereas that of the BR/SBR ones decreases with an increase of the BR content ratio. The variation of the $1/Q$ shows trends that are to some extent similar to the variation of the migration behaviors. This means that the migration behaviors of the antiozonants in the binary rubber-based rubber vulcanizates are related with the solvent swelling.

CONCLUSIONS

Migration rates of IPPD and HPPD in the SBR/NR and BR/NR vulcanizates become, on the whole, faster as the NR content decreases in the

vulcanizates. Migration rates of the antiozonants in the BR/SBR vulcanizates become, on the whole, slower by increasing the BR content in the vulcanizates, except those at 60°C. The migration rates of the antiozonants in the SBR/NR vulcanizates at 80°C and outdoors are faster than those in the BR/NR ones when the NR content ratio is the same. The migration behaviors of the antiozonants in the SBR/NR and BR/NR vulcanizates can be explained by the interface formed between dissimilar rubbers and the disperse phase sizes. The interface formed between the dissimilar rubbers in the blends is more and more developed by increasing the disperse phase size. Since the disperse phase sizes in the SBR/NR and BR/NR blends are larger when the NR is disperse phase than when the NR is continuous phase, the migration rates of IPPD and HPPD in the vulcanizates become faster with a decrease of the NR content.

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