

Migration Behaviors of Antiozonants in Triblend Vulcanizates of NR, SBR, and BR

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NR, SBR, BR의 세가지 고무로 이루어진 가류물에서 노화방지제의 이동 거동

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ABSTRACT: Influence of rubber composition on migration of antiozonants to the surface in ternary rubber-based vulcanizates composed of natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR) was studied. Of the three rubbers, contents of two rubbers were same and only the other one content was different (variable rubber). IPPD and HPPD were employed as antiozonants. Migration experiments were performed at 60°C for 21 days and outdoors for 4 months. Migration rates of the antiozonants increase by increasing the content ratio of the variable rubber in the vulcanizates from NR/SBR/BR=1/1/0.2 to 1/1/1 and then decrease with an increase of the content ratio of the variable rubber from 1/1/1 to 1/1/5. Migration behaviors of the antiozonants in the ternary rubber-based vulcanizates depending on the rubber composition were explained by the intermolecular interactions between rubber and antiozonant, by the solubility difference of the antiozonants for the rubbers, and by the interface formed between dissimilar rubbers in the triblend.

요약: NR, SBR, BR 등 3가지 고무로 이루어진 가류물에서 고무 조성비가 노화방지제의 이동 거동에 미치는 영향에 대해 연구하였다. 3가지 고무 중 2가지의 함량은 동일하게 하였고 나머지 하나만 다르게 하였다. IPPD와 HPPD를 오존노화방지제로 사용하였다. 실험은 60°C에서 21일간 방치하는 것과 옥외에서 4개월간 방치하는 것으로 진행하였다. 노화방지제의 이동 속도는 고무 조성비가 NR/SBR/BR = 1/1/0.2에서 1/1/1로 증가함에 따라 증가하다가 1/1/1에서 최대를 나타낸 후 다시 감소하였다. 3가지 고무로 이루어진 가류물에서 고무 조성비에 따른 노화방지제의 이동 거동의 변화는 고무와 노화방지제 간의 친화력, 고무에 대한 노화방지제의 용해도, 그리고 이질 고무간에 형성된 경계면 등으로 설명할 수 있었다.

Keywords: migration, vulcanizate, antiozonant.

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I. Introduction

Ozone attack on rubber compounds causes characteristic cracking perpendicular to the direction of applied stresses. This degradation is caused by reactions of ozone with the double bonds in the rubber molecules. These reactions lead to chain scission and the formation of various decomposition products. Several theories have been discussed in the literatures regarding the mechanism of antiozonant protection. In order to control the effects of rubber ozonation, either paraffin waxes or chemical antiozonants are added to unsaturated rubbers. The scavenger model states that the antiozonant blooms to the surface and preferentially reacts with ozone so that the rubber is not attacked until the antiozonant is exhausted.¹⁻³ The protective film theory is similar, except that the ozone-antiozonant reaction products form a film on the rubber surface that prevents (physically and perhaps chemically as well) ozone attack on the rubber.² A third relinking theory states that the antiozonant prevents scission of the ozonied rubber or else recombines severed double bonds.⁴ Currently, the most accepted mechanism of antiozonant action is a combination of the scavenger and protective film theories.^{5,6}

Migration behaviors of antidegradants in rubber vulcanizates are influenced by kinds of rubber and filler.⁷⁻¹⁰ 2,6-Di-*t*-butyl-4-methylphenol (BHT), *N*-phenyl-*N'*-isopropyl-*p*-phenylenediamine (IPPD), and *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (HP-

PD) migrate faster in SBR vulcanizates than in NR and BR vulcanizates.⁷ Migration rates of antidegradants in silica-filled rubber vulcanizates are slower than those in carbon black-filled ones.⁸⁻¹⁰ Migration rates of the antidegradants become slower and slower by increasing the filler content in the vulcanizates. One of the principal sources to influence migration behaviors of antidegradants in rubber vulcanizates are intermolecular interactions between the antidegradants and 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 elastomers¹¹⁻¹⁵ 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 of antiozonants to the surface in ternary rubber-based vulcanizates with natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR) was investigated. Experiments were performed outdoors and in a convection oven. IPPD and HPPD were employed as the antiozonants.

II. Experimental

In order to investigate the influence of rubber composition on migration of IPPD and HPPD to the surface in ternary rubber-based vulcanizates, thirteen carbon black-

Table 1. Formulations (phr)

Compound No.	1	2	3	4	5	6	7	8	9	10	11	12	13
SMR 20	33.4	25.0	25.0	50.0	40.0	40.0	20.0	14.0	14.0	72.0	45.5	45.5	9.0
SBR 1500	33.3	25.0	50.0	25.0	40.0	20.0	40.0	14.0	72.0	14.0	45.5	9.0	45.5
BR 01	33.3	50.0	25.0	25.0	20.0	40.0	40.0	72.0	14.0	14.0	9.0	45.5	45.5
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
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	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	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
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
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
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
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	1.2

filled rubber compounds composed of NR, SBR, and BR were prepared. The content ratios of rubbers of the compounds were NR/SBR/BR = 1/1/1, 1/1/2, 1/2/1, 2/1/1, 1/1/0.5, 1/0.5/1, 0.5/1/1, 1/1/5, 1/5/1, 5/1/1, 1/1/0.2, 1/0.2/1, and 0.2/1/1. Among the three rubbers, the content ratios of two rubbers are the same and that of only the other one is different (variable rubber). The content ratios of the variable rubber are 0.09, 0.20, 0.33, 0.50, 0.72. The formulations are given in Table 1. *N-tert*-Butyl-2-benzothiazole sulfenamide (TBBS) was used as a curing agent. The vulcanizates were prepared by curing at 160°C for 20 minutes.

The migration experiments were performed at constant temperatures of 60°C for 21 days in a convection oven. The experiments were also performed outdoors for 4 months. During the outdoor experiment (120 days), the average low and high temperatures were 10.39°C (range: 1–20°C) and 21.05°C (range: 6–30°C), respectively. Of the 120 days, the rainy days were 30 days.

Amounts of the antiozonants that migrated to the surface in the vulcanizates were

determined by the differences 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 gas chromatography after extraction of the antiozonants with THF. Experiments were carried out three times and averaged.

III. Results and Discussion

Experimental results for migration were plotted as a function of the rubber composition. The x-axis in Figures 1–4 is the content ratio of the variable rubber. For example, the content ratios of the variable BR are 0.33 (Compound 1), 0.50 (Compound 2), 0.20 (Compound 5), 0.72 (Compound 8), and 0.09 (Compound 11).

1. Migration Behaviors at 60°C

Migration behaviors of IPPD at 60°C depending on the rubber composition (Figure 1) show a specific trend that migration rates of IPPD increase with an increase of the content ratio of the variable rubber from

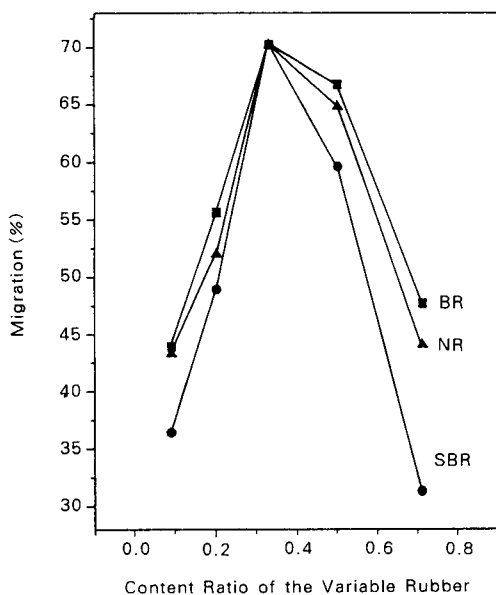


Fig. 1. Variation of amounts of IPPD that migrated in the triblend vulcanizates at 60°C for 21 days as a function of the content ratio of the variable rubber. Squares, circles, and triangles stand for the vulcanizates with the variable BR, SBR, and NR, respectively.

0.09 to 0.33 and then decrease by increasing the content ratio of the variable rubber irrespective of the rubber composition. Change of the migration rates of IPPD with the content ratio of the variable SBR is larger than that with the content ratio of the variable NR or BR. The amounts of IPPD migrated in the vulcanizates increase from 36.4, 43.3, and 43.9% (for the variable SBR, NR, and BR, respectively) to 70.2% by increasing the variable rubber content ratio from 0.09 to 0.33. The migration rates show the maximum at the rubber composition of NR/SBR/BR = 1/1/1 and then the amounts of the migrated IPPD decrease to 31.3, 44.1,

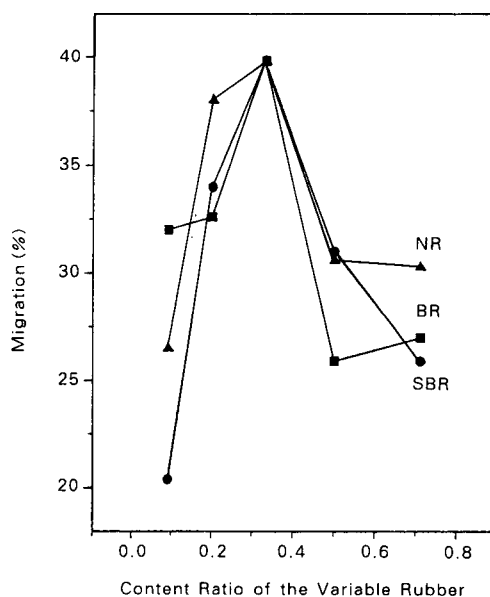


Fig. 2. Variation of amounts of HPPD that migrated in the triblend vulcanizates at 60°C for 21 days as a function of the content ratio of the variable rubber. Squares, circles, and triangles stand for the vulcanizates with the variable BR, SBR, and NR, respectively.

and 47.7%, respectively, by increasing the variable rubber content ratio from 0.33 to 0.72. Change of the migration rates of IPPD with the content ratio of the variable NR is larger than that with the content ratio of the variable BR. This may be due to the intermolecular interaction between IPPD and rubber. The intermolecular interaction of IPPD with SBR is stronger than that with NR or BR, while the intermolecular interaction of IPPD with NR is stronger than that with BR.⁷

Variation of migration behaviors of HPPD at 60°C with the rubber composition (Figure 2) shows the similar trend to that of IPPD.

The amounts of HPPD that migrated under the same experimental conditions are much less than those of IPPD. This is because HPPD and IPPD are the same species of N-phenyl-N-alkyl-p-phenylenediamines and HPPD (m/z 268) is larger than IPPD (m/z 226). The amounts of HPPD that migrated in the vulcanizates with the variable SBR, NR, and BR increase from 20.4, 26.5, and 32.0% (for the variable SBR, NR, and BR, respectively) to 39.8% by increasing the variable rubber content ratio from 0.09 to 0.33. The migration rates show the maximum at the rubber composition of NR/SBR/BR = 1/1/1 and then decrease to 25.9, 30.3, and 25.9%, respectively, by increasing the variable rubber content ratio.

Migration rate of a migrant in a rubber vulcanizate is largely affected by intermolecular interactions of the migrant with matrices of rubbers and fillers.⁷⁻¹⁰ Migration rate of a migrant in a rubber vulcanizate becomes slower as the intermolecular interactions of the migrant with the matrices become stronger. If migration behaviors of the antiozonants in the ternary rubber-based vulcanizates are affected mainly by the intermolecular interactions of the migrant with the matrices, the experimental results will be different from Figures 1 and 2. The migration rates of the antiozonants must increase by increasing the BR content ratio in the vulcanizate while those will decrease* with an increase of the SBR content ratio since the intermolecular interactions of the antiozonants with SBR are stronger than those with BR.⁸ As discussed above, the

experimental results can not be explained only by the intermolecular interactions of the antiozonants with the rubbers since variation of the migration rates shows a maximum point at the rubber composition of NR/ SBR/BR=1/1/1. What is the influencing factor on the migration behaviors of the antiozonants in the ternary rubber-based vulcanizates?

Variation of migration behaviors of the antiozonants in the triblend with the rubber composition can be explained by the solubility difference and the interface between dissimilar rubbers. There is an increased technological interest in the use of blends of various dissimilar rubber. However, there are technological problems which are frequently the result of some types of mutual incompatibility which can exist between dissimilar elastomers.¹⁶ Three types of incompatibility have generally been noted: incompatibility due to viscosity mismatch, thermodynamic incompatibility, and incompatibility due to cure rate mismatch. Due to these incompatibilities, the discontinuous interface is formed between dissimilar rubbers in rubber blends. Gardiner studied diffusion gradient of curatives in two rubbers.¹⁷ In similar rubbers, curative concentration showed a continuous gradient. But, in dissimilar rubbers, curative concentration showed a discontinuous gradient at the interface. Phase separation appears remarkably in immiscible elastomer blends when content ratios of two rubbers are nearly same. For the NR/SBR blends, phase separation appeared in 50/50 blend but did not appear in 25/75

blend.¹⁸ The phase separation will also appear clearly in the ternary rubber-based vulcanizates as the rubber content ratio is close to NR/SBR/BR = 1/1/1. The interface formed between dissimilar rubbers will be growing as the phase separation in the rubber blend appear. In the ternary rubber-based vulcanizates, the interface between dissimilar rubbers in the vulcanizate with the same content ratio of the three rubbers will be more developed than that in the vulcanizate with the different one. The antiozonants may migrate to the surface through the matrices of rubbers and filler or migrate along the interface formed between the dissimilar rubbers. Since the migration along the interface will be more faster than that through the matrices, the antiozonants migrate to the surface along the interface rather than through the matrix.

2. Migration Behaviors Outdoors

The outdoor experiments were carried out by putting the samples in the sun for 4 months. The outdoor migration experiments have a merit (reflection of the real conditions) in comparison with the experiments in a convection oven although they 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 behaviors of the antiozonants outdoors, on the whole, show the similar trend to those at 60°C. (Figures 3 and 4) The migration behaviors of the antiozonants in the ternary

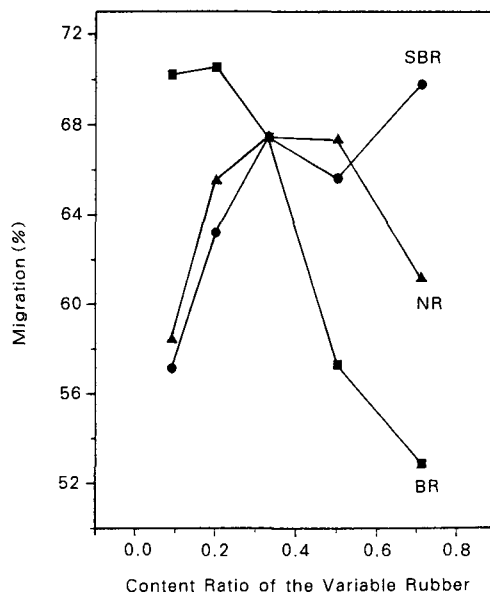


Fig. 3. Variation of amounts of IPPD that migrated in the triblend vulcanizates outdoors for 4 months as a function of the content ratio of the variable rubber. Squares, circles, and triangles stand for the vulcanizates with the variable BR, SBR, and NR, respectively.

rubber-based vulcanizates outdoors can be also explained by the solubility difference and the interface between dissimilar rubbers as similar to the case of the migration behaviors at 60°C.

The amounts of IPPD that migrated in the vulcanizates outdoors increase from about 57 and 58% (for the variable SBR and NR, respectively) to 67% and then decrease to 65 and 61%, respectively, by increasing the content ratios of the variable rubbers. However, migration rates of IPPD in the vulcanizates with the variable BR, on the whole, decrease by increasing the BR con-

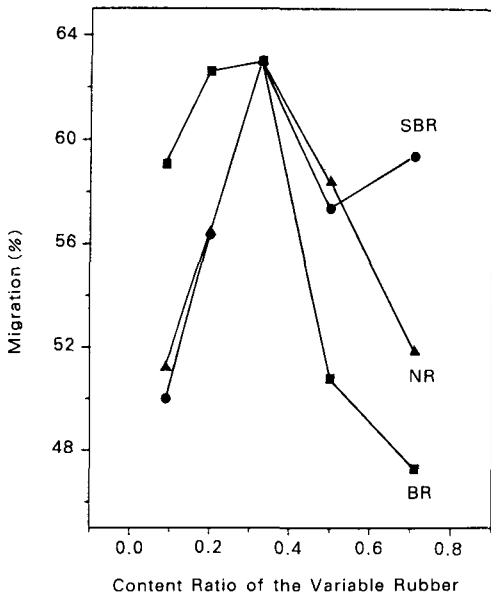


Fig. 4. Variation of amounts of HPPD that migrated in the triblend vulcanizates outdoors for 4 months as a function of the content ratio of the variable rubber. Squares, circles, and triangles stand for the vulcanizates with the variable BR, SBR, and NR, respectively.

tent ratio in the vulcanizates. This is different from the results at 60°C. This can not be explained by the intermolecular interactions between the antiozonants and the rubbers. The migration behaviors of IPPD in the vulcanizates with the BR content ratio of 0.33-0.72 can be explained by the interface between dissimilar rubbers as similar to the behaviors at 60°C. The migration behaviors of IPPD in the vulcanizates with the BR content ratio of 0.09-0.33 may be explained by the migrant concentration difference at the NR/SBR interface. Deviney and coworkers¹⁹ studied dependence of

diffusion rates on ingredient concentration and elastomer blend ratios. They reported that the ingredient concentration difference at the interface in NR/SBR blend (17%) was larger than that in NR/BR blend (8%). There are a lot of NR/SBR interfaces in the triblends with the low BR content ratios of 0.09 - 0.20 since contents of NR and SBR are much larger than that of BR in the triblends. Thus, IPPD will migrate mainly along the interface so its migration rates in those vulcanizates are faster than that in the vulcanizates with the rubber composition of NR/SBR/BR=1/1/1 since in the triblends the IPPD concentration difference at the interface between NR/SBR is large. This phenomenon was not observed at 60°C. This may be because the outdoor temperature is much lower than the oven-experimental temperature of 60°C. This phenomenon was not also observed in the migration behaviors of HPPD outdoors. This may be due to the difference of the intermolecular interactions of IPPD and HPPD with SBR. Since HPPD has a larger alkyl group (C₆H₁₃) than IPPD (C₃H₇), the intermolecular interaction of HPPD with styrene units of SBR is weaker than that of IPPD. Thus, the IPPD concentration difference at the interface between NR and SBR is larger than the HPPD one.

IV. Conclusion

Variation of migration behaviors of IPPD and HPPD in the ternary rubber-based vulcanizates of NR, SBR, and BR with the

rubber composition in the triblends was investigated. Migration rates of the antiozonants in the triblends with the rubber composition of NR/SBR/BR=1/1/1 are faster than those in the other vulcanizates. This can be explained by the intermolecular interactions of the antiozonants with the rubbers, by the solubility difference of the antiozonants in the dissimilar rubbers, and by the interface formed between dissimilar rubbers in the triblends. Migration behaviors of IPPD and HPPD outdoors show similar trends to those at 60°C.

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