# Migration of Antidegradants to the Surface in NR Vulcanizates: Influence of Content of Carbon Black

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Migration properties of antidegradants to the surface in NR vulcanizates containing carbon black of 30, 50, and 70 phr were studied using the migration-generating equipment with a vacuum technique. The migration was carried out at 60, 80, and 100 °C for 20 h. BHT, IPPD, HPPD, and wax were used as migrants. IPPD migrates faster than the other migrants. Amounts of BHT, IPPD, and HPPD that migrated at 60 and 80 °C decrease as the content of carbon black in the vulcanizate increases. Migrations of antidegradants in the NR vulcanizate containing carbon black of 50 phr are faster than those containing carbon black of 30 and 70 phr at 100 °C. Although $n$-$C_{21}H_{48}$ is heavier than HPPD, it migrates faster than HPPD and even faster than BHT at 100 °C. Influencing factors of carbon black on the migrations are its porous structure and polar functional groups on the surface.

## 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.[1] 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 most effective antiozonants are $N$, $N'$-disubstituted-$p$-phenylenediamines, in which at least one of the side groups is alkyl (preferably secondary alkyl).[2,3]

There are several theories about the mechanism of protection by chemical antiozonants. 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.[2,4,5] 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.[4] A third relinking theory states that the antiozonant prevents scission of the ozonized rubber or else recombines severed double bonds.[6] Currently, the most accepted mechanism of antiozonant action is a combination of the scavenger and protective film theories.[1,7]

Major characteristics required as antiozonant properties are migration to the surface of an object and reactivity with ozone. To measure migration of organic additives in a rubber compound, various methods such as solvent extraction,[8] the techniques of tagging the additives with a $^{13}C$ or a $^{35}S$ isotope before mixing it in a compound,[9,10] and compression set plates[11] were used. But, these methods are time consuming or do not consider a real tire conditions of inflation. Internal pressure of tire for passenger car is about 30 psi in driving conditions and pressure difference between inner and outer parts of tire might be more than twice. Recently, diffusion of antioxidants in rubber using rubber films and UV analysis was studied, in which rubber compounds without antioxidants were used.[12]

In this study, experiments were carried out with the migration-generating equipment using a vacuum technique.[13] This equipment has the following unique characteristics: First, pressure difference between inner and outer parts of compounded rubber sheet is considered. If pressure of vacuum chamber is about $10^{-6}$ Torr, then the pressure difference is about $10^8$ times. Second, organic additives on the surface are well vaporized in vacuum, so migration is accelerated. Third, migration has a direction from atmosphere to vacuum. Using this migration equipment, migration of antidegradants in rubber vulcanizates to the surface is strikingly accelerated. The loss of HPPD at 80 °C using this equipment is faster than that using a convection oven by about 10 times.[13]

In the previous work,[13] the influences of initial concentrations of antidegradants and kinds of rubber on the migration of antidegradants in rubber vulcanizates had been studied. Migration of antidegradants in rubber vulcanizates to the surface is independent of initial concentrations of antidegradants. Migrations of antidegradants in NR vulcanizates are faster than that in SBR ones.[13] Several groups studied effects of contents[14] and kinds[9] of carbon black. Diffusion coefficients of sulfur decrease by increasing the content of carbon black.[14] Diffusion coefficients of phenyl-2-naphthylamine in rubber vulcanizates containing carbon black with high surface area are smaller than those with low surface area.[9] In this study, with the migration-generating equipment, the influences of the content of carbon black on migration of antidegradants to the surface in NR vulcanizates were investigated. BHT (2,6-di-*tert*-butyl-4-methylphenol), IPPD ($N$-phenyl-$N'$-isopropyl-$p$-phenylenediamine), HPPD ($N$-phenyl-$N'$-(1,3-dimethyl-butyl)-$p$-phenylenediamine), and wax were used as migrants.

## Experimental

NR vulcanizates with three different contents of carbon black of 30, 50, 70 phr (Compound 1, 2, and 3, respectively) were prepared as demonstrated in Table 1. Each com-

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**Table 1.** Formulations. Units are phr

| Compound | 1 | 2 | 3 |
|---|---|---|---|
| SMR20 | 100.0 | 100.0 | 100.0 |
| N330 | 30.0 | 50.0 | 70.0 |
| Zinc oxide | 5.0 | 5.0 | 5.0 |
| Stearic acid | 3.0 | 3.0 | 3.0 |
| Wax | 4.0 | 4.0 | 4.0 |
| BHT | 2.0 | 2.0 | 2.0 |
| IPPD | 2.0 | 2.0 | 2.0 |
| HPPD | 2.0 | 2.0 | 2.0 |
| Sulfur | 1.2 | 1.2 | 1.2 |
| TBBS | 1.2 | 1.2 | 1.2 |

pounds contain 4 phr of wax and each 2 phr of BHT, IPPD, and HPPD. The NR compounds were cured at 160 °C for 15 minutes.

The migration-generating equipment used in this work has been described in detail elsewhere.[13] The dimension of the sample is 2.0 mm thick and 4.0 cm diameter. The migration experiments were carried out at constant temperatures of 60, 80, and 100 °C for 20 h. The base pressure in the vacuum chamber is typically lower than $1 \times 10^{-6}$ Torr and rises to about $5 \times 10^{-6}$ Torr during migration. The amount of antidegradants migrated to the surface was determined by the difference between the amounts of antidegradants that remained in the rubber vulcanizates before and after migration. The amount of antidegradants remaining in the rubber vulcanizates was analyzed using gas chromatography after extraction of the antidegrants with THF. Experiments were carried out three times and averaged.

## Results and Discussion

The experimental results were summarized in Tables 2, 3, and 4 for NR vulcanizates containing carbon black of 30, 50, and 70 phr, respectively. Values in parentheses in Tables 2-4 are migration rates calculated by the Eq. (1).[13]

$$C_t = C_0 \cdot (1 - k)^t \tag{1}$$

where, $C_0$ and $C_t$ are the concentrations of migrant that remained in a sample before and after migration, respectively, $k$ is the migration rate in $\% \cdot \sec^{-1}$, and $t$ is the migration time in second. Wax used in this study has a molecular weight distribution from $C_{21}H_{44}$ to $C_{40}H_{82}$. Migration rate of wax with a molecular weight equal or higher than $C_{27}H_{56}$ is

**Table 2.** Amounts of antidegradants migrated to the surface in NR vulcanizate containing carbon black of 30 phr (%). Values in parentheses are migration rate ($\times 10^{-6} \% \sec^{-1}$)

| Temperature (°C) | 60 | 80 | 100 |
|---|---|---|---|
| BHT | 51.98 (10.2) | 66.95 (16.6) | 73.69 (19.4) |
| IPPD | 61.62 (13.3) | 79.38 (24.4) | 83.43 (26.5) |
| HPPD | 35.04 (6.00) | 64.20 (15.3) | 77.25 (21.6) |
| Wax ($n$-$C_{23}H_{48}$) | 31.30 (5.21) | 67.33 (16.8) | 80.85 (24.2) |
| Wax ($n$-$C_{24}H_{50}$) | 10.78 (1.58) | 52.12 (11.0) | 72.96 (18.9) |
| Wax ($n$-$C_{25}H_{52}$) | 7.17 (1.03) | 37.83 (6.96) | 67.40 (16.2) |
| Wax ($n$-$C_{26}H_{54}$) | 2.17 (0.30) | 25.25 (4.24) | 59.00 (12.8) |

**Table 3.** Amounts of antidegradants migrated to the surface in NR vulcanizate containing carbon black of 50 phr (%). Values in parentheses are migration rate ($\times 10^{-6} \% \sec^{-1}$)

| Temperature (°C) | 60 | 80 | 100 |
|---|---|---|---|
| BHT | 51.06 (9.93) | 66.51 (15.2) | 77.27 (20.6) |
| IPPD | 55.53 (11.3) | 74.69 (19.1) | 89.03 (30.7) |
| HPPD | 31.41 (5.24) | 57.72 (12.0) | 81.21 (23.2) |
| Wax ($n$-$C_{23}H_{48}$) | 34.07 (5.79) | 64.61 (14.4) | 88.23 (29.7) |
| Wax ($n$-$C_{24}H_{50}$) | 16.73 (2.54) | 49.42 (9.47) | 75.45 (19.5) |
| Wax ($n$-$C_{25}H_{52}$) | 9.89 (1.45) | 32.55 (5.47) | 70.76 (17.1) |
| Wax ($n$-$C_{26}H_{54}$) | 4.46 (0.63) | 21.34 (3.33) | 61.81 (13.4) |

**Table 4.** Amounts of antidegradants migrated to the surface in NR vulcanizate containing carbon black of 70 phr (%). Values in parentheses are migration rate ($\times 10^{-6} \% \sec^{-1}$)

| Temperature (°C) | 60 | 80 | 100 |
|---|---|---|---|
| BHT | 47.29 (8.90) | 62.48 (13.6) | 73.41 (18.4) |
| IPPD | 48.10 (9.11) | 71.12 (17.2) | 83.79 (25.3) |
| HPPD | 26.81 (4.33) | 55.27 (11.2) | 76.48 (20.1) |
| Wax ($n$-$C_{23}H_{48}$) | 31.29 (5.21) | 63.41 (14.0) | 87.90 (29.3) |
| Wax ($n$-$C_{24}H_{50}$) | 14.86 (2.23) | 49.14 (9.39) | 72.80 (18.1) |
| Wax ($n$-$C_{25}H_{52}$) | 7.72 (1.12) | 31.42 (5.24) | 65.41 (14.7) |
| Wax ($n$-$C_{26}H_{54}$) | 2.31 (0.32) | 20.35 (3.16) | 58.65 (12.3) |

so slow that it is hard to measure the amounts of the wax that migrated under the experimental conditions. Since the $C_{21}H_{44}$ and $C_{22}H_{46}$ is contained with few amount in the wax, we did not measure their migration. Wax is a mixture of normal alkanes and their isomers. The number of the isomers is so many that it is very hard to separate them with each components and their content is lower than the normal alkanes. Thus, migration properties of only $n$-$C_{23}H_{48}$, $n$-$C_{24}H_{50}$, $n$-$C_{25}H_{52}$, and $n$-$C_{26}H_{54}$ were measured.

**Comparison of wax and antiozonants (BHT, IPPD, and HPPD).** Among the migrants (BHT, IPPD, HPPD, $n$-$C_{23}H_{48}$, $n$-$C_{24}H_{50}$, $n$-$C_{25}H_{52}$, and $n$-$C_{26}H_{54}$), the migration of IPPD is the fastest. BHT migrates faster than HPPD (m/z 268) at 60 and 80 °C, but migrates slower than HPPD at 100 °C. As the migration temperature increases, the amounts of antidegradants migrated continuously increase. In general, the migration of antidegradant with a lower molecular weight is faster than that with a higher molecular weight. For the normal alkanes ($n$-$C_{23}H_{48}$, $n$-$C_{24}H_{50}$, $n$-$C_{25}H_{52}$, and $n$-$C_{26}H_{54}$), the one with a low molecular weight migrates faster than that with a high molecular weight. But, BHT migrates slower than IPPD though the molecular weight of BHT (m/z 220) is lower than that of IPPD (m/z 226).

Wax with a molecular weight equal or higher than $n$-$C_{24}H_{50}$ migrates slower than BHT, IPPD, and HPPD. Wax with a molecular weight of $n$-$C_{23}H_{48}$ migrates faster than HPPD, although it is heavier than HPPD. Only HPPD in the vulcanizate containing 30 phr of carbon black at 60 °C migrates faster than $n$-$C_{23}H_{48}$. Differences between amounts of $n$-$C_{23}H_{48}$ and HPPD that migrated increase with increases of the migration temperature and the content of carbon black in the vulcanizates. Amounts of $n$-$C_{23}H_{48}$ that migrated in the vulcanizate containing 70 phr of carbon black are more than those of HPPD by about 5, 8, and 11% at 60, 80, and 100 °C, respectively. Amounts of $n$-$C_{23}H_{48}$ that mi-

grated at 80 °C are more than those of HPPD by about 3, 7, and 8% in the vulcanizate containing 30, 50, 70 phr of carbon black, respectively. This may be due to the difference of interactions of carbon black with them. One of the principal factors to affect the migration behaviors of antidegradants in a rubber vulcanizate is interactions between the antidegradants and matrices (rubber, carbon black, and silica).[13] Carbon black surface has graphite-like structures with functional groups such as hydroxyl, carboxyl, ketone, and so forth.[15] HPPD has an aromatic ring and amine group. The aromatic ring of HPPD will $\pi-\pi$ interact with graphite-like surface[16] and the amine group may interact well with polar functional groups by a hydrogen bond. Thus, interactions of HPPD with carbon black increase by increasing the content of carbon black in the vulcanizate. The strong interactions between HPPD and carbon black make migration of HPPD slow. $n$-$C_{23}H_{48}$ migrates slower than BHT and IPPD at 60 and 80 °C, but faster than BHT at 100 °C. Differences of amounts of $n$-$C_{23}H_{48}$ and BHT that migrated at 100 °C increase from 7 to 14% with an increase of the content of carbon black in the vulcanizate from 30 to 70 phr. This can be also explained by interactions between carbon black and migrants as similar to the comparison of HPPD and $n$-$C_{23}H_{48}$.

**Migration behaviors of BHT, IPPD, and HPPD.**
Migration behaviors of BHT, IPPD, and HPPD show similar trends depending on the contents of carbon black and the migration temperatures. Amounts of BHT, IPPD, and HPPD that migrated at 60 and 80 °C decrease by 4-14% with an increase of the content of carbon black from 30 to 70 phr as shown in Figure 1. This can be explained by the intermolecular interactions between them and matrices, carbon black and rubber. One of important parameters which
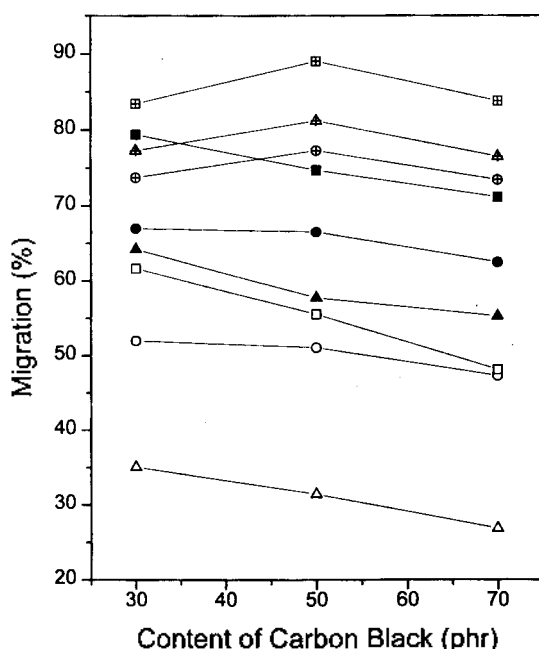


**Figure 1.** Varition of migration of BHT, IPPD, and HPPD depending on the content of carbon black. Open, solid, and cross-centered symbols stand for the migrations at 60, 80, and 100 °C, respectively. Circles, squares, and triangles indicate BHT, IPPD, and HPPD, respectively.

influence on migration properties of anitidegradants in a compounded rubber is an intermolecular interaction between antidegradants and matrices.[13] Migrations of phenylenediamines (IPPD and HPPD) in compounded BR are much faster than those in compounded SBR.[9,13] This is due to the strong interactions between styrene units of SBR and phenylenediamines. There are polar functional groups such as -OH, -$CO_2H$, and -CO- on the surface of carbon black.[15] These polar groups of carbon black may hydrogen-bond with the hydroxyl group of BHT or the amine group of IPPD and HPPD. Since the intermolecular interactions of BHT, IPPD, and HPPD with carbon black are stronger than those with NR, the migrations of BHT, IPPD, and HPPD decrease by increasing the content of carbon black.

For the migrations at 100 °C, the amounts of BHT, IPPD, and HPPD that migrated in the vulcanizate containing carbon black of 50 phr are more than those containing carbon black of 70 phr, as well as 30 phr, by about 4-6% as shown in Figure 1. The migration rates at 100 °C of BHT, IPPD, and HPPD in the NR vulcanizates containing carbon black of 30 phr are very close to those containing carbon black of 70 phr. This could not be explained only by the intermolecular interactions between carbon black and the migrants. It can be considered due to the shift of the distribution of the hole size in a rubber vulcanizate and the activation of segmental motion of the rubber at high temperatures. The holes are made by sulfur-crosslinking and the hole size distribution is shifted to a larger size as the temperature increases.[16] The higher the total crosslink density is, the smaller the hole size is. Total crosslink densities $(X_c)$ of Compounds 1-3 were measured by swelling method.[17] The total crosslink densities of NR vulcanizates containing carbon black of 30, 50, and 70 phr were 0.001867, 0.002280, and 0.002182 g·moles crosslinks/mL of rubbers, respectively. Since the total crosslink density of the vulcanizate containing carbon black of 50 phr is higher than those containing carbon black of 30 and 70 phr, the hole sizes in the vulcanizate containing 50 phr of carbon black are smaller than those containing 30 and 70 phr of carbon black. Thus, the vulcanizate containing carbon black of 50 phr may affect migration of the antidegradants more than those of 30 and 70 phr. Since the hole size distribution, at the high temperature, is shifted to a larger size, the migration may be accelerated. And it can be considered that the activated segmental motions of rubber at the high temperature may squeeze the migrants from the small holes so that the migration will be accelerated.

IPPD migrates faster than BHT and HPPD, irrespective of the temperature and the contents of carbon black. HPPD migrates slower than BHT at 60 and 80 °C, irrespective of the contents of carbon black, but this situation is reversed when the temperature is 100 °C. This is very interesting facts since HPPD is heavier than BHT by about 20%. However, the reasons could not be explained exactly. Only it is considered due to changes of intermolecular interactions, mainly van der Waals interactions, between the migrants and matrices, since the intermolecular interactions become weak by increasing the temperature. In Compound 2, differences of amounts migrated between BHT and HPPD decrease from about 20 to 9 and -4% with an increase of the temperature from 60 to 80 and 100 °C. This is
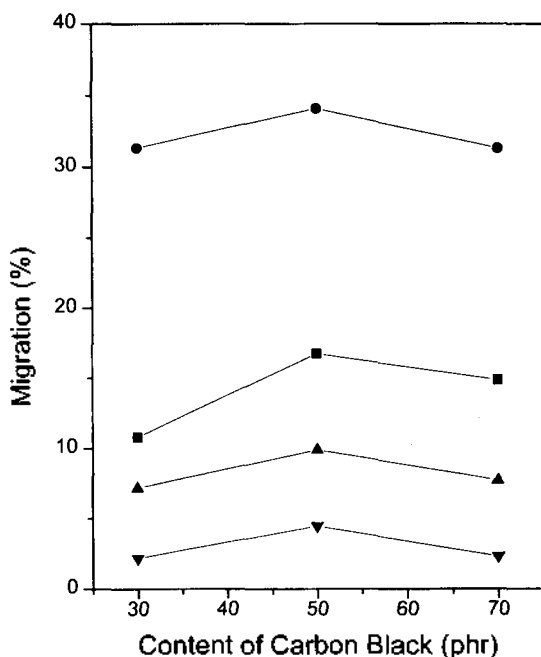
**Figure 2.** Varition of migration of wax depending on the content of carbon black at 60 °C. Circles, squares, up-triangles, and down-triangles indicate $n$-$C_{23}H_{48}$, $n$-$C_{24}H_{50}$, $n$-$C_{25}H_{52}$, and $n$-$C_{26}H_{54}$, respectively.

an evidence that the intermolecular interactions of HPPD with the matrices decrease more than those of BHT as the temperature increase.

**Migration behaviors of the normal alkanes.** Migrations of the normal alkanes ($n$-$C_{23}H_{48}$, $n$-$C_{24}H_{50}$, $n$-$C_{25}H_{52}$, and $n$-$C_{26}H_{54}$) at 80 and 100 °C show similar trends to those of BHT, IPPD, and HPPD. Amounts of the normal alkanes that migrated at 80 °C decrease with an increase of the content of carbon black in the vulcanizate. At 100 °C, amounts of the normal alkanes that migrated in the vulcanizate cotaining carbon black of 50 phr are more than those containing carbon black of 30 and 70 phr as similar to the migrations of BHT, IPPD, and HPPD as demonstrated previously. The amounts of $n$-$C_{23}H_{48}$, $n$-$C_{24}H_{50}$, $n$-$C_{25}H_{52}$, and $n$-$C_{26}H_{54}$ that migrated at 80 °C decrease by about 4, 3, 6, and 5%, respectively, as the contents of carbon black increase from 30 to 70 phr. The migrations of the normal alkanes at 60 °C show a different trend to those of BHT, IPPD, and HPPD. Amounts of BHT, IPPD, and HPPD migrated at 60 °C decrease with an increase of the content of carbon black as discussed previously. However, amounts of the normal alkanes that migrated at 60 °C in the vulcanizate cotaining carbon black of 50 phr are more than those containing carbon black of 30 and 70 phr as shown in Figure 2. This is a similar trend to the migrations of wax at 100 °C not at 80 °C.

The migration behaviors of the normal alkanes at 100 °C can be also explained by the shift of the hole size distribution in the vulcanizates and the activation of the segmental motion of rubber, similar to the case of BHT, IPPD, and HPPD, as discussed previously. The reason about the decrease of the amounts of the normal alkanes that migrated at 80 °C with an increase of the content of carbon black could not be explained by the intramolecular interactions between them and carbon black. Because the intermolecular

interactions between nonpolar normal alkanes and polar functional groups on the surface of carbon black is not strong. This may be explained by a path length of the migrants. Since carbon black is porous,[18] a path length that the normal alkanes migrates becomes long in the vulcanizate with a high content of carbon black. Thus, their migration rates in the vulcanizate with a high content of carbon black are slower than those with a low content of carbon black. The migration behaviors of the normal alkanes at 60 °C could not be explained by the shift of the hole size distribution, although those at 60 °C show a similar trend to those at 100 °C. This is because the shift of the hole size distribution becomes important only at high temperatures and the migration behaviors of wax at 80 °C do not follow those at 60 and 100 °C. The migration behaviors of wax at 60 °C could not be also explained by only the path length. This may be explained by combination of the path length and interactions between NR and the normal alkanes. By increasing the content of carbon black in the vulcanizate, the path length increases but the interactions of the normal alkanes with NR decrease. Thus, it can be considered that their migrations are mainly subject to the interactions between them and NR when the content of carbon black is low, while those are mainly subject to the path length when the content of carbon black is high.

## Conclusion

Migration rates of BHT, IPPD, and HPPD in carbon black-filled NR vulcanizates at 60 and 80 °C become slower with an increase of the content of carbon black in the vulcanizate from 30 to 70 phr. This is due to the intermolecular interactions between the surface of carbon black and the migrants. At 100 °C, migration rates of the antidegradants in the vulcanizate containing carbon black of 50 phr are faster than those containing carbon black of 30 and 70 phr. This may be explained by the shift of the hole size distribution in the vulcanizates and the activation of segmental motion of rubber. Migration behaviors of wax at 60 and 80 °C can be explained by the path length and interactions between NR and wax.

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# Blowout of Rubber Vulcanizates:
# Influences of Cure Systems, Content of Carbon Black, and Organic Additives

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Blowout of NR and SBR vulcanizates was studied using a microwave oven. Rubber vulcanizates with different contents of carbon black (0, 30, 50, 70 phr) and various cure systems (conventional, semi-EV, and EV) were prepared. Unfilled rubber vulcanizates did not exploded by irradiation of microwave, while carbon black-filled ones exploded within 10 min. A blowout time of the carbon black-filled rubber vulcanizate decreases with an increase of the content of carbon black in the vulcanizate. A blowout temperature of the organic additive-extracted vulcanizate is higher than that of the not-extracted one, but the extracted vulcanizate blows out faster than the not-extracted one. A blowout temperature of the overcured vulcanizate is higher than that of the undercured one with the same cure system. Temperatures of unfilled SBR vulcanizates heated by the microwave irradiation are lower than those of unfilled NR ones. The carbon black-filled SBR vulcanizates blow out at higher temperatures than the carbon black-filled NR ones. Blowout times of the carbon black-filled SBR vulcanizates are longer than those of the carbon black-filled NR ones.

## Introduction

When rubber is deformed, some part of the energy of deformation is transformed into heat as a result of various dissipative processes. When thick rubber blocks are subjected to repeated deformations, they can become so hot in the interior that they explode. This phenomenon is known as *blowout*. It is an important mode of failure in thick rubber articles, such as tire treads and tank track pads.[1] It is attributed to thermal decomposition of the rubber compound when the heat generated internally is not conducted away rapidly enough and the internal temperature becomes high enough to cause decomposition. Volatile products then develop an internal pressure sufficiently large to tear open a path to the exterior.

It should perhaps be pointed out that there is not at present a single, well-accepted, mechanism for blowout. It was first thought to be a mechanical fatigue cracking process, aggravated by the high temperatures set up by cycling stressing.[2] Other studies have attributed the failure to a biaxial tensile fracture in the center of the block, where the material is also weakened by high temperature.[3] Failure is attributed to the development of an internal pressure large enough to expand any pre-existing internal cavity to the

point of rupture. A similar hypothesis has been shown to account for internal fractures produced in rubber by superheating dissolved liquids.[4]

Engelhardt reported variation of blowout times of NR vulcanizates due to types of carbon balck using a flexometer.[5] Gent and Hindi studied blowout phenomena of NR (natural rubber), SBR (styrene butadiene rubber), BR (butadiene rubber), and IIR (butyl rubber) vulcanizates using a flexometer and a microwave oven.[6] They found that the blowout temperatures measured using a flexometer were consistent with those measured using a microwave oven, although the times taken to reach blowout were quite different. The times taken to reach blowout in the microwave oven are much faster than those in the flexometer experiments by over 10 times. In this study, blowout experiments were carried out using a microwave oven to study the influences of organic additives in rubber vulcanizates, content of carbon black, and cure system and time on blowout.

## Experimental

Thick rubber specimens, 12 mm thick, were made in a compression mold. The mix formulations and vulcanizing