Migration Behaviors of Wax to Surface in Rubber Vulcanizates

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ABSTRACT: The migration behaviors of wax to the surface in rubber vulcanizates were studied using natural (NR), styrene–butadiene (SBR), and butadiene rubber (BR) vulcanizates. The migration experiments were performed in a convection oven at 60 and 80°C for 14 days. There were less than 10% of the normal alkanes of n-$C_{22}H_{46}$ to n-$C_{38}H_{78}$ that migrated to the surface in the vulcanizates and evaporated at 60°C for 14 days. The amount of normal alkanes that migrated to the surface in the vulcanizates and evaporated at 80°C for 14 days was decreased by increasing the molecular weight of the normal alkanes. The migration of the normal alkanes in the NR vulcanizate was more sensitive to the variation of the molecular size of the normal alkanes than those in the BR and SBR vulcanizates. The migration behaviors of the normal alkanes in the vulcanizates were very similar to their evaporation behaviors. Major factors influencing the migration behaviors of the wax were discussed using the calculations of structures of the normal alkanes and evaporation experiments of wax. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2587–2593, 1999

Key words: wax; migration; rubber vulcanizate; evaporation

INTRODUCTION

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 parameters influence the solubility and mobility characteristics of each specific wax.[1] In general, substituted *papa*-phenylenediamine antiozonants are used with wax to protect for ozonation of rubber.[2]

The wax migrates to the surface in the natural rubber (NR) vulcanizate and forms a protection film on the surface.[1] The thickness of the paraffin wax film on the surface of the vulcanizate is increased by increasing the content of wax in the

vulcanizate. The thickness of the paraffin wax increases and then decreases with an increase of the melting point of the paraffin wax. 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 μm.

The chemical structures[3,4] and melting points[5] of the normal alkanes depend on their size. The normal alkanes with a molecular weight heavier than n-$C_{36}H_{74}$ have a structure of end-chain bending and folding.[4] The melting points of the normal alkanes are increased by increasing their size. The melting points of n-$C_{21}H_{44}$, n-$C_{24}H_{50}$, n-$C_{27}H_{56}$, n-$C_{30}H_{62}$, n-$C_{33}H_{68}$, n-$C_{36}H_{74}$, and n-$C_{40}H_{82}$ are 39, 51, 58, 63, 70, 75, and 79°C, respectively.[5] Consider that the composition of waxes affects the formation of a wax film because the alkanes have different structures and melting points, depending on their molecular weight.

In the present work, the migration behaviors of wax in carbon black filled NR, styrene–butadiene rubber (SBR), and butadiene rubber (BR) vulca-

Table I   Formulations (phr)

	Compound No.		
	1	2	3
SMR 20	100.0	0.0	0.0
BR 01	0.0	100.0	0.0
SBR 1500	0.0	0.0	100.0
N330	50.0	50.0	50.0
HPPD	3.0	3.0	3.0
Wax	3.0	3.0	3.0
Stearic acid	2.0	2.0	2.0
Zinc oxide	4.0	4.0	4.0
TBBS	2.0	2.0	2.0
Sulfur	1.2	1.2	1.2

TBBS, *N-tert*-butyl-2-benzothiazole sulfenamide.

nizates were studied. The structural characteristics of normal alkanes were calculated to investigate the influence of their structures on their migration in a rubber vulcanizate. Experiments of the evaporation of the normal alkanes dependent on molecular weight were carried out to investigate the influence of evaporation of the normal alkanes on their reduction during thermal aging.

EXPERIMENTAL

In order to investigate the migration behaviors of wax to the surface in a rubber vulcanizate, three carbon black filled rubber compounds with different rubber bases of NR, BR, and SBR were prepared. The formulations are given in Table I. The rubber vulcanizates were prepared by curing at 160°C for 20 min. The three compounds contain wax of 3.0 phr. The molecular weight distribution of the wax was obtained using gas chromatography. Figure 1 gives the molecular weight distribution of the wax. The wax was a mixture of normal alkanes and their isomers.

The migration experiments were performed in a convection oven for 14 days. The experimental temperatures were 60 and 80°C. The amount of wax that migrated to the surface in the rubber vulcanizates was determined by the differences between the amount of wax that remained in the vulcanizates before and after migration. The amount of wax remaining in the vulcanizates was analyzed using gas chromatography after extraction of the wax with *n*-hexane. Experiments were carried out 3 times and the results averaged.

RESULTS AND DISCUSSION

Wax is a mixture of normal alkanes and their isomers. Wax has a lot of isomers and it is hard to completely separate the isomers from each other with chromatography. Thus, in this study, only the normal alkanes of wax were employed as the experimental targets. The wax used in this study has a molecular weight distribution from $C_{20}H_{42}$ to $C_{42}H_{86}$. Because the $C_{20}H_{42}$, $C_{21}H_{44}$, and $C_{39}H_{80}$ to $C_{42}H_{86}$ are contained in a small amount in the wax, we did not measure their migrations.

The migration experiments of the normal alkanes of $C_{22}H_{46}$ to $C_{38}H_{78}$ were carried out at 60 and 80°C for 14 days. The amount of the normal $C_{22}H_{46}$ to $C_{38}H_{78}$ that migrated to the surface in the rubber vulcanizates at 60°C for 14 days was less than 10%. The amount of the n-$C_{22}H_{46}$ that migrated to the surface in the NR, BR, and SBR vulcanizates at 60°C for 14 days was about 6, 7, and 5%, respectively.

Migration at 80°C

Figure 2 gives a variation of amount of normal alkanes that migrated to the surface in the vulcanizates and evaporated at 80°C for 14 days as a function of the size of the normal alkanes. The amount of normal alkanes that migrated to the surface in the vulcanizates and evaporated at 80°C for 14 days was decreased continuously from about 30 to about 1% by increasing the molecular size of the normal alkanes from n-$C_{22}H_{46}$ to n-$C_{28}H_{58}$. The amount of the n-$C_{29}H_{60}$ to

Figure 1   Gas chromatography chromatogram of the wax used in this study. The numbers written above the peaks indicate the number of carbon atoms of the normal alkanes.

Figure 2 Variation of amounts of normal alkanes that migrated to the surface in the rubber vulcanizates at 80°C for 14 days: (■) NR, (●) BR, and (▲) SBR vulcanizates.

n-$C_{38}H_{78}$ that migrated to the surface in the vulcanizates and evaporated at 80°C for 14 days (about 1–6%) was larger than that of the n-$C_{28}H_{58}$ (about 1%).

In general, the amount of antidegradants that migrate to the surface in a rubber vulcanizate is increased by increasing the temperature and that of a small molecule is more than that of a large molecule when they are the same species chemically.[6–8] The principal factors influencing the migration of antidegradants in a rubber vulcanizate are intermolecular interactions between the antidegradants and matrices (rubber and filler).[6–8] However, in this study, the big difference in the migration of the normal alkanes in the vulcanizates, depending on the rubber base of the vulcanizate, was not found. Variation of the migration of the normal alkanes, depending on the alkane size, shows a local minimum at n-$C_{28}H_{58}$. The fact that the amount of the migrated n-$C_{28}H_{58}$ is smaller than those of the migrated n-$C_{29}H_{60}$ to n-$C_{38}H_{78}$ is very interesting because the n-$C_{28}H_{58}$ is smaller than the n-$C_{29}H_{60}$ to n-$C_{38}H_{78}$. What is the source of the occurrence of the local minimum?

Influence of Rubber Base

Because the amount of normal alkanes that migrated to the surface in the rubber vulcanizate

and evaporated decrease with an increase of the size of the normal alkanes, the migration equation dependent on the molecular weight of the normal alkanes can be established as eq. (1).

$$M_m = a + b/M_w + c/M_w^2 + d/M_w^3 + \cdots \quad (1)$$

The M_m is the amount (%) of the normal alkane with a molecular weight of m that migrated to the surface of a rubber vulcanizate and evaporated in; M_w is the molecular weight of the normal alkane; and a, b, c, and d are the parameters. Figure 3 gives the variation of the amount of the normal alkanes that migrated to the surface in the vulcanizates and evaporated at 80°C for 14 days as a function of $1/M_w$. Equation (1) was fitted to the experimental results, and the fitting results are displayed with solid curves in Figure 3.

Table II gives values of the parameters of eq. (1) for the NR, BR, and SBR vulcanizates obtained from the fitting of eq. (1). The r^2 for the fitting was close to 1.00. This means that eq. (1) well describes the migration behaviors of the normal alkanes in the rubber vulcanizates. Of the parameters a, b, c, and d, b is the principal parameter influencing the migration of the nor-

Figure 3 Curve fitting of eq. (1) to the experimental results of the migration at 80°C for 14 days: (■) NR, (●) BR, and (▲) SBR vulcanizates.

Table II   Parameters for $M_m = a + b/M_w + c/M_w^2 + d/M_w^3$ Obtained by Fitting to Experimental Results

Compound No.	a (10^3)	b (10^6)	c	d	r^2
1	−4.74	5.12	−1.84	2.21	0.998
2	−3.94	4.24	−1.52	1.83	0.998
3	−3.39	3.67	−1.33	1.61	0.986

mal alkanes in a rubber vulcanizate because the value of b is the largest. The b values for the migration at 80°C for 14 days in the NR, BR, and SBR vulcanizates are 5.12, 4.24, and 3.67 × 10⁶, respectively. The b for the NR vulcanizate is larger than those for the BR and SBR vulcanizates. This means that the migration of the normal alkanes in the NR vulcanizate is more sensitive to the change of the molecular size of the normal alkanes than those in the BR and SBR vulcanizates. The b for the BR vulcanizate is larger than that for the SBR one.

The crosslink densities of the rubber vulcanizates can affect the migration behaviors of wax. The migration rates of IPPD and HPPD in a NR vulcanizate with high crosslink density are faster than those with a low crosslink density.[9] In order to investigate the degree of crosslinks of the three vulcanizates, the swelling ratios of the vulcanizates were measured with n-decane after extraction of the organic materials from the vulcanizates. The crosslink density of the vulcanizate with a high swelling ratio is lower than that with a low swelling ratio. The swelling ratios of the NR, SBR, and BR vulcanizates are 1.924, 0.851, and 0.995, respectively. The crosslink density of the NR vulcanizate is much lower than those of the SBR and BR ones. The amount of the normal alkanes that migrated in the NR vulcanizate is not more than that in the SBR and BR as shown in Figure 3. The blooming rate of wax in an NR vulcanizate with high crosslink density was more sensitive than that with a low one.[10] As discussed above, however, the migration of the normal alkanes in the NR vulcanizate is more sensitive to the molecular size than those in the SBR and BR ones. Therefore, it can be considered that the migration sensitivity to the molecular size of wax, depending on the rubbers, is a specific property of rubber.

Influence of Structure and Size of Normal Alkanes

In order to investigate the source influencing the migration of the normal alkanes in the rubber

vulcanizates, the structures of the normal alkanes of n-$C_{22}H_{46}$ to n-$C_{32}H_{66}$ were calculated using molecular mechanics and molecular dynamics.

The initial structures of the input molecules were generated using the Insight II software package. Calculations were carried out by molecular mechanics and molecular dynamics using the Discover program of MSI. The CFF91 force field[11] was employed. A potential cutoff distance of 10.0 Å and a dielectric constant of 2.94 were employed. The dielectric constant of the vulcanized Hevea (one of the NRs) is 2.94.[12] The energy-minimized structures of the normal alkanes were obtained by conformational search. The conformational search was done by the annealing technique consisting of 100 ps of molecular dynamics at 900 K and 100-fold sampling for further minimizations. With the lowest energetic conformation among 100 conformers, the molecular dynamic simulations were performed at 353 K for 1000 ps to investigate the end-to-end distances of the normal alkanes. The end-to-end distance is the distance between the end carbon atoms of the normal alkanes.

Figures 4, 5, and 6 give the energy-minimized structures and the structures at 353 K of the n-$C_{24}H_{50}$, n-$C_{28}H_{58}$, and n-$C_{30}H_{62}$, respectively. The end-to-end distances of the normal alkanes are also displayed in Figures 4–6. When a normal alkane is composed of unique species (one molecular weight), a single normal alkane, it has a well-packed crystalline structure and mostly trans configurations.[3,4,13,14] The long normal alkanes exhibit chain folding[15] and the single normal alkanes with a molecular weight equal or more than n-$C_{36}H_{74}$ have end-chain bending and folding structures.[4] However, the normal alkanes obtained from this calculation had bending and folding structures as shown in Figures 4–6, although they were smaller than n-$C_{36}H_{74}$. This was because the normal alkanes calculated in this study were not under the condition of the single normal alkanes but under the condition of a mixture in a rubber vulcanizate.

The normal alkanes on the surface may contact with the rubber chains or form a wax film with their isomers. Because the dielectric constants of alkanes are close to that of an NR, the normal alkanes on the surface will also have the bending and folding structures similar to those in the vulcanized NR. The dielectric constants of nonadecane ($C_{19}H_{40}$), docosane ($C_{22}H_{46}$), 9-octylheptadecane ($C_{25}H_{52}$), and 11-decylheneicosane ($C_{31}H_{64}$) are 2.07, 2.08, 2.11, and 2.13, respectively.[12]

Figure 4   Structures of the n-$C_{24}H_{50}$ obtained from (a) the conformational search and (b) the molecular dynamics at 353 K: (a) the energy-minimized structure and (b) one of 100 conformers obtained from dynamic fluctuation for 1000 ps. The end-to-end distances are (a) 4.46 and (b) 15.98 Å.

Table III gives ranges of the end-to-end distances of the n-$C_{22}H_{46}$ to n-$C_{32}H_{66}$ obtained from the dynamic fluctuation at 353 K for 1000 ps. The end-to-end distances of the normal alkanes of the n-$C_{22}H_{46}$ to n-$C_{29}H_{60}$ are made longer by increasing their size. Thus, the decrease of the amount of the normal alkanes that migrated in the vulcanizates with an increase of their molecular weights from the n-$C_{22}H_{46}$ to the n-$C_{28}H_{58}$ can be explained by their end-to-end distances. The amount of the normal alkanes of the n-$C_{22}H_{46}$ to n-$C_{28}H_{58}$ that migrated in the vulcanizates increased with an increase of their end-to-end distances. However, the local minimum at the n-$C_{28}H_{58}$ of the migration of the normal alkanes cannot be exactly explained by the end to end distances because the end-to-end distances of the n-$C_{28}H_{58}$ are shorter than those of the n-$C_{29}H_{60}$ to n-$C_{32}H_{66}$. The end-to-end distance of the n-$C_{29}H_{60}$ is longer than those of the n-$C_{30}H_{62}$ to n-$C_{32}H_{66}$. The migrations of the n-$C_{29}H_{60}$ to n-$C_{32}H_{66}$ in the BR and SBR vulcanizates were not consistent with the end-to-end distances. The amount of the n-$C_{29}H_{60}$ that migrated in the BR and SBR vulcanizates is more than those of the n-$C_{30}H_{62}$ to n-$C_{32}H_{66}$, while the amount of the n-$C_{29}H_{60}$ that migrated in the NR vulcanizate is smaller than those of the n-$C_{31}H_{64}$ and n-$C_{32}H_{66}$.

Influence of Evaporation of Normal Alkanes

When evaporation of migrants on the surface of a rubber vulcanizate is accelerated, their migrations become faster. For example, the migration of antidegradants using the migration generating

Figure 5   Structures of the n-$C_{28}H_{58}$ obtained from (a) the conformational search and (b) the molecular dynamics at 353 K: (a) energy-minimized structure and (b) one of 100 conformers obtained from dynamic fluctuation for 1000 ps. The end-to-end distances are (a) 10.13 and (b) 15.88 Å.

Figure 6 Structures of the n-$C_{30}H_{62}$ obtained from (a) the conformational search and (b) the molecular dynamics at 353 K: (a) the energy-minimized structure and (b) one of 100 conformers obtained from dynamic fluctuation for 1000 ps. The end-to-end distances are (a) 11.47 and (b) 16.80 Å.

Table III   Range of End-to-End Distances of Normal Alkanes Obtained from Dynamic Fluctuation at 353 K for 1000 ps (Å)

Normal Alkane	End-to-End Distance
n-$C_{22}H_{46}$	4.37–25.36
n-$C_{23}H_{48}$	4.57–25.52
n-$C_{24}H_{50}$	4.86–25.21
n-$C_{25}H_{52}$	3.66–26.66
n-$C_{26}H_{54}$	3.95–26.81
n-$C_{27}H_{56}$	5.12–29.51
n-$C_{28}H_{58}$	4.23–31.05
n-$C_{29}H_{60}$	5.20–34.58
n-$C_{30}H_{62}$	4.62–31.42
n-$C_{31}H_{64}$	3.91–32.49
n-$C_{32}H_{66}$	4.08–32.59

The experimental results of the evaporation of the normal alkanes were fitted to eq. (1) and the values for the parameters a, b, c, and d of eq. (1) were obtained. The r^2 for the fitting was 1.00. This means that the evaporation behaviors of the normal alkanes of n-$C_{22}H_{46}$ to n-$C_{28}H_{58}$ are agree

equipment with a vacuum technique[6] is much faster than that in a convection oven because of the fast evaporation of the antidegradants on the surface facing the vacuum (about 10^{-6} torr). If the wax on the surface of the vulcanizate does not evaporate, it will remain on the surface of the vulcanizate or in the vulcanizate, although it migrates to the surface in the rubber vulcanizate. In order to investigate the degree of evaporation of the normal alkanes, depending on their size, evaporation experiments of the normal alkanes were performed in a convection oven. A wax film with about 8-μm thickness was prepared by spreading the wax solution in n-hexane on a glass plate and drying the solvent. The wax film was thermally aged at 60 and 80°C for 6 days. Figure 7 gives the variation of the amount of the normal alkanes of n-$C_{22}H_{46}$ to n-$C_{28}H_{58}$ that evaporated at 60 and 80°C as a function of $1/M_w$.

Figure 7 Variation of amounts of normal alkanes that evaporated from the wax film (8-μm thickness) at 60 and 80°C for 6 days as a function of the inverse of the molecular weight of the normal alkanes: (■) 60°C, (●) 80°C, and (—) the results of curve fitting of eq. (1).

Table IV   Parameters for $M_m = a + b/M_w + c/M_w^2 + d/M_w^3$ Obtained by Fitting to Experimental Results of Evaporation of Wax

Temperature (°C)	a (10^3)	b (10^6)	c	d	r^2
60	−3.99	4.58	−1.76	2.24	1.000
80	−1.65	2.00	−8.12	1.11	0.999

well with eq. (1). Table IV gives the parameters of eq. (1) for the evaporation of the normal alkanes. The b values for the evaporation at 60 and 80°C are 4.58 and 2.00×10^6, respectively. The b at 60°C is higher than that at 80°C. This means that the evaporation of the normal alkanes at low temperature is more sensitive to the change of the size of the normal alkanes than that at high temperature. The migration behaviors and the evaporation behaviors of n-$C_{22}H_{46}$ to n-$C_{28}H_{58}$ are well described by eq. (1). Thus, this can lead to the conclusion that the migration behaviors of n-$C_{22}H_{46}$ to n-$C_{28}H_{58}$ are well explained by the evaporation behaviors of n-$C_{22}H_{46}$ to n-$C_{28}H_{58}$.

The amount of the normal alkanes that evaporated at 60 and 80°C was continuously decreased until n-$C_{29}H_{60}$ by increasing their molecular weight and then increasing them slightly until n-$C_{32}H_{66}$ or n-$C_{33}H_{68}$. The decrement of the amount of n-$C_{22}H_{46}$ to n-$C_{29}H_{60}$ evaporated with an increase of their molecular weight can be explained by their melting and boiling points. The melting and boiling points become higher when increasing their molecular weight. The normal alkanes with a low melting point may evaporate better than those with a high one. However, the amounts of n-$C_{29}H_{60}$ that evaporated at 60 and 80°C were smaller than those of the n-$C_{30}H_{62}$ to n-$C_{32}H_{66}$. The amount of the normal alkanes that evaporated at 60°C were about 1.4, 4.0, 5.1, and 2.3% for the n-$C_{29}H_{60}$, n-$C_{30}H_{62}$, n-$C_{31}H_{64}$, and n-$C_{32}H_{66}$, respectively, and those at 80°C are about 5.4, 7.2, 8.4, and 5.9%, respectively. This cannot be explained by only the melting points of the normal alkanes; it can be explained by the end-to-end distances of the normal alkanes. The end-to-end distances of the normal alkanes increase until n-$C_{29}H_{60}$ by increasing the molecular

size of the normal alkanes and then decrease until n-$C_{32}H_{66}$. The end-to-end distances of n-$C_{29}H_{60}$ are longer than those of the n-$C_{30}H_{62}$, n-$C_{31}H_{64}$, and n-$C_{32}H_{66}$ as listed in Table III.

CONCLUSIONS

The amount of normal alkanes that migrated in the NR, BR, and SBR vulcanizates decreased remarkably until n-$C_{28}H_{58}$ and then was increased slightly by increasing their molecular weight. The migration behaviors of the normal alkanes in the NR vulcanizate were more sensitive to the variation of the molecular size of the normal alkanes than those in the BR and SBR vulcanizates. The migration behaviors of the normal alkanes in the rubber vulcanizates were consistent with the evaporation behaviors of the normal alkanes. The migration and evaporation behaviors of the normal alkanes were found to be closely related to the end-to-end distances of the normal alkanes.

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