Influence of Silica Content on Migration of Antidegradants to the Surface in NR Vulcanizates

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ABSTRACT: Migration of antidegradants to the surface in silica-filled natural rubber (NR) vulcanizates was studied with migration-generating equipment using a vacuum technique. 2,6-Di-t-butyl-4-methyl phenol (BHT), N-phenyl-N'-isopropyl-p-phenylenediamine (IPPD), N-phenyl-N'-(1,3-dimethylbutyl-p-phenylenediamine (HPPD), and wax (n-$C_{23}H_{48}$, n-$C_{24}H_{50}$, n-$C_{25}H_{52}$, and n-$C_{26}H_{54}$) were employed as antidegradants. The migration rate was found to be dependent on the content of silica in the vulcanizates. IPPD migrates faster than BHT and HPPD irrespective of the content of silica. BHT migrates faster than HPPD at 60 and 80°C, but slower than HPPD at 100°C. The migration rates of BHT, IPPD, and HPPD decrease with increase of the silica content from 30 to 70 phr. Wax with a low molecular weight migrates faster than that with a high molecular weight. The migration rate of n-$C_{23}H_{48}$, irrespective of migration temperature, decreases with increase of the silica content, similar to BHT, IPPD, and HPPD, but those of n-$C_{25}H_{52}$ and n-$C_{26}H_{54}$ have a local maximum at 50 phr silica content. The activation energies for migration to the surface in the vulcanizate containing 50 phr of silica are 19.3, 28.7, 40.1, 42.2, 51.6, 58.8, and 65.5 kJ/mol for BHT, IPPD, HPPD, n-$C_{23}H_{48}$, n-$C_{24}H_{50}$, n-$C_{25}H_{52}$, and n-$C_{26}H_{54}$, respectively. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1821–1828, 1998

Key words: antidegradants; migration; NR vulcanizate; vacuum technique; silica

INTRODUCTION

Ozone attack on rubber compounds causes characteristic cracking perpendicular to the direction of the 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 literature regarding the mechanism of antiozonant protection. To control the effects of rubber ozonation, either paraffin waxes or chemical antiozonants are added to unsaturated rubbers.

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.[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]

The major characteristics required as antiozonant properties are the migration to the surface of an object and reactivity with ozone. To measure the migration of organic additives in a rubber compound, various methods such as solvent ex-

traction,[7] the techniques of tagging the additives with a ^{13}C or a ^{35}S isotope before mixing it in a compound,[8,9] and compression set plates[10] and the techniques using a vacuum chamber[11] were used. The use of precipitated silica as a high-quality reinforcing filler in carbon black-filled rubber components of tires and mechanical goods has significantly increased over the years.

In this study, the migration of antidegradants in silica-filled natural rubber (NR) vulcanizates was measured with migration-generating equipment using a vacuum technique.[11] This equipment has several characteristics: First, the pressure difference between the inner and outer parts of a compounded rubber sheet is considered. If the pressure of a 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 a vacuum, so migration is accelerated. Third, the migration has a direction from the atmosphere to the vacuum. 2,6-Di-*t*-butyl-4-methyl phenol (BHT), *N*-phenyl-*N'*-isopropyl-*p*-phenylenediamine (IPPD), *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD), and wax were used as migrants.

EXPERIMENTAL

The details of the migration-generating equipment using a vacuum technique were described elsewhere.[11] The dimension of the sample was 2.0 mm thick and 4.0 cm in diameter. Migration experiments were carried out at constant temperatures of 60, 80, and 100°C for 20 h. The vacuum pressure for migration was about 5×10^{-6} Torr. Silica-filled NR vulcanizates were prepared by curing at 160°C for 15 min. The formulations are given in Table I. To investigate the effect of the content of silica on the migration to the surface, NR vulcanizates containing different contents of silica (30, 50, and 70 phr) were prepared (compounds 1, 2, and 3 in Table I, respectively).

The amount of antidegradants that migrated to the surface was determined by the difference in the amounts of antidegradants that remained in the rubber vulcanizates before and after migration. The amount of antidegradants that remained in the rubber vulcanizates was analyzed by gas chromatography after extraction of the antidegradants with THF. Experiments were carried out three times and averaged.

Table I   Formulations

Antidegradants	Compound No.		
	1	2	3
SMR20	100.0	100.0	100.0
Coupsil VP 8108	30.0	50.0	70.0
ZnO	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	1.5	1.5	1.5
TBBS	2.0	2.0	2.0

RESULTS AND DISCUSSION

The experimental results are summarized in Tables II, III, and IV for migrations in the vulcanizates containing silica of 30, 50, and 70 phr, respectively. The values in parentheses are migration rates calculated using eq. (1)[11]:

$$C_t = C_0(1 - k)^t \qquad (1)$$

where C_0 and C_t are the concentrations of a migrant that remained in a sample before and after migration, respectively; k, the migration rate in % s^{-1}; and t, the migration time in seconds. This rate, k, will be used to calculate the activation energy for migration to the surface from an Arrhenius plot.

Migration of BHT, IPPD, and HPPD

The amounts of BHT, IPPD, and HPPD that migrated in the silica-filled NR vulcanizates increased from 36–44 to 59–67%, from 39–51 to 74–89%, and from 22–30 to 67–80%, respectively, by increasing the temperature from 60 to 100°C. In general, the migration rates of an antidegradant with a low molecular weight are faster than those with a high molecular weight. IPPD (m/z 226) migrates faster than does HPPD (m/z 268) as shown in Tables II–IV. However, although IPPD is heavier than is BHT (m/z 220), IPPD migrates faster than does BHT at high temperatures (over about 50°C). BHT migrates at 60 and 80°C faster than does HPPD, but at 100°C, slower than does HPPD. This is due to the acceleration of the migration of HPPD by increasing the temperature. The amounts of HPPD and BHT

Table II Amounts of Antidegradants that Migrated in NR Vulcanizates Containing Silica of 30 phr (%) Depending on Temperature

Antidegradants	Temperature (°C)		
	60	80	100
BHT	44.5 (8.25)	59.3 (12.5)	67.4 (15.6)
IPPD	51.8 (10.1)	75.3 (19.4)	88.5 (30.0)
HPPD	30.3 (5.02)	58.5 (12.2)	79.9 (22.3)
Wax (n-$C_{23}H_{48}$)	29.3 (4.80)	59.7 (12.6)	80.1 (22.4)
Wax (n-$C_{24}H_{50}$)	6.1 (0.87)	44.1 (8.07)	74.1 (18.7)
Wax (n-$C_{25}H_{52}$)	3.8 (0.54)	28.2 (4.61)	64.7 (14.5)
Wax (n-$C_{26}H_{54}$)	1.6 (0.22)	13.6 (2.03)	53.0 (10.5)

Values in parentheses are migration rates ($\times 10^6\%$ s^{-1}).

that migrated at 80°C are more than those at 60°C by about 2.0 and 1.4 times, respectively. The amounts of HPPD and BHT that migrated increased by about 1.4 and 1.1 times, respectively, with increase of the temperature from 80 to 100°C.

To investigate the influence of the content of silica on the migrations of BHT, IPPD, and HPPD in detail, their migrations were graphed as a function of the content of silica. Figures 1, 2, and 3 show variation of their migrations at 60, 80, and 100°C, respectively. The amounts of BHT, IPPD, and HPPD that migrated at 60°C decreased from 44.5, 51.8, and 30.3% to 36.3, 39.1, and 21.6%, respectively, with increase of the silica content from 30 to 70 phr. This can be due to intermolecular interactions between the surface of the silica and the antidegradants. The surface of silica is composed of many hydroxyl groups,[12,13] and BHT, IPPD, and HPPD have a hydrogen-bonding site, —OH or —NH. Thus, the hydroxyl groups of silica can hydrogen bond with the —OH (BHT) and

—NH (IPPD and HPPD). These hydrogen bonds make their migrations slowly.

The migration rates of BHT, IPPD, and HPPD decreased with increase of the content of silica in the vulcanizates. The difference of the migration rate in the vulcanizates containing silica of 30 and 70 phr for IPPD is larger than those for BHT and HPPD. The difference of the migration rate for HPPD is larger than that for BHT. Average differences (at 60, 80, and 100°C) of the amounts of BHT, IPPD, and HPPD that migrated in the vulcanizates containing silica of 30 and 70 phr are 7.5, 15.1, and 11.4%, respectively. This may be explained by the strength of the intermolecular hydrogen bonds of the antidegradants with silica. The strength of the intermolecular hydrogen bonds can be due to the polarity and dipole moment of the molecule. If the antidegradant is more polar, the hydrogen bond may be stronger. Dipole moments of BHT, IPPD, and HPPD were calculated using an AM1 semiempirical method.[14] The

Table III Amounts of Antidegradants that Migrated in NR Vulcanizates Containing Silica of 50 phr (%) Depending on Temperature

Antidegradants	Temperature (°C)		
	60	80	100
BHT	40.5 (7.21)	56.6 (11.0)	66.4 (15.1)
IPPD	45.1 (8.32)	69.1 (16.3)	84.2 (25.6)
HPPD	28.0 (4.55)	54.6 (11.0)	78.5 (21.3)
Wax (n-$C_{23}H_{48}$)	26.7 (4.31)	57.0 (11.7)	79.2 (21.8)
Wax (n-$C_{24}H_{50}$)	15.9 (2.40)	44.0 (8.05)	71.5 (17.4)
Wax (n-$C_{25}H_{52}$)	11.0 (1.62)	33.8 (5.73)	67.4 (15.5)
Wax (n-$C_{26}H_{54}$)	6.5 (0.93)	20.1 (3.66)	56.5 (11.5)

Values in parentheses are migration rates ($\times 10^6\%$ s^{-1}).

Table IV   Amounts of Antidegradants that Migrated in NR Vulcanizates Containing Silica of 70 phr (%) Depending on Temperature

Antidegradants	Temperature (°C)		
	60	80	100
BHT	36.3 (6.27)	53.4 (10.6)	58.9 (12.3)
IPPD	39.1 (6.89)	56.9 (11.7)	74.3 (18.9)
HPPD	21.6 (3.37)	45.7 (8.47)	67.1 (15.4)
Wax (n-$C_{23}H_{48}$)	22.6 (3.55)	55.4 (11.2)	68.8 (16.2)
Wax (n-$C_{24}H_{50}$)	10.0 (1.47)	36.4 (6.37)	66.0 (15.0)
Wax (n-$C_{25}H_{52}$)	8.7 (1.26)	30.9 (5.12)	61.5 (13.3)
Wax (n-$C_{26}H_{54}$)	2.7 (0.38)	13.8 (2.07)	50.1 (9.65)

Values in parentheses are migration rates ($\times 10^6 \%$ s^{-1}).

dipole moments of BHT, IPPD, and HPPD are 1.30, 2.48, and 1.43 Debye, respectively. Thus, the migration of IPPD can be more influenced than can those of BHT and HPPD since the hydrogen bond between silica and IPPD is stronger than those of BHT and HPPD.
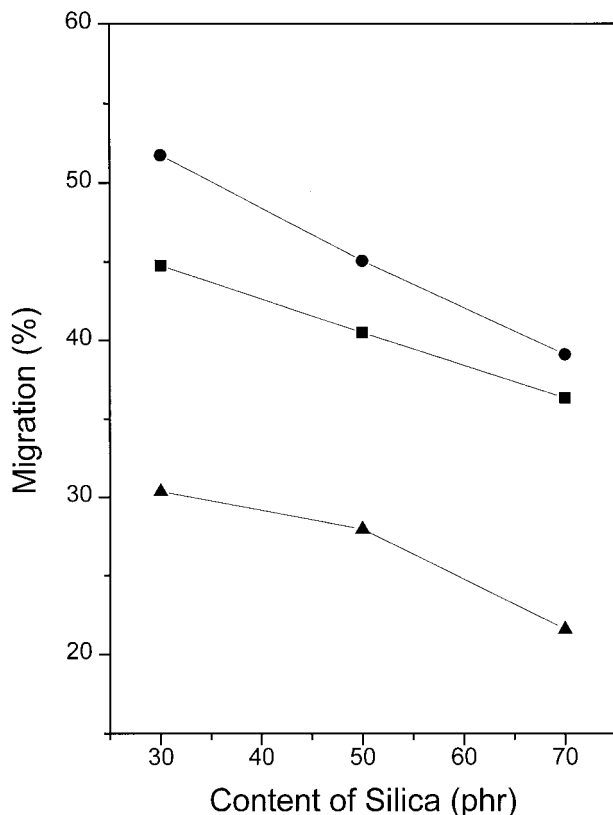
Migration of Wax

The wax used in this study has a molecular weight distribution from $C_{21}H_{44}$ to $C_{40}H_{82}$. The migration rate of wax with a high molecular weight equal or more than $C_{27}H_{56}$ under the experimental conditions is so slow that it is hard to measure the

Figure 1 Variation of amounts of antidegradants that migrated at 60°C as a function of the content of silica. (Squares, circles, triangles) BHT, IPPD, and HPPD, respectively.
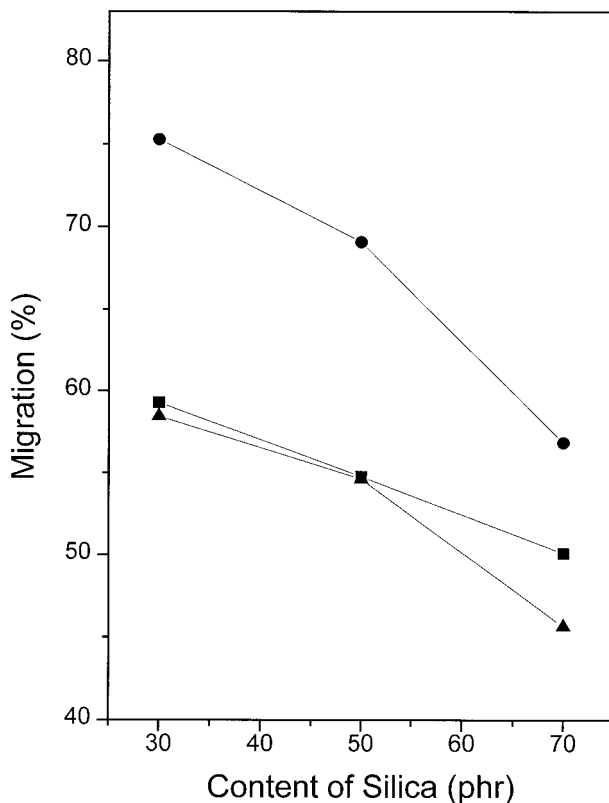

Figure 2 Variation of amounts of antidegradants that migrated at 80°C as a function of the content of silica. (Squares, circles, triangles) BHT, IPPD, and HPPD, respectively.
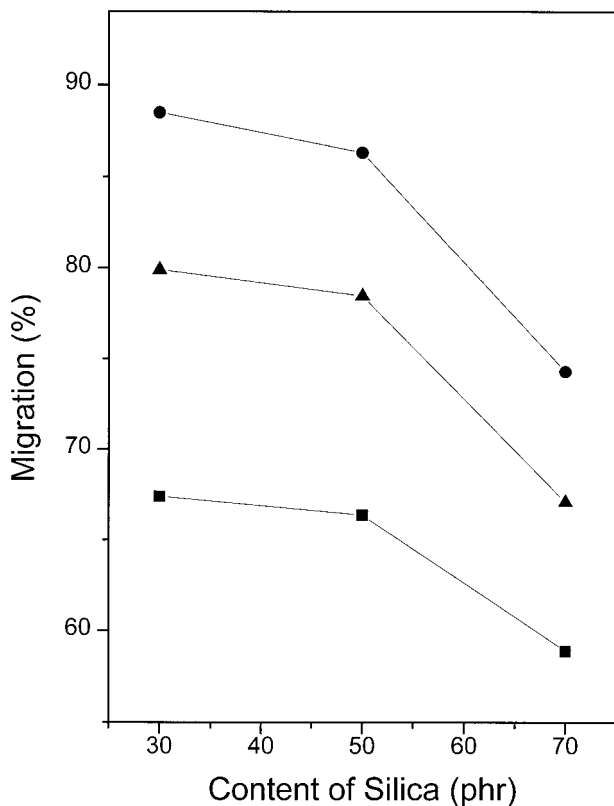
Figure 3 Variation of amounts of antidegradants that migrated at 100°C as a function of the content of silica. (Squares, circles, triangles) BHT, IPPD, and HPPD, respectively.

amounts of the wax that migrated. Since $C_{21}H_{44}$ and $C_{22}H_{46}$ is contained only in a small amount in the wax, we did not measure their migrations. 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 each of their components and their content is lower than that of the normal alkanes. Thus, the 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. The migration rates of wax decrease under the same conditions with increase of the molecular weight. 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 in the silica-filled NR vulcanizates increased from 23–29 to 69–80%, from 6–16 to 66–74%, from 4–11 to 62–67%, and from 2–7 to 50–57%, respectively, by increasing the temperature from 60 to 100°C.

To investigate the influence of the content of silica on the migration of n-$C_{23}H_{48}$, n-$C_{24}H_{50}$, n-$C_{25}H_{52}$, and n-$C_{26}H_{54}$ in detail, their migrations were graphed as a function of the content of silica.

Figures 4, 5, and 6 show the variation of their migrations at 60, 80, and 100°C, respectively. The amount of n-$C_{23}H_{48}$ that migrated, irrespective of the temperature, decreased by increasing the silica content from 30 to 70 phr. The amounts of n-$C_{25}H_{52}$ and n-$C_{26}H_{54}$ that migrated, irrespective of the temperatures, increased with increase of the silica content from 30 to 50 phr and then decreased by increasing the silica content from 50 to 70 phr. The migration of n-$C_{24}H_{50}$ has a specific trend. The amount of n-$C_{24}H_{50}$ that migrated at 60°C increased with increase of the silica content from 30 to 50 phr and then decreased by increasing the silica content from 50 to 70 phr, similar to the migrations of n-$C_{25}H_{52}$ and n-$C_{26}H_{54}$. But the migration of n-$C_{24}H_{50}$ at 100°C has a similar trend to that of n-$C_{23}H_{48}$. The amount of n-$C_{24}H_{50}$ that migrated at 100°C decreased from 74.1 to 66.0% with increase of the silica content from 30 to 70 phr. The amounts of n-$C_{24}H_{50}$ that migrated at 80°C in the vulcanizate containing silica of 30 and 50 phr is very close; its difference is 0.1%.
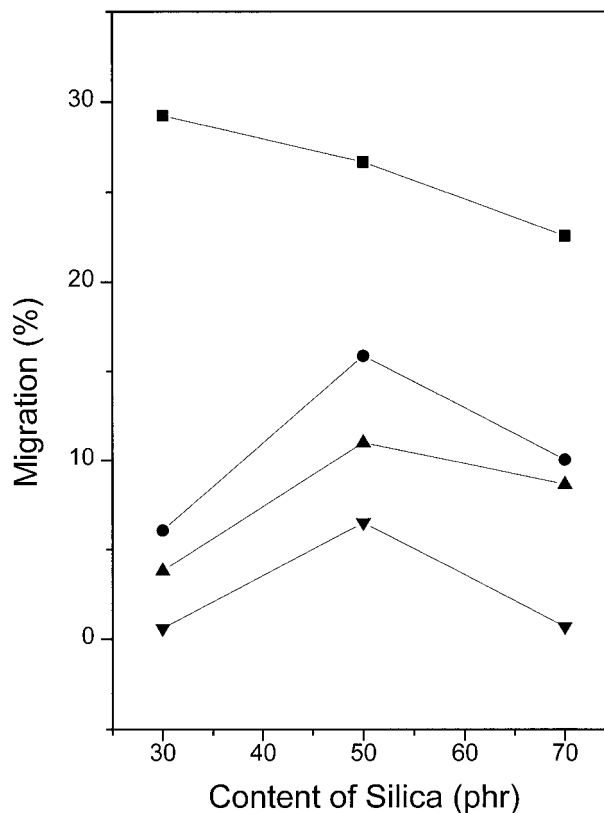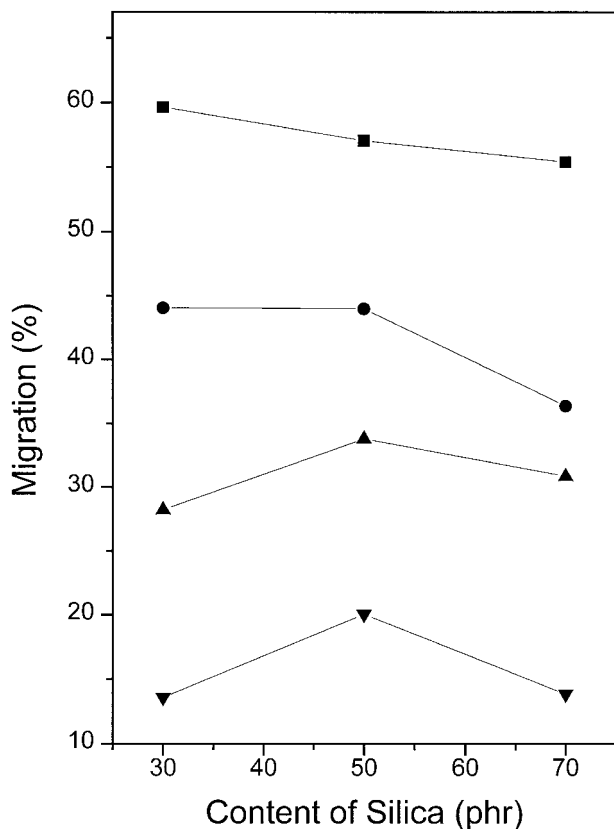

Figure 4 Variation of amounts of wax that migrated at 60°C as a function of the content of silica. (Squares, circles, up-triangles, down-triangles) n-$C_{23}H_{48}$, n-$C_{24}H_{50}$, n-$C_{25}H_{52}$, and n-$C_{26}H_{54}$, respectively.

Figure 5 Variation of amounts of wax that migrated at 80°C as a function of the content of silica. (Squares, circles, up-triangles, down-triangles) n-$C_{23}H_{48}$, n-$C_{24}H_{50}$, n-$C_{25}H_{52}$, and n-$C_{26}H_{54}$, respectively.

The migration rate of n-$C_{24}H_{50}$ that migrated in the vulcanizate containing silica of 50 phr is faster than that containing silica of 70 phr, similar to the other normal alkanes.

The migration rates of n-$C_{23}H_{48}$, n-$C_{24}H_{50}$, n-$C_{25}H_{52}$, and n-$C_{26}H_{54}$ decreased with increase of the silica content from 50 to 70 phr. This may be due to a path length of wax in the silica-filled NR vulcanizate. Since there are many pores in silica, the path length of the wax through silica becomes long with increase of the content of silica. Figure 7 shows the pore-size distribution of Coupsil VP 8108. The migration behaviors of n-$C_{23}H_{48}$, the decrease of its migration rate with increase of the content of silica, can be explained by the porosity of the silica. The long path length by increasing the silica content gives a long time taken for n-$C_{23}H_{48}$ to migrate to the surface in the silica-filled vulcanizate. However, since the migration rates of n-$C_{25}H_{52}$ and n-$C_{26}H_{54}$ increased with increase of the silica content from 30 to 50 phr, the migra-

tion behaviors of n-$C_{25}H_{52}$ and n-$C_{26}H_{54}$ cannot be explained only by the variation of the path length.

A major factor influencing the migration of antidegradants in rubber vulcanizates is an interaction between the rubber and antidegradants.[11] Thus, the increase of the migration rates of n-$C_{25}H_{52}$ and n-$C_{26}H_{54}$ with increase of the silica content from 30 to 50 phr may be explained by the path length and the intermolecular interactions between rubber and the normal alkanes. Since wax and NR are all hydrocarbons, they can interact by van der Waals force. The van der Waals interactions strengthen more and more as the temperature becomes low or the wax size becomes large. Since the intermolecular interactions of n-$C_{23}H_{48}$ with NR are relatively weaker than those of n-$C_{25}H_{52}$ and n-$C_{26}H_{54}$, the migration behaviors of n-$C_{23}H_{48}$ may be mainly subject to the path length. However, since the intermolecular interactions of n-$C_{25}H_{52}$ and n-$C_{26}H_{54}$ with NR are relatively strong, the migration behaviors of n-$C_{25}H_{52}$ and n-$C_{26}H_{54}$ in the vulcanizate with a
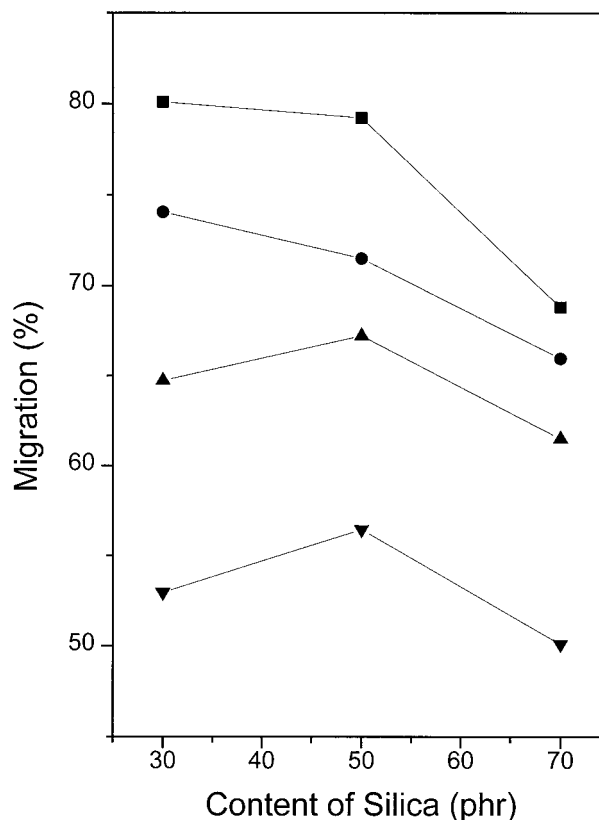

Figure 6 Variation of amounts of wax that migrated at 100°C as a function of the content of silica. (Squares, circles, up-triangles, down-triangles) n-$C_{23}H_{48}$, n-$C_{24}H_{50}$, n-$C_{25}H_{52}$, and n-$C_{26}H_{54}$, respectively.

high content of NR may be subject to the intermolecular interactions and to not the path length. The interactions of wax with rubber increased with increase of a portion of the rubber in the vulcanizates. Thus, the migration rates of n-$C_{25}H_{52}$ and n-$C_{26}H_{54}$ in the vulcanizate containing silica of 30 phr are slower than those containing silica of 50 phr. Since the van der Waals interactions become weak as the temperature increased, differences in the amounts of the normal alkanes that migrated in the vulcanizates containing silica of 50 and 30 phr decreased with increase of the temperature from 60 to 100°C. Even migration at 100°C of n-$C_{24}H_{50}$ in the vulcanizate containing silica of 30 phr is faster than that containing silica of 50 phr.

Activation Energy

The activation energies for the migration of antidegradants to the surface in a rubber vulcanizate were calculated by the Arrhenius plot with the migration rates. The Arrhenius equation is eq. (2):

$$k = A \exp(-E_a/RT) \qquad (2)$$

where k is the rate constant; A, the Arrhenius parameter; E_a, the activation energy; R, the gas constant; and T, the temperature in Kelvin. In this study, k is the migration rate in % s^{-1} as listed in Tables II–IV. The logarithm of eq. (2) gives
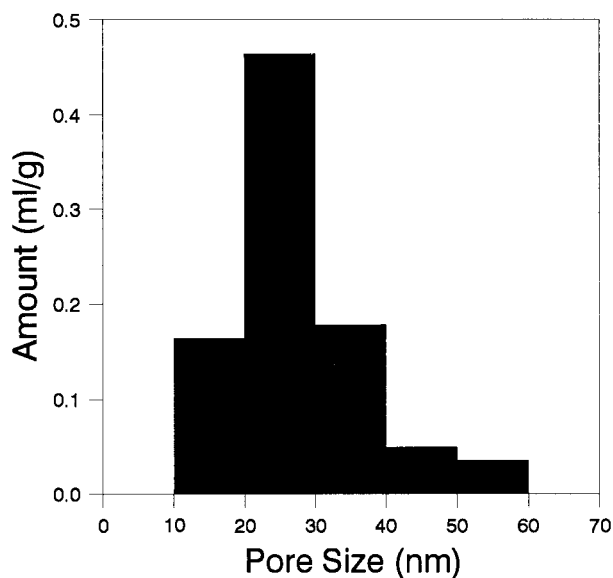
Table V   Activation Energy for Migration of Antidegradants in NR Vulcanizates (kJ/mol) Depending on Content of Silica

Antidegradants	Content of Silica (phr)		
	30	50	70
BHT	16.71	19.32	17.60
IPPD	26.15	28.68	26.23
HPPD	38.82	40.08	39.61
Wax (n-$C_{23}H_{48}$)	40.18	42.23	39.86
Wax (n-$C_{24}H_{50}$)	80.15	51.61	60.53
Wax (n-$C_{25}H_{52}$)	85.90	58.78	61.22
Wax (n-$C_{26}H_{54}$)	100.72	65.51	83.89

$$\ln k = \ln A - E_a/RT \qquad (3)$$

The activation energy can be calculated by multiplying the gas constant to the slope obtained from the Arrhenius plot of $\ln k$ versus $1/T$. The activation energies calculated from the Arrhenius plot are listed in Table V. The activation energies for migration to the surface in the NR vulcanizate containing silica of 30–70 phr are 16.7–19.3, 26.2–28.7, 38.8–40.1, 39.9–42.2, 51.6–80.2, 58.8–85.9, and 65.5–100.7 kJ/mol for BHT, IPPD, HPPD, n-$C_{23}H_{48}$, n-$C_{24}H_{50}$, n-$C_{25}H_{52}$, and n-$C_{26}H_{54}$, respectively. The activation energy for BHT is much lower than those for the other migrants. The activation energies for the wax increase with increase of its molecular weight.

CONCLUSIONS

Among the migrations of BHT, IPPD, HPPD, n-$C_{23}H_{48}$, n-$C_{24}H_{50}$, n-$C_{25}H_{52}$, and n-$C_{26}H_{54}$ in the silica-filled NR vulcanizates, the migration of IPPD is the fastest. The migration rates of BHT, IPPD, and HPPD decrease with increase of the silica content in the vulcanizate. This is due to the hydrogen bonds between the antidegradants and the surface of silica. The amount of n-$C_{23}H_{48}$ that migrated also decreases by increasing the silica content. This is explained by the path length. The migrations of n-$C_{25}H_{52}$ and n-$C_{26}H_{54}$ become fast with increase of the silica content from 30 to 50 phr and then slow by increasing the silica content from 50 to 70 phr. This can be explained by a combination of the path length and the van der Waals interactions of the normal alkanes with NR.

Figure 7   Pore-size distribution of Coupsil VP 8108.

REFERENCES

1. W. L. Cox, *Rubb. Chem. Technol.,* **32,** 364 (1959).
2. E. R. Erickson, R. A. Bernsten, E. L. Hill, and P. Kusy, *Rubb. Chem. Technol.,* **32,** 1062 (1959).
3. S. D. Razumovskii and L. S. Batashova, *Rubb. Chem. Technol.,* **43,** 1340 (1970).
4. M. Braden and A. N. Gent, *Rubb. Chem. Technol.,* **35,** 200 (1962).
5. R. W. Layer and R. P. Lattimer, *Rubb. Chem. Technol.,* **63,** 426 (1990).
6. R. P. Lattimer, R. W. Layer, E. R. Hooser, and C. K. Rhee, *Rubb. Chem. Technol.,* **64,** 780 (1991).
7. J. B. Gardiner, *Rubb. Chem. Technol.,* **42,** 1058 (1969).
8. J. E. Lewis, M. L. Deviney, and L. E. Whittington, *Rubb. Chem. Technol.,* **42,** 892 (1969).
9. M. L. Deviney, L. E. Whittington, C. W. Good, and R. J. Sperley, *Rubb. Chem. Technol.,* **47,** 127 (1974).
10. A. J. M. Sumner, in *Proceedings of the Rubber Division 136th Meeting, American Chemical Society,* Detroit, MI, October 17–20, 1989, Paper No. 37.
11. S.-S. Choi, *J. Appl. Polym. Sci.,* **65,** 117 (1997).
12. T. A. Okel and W. H. Waddell, *Rubb. Chem. Technol.,* **67,** 217 (1994).
13. Y.-C. Ou, Z.-Z. Yu, A. Vidal, and J. B. Donnet, *Rubb. Chem. Technol.,* **67,** 834 (1994).
14. M. J. S. Dewar, F. F. Zoebisch, E. F. Henly, and J. J. Stewart, *J. Am. Chem. Soc.,* **107,** 3092 (1985).