Correlation Between Migration Behaviors of Antiozonants and Temperature

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Received 23 March 2000; accepted 28 May 2000

ABSTRACT: Migration behaviors of antiozonants depending on temperature were studied using a carbon black-filled NR vulcanizate containing *N*-phenyl-*N*′-isopropyl-*p*-phenylenediamine (IPPD) and *N*-phenyl-*N*′-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD) as antiozonants. The experimental temperatures were 100, 90, 80, and 70°C. Migration rates of them increased steeply by increasing the temperature. The correlation between the migration rates and the temperature was investigated using the half ($t_{1/2}$)- and quarter ($t_{1/4}$)-lifetimes of the migrants remaining in the vulcanizate after the migration. The plot of log t versus $1/T$ was well fitted by the linear equation: The correlation coefficients were higher than 0.995. It was found that the migration behavior and temperature had a correlation of log $t = b/T + c$, where t and T are the migration time and temperature, b is E_a/R, and c is the constant. The activation energies for the migration were 36.48 and 37.93 kJ/mol for IPPD and HPPD, respectively. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1566–1570, 2001

Key words: antiozonants; migration; correlation with temperature; half-life

INTRODUCTION

Migration behaviors of antidegradants in rubber vulcanizates are influenced by matrices of the rubber and the filler.[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 slower in styrene–butadiene rubber (SBR) vulcanizates than in natural rubber (NR) and butadiene rubber (BR) vulcanizates.[1] Migration rates of antidegradants in silica-filled rubber vulcanizates are much slower than in carbon black-filled ones.[2–4] Migration rates of the antidegradants become slower and slower by increasing the filler content in the vulcanizates. Intermolecular interactions between the antidegradants and the matrices of the rubber and the filler affect the migration rates in filled rubber vulcanizates,[1–4] that is, the stronger the intermolecular interactions are, the slower are the migration rates in rubber vulcanizates.

Migration rates of migrants in rubber vulcanizates to the surface become faster and faster as the temperature increases.[1–6] Since migration rates of antidegradants in rubber vulcanizates are very slow at low temperatures below 40°C,[6] observation of the migration behaviors at low temperatures requires a long time. It is important to predict the consuming rate of antidegradants and the service life of rubber goods. The service life is the use period of rubber goods without any crack in them by oxidation and degradation of the polymer. However, since rubber goods are used generally below 40°C, estimation of the service life of rubber goods requires a very long time. In this study, variation of the migration behaviors of antiozonants in an NR vulcanizate with temperature was studied. The migration behaviors at low temperatures were predicted by the correlation obtained at high temperatures. In general,

Journal of Applied Polymer Science, Vol. 80, 1566–1570 (2001)

substituted *para*-phenylenediamine antiozonants were used with wax to protect against ozonation of the rubber.[7] In the present work, IPPD and HPPD were employed as antiozonants.

EXPERIMENTAL

To investigate the correlation between the migration behaviors of antiozonants to the surface in a rubber vulcanizate and temperature, a carbon black-filled NR compound was prepared. The formulation was as follows (unit is phr): NR (SMR 20, 100.0), carbon black (N330, 50.0), zinc oxide (5.0), stearic acid (3.0), wax (1.0), IPPD (2.0), HPPD (2.0), *N-tert*-butyl-2-benzothiazole sulfenamide (TBBS, 2.6), and sulfur (0.6). The rubber vulcanizate was prepared by curing at 160°C for 20 min.

The migration experiments were performed at constant temperatures of 100, 90, 80, and 70°C for 5 (0.5-day interval), 10 (1.0-day interval), 20 (2.0-day interval), and 40 (4.0-day interval) days, respectively, in a convection oven. The dimension of the sample was 3 × 5 cm (2 mm thickness). The samples were hung in the oven in order to make evaporation of the antiozonants occur on both sides of the sample. Amounts of the antiozonants that migrated to the surface in the vulcanizates were determined by the differences between the 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 from the sample with THF. HP 5890 gas chromatography was used. Temperatures of the injector and detector (FID) were 250 and 260°C, respectively. The initial oven temperature was 150°C (holding for 2 min) and the temperature was increased at rate of 8°C/min. An Ultra 1 (10 m × 0.2 mm) capillary column was used. Experiments were carried out three times and averaged.

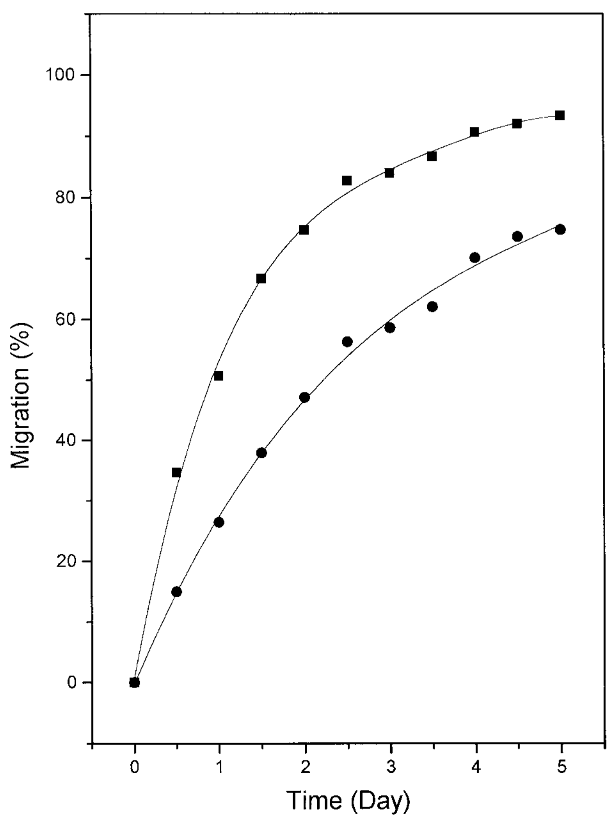

Figure 1 Variation of amounts of IPPD (rectangles) and HPPD (circles) migrated at 100°C as a function of time. Solid lines were obtained by curve fitting of the fourth-power series.

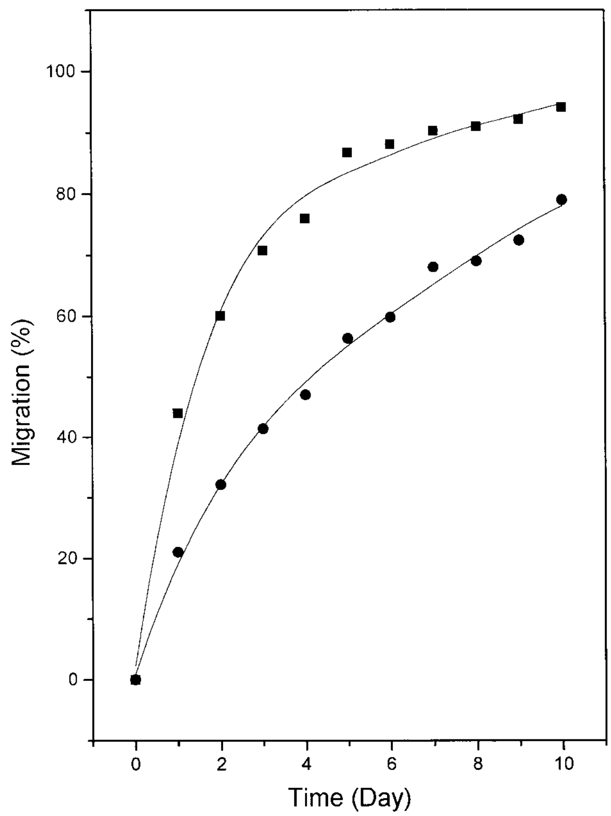

Figure 2 Variation of amounts of (rectangles) IPPD and (circles) HPPD migrated at 90°C as a function of time. Solid lines were obtained by curve fitting of the fourth-power series.

RESULTS AND DISCUSSION

The migration rates of the antiozonants at over 100°C are too fast and those at below 60°C are so

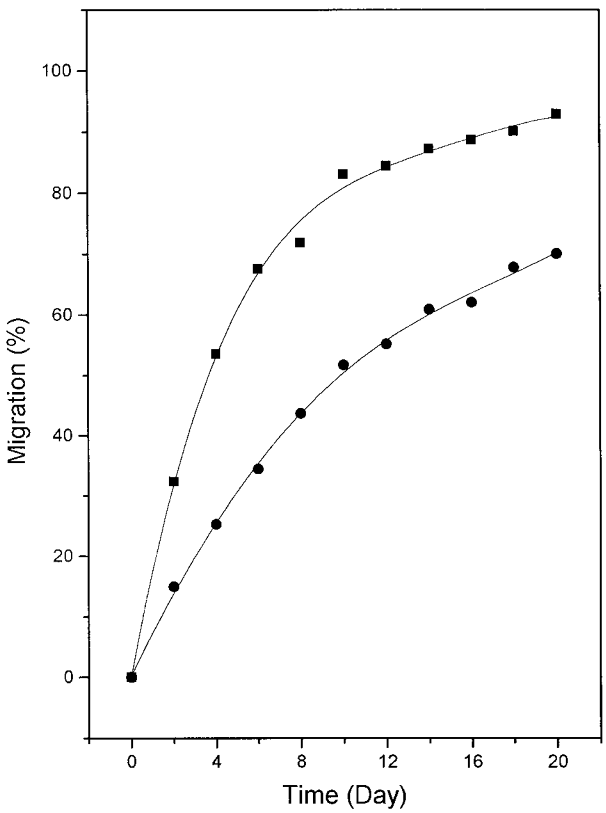

Figure 3 Variation of amounts of (rectangles) IPPD and (circles) HPPD migrated at 80°C as a function of time. Solid lines were obtained by curve fitting of the fourth-power series.

slow that a long time is required to obtain a migration plot depending on the time variation. Thus, the experimental temperatures were 70–100°C. The experimental results are summarized in Figures 1–4. The amounts of the antiozonants that migrated to the surface in the rubber vulcanizate and evaporated increase steeply at the beginning and then increase slightly by increasing the migration time. The amounts of the antiozonants that migrated and evaporated decrease remarkably as the temperature decreases. The amount of IPPD that migrated and evaporated is larger than that of HPPD.

The solid lines in Figures 1–4 were obtained by curve fitting of the fourth polynomial equation. The fourth polynomial equations are summarized in Table I. To investigate the variation of the migration behaviors depending on the temperature in detail, the half-life time ($t_{1/2}$) was calculated from the curve-fitting equation. The half-lifetime implies the time taken until the amounts of the antiozonants remaining after the migration in the rubber vulcanizate become half of the initial concentrations. In general, the half-lifetime is used to compare or determine the service life of materials and goods. Table II gives the half-lifetimes of the antiozonants. The $t_{1/2}$ of the antiozonants increase notably as the temperature decreases. Besides the half-lifetime, the quarter-lifetime ($t_{1/4}$) was measured from the experimental results. The quarter-lifetime implies the time taken until the amounts of the antiozonants remaining after the migration in the rubber vulcanizate become a quarter of the initial contents. The $t_{1/4}$ of the antiozonants are also listed in Table II. The $t_{1/4}$'s of HPPD at 80 and 70°C were not listed since its amount remaining in the vulcanizate after the migration did not reach to the $t_{1/4}$ under the experimental conditions.

The Arrhenius equation shows the correlation between the rate constant and the temperature:

$$k = A \exp(-E_a/RT) \qquad (1)$$

where k is the rate constant; A, the Arrhenius parameter; E_a, the activation energy; R, the gas constant; and T, the temperature. Since the rate

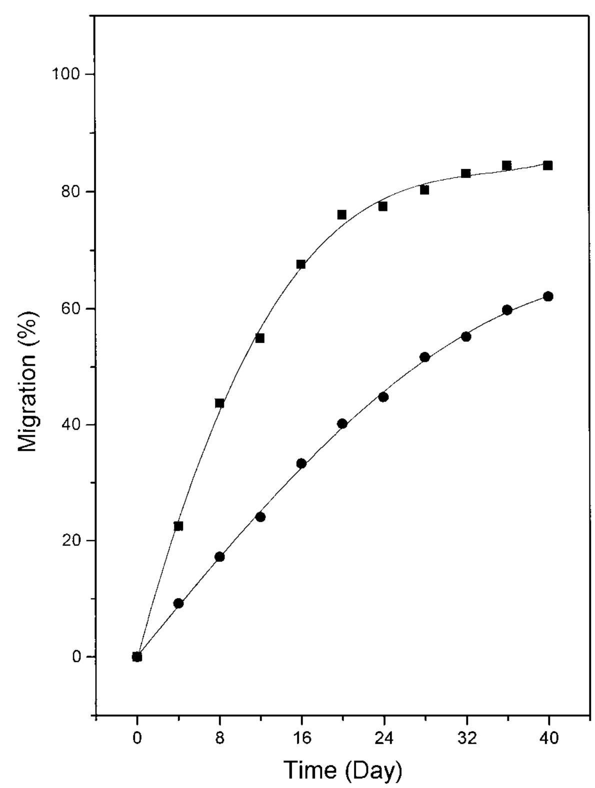

Figure 4 Variation of amounts of (rectangles) IPPD and (circles) HPPD migrated at 70°C as a function of time. Solid lines were obtained by curve fitting of the fourth-power series.

Table I Curve-fitting Equations Obtained from Figures 1–4

Antiozonant	Temperature	Equation	Correlation Coefficient
IPPD	100°C	$y = 0.811 + 74.881x - 27.177x^2 + 4.828x^3 - 0.330x^4$	0.999
	90°C	$y = 2.239 + 45.792x - 10.225x^2 + 1.070x^3 - 0.045x^4$	0.995
	80°C	$y = 0.393 + 18.772x - 1.663x^2 + 0.070x^3 - 0.001x^4$	0.999
	70°C	$y = -0.307 + 6.606x - 0.170x^2 + 0.002x^3 - 0.00001x^4$	0.999
HPPD	100°C	$y = -0.169 + 32.465x - 5.253x^2 + 0.383x^3 - 0.005x^4$	0.998
	90°C	$y = 0.931 + 21.185x - 3.343x^2 + 0.310x^3 - 0.011x^4$	0.998
	80°C	$y = 0.409 + 7.151x - 0.209x^2 - 0.002x^3 - 0.0002x^4$	0.999
	70°C	$y = 0.156 + 2.174x - 0.003x^2 - 0.0004x^3 + 0.000002x^4$	0.998

constant implies variation per unit time, the reciprocal of the rate constant ($1/k$) can be the reaction time (t). By making the Arrhenius equation reciprocal, eq. (1) can be eq. (2):

$$1/k = t = (1/A)\exp(E_a/RT) \qquad (2)$$

By taking the logarithms of eq. (2), eq. (3) will be obtained:

$$\log t = b/T + c \qquad (3)$$

where b is the E_a/R and c is the constant.

To investigate the correlation between the migration behavior and the temperature, log t versus $1/T$ was plotted as shown in Figures 5 and 6 for the half-lifetimes and quarter-lifetimes, respectively. Figure 5 gives the variation of logarithm of the half-lifetime ($\log t_{1/2}$) as a function of the inverse temperature ($1/T$). The variation of $\log t_{1/2}$ with $1/T$ was fitted well to the linear equation. The results of the curve fittings are summarized in Table III. The correlation coefficients for the curve fitting of the half-lifetime of IPPD is 0.995, while those of HPPD is 0.999. Figure 6 gives the variation of $\log t_{1/4}$ of IPPD as a function of $1/T$. The result of the curve fitting is also summarized in Table III. Since the slopes obtained from Figure 5 are equal to the E_a/R, we can calculate the activation energy for the migration. The activation energies are 36.48 and 37.93 kJ/mol for IPPD and HPPD, respectively. The

Table II Half ($t_{1/2}$)- and Quarter ($t_{1/4}$)-Lifetimes for Amounts of the Antiozonants Remaining in the Vulcanizate

Antiozonant	Temperature (°C)	$t_{1/2}$	$t_{1/4}$
IPPD	100	0.914	1.985
	90	1.441	3.284
	80	3.652	7.759
	70	9.805	17.742
HPPD	100	2.214	4.906
	90	4.125	9.088
	80	9.829	—
	70	27.106	—

Units are days.

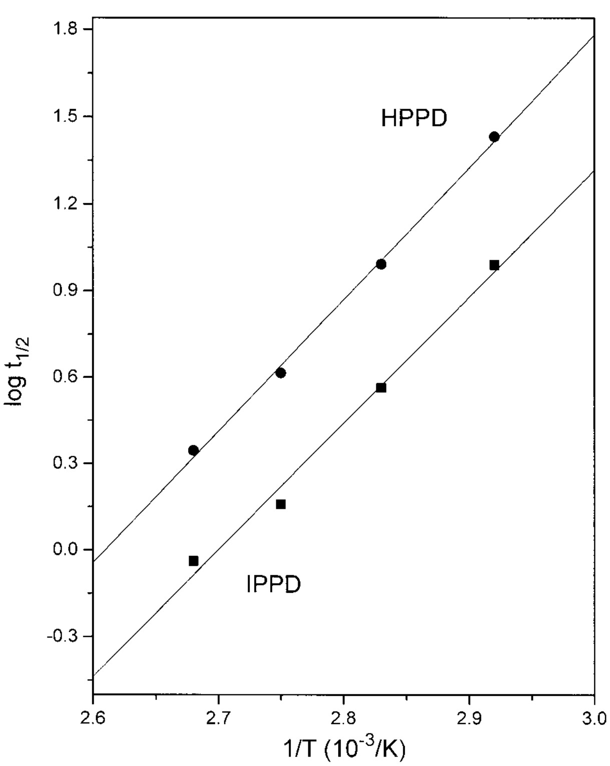

Figure 5 Variation of $\log t_{1/2}$ of (rectangles) IPPD and (circles) HPPD as a function of $1/T$. The lines were obtained by curve fitting. The correlation coefficients are 0.995 and 0.999 for IPPD and HPPD, respectively.

activation energy for HPPD is higher than for IPPD. This implies that the migration of HPPD to the surface in a rubber vulcanizate needs higher energy than for IPPD.

From the curve-fitted equations, the half-lifetime of the migrant at a certain temperature can be calculated. Using the curve-fitted linear equations, it is possible to predict the half-lifetime at low temperatures. For example, the half-lifetimes of IPPD at 30 and 40°C calculated from the curve-fitted equation are about 433 and 149 days, respectively, while those of HPPD are about 1467 and 470 days, respectively. It is important to know the consumption rate of antiozonants in a rubber vulcanizate to determine the initial dosage of the antiozonants. However, the consumption rate of the antiozonants at low temperatures is so slow that it needs a long time to determine the consumption rate at low temperatures. For example, the amount of HPPD that migrated and evaporated in the NR vulcanizates outdoors during the hot summer (for 2 months) was about 5–11%.[6] Thus, it is possible to predict the consumption rates of the antiozonants in a short time using the well-fitted equation obtained from the experimental data at high temperatures. Thus, it can lead to the conclusion that it is possible to predict the half-lifetime of an antiozonant in a rubber vulcanizate at low temperatures using experimental results obtained at high temperatures, as done in this study.

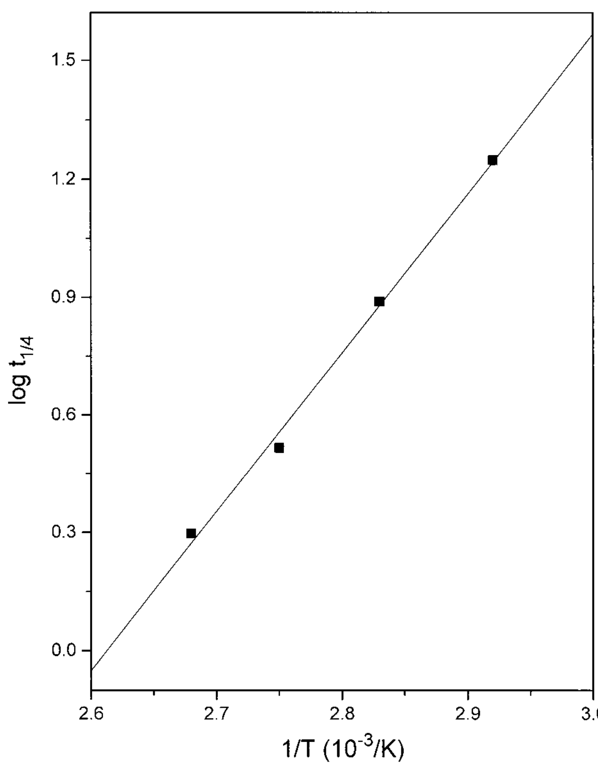

Figure 6 Variation of log $t_{1/4}$ of IPPD as a function of $1/T$. The line was obtained by curve fitting. The correlation coefficient is 0.998.

Table III Curve-fitting Equations of Figures 5 and 6

Antiozonant	Equation	Correlation Coefficient
IPPD	$\log t_{1/2} = 4389.72/T - 11.8508$	0.995
	$\log t_{1/4} = 4122.70/T - 10.7837$	0.998
HPPD	$\log t_{1/2} = 4564.80/T - 11.9121$	0.999

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