

# Sorption and Diffusion of a Brake Fluid in EPDM Elastomers

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**ABSTRACT:** This article reports on an investigation into how the morphology of four commercially available ethylene propylene diene monomer (EPDM) elastomers was affected by exposure to a brake fluid. The sorption and diffusion coefficients as a function of carbon-black content as well as the EPDM type were determined at 23°C, 60°C, 100°C and 150°C. It was found that variation in carbon-black loading showed an effect on the transport characteristics of EPDM elastomers. The sorption data at room temperature were not reported since these took too long a time. The leaching out of the indigenous additives might be due to the paraffin oil migrating to the surface of the specimens. The diffusion of the brake fluid in the EPDM membranes follows non-Fickian transport. The results of this investigation are discussed in terms of the morphological differences in the EPDM formulations. The diffusion coefficients showed a dependence on the morphology of EPDM, as studied by the glass-transition temperature of the elastomers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 000–000, 2001

**Key words:** EPDM elastomers; diffusion; brake fluid

## INTRODUCTION

The molecular transport of organic liquids through polymer membranes has been the subject of intense investigation over the past several years.<sup>1–12</sup> The solvent resistivity of these membranes is extremely important for applications including the construction of brake diaphragms. Thus, an understanding of the membrane transport properties—namely, sorption, diffusion, and permeation with respect to brake fluids—is essential in order to commercialize a brake system. Therefore, we have undertaken an investigation of the effect of poly(ether glycol) brake fluid, commercially known as DOT 3, toward an EPDM (ethylene propylene diene monomer) brake membrane. Four types of EPDM elastomers with different morphologies were selected for the study.

The molecular transport of organic liquids depends on (1) the density of chain entanglements and chain ends, (2) crosslink density, (3) compatibility of both polymer and liquid, and (4) type and amount of filler, in addition to viscosity of the penetrant liquid and the functionality of crosslinks.<sup>13–14</sup> Excellent reports on the effect of fillers on the diffusion and sorption processes have been published.<sup>15–17</sup> Since carbon-black loading is crucial to the transport properties of EPDM elastomers for our investigation, different types of fillers were used with the other compounding ingredients that the EPDM manufacturing suppliers utilized for brake parts.

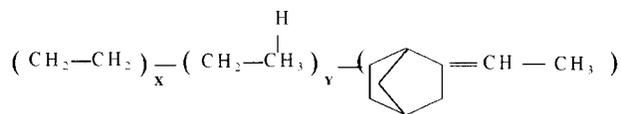
## EXPERIMENTAL

### Materials

Four commercial EPDMs were used to investigate the transport characteristics of brake fluid through the polymer structure, shown schematically in Figure 1. Table I illustrates the contents

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**Figure 1** Chemical formulas of ethylene propylene diene monomer (EPDM).

of the monomer as well as the morphology differences existing between each EPDM elastomer supplied.

These EPDMs were compounded as per the existing formulations that showed better resistance to brake fluid DOT 3 and DOT 4. The carbon-black content was varied from 0 to 110 phr to show the effect of carbon-black loading on the transport characteristics of the brake fluid in EPDMs. Mainly three types of carbon black were used: N550, N762, and N774 (ASTM D 1765). Table II illustrates the detailed compounding ingredients added for each type of polymer.

### Immersion Experiment

The EPDM samples were compression-molded in sheets ~2 mm thick. The curing was completed to  $t_{90}$ , which represents the time at which a sample was cured to 90% of the maximum rheometric torque. For diffusion experiments, EPDM samples were cut into circular pieces uniform in size (2 cm in diameter) using a steel die. Dry weights of the cut samples were taken before immersion into the brake fluid (SAE RM-66-03) in airtight bottles. At specified time intervals the samples were taken out, immersed in ethyl alcohol, and then dried between filter paper wraps, weighed to the nearest  $\pm 0.1$  mg using an analytical balance (Ohaus Explorer Model E00640). Samples were immediately placed back into the test bottles and returned to the oven. This procedure was continued until equilibrium. The experiments were

conducted at room temperature, 60°C, 100°C, and 150°C. A minimum of three specimens were tested for better reproducibility for each EPDM formulation.

The gravimetric data were edge-corrected for finite dimensions of the sample using the procedure suggested in the literature.<sup>18</sup> For the case of a constant diffusion coefficient,  $D$  (mm<sup>2</sup>/min) in the direction normal to the surface, the following relation was used<sup>19</sup>:

$$D = \pi \left( \frac{h \cdot \theta}{4 \cdot Q_{\infty}} \right)^2 \quad (1)$$

where  $\theta$  is the slope of the straight line fit to a plot of mass gain,  $Q_t$  (in mass %), versus square root of time,  $t^{1/2}$ ;  $h$  is the sample thickness; and  $Q_{\infty}$  is the limiting quantity, which is related to the equilibrium solubility.

A Du Pont 2100 Thermo Mechanical Analyzer (TMA) instrument was used to determine the glass-transition temperature,  $T_g$ , of the EPDM membranes. A 6.4-mm probe diameter and a force of 0.025N were used in order to avoid the penetration phenomenon<sup>20</sup> observed near  $T_g$ . Cooling to  $-90^{\circ}\text{C}$  was performed using liquid nitrogen.

## RESULTS AND DISCUSSION

Sorption results are expressed in terms of mass increase per 100 g of the EPDM rubber. Typical plots of  $Q_t$  versus square root of time,  $t^{1/2}$ , at 60°C are presented in Figure 2(a–d). It can be seen that the loading of EPDM with carbon black reduces the  $Q_t$  values. The carbon black-filled samples absorbed lesser amounts of the brake fluid compared to the unfilled ones. The same trend is shown at other temperatures (100°C and 150°C), as illustrated in Figures 3 and 4. The results of

**Table I** Molecular Mass Distributions and Ethylene/Ethylidene Norbornene (ENB) Contents in EPDM Polymers

EPDM Type	$\bar{M}_w$ ( $\times 10^3$ )	$\bar{M}_n$ ( $\times 10^3$ )	$\bar{M}_z$ ( $\times 10^3$ )	$\bar{M}_w/\bar{M}_n$	Ethylene Content (x)	ENB Content (z)	Catalyst Type EPDM
EPDM 1 <sup>a</sup>	205	41	760	5.0	56	4.5	Z.N. EPDM
EPDM 2 <sup>a</sup>	225	48	830	4.7	54	4.5	Z.N. EPDM
EPDM 3 <sup>b</sup>	135	47	—	2.9	50	5.0	C.G.C. EPDM
EPDM 4 <sup>b</sup>	130	54	—	2.4	69.5	0.15–0.95	C.G.C. EPDM

<sup>a</sup> Ziegler-Natta Catalyst EPDM from DSM company.

<sup>b</sup> Constrained geometry Catalyst EPDM from DuPont Company.

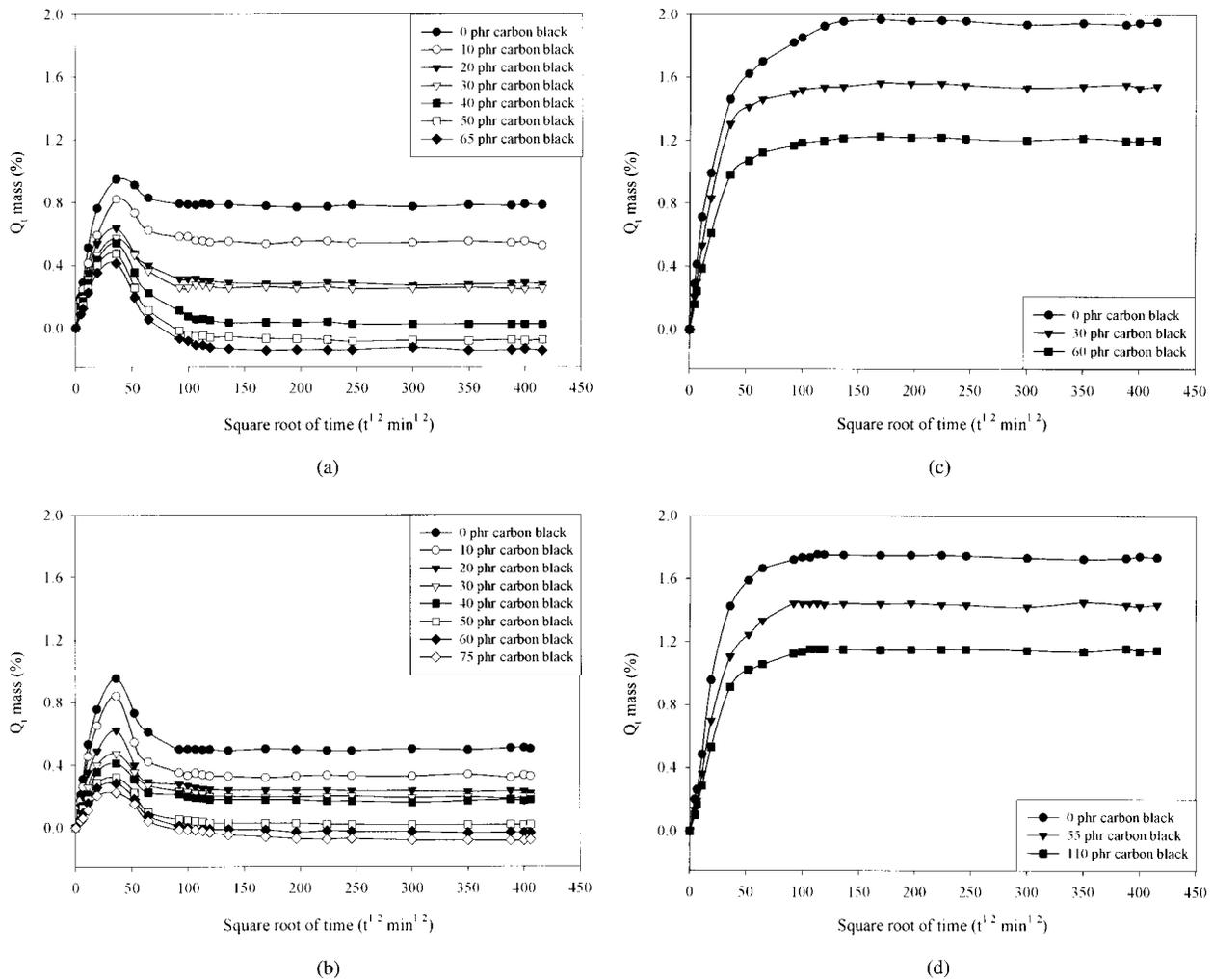
**Table II Compounding Formulations Expressed in phr**

Ingredients	Formulation 1	Formulation 2	Formulation 3	Formulation 4
EPDM 1	100			
EPDM 2		100		
EPDM 3			100	
EPDM 4				100
Carbon black N550			0-60	
Carbon black N762	0-65			0-110
Carbon black N774		0-75		
Sunpar 2280	10.0	10.0	No	No
Di-Cup 40 C	8.0	8.0	10.0	
Di Cup 40 KE				7.0
Agerite Resin D	1.5	1.5	1.0	1.0
Zinc Oxide	5.0	5.0	5.0	5.0

the room temperature immersion experiment were not completed since sorption was extremely slow, and it took too long a time to observe the appreciable mass change compared to other temperatures. This was too low to be reliably reported because of the limit ( $\pm 0.1$  mg) imposed on the precision of the balance used. From the above figures, it can be seen that true equilibrium saturation is reached only in the cases of the EPDM-3 and EPDM-4 formulations. However, the sorption behavior of other EPDM membranes showed an anomalous pattern. At 150°C, EPDM-1 formulations reached the maximums of 3.29% and 1.27% sorption for 0 phr and 65 phr carbon-black loading. They then showed a sudden decrease with time, possibly creating the additional free volume necessary for the diffusing molecules of brake fluid so that the advancing boundary travels faster than the rate of relaxation of EPDM chain segments. However, this pattern leveled off, reaching saturation in which no more leaching was observed. Although there is a general trend of this leveling off in  $Q_t$  values with time, it is not very systematic for all the formulations. In a similar way, this phenomenon was seen with EPDM-2 membranes with sorption reaching the maximums of 3.76% and 1.77%, corresponding to 0 phr and 75 phr carbon-black loading, respectively, at the same temperature. This behavior is more pronounced at higher temperatures based on comparing 100°C with 60°C. It should be noted that the test experiments were run for longer periods of time after saturation (as can be seen for the sorption data at 60°C, run for 4 months) to check if there was any appreciable polymer degradation. The results of such a longer period of immersion are satisfactory, since almost no appreciable deterioration of the EPDM elastomers was observed.

Actually, the decrease in  $Q_t$  values over an extended period of time, observed only in EPDM-1 and EPDM-2 formulations after reaching maximum sorption, is striking. The same phenomenon has been documented in the literature and is attributed to the loss of low-molecular-mass indigenous compounds in the presence of aggressive solvents.<sup>5,9</sup> It is worth mentioning that the main difference between EPDM membranes is the paraffin oil (Sunpar 2280) added to some of these compounding formulations. The loss of these indigenous additives was checked by drying the samples after complete desorption and weighing them again.<sup>5</sup> In order to explain the above trend, the EPDM-3 and EPDM-4 compounding formulations were modified by adding 10 phr and 20 phr Sunpar 2280. In fact, the same anomalous pattern of leaching out was observed even with the modified EPDM-3 and EPDM-4 membranes, that is, sorption reached its maximum and then decreased with time, as shown in Figure 5. The addition of paraffin oil to the above formulations resulted in a decrease of  $Q_t$  values, suggesting that Sunpar 2280 was dissolved by the brake fluid. Tests using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) showed that both the brake fluid and the paraffin oil were immiscible and no appreciable information was obtained from these tests. Even though there has been no systematic study to check the above statement, it is likely that when the brake fluid diffuses into the EPDM elastomer network, it might replace the paraffin oil and act as a plasticizer without any change in the hardness property.

The sorption of EPDM-1 and EPDM-2 is identical until the attainment of equilibrium, suggesting that polymer chains respond almost identi-



**Figure 2** Sorption  $Q_t$  versus square root of time,  $t^{1/2}$ , at 60°C: (a) EPDM-1, (b) EPDM-2, (c) EPDM-3, (d) EPDM-4.

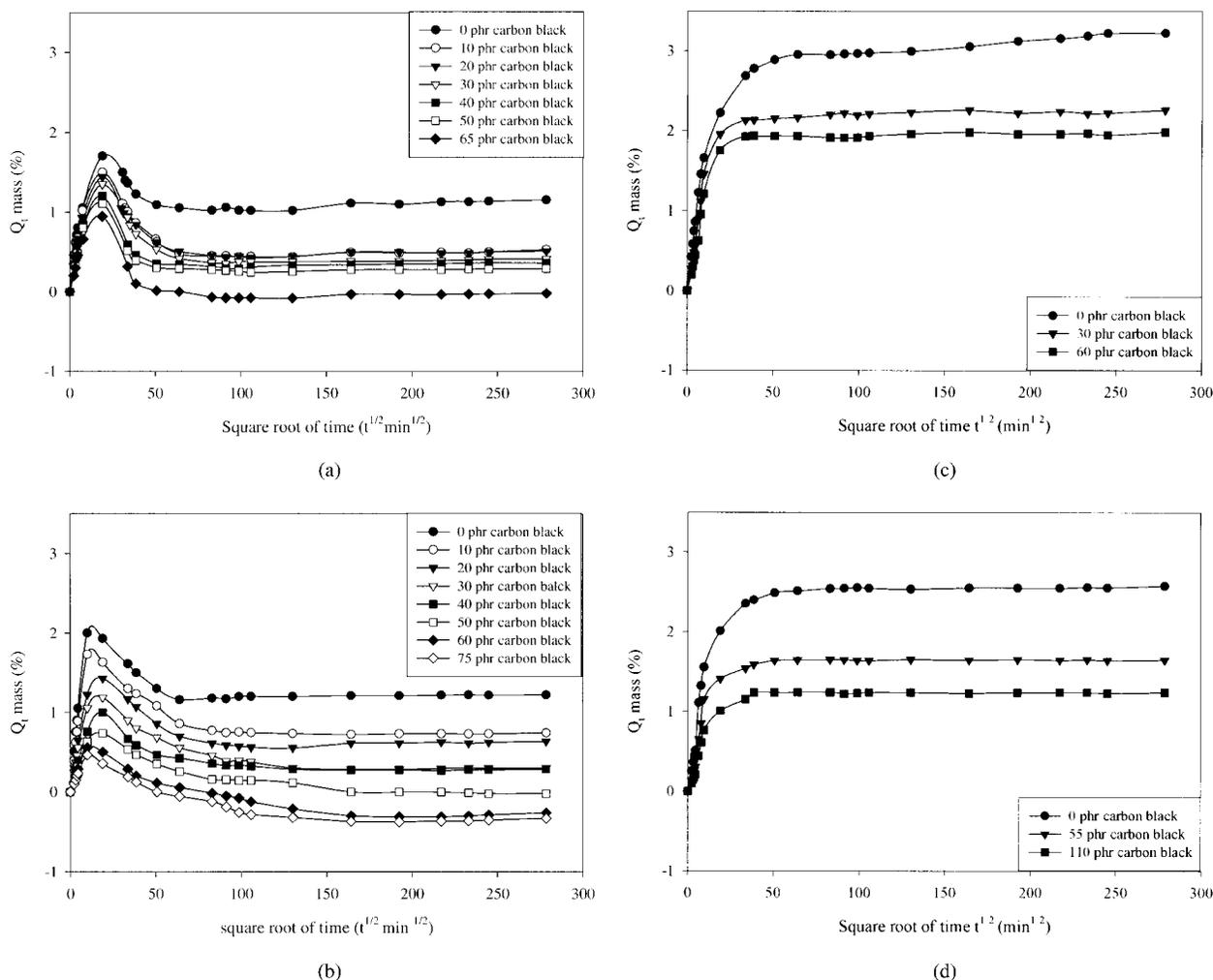
cally during sorption. However, at the initial stages, the sorption plots are slightly sigmoidal, suggesting a slow relaxation of the polymer chain segments in the presence of a brake fluid. This supports the idea of an anomalous-type pattern.<sup>21–22</sup> Similarly, EPDM-3 and EPDM-4 membranes exhibit sigmoidal trends but behave somewhat differently near equilibrium. The results of temperature dependence of sorption are presented in Figures 2–4. The attainment of equilibrium sorption is slower at 60°C than at higher temperatures. An increase of 40°C (i.e., from 60°C to 100°C) caused a considerable increase in sorption of the filled and unfilled EPDM elastomers. Sorptivity of all the EPDM membranes at 150°C was almost twice as high as that observed at 100°C and approximately three times as high as that observed at 60°C.

### Sorption Kinetics

In order to investigate the transport mode, the sorption results have been analyzed using the empirical relationship<sup>11–12</sup>

$$\log\left(\frac{Q_t}{Q_\infty}\right) = \log k + n \log t \quad (2)$$

where  $Q_t$  and  $Q_\infty$  are the sorption uptake values (in mass %) at, respectively, time  $t$  and equilibrium time; and  $k$  is a kinetic parameter, which depends on the nature of the polymer–solvent interactions. The value of  $n$  indicates the type of transport, that is, if  $n = 0.5$ , then the transport is Fickian; if  $n = 1$ , it is non-Fickian. For values of  $n$  between 0.5 and 1.0, the transport follows anomalous-type pattern.<sup>11–12</sup> A typical plot of  $\ln(Q_t/Q_\infty)$



**Figure 3** Sorption  $Q_t$ , versus square root of time,  $t^{1/2}$ , at 100°C: (a) EPDM-1, (b) EPDM-2, (c) EPDM-3, (d) EPDM-4.

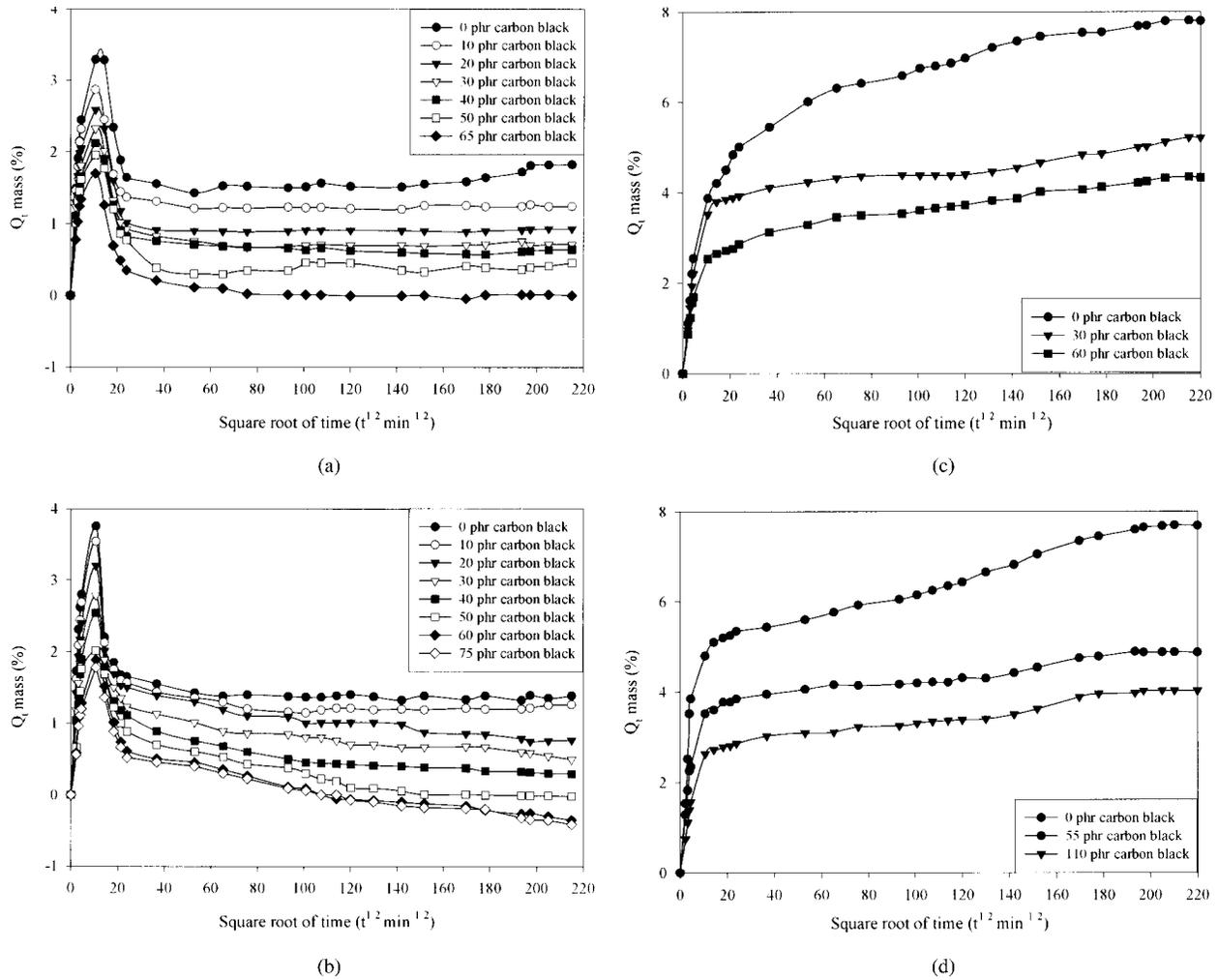
versus  $\ln t$  is illustrated in Figure 6. Since only the EPDM-3 and EPDM-4 membranes showed equilibrium saturation and EPDM-1 and EPDM-2 did not attain a true equilibrium [Figs. 2–4(a,b)], the values of  $n$  and  $k$  were estimated only for EPDM-3 and EPDM-4. The results of  $n$  and  $k$ , as estimated from the least-squares method at 60°C, 100°C, and 150°C, are summarized in Table III. The values of  $n$  for all the systems range between 0.55 and 0.60, indicating an anomalous-type transport and that these values were not affected by the temperature. On the other hand, the values of  $k$  increased with temperature for all the formulations, but no systematic trend was observed with the carbon-black loading. Generally, smaller values of  $k$  at 60°C support lesser interactions between the brake fluid and polymer chain segments.

### Diffusion Coefficients

Diffusion coefficients of the polymer–penetrant systems have been calculated using eq. (1). The effect of carbon-black loading has a crucial effect on the diffusion coefficient. This can be approached theoretically by assuming that each filler particle behaves as an obstacle to the diffusing molecule. By analogy to electric conductivity using the Maxwell model, the effective diffusion coefficient of a composite consisting of spherical particles in a matrix can be estimated and is given by<sup>23</sup>

$$D_{i,m} = D_{i,p} \left[ \frac{2 - 2V_f + (1 + 2V_f)D_{i,f}/D_{i,p}}{2 + V_f + (1 - V_f)D_{i,f}/D_{i,p}} \right] \quad (3)$$

where  $V_f$  is volume fraction of the particulate fillers, and  $D_{i,f}$  and  $D_{i,p}$  are the diffusion coeffi-



**Figure 4** Sorption  $Q_t$ , versus square root of time,  $t^{1/2}$ , at 150°C, (a) EPDM-1, (b) EPDM-2, (c) EPDM-3, (d) EPDM-4.

coefficients of the particles and the matrix, respectively. For very small values of  $V_f$ , as in the present situation, and with the limit that  $D_{i,f}/D_{i,p}$  is very small, eq. (3) can be approximated by<sup>20</sup>

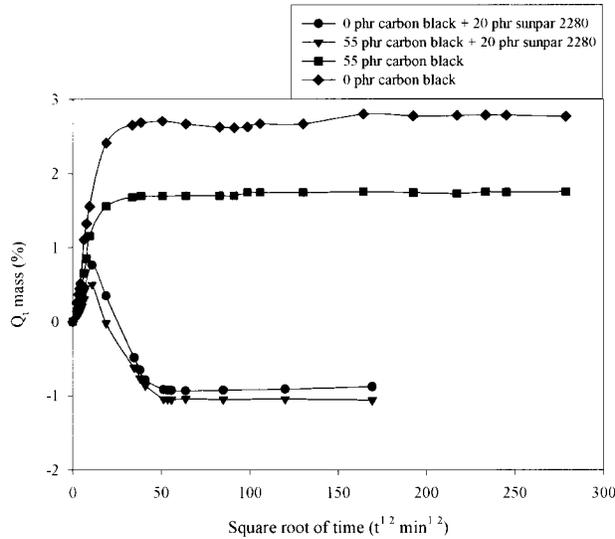
$$D_{i,m} = D_{i,p} \left[ \frac{2 - 2V_f}{2 + V_f} \right] \quad (4)$$

where  $D_{i,m}$  is diffusivity of a substance  $i$  in the filled polymer membrane and  $D_{i,p}$  is diffusivity of a molecule  $i$  in the unfilled polymer.

LaPack et al.<sup>24</sup> have reported on an equation to study the effect of fillers on the permeability of membranes, which relates diffusivity of a filled membrane to an unfilled one as follows:

$$D_{i,m} = D_{i,p} / (1 + V_f/2) \quad (5)$$

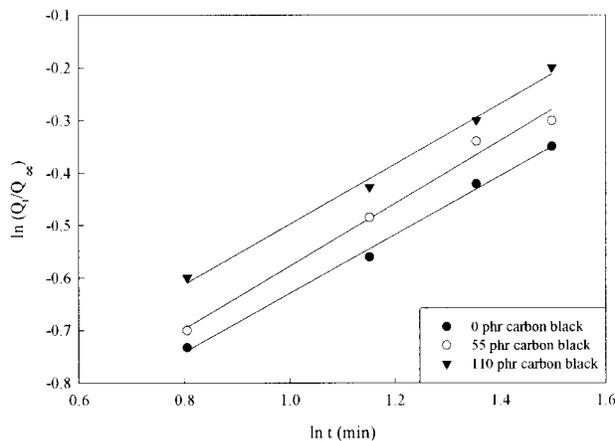
The present work has done a comparable study using both equations in order to estimate the diffusion coefficients for different EPDM formulations. Both eqs. (4) and (5) predict that the diffusion coefficient decreases with an increasing filler concentration. Eq. (5) has an error rate<sup>24</sup> of up to 16% in diffusivity for the filled polymers at  $V_f \sim 0.3$ . Generally, the decrease in diffusion coefficients in loaded elastomers is logical because the brake fluid absorption by the carbon-black filler is negligible and the Maxwell theory assumes a perfect bonding at the particle–matrix interface. No appreciable difference was found between the experimental results and the theoretical models, as illustrated in Figures 7–9 for the EPDM-1 at 60°C, 100°C, and 150°C, respectively. The same trend was observed for the remaining EPDM membranes. The lower diffusion coefficients of



**Figure 5** Sorption  $Q_t$ , versus square root of time,  $t^{1/2}$ , at 100°C: comparison between EPDM-4 and modified one showing the leaching-out phenomenon.

the brake fluid in the case of highly loaded EPDM do not agree with the recent work of Aminabhavi et al.,<sup>17</sup> who reported that diffusion coefficients of the filled fluoroelastomers do not exhibit any systematic dependence on the amount of carbon black.

The estimated diffusion coefficients using eq. (1) agree well with the Maxwell model though, some deviations were recorded, which may be attributed to the presence of pores in the molded rubber sheets, favoring a higher diffusion of the brake fluid. On the other hand, agglomerates of the high carbon-black content specimens produce a lower diffusion of the brake fluid, as seen in

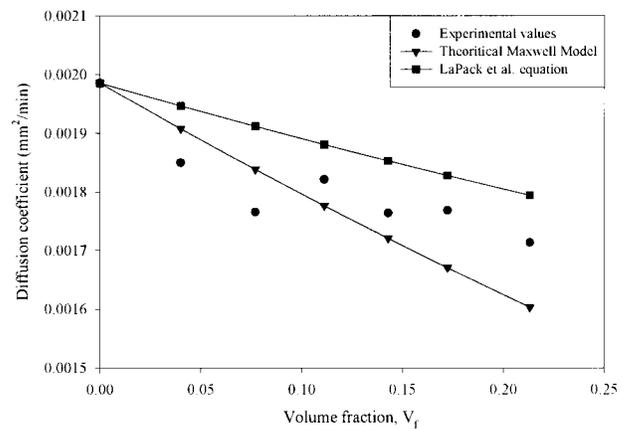


**Figure 6**  $\ln(Q_t/Q_\infty)$  versus  $\ln t$  plots for EPDM-4 at 150°C.

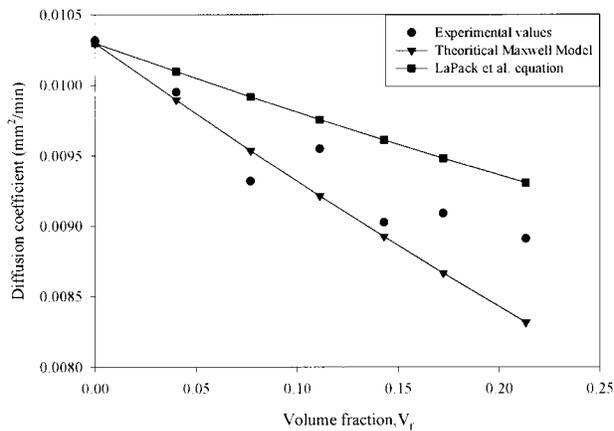
**Table III** Analysis of Sorption Data of EPDM-3 and EPDM-4 (using Eq. 2)

EPDM/phr Carbon Black	Temperature (°C)	$n$	$k \times 10^2$ (min <sup>-n</sup> )
EPDM-3/0	60	0.55	3.73
	100	0.57	5.61
	150	0.56	6.78
EPDM-3/30	60	0.56	3.85
	100	0.56	5.33
	150	0.57	7.03
EPDM-3/60	60	0.57	2.98
	100	0.58	5.41
	150	0.58	7.01
EPDM-4/0	60	0.58	2.12
	100	0.57	3.18
	60	0.59	6.76
EPDM-4/55	60	0.60	1.71
	100	0.56	3.23
	150	0.57	6.87
EPDM-4/110	60	0.58	1.79
	100	0.56	2.68
	150	0.56	6.45

Figures 7–9, where the values are lower than the limit of the Maxwell model or are approaching the trend suggested by LaPack.<sup>24</sup> The Maxwell model for predicting the diffusion coefficient in composite materials has been used with some success in thermoset composites, as reported earlier.<sup>20</sup> Since



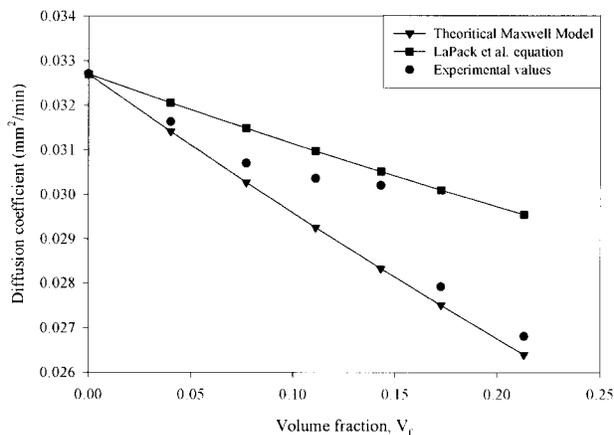
**Figure 7** Diffusion coefficient versus volume fraction of carbon-black filler for EPDM-1 at 60°C: a comparison between theoretical and experimental results.



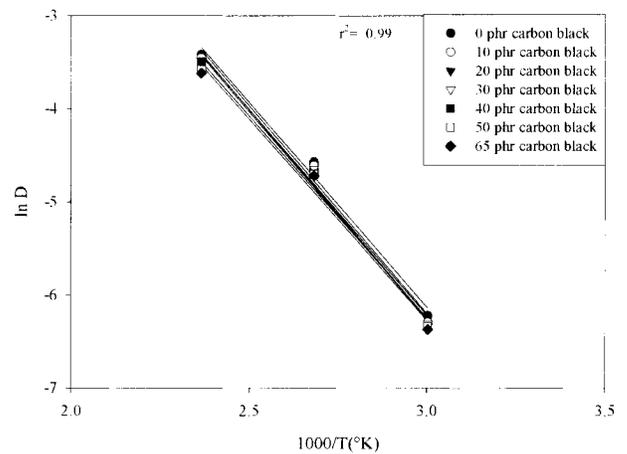
**Figure 8** Diffusion coefficient versus volume fraction of carbon-black filler for EPDM-1 at 100°C: a comparison between theoretical and experimental results.

the composite itself contains a large number of pores, this in turn increases the diffusion coefficients.

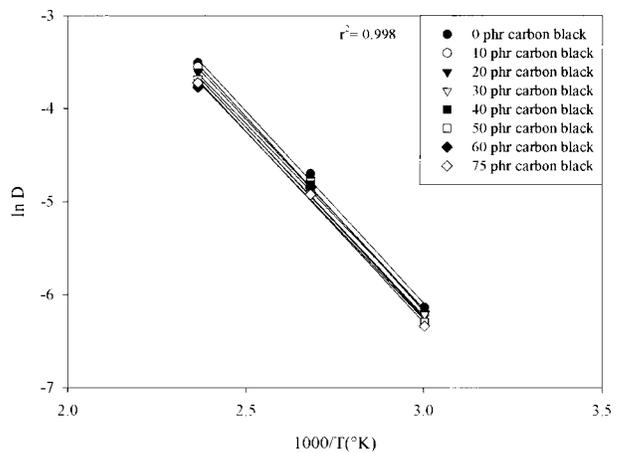
Diffusion coefficients of this study exhibit a systematic dependence on temperature. This dependency is represented by the Arrhenius relationship, shown by plotting  $\ln D$  versus  $1/T$  (Figs. 10 and 11). For all formulations, it was found that the diffusion coefficient increases with an increase in temperature. Values of activation energy  $E_D$ , for diffusion were calculated using the least-squares method by fitting the  $\ln D$  results with  $1/T$ . The  $E_D$  values for EPDM-1 and EPDM-2 fall in the range of 17–19 kJ/mol. But,  $E_D$  values for EPDM-3 and EPDM-4 fall in the range of 20–22 kJ/mol, an expected range for most elastomers. No systematic dependency of  $E_D$  on car-



**Figure 9** Diffusion coefficient versus volume fraction of carbon-black filler for EPDM-1 at 150°C: a comparison between theoretical and experimental results.



(a)

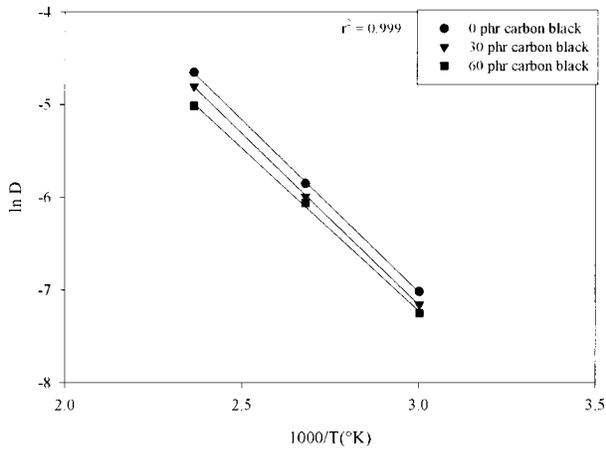


(b)

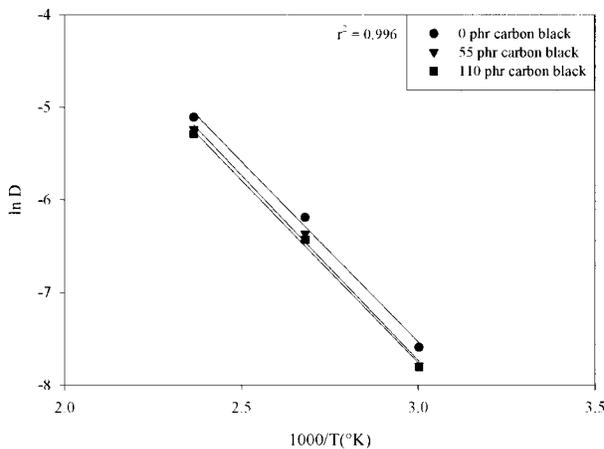
**Figure 10** Arrhenius plots for diffusivity of brake fluid through (a) EPDM-1 and (b) EPDM-2.

bon-black loading was observed, but the small observed difference between EPDM-1, EPDM-2 and EPDM-3, and EPDM-4 may be the result of the molecular-weight difference of the polymers (Table I).

The filler-polymer interaction in carbon-black loaded EPDM is quite high, thus restricting the mobility of the individual polymer chains and causing the rubber to exhibit a lower sorption (Fig. 12). The increase in  $T_g$  with an increase of carbon-black loading is logical because intrusion of filler particles hinders the molecular mobility of the chain segments—this is in agreement with numerous examples in the literature<sup>25–27</sup> on  $T_g$ -versus-filler content. A plot of the apparent diffusion versus the  $T_g$  of the polymers would show the effect of morphology on diffusion. However, this dependence was not linear when compared to the previous studies.<sup>28</sup> This prompted us to use a



(a)



(b)

**Figure 11** Arrhenius plots for diffusivity of brake fluid through (a) EPDM-3 and (b) EPDM-4.

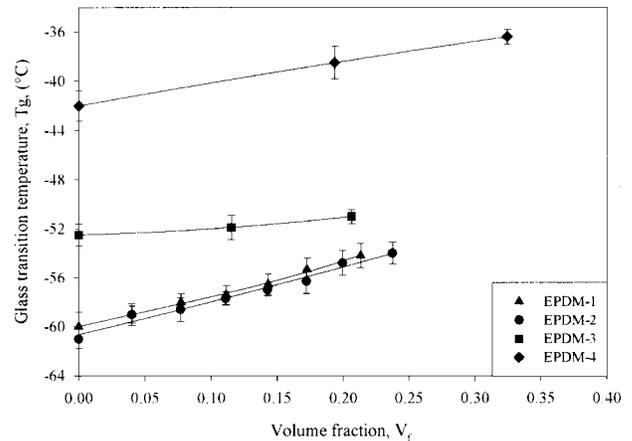
semilogarithmic plot of the apparent diffusion coefficients versus  $1/(T - T_g)$ , as shown in Figure 13. Statistical variations are also indicated in the same figure, which shows confidence intervals of 99% as well as the correlation coefficient. However, the analysis of such results suggests that the diffusion coefficient obeys the Arrhenius equation:

$$\ln D = \ln D_0 - B/(T - T_g) \quad (6)$$

Upon rearrangement, we get:

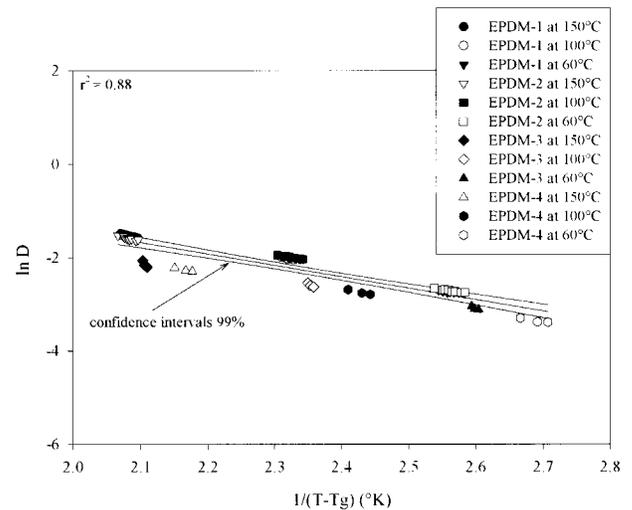
$$D = D_0 \exp[-B/(T - T_g)] \quad (7)$$

where  $A$  is a constant and  $B$  is related to the activation energy. This relationship shows the temperature dependence of the diffusion coefficient.



**Figure 12** Glass-transition temperature as a function of carbon-black concentration for different EPDM formulations.

cient on the  $T_g$  of EPDM as well as the diffusivity dependency on the morphology of polymers. It can be observed that the higher the  $T_g$ , the lower the penetrant diffusivity. By analyzing the molecular mass of the EPDM matrix (Table I), it can be seen that EPDM-1 and EPDM-2 have molecular-weight distributions different than EPDM-3 and EPDM-4. In fact, EPDM-1 and EPDM-2 show lower diffusivity of brake fluid, suggesting that the molecular mass of the polymers may contribute to lowering the diffusion coefficients. However, this statement alone is not sufficient to explain the low diffusivity of brake fluid observed with EPDM-4. Frensdorff has established that the diffusivity of lower hydrocarbons in ethylene-



**Figure 13** Logarithm curve of diffusion coefficient versus  $1/(T - T_g)$  for the different formulations.

propylene copolymers decreases as the propylene content of the copolymer increases.<sup>29</sup> However, the higher ethylene content in EPDM-4 disagrees with the above statement. This may be explained by the low content of ENB monomer in EPDM-4, with fewer double bonds in the molecules than other elastomers have. Thus, the low ENB content contributes considerably to a decrease in diffusivity. This is in agreement with the work of Auerbach et al.,<sup>30</sup> who showed that the presence of double bonds in the rubber tends to increase the diffusivity for octadecane in the unsaturated rubber and the hydrogenated polymers. However, more investigation is needed to quantify the contribution of each of the above factors—that is, the molecular weight and the ENB content—in lowering the diffusivity.

## CONCLUSIONS

The transport properties of a brake fluid (DOT 3) in four commercial EPDM elastomers loaded with 10–110 phr carbon blacks were investigated by immersion and mass gain experiments at 60°C, 100°C, and 150°C. It was observed that both sorption and diffusion coefficients are affected by the presence of carbon blacks, such effects decreasing with an increasing amount of carbon black. The sorption data show that the leaching out of the indigenous additives occurs for formulations embedded with paraffin oil. Observations on the  $T_g$  of the EPDM membranes reveal that the higher the  $T_g$ , the lower the diffusion coefficients. The current study also examined the contribution of molecular mass and the ENB content in EPDM elastomers on sorption and diffusion results.

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