Diffusion of a Volatile Liquid in Polychloroprene Rubber

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Synopsis

The penetration rate of chloroform (highly volatile solvent) in chloroprene rubber vulcanizate, based on different carbon black type and loading, has been studied. The results relevent to carbon black loading have shown an increase in the penetration rate with the increase in loading percentage. Other factors affecting the penetration rate, such as particle size and aggregate structures of carbon black, have shown some confusing results, such as the decrease in penetration rate with the increase of particle size and the decrease in penetration rate at a higher degree of equilibrium volume swelling. These results were attributed to the wrinkles formed at the surface of the rubber at these high equilibrium swellings.

INTRODUCTION

The swelling of rubber involves a diffusion process by which liquid is transported from one part of the sample to another. The diffusion theory in elastomers[1,2] is based on the assumption that the swelling commences by the absorption of liquid in the surface layer of the test piece to a certain concentration equal to that of whole test piece at final equilibrium; then it proceeds by increasing the depth of the swollen layers at a penetration rate[3,4]

$$P = \lim \frac{1}{2} \frac{d(M_t/M_e)}{d(t^{1/2}/d)} \tag{1}$$

for a sheet of large area compared with thickness d; M_e and M_t are weight uptakes of liquid at equilibrium and after time t, respectively.

The diffusion of a liquid in the bulk of the rubber depends on the homogenity of the mix and the way that the carbon black aggregates. Hence, the diffusion values are appropriate averages over the concentration and space. The relation between these average diffusion coefficients D_{av} and the penetration rate P is given as[5]

$$D_{av} = \frac{\pi P^2}{4} \tag{2}$$

A considerable number of investigations were carried out by Southern and Thomas[5] to determine the diffusion coefficient in natural rubber vulcanizate for liquids varying in viscosity. Another study for six other synthetic elastomers was made by the same authors.[3] They showed that the penetration rate of decane through these elastomers decreased as the glass transition

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temperature increased. Blow et al.[4] studied the effect of test piece shape and size, test temperature, rubber-liquid ratio, chemical composition of rubber and liquid, and evaporation on the penetration rate of acetone in fluorocarbon rubber vulcanizate. They found that the penetration rate is relevant to these factors.

However, the problem is more complicated when using a highly volatile liquid, such as chloroform. The present work is concerned with the method that can be used to avoid errors arising from the deswelling that occurs to the swollen rubber by evaporation when these measurements are carried out at room temperature.

The study will involve the effect of carbon black particle size and concentration on the penetration rate of chloroform in chloroprene rubber.

MATERIALS AND EXPERIMENTAL PROCEDURE

Rubber Mix Formulation

The mixes examined were based on neoprene elastomer, which is the generic name for chloroprene polymer (2-chloro-1,3-butadiene) supplied by E. I. duPont de Nemours and Company. The grade used in this study is Neoprene WRT. The basic formulation is given in Table I. The flectol H that was used in the mix is a Monsanto product and is used to improve flexing properties of the rubber. The tetramethyl thiourea is a very fast vulcanizing agent. Four types of carbon black were used: thermal medium (MT), semireinforcing furnace (SRF), high abrasion furnace (HAF), and superabrasion furnace (SAF). The properties of these blacks[6] are given in Table II. The particle size concentration was also studied at 0, 10, 20 40, and 60 phr. These concentrations were used with each carbon black mentioned before.

MIXING PROCEDURE AND TEST PIECE PREPARATION

Mastication and mixing were carried out on a two-roll mill (300 × 130 mm) operating at a friction ratio of 1.25 : 1 with water cooling. Vulcanized sheets (from which test pieces were cut) were produced by molding in an electrically heated platean press at 170°C. Rheometer (Monsanto type TM100) tests at 170°C indicating that 90% cross-linking occurs at a cure time of 9 min was given in all cases.

TABLE I
Mix Formulation

Neoprene WRT	100
Flectol H (Monsanto)[a]	1.0
MgO	4.0
Stearic acid	0.75
Zinc oxide	5.0
TMTU[b]	0.75
Carbon black	As indicated

[a]Acetone-aniline products.
[b]Tetramethyl thiourea.

TABLE II
Carbon Black Properties, Penetration Rate, and Diffusion Coefficient[a]

Carbon black (phr)	MT (470, 33)		SRF (60, 65)		HAF (29, 105)		SAF (20, 115)	
	$P \times 10^{4}$ [b]	$D \times 10^{8}$ [c]	$P \times 10^{4}$	$D \times 10^{8}$	$P \times 10^{4}$	$D \times 10^{8}$	$P \times 10^{4}$	$D \times 10^{8}$
10	8.1	51.6	5.9	27.5	8.3	54.2	8.7	59.6
20	8.8	60.9	6.8	36.5	9.7	74.1	8.3	54.2
40	10.6	88.4	7.5	44.3	12.4	121.0	9.9	77.1
60	13.1	135.1	8.9	62.3	16.2	206.5	11.6	105.9

[a] The first value in parentheses is particle size; the second is structure.
[b] P is the penetration rate expressed as $cm/s^{1/2}$.
[c] D is the diffusion coefficient expressed as cm^{2}/s.

SWELLING MEASUREMENTS

Rectangular test pieces ($15 \times 15 \times 2$ mm) are allowed to swell at room temperature for 48 h in stoppered glass bottles containing 40 cm^{3} of chloroform. The sample was weighted in chloroform to determine M'_{e}, picked up from the liquid, and hung by a fine wire in air from the arm of a sensitive automatic balance. The weight was then recorded each 30 s. The evaporation curve is plotted as the weight of sample versus the square root of time. The relation is almost linear (see Fig. 1) and by extrapolating to zero time (the time at which the test piece is removed from the liquid), the weight of the sample at equilibrium state, M_{e}, can be obtained.
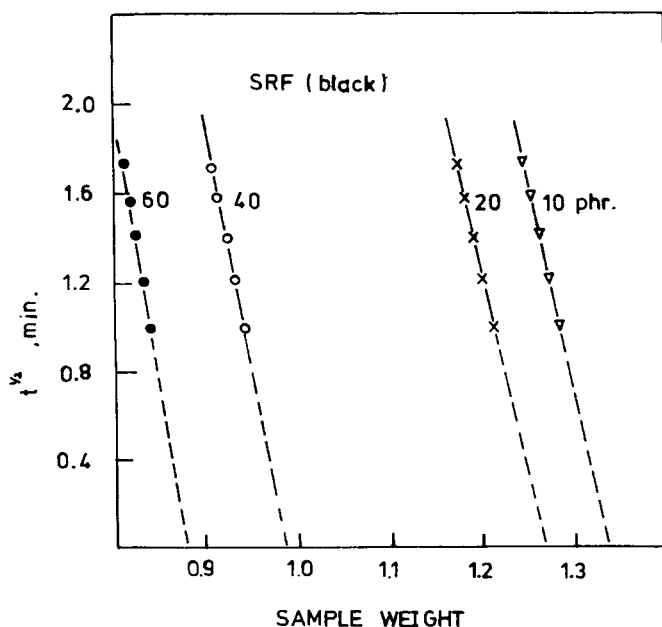

Fig. 1. Evaporation curves. Plot of square root of time versus sample weight.

The deswelling of the rubber vulcanizate is a reverse process to the swelling phenomenon. So, the slope of the evaporation curve can be used to evaluate $M_t/t^{1/2}$ given in eq. (1).

The sample used for swelling measurements is first dried at room temperature for 72 h, then at 70°C to constant weight M_d, and then in chloroform to M_d'.

The percentage volume swelling ΔV was calculated as

$$\Delta V = \frac{(M_e - M_e') - (M_d - M_d')}{M_d - M_d'} \times 100 \qquad (3)$$

The experimental errors associated with these procedures were estimated by replicate swelling measurements using 10 samples cut from the same rubber sheet. The standard deviation was calculated and the coefficient of variation was found to be 0.025. This variation is quite reasonable to conclude that the evaporation method is quite satisfactory.

RESULTS AND DISCUSSION

The penetration rate of organic liquids into a rubber vulcanizate depends on many factors. These factors are (1) the density of chain entanglements and
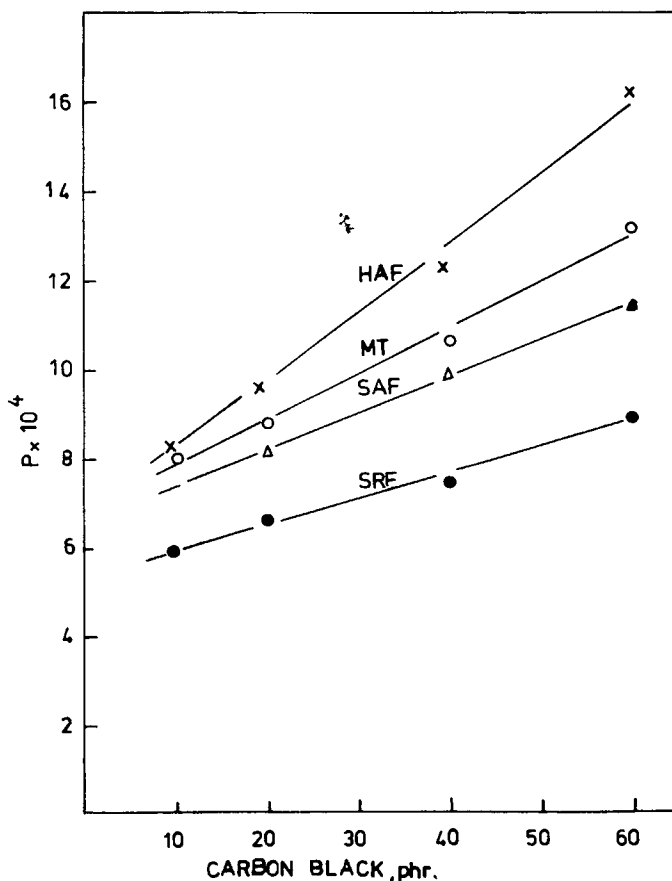

Fig. 2.   Penetration rate versus carbon black concentration.

chain ends, (2) the cross-link density of rubber, (3) the solubility parameter of both polymer and liquid, and (4) the type and amount of filler..

However, these concepts are by no means the whole story. Other factors can affect the penetration rate and the degree of equilibrium swelling, such as the viscosity of liquid, the network three-dimensional structure of the rubber, and the functionality of cross-links.

Functionality of 2   Functionality of 3
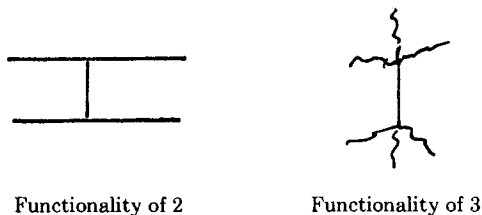
In the present work a trial was made to fix most of these factors by using a specific polymer (Neoprene) and a specific mix formulation, which is given in Table I. The only variables were the carbon black types and amounts.

The most important five properties of carbon black are (1) the particle size, (2) the structure, (3) the physical nature of particle surface, and (4) the chemical nature of the surface and the particle porosity.

It is convenient to explain here the term "structure" and how it can be measured. *Structure* refers to the joining together of carbon black to form three-dimensional aggregates. This is normally measured by determining the
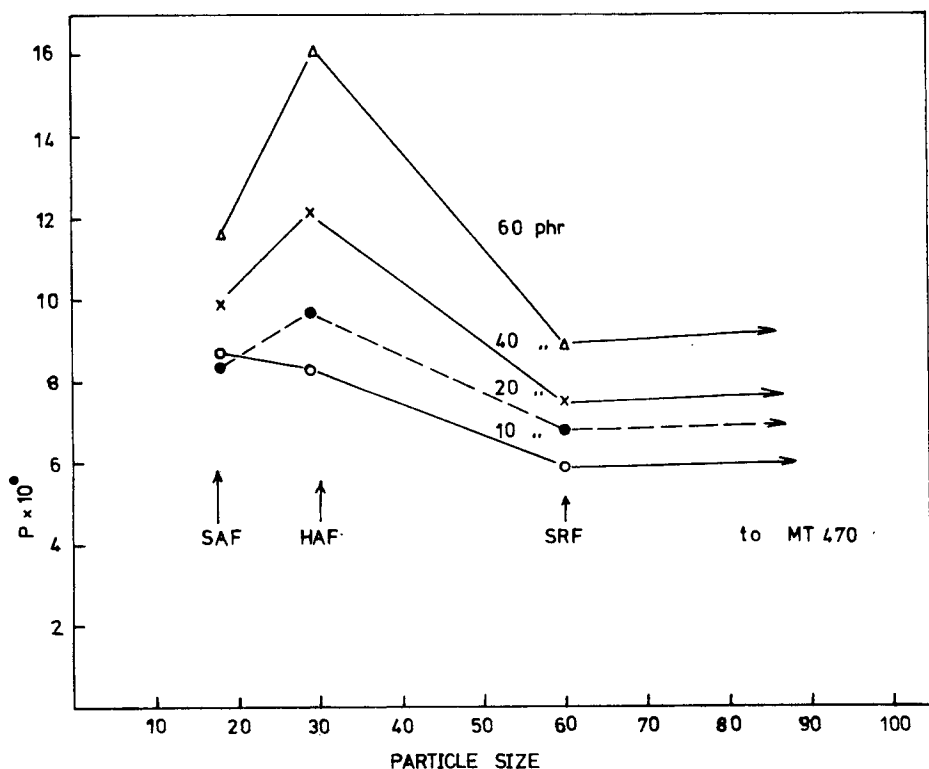

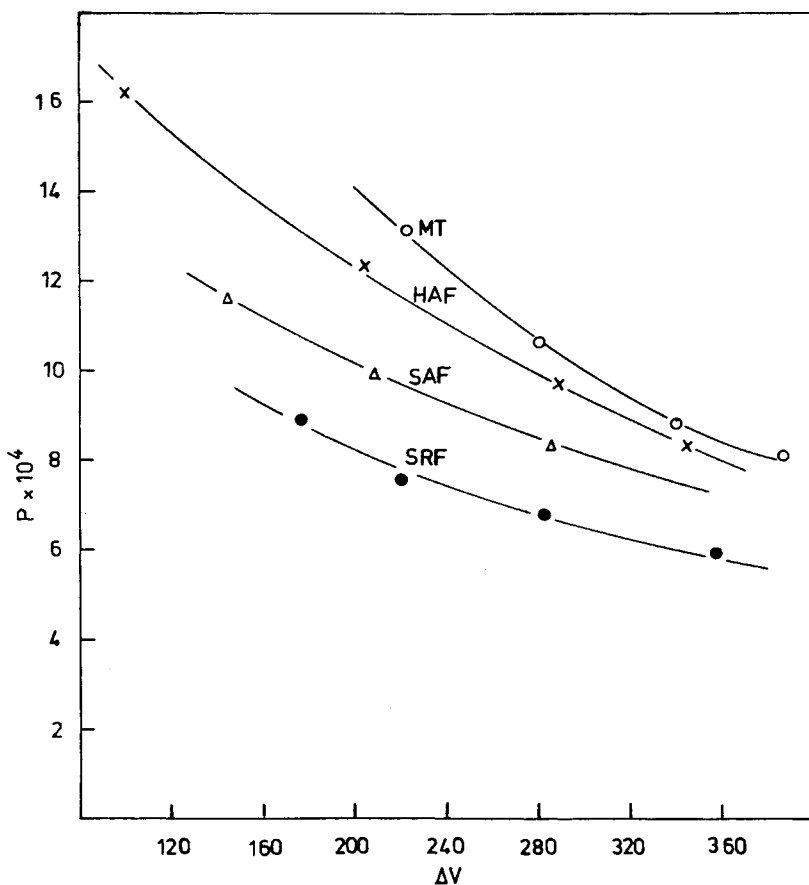Fig. 3.   Penetration rate versus carbon black particle size.

Fig. 4.   Penetration rate versus percentage volume swelling.

total volume of air spaces between aggregates per unit weight of black. The test is done by measuring the volume of liquid (dibutyl phthalate, DBP) required to fill the void and is recorded as cm^3 per 100 g of black. Values for different types of carbon black were given by Gaton and Middleton[7] and Horn.[8] These values are shown in Table II.

The effect of various loading of carbon black on the penetration rate of chloroform in the chloroprene rubber vulcanizates has been examined. The penetration rate is calculated as before. These results are shown in Fig. 2. This relation is found to be linear, and the penetration rate is found to increase with the increase of the carbon black concentration in the mix. These linear relations are of different slopes depending on the carbon black type.

Figure 3 shows that the penetration rate is not simply related to the carbon black particle size. It seems that the penetration rate is often increased when the particle size decreases; the opposite was expected. However, these confusing results can be explained when the penetration rate of the solvent in the rubber is plotted against the percentage equilibrium volume swelling. This is shown in Fig. 4. This figure shows three important aspects. First, each carbon black type has its own curve and the curves are of different levels. Second, the percentage equilibrium volume swelling is considerably high for all types and
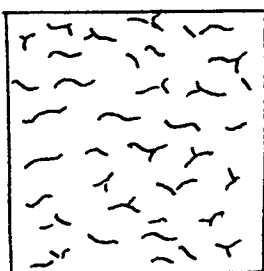
Surface wrinkles

concentration of carbon black. Third, the penetration rate decreases with the increase in swelling percentage.

The results given by Fig. 4 make it possible to explain the results of Fig. 3 as follows. At a high swelling ratio the surface of the rubber become unstable and several wrinkles are formed at the surface.[9] Thus, there is some uncertainty in the surface concentration, especially for samples containing relative large carbon black particles in which the possibility of forming large numbers of wrinkles at the surface is great. These wrinkles reduce the rate of penetration of the solvent in the rubber vulcanizates.
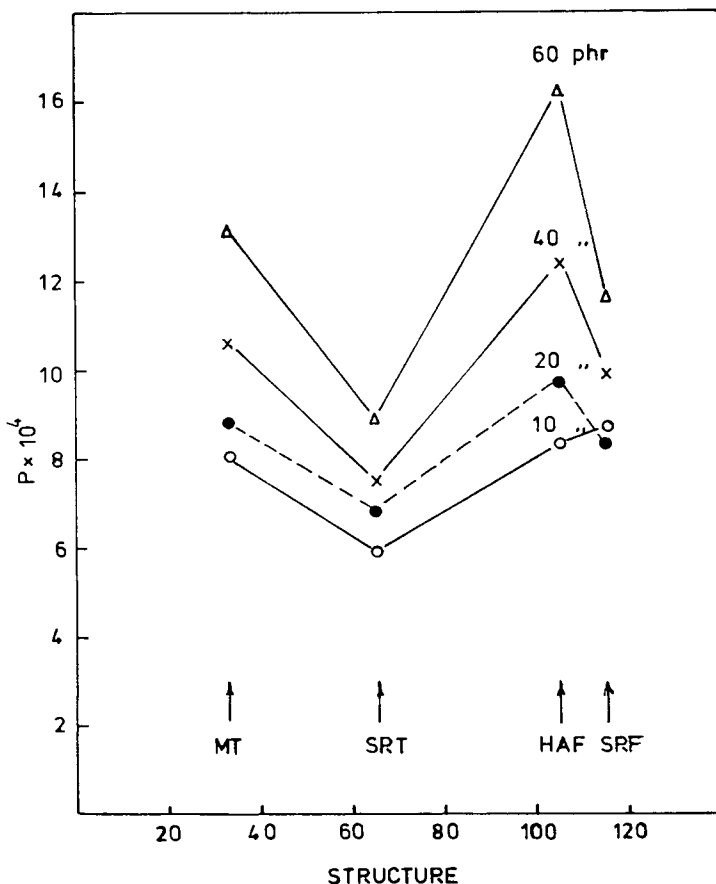

Fig. 5.   Penetration rate versus carbon structure.

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Similar results were obtained by Aitken and Barrer[10] and Southern and Thomas[5] when they used mixes of different cross-linked densities. They showed that the diffusion of some solvents increased with the increase of chemical cross-links in the mix, although the opposite was expected. They also attributed these results to the wrinkles formed at the surface of the rubber when the equilibrium volume swelling of rubber by a solvent was high. However, it must be mentioned here that solvents and polymers of the same cohesive energy densities possess higher swelling values.[11]

Finally, in Fig. 5, the penetration rate is plotted against the average structure of carbon black. The curve does not follow a certain relation. There are many factors affecting this relation, such as the aggregates of carbon black and whether it is dispersed well or badly in the polymer, the physical and chemical nature of the carbon black particle surface, and the particle porosity of the carbon molecules. These factors together widely affect the hydrodynamic forces between the polymer chain and the carbon black aggregates. Also, these forces add physical cross-links to the rubber vulcanizate; these additional crosslinks affect the percentage volume swelling and, in turn, the penetration rate.

CONCLUSION

The diffusion of a volatile liquid in a filled rubber vulcanizate depends on the carbon black type and amount. Different types of carbon black aggregate at the bulk of the rubber at different shapes and concentrations. These aggregates are attached to the polymer chain by different hydrodynamic forces. The diffusion of a liquid in an elastomer depends on the final three-dimensional network product and the concentration of materials in the substrate.

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