Penetration of Oils into Polychloroprene Rubber

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Synopsis

A number of factors which influence the penetration rate of motor oils in polychloroprene rubber have been investigated. These are relevant to carbon black concentration, carbon black particle size and oil characterization.

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 sample to a certain concentration equal to that of the whole sample at final equilibrium; then the swelling proceeds by increasing the depth of the swollen layers at a penetration rate P,[3-5]

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

for a rubber sheet of thickness d. M_e and M_t are the weight uptake of liquid at equilibrium and after time t, respectively.

The diffusion of a liquid in the bulk of the rubber depends on the homogeneity of the mix and the way that the carbon black is aggregated. Hence, the diffusion values are approximate averages over the concentration of liquid and dimensions of the sample. The relation between the average diffusion coefficient D_{av} and the penetration rate P is given as[5]

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

MATERIALS AND EXPERIMENTAL PROCEDURE RUBBER MIX FORMULATION

The mixes examined were based on neoprene elastomer, which is the generic name of chloroprene polymer (2-chloro-1,3-butadiene) supplied by E. I. DuPont de Nemours and Co. 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

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TABLE I
Mix Formulation

	phr
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[c]	as indicated

[a]Acetone–aniline products.
[b]Tetramethyl thiourea.
[c]TM, SRF, HAF, and SAF

TABLE II
Carbon Black Properties

Property	TM	SRF	HAF	SAF
Average particle size (nm)	470	60	29	20
Aggregation structure[a] ($cm^3/100$ g)	33	65	105	115

[a]Volume of air spaces between carbon black aggregates per unit weight of carbon black.[6]

carbon black were used: thermal medium (MT), semireinforcing furnace (SRF), high abrasion furnace (HAF), and superabrasion furnace (SAF). These were used at concentrations of 0, 10, 20, 40, and 60 phr. The characteristics of these blacks are given in Table II.

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 the test pieces were cut) were produced by molding in an electrically heated platen press at 170°C. Rheometer (Monsanto type TM 100) tests at 170°C indicated that 90% crosslinking occurs at a cure time of 9 min in all cases.

Swelling Measurements

Rectangle test pieces (15 × 15 × 2 mm) were immersed in 20 mL of oil. The swelling tests were carried out in stoppered-glass bottles placed in a fan-assisted air circulating oven at 100°C. The samples were removed from the oil at time intervals. The excess oil on the surface of the sample was removed by blotting with filter paper then weighed by hanging in a sensitive balance (Sartorius type 4800) and reimmersed in oil until constant weight was reached. The characteristics of oils used for swelling measurements are given in Table III.

TABLE III
Oil Characteristics

Commercial name	Code	Molecular weight	Specific gravity	Viscosity (P)
Misr oil super	A	202	0.81	2.425
Misr oil diesel	B	243	0.89	2.236
Esso	C	166	0.89	2.000
Lockheed 105	D	191	0.96	0.005

RESULTS AND DISCUSSION

The penetration rate and the percentage volume swelling of an oil into a rubber vulcanizate depend on many factors among which are: (1) the density of chain entanglements and chain ends, (2) the crosslink density of the rubber, (3) the type and amount of filler, (4) the network three-dimensional structure, (5) the functionality of crosslinks, (6) the viscosity of the oil, and (7) the solubility of both polymer and oil.

In this paper a trial was made to fix most of these factors by using a specific polymer and specific mix formulation. The only variables are the carbon black type and amount and the oil characteristics.

Effect of Carbon Black Concentration on the Penetration Rate

The effect of various loading of carbon black on the penetration rate was carried out using HAF black of concentration 0, 10, 20, 40, and 60 phr added

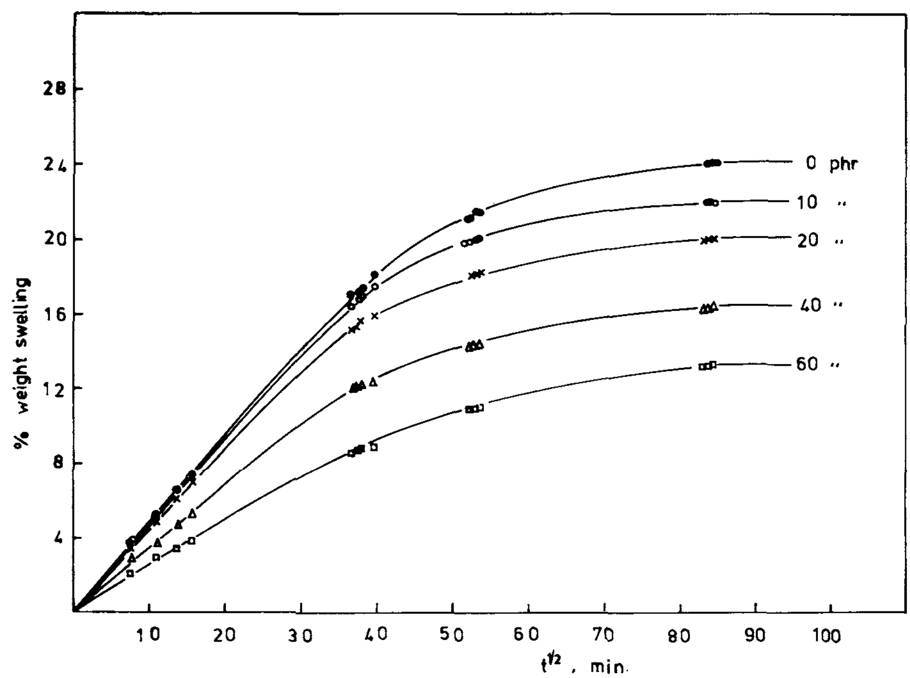

Fig. 1. Percentage weight swelling vs. square root of time for samples containing different concentration of HAF black.

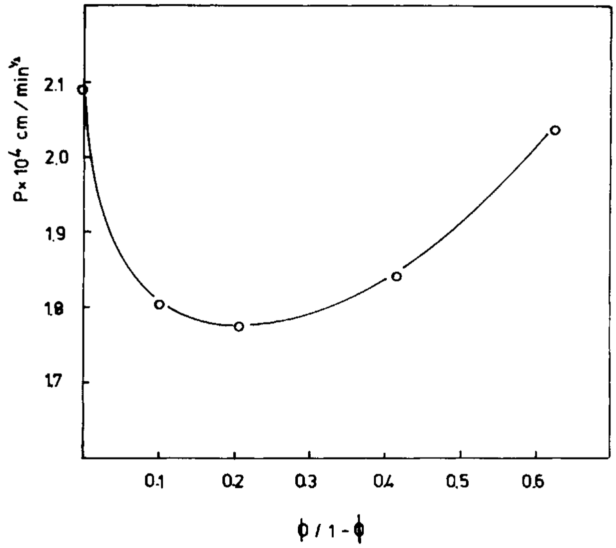

Fig. 2. Penetration rate vs. $\phi/1 - \phi$; ϕ is the volume fraction of HAF black in the mix.

to the mix given in Table I and one type of oil A. The percentage increase in weight due to swelling is plotted against the square root of time, in minutes. The curves are shown in Figure 1; the curves are similar in character but differ in magnitude. The nearly linear portion at the early part of the curves represent about 60% or more of the equilibrium volume swelling values. It usually happens that the early part of the curve is sigmoidal.[7,8] This sigmoidal shape is attributed to the resistance of the unswollen portion of the sample. The sigmoidal shape becomes linear when the equilibrium volume swelling is low as in the case of highly viscous solutions; for example oils, or when the solubility parameter of the solvent is far from that of the polymer; or when restrain is applied to the sample during the course of swelling, which causes a decrease in the subsequent equilibrium swelling values.[9,10] However, the early linearity of our diffusion curves may be due to the low equilibrium volume swelling values, for this specific mix and oil, and that the samples used was of uniform thickness and of parallel leveled surface edges. The nearly horizontal part of the curve means that the rubber degradation or extraction of its soluble ingredients are extremely small.

The slope of the straight lines obtained at the early part of the curves was calculated. This slope is equal to $M_t/t^{1/2}$; and at equilibrium volume swelling, M_e values were obtained. Using eqs. (1) and (2) the penetration rate and diffusion coefficients were calculated. Figure 2 is a plot of $\phi/1 - \phi$ vs. the penetration rate P, where ϕ is the volume concentration of filler in the mix. From this figure, the penetration rate decreases with the increase of carbon black concentration. This may be attributed to the aggregation of carbon black at the bulk of the rubber mix. These aggregations happen at different plate levels which act as screens, delaying the penetration rate of oil molecules into the bulk of the rubber mix. In addition the carbon black–rubber reinforcement causes restriction to the equilibrium volume swelling. At higher

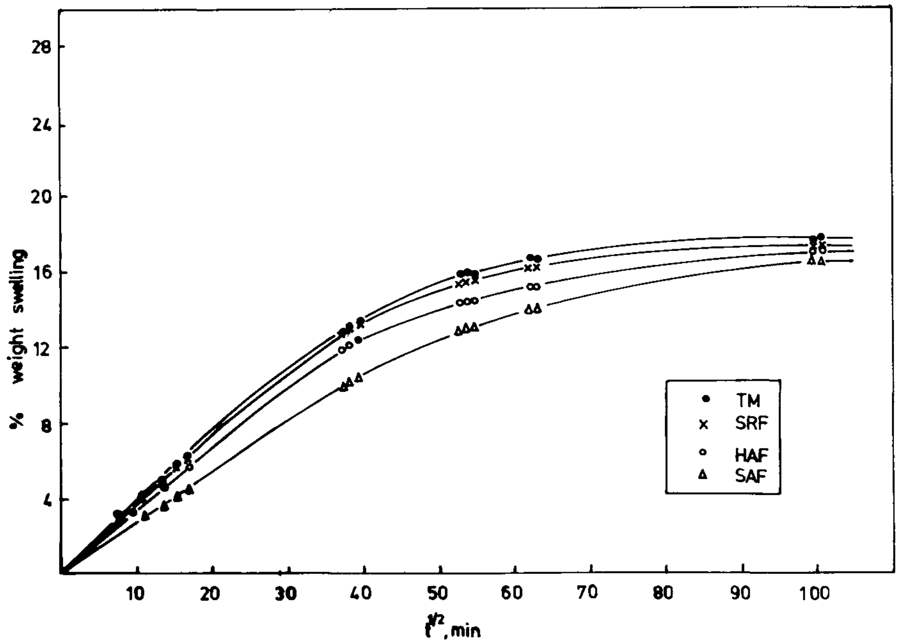

Fig. 3. Percentage weight swelling vs. square root of time for samples containing different types of carbon black (40 phr): (●) TM; (×) SRF; (○) HAF; (△) SAF.

carbon black concentration (> 20 phr) the volume fraction of polymer in the mix decreases, causing an increase in the penetration rate of the oil.

Effect of Carbon Black Type on the Penetration Rate

In this study, a master batch of the mix given in Table I was divided into four portions and each portion was loaded by an equal amount (40 phr) of MT, SRF, HAF, and SAF blacks, varying in particle size. These samples were cured at the same temperature, 170°C, and same cure time, 9 min. The effect of various types of carbon blacks on the penetration rate was studied using one type of oil A, (Table III). The penetration curves are similar in character

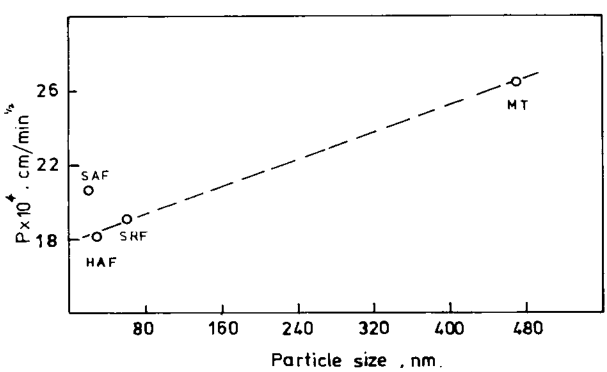

Fig. 4. Penetration rate vs. particle size of carbon black.

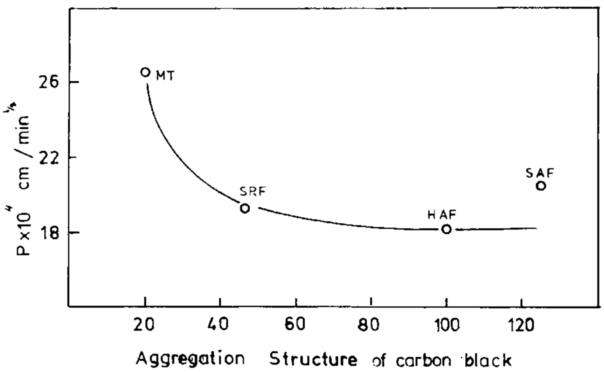

Fig. 5. Penetration rate vs. aggregation structure of carbon black

(Fig. 3). The SAF curve shows some different behavior than the three other blacks, due to its superior adhesion force with the polymer. Figure 4 shows the relation between carbon black particle size and the penetration rate; the latter increases with an increase in particle size. But, this linear relation is not always followed as in the case of SAF black. Figure 5 represents the relation between the aggregation structure of carbon black and the penetration rate. The lower the aggregation structure, the higher the penetration rate. This relation is not valid for SAF black where a sudden increase in the penetration rate occurs at higher structure. This may be due to the carbon black chain aggregation reduction during mixing. However, this reduction was observed before.[11,12] We may conclude here that the penetration rate values can be

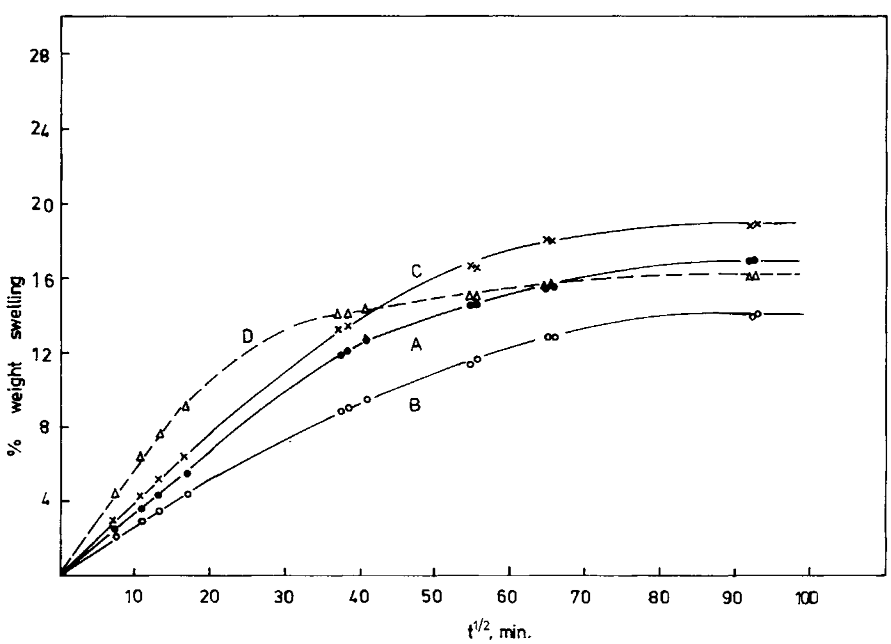

Fig. 6. Percentage weight swelling vs. square root of time. Different types of oils and one mix containing 40 phr of HAF black.

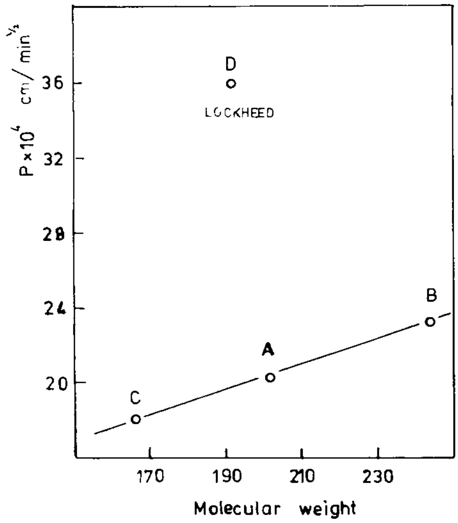

Fig. 7. Penetration rate vs. molecular weight of oils.

used as a measure of comparing the degree of carbon black aggregation in a certain mix.

Effect of Oils Characteristics on the Penetration Rate

The chloroprene rubber mix given in Table I and containing 40 phr of HAF black is used to study the penetration rate of four commercial oils in the rubber mix. Three of these oils are highly viscous (motor oils) and the fourth is a motor vehicle brake fluid which conforms to Federal motor vehicle safety standard number 116. This oil is Lockheed super 105 hydraulic fluid

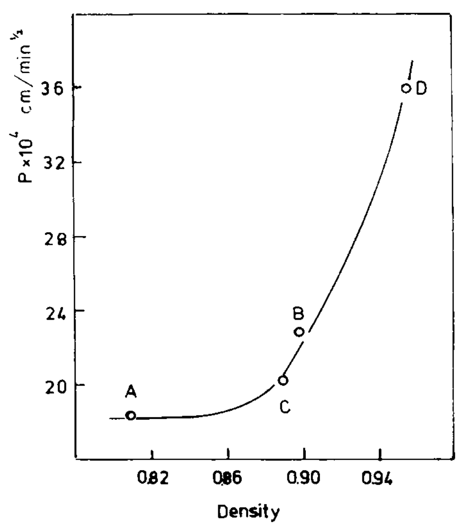

Fig. 8. Penetration rate vs. oil densities.

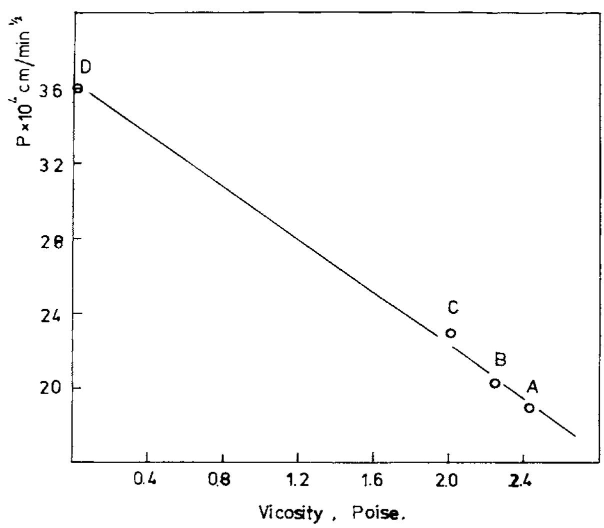

Fig. 9. Penetration rate vs. oil viscosities.

(Banbury, U.K.). The molecular weight, viscosity, and specific gravity of the four oils were measured accurately and are given in Table III.

The percentage weight uptake of these oils are plotted against the square root of immersion time as shown in Figure 6. It is apparent that the three motor oils A, B, and C show similar curves of different levels depending on their viscosities. However, the clutch brake fluid, which is of a very low viscosity compared with the other oils, shows different properties during the penetration process and an early equilibrium volume swelling than the other three oils. Plotting the penetration rate P vs. the molecular weight of oils (Fig. 7), we can notice that the mobility of a solvent in a polymer depends greatly on its molecular weight, as long as these solvents are of the same chemical constitution. In fact, three of these oils are of the same base oil but differ only in the ratio of additives. These additives are the detergent, the sludge dispersant, and the antioxidant. The clutch brake oil is of completely different chemical composition than that of the motor oils, and, of course, the mobility of its molecules in the rubber mix is completely different.

From a plot of the penetration rate P against the density of the examined four oils (Fig. 8), it is clear that there is a reasonable relation than that obtained between P and oil molecular weights.

The relation between P and oil viscosities is more common. This relation is shown in Figure 9. A similar relation was observed by Southern and Thomas[6] and Allen et al.[13] when they measured the penetration rate of a large number of liquid hydrocarbons in natural rubber. They found that the penetration rate decreased as the viscosity of the swelling liquid increased. They also reported that the amount of liquid absorbed is independent on its viscosity but dependent on its chemical nature. For example, it was shown that hexane and liquid paraffin exhibit similar equilibrium swelling values in natural rubber vulcanizates, but the rate of penetration of the latter is one-ninth that of the former.

TABLE IV
Penetration Rate P Expressed as $cm/s^{1/2}$ and Diffusion Coefficient D Expressed as cm^2/s

HAF phr	0	10	20	40	60
$P \times 10^4$	20.0	18.1	17.8	18.4	20.4
$D \times 10^8$	314	257	249	266	328
Carbon black	MT	SRF	HAF	SAF	
$P \times 10^4$	26.3	19.1	18.4	20.6	
$D \times 10^8$	543	286	266	233	
Oil code	A	B	C	D	
$P \times 10^4$	18.4	16.9	17.4	30.9	
$D \times 10^8$	266	224	238	750	

CONCLUSIONS

1. The penetration rate of the oil in polychloroprene rubber decreases with an increase of carbon black concentration up to 20 phr. For concentrations > 20 phr there is a remarkable increase in the penetration rate.

2. The penetration rate increases with an increase in particle size and a decrease of aggregation structure of carbon black. However, this relation is not valid in the case of SAF black; this was attributed to the aggregation reduction either during mixing or during vulcanization.

3. The penetration rate increases with an increase of molecular weight and density of oil, while it decreases with an increase of oil viscosity provided that these oils belong chemically to the same group of hydrocarbons.

4. The penetration rates and diffusion coefficients of all samples used in this study are given in Table IV.

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