

New Results on the Kinetic Aspect of the Permeation Resistance of Elastomers, Using an Original Testing Cell and Methanol as Model Permeating Fluid

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SYNOPSIS

This work describes a method developed to study the permeation of fluids through rubber membrane in a semiautomatic manner, in such a way that information regarding the complete process is obtained. Using this technique, several permeation parameters were assessed with fluoroelastomer and hydrogenated nitrile rubber membranes. A phenomenological model for the permeation process is proposed that includes two concomitant physical phenomena: the swelling of the membrane and the permeation itself. Simple mathematical relationships are derived from the experimental data, with the permeation rate as the key parameter.

INTRODUCTION

The resistance to methanol-containing fuels, which is now required for various rubber applications in the automotive field, has again focused attention on the evaluation methods for the fuel resistance of rubber. Basically chemical and physical effects have to be considered when a rubber is in contact with a fluid. When chemical effects occur, they are likely to strongly affect the structure of the elastomer and ultimately lead to a destruction of the network; in such a case the rubber is not suitable for the application. Physical effects refer essentially to the diffusion of the fluid into the elastomer, which contributes to permeation and/or swelling.

Permeation is the key parameter when only one face of the rubber item is in contact with the fluid, such as in hoses, seals, membranes, diaphragms, etc. Permeation cannot be considered as a mere diffusion process since several physical phenomena are involved, i.e., absorption of the fluid by the exposed face of the rubber item, diffusion through the rubber, and eventually desorption on the other face. Usual

liquid permeation methods are based on weight variation of a vessel containing the permeating fluid and closed by the tested rubber membrane, such as with the Payne cup method described in ASTM D1653-72. This method requires periodic weighing of the test vessel in order to determine the steady-state equilibrium to allow the constant rate of weight loss to be assessed. Several authors have used this method to study the permeability of rubber items (membranes, laminates) to fuels and gasohol,^{1,2} and a review of the various aspects of permeation through rubbers and plastics has been published.³ Other methods consist essentially in the periodic weighing of hoses containing the permeating fluid.

The most popular method to assess the fluid resistance of rubber parts is the swelling method, i.e., the measure of the fluid up-take by a piece of rubber immersed in the fluid. There are numerous publications available concerning this method,⁴⁻⁶ but if swelling and permeation are obviously related phenomena, it must be noted that swelling results give no information regarding the permeation resistance of the rubber to the fluid or to certain components of the fluid, as commented in a recent work.⁷

The purpose of this work is to describe a method developed to study the permeation of fluids through rubber membrane in a semiautomatic manner, in

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such a way that information regarding the complete process is obtained. In other words the method hereafter described allows us to consider the transient as well as the steady-state permeation.

THEORETICAL ASPECTS OF PERMEATION AND DIFFUSION

The basic mathematical aspects of diffusion are extensively described in textbooks^{8,9} and in review papers.¹⁰ Only some basic aspects of the permeation of liquid through elastomer membranes will be briefly discussed here.

Permeation is a transport phenomenon that describes the crossing of a (rubber) membrane by a foreign molecule, the driving force being the absence of concentration equilibrium in the foreign molecule between the two media on both sides of the rubber membrane. Practical cases of permeation concern, for instance, the fuel vapor loss through pipe and hose walls in automotive applications. With respect to the schematic description given in Figure 1, there are at least four distinct processes to be considered when a foreign molecule permeates through a rubber membrane:

1. The absorption of the foreign molecule on face A of the membrane.

FLUID PERMEATION IN RUBBER MEMBRANE

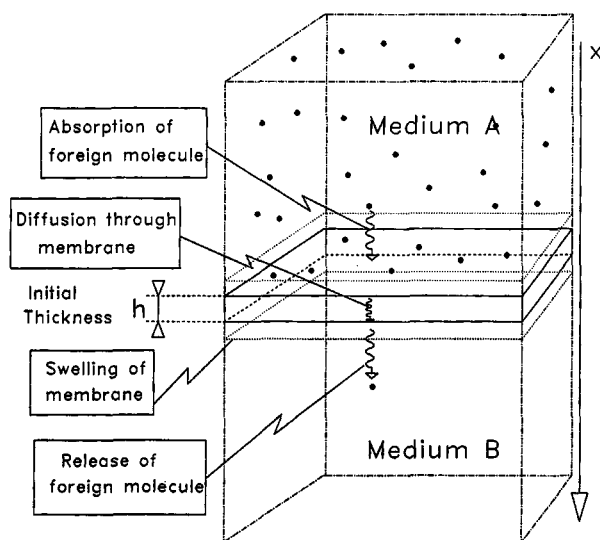


Figure 1. Schematic description of the permeation process.

2. The diffusion through the membrane, from face A to face B.
3. The swelling of the membrane, concomitant with the diffusion.
4. The evaporation (or extraction) of the foreign molecule on face B of the membrane.

Assuming an instantaneous contact of the medium A (containing the permeating molecules) with the face A of the membrane at time $t = 0$, it is obvious that the above processes are not taking place all in the same time. There is thus an important *kinetic aspect* in the permeation problem.

The well-known Fick equations offer a basic theoretical approach to the permeation problem. i.e.:

$$F_x = D \frac{\partial C}{\partial x} \quad (\text{first Fick law})$$

$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \quad (\text{second Fick law})$$

where F_x is the rate of diffusion through unit area of material, D the diffusion coefficient of the diffusing substance, and C the concentration ($\partial C/\partial x$ is therefore the concentration gradient along the diffusion direction x). Implicitly the Fick laws assume that the diffusion coefficient D is constant, irrespective of the concentration. This is obviously not the case with rubber membranes that swell when in contact with a permeating fluid.

The diffusing substances loosen the rubber structure, which facilitates the movement of the diffusing molecule and hence a variation of the diffusion coefficient. In addition there are, with rubbers, time-dependent processes caused by the swelling of the elastomer by the permeating fluid that are likely to render D not only concentration dependent but also time dependent.

In dealing with the particular problem of the permeation of certain components of modern fuels through rubber membrane (methanol, for instance), it has been shown that the kinetic aspects are rather important.⁷ The transient-state permeation is therefore as important as the steady-state permeation. The concentration dependence (not to mention the time dependence) of the diffusion coefficient complicates the theoretical approach of the permeation-diffusion process not only because it makes the mathematics difficult to handle but also because one has to determine the dependence law of D . Several attempts are reported in the literature (see Ref.

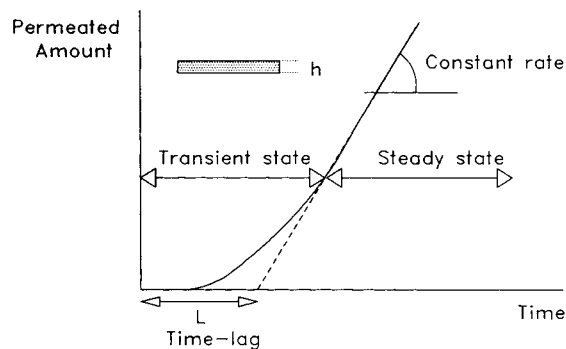


Figure 2. Theoretical permeation curve.

10), the simplest one being to consider a linear relationship of the type¹¹

$$D_C = D_{C=0}(1 + AC)$$

where A is a constant. An equation can then be derived relating the diffusion coefficient $D_{C=0}$ with the thickness h of a permeated membrane and the time lag L of the permeation, i.e., the time necessary for the steady-state permeation to be established (see Fig. 2):

$$D_{C=0} = \left(\frac{h^2}{6L} \right) \left[\frac{\left(1 + \frac{AC_e}{4} \right)}{\left(1 + \frac{AC_e}{2} \right)} \right]$$

where C_e is the equilibrium concentration of the permeating fluid in the membrane interface. The interesting aspect of this approach is the reference

to the time lag L of the permeation, which is likely to be an important experimental parameter with respect to practical situations. As we will show, our experimental method does allow a similar time lag parameter to be determined.

PERMEATION CELL

Principle of the Method

The method has been developed to study more accurately the kinetic parameters of liquid permeation through a rubber membrane in contact on one side with a solvent.

As shown in Figure 3, the permeation cell consists of a two-part glass vessel separated by the rubber membrane; the upper part is filled with the solvent while the pressure is reduced in the lower compartment. The permeation through the membrane is assessed by measuring the pressure variation versus time in the lower compartment with an electronic gauge connected to a recorder. With this technique the permeation process is thus followed in a continuous way. Moreover, since very small pressure variations can be measured, minute permeating amounts can be detected, and the method is suitable to study the permeation kinetics with accuracy and sensitivity.

Test Method

The rubber membrane, whose thickness map has been previously measured, is first mounted in the cell and the pressure is reduced in the lower com-

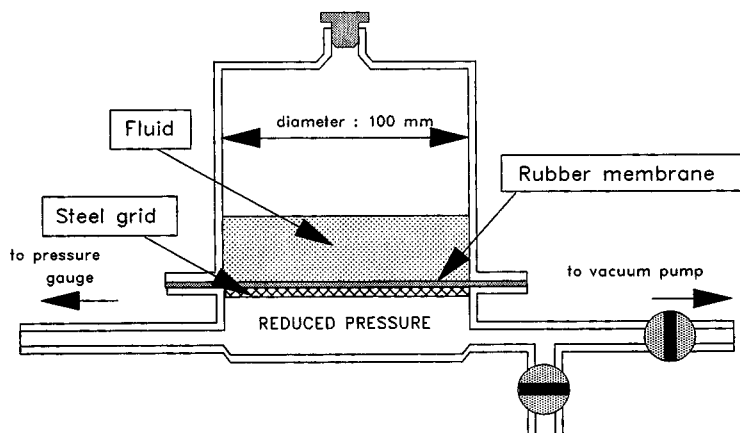


Figure 3. Description of the permeation cell.

partment, at the desired level (usually 0.200 bar). A delay of at least 24 h is observed during which no significant pressure variation must be detected before the system is considered as perfectly tightened. Then the solvent is poured in the upper part of the cell and a stopper is used to close it and thus avoid evaporation. The experiment lasts for several days to a few months depending on the permeation resistance of the membrane. When the permeation test is completed the membrane is carefully removed from the cell, blotted with filter paper, and the final thicknesses map is measured.

The results reported here were obtained with pure methanol as permeating fluid, and all tests were performed at 23°C.

Data Treatment

The test data are treated as follows: From the recorded pressure curve, a pressure variation curve is drawn with respect to the initial reduced pressure. The amount of permeating gas moles, n , is calculated according to the perfect gas law:

$$n = \frac{PV}{RT}$$

where P = pressure variation read (atm)
 V = volume of the lower part of the cell (L)
 R = gas constant (0.082 atm/L K)
 T = test temperature (K)

When dividing n by the membrane area, the specific permeation (at given thickness) is eventually obtained.

EXPERIMENTAL RESULTS

Tested Samples

Two different types of elastomers were used in preparing various test membranes: fluoroelastomer (FKM) and hydrogenated nitrile rubber (HNBR), with respect to known applications of such materials in manufacturing rubber parts for which a resistance to methanolated fuels is required.

The characteristics of the different elastomers tested are given in Table I. All formulations were compounded according to standard practices and the membranes were compression molded with a special mold offering high-quality metal surfaces and a tight control of the cavity depth. The optimal curing conditions were determined from oscillating disk rheometer data.

Table I Test Membranes

Sample Coding	Elastomer Type	Curing System	Filler Type and Content	Sheet Thickness (mm)
FKM68Bb	Fluoroelast. 68%F	Bisphenol A	Carbon black N990 30phr	1; 1.2; 2
FKM68Bw	Fluoroelast. 68%F	Bisphenol A	Wollastonite* NYAD400 30phr	1; 2
FKM68Pb	Fluoroelast. 68%F	Peroxide	Carbon black N990 30phr	1; 1.2; 2
FKM68Pw	Fluoroelast. 68%F	Peroxide	Wollastonite* NYAD400 30phr	1; 2
FKM70Bb	Fluoroelast. 70%F	Bisphenol A	Carbon black N990 30phr	1; 1.2; 2
HNBRb	Hydrogenated nitrile rubber 38%AN 95% sat.	Peroxide	Carbon black N660 50phr	1.1; 1.3; 1.7

* Wollastonite = Calcium metasilicate

Results

Typical Permeation Curve

Figure 4 is a typical specific permeation curve in terms of millimole of permeating fluid (i.e., methanol) per cm^2 . The curve has a typical shape and at least four different zones can be distinguished:

1. First, an induction region (A) is observed, during which the solvent is penetrating through the rubber membrane; swelling of the membrane is likely to occur but no permeating molecule is detected.
2. The beginning of the second region (B) corresponds to the early detection of pressure increase in the lower compartment of the cell; during the following stabilization period, growing amounts of permeating molecules are detected in an essentially unsteady manner.
3. The third zone (C) corresponds to a steady-state regime; the slope is maximum and constant and allows an average permeation rate to be calculated.
4. In the last part (D) the slope decreases but cannot be any more related to the permeation process since at this stage the methanol partial pressure has reached its saturation value at the test temperature.

In the best cases the method thus gives access to three basic parameters for any given test membrane:

the induction time (t_i), the stabilization time (t_s), and the average permeation rate (V_p). However, with certain membranes, the stabilization period is somewhat ambiguous because the experimental curve does not exhibit the simple shape of Figure 4. In such cases the stabilization time may be ill-defined.

Fluoroelastomers Test Results

Typical experimental curves are shown in Figure 5, as obtained with membranes of 68% fluorine carbon black filled compounds, vulcanized with a peroxide curing system. Similar curves are obtained with the other test samples. The permeation parameters t_i , t_s , and V_p , as defined above, were read on the experimental permeation curves (Table II).

As expected, the permeation parameters are depending on the membrane thickness for the three FKM tested. The time parameters, i.e., t_i and t_s , are increasing with the initial thickness of the membrane, while the permeation rate V_p is inversely proportional to the initial thickness, as illustrated in Figure 6. The fluorine content of the elastomer has a drastic effect of these parameters. Indeed, just two percent more fluorine allow the induction time to be multiplied by a factor of 4–5 at equal thickness. The influence of the vulcanization system is nearly negligible; the compound vulcanized with the peroxide system exhibits slightly lower induction time

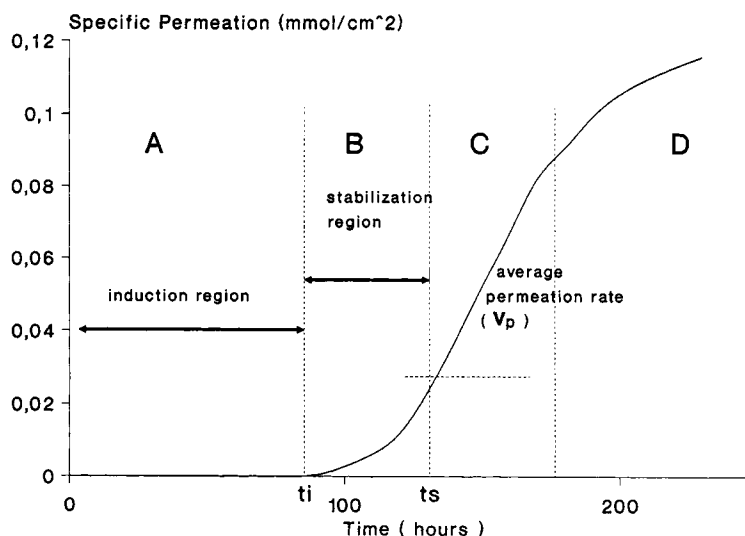


Figure 4. Typical permeation curve obtained with the method described in this work.

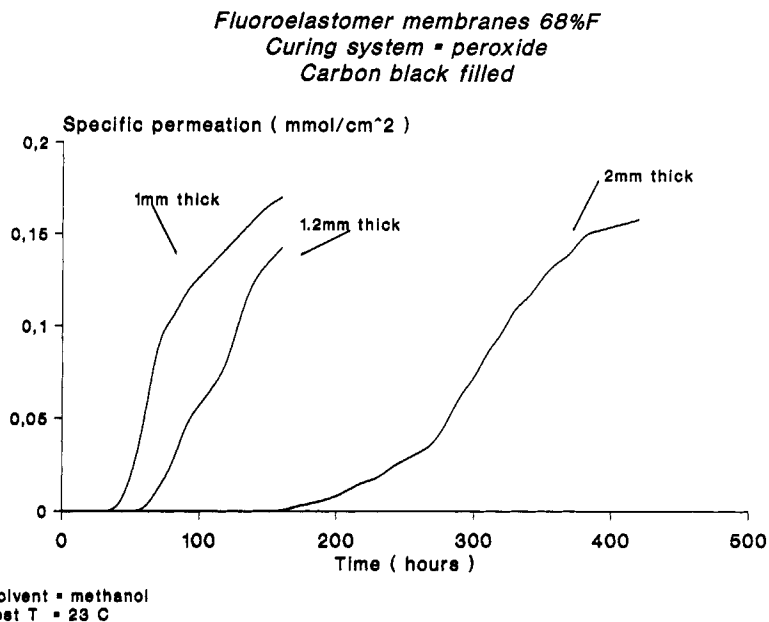


Figure 5. Example of experimental permeation curves obtained for FKM68Pb at various membrane thicknesses.

and higher permeation rate but such differences are close to the experimental scatter. The wollastonite formulations behave rather similarly to the carbon black ones for the FKM68, particularly with the thinner membranes (1 mm); when the thickness increases, small differences are observed.

The average thickness of the membranes were measured after completion of the permeation test.

As seen in Table II, the thickness variation with respect to the initial thickness depends essentially on the fluorine content, and on the vulcanization system. Indeed, the thickness variation is around 11.2% for the 68% fluorine membranes vulcanized with bisphenol AF, 7.5% for the 68% F membranes cured with peroxide and 4.2% for the 70% F membranes. The type of filler (carbon black or wollas-

Table II FKM Permeation Results

	Thickness variation Δh (%)	Induction time (hours)	Stabilization time (hours)	Permeation rate (mmol/cm ² *h)
FKM69Pb 1 mm	11	40	45	0.0027
FKM68Pb 1.2 mm	11.5	60	80	0.0014
FKM68Pb 2 mm	10	160	255	0.0010
FKM68Pw 1 mm	11.5	50	55	0.0026
FKM68Pw 2 mm	12	150	220	0.0013
FKM68Bb 1 mm	7.5	55	60	0.0019
FKM68Bb 1.2 mm	7.5	95	120	0.0012
FKM68Bb 2 mm	7	180	280	0.0006
FKM68Bw 1 mm	8	60	70	0.0017
FKM68Bw 2 mm	7.5	160	220	0.0005
FKM70Bb 1 mm	4	180	200	0.0003
FKM70Bb 1.2 mm	4.5	230	310	0.00021
FKM70Bb 2 mm	4	350	490	0.00019

PERMEATION THROUGH FLUOROELASTOMER MEMBRANES

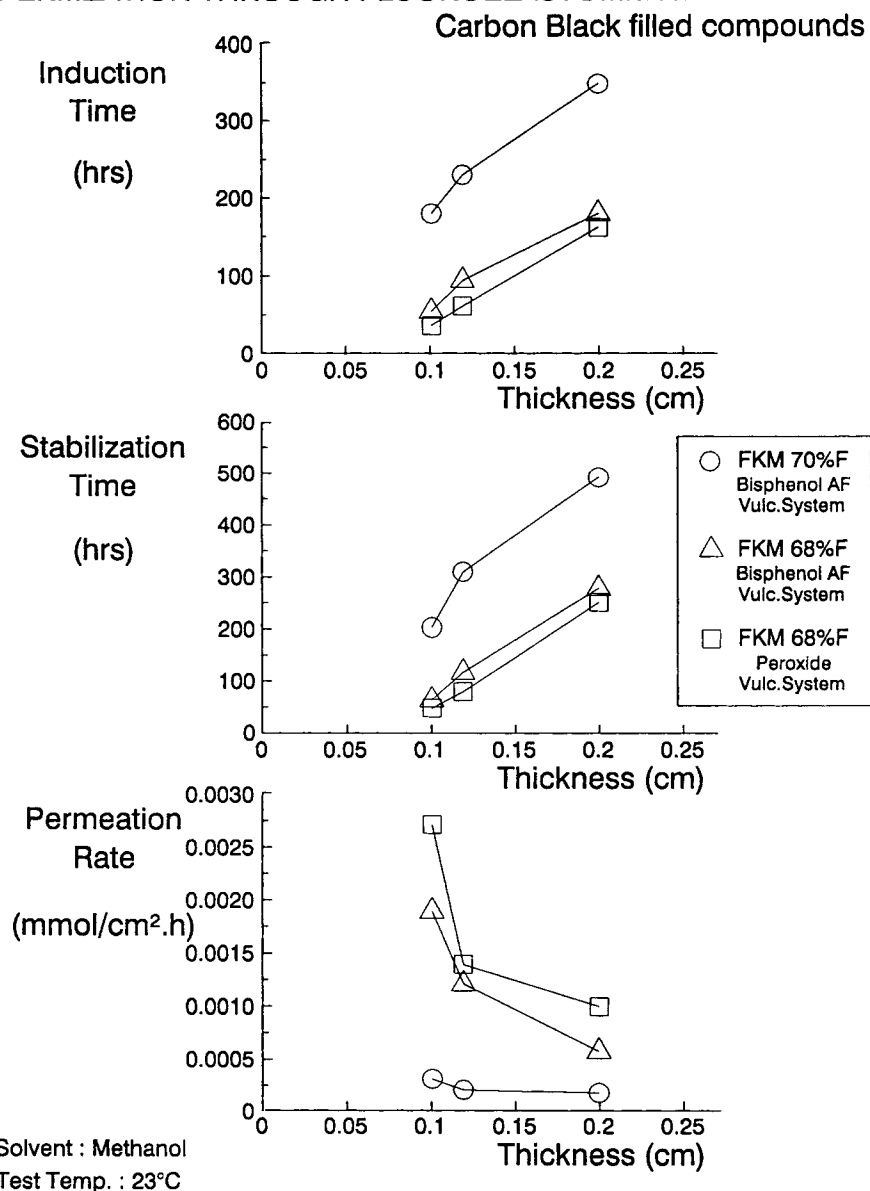


Figure 6. Effect of the membrane thickness on the permeation parameters for various FKM.

tonite) has no significant effect. All these formulation effects are summarized in Table III.

Hydrogenated Nitrile Rubber Test Results

The permeation behaviour of HNBR is qualitatively similar to FKM. Indeed the experimental curves exhibit essentially the same shape and the permeation parameters t_i , t_s , and V_p also depend on the initial

thickness in the same way, as shown in Figure 7. The thickness variation (in %), as well as the weight variation, are not affected by the initial thickness of the membrane, as shown in Table IV.

The simple comparison of the permeation data, as obtained for the FKM and HNBR membranes, shows directly that the latter is much more permeable to methanol than the former. Particularly, the permeation rate is considerable higher and the induction time is lower for the HNBR.

Table III FKM Results: Summarized Effects

Membrane parameter modification	Variation of t_i	Variation of t_s	Variation of V_p	Variation of Δh
↑ of % Fluor	↑↑↑	↑↑↑	↓↓↓	↓↓
Filler type: replacing CB by Wollastonite	—	—	—	—
Curing system: replacing BA by peroxide	↓	↓	↑	↑↑
↑ Initial thickness	↑↑	↑↑	↓↓	—

DISCUSSION

Whatever the membrane tested, the permeation curve presents always the same pattern, which is best described with respect to the measured time parameters of the experiment, i.e., the induction time t_i and the stabilization time t_s . For instance, the observed phenomena can be described by the following sequence of events: from time zero to t_i , only swelling of the membrane is occurring and es-

entially no permeant molecule is passing; from t_i to t_s , the swelling process continues but the permeation occurs; beyond t_s , the equilibrium swollen state is reached and the permeation proceeds at constant rate. In other words, the test results can be interpreted with respect to two simple *concomitant* physical phenomena, i.e., (i) the swelling of the membrane as the fluid penetrates into it and (ii) the permeation itself. As illustrated in Figure 8, the swelling competes thus with the permeation process until an equilibrium swollen state is reached. Consequently the actual amount of permeating molecules having readily passed through the membrane—and therefore detectable on the other side—is depleted until time t_s , i.e., until the steady-state is established. At this stage, the maximum swollen thickness of the membrane h_f is reached, and therefore the time t_s is likely to be the time for maximum swelling to be reached.

With respect to the above modeling of the permeation–swelling process, it is clear that the key parameter is the *permeation rate* V_p . Consequently, there must be a relationship between the time parameters, i.e., t_i and t_s , and V_p providing the actual thickness at the time considered is taken into account. With the assumption that the final thickness h_f of the membrane is reached at t_s , the ratio of t_s versus the thickness variation can be expected to be inversely proportional to the permeation rate, whatever the initial membrane thickness and the formulation, for a given rubber. Indeed, as shown in Figure 9, all the fluoroelastomer membranes data can be well fitted with such a simple relationship, i.e.:

$$\frac{t_s}{h_f - h_0} = \frac{A}{V_p}$$

where t_s = stabilization time (h)
 h_f = final thickness (cm)

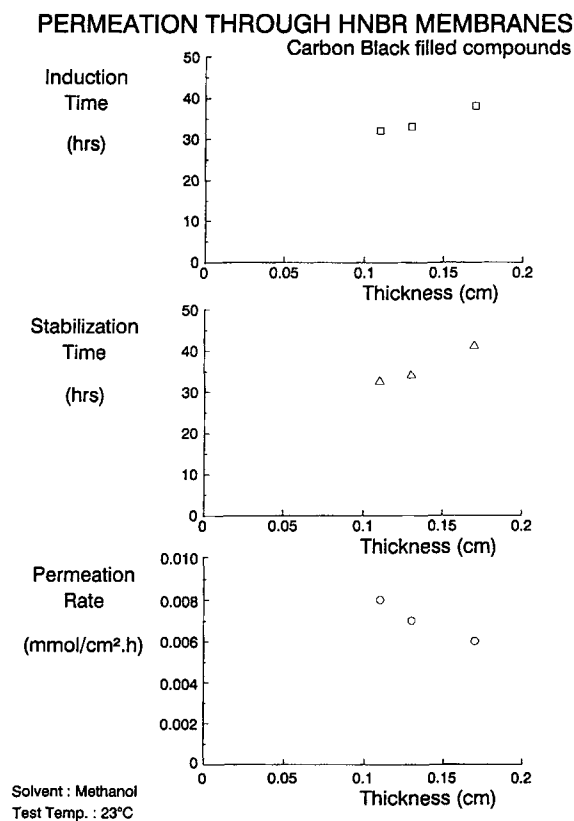


Figure 7. Effect of the membrane thickness on the permeation parameters for HNBRb.

Table IV HNBRb: Permeation Results

Membrane Thickness	Thickness Variation (%)	Weight Variation (%)	Induction Time (hours)	Stabilization Time (hours)	Permeation Rate (mmol/cm ² *h)
1.1 mm	3.1	3.7	32	32.5	0.008
1.3 mm	3.5	3.9	33	34	0.007
1.7 mm	3.3	4.2	38	41	0.006

h_0 = initial thickness (cm)
 V_p = permeation rate (mmol/cm² h)
 A = coefficient

The data point with the hydrogenated nitrile rubber membranes have been plotted in Figure 9 but were not included in the fitting. Indeed the nature of the rubber is controlling the permeation–swelling process, and while a similar relationship is likely to hold for all material, the coefficient is surely different.

The proximity of the HNBR data points from the curve fitted to the FKM data has therefore no particular meaning, except that they reflect the poor permeation resistance of HNBR to methanol.

The induction time t_i corresponds to the first detection of permeant molecules having passed through the membrane. At this stage, the swollen state of the membrane is still transitory, and, if the actual thickness h_i of the membrane could be assessed, one would expect the corresponding ratio,

ONE SIDE ELASTOMER MEMBRANE PERMEATION MECHANISM

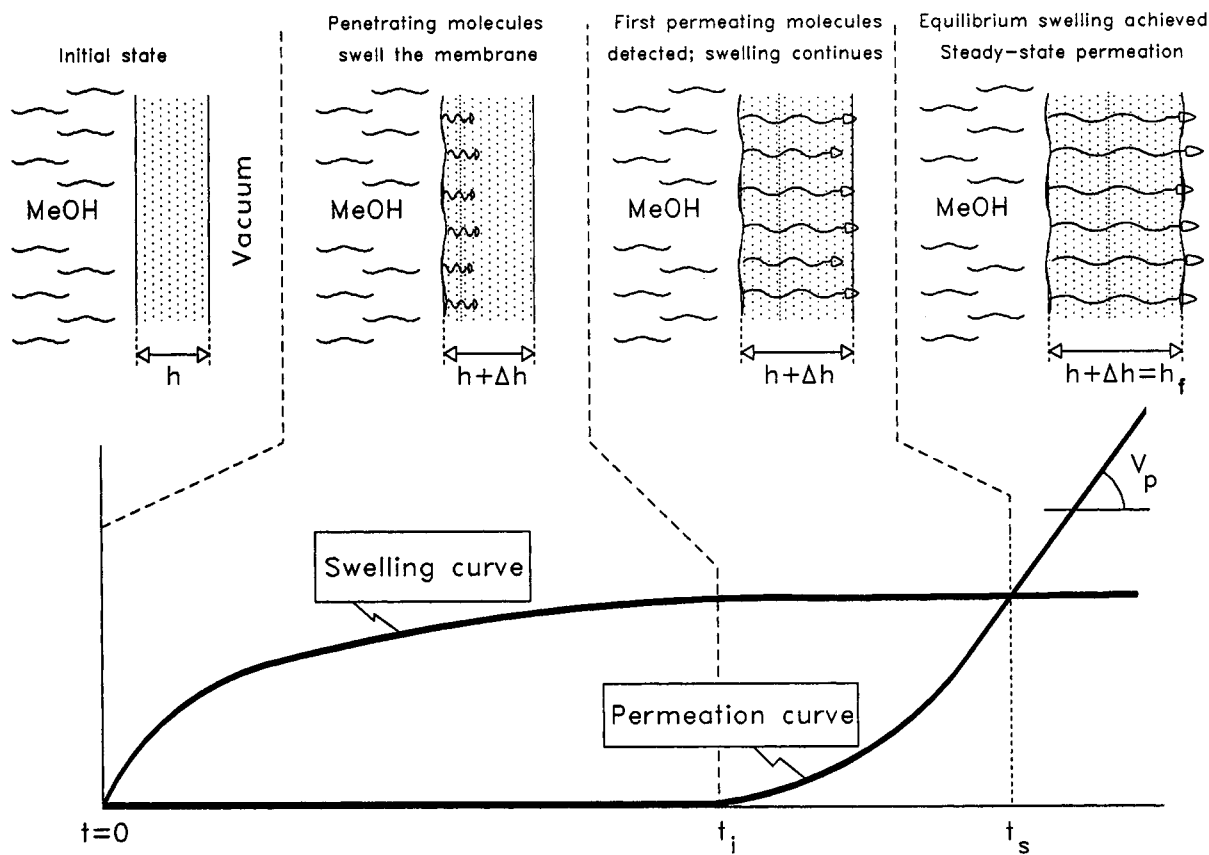


Figure 8. Schematic model proposed for the permeation process taking into account the concomitant swelling process.

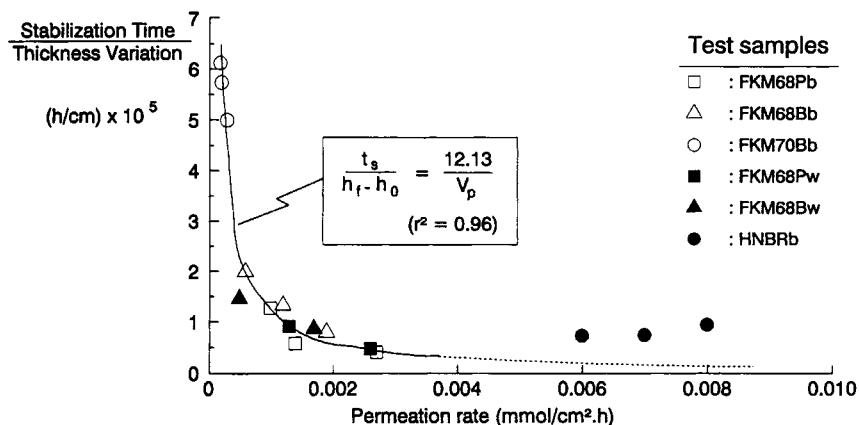


Figure 9. Relationship between the stabilization time and the permeation rate for various FKM.

i.e., $t_i / (h_i - h_0)$, to fit the same relationship. The thickness h_i at time t_i can be estimated with respect to the observed swelling kinetics of FKM membranes in methanol-containing fuels, as previously reported.⁷ With respect to the expected swelling curve drawn in Figure 8, the membrane swelling can be modeled with a relatively simple equation using the available experimental data, i.e.:

$$h = h_0 + (h_f - h_0) \left[1 - \left(\frac{t_s - t}{t_s} \right)^m \right]$$

where h = membrane thickness at time t
 t_s = stabilization time (h)
 h_f = final thickness (cm)
 h_0 = initial thickness (cm)
 m = swelling kinetics coefficient

In such a model the swelling kinetics (from the initial thickness h_0 to the final thickness h_f) depends on the coefficient m and on the stabilization time t_s . With respect to the observation that fluid absorption processes in the earlier stage are proportional to the square root of time,¹⁰ the most logical choice for m is 2, since a time difference ($t_s - t$) is considered in the model. Plots of this relationship for various values of the h_0 , h_f , and t_s give indeed smoothly increasing curves corresponding well with the observed swelling kinetics. The actual thickness h_i at time t_i , were then calculated for all the tested membranes and, as shown in Figure 10, the ratio $t_i / (h_i - h_0)$ gives data point that fit nearly the same curve as the ratio $t_s / (h_f - h_0)$. The permeation rate appears thus as the key parameter, controlling not only the passage of methanol molecules through the

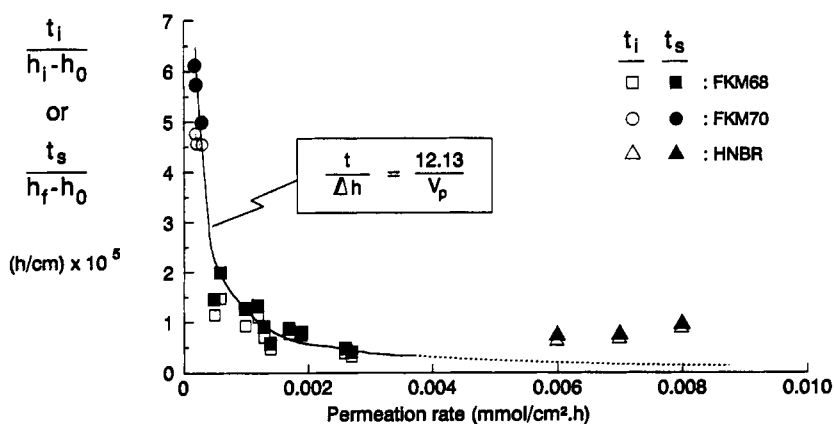


Figure 10. Relationships between the induction and stabilization times and the permeation rate for various FKM.

FKM membranes but also the swelling mechanism itself, since all test results fit the following simple equation

$$\Delta h = \frac{tV_p}{12.13}$$

where Δh = thickness variation (cm) at time t

t = time (h)

V_p = permeation rate (mmol/cm² h)

CONCLUSIONS

The permeation cell technique allows more information to be obtained than standard methods on the behavior of elastomer products exposed to (nonchemically destructive) fluids. Several permeation parameters can be assessed, i.e., the induction time, the stabilization time, and the permeation rate. Furthermore test results can be interpreted with respect to two concomitant physical phenomena taking place during the process: (i) the swelling of the membrane as the fluid penetrates into it and (ii) the permeation itself. The swelling clearly competes with the permeation process until the former is completed, i.e., until an equilibrium swollen state is achieved.

Through a suitable data treatment, it has been demonstrated that the permeation rate—which can be readily assessed when the swelling is completed—is the key parameter of the whole process. For a given type of rubber, it has been shown that the actual thickness at any time during the swelling stage can be assessed with a relatively simple model, providing the stabilization time and the final swollen thickness is known. Moreover the thickness variation is essentially controlled by the permeation rate for a given type of rubber, whatever the formulation of the compound.

According to the reported results and the phenomenological model for the permeation, all observed effects are clearly understood. Since swelling

and permeation are related phenomena, the parameters affecting the former affect also the later. While further works with other families of polymer should be made to confirm the general validity of the reported observation, it is nevertheless clear that any realistic mathematical simulation of the permeation–swelling processes of fluids through elastomer membranes should take into consideration the concomitant physical phenomena as identified with the testing technique described.

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REFERENCES

1. P. E. Cassidy, T. M. Aminabhavi, and J. C. Brunson, *Rubb. Chem. Technol.*, **56**, 357 (1983).
2. P. E. Cassidy and T. M. Aminabhavi, *Rubb. Chem. Technol.*, **59**, 779 (1986).
3. P. E. Cassidy, T. M. Aminabhavi, and M. C. Thompson, *Rubb. Chem. Technol.*, **56**, 594 (1983).
4. E. Southern and A. G. Thomas, *Trans. Faraday Soc.*, **63**, 1913 (1967).
5. I. A. Abu-isa, *Rubb. Chem. Technol.*, **56**, 135 (1983).
6. Y. Khatir, J. Bouzon, and J. M. Vergnaud, *J. Polym. Eng.*, **7**(4), 275 (1987).
7. J. L. Leblanc, Resistance of Fluoroelastomers to Methanol Containing Fuels—Chemical and Physical Aspects of the Problem, SAE Intern. Congress, Feb. 26–March 2, 1990, Detroit, Michigan, Paper Nr 900197.
8. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Clarendon Press, Oxford, 1975.
9. D. W. Van Krevelen, *Properties of Polymers*, 2nd ed. Elsevier, New York, 1976, Chapter 18.
10. G. J. Van Amerongen, *Rubb. Chem. Technol.*, **37**, 1065 (1964).
11. H. L. Frisch, *J. Chem. Phys.*, **61**, 93 (1957); **62**, 401 (1958); **63**, 1022 (1959).

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