Review of the Permeation of Organic Substances through Rubber Latex Films

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Literature describing experimental methods, reporting data and discussing theory relating to permeation is reviewed Emphasis is placed on data from natural rubber latex films and comparison of such films with other materials used in elastomeric gloves In total, permeation data for 40 permeants and 30 glove materials is covered Large discrepancies are noted in results obtained from different laboratories and these can only partly be attributed to differences in experimental methods Overall, natural rubber generally provides better resistance than silicone or PVC materials but are inferior to nitrile or Neoprene-based materials, particularly in resistance to hydrocarbons Theories describing permeation rate and lag time in terms of Ficks laws are described, and the dependence of diffusion coefficient on concentration is discussed

One of the major uses for natural and synthetic rubber latices is in the production of gloves for barrier protection. Barrier protection is taken to mean providing both a physical and a chemical barrier It is well known that properly made rubber gloves provide an excellent physical barrier, even to sub-micron sized particles the size of the AIDS virus, HIV. The effectiveness of glove materials as barriers to small molecules such as solvents, however is seldom complete because of the ability of these molecules to diffuse through the polymer itself. A considerable amount of work has been carried out on measuring and understanding the permeation of substances through rubber films or membranes The research falls into two distinct categories Firstly, there are empirical studies aimed at evaluating the barrier performance of various types of gloves and other similar products The other area of interest has been in understanding and developing the theory of permeation. This review aims to cover both areas of research,

with particular emphasis on the behaviour of films made from natural rubber latex

When a polymer membrane is challenged by a fluid (liquid or vapour), the permeation behaviour is generally described by the curves given in *Figures 1* and *2*. The two important characteristics of any membrane/permeant combination are the steady-state permeation rate and the breakthrough and/or lag time These terms will be used throughout this review

EXPERIMENTAL METHODS

The methods used to determine permeation characteristics of elastomeric materials have been reviewed recently[1] The principle in all of the methods is that a sample of the material with defined surface area is held firmly in a device usually called a permeation cell The permeating substance is admitted on one side of the membrane and some detection system detects the substance on the other side. Two

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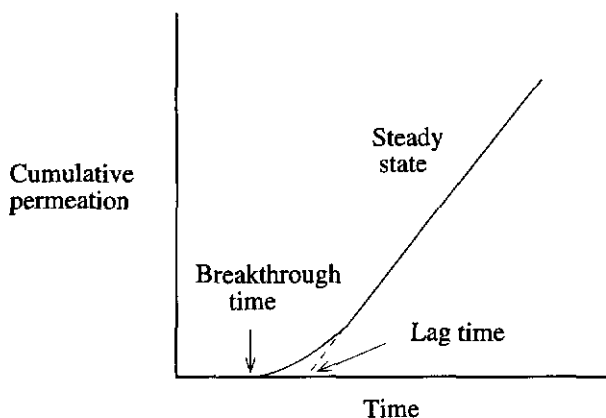**Rubber Research Institute of Malaysia, P O Box 10150, 50908 Kuala Lumpur, Malaysia

Figure 1. Model permeation curve showing cumulative permeation against time.
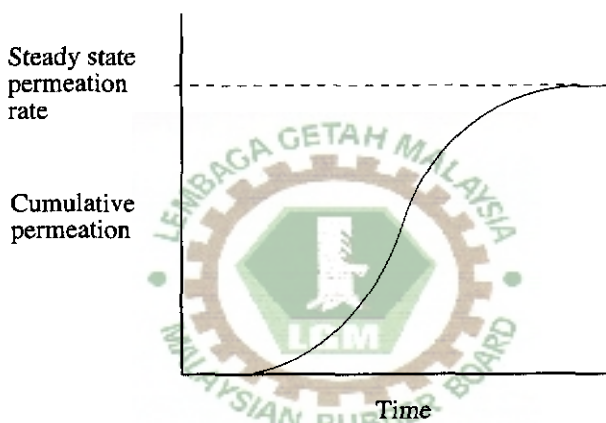

Figure 2. Model curve of permeation rate against time.

fundamental types of permeation cell exist. The preferred type is the open-loop set-up in which permeant is continuously removed from the reception side of the membrane and taken to a detector so that no build up in concentration is allowed. The alternative type of permeation cell is the closed-loop cell. In this set-up the collection chamber is essentially closed and concentration determination is carried out either continuously or periodically on that chamber's contents. This close-loop arrangement requires a different theoretical treatment which has been well covered in a recent review[2].

A number of standard permeation cells have been described in recent years. The first was documented in the *ASTM* test method[3] of 1981

which has since been twice updated[4], and also appears in *EN 374-3:1994*[5]. An alternative method was developed by the British Occupational Hygiene Technology Committee[6] and submitted to both the *BSI* and *ISO*. This cell has been described in recent European and *ISO* Standards[7]. A number of variables still exist when a standard cell is used and a standard procedure followed. The chief variables are the nature of the collecting medium, temperature, collecting medium flow rate and method of analysis. The dependence on temperature is unsurprising since diffusion is known to be temperature dependant. The nature of the collection fluid and its flow rate however, should ideally not affect the results as the aim is to maintain zero concentration of the permeant at the membrane surface. In practice, an infinite flow rate would be required to achieve that situation. If non-standard cells are used, exposed sample area, collecting chamber volume and sampling mode become other important variables. It has been necessary to use cells other than of a standard design, for example for the study of highly toxic or hazardous chemicals[8], or for testing of complete gloves[9].

A number of comparisons have been made between different permeation cells and the effect of different variables on the results. The most complete study is that by Mellstrom who tested both the two standard cells and another cell design with gaseous collection in an open-loop[10]. The main findings were that breakthrough times were little affected by cell design or collection gas flow rate within reasonable limits (120–500 ml/min through the *ASTM* and *ISO* cells) but that steady-state permeation rates were dependant on cell design and gas flow rate. For example, the *ISO* cell at 500 ml/min gave permeation rates 2.6-5.2 times higher than those obtained from the *ASTM* cell at 120ml/min. It was found that the two important factors affecting permeation rates in open-loop systems

are the exposed surface area of the test piece and the collecting fluid flow rate.

The method of detection chosen for permeation studies depends on the nature of the permeant, whether an open- or closed-loop is used and whether continuous or periodic monitoring is required. In the simplest open-loop set-up, the reception side can be open to the atmosphere and permeation levels measured by weight changes[11-13]. Likewise, the amount of permeated substance in a simple closed-loop system can be measured by pressure changes in the closed reception chamber[14]. The preferred method of analysis for quantitative work with an open-loop is flame ionisation detection, usually *via* a gas chromatograph (GC)[1,15-18]. Infra-red[18-20] and ultra-violet[18] analytical methods have also been employed for the same purpose. Specific, non-continuous detection methods have been used for the detection of specific permeants. These include charcoal air-sampling tubes[16], Drager tubes[16], mutagenicity testing[21] and non-continuous gas chromatograph analysis[22].

Permeation Data for Elastomeric Glove Materials

The most comprehensive study of the permeation behaviour of glove materials, in terms of materials covered, is that by Nelson *et al.*[19] The breakthrough times and steady-state permeation rates of 29 common organic chemicals through 28 different glove materials were determined. Six of the gloves tested were made from natural rubber latex, seven from Neoprene and the others were made from nitrile, PVC, polyethylene or a Neoprene/natural rubber blend. It was found that both breakthrough times and permeation rates varied considerably, even between gloves made from the same polymer. Glove thickness was identified as one important variable. Tests on materials of identical origins with different

thicknesses revealed the inverse propor-
tionality of permeation rate with thickness
expected from theory[19]. Whilst thickness was
an important factor, it could not account for all
of the differences in permeation rates between
gloves of the same polymer composition
(*Table 1*). Clearly, factors other than the nature
of the polymer are important in determining
permeation characteristics.

Breakthrough times for the various
substances through the six types of natural
latex gloves could be grouped into three
categories (*Table 2*). More precise ranking of
breakthrough times could not be achieved
because of discrepancies between different NR
gloves. Also the differences in breakthrough
times between different solvents tended to be
small. Overall, *some correlation seems to exist*
between breakthrough time, permeation rate
and permeant polarity. Thus, non-polar
solvents tend to have short breakthrough times
and high permeation rates whilst more polar

substances have longer breakthrough times and
lower rates. Within the overall trend however,
some anomalies exist. For example,
cyclohexane, carbon tetrachloride and xylene
are generally considered to be non-polar, yet
are in the intermediate group with respect to
breakthrough times whilst butyl acetate, which
is more polar than many of the other permeants
studied, has one of the highest permeation
rates.

Molecular weight or molecular size of
permeant does not seem to be an important
factor in determining breakthrough time or
permeation rate. Toluene and phenol, which
have almost the same molecular weight and
similar molecular structures, have widely
differeing breakthrough times. Even for
homologues with the same functional group,
molecular weight does not seem to be the
decisive factor. This is illustrated by the
permeation rate of methyl ethyl ketone being
higher than that of acetone, and that of ethanol

TABLE 1. SELECTED PERMEATION DATA FOR ORGANIC SOLVENTS
THROUGH NATURAL RUBBER GLOVE MATERIALS[a]

Glove number	1	2	3	4	5	6
Av. thickness (mm)	0.21	0.31	0.47	0.52	0.45	0.59
Permeation rate (μg/min/cm^2)						
Acetone	210	110	82	46	66	45
Butyl acetate	2900	1400	940	640	880	510
Chloroform	15	4	7.6	4.4	5.6	7.0
Ethanol	14	4	<4	<4	<4	<4
Toluene	9.2	4.7	2.7	3.8	3.6	2.8
Breakthrough time (min)						
Acetone	2.2	5.2	6.0	8.0	15	27
Butyl acetate	2.0	4.0	6.4	9.2	8.0	14
Chloroform	0.8	1.6	2.6	6.4	3.2	2.8
Ethanol	12	28	>60	>60	>60	>60
Methanol	2	20	>60	24	18	>60
Toluene	0.5	2.0	3.5	5.0	3.0	4.1

[a]Reference 19

TABLE 2. OVERALL RANKING OF PERMEATION RATES AND BREAKTHROUGH TIMES OF
ORGANIC SOLVENTS THROUGH NATURAL RUBBER GLOVES[a]

	Breakthrough time		Permeation rate
Short	Pentane Toluene Methylene chloride Chloroform Trichloroethylene Benzene Methyl iodide Ethylene dichloride Tetrahydrofuran		Pentane Cyclohexane Butyl acetate Freon TF Isoamyl acetate Methyl ethyl ketone Dioxane Acetone Tetrahydrofuran
Medium	Acetone Butyl acetate Carbon tetrachloride Cyclohexane Methyl ethyl ketone Pyridine Tetrachloroethane 111-Trichloroethane Xylene Dioxane Isoamyl acetate Freon TF	Increasing rate	Methyl iodide Trichloroethylene Chloroform Carbon tetrachloride Methylene chloride Benzene Tetrachloroethane Toluene 111-Trichloroethane Xylene Aniline m-Cresol
Long	Aniline m-Cresol Ethanol Ethylene glycol Methanol Phenol Trifluoroethanol Dimethyl sulphoxide		Dimethyl sulphoxide Ethanol Ethylene dichloride Ethylene glycol Methanol Phenol Pyridine Trifluoroethanol

[a]Reference 19

being higher than the permeation rate of methanol. Although the overall trend for permeation rates is the same as that for breakthrough times, no clear correlation can be established between the two parameters. The relatively high permeation rates of the esters butyl acetate and isoamyl acetate, for instance, does not tie in with either the moderate breakthrough times or the known polarity of these compounds. Yet the fact that both of the

esters tested exhibited similar behaviour suggests that it is more than an anomaly of a particular solvent.

A comparison of the data obtained from NR glove materials with those from synthetic glove materials (*Tables 3* and *4*) shows that natural rubber performs reasonably well against most permeants. For example, acetone has a longer breakthrough time for NR than for

TABLE 3. PERMEATION RATES OF SELECTED SOLVENTS THROUGH FOUR TYPES
OF GLOVE MATERIAL OF SIMILAR THICKNESS[a]

Material	NR	PVC	Neoprene	Nitrile
Thickness (mm)	0.31	0.31	0.29	0.32
Acetone	110	C	140	1500
Butyl acetate	1400	3300	350	880
Chloroform	4	5.4	4.4	7
Ethanol	4	28	<4	<4
Methanol	8	18	<4	29
Toluene	4.7	2.1	2.5	0.8
Pentane	2700	100	21	10

[a]Reference 19
All figures are in $\mu g/min/cm^2$
C indicates catastrophic failure

TABLE 4. BREAKTHROUGH TIMES OF SELECTED SOLVENTS THROUGH
FOUR TYPES OF GLOVE MATERIAL OF SIMILAR THICKNESS[a]

Material	NR	PVC	Neoprene	Nitrile
Thickness (mm)	0.31	0.31	0.29	0.32
Acetone	5.2	C	16	3.0
Butyl acetate	4.0	2.4	11	20
Chloroform	1.6	0.4	3.6	4.4
Ethanol	28	11	>60	>60
Methanol	20	3	>60	39
Toluene	2.0	2.9	4.0	10
Pentane	1.7	9.2	20	5.6

[a]Reference 19
All figures are in minutes
C indicates catastrophic failure

nitrile, and a lower permeation rate through NR than through Neoprene or nitrile. It is only in resistance to permeation by hydrocarbons like toluene and pentane that the oil-resistant materials clearly outperform NR.

Permeation of hydrocarbon liquids through elastomeric materials was the subject of a separate study[11]. Permeation rates of benzene, cyclohexane, heptane and isooctane through 10 different rubber materials were measured. The results (Table 5) show that natural rubber provided less resistance to permeation than any of the synthetic rubbers apart from silicone. The permeation rate of benzene was about twice as high through NR as it was through

TABLE 5. RELATIVE PERMEATION RATES OF FOUR HYDROCARBONS
THROUGH VARIOUS ELASTOMERS[a]

Elastomer	Benzene	Cyclohexane	Heptane	Isooctane
Hexafluoropropylene/vinyl-idine fluoride copolymer	1	1	1	1
Nitrile (48% acrylonitrile)	439	2	2	1
Polysulphide	300	90	40	24
Nitrile (32% acrylonitrile)	1418	365	220	50
Chlorosulphonated PE	104	5000	1000	240
Polyurethane	1525	6000	2000	1000
Polychloroprene	1739	24000	6000	1000
SBR	2832	182000	117000	40000
NR	2714	327000	315000	294000
Silicone (50 Shore A)	4070	1120000	1580000	2580000

[a]Reference 11

TABLE 6. PERMEATION CHARACTERISTICS OF A PARTICULAR NITRILE GLOVE
OBTAINED FROM SEPARATE STUDIES

Reference	Breakthrough time (min)	Steady-state permeation rate (μg/min/cm²/mm)
9	3.84	3.4
15	2.80	43.1
23	2.61	67.2
24	1.27	21.0

Neoprene, nitrile or polyurethane, but the difference was much greater for the saturated hydrocarbons. These results provide further proof, if required, that natural rubber provides a poor barrier to hydrocarbon solvents.

Jencen and Hardy measured the permeation characteristics of six common solvents through NR, polyurethane, polychloroprene, PVC and nitrile materials[15]. In general, breakthrough times were shorter and permeation rates higher for NR than for the other materials except for PVC. Some of the data obtained for poly-urethane were also inferior to comparable NR

results. This study was able to identify several elastomer/permeant combinations which had been examined by other researchers in the field, allowing direct comparison of data. Such a comparison gives cause for concern. For instance, a particular nitrile glove (*Edmont 37-175*) was studied by four different groups with widely differing results *(Table 6)*.

A possible reason for such large discrepancies is provided by Henry and Schlatter[18] who studied the permeation of toluene and dimethylformamide through three types of elastomeric material. Using the same

basic equipment, major differences in results were found between experiments when different collecting fluids or different methods of analysis were used. For example, the permeation rate of toluene through Neoprene was found to be 2727 mg/min/cm^2 with isopropanol as the collection fluid and GC detection. When UV detection was employed with the same collection liquid, the respective result was 400 mg/min/cm^2. With IR detection and nitrogen as the collection fluid, a higher permeation rate of 3502 mg/min/cm^2 was recorded. Different laboratories using exactly the same protocol generally produced permeation rates agreeing within 20%-30%. Breakthrough times however, tended to vary widely between laboratories, even when measured under nominally identical conditions.

One further wide-ranging permeation study reported in the literature covers the permeation of four solvents through eleven different glove materials, excluding NR[16]. The solvents were benzene, chloroprene, dichloromethane and carbon tetrachloride, and the best glove material in terms of overall solvent resistance was a supported PVA glove. Polychloroprene gloves performed worst in this particular study. Other studies in this area provide qualitative or semi-quantitative data for solvent permeation through elastomeric materials[12,13,27,28].

Taken together, the research described above has reported permeation data for a total of 40 common organic liquids through at least 30 glove materials covering all of the major polymers. Other papers have reported data of a more specialised nature, generally where a practical need for barrier protection existed. The permeation of several N-nitrosamines through glove materials has been studied[22] as has that of the petrol additives ethylene bromide and tetraethyllead[25]. In the medical field, Laidlaw *et al.* obtained qualitative data on the permeation of 20 antineoplastic drugs through latex and PVC gloves[21]. Another investigation produced semi-quantitative data for the permeation of fluorouracil and methotrexate through the same materials[26], those being the glove materials normally encountered in medical environments.

The overall picture which emerges from the permeation testing of a wide range of materials by various laboratories is characterised by the following features:

• Breakthrough times generally exhibit poor reproducibility and poor agreement between laboratories. This parameter seems to be critically dependent on experimental protocol as well as being seriously affected by minor differences in sample characteristics such as surface irregularities.

• Steady-state permeation rates show reasonable consistency and agreement between laboratories provided the same experimental conditions are used. Differences in some of the important experimental conditions however, such as the collecting fluid or detection method, can lead to widely differing results.

• Natural rubber based materials show good permeation resistance to polar liquids such as alcohols, phenols, amines and dimethyl sulphoxide, but poor resistance to hydrocarbons, particularly the aliphatics.

• The permeation resistance of NR latex-derived glove materials to most organic solvents is generally inferior to that of Neoprene and nitrile based products but better than that of silicone or PVC materials. Polyurethane materials perform better than NR under some circumstances but worse under others.

Theory of Permeation

The theory of permeation in general, and permeation of organic molecules through elastomeric films in particular, has been covered in a number of excellent reviews[2,29,30]. The theory will not be covered in detail in this review, but certain aspects which are particularly relevant will be highlighted.

Permeation can be considered as consisting of three distinct processes, namely absorption at one face, diffusion through the polymer layer and evaporation or desorption at the other face.

Desorption does not generally play a significant part in the overall process, so that permeation is usually described by the solution-diffusion model. The diffusion of liquids through polymers which are well above their glass transition temperature is known to be Fickian in character, so equations derived from Fick's first and second laws are applicable. The permeation rate, q is therefore given by:

$$q = -D \frac{dc}{dx} \qquad \ldots 1$$

where D is the diffusion coefficient and dc/dx is the concentration gradient acorss the membrane.

Integration of *Equation 1* between c_1 and c_2 with l as the membrane thickness we obtain:

$$q = \frac{D (c_1 - c_2)}{l} \qquad \ldots 2$$

where D is in fact an average diffusion coefficient.

The specific permeation rate, Q is defined as:

$$Q = ql = D (c_1 - c_2) \qquad \ldots 3$$

If $c_1 \gg c_2 = 0$ as is usually the case, then

$$Q = Dc_1 \qquad \ldots 4$$

In the case where the exposed surface of the membrane is in contact with the pure permeant, or at least saturated, c_1 is given by the solubility of the permeant, S. *Equation 4* then becomes:

$$Q = DS \qquad \ldots 5$$

The lag time, L which is defined as the extrapolation of the steady-state portion of the cumulative permeation curve to zero time, can be shown to be:

$$L = l^2 / 6D \qquad \ldots 6$$

The main complication to the theory described above arises due to the concentration dependence of D. In order for a molecule of size comparable to a monomer unit to diffuse through a polymer, co-operative motion of a polymer segment consisting of several monomer units is required. As the concentration of the diffusant increases, the polymer mobility tends to increase, so the diffusion coefficient also increases.

When D is dependent only on concentration, the time lag, L was derived by Frisch[31] as:

$$L = \frac{l^2 \int_0^{c_e} cD(c) \left[\int_0^{c_e} D(u)du \right] dc}{\left[\int_0^{c_e} D(c)dc \right]^3} \qquad \ldots 7$$

where c_e is the equilibrium or saturation concentration.

This equation can, in principle, be converted to find D as a function of concentration. In practice, however, this requires prohibitively accurate knowledge of L. It is more useful as a means of checking whether D is in fact only dependant on concentration.

Breakthrough time which, unlike lag time, can be directly measured experimentally, is a

complex function of several experimental parameters. For any chemical-material pair, breakthrough time is a function of thickness, analytical sensitivity, flow rate and surface area[2]. This parameter has not been amenable to theoretical analysis. It must therefore be accepted that comparison of breakthrough times is valid for comparing permeation behaviour of different materials under the same conditions but not as a means of obtaining fundamental information about a chemical-material pair.

The theory of permeation through polymer blends has been well described in two reviews[32,33] and agreement between theory and experiment is generally good. Most of the blends studied have consisted of synthetic polymers, but Barbier did study the permeability of nitrogen through natural rubber - nitrile rubber blends[34]. Although the author did not analyse the data in terms of a theoretical model, later analysis showed the results to agree well with the Maxwell model theory[33].

In addition to polymer blends, permeation through polymer laminates or composites has been studied from a theoretical point of view. The work of Frisch[35] who first derived expressions for time lags of permeation through laminae, and others is discussed by Barrer[32]. Good agreement has again been found between theory and experiment, including results on the diffusion of propane through natural rubber/ silicone rubber laminates of the AB and ABA types[36].

Date of receipt: June 1994
Date of acceptance: August 1994

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