Water permeation through elastomer laminates: 3. Neoprene/styrene–butadiene rubber

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Permeation rates and activation parameters for the transport of water and 3.5% sodium chloride solution through laminates comprised of Neoprene (CR) and styrene–butadiene rubber (SBR) have been measured at 23°C, 40°C and 60°C. Sodium chloride solution exhibited higher permeation rates than distilled water and the laminates showed a slight directional character with salt water. Also for salt water a reduction of permeation rates compared with the calculated average was observed. However, for the distilled water, essentially no directional behaviour (valving) was observed and no significant differences from calculated averages occurred, except at 60°C. These findings for distilled water are contrary to those found for other laminates. The temperature dependence of permeation rate had an Arrhenius behaviour. Observed activation energies were found to be lower for membranes which exhibited high permeation rates. Furthermore, the measured permeation rates are satisfactorily explained in the light of free volume concepts of diffusion.

(Keywords: permeation; water; laminates; Neoprene; rubber)

INTRODUCTION

Water permeation through exposed rubber surfaces is a major determinant of reliability in underwater devices such as undersea and well-logging cables, sonar transducers, etc. The consequences may range from a just detectable loss in signal-to-noise, to catastrophic failure of the encapsulated component. Several factors must be considered: the rate of permeation *versus* the composition of the elastomer and/or the permeant; the effect of temperature on permeation rate; compositional changes in the elastomer caused by the permeant; and effect of elastomeric stress on permeation. Any process that alters the permeability of the elastomer will, of course, affect all of these factors. Recently[1–5], the ultimate goal of polymer scientists in this area has been to find suitable barriers to water permeation. Great advances are now being made in the development of commercial materials for undersea applications and in accelerated test methods to predict long-term life expectancy.

Previous papers[2,3] in this series involving Neoprene/ethylene-propylene-diene terpolymer (EPDM) and SBR/EPDM laminates, demonstrated a strictly directional behaviour of permeability to distilled water and a 3.5% sodium chloride solution (simulated seawater). As an extension of this research, the permeation properties were studied for single, as well as laminated elastomers comprising Neoprene (CR) and styrene–butadiene rubber (SBR) at 23°C, 40°C and 60°C. Distilled water and a 3.5% sodium chloride solution were used as permeants and permeation rates were measured using the gravimetric cup method (ASTM D1653-72). The effects of temperature and directional flow behaviour of permeants through laminates were studied and the results were discussed on the basis of free volume theories[6–10].

EXPERIMENTAL

Neoprene, SBR, and their laminates were supplied by Mr A. Kutack, Utex, Weimer, Texas. In the processing, a 30.5 cm (12 inch) laboratory mill was used to mix and prepare the rubber compounds for moulding. The compounds were made into 2.0–2.3 mm (0.08 to 0.09 inch) thick sheets and the homogeneous rubber samples were moulded in a 15.25 cm × 15.25 cm (6 × 6 inch) ASTM tensile slab mould. The thickness of the membrane was measured by means of a micrometer within the accuracy of ±0.001 cm. The curing was done at 160°C for about 20 min. Composition and mechanical properties are compiled in *Tables 1* and *2*.

The permeation experiments were carried out by the gravimetric cup method (ASTM D1653-72) with an area of exposure 25 cm². Either distilled water or a 3.5% sodium chloride solution was used as permeant. To eliminate leakage problems a thin layer of silicone RTV sealant was applied along the sealing circular edges of the cups. These cups were then placed in a desiccator over silica gel, and the whole assembly was kept in an oven maintained at the desired constant temperature (23°C, 40°C or 60°C). The weight loss (in mg) was noted daily until equilibrium was reached. Permeation rate $\mathrm{mg\,cm^{-1}\,day^{-1}}$, Q, was calculated from a least-squares analysis of the steady-state portion of a plot of weight loss (in mg) *versus* time (in days) using:

$$\text{Permeation rate} = Q = \frac{qL}{At} = P(p_1 - p_2) \qquad (1)$$

Here, p_1 and p_2 are respectively the vapour pressure (in

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cmHg) on the wet side and on the dry side of the membrane; L and A represent respectively the thickness (in cm) and area (in cm^2) of the membrane exposed to water; q is the amount of liquid (in mg) permeating through the membrane, t is the time (in seconds) and P is called the permeability coefficient, usually expressed in $g\,cm^{-1}\,s^{-1}\,cmHg^{-1}$.

RESULTS AND DISCUSSION

Permeation rates (a phenomenological quantity) and permeation coefficients are presented in *Tables 3* and *4* respectively for distilled water and sodium chloride solutions. It is seen that for all samples studied at different temperatures the observed permeation rates are higher in case of sodium chloride solution than for distilled water. However, at 60°C the differences between salt water and fresh water permeabilities are greatly diminished. This non-equilibrium behaviour may be attributed to be one or more of several causes.

Table 1 Elastomer composition (pHr)[a]

	Elastomer	
Compound	CR	SBR
Ameripol	–	100
Neoprene W	100	–
Zinc oxide	5	5
Stearic oxide	0.5	1
Sulphur	–	2
N550 Carbon black	50	50
Aranox[b]	2	–
NA-22[c]	0.5	–
Magnesium oxide	4.0	–
CBTs[d]	–	1

[a] Parts per hundred of elastomer
[b] *N*-phenyl-*N*′-(*p*-toluenesulphonyl)-*p*-phenylene diamine
[c] Ethylene thiourea
[d] *N*-cyclohexyl-2-benzothiozolesulphonamide

Table 2 Mechanical properties of elastomers

	Elastomer	
Property	CR	SBR
Hardness, Shore A	76	65
% Elongation	190	420
100% Modulus, kPa (psi)	900 (1310)	290 (420)
200% Modulus, kPa (psi)	–	900 (1300)
300% Modulus, kPa (psi)	–	1620 (2350)
Tensile strength, kPa (psi)	2250 (3260)	2270 (3300)
Tear, die C, $kg\,cm^{-1}$ (psi)	54 (300)	61 (340)

Because permeability is a linear function of diffusivity, any change in the latter will have a corresponding effect in the former. The experimental data may be more satisfactorily discussed in terms of the free volume theories of diffusion[6–10]. According to free volume concepts, diffusion or migration is governed by the amount of free volume and size of the migrating molecule. In the system studied here, sodium and chloride ions, being smaller in size than water dipoles, might have moved at a faster rate than water dipoles. While doing so, these sodium and chloride ions might carry the surrounding water hydration layer as a whole unit thus resulting in higher permeation rates in case of sodium chloride solution. Before transport takes place the membrane structure might be in a collapsed form. However, when it is exposed to either water or sodium chloride solution, a swelling takes place due to the expansion of the polymer membrane and due to the availability of more free volume to facilitate the transport of solvent molecules. Theoretically, however, local equilibrium is assumed to occur at all points during the process of diffusion and this equilibrium is equivalent to a swollen state[11,12]. Free volume increases as the temperature increases and the free volume theory therefore predicts that diffusion coefficient increases with temperature thus resulting in an increased permeation rate.

In order to evaluate the effect of temperature on permeation rate the Arrhenius relationship is used. The results summarized in *Tables 3* and *4* show an increase in permeation rate with temperature for elastomers CR, SBR and their laminates. The increase is appreciable for elastomer CR in both distilled water and sodium chloride solution. A slightly smaller increase occurs with SBR. Both laminates, $\overrightarrow{\mathrm{CR/SBR}}$ and $\overrightarrow{\mathrm{SBR/CR}}$, also display increases in permeation rates with increasing temperature. The $\overrightarrow{\mathrm{SBR/CR}}$ with sodium chloride solution shows a greater increase in permeation rate as compared with $\overrightarrow{\mathrm{CR/SBR}}$ laminate, and this difference vanishes when distilled water is used as permeant suggesting that the rate of permeation of water is almost identical for the laminates irrespective of the direction of permeant. This may be due to the fact that there should be some residual charges within the polymer membrane being not much affected in the presence of water molecules. However, no systematic trend in permeation rate versus temperature was observed for any of the membranes studied here. This could have been the result of their nonuniform ageing at higher temperatures[1].

The activation energies E_p shown in *Tables 3* and *4* were

Table 3 Permeation data and activation parameters for elastomer–water system

		Permeation rate ($mg\,cm^{-1}\,day^{-1}$) at			Permeation coefficient × 10^{11} ($g\,cm^{-1}\,s^{-1}\,cmHg^{-1}$) at			
Elastomer	Thickness (cm)	23°C	40°C	60°C	23°C	40°C	60°C	Activation energy[b] ($kcal\,mol^{-1}$)
CR	0.221	0.016	0.085	0.699	8.97	17.82	55.22	20.50 ± 0.25[b]
SBR	0.216	0.011	0.050	0.195	6.17	10.49	15.14	15.08 ± 0.30
$\overrightarrow{\mathrm{CR/SBR}}$[a]	0.394	0.012	0.062	0.275	6.72	13.00	21.36	16.89 ± 0.22
$\overrightarrow{\mathrm{SBR/CR}}$[a]	0.394	0.014	0.061	0.268	7.85	12.79	20.81	15.08 ± 0.20

[a] Direction of flow of permeant through laminates
[b] Standard error at 95% confidence level

Table 4 Permeation data and activation parameters for elastomer–aqueous sodium chloride system

Elastomer	Permeation rate ($mg\,cm^{-1}\,day^{-1}$) at 23°C	40°C	60°C	Permeability coefficient × 10^{11} ($g\,cm^{-1}\,s^{-1}\,cmHg^{-1}$) at 23°C	40°C	60°C	Activation energy ($kcal\,mol^{-1}$)
CR	0.098	0.309	0.861	54.94	64.79	66.86	10.73 ± 0.24
SBR	0.019	0.052	0.200	10.65	10.90	15.53	12.66 ± 0.21
$\overrightarrow{\text{CR/SBR}}$	0.071	0.115	0.252	39.81	24.11	19.57	6.63 ± 0.30
$\overrightarrow{\text{SBR/CR}}$	0.092	0.128	0.270	51.58	26.84	20.97	5.79 ± 0.34

calculated from Arrhenius plots by a linear regression of equation (2).

$$\log p = \log p_0 - \frac{E_p}{2.303\,RT} \tag{2}$$

Several important findings resulted from the data obtained. For both single membranes (CR and SBR) or the laminates, E_p was greater in distilled water than in sodium chloride solution. This is attributed to higher permeation rates of sodium chloride than that of water. However, the numerical values in the range 5–11 kcal mol^{-1} for sodium chloride solution and 15–21 kcal mol^{-1} for distilled water are indicative of the values closer to activated transport mechanism.

Similar to our earlier findings[2,3], the laminates showed a somewhat directional dependence towards permeation rates when sodium chloride solution was used as a permeant, but less than found previously. Intuitively, the permeation rate of a laminate should be the sum (or a weighted sum) of the rates of the individual components, and there should be no dependence on direction of permeation. However, this assumption is apparently too simplistic. For example, when the direction of the flow of permeant is from $\overrightarrow{\text{CR/SBR}}$, it showed a greater resistance (lower permeation rate with sodium chloride solution than for $\overrightarrow{\text{SBR/CR}}$ system). This directional dependence can be best understood by considering the low permeability material (SBR) to be the value of restrictive force in the laminate. If the permeant encounters SBR first, the rate and amount of water transmitted to the CR interface will be low; CR in comparison to SBR has a high permeability, so that the small amount of permeant delivered to it is transmitted rapidly. When the permeant flows in the reverse direction, i.e. when it encounters CR first, the principal consequence will be decreased rate and amount of permeant flow to SBR interface, with SBR then controlling further transmission. Although the elastomer SBR is the controlling component in permeation through the laminate, it is more effective in the $\overrightarrow{\text{CR/SBR}}$–sodium chloride situation than it is in the $\overrightarrow{\text{SBR/CR}}$–sodium chloride situation.

On the other hand, when water was used as a permeant, no significant directional dependency was observed, contrary to earlier work[2,3]. This helps to confirm the above explanation of valving, because for the single layers in fresh water, very little difference is seen in permeation rates. Therefore, neither layer can act as a primary restricting or controlling agent for a less permeable second layer.

Table 5 Calculated permeation rates ($mg\,cm^{-1}\,day^{-1}$)

Temperature (°C)	Roger *et al.*[13,14] formula: Water	Salt solution	Arithmetic mean: Water	Salt solution
23	0.0118	0.029	0.0135	0.0585
40	0.0569	0.0809	0.0675	0.1805
60	0.2767	0.2948	0.4470	0.5305

Furthermore, as is evident from *Table 5*, in all cases the laminates exhibited somewhat lower permeation rates than the arithmetic mean of the individual components. Permeation rates were also calculated for the laminates using Rogers *et al.*[13,14] relation:

$$Rate_{(C)} = L_{(C)}\frac{L_{(C)}}{Rate_{cr}} + \frac{L_{SBR}}{Rate_{SBR}} \tag{3}$$

where *L* is the thickness of the composite (C), CR or SBR and *Rate* is the permeation rate of the composite (C) or the individual membranes. For CR/SBR–water situation the calculated rate (from equation (3)) was very close to the experimentally observed rate but for the CR/SBR–sodium chloride situation no systematic trend in permeation was observed (*Table 5*).

CONCLUSIONS

Results from a study of the transport of water and sodium chloride solution through CR, SBR and their laminates obtained at 23°C, 40°C and 60°C indicated a directional character but only in case of sodium chloride solution. These rates were lower than the arithmetic mean of two single layers and no systematic trend was observed for the theoretically calculated permeation rate. The temperature dependence had an Arrhenius behaviour. Sodium chloride solution had higher permeation rate than distilled water and consequently the calculated activation energies were lower for sodium chloride solution than for distilled water; these values being within the range that follow the activated transport mechanism. The experimental results were explained on the basis of free volume concepts of diffusion.

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