

SHORT COMMUNICATION

Oxygen Transport in Epoxidised Natural Rubber

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Permeability and diffusion coefficients have been measured in the range 30°C to 50°C for oxygen in natural rubber and a series of epoxidised natural rubber (ENR) membranes. The dependence of ENR permeability and diffusivity on level of epoxidation was significant and a reduction of about 96% in diffusivity at 50% epoxidation level was observed.

Epoxidised natural rubber being a 'new' class of rubber has been a subject of extensive investigation related to its mechanical, chemical and physical properties¹⁻⁵. Molecular diffusion study is one area which has received attention but very few studies have been reported apart from that of the air permeation^{1,6}. It is felt that study should be extended to all types of gases because such data are as important for epoxidised natural rubber as they are for the other polymer systems which have already been

established. This paper reports on the first part of our study on the transport of oxygen and the effect of level of epoxidation of the epoxidised natural rubber membranes.

EXPERIMENTAL

Sample

The system investigated was a series of epoxidised natural rubber vulcanisates including

TABLE 1. CURE FORMULATIONS FOR ENR SAMPLES^a

Ingredient and curing	Sample			
	NR	ENR 10	ENR 20	ENR 50
SMR L	100	—	—	—
ENR 10	—	100	—	—
ENR 20	—	—	100	—
ENR 50	—	—	—	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Permanax TQ	2	2	2	2
Sulphur	1.5	1.5	1.5	1.5
MOR	1.5	1.5	1.5	1.5
Cure time at 150°C (min)	21	21	17	13

^aWith permission from the Rubber Research Institute of Malaysia

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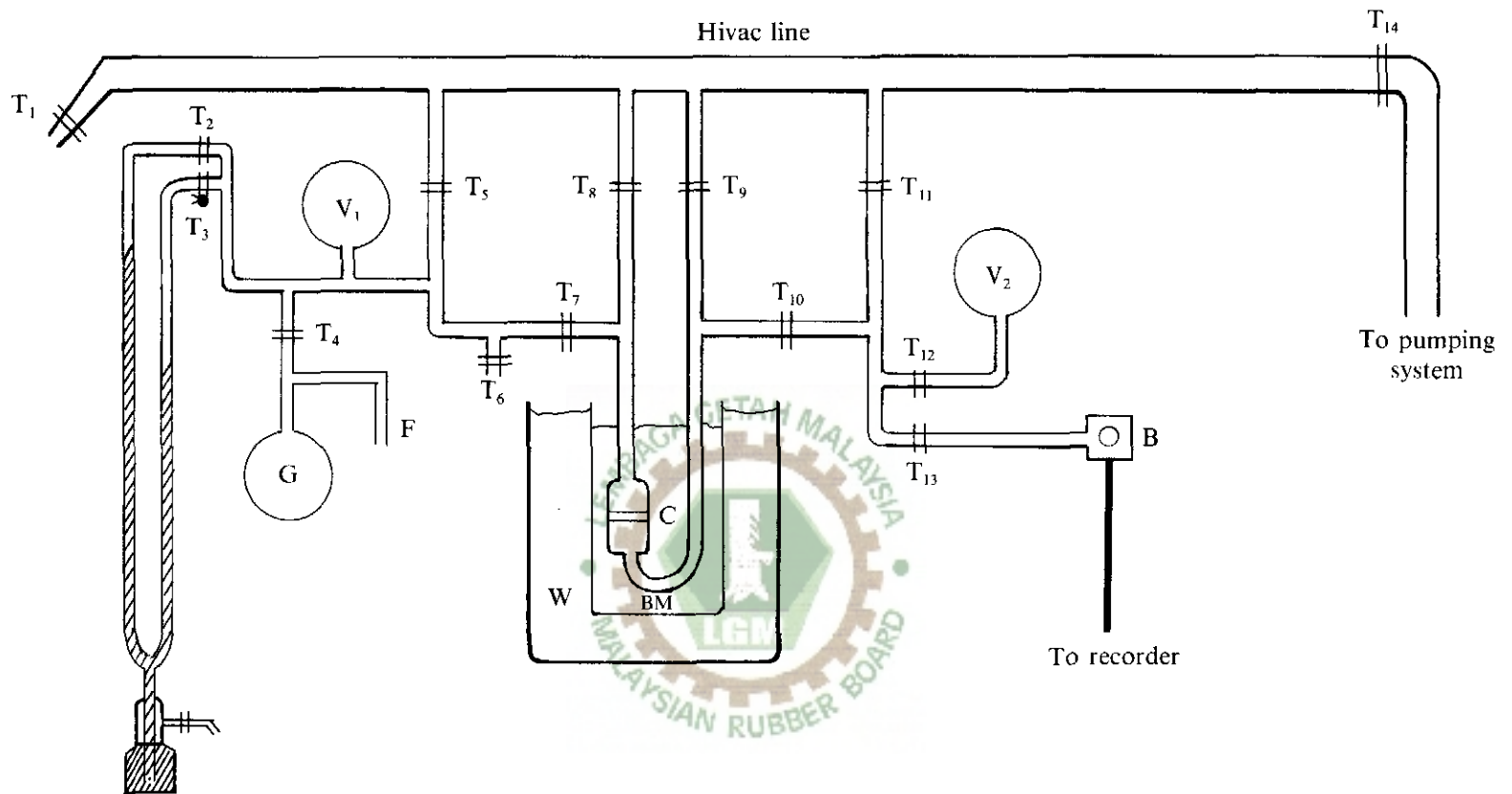


Figure 1. Permeation apparatus.

the natural rubber which were supplied in sheets of thickness in the range 0.70 mm to 0.76 mm by the Rubber Research Institute of Malaysia. All samples, prepared based on the semi-EV system⁶, were crosslinked by hot pressing at 150°C and the exact formulations are shown in Table 1. The notations ENR 10, ENR 25 and ENR 50 denote natural rubber samples with 10, 25 and 50 mol percent epoxidation respectively. A research grade oxygen gas (99.985% purity) was used without further purification.

Apparatus

The permeation apparatus used in the present study is a modification of that used by Barrer *et al*⁷. This is shown schematically in Figure 1.

It comprises essentially of two sections; the high pressure side (the ingoing side) which is connected to the low pressure side (the outgoing side) via a diffusion cell, C. Both sections are connected via taps T_8 and T_9 to the high vacuum line 'hivac' which is serviced by a pumping system. Before making measurements, the membrane was outgassed at 50°C with all taps opened to the pumping system until the 'leak rate', with all taps opened except T_2 , T_3 , T_5 , T_8 , T_9 , and T_{11} , was negligible (generally of the order 10^{-4} mm Hg per hour). During measurement, the ingoing face of the membrane was subjected to a constant pressure of oxygen (pressures used in this work range from 3 cm to 22 cm Hg) and the pressure of the outgoing face was recorded as a function of time by an

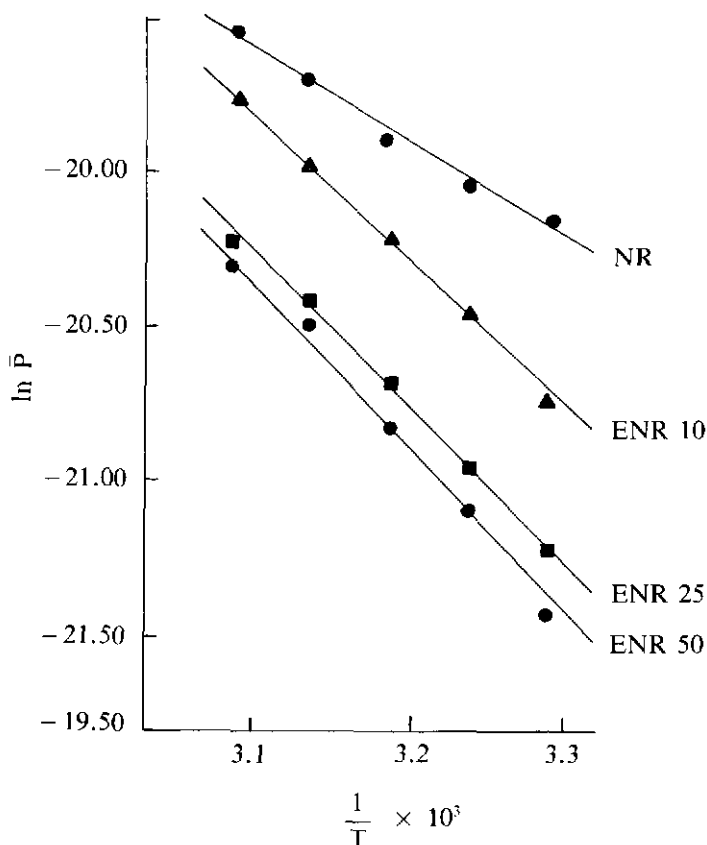


Figure 2. Epoxidised natural rubber oxygen permeabilities.

absolute pressure sensor, MKS Baratron. From the slope of the linear portion of such a plot, the steady-state flux, J (cm^3 stp/ cm^2/s) and

the time lag, L (s), are readily obtained. Measurements were carried out at several temperatures in the range 30°C to 50°C . The

TABLE 2. TRANSPORT PARAMETERS AT 40°C

Polymer	$\bar{P} \times 10^9$ (cm^3 (STP)/ $\text{cm}/\text{cmHg}/\text{s}$)	\bar{E}_p (kJ/mol)	$D \times 10^6$ (cm^2/s)	E_D (kJ/mol)
NR	2.26 (16.95×10^{-17})	26.6	2.40 (2.40×10^{-10})	31.4
ENR 10	1.64 (12.3×10^{-17})	32.2	1.75 (1.75×10^{-10})	34.1
ENR 25	1.02 (7.65×10^{-17})	41.9	1.21 (1.21×10^{-10})	48.6
ENR 50	0.89 (6.68×10^{-17})	44.9	0.08 (0.08×10^{-10})	68.2

Figures within brackets are values expressed in SI units: \bar{P} ($\text{m}^4\text{s}^{-1}\text{N}^{-1}$), D (m^2s^{-1}).

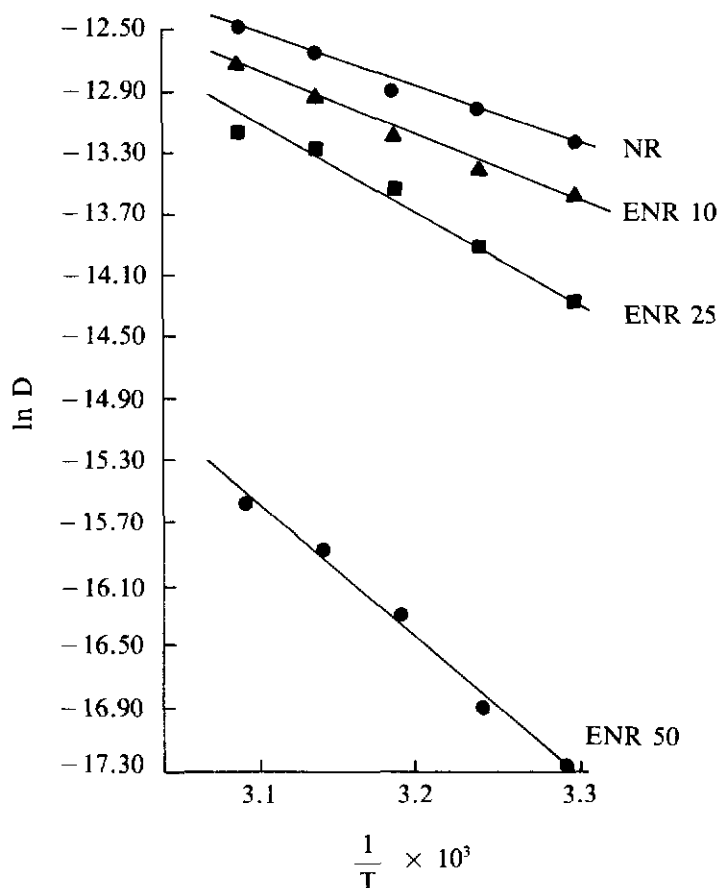


Figure 3. Epoxidised natural rubber oxygen diffusivities.

required temperature was achieved by immersing the cell in a beaker of mercury, *BM*, placed in a water bath, *W*, which was regulated to within 0.01 °C by an integrated heating and stirrer unit, Grant SU 6.

RESULTS AND DISCUSSION

For the natural rubber and the epoxidised samples, permeabilities, \bar{P} , were independent of pressure and obeyed the relation $\bar{P} = \bar{P}_0 \exp(-E_{\bar{P}}/RT)$. The transient diffusion coefficients⁸, \bar{D} , were obtained from the relation $D = l^2/6L$ where L the time lag, was determined from the permeation experiment, and l was the membrane thickness. The diffusion coefficients were in good agreement with the relation $D = D_0 \exp(-E_D/RT)$. The absolute determination of P and D is accurate to 3.0% and 4.8% respectively while the reproducibility of measurements performed with one and the

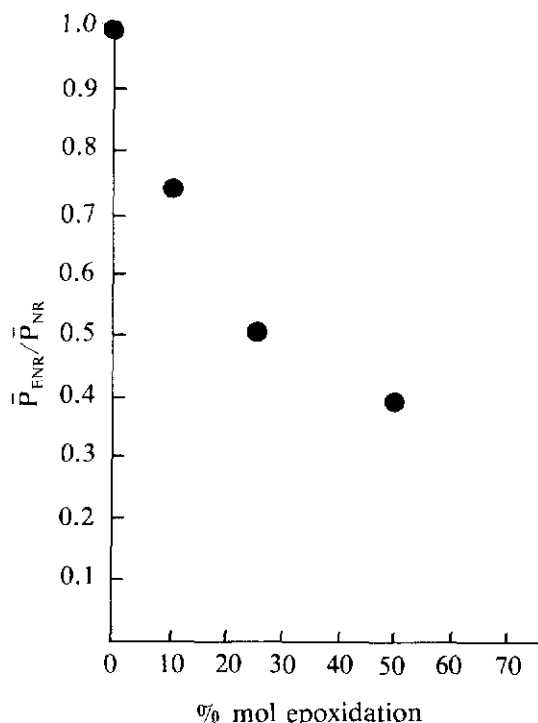


Figure 4. Epoxidised natural rubber permeability ratio at 40.0 °C.

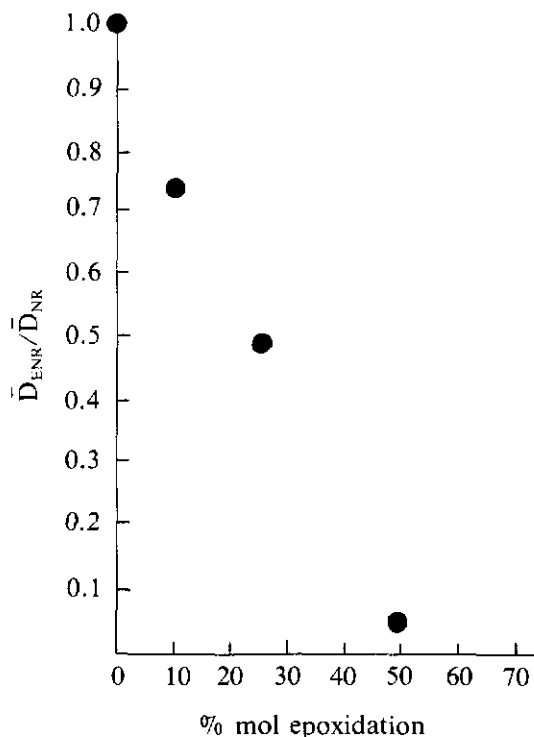


Figure 5. Epoxidised natural rubber diffusivity ratio at 40.0 °C.

same membrane at different pressures is within 1%. The transport parameters are summarised in Table 2. The Arrhenius plots for P and D for all samples are shown in Figures 2 and 3 respectively. The values of $E_{\bar{P}}$ and E_D were computed using the least mean squares method.

The dependence of permeability on the level of epoxidation is shown in Figure 4. Permeability decreases as the level of epoxidation increases. The dependence of diffusivity on the level of epoxidation as shown in Figure 5 exhibits a similar trend with a sudden drop of about 96% in D at 50% epoxidation level. This behaviour is typical of gas transport in heterogeneous polymer systems such as filled rubbers, rubber copolymers and rubber blends in which the dispersed phase is relatively impermeable compared to the continuous phase⁹. In so far as the ENR system is concerned, no occurrence of heterogeneity of the sort related to phase

separation of the rubber chains as a result of epoxidation has ever been reported, except in the stretched ENR⁴. Thus, treatment of the present data based on the empirical relation used by Barrie *et al.*⁹ was not attempted.

The increase in the activation energy of diffusion seems to suggest that more energy is required in order to achieve segmental mobility necessary for the oxygen molecule diffusion as the level of epoxidation is increased. In other words, the observed decrease in diffusivity and increase in its activation energy are likely to be the result of chain stiffening effect imparted by increasing the level of epoxidation. This is in good agreement with the observed linear increase in the glass transition temperature, T_g , with the level of epoxidation^{4,5} which was attributed to the reduction in molecular flexibility probably due to the inter-molecular hydrogen bonding⁴.

In conclusion, the increase in level of epoxidation has decreased the diffusion and permeation of oxygen molecule across the epoxidised natural rubber membranes. Presently, study has been extended to using nitrogen and air with additional samples of higher epoxidation levels and at additional temperatures below 30°C.

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REFERENCES

1. BAKER, C.L.S., GELLING, I.R. AND NEWELL, R. (1985) *Rubb. Chem. Technol.*, **58**(1), 67.
2. GELLING, I.R. (1985) *Rubb. Chem. Technol.*, **58**(1), 86.
3. GELLING, I.R. AND MORRISON, N.J. (1985) *Rubb. Chem. Technol.*, **58**(1), 243.
4. DAVIES, C.K.L., WOLFE, S.V., GELLING, I.R. AND THOMAS, A.G. (1983) *Polim.*, **24**, 107.
5. DAVEY, J.E. AND LOADMAN, M.J.R. (1984) *Br. Polym. J.*, **16**, 134.
6. RUBBER RESEARCH INSTITUTE OF MALAYSIA (1984) *Epoxidised Natural Rubber*.
7. BARRER, R.M. AND SKIRROW, G. (1948) *J. Polym. Sci.*, **3**, 549.
8. BARRER, R.M. (1939) *Trans. Faraday Soc.*, **35**, 628.
9. BARRIE, J.A., MUNDAY, K., KUO, D., JAMIL, I., WILLIAMS, M. AND SPENCER, H.G. (1982) *Proc. 28th IUPAC Macromol. Symp.*, 747.