Gas transport in epoxidized natural rubber

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The diffusion and solution of CO_2 and CH_4 in epoxidized natural rubber has been studied over the temperature range of 30–60°C. The dependence of the solubility constant on the degree of epoxidation is weak for CO_2 and the corresponding dependence of the permeability is determined largely by that of the diffusion constant. For CH_4 there is a significant decrease in the solubility with the degree of epoxidation which can be attributed to the corresponding variation in the heat of sorption.

(Keywords: gas transport; epoxidized natural rubber)

Introduction

Under controlled conditions natural rubber (NR) can be epoxidized to any desired level[1,2]. It is established that epoxidation reduces gas permeability and for levels of epoxidation of ~50 mol% or more the permeability approaches that of butyl rubber. The purpose of this communication is to examine in more detail the dependence of gas permeability on degree of epoxidation and in particular to determine the contributions from the diffusion and solubility coefficients. For this purpose the transport of CO_2 and to a lesser extent CH_4 has been studied in NR and NR with 25 and 50 mol% levels of epoxidation.

Experimental

Thin sheets of NR and of epoxidized NR (ENR25 and ENR50 with 25 and 50 mol% levels of epoxidation, respectively) were supplied by the Malaysian Rubber Producers' Research Association. Each sample was crosslinked with dicumyl peroxide (3 g per 100 g rubber) in the absence of antioxidants. Prior to use the sheets were stored in sealed bags in a refrigerator to minimize degradation. The thickness of the sheets was ~0.1 cm.

Gas permeabilities and diffusion time lags were measured using a conventional vacuum system. The membranes were supported in glass cells with effective cross-sections in the range of 4–6 cm^2. The pressure on the upstream face of the membrane was practically constant. The downstream pressure relative to the upstream pressure was effectively zero and was monitored as a function of time using a capacitance pressure transducer ('Baratron' MKS). The CO_2 and CH_4 were of research grade quality.

Glass transition temperatures (T_gs) were measured with a differential scanning calorimeter (Du Pont 9000) operating with a heating rate of 10°C min^{-1}. The T_gs were -62, -40 and -15°C for NR, ENR25 and ENR50, respectively. As reported earlier, the increase in the T_g with the degree of epoxidation (mol%) was virtually linear[1,2]. The values of the T_gs recorded in this study are ~10°C higher than corresponding literature values reflecting possible differences in heating rates and degrees of crosslinking.

Results and discussion

Steady state permeabilities $\bar{P}$ and diffusion constants D obtained from the time lag were determined at several temperatures over the range of 30–60°C and were independent of upstream pressure. The solubility constant σ was obtained from the relation $\bar{P} = D\sigma$. The system ENR50/CH_4 was studied at 60°C only. The temperature dependence of $\bar{P}$, D and σ was well represented by the expressions, $\bar{P} = \bar{P}_0 \exp(-E_P/RT)$, $D = D_0 \exp(-E_D/RT)$ and $\sigma = \sigma_0 \exp(-\Delta H^\theta/RT)$, respectively. The dependence on degree of epoxidation of $\bar{P}$, D and σ for CO_2 and CH_4 is shown in *Figure 1* and values of the transport and solubility parameters interpolated at 40°C are given in *Table 1*. The standard partial molar free energy of solution is given by $\Delta G^\theta = -RT\ln\sigma$ and corresponds to the transfer of 1 mole of gas at a pressure of 1 cmHg to a solution phase of unit concentration [cm^3(STP) cm^{-3}]. The corresponding entropy of solution was obtained from $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$.

The decrease in D with degree of epoxidation is largely a reflection of the decrease in segmental mobility accompanying epoxidation as indicated by the change in the T_g. This behaviour is also reflected in the increase of the activation energy for diffusion, E_D, with degree of epoxidation. The results indicate that with CO_2 as penetrant the dependence of $\bar{P}$ on the degree of epoxidation is governed largely by that of D. Both the solubility and the standard partial molar heat of solution ΔH^θ are only weakly dependent on the degree of epoxidation.

The process of gas sorption may be considered as comprising two steps, namely, the exothermic absorption of a gas molecule into a 'hole' or region of high free

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Table 1 Values of transport and solubility parameters interpolated at 40°C

Membrane/gas	E_P (kJ mol^{-1})	E_D (kJ mol^{-1})	$10^4\bar{P}_o$ [cm^3 (STP) cm cmHg^{-1} cm^{-2} s^{-1}]	D_o (cm^2 s^{-1})	σ_o [cm^3 (STP) cm^{-3} cmHg^{-1}]	ΔH^θ (J mol^{-1})	ΔS^θ (J mol^{-1} K^{-1})
NR/CO_2	25	39	4.13	7.23	1.3	−12000	−81
ENR25/CO_2	33	45	29.10	22.30	3.3	−14000	−71
ENR50/CO_2	46	60	998.00	1547	2.9	−14000	−74
NR/CH_4	33	37	27.40	2.32	0.0012	−4000	−56
ENR25/CH_4	47	48	977.00	56.40	0.002	−1000	−53

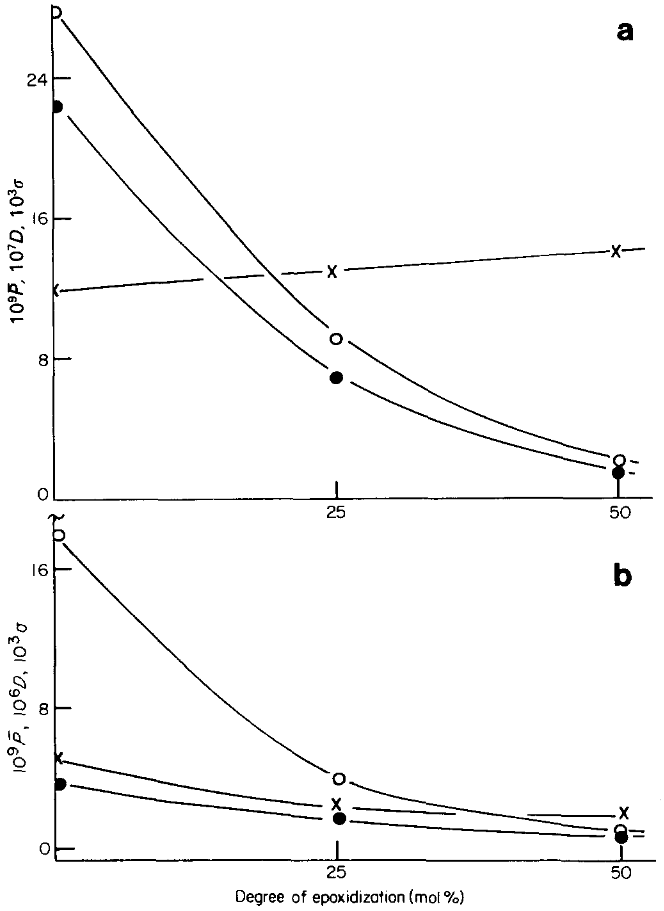

Figure 1 Dependence of $\bar{P}$, D and σ for (a) CO_2 at 40°C and (b) CH_4 at 60°C on the degree of epoxidation: ○, $\bar{P}$; ●, D; ×, σ

volume and the endothermic formation of an equivalent 'hole' in order to maintain the level of free volume at any one temperature. With CO_2 as penetrant the exothermic step is expected to become increasingly exothermic and the endothermic step increasingly endothermic as the degree of epoxidation increases. It would appear that the dependence on the degree of epoxidation in both steps virtually cancel each other to give a heat of solution which is only weakly dependent on the extent of epoxidation but which is decidedly exothermic suggesting that the exothermic step provides the more dominant contribution.

The entropy of 'hole' formation is expected to increase while the entropy of gas sorption into a pre-existing hole may be expected to decrease with increasing epoxidation. For CO_2, these two effects again tend to counteract each other to give a resultant entropy of solution depending weakly on the degree of epoxidation.

For CH_4 the solubility constant is relatively lower and decreases with the degree of epoxidation, also, ΔH^θ is close to zero so that the exothermic step, as expected, is less dominant. The solubility decrease accompanying epoxidation can be attributed to the corresponding variation of ΔH^θ as ΔS^θ is virtually independent of the degree of epoxidation. ΔH^θ tends to become more endothermic with increasing epoxidation which suggests that for the less polar CH_4 molecule the enthalpy of sorption in a 'hole', the exothermic step, does not depend so strongly on the degree of epoxidation as for CO_2.

References

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