

Dimensional response of engineering polymeric elastomers in the presence of halo-substituted benzenes

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Received 20 February 1990; revised 4 September 1990; accepted 22 October 1990

Dimensional response of several engineering polymers in the presence of halo-substituted benzenes has been studied by weight-gain and swelling measurements. The experimental data have been used to estimate the diffusion coefficients, kinetic rate constants, activation parameters and molar mass between crosslinks for all the polymer-solvent systems.

The swelling of a crosslinked network polymeric elastomer by a solvent is one of the possible structural changes which measure the dimensional stability of a polymer in the presence of a solvent. These structural changes require a rearrangement of chain segments which can dominate the sorption kinetic behaviour and solvent transport into the polymer matrix. The mechanism of liquid transport in rubbery polymers has been fairly well understood, yet the exact mathematical modelling of the phenomenon is still not available¹⁻³

Styrene butadiene rubber (SBR), nitrile butadiene rubber (NBR), natural rubber (NR), polychloroprene (CR) and ethylene propylene diene terpolymer (EPDM) have been widely used as engineering polymers. In a variety of applications, these polymers may come into contact with organic solvents in addition to other foreign ingredients. On coming in contact with such liquids, many polymers have a tendency to swell thereby restricting their usage. In view of this, a study has been initiated in our laboratory to assess the transport behaviour of polymer membranes in the presence of organic solvents^{4,7}. In continuation of this work, we now present results of experimental and theoretical studies on the transport characteristics of SBR, NBR, CR, NR and EPDM elastomeric polymer membranes with respect to chlorobenzene, bromobenzene and fluorobenzene.

Materials and Methods

Polymer sheets of SBR, NBR, CR, NR and EPDM in dimensions of $1/16'' \times 6'' \times 6''$ were supplied as gift samples by UTEX Industries, Texas (courtesy of Mr A. Kutac). Mixing and moulding of the polymer compounds was done in a 12'' laboratory mill and the polymer sheets were cured at 160°C for 20 min.

Reagent grade solvents, namely chlorobenzene, bromobenzene and fluorobenzene were doubly distilled before use.

Diffusion experiments

Circular samples of polymers were cut (diameter = 1.94 cm) by means of a sharp-edged steel die and their thicknesses were measured at several points on the membranes using a micrometer (accuracy ± 0.001 cm). The diffusion experiments were performed for each polymer-solvent system by soaking the samples in the respective solvents (≈ 20 ml) taken in test bottles maintained at $25 \pm 0.5^\circ\text{C}$ in a thermostatic oven (Mettler, Germany). The mass-gain of the samples and changes in their thickness were measured at periodic intervals by removing the samples out of the test bottles. Details of the experimental procedures have been published earlier⁴.

Results and Discussion

The output data from a diffusion experiment is the per cent weight gain, $Q(t)$ (expressed as mol per cent increase) and per cent increase in thickness, $L(t)$, of the sample versus square root of time, $t^{1/2}$. Such plots (Fig. 1), referred to as sorption curves, are independent of material thickness for a Fickian diffusion process³. Similarly, the curves for percentage increase in thickness are shown in Fig. 2. It is, however, clear that either $Q(t)$ or $L(t)$ increases linearly with $t^{1/2}$, during early stages of diffusion experiments; at longer time intervals, these curves level off. For all the solvents, either $Q(t)$ or $L(t)$ values are found to be higher in the case of SBR, whereas lower values are observed for EPDM membrane (see Fig. 2). This suggests that EPDM would be a better barrier membrane in view of its lower values of swelling. The sorption behaviour of EPDM and CR membranes is almost identical (see Fig. 1) and the

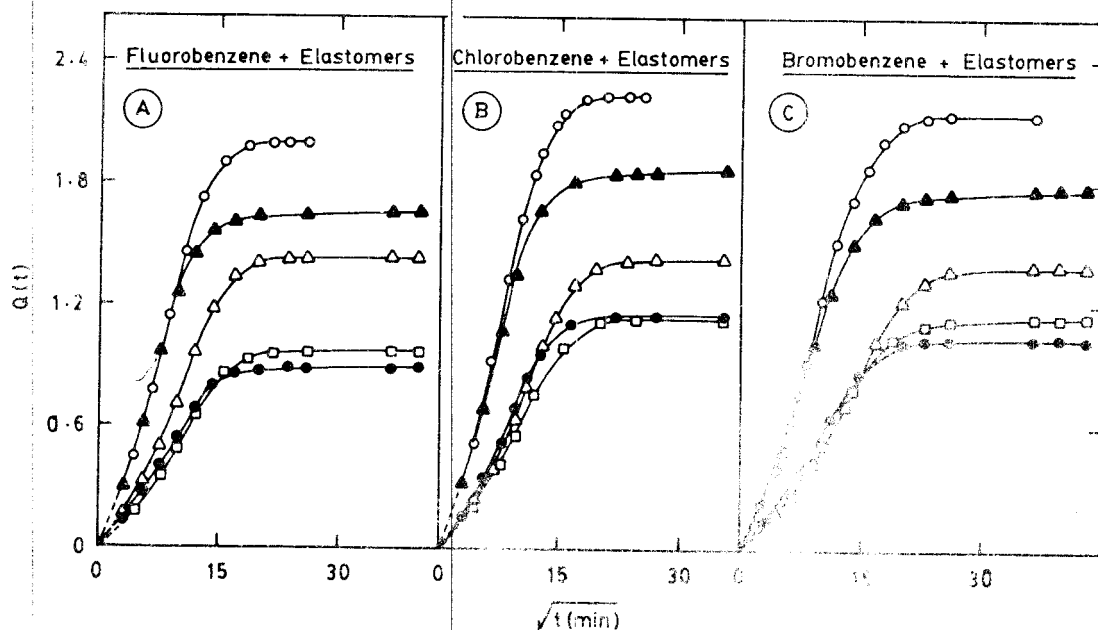


Fig. 1—Sorption curves, i.e., $Q(t)$ vs $t^{1/2}$ for (A) fluorobenzene with (O) SBR, (Δ) NBR, ($\square$) CR, ($\bullet$) EPDM and ($\blacktriangle$) NR; (B) chlorobenzene with the same polymer membranes as in (A); and (C) bromobenzene with the same polymer membranes as in (A).

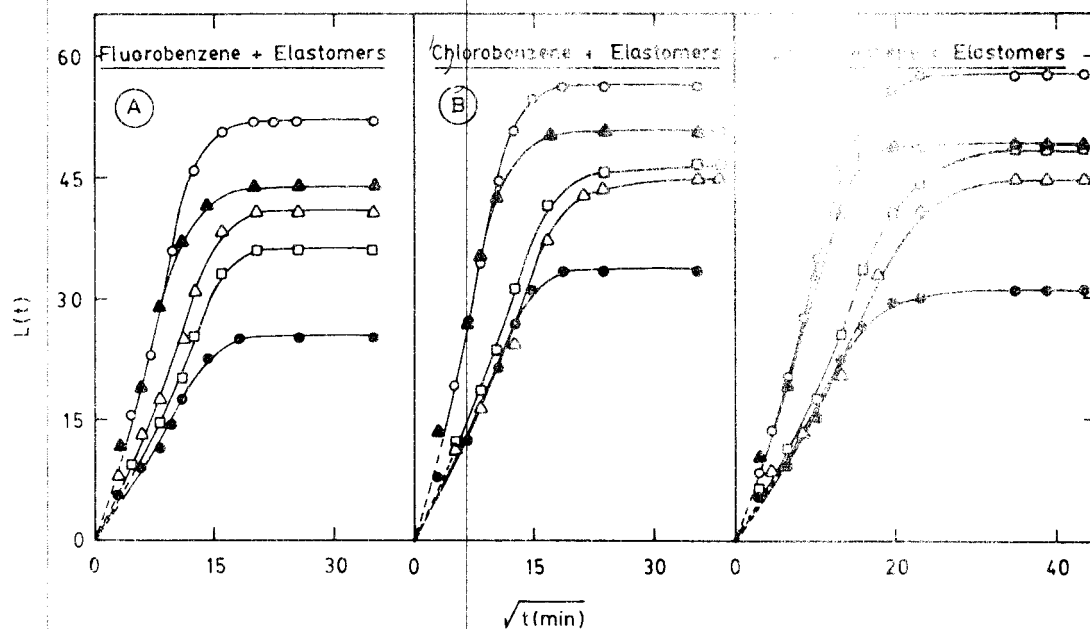


Fig. 2—Sorption curves, i.e., $L(t)$ vs $t^{1/2}$ for (A) fluorobenzene with (O) SBR, (Δ) NBR, ($\square$) CR, ($\bullet$) EPDM and ($\blacktriangle$) NR; (B) chlorobenzene with the same polymer membranes as in (A); and (C) bromobenzene with the same polymer membranes as in (A).

sorption curves for such membranes may be rationalized in terms of chain segment motions relative to the concurrent solvent diffusion rates³.

The sorption curves of Figs 1 and 2 suggest that the transport phenomenon follows the Fickian mechanism. It is, therefore, possible to estimate the

concentration-independent diffusion coefficients⁴ (D_0) by using Eq. 1:

$$D_0 = \pi (h \theta / 4 Q_\infty)^2 \quad \dots (1)$$

where h is polymer thickness, θ is the slope of the initial linear portion of the sorption curves shown in

Fig. 1 and Q_{∞} represents the maximum sorption values (saturation equilibrium values) of the polymer-solvent systems as obtained from the plateau regions.

In an analogous manner, diffusion coefficients can also be estimated from the maximum swelling data (L_{∞}) (see Fig. 2) as⁴,

$$D_L = (h \theta / 4 L_{\infty})^2 \quad \dots (2)$$

where θ is the slope of the initial linear portion of the sorption curves given in Fig. 2. Due to the significant swelling of the polymer samples in the presence of liquids considered, an attempt was made to apply correction to diffusion coefficients, D_L , to include 3-dimensional transport. This can be done by following the procedure suggested by Shen and Springer⁸ for a rectangular geometry of the sample. For disc shaped polymer samples, the modified relation would be,

$$\bar{D}_L = D_L \left[1 + \frac{\bar{h}}{\bar{r}} + \frac{\bar{h}}{2\pi\bar{r}} \right]^2 \quad \dots (3)$$

where $\bar{D}_L$ is the average value of the diffusion coefficient, $\bar{h}$ and $\bar{r}$ represent, respectively, average thickness and radius of polymer samples. The maximum equilibrium data, i.e., Q_{∞} and L_{∞} along with D_O and $\bar{D}_L$ values are summarized in Table 1. It is heartening to note that there is an excellent agreement between the D_O and $\bar{D}_L$ values for the majority of polymer-solvent systems.

From the foregoing discussion, it is apparent that the sorption is a rate controlled kinetic process

which can be studied by the first order kinetic rate equation⁹. Thus,

$$\frac{dc}{dt} = k(C_{\infty} - C_t) \quad \dots (4)$$

where k (min^{-1}) is the first order rate constant; C_t and C_{∞} are the concentrations at time t and at infinite time t_{∞} respectively. Upon integration, Eq. 1 yields,

$$kt = 2.303 \log \left(\frac{C_{\infty}}{C_{\infty} - C_t} \right) \quad \dots (5)$$

In order to investigate the temperature-dependent kinetic rate behaviour, sorption experiments were carried out at 44° and 60°C in addition to room temperature. The estimated rate constants at 25°, 44° and 60°C and the activation energies (E_a) as estimated from the Arrhenius relationship¹⁰ are given in Table 2.

Some useful kinetic plots are given in Figs 3 and 4. From the results of rate constants and activation energies given in Table 2 and evaluated from Fig. 5, we could not conclude any quantitative relationship, yet some general tendencies could be observed. For instance, lower E_a values as observed in the cases of SBR and NR compared to those for CR and EPDM are attributed to the easy transport of solvents through the membranes. This fact is also supported by the higher values of $\bar{D}_L$ or D_O for SBR and NR than those for CR and EPDM membranes. For NBR, however, diffusion coefficients are small and the E_a values are somewhat high (see Table 2).

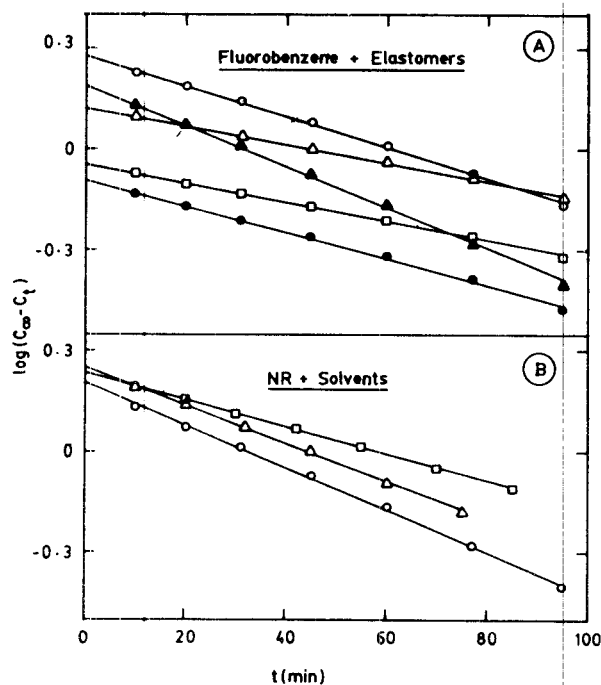
Table 1—Some transport data of polymer-solvent systems at 25°C

Solvent	Property	Polymer membranes				
		NBR	CR	EPDM	SBR	NR
Fluorobenzene	Q_{∞} (mole %)	1.42	0.97	0.88	1.99	1.65
	L_{∞} (%)	40.80	36.10	25.10	51.90	44.10
	$D_O \cdot 10^7$ (cm^2/s)	5.30	6.47	6.94	8.32	10.67
	$\bar{D}_L \cdot 10^7$ (cm^2/s)	4.40	5.52	4.90	6.78	9.75
Bromobenzene	Q_{∞} (mole %)	1.39	1.14	1.03	2.14	1.78
	L_{∞} (%)	44.70	48.40	30.90	57.50	48.60
	$D_O \cdot 10^7$ (cm^2/s)	2.76	4.47	4.91	5.09	5.98
	$\bar{D}_L \cdot 10^7$ (cm^2/s)	2.81	4.04	4.16	8.82	7.51
Chlorobenzene	Q_{∞} (mole %)	1.42	1.14	1.15	2.22	1.87
	L_{∞} (%)	44.90	46.50	33.30	56.10	50.50
	$D_O \cdot 10^7$ (cm^2/s)	4.43	6.55	7.49	8.90	9.93
	$\bar{D}_L \cdot 10^7$ (cm^2/s)	4.20	6.58	3.91	8.01	9.61

Table 2—Sorption kinetic data for polymer-solvent systems, activation energies and molar mass between crosslinks

Polymer	Property ^a	Solvent								
		Fluorobenzene			Chlorobenzene			Bromobenzene		
		25°C	44°C	60°C	25°C	44°C	60°C	25°C	44°C	60°C
NBR	$k \cdot 10^3$	7.29	11.53	16.15	6.47	8.64	11.17	3.68	6.02	8.59
	E_a	18.82 $\pm$ 0.29 ^b			12.87 $\pm$ 0.25			20.11 $\pm$ 0.30		
	M_c	175			589			639		
CR	$k \cdot 10^3$	7.37	9.52	13.22	7.03	9.68	12.88	5.28	7.59	9.45
	E_a	13.64 $\pm$ 0.27			14.24 $\pm$ 0.31			13.80 $\pm$ 0.36		
	M_c	458			820			933		
EPDM	$k \cdot 10^3$	9.59	14.07	19.02	9.66	14.07	17.19	6.95	9.71	13.00
	E_a	16.16 $\pm$ 0.26			13.72 $\pm$ 0.40			14.75 $\pm$ 0.25		
	M_c	819			823			1109		
SBR	$k \cdot 10^3$	11.20	16.01	18.04	11.92	14.35	17.02	7.59	10.46	12.72
	E_a	11.46 $\pm$ 0.24			8.39 $\pm$ 0.31			12.25 $\pm$ 0.22		
	M_c	619			968			1591		
NR	$k \cdot 10^3$	14.56	19.18	23.07	13.36	17.14	19.83	9.19	11.90	14.06
	E_a	10.91 $\pm$ 0.25			9.38 $\pm$ 0.33			10.09 $\pm$ 0.23		
	M_c	871			1333			1728		

^a k in min^{-1} ; E_a in kJ/mol .

^brelative standard error at 95% confidence level.

 Fig. 3—Plots of $\log(C_\infty - C_t)$ vs t for (A) fluorobenzene with elastomers: ($\circ$) SBR, (Δ) NBR, ($\square$) CR, ($\bullet$) EPDM, ($\blacktriangle$) NR; (B) NR with solvents: ($\circ$) fluorobenzene, (Δ) chlorobenzene, ($\square$) bromobenzene.

For a comprehensive understanding of the structure-property relationships of the elastomers in the presence of a solvent, it is necessary to know the magnitude of polymer-solvent interaction parameter (χ) and hence the molar mass between crosslinks (M_c). The criterion for swelling equilibrium was first recognized by Frenkel¹¹ and was later developed by Flory and Rehner¹² (FR). For a successful calculation of M_c by this theory, we need reliable values of χ for the solvent-polymer pair. A number of methods of determining χ have been suggested in the literature¹³. All these methods are empirical and require the use of solubility parameter of the solvent. Instead, we suggest calculation of χ based on the phenomenological approach. This method is based on expressing the FR equation into a derivative of volume fraction of the polymer (ϕ_p) in the completely swollen state with respect to temperature. Thus,

$$\left(\frac{d\phi_p}{dT}\right) = \frac{\chi\phi_p^2/T}{2\chi\phi_p - \frac{\phi_p}{1-\phi_p} - [\ln(1-\phi_p) + \phi_p + \chi\phi_p^2]N} \quad \dots (6)$$

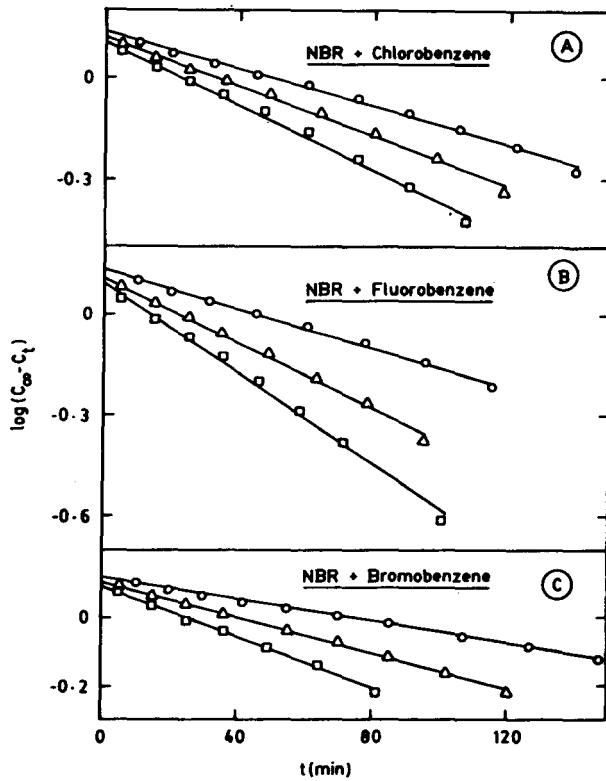


Fig. 4—Plots of $\log (C_{\infty} - C_t)$ vs t for (A) NBR with chlorobenzene at (○) 25°C, (△) 44°C, (□) 60°C; (B) NBR with fluorobenzene at (○) 25°C, (△) 44°C, (□) 60°C; (C) NBR with bromobenzene at (○) 25°C, (△) 44°C, (□) 60°C.

$$\text{where } \left(\frac{\phi_p^{2/3} - 2}{3} \right) \\ N = \frac{(\phi_p^{1/3} - 2\phi_p/3)}{(\phi_p^{1/3} - 2\phi_p/3)} \quad \dots (7)$$

so that

$$\alpha = \frac{(d\phi_p/dT)[\{\phi_p/(1-\phi_p)\} + N \ln(1-\phi_p) + N\phi_p]}{[2\phi_p(d\phi_p/dT) - \phi_p^2 N(d\phi_p/dT) - \phi_p^2/T]} \quad \dots (8)$$

The volume fraction ϕ_p of the swollen polymer can be calculated as:

$$\phi_p = \left[1 + \frac{\rho_p}{\rho_s} \left(\frac{M_a}{M_b} \right) - \left(\frac{\rho_p}{\rho_s} \right) \right]^{-1} \quad \dots (9)$$

Here, M_b and M_a are respectively the mass of polymer before and after swelling, ρ_s is solvent density and ρ_p is density of the polymer (ρ_p values are: SBR = 1.15; EPDM = 1.09; NBR = 1.21; CR = 1.42; and NR = 1.14). Computation of $(d\phi_p/dT)$ can be done from a least-squares fit of the ϕ_p data versus temperature (T).

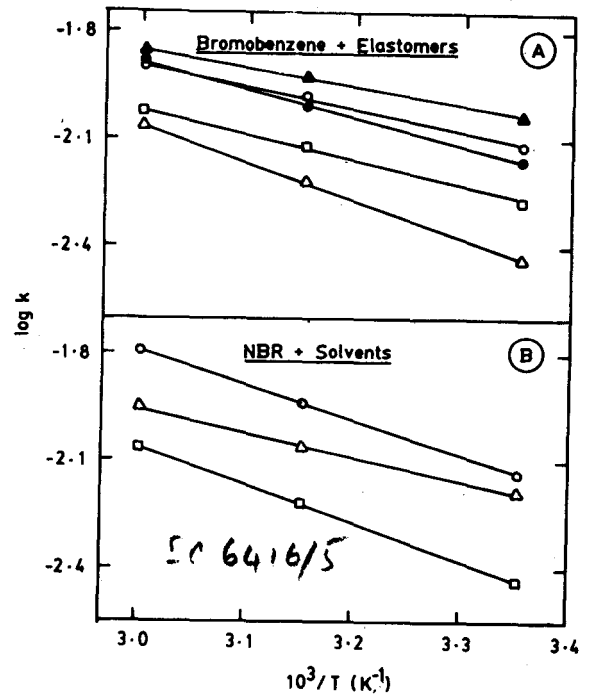


Fig. 5—Arrhenius plots of $\log k$ vs $1/T$ for (A) bromobenzene with elastomers: (○) SBR, (△) NBR, (□) CR, (●) EPDM, (▲) NR; (B) NBR with solvents: (○) fluorobenzene, (△) chlorobenzene, (□) bromobenzene.

The molar mass between crosslinks can then be obtained from the FR model as:

$$M_c = \frac{-\rho_p V_s [(\phi_p)^{1/3} - \phi_p/2]}{[\ln(1-\phi_p) + \phi_p + \alpha \phi_p^2]} \quad \dots (10)$$

where V_s is molar volume of solvent and the parameter α used here has been estimated from Eq. 8. The estimated M_c values are also included in Table 2.

Wide variations in M_c values are observed, which depend on the nature of interacting solvents. For instance, in the case of NBR + fluorobenzene system, M_c is about 175 whereas higher values are observed for NBR with chloro- and bromobenzene, i.e., 589 and 639 respectively. In general, for fluorobenzene, M_c values are smaller than those observed for either chlorobenzene or bromobenzene. To some extent, this discrepancy may be attributed to the limitations of the FR theory.

It should be realized that if we can calculate the α values directly from the classical relationship given by Hildebrand *et al.*¹⁴ based on the solubility parameter concept, further calculations of M_c from Eq. 10 are somewhat identical to those based on our values of α from Eq. 8. For instance, in the case of CR + bromobenzene a value of $M_c = 869$ agrees

somewhat with our calculated M_c (933). At any rate, our method of sorption and hence the computed M_c data given in Table 2 may be regarded as realistic.

The status of the FR theory is still unresolved. It appears that the interaction of the solvent with the crosslinks is different from that with mid chain segments. If this is the case, the elastic modulus may be solvent-dependent because inappropriate account had been taken of the crosslink-solvent mixing term. However, calculations made to estimate α on swelling showed that this is an unlikely source of the limitation of the FR theory. A need for the modification of FR model has been recently suggested¹⁵ in a study where it has been demonstrated that the assumption of separability of mixing and elastic free energies is incorrect. Our present data suggest that the elastic free energy of isotropically swollen elastomer cannot be evaluated without a viable theory. We hope to continue these measurements in the future with other systems to explore the thermodynamic variables which influence such results.

Acknowledgement

The authors appreciate the generous support from the UGC, New Delhi, India in the form of

teacher fellowship to Mr. S.B. Harogopad to study at Karnatak University, Dharwad.

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