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

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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 available.

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. 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.

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 ± 0.5°C in a thermostatic oven (Memmert, 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 earlier.

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 process. 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., $Q(t) \times t^{1/2}$ for (A) fluorobenzene with (○) SBR, (△) NBR, (△) IEM and (▲) 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 (○) SBR, (△) NBR, (△) CR, (●) EPDM and (▲) 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 rates.

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 coefficients $D_0$ by using Eq. 1:

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

(1)

where $h$ is polymer thickness, $\theta$ is the slope of the initial linear portion of the sorption curves shown in
Fig. 1 and $Q_\infty$ 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 ($L_\infty$) (see Fig. 2) as

$$D_L = (h \, \theta / 4L_\infty)^2$$

where $\theta$ 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 Springer for a rectangular geometry of the sample. For disc shaped polymer samples, the modified relation would be,

$$\bar{D}_L = D_L \left[ 1 + \frac{\bar{h}}{\bar{r}} + \frac{\bar{r}}{2 \pi \bar{t}} \right]^2$$

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., $Q_\infty$ and $L_\infty$ along with $D_0$ and $D_L$ values are summarized in Table 1. It is heartening to note that there is an excellent agreement between the $D_0$ 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 equation. Thus,

$$\frac{dc}{dt} = k \left( C_\infty - C_t \right)$$

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

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

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 relationship 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 $D_1$ or $D_0$ 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>
<thead>
<tr>
<th>Solvent</th>
<th>Property</th>
<th>NBR</th>
<th>CR</th>
<th>EPDM</th>
<th>SBR</th>
<th>NR</th>
</tr>
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<tbody>
<tr>
<td>Fluorobenzene</td>
<td>$Q_\infty$ (mole %)</td>
<td>1.42</td>
<td>0.97</td>
<td>0.88</td>
<td>1.99</td>
<td>1.65</td>
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<tr>
<td></td>
<td>$L_\infty$ (%)</td>
<td>40.80</td>
<td>36.10</td>
<td>25.10</td>
<td>51.90</td>
<td>44.10</td>
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<td></td>
<td>$D_0$, 10$^7$ (cm$^2$/s)</td>
<td>5.30</td>
<td>6.47</td>
<td>6.94</td>
<td>8.32</td>
<td>10.67</td>
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<tr>
<td></td>
<td>$\bar{D}_L$, 10$^7$ (cm$^2$/s)</td>
<td>4.40</td>
<td>5.52</td>
<td>4.90</td>
<td>6.78</td>
<td>9.75</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>$Q_\infty$ (mole %)</td>
<td>1.39</td>
<td>1.14</td>
<td>1.03</td>
<td>2.14</td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td>$L_\infty$ (%)</td>
<td>44.70</td>
<td>48.40</td>
<td>30.90</td>
<td>57.50</td>
<td>48.60</td>
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<td>$D_0$, 10$^7$ (cm$^2$/s)</td>
<td>2.76</td>
<td>4.47</td>
<td>4.91</td>
<td>5.09</td>
<td>5.98</td>
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<td>$\bar{D}_L$, 10$^7$ (cm$^2$/s)</td>
<td>2.81</td>
<td>4.04</td>
<td>4.16</td>
<td>8.82</td>
<td>7.51</td>
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<tr>
<td>Chlorobenzene</td>
<td>$Q_\infty$ (mole %)</td>
<td>1.42</td>
<td>1.14</td>
<td>1.15</td>
<td>2.22</td>
<td>1.87</td>
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<tr>
<td></td>
<td>$L_\infty$ (%)</td>
<td>44.90</td>
<td>46.50</td>
<td>33.30</td>
<td>56.10</td>
<td>50.50</td>
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<td>$D_0$, 10$^7$ (cm$^2$/s)</td>
<td>4.43</td>
<td>6.55</td>
<td>7.49</td>
<td>8.90</td>
<td>9.93</td>
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<td></td>
<td>$\bar{D}_L$, 10$^7$ (cm$^2$/s)</td>
<td>4.20</td>
<td>6.58</td>
<td>3.91</td>
<td>8.01</td>
<td>9.61</td>
</tr>
</tbody>
</table>
Table 2—Sorption kinetic data for polymer-solvent systems, activation energies and molar mass between crosslinks

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Property</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fluorobenzene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25°C 44°C 60°C</td>
</tr>
<tr>
<td>NBR</td>
<td>$k \cdot 10^3$</td>
<td>7.29  11.53  16.15</td>
</tr>
<tr>
<td></td>
<td>$E_a$ (kJ/mol)</td>
<td>18.82 ± 0.29</td>
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<tr>
<td></td>
<td>$M_c$ (g/mol)</td>
<td>175</td>
</tr>
<tr>
<td>CR</td>
<td>$k \cdot 10^3$</td>
<td>7.37  9.52  13.22</td>
</tr>
<tr>
<td></td>
<td>$E_a$ (kJ/mol)</td>
<td>13.64 ± 0.27</td>
</tr>
<tr>
<td></td>
<td>$M_c$ (g/mol)</td>
<td>458</td>
</tr>
<tr>
<td>EPDM</td>
<td>$k \cdot 10^3$</td>
<td>9.59  14.07  19.02</td>
</tr>
<tr>
<td></td>
<td>$E_a$ (kJ/mol)</td>
<td>16.16 ± 0.26</td>
</tr>
<tr>
<td></td>
<td>$M_c$ (g/mol)</td>
<td>819</td>
</tr>
<tr>
<td>SBR</td>
<td>$k \cdot 10^3$</td>
<td>11.20  16.01  18.04</td>
</tr>
<tr>
<td></td>
<td>$E_a$ (kJ/mol)</td>
<td>11.46 ± 0.24</td>
</tr>
<tr>
<td></td>
<td>$M_c$ (g/mol)</td>
<td>619</td>
</tr>
<tr>
<td></td>
<td>$E_a$ (kJ/mol)</td>
<td>10.91 ± 0.25</td>
</tr>
<tr>
<td></td>
<td>$M_c$ (g/mol)</td>
<td>871</td>
</tr>
</tbody>
</table>

* $k$ in min$^{-1}$; $E_a$ in kJ/mol.
* Relative standard error at 95% confidence level.

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 ($\chi$) and hence the molar mass between crosslinks ($M_c$). The criterion for swelling equilibrium was first recognized by Frenkel$^9$ and was later developed by Flory and Rehner$^{10}$ (FR). For a successful calculation of $M_c$ by this theory, we need reliable values of $\chi$ for the solvent-polymer pair. A number of methods of determining $\chi$ have been suggested in the literature$^{11}$. All these methods are empirical and require the use of solubility parameter of the solvent. Instead, we suggest calculation of $\chi$ based on the phenomenological approach. This method is based on expressing the FR equation into a derivative of volume fraction of the polymer ($\phi_p$) in the completely swollen state with respect to temperature. Thus,

$$
\frac{d\phi_p}{dT} = \frac{\chi \phi_p^2}{T} - \frac{2 \chi \phi_p}{1 - \phi_p} - \ln(1 - \phi_p^2) + \phi_p + \chi \phi_p^2
$$

... (6)
where

\[
N = \frac{\left(\frac{\varphi_p^{2/3}}{3} - \frac{2}{3}\right)}{\left(\frac{\varphi_p^{1/3} - 2\varphi_p/3}{3}\right)}
\]

so that

\[
\alpha = \frac{\left[\frac{d\varphi_p}{dT}\right] \left[\varphi_p/(1 - \varphi_p)\right] + N \ln(1 - \varphi_p) + N \varphi_p}{2\varphi_p(d\varphi_p/dT) - \varphi_p^2 N (d\varphi_p/dT) - \varphi_p^2/T}
\]

The volume fraction \(\varphi_p\) of the swollen polymer can be calculated as:

\[
\varphi_p = \left[1 + \frac{\rho_s}{\rho_p} \left(\frac{M_p}{M_s}\right) - \left(\frac{\rho_p}{\rho_s}\right)\right]^{-1}
\]

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

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

\[
M_c = -\frac{\rho_s V_s [\varphi_p^{1/3} - \varphi_p/2]}{\ln(1 - \varphi_p) + \varphi_p + \alpha \varphi_p^2}
\]

where \(V_s\) is molar volume of solvent and the parameter \(\alpha\) 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 \(\alpha\) values directly from the classical relationship given by Hildebrand \textit{et al.} based on the solubility parameter concept, further calculations of \(M_c\) from Eq. 10 are somewhat identical to those based on our values of \(\alpha\) from Eq. 8. For instance, in the case of CR + bromobenzene a value of \(M_c = 869\) agrees
somewhat with our calculated \( M_e \) (933). At any rate, our method of sorption and hence the computed \( M_e \) 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 \( x \) 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 suggested 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 elastomers 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.

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References