Chapter 7 Results and Discussion

In the current chapter, the results from the FTIR-ATR diffusion study (Chapter 4), the kinetic absorption analysis (Chapter 5), and the dynamic mechanical analysis (Chapter 6) are discussed in view of each other. The relevance of these has been placed in the context of a much larger study investigating the inter-relationship between chemical structure of a penetrant, its transport properties, and their effect on mechanical properties. Details on how all three studies can be utilized in conjunction with one another to understand the transport process and provide extremely valuable structure-property relationships are given.

The meticulous development of the FTIR-ATR experimental apparatus and procedure of diffusion analysis yielded useful information regarding the specific interactions involved in the transport of ester penetrants. The increased polarity of these penetrants resulted in greater attractions which, in turn, led to higher solubility of the systems. These effects were manifested in the chemical shifts associated with the carbonyl (C=O) and amide nitrogen (N-H) stretches of the polymer, toward lower wave numbers. Similar trends were exhibited by the penetrant equilibrium IR absorption ($A_\infty$) values obtained from these IR studies.

Mass uptake of the esters and alkanes proved to be a simple and informative technique to probe their transport processes. Equilibrium sorption data showed higher solubility for the lower molecular weight alkanes and esters. Furthermore, enhanced solubility was observed for the esters, compared to the alkanes. These results were attributed to an increase in specific interactions between the polymer and the polar esters, and are consistent with those from the IR analysis.

The diffusivities ($D$) of the penetrants were evaluated based on a Fickian model of transport. The values of $D$ for both types of penetrants decreased with increasing molecular size (i.e. mass or molar volume). This is due to the fact that a large molecule requires greater cooperative motion of polymer segments in order to be accommodated in the matrix, resulting in slower diffusion. A comparison of the esters and alkanes showed obvious signs of the effect of the polar group in the form of greater diffusion coefficients for the esters. However, the lowest molecular weight penetrants of both series exhibited identical behavior, indicating that the diffusion processes for these small molecules are similar in nature. This behavior in $D$ was dominated by the size of the molecule, rather than its chemical nature. Furthermore, the diffusion behaviors of the higher molecular weight esters (longer $n$-alkyl groups attached) approached those of the $n$-alkanes. For example, the nonpolar-to-polar characters of isopropyl myristate (IPM) and isodecyl pelargonate (IDP) (number of $\text{CH}_2$ units = 12) were much larger than that of ethyl propionate (EP) (number of $\text{CH}_2$ units = 2). The longer hydrophobic segment in IPM and IDP resulted in a “dilution” of the overall polarity of these ester molecules. In addition, the increased flexibility of the $n$-alkyl chains resulted in more effective shielding of the
polar group, thereby decreasing the likelihood of interactions with the polymer. Such a “dilution” of the polar ester functionality is also supported by the IR chemical shift data.

The activation energies of diffusion (E_d) for the penetrants were evaluated using an Arrhenius approximation. Values of E_d for both series were found to increase with increasing molecular size, in agreement with the trends observed for the diffusion coefficients. However, the E_d’s for the esters were typically lower than those of the alkanes, indicative of a less complex process for the diffusion of esters. Size effects dominated the behaviors of the lower and higher molecular weight esters, while chemical effects played the major role in the intermediate molecular range. The activation energies for the extreme molecular weight esters approached those of the corresponding n-alkanes. The lowest molecular weight penetrants of both series converged upon a “plateau” region. This was attributed to a “critical size” below which the diffusion process occurred in a simpler, elemental step, in which the molecule diffused as a whole. Such an interpretation is consistent with the observations of Aminabhavi et al.\textsuperscript{1} in their study of diffusion of linear alcohols in fluoroelastomeric polymers. It is also in agreement with the results of van Krevelen\textsuperscript{2} from a diffusion study of low molecular weight penetrants through polyethylene.

Basic relationships between the molecular structures of penetrants and their observed diffusion properties have been established in Chapter 5. These relationships are correlated with the concept of a double reduction in variables for the dynamic mechanical data that has been described in Chapter 6. This is possible since the diffusion coefficient relates penetrant concentration to exposure time; the dynamic mechanical response has also been shown to depend upon the same two parameters. These correlations enable the prediction of the transport properties as well as the dynamic mechanical response of a polymer-penetrant system based upon knowledge of the penetrant structure. The steps involved in the above procedure are outlined below.

**Step 1: Determination of E_d**

Relationships describing the effects of molecular size on the activation energy of diffusion (E_d) for both the n-alkanes and esters were discussed in Chapter 5. The value of E_d for a selected penetrant of known molar volume (V_m) is derived from a plot of E_d versus V_m (Figure 5-46) or from a plot of E_d versus χ * V_m (Figure 5-73), both of which are shown in Chapter 5.

**Step 2: Determination of Arrhenius front factor, D_0**

The Arrhenius front factor (D_0) for a penetrant is evaluated from a plot of log D_0 versus E_d, as shown in Figure 7-1. This plot is based on equation 5-12 that relates D_0 to E_d. In Figure 7-1, both series of penetrants are represented by a single line of slope = 0.11. This is in excellent agreement with the literature value for this slope = 0.10 for elastomeric materials, as described by van Krevelen\textsuperscript{2}.
Step 3: Evaluation of Diffusion coefficients, $D$

Having calculated the values of $E_d$ and $D_0$ as described above, the value of the diffusion coefficient ($D$) for a penetrant at any temperature is determined based upon the Arrhenius expression,

$$D = D_0 \exp\left(-\frac{E_d}{RT}\right)$$

Step 4: Evaluation of concentration profile

The concentration-time profile (as a function of time) for a particular matrix geometry and boundary conditions, is evaluated from the diffusion coefficient of step (3). Such concentration profiles for a thin-film geometry based upon various D’s are shown in Figure 7-2. From these curves, the fractional composition of a penetrant for any time and geometry is obtained.
Step 5: Evaluation of penetrant composition

In order to develop the correlations discussed earlier, the actual composition of the penetrant as a function of time is evaluated. Such a composition in terms of weight percent of the penetrant is derived from its equilibrium weight uptake ($M_\infty$). $M_\infty$ is a measure of the solubility of the penetrant in the polymer and is directly related to the Flory-Huggins interaction parameter, $\chi$.

The $M_\infty$ values for the $n$-alkanes and esters are plotted as a function of $\chi$ in Figure 7-3. It can be seen that both series of penetrants are represented by a single curve, whose equation is given as:

$$\text{Weight \% Uptake} = 2.34 + 24.76\exp\left(-\frac{(\chi - 1.05)}{0.39}\right)$$

This equation is used to calculate the equilibrium weight uptake values for similar types of penetrants, if their $\chi$ values are known. If not, they are determined experimentally.
**Step 6: Evaluation of dynamic mechanical response**

The diffusion coefficient and penetrant composition evaluated as shown above are utilized to predict the dynamic mechanical response of the polymer-penetrant system, taking into account the effects of both, temperature and diffusion.

Modulus-frequency master curves that have been shifted with respect to temperature were further shifted with respect to exposure times to yield doubly-reduced master curves. The corresponding diffusion-time shift factors (log $a_{Dt}$) are plotted as a function of penetrant concentration in Figure 7-4. Both the $n$-alkanes and esters are represented by a single curve, described by a power law expression, $y = a x^b$, where $a = 1.01$ and $b = 0.53$ (statistical $\chi^2 = 0.39$). This behavior is analogous to dependence of the compositional shift factor on weight fraction of diluent, described by Schausberger$^3$ and Onogi$^4$. These results indicate that the chemical nature of the penetrant does not alter the mechanism of mechanical relaxation of the polymer. However, it determines the penetrant concentration incorporated into the polymer matrix, which in turn has been shown to be the controlling factor in determining the final mechanical response.

In order to obtain the dynamic mechanical response of the polymer exposed to a similar penetrant (due to temperature and diffusion), it is necessary to construct a modulus-frequency master curve of the material, referenced to the temperature of interest. Then, a doubly-reduced master curve shifted with respect to temperature as well as exposure time, is obtained by:
1) Incorporating the weight percent uptake of the penetrant evaluated in Step 5 into the plot of Figure 7-4.

2) Determining its diffusion-time shift factor \( \log a_{Dt} \) for a given diffusion coefficient and time, from that plot.

3) And finally, shifting the temperature-shifted master curves through a factor of \( \log a_{Dt} \) along the log (frequency) axis.

![Figure 7-4. Diffusion-time shift factors for both \( n \)-alkane and ester penetrants as a function of weight percent uptake](image)

In devising the relationships shown above, three major assumptions were utilized:

1) existence of a temperature-independent \( E_d \)
2) validity of the Frenkel-Flory-Rehner hypothesis in determining \( \chi \) and
3) that dynamic mechanical response constitutes an “average” from the entire thickness of the film.

Based upon these, the “sensitivity” of the proposed correlations was investigated in order to determine their applicability. It was found that a 3 to 8% deviation in the determination of \( E_d \) resulted in \( \sim 11\% \) deviation in the final diffusion-time shift factor \( \log a_{Dt} \) evaluated. Deviations of this magnitude are highly acceptable due to the complexity of the transport and mechanical processes and the difficult nature of the experiments themselves.
Thus, it has been demonstrated that a quantitative prediction of the dynamic mechanical response of a polymer-penetrant system may be made based on knowledge of the chemical structure of the penetrant.

Qualitative relationships describing the ability to predict the diffusivity and activation energy of diffusion, $E_d$, for both series of penetrants have also been shown in Chapter 5 (Figures 5-73). These preliminary relationships are based upon both the interaction parameter ($\chi$) and molar volume ($V_m$) of the penetrants, thereby accounting for both polymer-penetrant energetics and penetrant size. This concept could be a precursor to the development of a more concise molecular model of diffusion that takes into account all of the factors that have been considered in this study. Such a model may be able to predict the behavior of any polymer-penetrant system of interest more easily and accurately than any model currently available.

Thus, this study has provided greater insight into the process of diffusion in the polymer-penetrant systems studied. This has been done through the use of various techniques in conjunction with each other. Furthermore, the effect of penetrant structure (size, shape, and chemical nature) on the transport behavior and on the dynamic mechanical response of the systems, has been investigated in great detail. Structure-property relationships for the above effects have been developed and successfully correlated to each other. Such a correlation has enormously improved the ability to predict either the transport or dynamic mechanical behavior of a similar type of penetrant, based only upon knowledge of its chemical structure.
Endnotes


