

Chapter 8 Conclusions

The transport properties of two series of penetrants - nonpolar *n*-alkanes and polar ester penetrants - in a polyamide-type polymeric adhesive have been thoroughly investigated. Mass uptake experiments for both series of penetrants have been carried out to provide kinetic as well as thermodynamic information on their transport processes. Equilibrium solubilities of the penetrants were characterized in view of the Flory-Huggins interaction parameter, χ .

It was concluded from this analysis that thermodynamic equilibrium (in the form of greater solubility) is a strong function of molecular size and chemical nature of the penetrant. The polar esters as well as the lower molecular weight alkanes yielded higher solubilities than the larger hydrocarbons. Furthermore, the esters were found to be more soluble than the corresponding *n*-alkanes due to the presence of the polar ester functionality.

An FTIR-ATR experimental setup apparatus was designed and successfully built to study the diffusion behavior of the esters, *in-situ*. Increased chemical shifts toward lower wavenumbers and higher solubilities (A_∞ values) with increasing polarity of the penetrant were observed from this analysis. These IR results were in excellent agreement with the results from the mass uptake experiments described above.

The mechanism of penetrant transport was found to be indicative of a Henry's law-type of process in which vacancies were created within the polymer matrix to permit diffusion of a penetrant. The size of a vacancy required in order to accommodate a penetrant was governed by both the size as well as shape of the molecule. This necessitated a study of the effect of penetrant shape on the transport behavior of the system. This was carried out

1. by using Monte-Carlo molecular simulations of the shapes of the penetrant molecules in a polar medium, and
2. by calculating the activation energies of diffusion per carbon atom added and comparing them to literature values of molecules whose shapes were well characterized.

These studies led to the conclusion that all the penetrant molecules (with the exception of isodecyl pelargonate (IDP)) assumed linear geometries during their diffusion through the polymer matrix. As a result, the transport of these molecules involved a linear translation, parallel to their long axes. However, the IDP molecule was found to possess a shape approaching that of a sphere, thereby giving rise to its "anomalous" behavior.

The effects of penetrant size as well as polymer-penetrant interactions have been taken into account in order to yield a *qualitative* relationship that allows the prediction of the Arrhenius diffusion parameters D_o and E_d for similar penetrant types. Knowledge of E_d and D_o , in turn, enables the evaluation of the diffusion coefficient (D) at a given temperature.

The process of diffusion and its effects on the resulting dynamic mechanical response of the polymeric adhesive have been studied in great detail using the method of reduced variables. The concept of a *diffusion-time shift factor* ($\log a_{Dt}$) has been introduced to account for the variations in the dynamic mechanical response as a result of the existence of a low molecular weight penetrant within the polymer matrix. It has been shown that the *mechanism* of mechanical relaxation is not influenced by the size or chemical nature of the penetrant. However, the *rate* of change in the relaxation is affected by both these parameters. Furthermore, these parameters determine the *equilibrium* penetrant composition, which in turn determines the *extent* of change in the relaxation.

Thus, in this study, information regarding penetrant structure such as molecular weight, molar volume and polymer-penetrant interactions has been utilized to develop predictive correlations of the transport behavior of two series of penetrants- alkanes and esters - in a polymeric adhesive. These correlations have been expanded to predict the resulting dynamic mechanical response of the polymer in the presence of these small molecular weight penetrants. This study could prove to be a powerful tool in predicting the transport properties of unknown systems. It could also be the precursor to a more theoretical molecular model of diffusion that can predict the behavior of *any* polymer-penetrant combination of interest.

Future Work

This study involved the transport of esters and alkanes through a polyamide type polymeric adhesive. It would be interesting to change the nature of the penetrant by:

1. introducing multifunctional moieties
2. changing the functionality to alcohols, amines, etc...
3. introducing shape effects via branching and/or location of functionality within penetrant backbone
4. changing the rigidity / flexibility of the backbone by suitable use of aromatic or unsaturated species,

and the nature of the polymeric matrix by:

1. varying crosslink density
2. the use of semicrystalline materials
3. modifying morphology, as in the case of random or block copolymers
4. varying the thermal history of the material in order to induce different extents of physical aging.

In this study, the effect of transport on the dynamic mechanical properties of the systems was thoroughly investigated and correlations were developed relating the two. It would be worthwhile to extend these correlations to include the effect of transport on the adhesive strength properties (such as peel strength) of a polymer-substrate system.

The above studies could lead to the evolution of a more general and universal model for predicting the transport and mechanical behavior of any polymer-penetrant system, based on the chemical structure of the polymer and the penetrant.