Penetrant Transport in Polyethylene–Polystyrene Semi-Interpenetrating Polymer Networks

SEONG-UK HONG,* J. L. DUDA

Departments of Materials Science and Engineering and of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

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ABSTRACT: In this study, diffusion behavior is investigated for polyethylene–polystyrene semi-interpenetrating polymer networks (PES-IPN) with toluene and chloroform and for a polyethylene/toluene system. The results show that diffusion in the semi-IPN material consists of a continuous polyethylene phase containing disperse polystyrene and that the transport in this material closely parallels transport in the homogeneous polyethylene. Consequently, the measured diffusion coefficients can be correlated, using the free-volume theory and parameters which characterize the free volume of the continuous phase, as a function of temperature and concentration. In addition, from the diffusivities of toluene in the polyethylene and the solubilities in the polyethylene and polystyrene, the diffusion coefficients of the PES-IPN/toluene system are predicted with an unsteady-state diffusion model developed in this study. Predictions with the new unsteady-state model are comparable with the experimental data. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 51–57, 1997

Key words: diffusion; semi-IPNs; polymer; solvent; free volume

INTRODUCTION

Interpenetrating polymer networks (IPNs) are generally defined as a combination of two or more polymers in network form, at least one of which is synthesized or crosslinked in the immediate presence of the other.[1,2] Many IPNs exhibit dual-phase continuity, which means that two or more polymers in the system form phases that are continuous on a macroscopic scale. Sometimes IPNs do not possess cocontinuity of networks; rather, one phase forms fine droplets dispersed in another phase, and the diameters range from 10 to 100 nm.[3] However, because the system has been prepared through the standard methods of IPN preparation, it is identified as an IPN material. The polyethylene (PE)–polystyrene (PS) semi-IPNs (PES-IPN) used in this study belong to the latter case.

When two or more polymers are combined, the resulting composition can be called a multicomponent polymer material. This combination can facilitate processing and may affect flexibility, tensile and impact strength, and chemical resistance. Furthermore, the transport of small molecules in multicomponent polymer materials is of technical importance in many areas where polymers are acting as barriers and in separation processes, such as selective diffusion. Consequently, reliable predictions of diffusion coefficients for small molecules in multicomponent polymer materials could be a useful tool in designing appropriate materials.

In this study, diffusion behavior is investigated for PES-IPN with toluene and chloroform and for a PE/toluene system. In addition, the diffusion coefficients of the PES-IPN/toluene system are predicted from the diffusivity data for toluene in the PE and the solubility data in the PE and PS.

Correspondence to: J. L. Duda.

* *Current address:* Department of Chemical Engineering, The Johns Hopkins University, Baltimore, MD 21218-2694.

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EXPERIMENTAL

Mutual diffusion coefficients were measured for toluene and chloroform in PES-IPN and for toluene in PE. The experiments were conducted over a temperature range of 75–140°C with a gravimetric vapor sorption balance in which polymer samples are exposed to a step change in the vapor pressure of the solvents while being maintained at constant temperature. The vapor sorption apparatus used in this study used a quartz spring, and isothermal conditions were maintained by a condensing vapor.[4] By setting the pressure above the reboiler fluid, the temperature at which the fluid boils is determined. The vapor of the boiling fluid surrounds the outer wall of the sorption chamber and thereby establishes experimental temperatures.

The polymers used in this study were provided by ARCO Chemical Company (Newtown Square, PA). The PES-IPN contained 30–35% PE with the balance being PS (the PS phase did contain a small amount of *n*-butyl acrylate as a comonomer to prevent phase inversion). The PES-IPN had 7% crystallinity, and both the melting temperature of PE and the glass transition temperature of PS in the PES-IPN were near 100°C.[5] Scanning electron microscopy indicates that fine droplets of PS are dispersed in a crosslinked PE phase.[6] The PE used in this study was the same as that used in the preparation of the PES-IPN.

The polymers were pressed with a laboratory press at 120°C. To conduct experiments, polymer disks were cut and fitted to aluminum buckets, which were then placed into the sorption column. In order to reduce the possibility of any internal stress which may have been introduced at the time of pressing, the solvent vapor was introduced into the polymer sample two to three times in a sorption/desorption cycle. Each experiment consisted of measuring the weight gain of the polymer sample as a function of time. If the data are plotted as a fractional approach to equilibrium versus the square root of time, the diffusivity can be obtained from the initial slope of the plot. Further details of the data analysis procedure are available elsewhere.[7]

THEORY

The diffusivity data obtained in this study are interpreted in terms of two different empirical models. The most successful theory for the correlation or prediction of diffusion in polymer/solvent systems is the free-volume theory.[8–10] Although this theory has been quite successful for describing molecular diffusion in homogeneous polymers, the applicability of this theory for the correlation of data obtained in the semi-IPN system is questionable because of the heterogeneities associated with the presence of a dispersed PS-rich phase in addition to crystals in the PE phase. However, the free-volume theory may still be useful as a correlation technique at temperatures above both the melting point of PE and the glass transition temperature of PS since the molecular diffusion of the solvent is probably dominated by the faster transport in the continuous PE phase.

According to one of the more popular versions of the free-volume model, the polymer/solvent binary mutual diffusion coefficient, D, is given by eqs. (1) and (2), with subscripts 1 and 2 referring to the solvent and polymer, respectively:

$$D = D_1(1 - \phi_1)^2(1 - 2\chi\phi_1) \tag{1}$$

$$D_1 = D_0 \exp\left(\frac{-E}{RT}\right) \exp \times \left(\frac{-(\omega_1 \hat{V}_1^* + \xi\omega_2 \hat{V}_2^*)}{\omega_1\left(\frac{K_{11}}{\gamma}\right)(K_{21} - T_{g1} + T) + \omega_2\left(\frac{K_{12}}{\gamma}\right)(K_{22} - T_{g2} + T)} \right) \tag{2}$$

Here, D_0 is a preexponential factor, E is the critical energy which a molecule must possess to overcome the attractive forces holding it to its neighbors, and γ is an overlap factor which is introduced because the same free volume is available to more than one molecule. $\hat{V}_i^*$ is the specific hole free volume of component i required for a diffusive jump, ω_i is the weight fraction of component i, and ξ is the ratio of the molar volume of the jumping unit of the solvent to that of the polymer. K_{11} and K_{21} are free-volume parameters for the solvent, while K_{12} and K_{22} are those for the polymer; ϕ_1 is the solvent volume fraction, and χ is the polymer-solvent interaction parameter.

Gravimetric sorption is an unsteady-state diffusion technique in which the diffusion coefficient can be determined by several procedures from the sorption weight versus time data. In a heterogeneous medium, different effective diffusion coefficients can be obtained from a sorption curve by alternative procedures.[11] Unfortunately, the preponderance of diffusion models in the literature for heterogeneous systems is specific to the steady-state diffusion mode.[12–18]

In addition to evaluation of the free-volume correlation model, an unsteady-state diffusion model to describe transport in a heterogeneous material with characteristics of the IPN system is developed below. This analysis is an extension of the diffusion-sorption model presented by Smith and Keller.[19] In this analysis, it is assumed that the main transport of the solvent through the polymer mixture takes place in the continuous PE-rich phase. If it is further assumed that at each position in the heterogeneous material, the solvent in the dispersed droplets is in local equilibrium with the solvent in the surrounding continuous phase, then the unsteady-state diffusion equation can be modified as

$$\phi_c \frac{\partial C_c}{\partial t} = \phi_c D_c \frac{\partial^2 C_c}{\partial x^2} - \phi_d \frac{\partial C_d}{\partial t} \tag{3}$$

where subscripts c and d refer to the continuous and dispersed phases, respectively, and C_i and ϕ_i are the concentration and volume fraction of phase i, respectively. Equation (3) can be rearranged to

$$\frac{\partial(\phi_c C_c + \phi_d C_d)}{\partial t} = \frac{\partial C}{\partial t} = \phi_c D_c \frac{\partial^2 C_c}{\partial x^2} \tag{4}$$

If we assume that a partition coefficient K can describe the relationship between solvent concentrations in the two phases, then

$$C_d = KC_c \tag{5}$$

From the insertion of eq. (5) into eq. (4), eq. (4) can be written as

$$\frac{\partial C}{\partial t} = \frac{D_c}{1 + vK} \frac{\partial^2 C}{\partial x^2} \tag{6}$$

where v is the volume fraction ratio (ϕ_d/ϕ_c), and the effective diffusion coefficient is given by the expression

$$D_{eff} = \frac{D_c}{1 + vK} \tag{7}$$

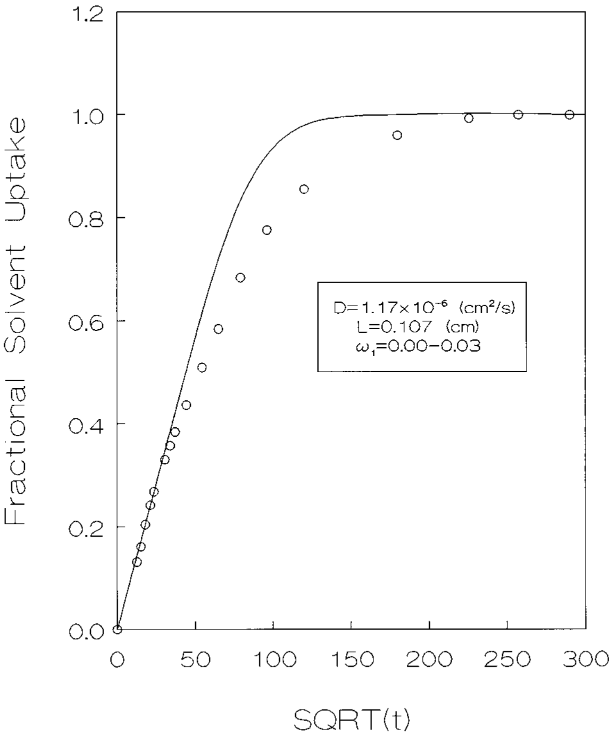

Figure 1 Experimental results for the sorption of toluene in PES-IPN at 75°C. The line represents the theoretical prediction for Fickian diffusion.

In the analysis of the data, the free-volume theory formulation is used as a correlation model using the free-volume characteristics of the PE-continuous phase. In contrast, experimental measurements of diffusivities of the solvent in the PE are used in the unsteady-state model developed in this article to predict the effective diffusion coefficients in heterogeneous IPN material.

RESULTS AND DISCUSSION

The diffusion characteristics of toluene and chloroform in the PES-IPN heterogeneous material were investigated over wide temperature and concentration ranges. Two kinds of sorption data from this study are presented in Figures 1 and 2. The solid lines correspond to the sorption behavior resulting from a solution of the standard unsteady-state diffusion equation:

$$\frac{\partial C}{\partial t} = D_{eff} \frac{\partial^2 C}{\partial x^2} \tag{8}$$

with the following initial and boundary conditions:

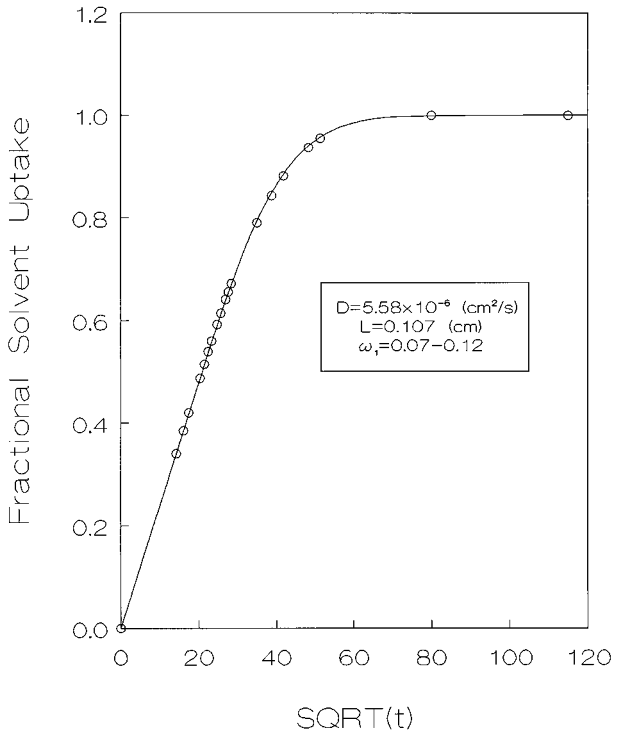

Figure 2 Experimental results for the sorption of toluene in PES-IPN at 88°C. The line represents the theoretical prediction for Fickian diffusion.

$$C = C_0 \quad \text{at } 0 < x < l, t = 0 \tag{9}$$

$$C = C_1 \quad \text{at } x = 0, t \geq 0 \tag{10}$$

$$\frac{\partial C}{\partial x} = 0 \quad \text{at } x = l, t \geq 0 \tag{11}$$

where l is the thickness of the polymer sample in the bucket, and D_{eff} is the effective diffusion coefficient. The first boundary condition indicates that the surfaces are kept at a constant concentration C_1, while the second one implies that there is no transport of the penetrant through the bottom of the bucket. The sorbed mass is obtained by integrating eq. (8) over the thickness of the film. The disagreement between the unsteady-state diffusion equation and the experimental results in Figure 1 indicates that the IPN system does not behave as a Fickian diffusion material at this temperature and concentration. Consequently, in this case, the conventional data analysis procedure based on the initial slope method[14] cannot be used to determine the mutual diffusion coefficients from the sorption data. In contrast, although the temperature used was still below the melting point of PE and the glass transition temperature of PS, the experimental data agree well with the diffusion equation in Figure 2. It is possible that the solvent is actually changing the morphology of the IPN at various temperatures and concentrations by melting out the PE crystals and plasticizing the PS phase to convert it from a glassy material to a rubbery polymer phase. Whatever the mechanism, it is very clear from Figures 1 and 2 that the diffusion behavior of the solvent in the IPN material is distinctly different in two cases. Therefore, the diffusion coefficient has hereafter been determined, using the initial slope method, only if the diffusion process is Fickian.

The experimental diffusivity measurements and correlation of these diffusivities with the free-volume theory are presented in Figure 3 and 4. The free-volume parameters used in these correlations are provided in Table I. Six of the 10 parameters in the free-volume theory were estimated *a priori* by the methods discussed elsewhere.[20] The χ values were obtained by correlating the solubility data with the Flory-Huggins equation.[21] The dependence of χ on temperature was ignored since, for the purpose of this study, single χ values were sufficient to describe the thermodynamic behavior of the solvents in the PES-IPN. It should be noted in these correlations as well as in the free-volume correlation of the

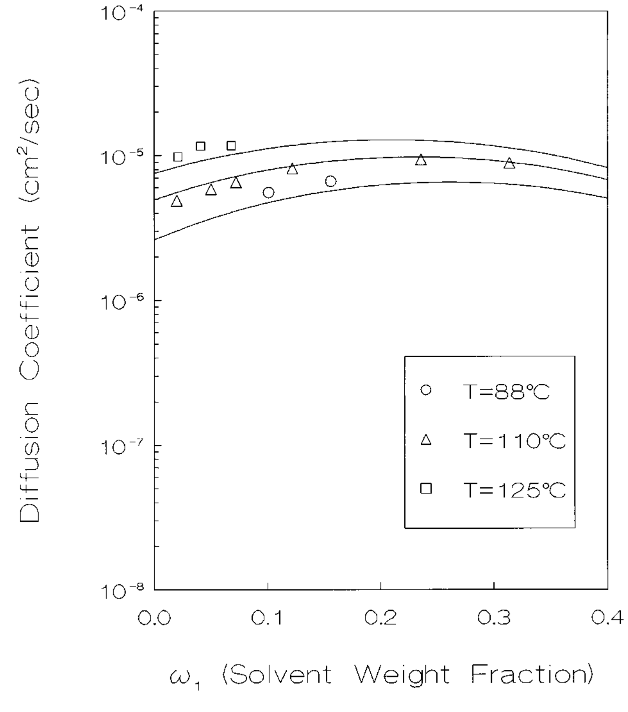

Figure 3 Experimental data and theoretical correlations for PES-IPN/toluene mutual diffusion.

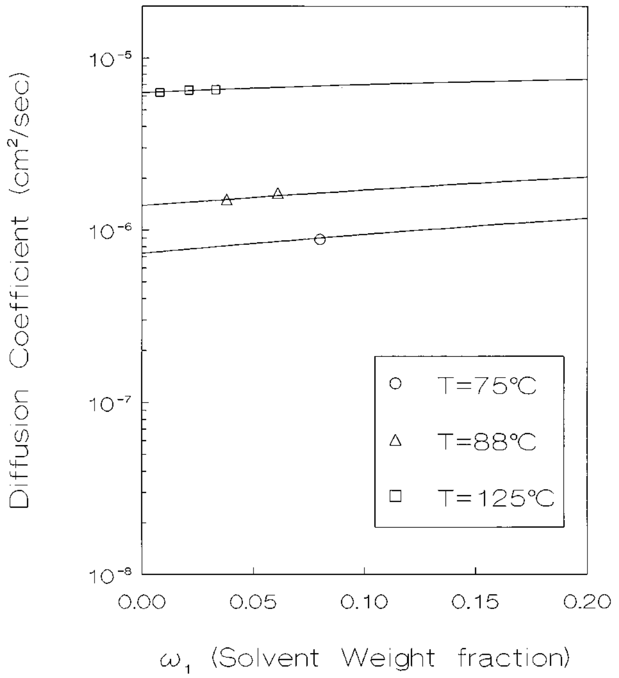

Figure 4 Experimental data and theoretical correlations for PES-IPN/chloroform mutual diffusion.

diffusivity data in the PE system that the free-volume characteristics of the PE were obtained from a nuclear magnetic resonance relaxation study.[22] Furthermore, in these free-volume correlations, the experimental diffusivity measurements as a function of temperature and concentration were correlated to determine three parameters in the free-volume theory, D_0, E, and ξ. For both systems, the free-volume theory does a reasonable job of correlating the diffusivity data at all temperatures and concentrations. At temperatures below 100°C, since chloroform is a better solvent for the system than toluene, the diffusion process becomes Fickian at lower solvent concentrations.

In order to evaluate the theories for predicting diffusion in heterogeneous media, the diffusion characteristics of toluene in PE were also investigated. Because of the anomalous behavior of toluene in the IPN below 100°C, the studies were conducted above this temperature. The free-volume correlation of the diffusivity data is presented in Figure 5. The free-volume parameters used in these correlations are provided in Table I.

The concentration dependence of toluene diffusivity in PE, PS, and PES-IPN is illustrated in Figure 6. Data for the PE and IPN system are from this study, while the diffusivity data for the PS/toluene system were obtained from the literature.[23] The solid lines in Figure 6 represent correlations using the free-volume theory. These results indicate that the diffusivity of the PES-IPN/toluene system is quite similar to that of the PE/toluene system. This behavior is consistent with the fact that the PE is a continuous phase in which the diffusion is fast compared with the PS phase. Because of the relatively low free-volume in PS at 110°C, the PS/toluene system shows the strongest concentration and temperature dependency.[23] In the temperature range investigated, the PS is within 50°C of its glass transition temperature, while the PE is more than 200°C above its glass transition temperature.

Finally, the predictive capability of the unsteady-state model developed in this study is evaluated. In these predictions, the solubilities for the toluene in the pure PE and PS and the diffusivit-

Table I Parameters Used in Correlations of Diffusion Coefficients for Polymer/Solvent Systems

Parameter	PES-IPN/ Toluene	PES-IPN/ Chloroform	PE/Toluene
$\hat{V}_1^*$ (cm^3/g)	0.917	0.510	0.917
$\hat{V}_2^*$ (cm^3/g)	0.905	0.905	1.006
K_{11}/γ (cm^3 g^{-1} K^{-1})	2.20×10^{-3}	7.12×10^{-4}	2.20×10^{-3}
K_{12}/γ (cm^3 g^{-1} K^{-1})	1.02×10^{-3}	1.02×10^{-3}	1.02×10^{-3}
$K_{21} - T_{g1}$ (K)	−102.72	−29.43	−102.72
$K_{22} - T_{g2}$ (K)	−138.70	−138.70	−138.70
χ	0.75	0.47	0.67
ξ	1.61	1.60	1.29
D_0 (cm^2/s)	7.28×10^{-3}	5.41×10^{-1}	2.85
E (cal/mol)	1,100	4,660	5,470

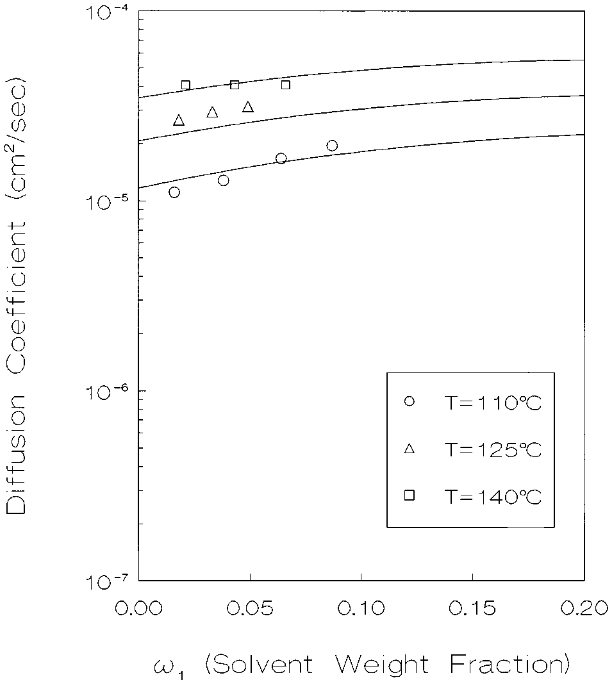

Figure 5 Experimental data and theoretical correlations for PE/toluene mutual diffusion.

ies in the pure PE are used to predict the effective diffusion coefficients in the heterogeneous IPN material. Figure 7 shows the comparison between the experimental data for the PES-IPN/toluene system and the unsteady-state model predictions as a function of temperature and concentration. This analysis indicates that predictions of diffusion in the IPN material using the unsteady-state model are comparable with the experimental data.

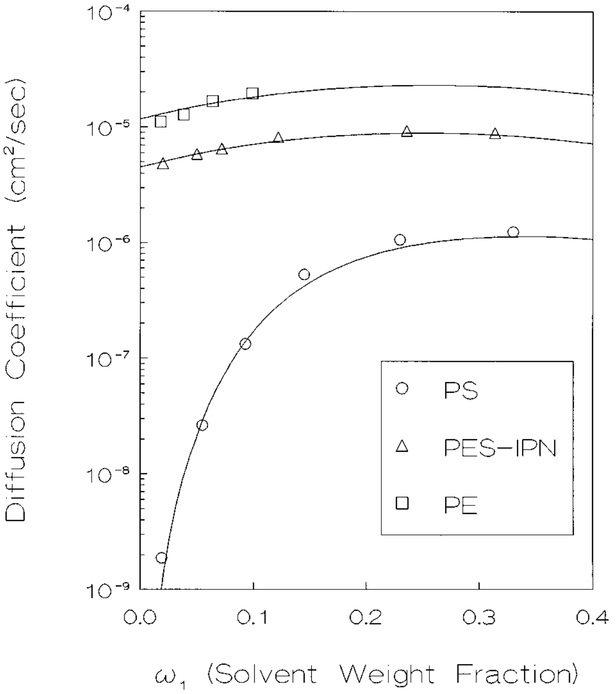

Figure 6 Concentration dependence of diffusivity at 110°C for toluene in PE, PS, and PES-IPN.

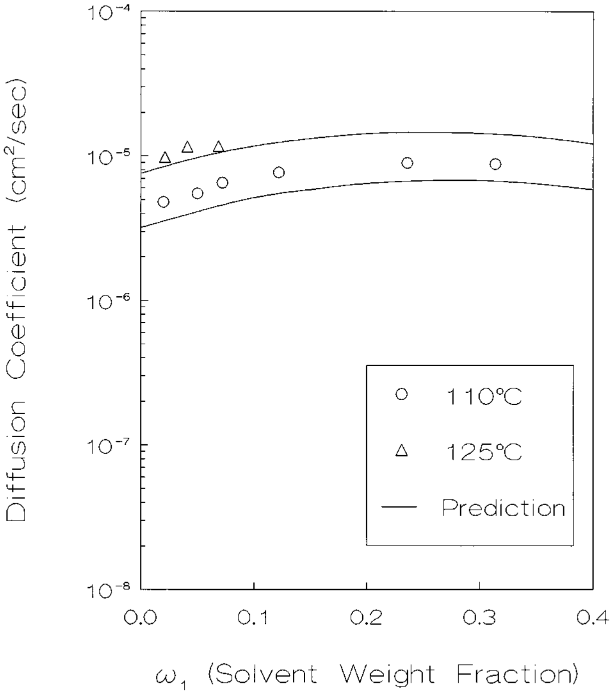

Figure 7 Experimental data and theoretical predictions for PES-IPN/toluene mutual diffusion.

CONCLUSIONS

These studies show that the semi-IPN material consists of a continuous PE phase containing dispersed PS and that transport in this material closely parallels transport in the homogeneous PE. Consequently, the concentration and temperature dependency of the measured diffusivities can be correlated using the free-volume theory and parameters which characterize the free volume of the continuous phase. The comparisons of the experimental results with the solutions of Fick's law indicate that the morphology of the IPN material changes when exposed to solvents at temperatures below 100°C. The evaluation of the unsteady-state model developed in this study shows that the model reasonably predicts the rate of transport in this heterogeneous material.

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