Solubility and Diffusivity of Cyclohexane in High Density Polyethylene

Justin L. Rausch, Taylor C. Schulz, Ronald P. Danner

Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

ABSTRACT: The diffusivity and solubility of cyclohexane in a high density polyethylene, HDPE, were studied using a gravimetric, quartz-spring, sorption balance. Solvent concentrations up to a weight fraction of 0.15 over a temperature range of 90 to 160°C were measured. Diffusion coefficients in the range of 10^{-6} to 10^{-7} were determined. Two types of polymer samples were used: a commercial bead form and flat sheets prepared by melting the polymer. Within the experimental error no differences were observed between the two forms indicating that there were no significant effects caused by the melting and compression. The solubility of cyclohexane in the HDPE as a function of the activity of the cyclohexane was linear. Above the melt temperature the solubility data were predicted better by the group-contribution, lattice-fluid equation of state (GCLF-EoS) than by the van der Waals free-volume (UNIFAC-vdw-FV) model. Below the melt temperature a correction factor for the elasticity significantly improved the predictions for both models. Although the HDPE has a crystallinity of 77.6%, the experimental data and the Vrentas-Duda free-volume theory indicated no significant tortuosity effects. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4315–4321, 2012

Key words: polyethylene (PE); solution properties; diffusion

INTRODUCTION

High-density polyethylene (HDPE) is an important polymer with many applications: plastic lumber, bags, furniture, pipes, bottles, fuel tanks, etc. HDPE is synthesized with a catalyst (e.g., Ziegler-Natta) that results in very little branching.[1] This allows tight packing of the polymer chains resulting in a high-density semicrystalline polyethylene in the range of 0.940 to 0.970 g/cm^3.

Polyethylene is frequently made by a solution polymerization process using solvents such as cyclohexane.[2] Design of effective methods of removing such solvents and other additives requires good estimates of the diffusivity and solubility of these compounds in the polymer. Theoretically, the crystallinity of the polymer can affect both the diffusivity and solubility of the solvent. The solvent is generally considered to be excluded from the crystals and the solubility can be reduced because of the elastic stress on chains in the amorphous phase.[3] The crystals have also been reported to reduce the free volume in the amorphous phase and create tortuous paths through the polymer and, thus, reduce the rate of diffusion.[4]

BACKGROUND

Diffusion

In contrast to binary liquid or gas systems where concentration has little effect on the diffusivity, in a polymer–solvent system the diffusivity can be greatly influenced by the solvent concentration. In small-molecule gas or liquid systems the free volume (essentially the actual volume minus the hard-core volume) is relatively large resulting in diffusivities of the order of 10^{-5} to 10^{-6} cm^2/s. In a pure amorphous polymer near its glass transition temperature such as polystyrene(PS) at 110°C there is comparably little free volume. The addition of small amounts of free-volume-carrying solvents can affect large changes in the diffusivity, e.g., in the PS/toluene system from 10^{-9} to 10^{-6} cm^2/s with an increase of toluene concentration from 0 to 0.2 weight fraction.[5] A semicrystalline polymer such as polyethylene far above its glass transition temperature ($T_g \approx -10$°C) generally has a lot of inherent free volume and the effects of added solvent are less significant.

In a semicrystalline polymer, the diffusion can be affected by the crystal structure. It is assumed that the solvent cannot penetrate into the crystals and only diffuses through the amorphous regions of the polymer.[3] At higher crystallinity values, the crystal structure would be expected to hinder the diffusion pathway, resulting in a reduction of the diffusivity.

Correspondence to: R. P. Danner (rpd@psu.edu).

Crank's model

Any quantitative method for determining the diffusivity must account for the shape of the material. Crank[6] derived various equations for diffusion based on the geometry. While the beads used in the current study were not strictly spherical (they had slightly "stubby" ends), careful analysis of the sorption uptake curves with various geometries proved that the spherical model was quite adequate. Thus,

$$\frac{M_t}{M_\infty} = 6\left(\frac{Dt}{R_{av}^2}\right)^{\frac{1}{2}}\left(\frac{1}{\pi^2} + \sum_{n=1}^{\infty} ierfc\frac{nR_{av}}{\sqrt{Dt}}\right) - 3\frac{Dt}{R_{av}^2} \quad (1)$$

Here M_t is the mass uptake at time t, and M_∞ is the uptake at equilibrium so M_t/M_∞ is the fractional mass uptake. R_{av} is the average radius of the particles. Below an M_t/M_∞ value of 0.5 the summation term is negligible compared with the other two terms, and this equation reduces to:

$$\frac{M_t}{M_\infty} = \frac{6}{\pi^2}\left(\frac{Dt}{R_{av}^2}\right)^{\frac{1}{2}} - 3\frac{Dt}{R_{av}^2} \quad (2)$$

This equation was regressed to determine the diffusivity for the pellet samples.

Crank developed a similar equation for a flat sheet geometry that was relevant for the polymer sheets used in this study. This equation corresponds to a sheet with a thickness that is small enough so that the other dimensions can be considered infinitely long.

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{L^2}\right)^{\frac{1}{2}}\left(\frac{1}{\pi^2} + 2\sum_{n=1}^{\infty}(-1)^n ierfc\frac{nL}{\sqrt{Dt}}\right) \quad (3)$$

In this equation, the length, L, is the diffusion length, and replaces the radius in the spherical equation. For diffusion from just one side of the sheet, as was the case in the present study, L is the thickness of the sheet. As in the spherical equation, the summation term is negligible below a fractional uptake value of 0.5 and therefore

$$\frac{M_t}{M_\infty} = \frac{2}{\pi^2}\left(\frac{Dt}{L^2}\right)^{\frac{1}{2}} \quad (4)$$

Alinear regression of the initial fractional uptake, M_t/M_∞, versus time, t, was used to determine the diffusion coefficients.

Vrentas-Duda free-volume theory

The Vrentas-Duda free-volume theory states that the free volume of a material controls the molecular transport. The free volume accounts for a portion of the total volume, with the remainder of the volume being described as the occupied volume. The occupied volume is the space taken up by the molecules, whereas the free volume is the portion of the volume between the molecules that is essentially open space. This free volume greatly depends on the temperature of the system.

The free volume is subdivided into the interstitial free volume and the hole free volume. The interstitial free volume cannot redistribute itself because the required energy is too great. On the other hand, the hole free volume can easily be rearranged, and the molecular diffusion can be defined as the movement of molecules into these holes. For this movement to happen, the molecule and a sufficient sized hole must be adjacent to each other, and the molecule must possess enough energy for the transition. Details of the Vrentas-Duda free-volume equation are given in Refs. 7 and 8. The equation for the mutual diffusion coefficient in an amorphous polymer is

$$D_a = \left[D_{01}\exp\left(-\frac{(\omega_{1a}\hat{V}_1^* + \omega_{2a}\hat{V}_2^*\xi)}{\hat{V}_{FH_a}/\gamma}\right)\right]$$
$$\times\left[(1 - 2\chi\varphi_{1a})(1 - \varphi_{1a})^2\right] \quad (5)$$

$$\frac{\hat{V}_{FH_a}}{\gamma} = w_{1a}\frac{K_{11}}{\gamma}\left[(K_{21} - T_{g1}) + T\right]$$
$$+ w_{2a}\frac{K_{12}}{\gamma}\left[(K_{22} - T_{g2}) + T\right] \quad (6)$$

Here D_a is the mutual binary diffusion coefficient in the amorphous polymer, D_{01} is the pre-exponential factor, ω_{ia}, is the weight fraction of the solvent (1) or the polymer (2) in the amorphous phase, $\hat{V}_i^*$ hole free volume of component i, $\hat{V}_{FH_a}$ is the hole free volume in the amorphous phase, γ is the overlap factor accounting for shared free volume, ξ is the ratio of the solvent and polymer jumping units, φ_{1a} is the volume fraction of the solvent in the amorphous phase, and χ is the Flory-Huggins interaction parameter. In eq. (5) the first bracketed term is the estimation of the self-diffusion coefficient and the second term is the thermodynamic term using the Flory-Huggins thermodynamic model[9] to relate the mutual binary diffusion coefficient to the self-diffusion coefficient. The characteristics of the free-volume parameters and ways to estimate them are given by Zielinski and Duda.[10]

The free-volume theory has been modified to describe mutual binary diffusion in a semicrystalline material to take into account tortuosity and the effect of crystals on the adjoining amorphous phase. Wong et al.[11] account for the increase in the characteristic diffusion length caused by the presence of crystals

using a tortuosity factor, τ. The mutual diffusion coefficient is thus

$$D = \frac{D_a}{\tau} \qquad (7)$$

Lützow, et al.[4] suggest that the effect of the crystals on the amount of free volume in the amorphous phase can be estimated from the volume fraction of the crystals, φ_c.

$$\hat{V}_{\mathrm{FH}_{2a}}/\gamma = f_a - f_b \varphi \qquad (8)$$

Here f_a is the free volume of the amorphous phase without the presence of crystals and f_b is the parameter which correlates the influence of crystallinity on the amorphous phase. Thus, eq. (6) becomes

$$\frac{\hat{V}_{\mathrm{FH}_a}}{\gamma} = w_{1a}\frac{K_{11}}{\gamma}\left[(K_{21} - T_{g1}) + T\right] + w_{2a}[f_a - f_b\phi_c] \qquad (9)$$

Furthermore, they assume the tortuosity to be a linear function of the crystallinity.

$$\tau = 1 + \phi_c \tau_a \qquad (10)$$

Lützow et al. developed estimates for polyethylene parameters as follows: $f_a = 0.164$, $f_b = 0.0849$, $\tau_a = 7.57$. Thus, for the current work where $\phi_a = 0.776$, $\hat{V}_{FH_{2a}}/\gamma = 0.098$ and $\tau = 6.87$, similar to values reported by Lützow et al.

Solubility

Predictions of the solubility were made with the UNIFAC van der Waals free-volume[12] (UNIFAC vdw-FV) and with the group-contribution lattice fluid equation of state[13] (GCLF-EoS). For the pure components these models require the densities of both components, the molecular weight of the polymer, and the vapor pressure of the solvent. For the mixture the only requirement is the specification of the groups in the components.

van der Waals free-volume model

The UNIFAC model of Fredenslund et al.[14] can be used to predict activity coefficients in polymer-solvent systems. However, this method does not account for the free volume of the material. Oishi and Prausnitz[15] extended the approach to include a free-volume term. Kannan et al.[12] introduced the van der Waals partition function to determine the free-volume contribution. The UNIFAC van der Waals free-volume (UNIFAC vdw-FV) model uses the following equation to determine the activity coefficient of species i (Ω_i):

$$\ln\Omega_i = \ln\Omega_i^c + \ln\Omega_i^r + \ln\Omega_i^{fv} \qquad (11)$$

Here, c, r, and f_v correspond to the combinatorial, residual, and free-volume contributions, respectively. The first two terms are the original UNIFAC expressions.[14] This additional free-volume term is:

$$\ln\Omega_i^{fv} = \ln\left[\frac{\varphi_i^{fv}}{\varphi_i^h}\right] + \left[\frac{\varphi_i^h - \varphi_i^{fv}}{x_i}\right] \qquad (12)$$

In this equation, φ_i^{fv} and φ_i^h are the free volume and hardcore volume fractions, respectively, and x_i is the mole fraction. The relationship between the activity and weight fraction activity coefficient is:

$$a_i = \Omega_i \omega_i \qquad (13)$$

Group-contribution, lattice-fluid equation of state

The GCLF-EoS can also be used to predict the activity for a polymer-solvent system.[13] The GCLF-EoS relies on the lattice fluid theory and takes into account the contributions of various functional groups. Using this technique, the activity coefficient can be calculated using the following equation.

$$\ln\Omega_i = \ln\varphi_i - \ln w_i + \ln\frac{\tilde{v}_i}{\tilde{v}} + q_i\ln\left(\frac{\tilde{v}}{\tilde{v}-1}\frac{\tilde{v}_i - 1}{\tilde{v}_i}\right)$$
$$+ q_i\left(\frac{2\theta_{i,p} - \theta}{\tilde{T}_i} - \frac{\theta}{\tilde{T}}\right) + \frac{zq_i}{2}\ln\dot{\Gamma}_{ii} \qquad (14)$$

In this equation, φ_i and w_i are the volume and weight fractions, respectively, $\tilde{v}_i$ and $\tilde{v}$ are the reduced volume of species i and the mixture, q_i is the effective chain length of species i, $\theta_{i,p}$, and θ are the surface area fractions of pure species i and the mixture, $\tilde{T}_i$ and $\tilde{T}$ are the reduce temperature of species i and the mixture, z is the coordination number, and $\dot{\Gamma}_{ii}$ is the nonrandomness parameter.

Elasticity effect

These theoretical models for predicting solubility are not complete in the case of semicrystalline polymers. In this case it has been proposed that a new contribution has to be incorporated due to the elastic effect that the crystalline phase has on the solubility of the solvent. With this goal Serna et al.[16] introduced a correction to the solubility prediction models based on the theory developed by Michaels and Hausslein.[17] An additional term was added to eq. (11) to account for the elasticity effect. The expression for the calculation of the solvent weight fraction activity coefficient taking into account this elastic contribution becomes

$$\ln\Omega_i = \ln\Omega_i^c + \ln\Omega_i^r + \ln\Omega_i^{fv} + \ln\Omega_i^{el} \qquad (15)$$

Since $a_i^C = \omega_i \Omega_i^C$ it follows that, for the elastic contribution, the activity is equal to the activity coefficient $a_i^{el} = \Omega_i^{el}$.

According to the theory of Michaels and Hausslein the tension on the intercrystalline tie chains affects the thermodynamic equilibrium. The assumption of Hookean behavior of the polymer tie chains was made. The final expression obtained is:

$$\ln a_1^{el} = \frac{\Delta H_2^f \rho_a V_1 \left(\frac{1}{T} - \frac{1}{T_m}\right) - (\phi_1 - \chi\phi_1^2)}{R\left(\frac{3}{2f_e\phi_2} - 1\right)} \qquad (16)$$

Here ΔH_2^f is the specific heat of fusion per gram of crystalline polymer, ρ_a is the density of the amorphous polymer, T_m is the melting point of the crystalline polymer, V_i is the molar volume of the solvent (i=1) and polymer (i=2), and f_e is the fraction of elastically effected chains in the amorphous region. In general, in this region different types of chains can be found: tie chains, loops, free ends, and floating chains. Only the former ones are stretched when the solvent penetrates into the polymer network, and they become elastically deformed. As a result, only the tie chains are considered to produce a constraint on the polymer crystallites, which results in a decrease in sorption of the solvent in the polymer compared to what occurs in a totally amorphous polymer.

Serna et al.[16] studied linear, low density polyethylene–solvent systems. They reported that the f_e parameter was not temperature dependent. They found significantly improved predictions for the UNIFAC-vdw-FV model with a value of f_e of 0.36, but for the GCLF-EoS a value of 0.5 was the optimum.

EXPERIMENTAL

The HDPE that was used in this study had a crystallinity of 77.6%, a melt temperature of 131.5°C, and a density of 0.9586 g/cm³ at room temperature. The heat of fusion for the crystalline polymer[16] was taken as 65 cal/g. This polymer was obtained in bead form. For the experimental temperatures above the melt (140, 150, and 160°C) the spherical shape began to deform and, thus, the beads were pressed into flat sheets. Below the melt (90, 100, and 105°C), data were obtained on both the beads as received and on the sheets. These data were compared to see if the melting and compression caused any significant changes.

The gravimetric sorption experiments were conducted in a cylindrical glass column with a quartz spring using the same apparatus made and described by Duda et al.[18] In all cases the HDPE samples were placed in aluminum pans which were hung from the quartz spring in the Pyrex column. For temperatures below the melt the beads were used directly. For temperatures above the melt the sheets were cut to fit snuggly into the pans resulting in one-sided diffusion. The temperature in the solvent boiler was set so as to establish the desired activity in the column, the ratio of the vapor pressure at the boiler temperature to that at the column temperature. At the beginning of each experiment, the solvent vapor was introduced into the column, and the interaction between the polymer and solvent was monitored by measuring the mass uptake using a cathetometer. The experiment was concluded when there was no further change in the extension of the spring.

The gravimetric sorption analysis was carried out at three activities for each of the six column temperatures. In the higher temperature range, the activity values were limited because of the pressure limitations of the gravimetric column (i.e., <1 bar).

RESULTS

Solubility

The solubilities were determined from the equilibrium data for the gravimetric sorption experiments. The data are detailed in Table I. The solubility is reported as the amorphous weight fraction, i.e., g cyclohexane/g amorphous polymer. The estimated error in these data is $\sim$ 8%. The equilibrium pressure of the cyclohexane, p_1, as listed in Table I was the vapor pressure at the boiler temperature. The equilibrium weight fraction was determined from the final spring extension. The prediction models for solubility focus on the activity, a_1.

$$a_1 = \frac{f_1}{f_1^o} \approx \frac{p_1}{p_1^{sat}} \qquad (17)$$

Here f_1 is the equilibrium fugacity, f_1^o is the standard state fugacity (pure liquid at the temperature of the column), and p_1^{sat} is the vapor pressure of the cyclohexane at the column temperature. For the low pressures of the experiments the ratio of the pressures is a quite adequate representation of the activity. The following figures representing the data are in terms of activity in order to facilitate the comparison with model predictions.

Figure 1 shows the solvent activity as a function of the equilibrium amorphous weight fraction above and below the melt temperature. The lines in this figure were drawn arbitrarily for clarity. Above the melt (140 and 160°C) there was only a small change

TABLE I
Amorphous Solubility and Diffusivity of Cyclohexane in High-Density Polyethylene

Temp(°C)	Sample type	Activity	Pressure (kPa)	Equilibrium weight fraction[a]	Diffusion weight fraction[b]	Diffusivity (cm^2/s)
90	Beads	0.299	5.29	0.059	0.041	5.01×10^{-7}
		0.451	7.97	0.109	0.076	5.78×10^{-7}
		0.601	10.62	0.149	0.121	6.48×10^{-7}
	Sheet	0.299	5.29	0.060	0.042	
		0.451	7.97	0.106	0.074	4.66×10^{-7}
		0.601	10.62	0.131	0.110	7.73×10^{-7}
100	Beads	0.200	4.66	0.047	0.033	7.49×10^{-7}
		0.300	6.98	0.076	0.053	7.98×10^{-7}
		0.400	9.31	0.103	0.072	8.28×10^{-7}
	Sheet	0.200	4.66	0.048	0.034	9.74×10^{-7}
		0.300	6.98	0.068	0.048	8.07×10^{-7}
		0.400	9.31	0.087	0.075	
105	Beads	0.200	5.31	0.052	0.037	7.87×10^{-7}
		0.300	7.97	0.079	0.055	8.70×10^{-7}
		0.399	10.59	0.104	0.089	8.73×10^{-7}
	Sheet	0.200	5.31	0.044	0.031	8.16×10^{-7}
		0.300	7.97	0.080	0.056	9.94×10^{-7}
		0.399	10.59	0.110	0.077	1.14×10^{-6}
140	Sheet	0.100	6.00	0.023	0.016	1.45×10^{-6}
		0.150	9.01	0.045	0.032	1.67×10^{-6}
		0.200	12.00	0.068	0.054	2.00×10^{-6}
150	Sheet	0.080	5.89	0.022	0.015	1.50×10^{-6}
		0.120	8.84	0.038	0.026	1.77×10^{-6}
		0.160	11.78	0.050	0.035	2.15×10^{-6}
160	Sheet	0.070	6.28	0.024	0.017	1.66×10^{-6}
		0.110	9.87	0.039	0.028	2.17×10^{-6}
		0.142	12.76	0.049	0.035	2.55×10^{-6}

[a] Based on the amorphous phase.
[b] Based on amorphous phase and adjusted for concentration step change as described in text.

in the solubility. Below the melt (90 and 105°C), however, the solubility for the same activity is significantly higher at the higher temperatures. While
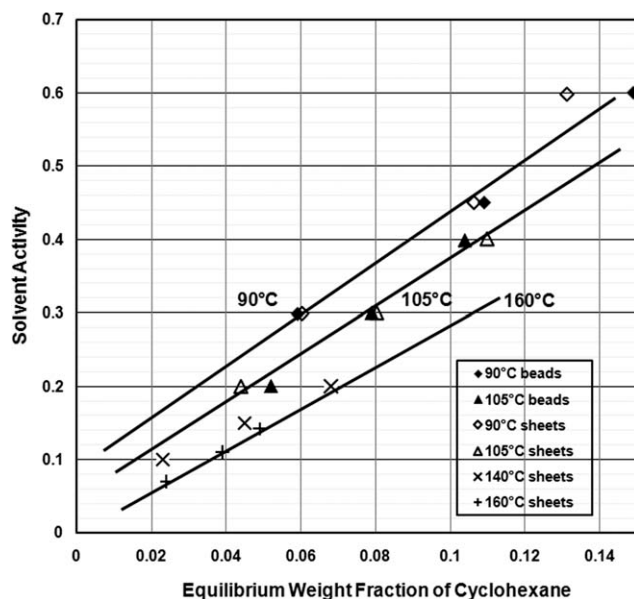

Figure 1 Cyclohexane solubility in HDPE. (Amorphous basis).

this may at first glance be counterintuitive, it is to be expected because to attain the same activity at a higher temperature a higher pressure is required. The data also indicate that within experimental error there is essentially no difference between the solubility in the beads and the sheets.

Predictions based on the UNIFAC-vdw-FV model and the GCLF-EoS were made for all the temperatures, 90–160°C. In all cases the temperature dependencies of the densities and vapor pressures were taken into account. The results above the melt temperature are characterized by the curves shown in Figure 2. The UNIFAC-vdw-FV model, eq (11), tends to predict weight fractions of cyclohexane which are a bit too low. The GCLF-EoS, eq. (14), predicts essentially the same values for both 140 and 160°C and are in better agreement with the experimental data than those of the UNIFAC-vdw-FV mode.

Typical results below the melt temperature (90°C) are shown in Figure 3. Both models predict weight fractions of cyclohexane which are too high if the elasticity effect is not taken into account. If the f_e factor is accounted for, eq. (16), much better predictions are obtained. The density of the amorphous phase in the semicrystalline region
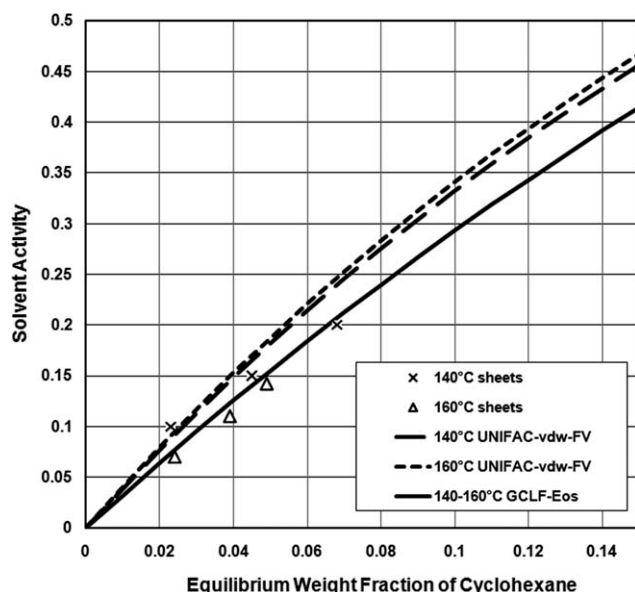
Figure 2 Prediction of cyclohexane solubility in HDPE above the melt temperature (Amorphous basis).

was calculated by extrapolation of the amorphous behavior above the melt temperature using the Tait equation.[19]

$$V(P, T) = V(0, T)\left[1 - C\ln\left(1 + \frac{P}{B(T)}\right)\right] \quad (18)$$

$$V(0, T) = A_0 + A_1(T - 273.15) + A_2(T - 273.15)^2 \quad (19)$$

$$B(T) = B_0 \exp[-B_1(T - 273.15)] \quad (20)$$

Here V is the specific volume of the polymer, T is the temperature, P is the pressure, and A_i and B_i are specific constants (See Table II).
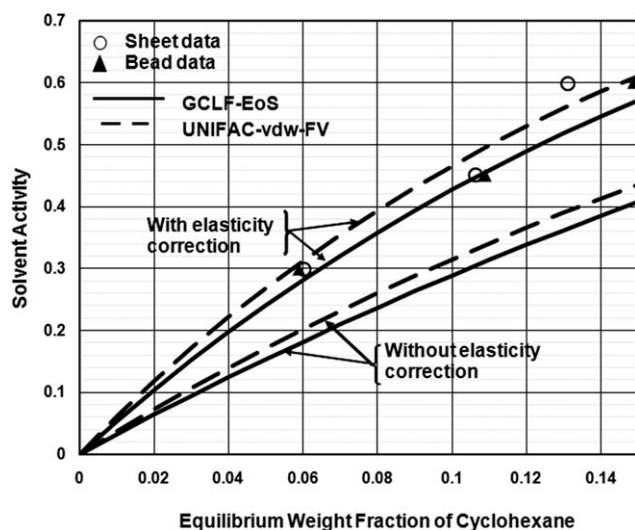

Figure 3 Prediction of cyclohexane solubility in HDPE below the melt temperature (90°C) (Amorphous basis).

TABLE II
Correlation Parameters For HDPE and Cyclohexane

Free-volume parameters	
Cyclohexane molecular weight	84.16
V_1^* (cm^3/g)	1.008
V_2^* (cm^3/g)	1.006
K_{11}/γ (cm^3/g K)	3.02×10^{-3}
K_{12}/γ (cm^3/g K)	1.02×10^{-3}
$K_{21}\text{-}T_{g1}$ (K)	-157.8
$K_{22}\text{-}T_{g2}$ (K)	-228.7
χ	0.364
ξ	0.5447
D_0 (cm^2/s)	2.39×10^{-5}

Tait equation constants[a] for amorphous HDPE[19]	
A_0 (cm^3/g)	1.16×10^{-3}
A_1 (cm^3/g K)	6.29×10^{-7}
A_2 (cm^3/g K^2)	1.13×10^{-9}
B_0 (Pa)	1.79×10^8
B_1 (1/K)	4.73×10^{-3}
C	0.0894

[a] Units: T in K, P in Pa.

Serna et al.[16] found that different values of the elasticity factor for linear, low-density polyethylene were needed for each of the models (0.36 for the UNIFAC-vdw-FV and 0.5 for the GCLF-EoS). In the present case a value of 0.55 was quite satisfactory for both models. Note that this value is a fitted parameter and means the models are no longer purely predictive. For polyethylenes, however, it appears a value around 0.4–0.5 will significantly improve the predictions. The elastic activity coefficient is not overly sensitive to the value of f_e.

Diffusivity

The diffusivity was calculated using Crank's model for the corresponding polymer geometry. The data were obtained by measuring very small changes in the quartz spring extension. The diffusion coefficient in turn is quite sensitive to the initial slope of the normalized uptake versus the square root of time. As a result the error in the diffusion data is of the order of 25%. As discussed earlier diffusivities in polymer-solvent systems can be very sensitive to solvent concentration. The variation of the diffusivity in the ranges of temperature and pressure studied in this work was over 500%. Thus, defining them with an absolute error of 25% is valuable.

For the diffusion experiments there is a step change in the concentration. As shown by Vrentas and Duda[20] the most appropriate concentration to represent the concentration over a given step is 70% of the change. This is given as the diffusion weight fraction in Table 1. Figure 4 shows the experimental diffusion coefficients as a function of the amorphous weight fraction of cyclohexane. Below the melt
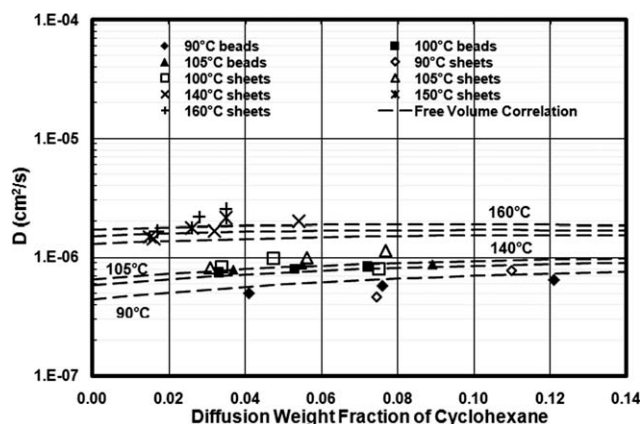
Figure 4 Diffusion coefficient of cyclohexane in HDPE—data and free-volume predictions (Amorphous basis).

temperature (131.5°C), the experiments were initially carried out using the polymer beads as they were received. Above the melt temperature, however, the shape of these beads deformed and stuck together, so the samples were pressed into thin sheets. The experiments below the melt temperature were repeated using the flat sheets. Within the experimental error there was essentially no difference between the geometries which indicates that the melting and compression of the polyethylene had no significant effects.

All the data both above and below the melt temperature were regressed using the Vrentas-Duda free-volume model without the tortuosity factor, eq. (5). The parameters obtained from this fit are given in Table II. The expectation was that this would not provide good fits below the melt temperature because of the crystallinity. The results, however, follow the trends of the data in both regions of temperature, indicating that the tortuosity and effect of the crystals on the amorphous phase free volume has little or no affect. In theory, the crystals within the polymer should deter the diffusion process because the solvent material cannot penetrate the crystalline region of the material. Thus, the solvent travels along the tortuous pathways that correspond to the amorphous portion of the polymer. If the tortuosity factor calculated from eq. (10) is introduced, the predicted diffusivities would be reduced by a factor of 6.87, significantly below the experimental data. This is contrary to the results reported by Lützow, et al.[4]

The cause of this phenomenon is unknown. One possible theory is that the crystals broke down before they could affect the diffusion. As the temperature approaches the melt temperature, the semicrystalline material will start to transform into a more amorphous material. Another factor is the presence of cyclohexane. The crystals within the polymer could partially dissolve after the solvent is introduced.

CONCLUSION

In this study, diffusion and solubility data were obtained for an HDPE-cyclohexane system using gravimetric sorption analysis. Temperatures ranging for 90–105°C below the melt and 140–160°C above the melt were examined up to a solvent weight fraction of 0.15. Both the solubility and diffusivity data depended on the temperature and the concentration. The crystallinity did not have the anticipated tortuosity effect on the diffusion.

Below the melt temperature a comparison was made between the data for the original beads and the melted, compressed sheets. Similar results were observed for both sample types. Above the melt temperature the GCLF-EoS was better than the UNIFAC-vdw-FV model for the prediction of the solubility of cyclohexane in the HDPE. Below the melt temperature a correction for the elasticity effect was necessary in order to provide good predictions by either model.

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