Ethylene Solubility and Diffusion in Low-Density Polyethylene and Ethylene Copolymers

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Synopsis

Evolution rate measurements were conducted to determine the solubility and the diffusion constants of ethylene in three semicrystalline polymers: low-density polyethylene (LDPE), ethylene–ethyl acrylate (EEA), and ethylene–vinyl acetate (EVA) copolymers. The apparatus for such measurements utilizes a flame ionization detector interfaced to a computer for continuous monitoring of the ethylene evolution from the polymer pellets. Solubilities are obtained by calculating the total ethylene evolved over a 12–48-hr period. Analysis of the evolution rate data in terms of the nonsteady-state diffusion equation for spheres yields the diffusivity. The ethylene solubility and diffusion constants in EVA and EEA are very similar to those in LDPE. This is due to compensating effects of decreased crystallinity and increased cohesive energy density with the incorporation of bulky polar groups into the polymer chain.

INTRODUCTION

Low-density polyethylene (LDPE), ethylene–vinyl acetate (EVA), and ethylene–ethyl acrylate (EEA) copolymers comprise a large fraction of the economic value of all manufactured polyolefins. Freshly made LDPE, EVA, and EEA pellets contain considerable amounts of ethylene, which must be purged to allow safe handling of the product. Therefore, ethylene solubility and diffusivity data are required to provide a rational basis for the design and operation of pellet devolatilization facilities. The temperature range of interest for such data is usually 20–75°C.[1]

In semicrystalline polymers, the diffusion of a supercritical gas depends on the nature of the diffusing molecule and the chemical structure of the polymer chain, as well as the morphology of the polymer matrix. Diffusion takes place in the amorphous regions, where cooperative motion of polymer segments allows molecules to jump thermally to neighboring sites in the matrix. Crystalline structures decrease the diffusivity by requiring the molecule to follow a tortuous path through the matrix and by restricting the motion of polymer segments in the amorphous regions. Comparison of gas diffusivity of LDPE, EVA, and EEA copolymers is especially interesting, because the random incorporation of bulky polar groups like VA and EA into the polyethylene chain disrupts the crystalline matrix, leading to higher amorphous fractions in which diffusion can occur. However, the polar groups also stiffen the polymer chains, as demonstrated by the higher glass transition temperatures of the homopolymers of EA (−24°C) and VA (28°C) compared with the predicted T_g of amorphous polyethylene (< −70°C). From this point of view, EVA and EEA chains should show more resistance to molecular diffusion relative to a completely amorphous LDPE sample. The interplay of these two opposing tendencies determines the relative magni-

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tude of the ethylene diffusion constants in ethylene polymers. Therefore, *a priori* predictions are difficult, and experimental determinations are necessary.

Crank and Park[2] have described several experimental techniques used to measure diffusivities. The most common approach is to separate measurements of the steady-state rate of gas transmission through the polymer film and of the equilibrium solubility coefficient. Using such a technique, Michaels and Bixler[3] measured the diffusion and solubility constants of 12 common gases in LDPE; however, ethylene was not included among the gases studied. We describe here a technique based on continuous monitoring of gas evolution rate out of polymer pellets which allows determination of the solubility and the diffusion constant from a single experiment. This method has been applied to the measurement of ethylene diffusivity and solubility in three commercial ethylene polymers—LDPE, EVA, and EEA—at temperatures from 20 to 75°C.

EXPERIMENTAL

The apparatus used in this work consists of a Thermal Evolution Analyzer (DuPont 916-TEA) equipped with an external sample holder and interfaced to a PDP-11/40 digital computer (Fig. 1). Approximately 7.5 g of spherical pellets of uniform size were charged to the Pyrex sample holder. A heating tape wrapped around the glass holder was used to control the temperature of the pellets. Temperature gradients in the pellet bed were minimized by preheating the purge gas to the temperature of the bed by passing the gas through a layer of steel wool positioned above the pellets. The total temperature variation was found to be less the ±1°C by moving a thermocouple to several horizontal and vertical positions in the sample holder. This thermocouple was also used to monitor the bed temperature during the course of each experiment.

Two purge streams were required in the experiments: (1) pure ethylene (25 cc/min) for saturating the pellets and (2) a high-purity nitrogen stream (30.0 ±

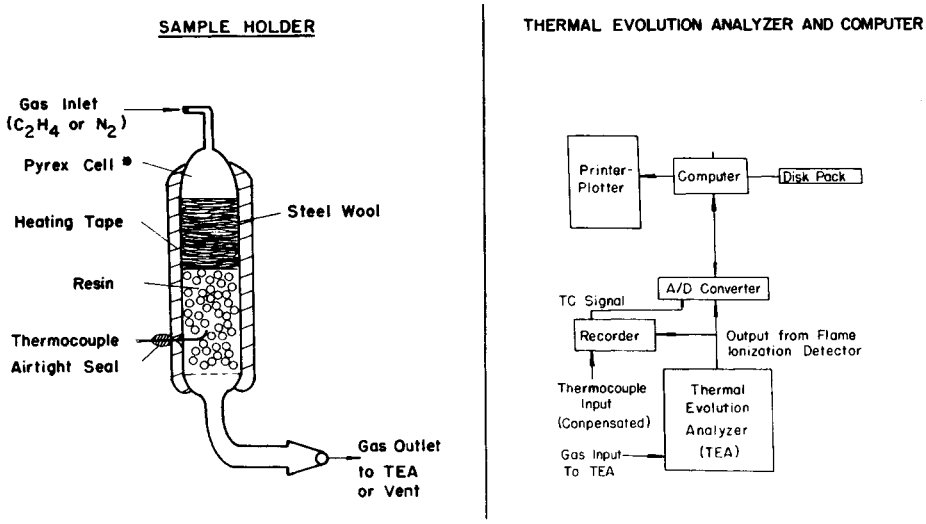

Fig. 1. Diagram of the apparatus used and schematic of the experimental setup.

0.2 cc/min) for desorption measurements. Prior to evolution rate measurements, the pellets were stripped of residual volatiles left over from production or processing (i.e., acetone, oils) by purging with nitrogen until the evolution rate was below detectable levels (10^{-11} g/min/g of polymer). The pellets were then saturated at the desired temperature by purging with high-purity ethylene for more than 48 hr. To begin the evolution rate measurements, the ethylene purge was replaced by a nitrogen purge (1000 cc/min), which quickly stripped the ethylene from the sample holder. After 30 sec, the rapid purge was replaced with a high-purity nitrogen stream of known volumetric flow rate (30.0 ± 0.2 cc/min), and the outlet from the sample holder was attached to the TEA inlet. From this point on, a flame ionization detector in the TEA continuously monitored the ethylene concentration in the nitrogen stream. The analog output from the detector was inputted to the computer system. A real-time data acquisition program[4] controlled the data sampling rate, changed the analogs to digital gain for optimum resolution, and stored the digital values on a disk for later analysis. Evolution rates were recorded at 1-min intervals until they fell below the detectable levels. This process required 12–48 hr, depending on the polymer type and the pellet temperature. The high sensitivity of the flame ionization detector and the large sample size that could be contained in the external cell allowed evolution rate measurements to less than 10^{-10} g of ethylene/min/g of polymer sample, as was required to follow the devolatilization to the low levels achieved in this work. The accuracy of the evolution rate measurements is estimated to be ±5% based on repeated calibrations of the flame ionization detector.

Evolution rate measurements were conducted at atmospheric pressure in the temperature range 23–74°C. Polymers used in this study were all commercial samples from Union Carbide Corporation with the characteristics shown in Table I. A differential scanning calorimeter (DuPont 990) was used to measure the melting curves and the heats of fusion. The fraction of crystalline polymer was estimated by assuming[5] 286 J/g for the heat of fusion of 100% crystalline polyethylene. Gill and Levy[6] have detailed this procedure for crystallinity determination in polyethylene and have indicated agreement with x-ray techniques.

TABLE I
Characteristics of the Polymer Samples

Parameter	LDPE	EVA	EEA
Density, g/cm^3 (25°C)	0.923	0.934	0.930
Comonomer content, wt. %			
VA	—	10	—
EA	—	—	18
Melting temperature, °C[a]	115	95	89
Heat of fusion, J/g[a]	137	86	54
Crystallinity, %[a] (reproducibility)	48 (±5)	30 (±3)	19 (±2)
Average pellet radius, cm[b]	0.192	0.153	0.183

[a] Measured by DSC.
[b] SD = ± 0.01 cm.

DISCUSSION

Evolution Rates

The evolution rates of ethylene from LDPE, EVA, and EEA pellets are presented in Figures 2–5. Evolution rate measurements were taken at 1-min intervals until more than 98.5% of the ethylene was evolved. During the first hour of desorption, the evolution rate decreases by more than an order of magnitude. Increasing the temperature results in larger evolution rates during the early phases of desorption; however, this trend is reversed at longer times due to rapid depletion of ethylene from the pellets (Fig. 2). All three polymers depict the same characteristic behavior towards the diffusion of ethylene molecules, as evidenced by Figures 2–5.

Ethylene Solubility

Solubilities at different temperatures were obtained by measuring the total ethylene evolved over a 12–48-hr period. These empirical solubilities represent the moles of ethylene dissolved per gram of bulk polymer under 1 atm of ethylene. No corrections were made for gas phase nonideality, which would be very small under these conditions, and no adjustments were made for crystallinity in the polymer. Repeated experiments yielded reproducible solubilities within ±8% (95% confidence limits). They are shown in Figure 6 as a function of reciprocal temperature. Ethylene solubilities in EEA copolymers are 10–40% larger than those in LDPE and EVA pellets, depending on the temperature.

In studying the gas solubility in polyethylene, Michaels and Bixler[3] observed that the solubility is strongly dependent on the volume fraction of the amorphous

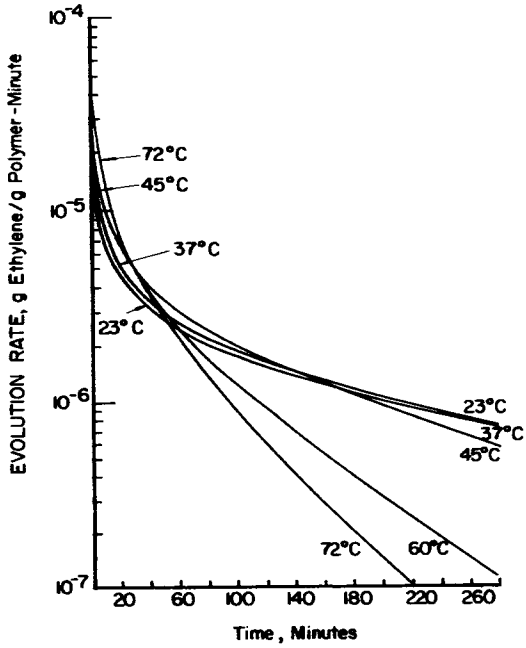

Fig. 2. Ethylene evolution from LDPE.

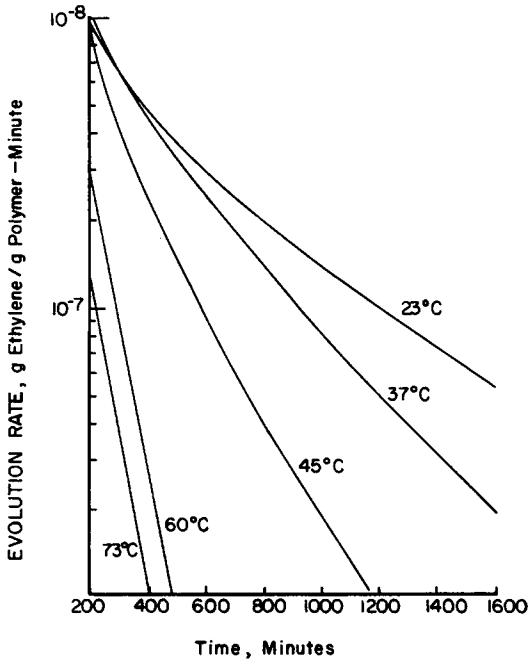

Fig. 3. Ethylene evolution from LDPE.

phase. The gases have little or no solubility in the crystalline phase. They were able to correlate gas solubilities with crystallinity for polymers of similar chemical structure (i.e., low- and high-density polyethylenes). A direct interpretation

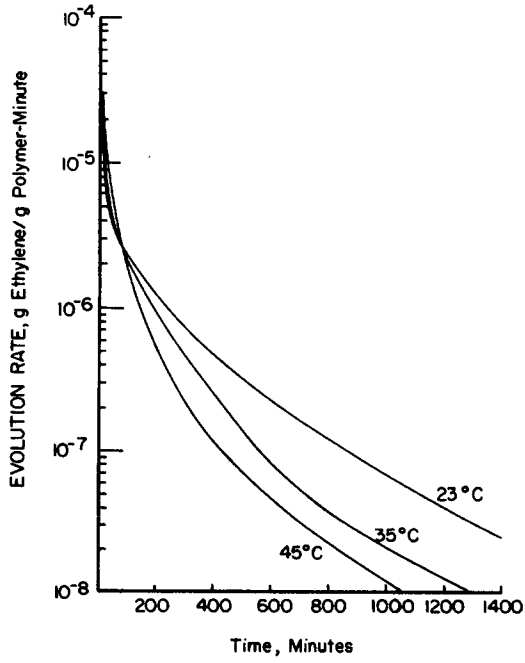

Fig. 4. Ethylene evolution from EVA.

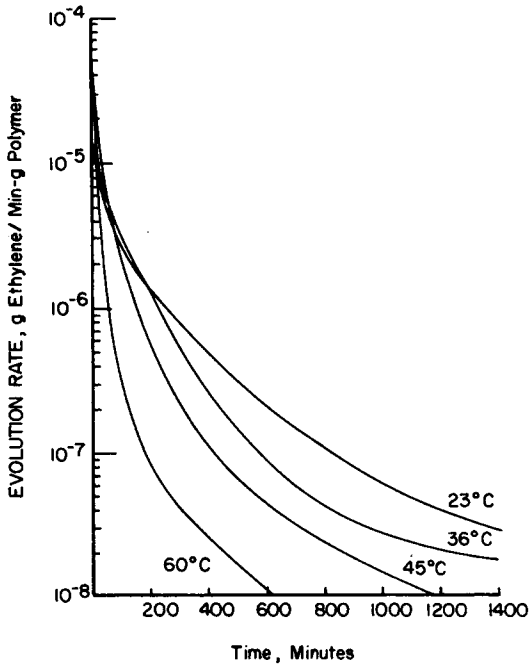

Fig. 5. Ethylene evolution from EEA.

of our results in terms of crystalline content of the polymer is not possible due to different affinities of acetate and acrylate groups in EVA and EEA copolymers towards ethylene. At 23°C the solubility of ethylene is almost equal in all three polymers, indicating that any increases in solubility due to the lower crystallinity in EEA or EVA at this temperature is offset by increased dissimilarity between ethylene and polar side groups. As the temperature increases, the effect of increased amorphous fraction in EEA outweighs the effects of chemical dissimilarity, leading to higher solubility compared to LDPE.

The temperature dependence of ethylene solubility can be described by the usual Arrhenius type relationship (Fig. 6). A least-squares fit of the data yields the following:

$$\ln S_{\mathrm{LDPE}} = -14.417 + 2440/RT \tag{1}$$

$$\ln S_{\mathrm{EEA}} = -12.713 + 1482/RT \tag{2}$$

The coefficient of reciprocal temperature in eqs. (1) and (2) is the apparent heat of solution.[7] For LDPE the apparent heat of solution is −10.5 kJ/mol, in excellent agreement with the values reported by Michaels and Bixler[3] for similar gases in LDPE. A direct comparison of ethylene solubilities reported here with those measured by Lui and Prausnitz[8] for LDPE and EVA melts is not possible due to the higher temperatures of their measurements; however, the extrapolation of the data in Figure 6 to 125°C and above yields good agreement with their data (after adjusting for crystallinity).

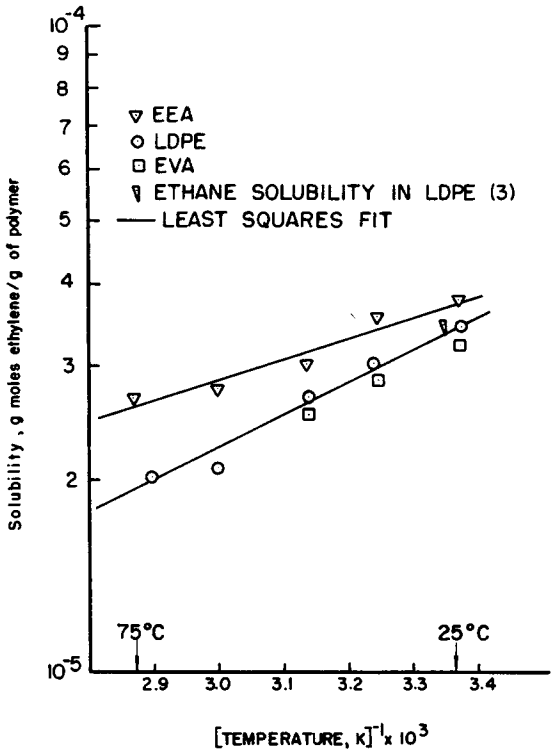

Fig. 6. Temperature dependence of ethylene solubility in LDPE, EVA, and EEA.

Diffusion Constant

The differential equations describing the sorption/desorption rates are amenable to analytical solutions for simple geometries like spheres. Therefore, to interpret the evolution rate measurements in terms of a diffusion constant, the following assumptions are made:

1. Diffusion in the polymer is Fickian with a constant diffusivity D. This implies that crystallinity in these polymers does not alter Fick's laws of diffusion, although D may, and probably will, be affected.
2. Gas phase resistance to mass transfer is negligible.

The derivation of the non-steady-state diffusion equation for gases in spherical solids is given in Ref. 9, and therefore it is not repeated here. The expression for the evolution rate as a function of time is

$$\frac{d(M_t)}{dt} = \frac{6M_\infty D}{r^2} \sum_{n=1}^{\infty} \exp\left(-\frac{Dn^2\pi^2 t}{r^2}\right) \tag{3}$$

To calculate the diffusion constant D, the evolution rate data were fitted to eq. (3) using a nonlinear optimization routine. This essentially involves finding the value of D which minimized the sum of the squares of the deviations between the predicted evolution rate and the measured values. The series in eq. (3) was terminated at $n = 5$. Higher values of n do not contribute significantly to the evolution rate except at the very beginning of the experiment. The calculated diffusivities are presented in Table II. The measured and calculated [from eq. (3)] evolution rates are within the experimental accuracy of the measurements.

TABLE II
Calculated Diffusion Constants for Ethylene in LDPE, EVA, and EEA Pellets

Polymer	Temperature, °C	Diffusion constant, $cm^2/min \times 10^5$
LDPE	23	0.86
	36	1.16
	45	2.20
	60	5.09
	73	7.18
EVA	23	0.84
	35	1.34
	45	2.57
EEA	23	1.42
	37	2.21
	45	3.35
	60	5.44
	74.5	7.77

A more stringent test is to calculate the amount of ethylene retained in the pellets as a function of time and then compare this with the measured values. Such a calculation can be performed by integrating eq. (3) with respect to time. The resulting equation is

$$\frac{M_\infty - M_t}{M_\infty} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{Dn^2\pi^2 t}{r^2}\right) \tag{4}$$

Figure 7 illustrates the results of such a calculation for LDPE at 23°C. Again the agreement between the predicted and the measured values is good, indicating the validity of the assumptions in using eq. (3) to represent the evolution rate data. We estimated the accuracy of the diffusion constants at ±10%, with variation in pellet diameter being the largest contributor to the uncertainty.

As illustrated in Figure 8, ethylene diffusivities in all three polymers are very

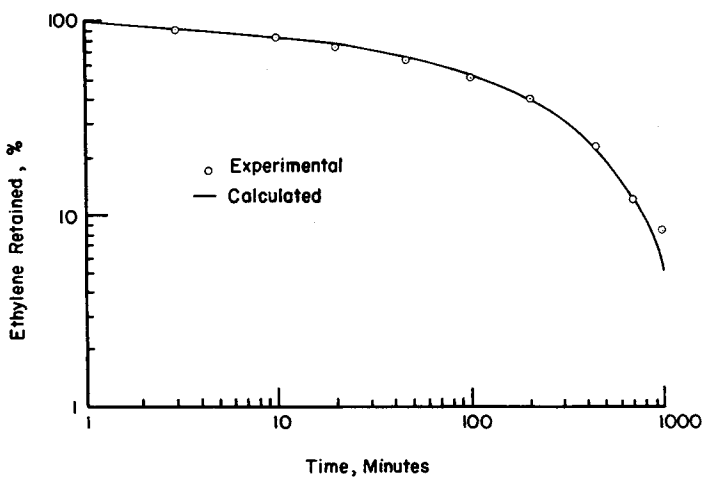

Fig. 7. Comparison of ethylene retention measured for LDPE at 23°C with that predicted from diffusion constant.

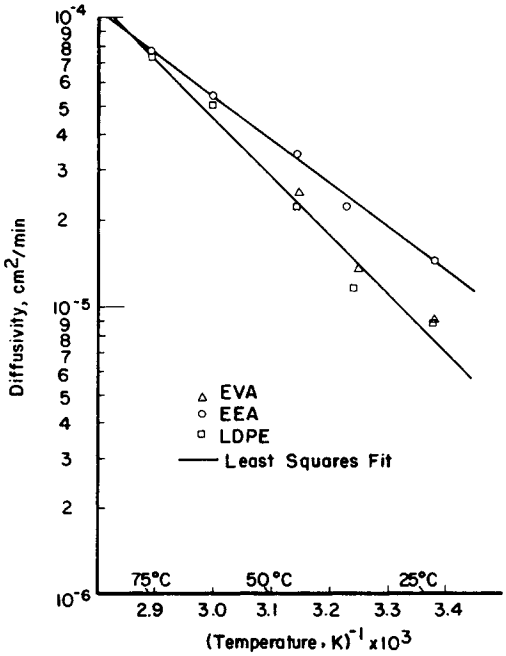

Fig. 8. Temperature dependence of ethylene diffusivity in LDPE, EVA, and EEA.

close in magnitude, but the differences become more apparent as the temperature decreases. At 23°C, ethylene diffusivity in EEA is twice of that in LDPE and EVA. Arrhenius plots of ethylene diffusion constants versus the reciprocal temperature yield 40 and 29 kJ/mol as the activation energies in LDPE and EEA, respectively. However, additional measurements on more refined samples are needed to verify the small differences in D and E_D between EEA and LDPE. (No activation energy is calculated for ethylene diffusivity in EVA pellets due to the limited temperature range of the data.)

If we assume that the solubility of ethylene in the polymers is proportional to the pressure (Henry's law region) and the diffusivity is independent of pressure, then permeability constants can be calculated using the expression

$$\overline{P} = DS \tag{5}$$

The permeability constants for ethylene in LDPE and EEA at 23°C are 1.0×10^{-7} and 1.7×10^{-7} cc(STP)/cm sec (atm), respectively, based on values of diffusivity and solubility determined in this work. The LDPE value is in good agreement with permeabilities of similar gases in LDPE measured directly by the time-lag technique.[3]

The results for LDPE and EEA are consistent with an interpretation based on compensating factors from crystallinity changes and polymer stiffness. At low temperatures, the high crystalline content of the LDPE pellets (48%) leads to lower diffusivities than those in EEA pellets (18% crystalline). The crystallites act as impermeable fillers, forcing gas molecules to follow tortuous paths through amorphous regions. As the temperature is increased, volumetric expansion and partial melting of the polymer lead to easier diffusion of gas molecules; however, the increase in diffusivity is larger in LDPE due to its lower cohesive energy

density. Bulky ethyl acrylate groups increase the cohesive energy density of the EEA chains, restricting the segmental movements required for a permeant molecule to diffuse through. Therefore, if measurements were extended to completely amorphous samples, we would anticipate that the ethylene diffusivity in LDPE would surpass that in EEA because of the differences in cohesive energy density. Further understanding of gas diffusion in semicrystalline polymers now depends on acquisition of more data to quantify these trends.

NOTATION

D = diffusion constant
M_t = gas concentration in polymer at time t
M_∞ = initial gas concentration in polymer
$\bar{P}$ = permeability constant
r = pellet radius
S = ethylene solubility in bulk polymer
T = absolute temperature
t = time

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