

Effects of Temperature, Repeated Exposure, and Aging on Polybutylene Permeation by Organic Chemicals

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SYNOPSIS

The permeation parameters, partition coefficient and diffusion coefficient, were obtained for polybutylene (PB) with toluene using a gravimetric method. A PB sample was repeatedly exposed and desorbed, and the partition coefficient and diffusion coefficient were measured. Permeation parameters were also measured at different temperatures. The results were compared with those obtained from a 12-year-old PB pipe sample, which had experienced structural failure. Tests at an elevated temperature of 45°C failed to simulate the effect of polymer aging, whereas repeated sorption/desorption tests produced permeation parameters compatible with those of a 12-year-old PB pipe in service.

INTRODUCTION

The major thermoplastic materials used for potable water transport and plumbing applications include poly(vinyl chloride) (PVC), chlorinated poly(vinyl chloride) (CPVC), polyethylene (PE), polybutylene (PB), and acrylonitrile-butadiene-styrene (ABS). Advantages claimed for plastic pipes include immunity to corrosion, ease of use, ductility, and durability. During the last decade, however, it has been found that plastic piping and gasket materials are susceptible to attack and/or permeation by certain organic chemicals.^{1,2}

Polymers are permeated by organic chemicals through a combination of partitioning (solubility) and diffusion phenomena. Prediction of a partition coefficient and diffusion coefficient has been attempted by other researchers.^{2,3} For aromatic organic chemicals, the vapor-phase partition coefficient was predicted from a logarithmic correlation with the saturation vapor concentration for PB and styrene butadiene rubber (SBR).² Also, the diffusion coefficient was estimated from the relationship between the molecular diameter and the logarithm of the diffusion coefficient for PVC,¹ PB, and SBR.²

During service, polymers may change their physical properties including strength, stiffness, strain at failure, and permeability. Attempts have been made to evaluate the changes of original properties over a long period of time. One method adopted by EPA is to raise the temperature to 50°C to test chemical compatibilities.⁴ It is not clear whether a test at an elevated temperature can produce permeation parameters comparable to those of samples exposed to organic chemicals for a long time. A technique should be developed to assess the effects the aging of a polymer has on its permeability. In other words, how does the performance of a polymer change when it is exposed to organic chemicals for a long service time.

The objective of this paper is to evaluate permeability of PB to toluene after long-term use. The results from 12-year-old specimens, repeated sorption-desorption tests, and various temperature conditions are compared.

MATERIALS AND METHODS

Materials

PB, trade name for poly(1-butene), is a member of the polyolefin group of polymers made of straight-chain hydrocarbons. PB is partially crystalline and

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has five different types of crystals.⁵ Usual crystallinity after pipe extrusion is 48–55%. The glass transition temperature for PB ranges from -17 to -25°C . The typical nominal average molecular weight is 70,000–75,000 g/mol, and the weight average molecular weight is 725,000–750,000 g/mol. PB has a stiffness similar to low-density PE, but its strength is higher than that of high-density PE. Its most significant feature is its better retention of strength with increasing temperature. Its highest service temperature is nearly 93°C for pressure uses and somewhat higher for nonpressure applications. The PB used in this experiment has a density of 0.93 g/cm^3 at 20°C and an average sample thickness of $63\text{ }\mu\text{m}$. Thin strips of PB were obtained from the water pipes with a lathe. Several rolls of PB pipe were purchased on the open market. Samples of PB also were obtained from the North Marin Water District, San Rafael, Ca. Some of the latter specimens had been in service for up to 12 years and had experienced structural failures. High-pressure liquid chromatography grade toluene was used without further purification.

Apparatus and Procedure

Microbalances are commonly used to determine the permeation of gases and vapors through polymers.^{2,3,6} The microbalance method consists of measuring the weight increase of a small specimen of polymer over time under exposure to the pure gas or vapor. The method is relatively rapid and does not require the determination of concentrations.

The system used in this study is shown schematically in Figure 1. The vapor of a pure organic chemical (liquid) stored in a 1 L flask was drawn through the microbalance with a vacuum pump. Two glass cold-traps were installed upstream of the pump, primarily to avoid contamination of the pump oil with the corrosive chemicals drawn through the microbalance. The vapor pressure was controlled by the two stainless steel needle valves designated as A and B in Figure 1. Vapor pressure was recorded continuously with time thanks to a pressure transducer located in the sample chamber of the microbalance. The pressure was also monitored by eye with a mercury manometer (see Fig. 1).

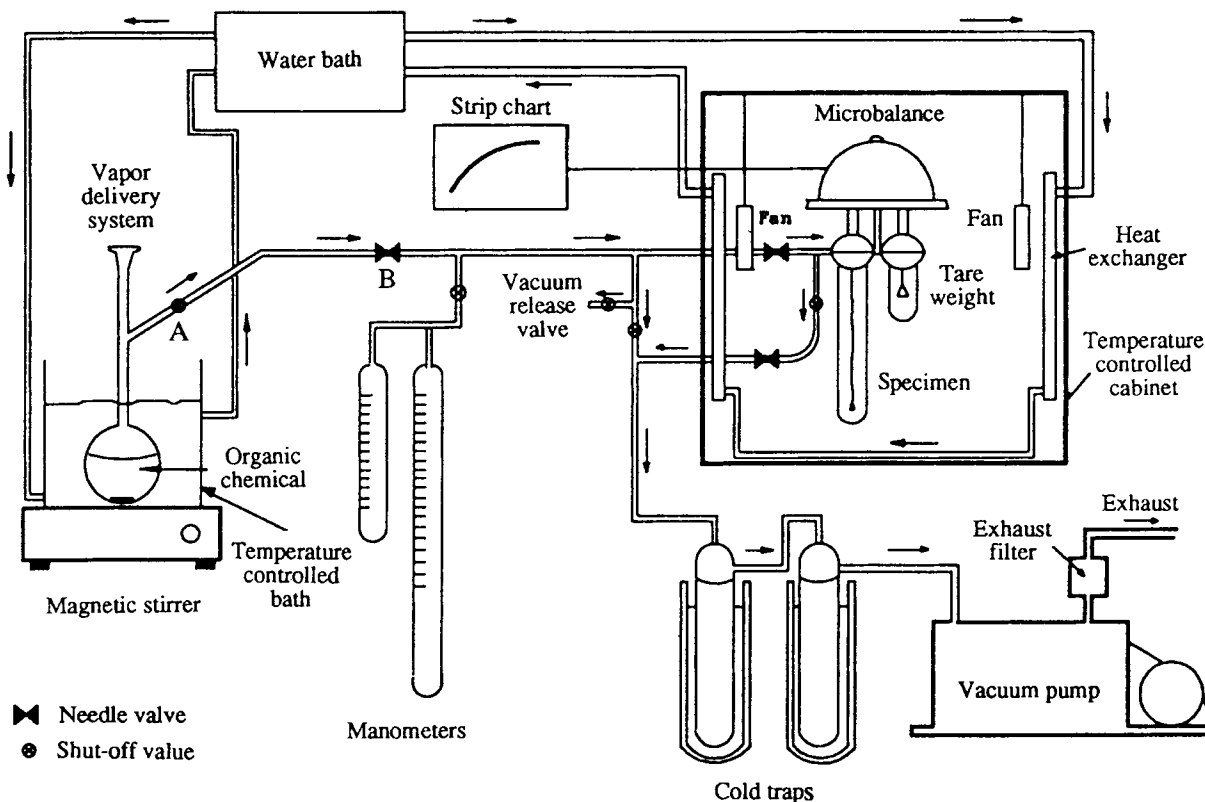


Figure 1 Schematic diagram of microbalance apparatus.

A mixture of water and ethylene glycol was circulated from a constant temperature water bath through a heat exchanger to control the temperature in the microbalance chamber. This arrangement sufficed to control the temperature within $\pm 0.5^\circ\text{C}$ over a range of $5\text{--}48^\circ\text{C}$. Finally, the microbalance proper was installed inside a thermally insulated wood cabinet. This cabinet rested on the concrete foundation slab of the building in which the work was being performed. The latter was necessary to minimize vibrations.

The procedures used to operate the apparatus were as follows:

1. A sample of the polymer was placed on the balance sample holder and valve A was closed (Fig. 1). A vacuum was then applied to the system (approx. 10^{-2} mmHg). The temperature was adjusted until steady-state conditions of weight and temperature were achieved. (The purpose of the vacuum was to remove the atmospheric moisture and other gases sorbed by most polymers under ambient conditions.)
2. Valve A was opened and adjusted in concert with valve B to obtain a steady vapor pressure as quickly as possible. The test was continued until the weight of the sample again became steady with time.
3. Step 2 was repeated over a range of pressures.
4. Valve A was then closed, and the test was continued under vacuum until the sample returned to its initial weight. This served as a check on the sample tare weight.

It was postulated that the aging process of a polymer may be enhanced by repeated sorption/desorption cycles. This treatment might lead to the release of materials that are soluble in the polymer such as plasticizers or processing aids. Therefore, a series of experiments was conducted in which the sequence Steps 2 through 4 was repeatedly applied to a single sample.

THEORY

The organic chemical vapor absorbed by the polymer can be considered as a solute. Assuming that the solute is approaching the limit of infinite dilution

in the polymer, the absorption isotherm will always be linear, or

$$C^* = KC_v \quad (1)$$

in which C^* = solute concentration in the polymer at equilibrium (mg/L); C_v = solute concentration in the gas surrounding the polymer sample (mg/L); and K = the vapor-polymer partition coefficient. The partition coefficient was then computed from the results of the microbalance studies by

$$K = \frac{\Delta M^*}{M_0} \cdot \frac{\rho_0}{MW} \cdot \frac{RT}{p} 7.6 \times 10^8 \quad (2)$$

in which ΔM^* = gain in weight of polymer sample at equilibrium (mg); ρ_0 = density of polymer at time zero (g/cm^3); M_0 = weight of polymer sample at time zero (mg); MW = molecular weight of solute (g/mol); R = ideal gas constant ($8.206 \times 10^{-5} \text{ m}^3 \text{ atm}/\text{K mol}$); T = absolute temperature (K); and p = pressure of solute vapor (mmHg).

The diffusion of a solute into the very thin sheets of polymer placed in the microbalance apparatus is essentially unidimensional. The diffusion coefficient is independent of solute concentration at the limit of infinite dilution of the solute in the polymer (pure-Fickian diffusion). Based on the following assumptions, the weight gain of the polymer sample with time t is⁷

$$\frac{\Delta M(t)}{\Delta M^*} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \times \exp\left(- (2n+1)^2 \pi^2 \frac{Dt}{l^2}\right) \quad (3)$$

in which $\Delta M(t)$ = gain in weight of the polymer sample at time t (mg); D = diffusion coefficient (m^2/day); t = elapsed time (days); and l = thickness of polymer sample (m). At half-sorption time, ($t_{0.5}$), $\Delta M(t)/\Delta M^* = 0.5$. Rearranging eq. 3 for this particular time gives

$$D = 0.049 \frac{l^2}{t_{0.5}} \quad (4)$$

This expression, called the half-saturation equation, was used to estimate the values of D in this work, in which $t_{0.5}$ = time required for the polymer sample to attain half of its maximum weight gain (days).

It was noted early in this study that the results obtained for K tended to follow a theoretically de-

rived absorption isotherm (similar to Langmuir isotherm) developed from phase equilibrium thermodynamics²:

$$K(a) = \frac{\omega}{\gamma - \beta a^*} \quad (5)$$

in which a^* = the equilibrium solute activity; γ and β = coefficients to be determined from experiments; and

$$\omega = \frac{\rho_0}{p_s} \frac{RT}{MW} \quad (6)$$

where p_s = saturation vapor pressure (atm). Note that γ must always be greater than βa^* and that

$$\lim_{a^* \rightarrow 0} K(a) = \frac{\omega}{\gamma} \quad (7)$$

The pressure of solute vapor should be expressed in terms of activity a , because the activity of a solute is constant within a multiphase system at equilibrium. If the solute vapor behaves as an ideal gas, the activity of the vapor at any pressure other than saturation vapor pressure p_s is

$$a = \frac{p}{p_s} \quad (8)$$

The results of sorption studies performed with various polymers tended to obey the exponential function⁸

$$D = D_0 e^{\alpha a} \quad (9)$$

in which D_0 = the diffusivity at the limit of infinite dilution of solute in the polymer (the intrinsic diffusion coefficient) (m^2/day) and $\alpha = a$ coefficient.

The mass flux of an organic chemical vapor at steady state can be expressed by the permeability coefficient (P) defined as

$$P = K \cdot D \quad (10)$$

Variations of P do not always reflect the variations of D and K . In some cases where K and D vary in opposite directions, P can remain fairly constant.

This coefficient may be used to compare the overall permeation characteristics of different solutes in a polymer or the same solute in different polymers.

The Arrhenius equation is commonly used to relate the changes in both K and D with absolute temperature T , or

$$K = \alpha_1 \cdot \exp\left(-\frac{\Delta H}{RT}\right) \quad (11)$$

$$D = \alpha_2 \cdot \exp\left(-\frac{E_d}{RT}\right) \quad (12)$$

and

$$P = \alpha_3 \cdot \exp\left(\frac{E_p}{RT}\right) \quad (13)$$

in which α_1 , α_2 , and α_3 = constants; ΔH = heat of solution (kcal/mol); E_d = activation energy for diffusion (kcal/mol); and $E_p = \Delta H + E_d$ (kcal/mol).

RESULTS AND DISCUSSION

Microbalance experiments were conducted at 10, 20, 33, and 45°C to investigate the effects of temperature on toluene permeation through PB. Figures 2 and 3

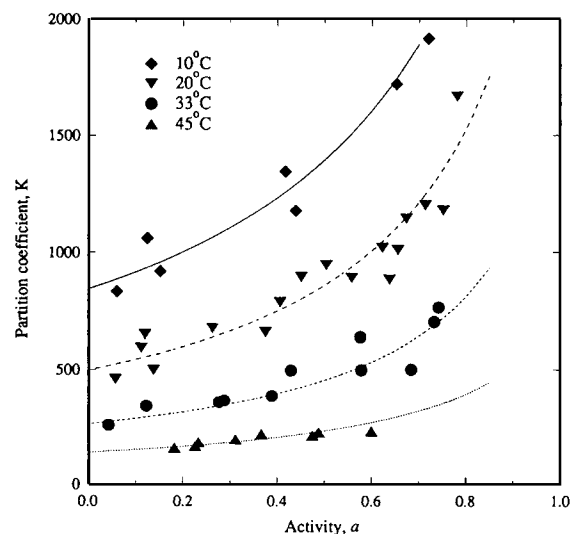


Figure 2 Effect of temperature on partition coefficients of toluene in PB.

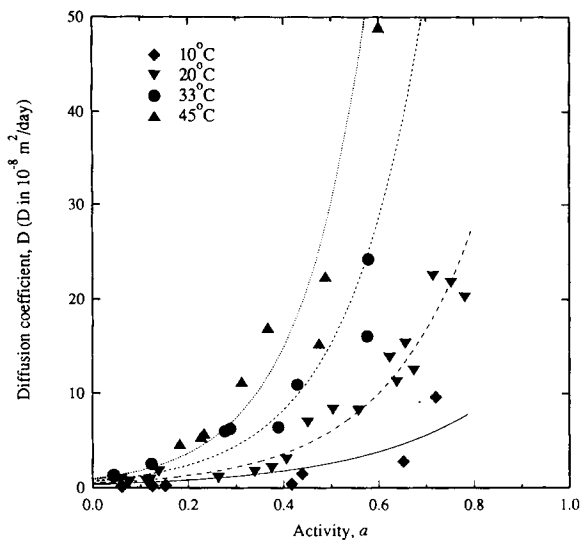


Figure 3 Effect of temperature on diffusion coefficients of toluene in PB.

show the variations of partition coefficients and diffusion coefficients at four different temperatures with respect to activity. The curves shown in Figures 2 and 3 were predicted from the thermodynamic model (eq. 5) and the exponential relationship (eq. 9), respectively. The partition coefficient (solubility) decreased and the plots of K versus activity became flatter as temperature increased. The diffusion coef-

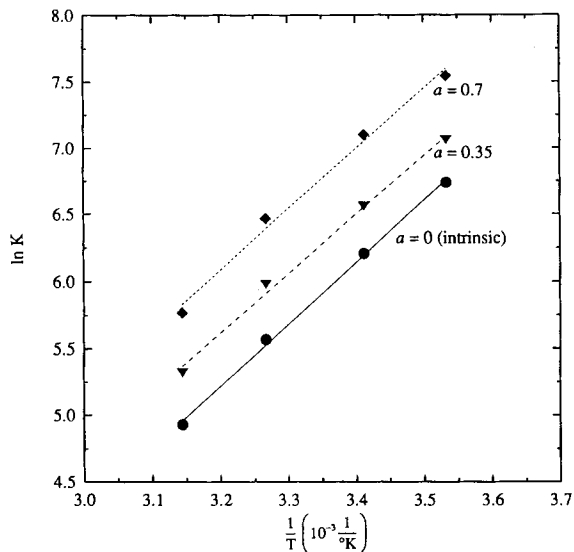


Figure 4 Arrhenius plots of the variation of the partition coefficients of toluene in PB with temperature. (The connecting lines are simple linear regressions.)

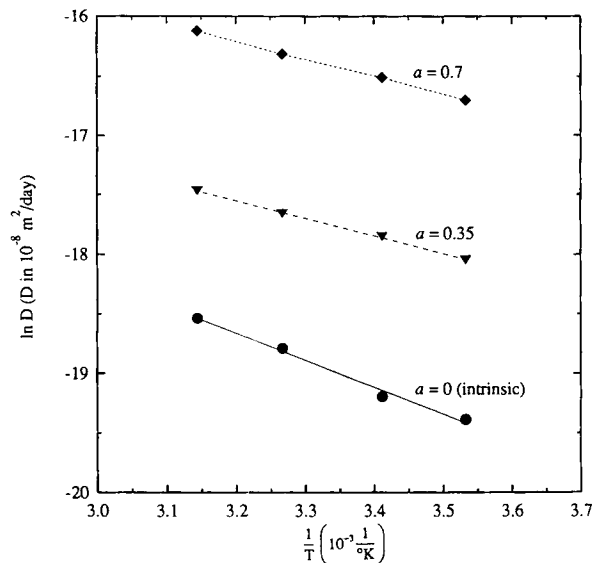


Figure 5 Arrhenius plots of the variation of the diffusion coefficients of toluene in PB with temperature. (The lines connecting the points are simple linear regressions.)

icient increased significantly with the increase in temperature. The increase of the diffusion coefficient with the increase in activity was marked at higher temperatures. For example, the intrinsic diffusion coefficient doubled, whereas the diffusion coefficient

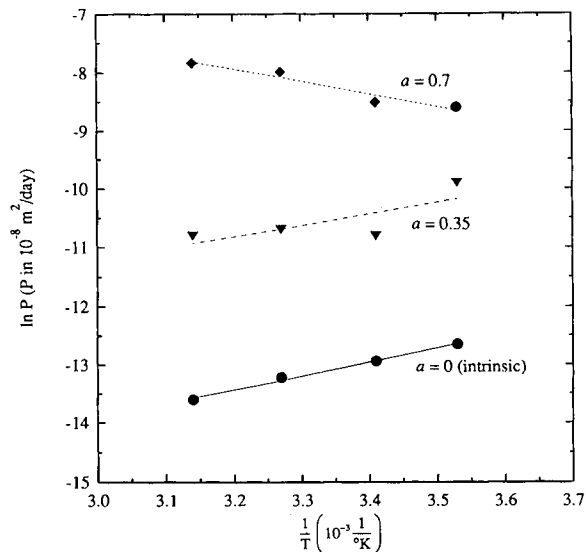


Figure 6 Arrhenius plots of the variation of the permeability coefficients of toluene in PB with temperature. (The lines connecting the points are simple linear regressions.)

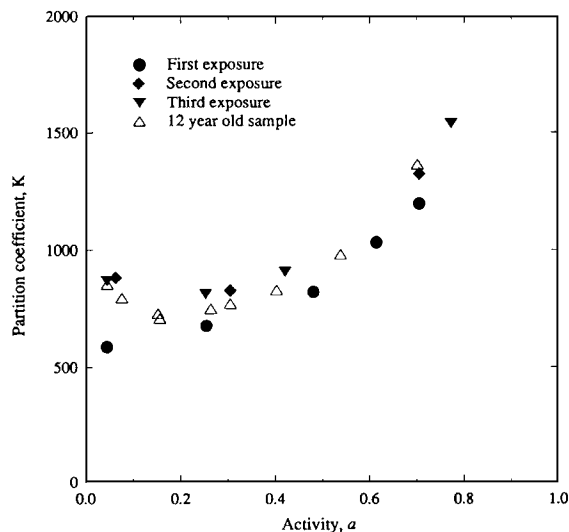
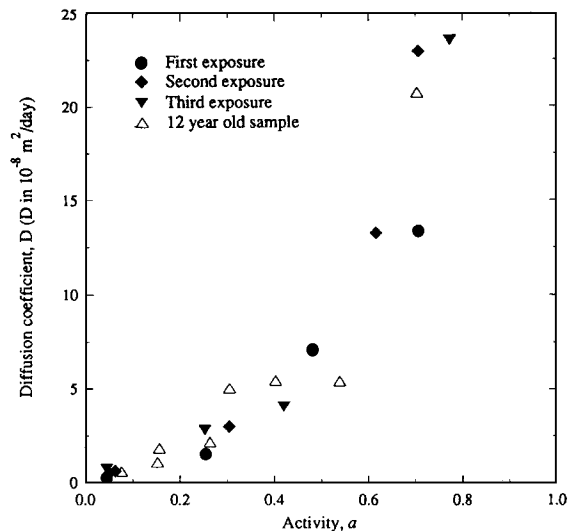
Table I Summary of Heat of Solution and Activation Energies for K , D , and P for Toluene in PB

	0.0	0.35	0.7
ΔH (kcal/mol)	-9.2	-8.8	-9.0
E_d (kcal/mol)	+4.5	+2.9	+2.9
E_p (kcal/mol)	-4.8	-3.8	+4.3

at an activity of 0.5 increased 15 times when the temperature was increased from 10 to 45°C.

The results were also fitted to the Arrhenius equations [eqs. (11) and (12)]. Figures 4–6 show regression lines at three different activities for K , D , and P . The net effect of decreased partition coefficients and increased diffusion coefficients was a decrease in P up to activity 0.35 but an increase in P at activity 0.7. The intrinsic heat of solution ΔH was about -9.2 kcal/mol for toluene in PB and remained approximately constant up to toluene activities 0.7 (Table I). The intrinsic activation energy of diffusion E_d , on the other hand, was about +4.5 kcal/mol, and the activation energy remained constant after activity 0.35.

Figures 7 and 8 show the results of repeated sorption/desorption experiments on a sample of a new PB and of a single sorption experiment on a 12-year-old sample. The 12-year-old sample exhibited

**Figure 7** Effect of repeated exposure and aging of PB on observed toluene partition coefficients at 20°C.**Figure 8** Effect of repeated exposure and aging of PB on observed toluene diffusion coefficients at 20°C.

greater partition coefficients than did the new sample (first exposure) at low activities and slightly greater at high activities. In general, the 12-year-old sample had slightly higher partition coefficients than did the new sample but lower than those of the second and third time exposed sample. Diffusion coefficients had a slight tendency to increase after each exposure. The diffusion coefficients at the second and third exposure were close to those obtained from the 12-year-old sample. Therefore, it can be said that accelerated aging of PB may be obtained by repeated sorption/desorption cycles.

CONCLUSIONS

1. The partition coefficient decreased and the diffusion coefficient increased with the increase in temperature.
2. The heat of solution of PB remained constant at approximately -9.0 kcal/mol over the activity, whereas the activation energy of diffusion decreased from +4.5 kcal/mol at activity 0 to +2.9 kcal/mol above an activity of 0.35.
3. The partition coefficient and the diffusion coefficient of PB after a long service period (12-year-old sample) were close to those obtained after repeated sorption/desorption cycles on a new PB sample.

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