

Carbon Tetrachloride Absorption in Low-Density Polyethylene Pellets: Concentration Profiles by Electron Microprobe Analysis

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Synopsis

The concentration profiles of carbon tetrachloride in low-density polyethylene pellets after various periods of absorption (1–6 h) at 40°C have been measured in a new application of electron probe microanalysis using energy dispersive x-ray spectroscopy (EDAX). The concentration profiles were determined from an EDAX scan of chlorine content along the diameter of a cylindrical pellet (4-mm diameter) mounted in a scanning electron microscope. The maximum chlorine content seen in the EDAX scan was presumed to reflect the equilibrium surface concentration, eliminating the need to calibrate the system and enabling direct interpretation of the EDAX scan as a concentration profile. The concentration profiles revealed that absorption of CCl_4 in LDPE pellets took place with a sharp moving boundary, with the depth of penetration proportional to $(\text{time})^{1/2}$ rather than to time as in case II diffusion. This behavior was attributed to a discontinuous relationship between diffusivity and concentration, resulting in a sharper than expected fickian diffusion profile. The EDAX technique, although requiring further refinement, appears to be a valuable method for assessing slow diffusion in thick polymer samples for those penetrants detectable by EDAX.

INTRODUCTION

Measurement of the diffusivity of a penetrant is frequently used to assess the effect of some parameter on polymer morphology.¹ Thick polymer samples, such as resin pellets or injection-molded parts, are important for these measurements because the morphological changes associated with the processing conditions are preserved in such specimens. Thus diffusion measurements with these samples enable the influence of processing conditions on polymer morphology and transport rates to be determined. However, diffusion is slow with thick samples and the standard sorption experiment takes a long time to come to equilibrium.² This experimental problem is further exacerbated if high-molecular-weight, slowly diffusing penetrants are used. Since many polymer additives fall in this category, characterization of the migration process in real samples is difficult. In this connection, concentration profiles of a diffusing molecule are useful for characterizing a slow diffusion process in a thick polymer sample. Moreover, concentration profiles may provide a more detailed picture of concentration, time, and/or position dependence of the diffusion process.

Concentration profiles of a diffusing molecule in a polymer have been measured in the past by using interferometric^{3,4} and Lamm scale tech-

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niques.⁵ These techniques suffered from various drawbacks, such as the difficulty in establishing the penetrant concentration-refractive index relationship for calibration, particularly when a maximum in the refractive index-concentration plot occurred, doubling of the interference fringes in the case of swelling, and the problem of correctly focusing the fringes for high and low refractive index gradients. Long and Watt⁶ measured the concentration profiles of a colored vapor by photomicrographic technique; however, this method is limited to suitable colored unreactive penetrants. Long and Richman⁷ used a technique of microradiography to generate concentration profiles of methyl iodide in polyvinyl acetate. This method utilized the marked difference in x-ray mass absorption coefficient of penetrant and polymer. Radiotracer methods⁸⁻¹¹ make use of diffusants labeled with radioactive atoms. This method is faced with the major shortcoming of having to obtain the required labeled material. A technique based on infrared microdensitometry¹² has also been used with limited success. In this technique, the broadening of the concentration profile of an additive in the polymer is monitored, yielding the diffusion coefficient.

In this paper we report on the use of electron probe microanalysis and energy dispersive x-ray spectroscopy (EDAX) to determine the concentration profile of carbon tetrachloride diffusing in low-density polyethylene pellets (LDPE). Carbon tetrachloride was used as a model compound since its chlorine atoms are detectable by EDAX.

EDAX utilizes the x-ray fluorescence induced when a high-energy electron beam is stopped by certain elements in a polymer specimen mounted in a scanning electron microscope. The x-rays are emitted with energies characteristic of the elements present in the specimen and the energy spectrum analyzed by an energy dispersive spectrometer to provide a qualitative analysis. Since the intensity of x-ray emission is proportional to the amount of element irradiated, spectrometric analysis of the radiation produced by electron bombardment at any point in a specimen also leads to a quantitative elemental analysis. Using electron beams focused electromagnetically to produce a finely focused probe at the specimen surface, elemental analyses of microvolumes typically of the order of a few cubic micrometers in bulk samples are possible. It is possible to detect less than 10^{-16} g of an element at slow scan rates or with multiple scans.

MATERIALS AND METHODS

Materials

Low-density polyethylene (CIL 300 GXN 7218) was supplied as nearly cylindrical pellets (4.0 mm diameter by 3.5 mm long; surface-volume ratio = 1.57 mm^{-1}). The melt index was 2.07 (ASTM D1238-73), density was 928.7 kg/m^3 (ASTM D1506-68), and crystallinity by DSC was $32 \pm 2\%$. Carbon tetrachloride (Caledon Laboratories Ltd., Ontario) was used with density $1583.0\text{--}1585.0 \text{ kg m}^{-3}$ at 25°C and boiling range $76.7 \pm 0.1^\circ\text{C}$.

SORPTION MEASUREMENT

The unsteady-state absorption kinetics of carbon tetrachloride in low-density polyethylene pellets at 40°C was measured with a Cahn electro-

balance (Model 2000, Cahn Instruments, Cerritos, California.¹³ The temperature was maintained at 40°C ($\pm 0.1^\circ\text{C}$) by circulating hot water (water bath circulator RC3, Lauda, FRG) through a jacketed tube surrounding the sample and CCl₄. The rate of mass uptake was determined by suspending a LDPE pellet from the balance, 1 cm above the level of carbon tetrachloride in the sample tube, and following until equilibrium. The mass uptake at each point in time M_t divided by that at equilibrium M_∞ was plotted against the square root of time $t^{1/2}$ in the standard fashion. The equilibrium uptake at 40°C was 0.5 g/g LDPE.

CONCENTRATION PROFILE MEASUREMENT

The ends of the pellets were capped with aluminum foil secured by epoxy resin so that only radial diffusion would occur. These pellets were exposed to pure carbon tetrachloride vapor at 40°C in a sorption apparatus as above. The pellets were removed from the sorption chamber after various predetermined times and stored on dry ice.

The pellet was held in a wooden die with a V notch and cut perpendicular to its axis into two halves by a sharp, thin chisel. The smoothness of the cut surface was very important to minimize topographical effects that would cause variations in the electron incidence and x-ray takeoff angles. Next, a thin layer of carbon (80–120 Å) was evaporated onto the cut surface of the sample to prevent charge buildup, to eliminate beam distortion, and to minimize the specimen heating (SEM coating unit, Polaron PS100, Polaron Equipment Ltd., Watford, England). The estimated time in all these operations was approximately 5–7 min. The sample was then placed on a carbon block (Fig. 1) and mounted on a scanning electron microscope (ISI-60, Hitachi, Japan). A 30-keV accelerated electron beam of approximately 0.25 μm diameter was used for scanning. The sample was scanned by the electron probe across the diameter of the pellet (line profile) with one 60-s pass from one edge of the sample to the other, as shown in Fig. 1. The intensity of the characteristic x-rays corresponding to chlorine atoms produced during the scan were analyzed by EDAX (γ -PGT-1000, Princeton Gamma-Tech., Princeton, New Jersey) in the line profile mode in each of the 1000 channels used to subdivide the pellet diameter, and the results were synchronously recorded on photographic film.

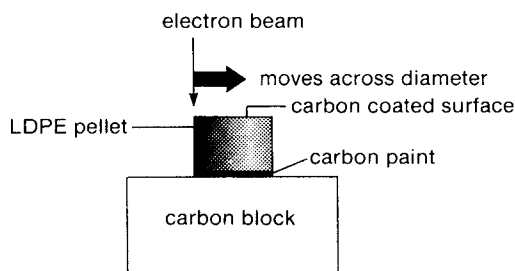


Fig. 1. Mounting of LDPE pellet on carbon block for EDAX analysis.

RESULTS

Typical EDAX photographs for four different times of absorption of carbon tetrachloride vapor in as-supplied low-density polyethylene pellets at 40°C are shown in Fig. 2. The semicircular images in these photographs are the edges of the cylindrical pellets. The height between the white dots and the baseline is proportional to the number of chlorine atoms detected by x-ray analysis at each point along the baseline (pellet diameter). The two regions near the circumference correspond to the annular ring in which the pellets contained CCl_4 ; the region between the peaks indicates pure polymer as yet free of penetrant. The proportionality constant between height above baseline and CCl_4 concentration was dependent on instrument setting (aperture, x-ray takeoff angle, and so on). Two samples were examined at each sampling time, and each sample provided identical results. Both peripheral regions in each EDAX photograph (Fig. 2) were nearly identical, indicating uniform distribution of the penetrant in the samples.

The outer edge of the peripheral regions should have been vertical, and the intensity should have been uniform throughout these regions where

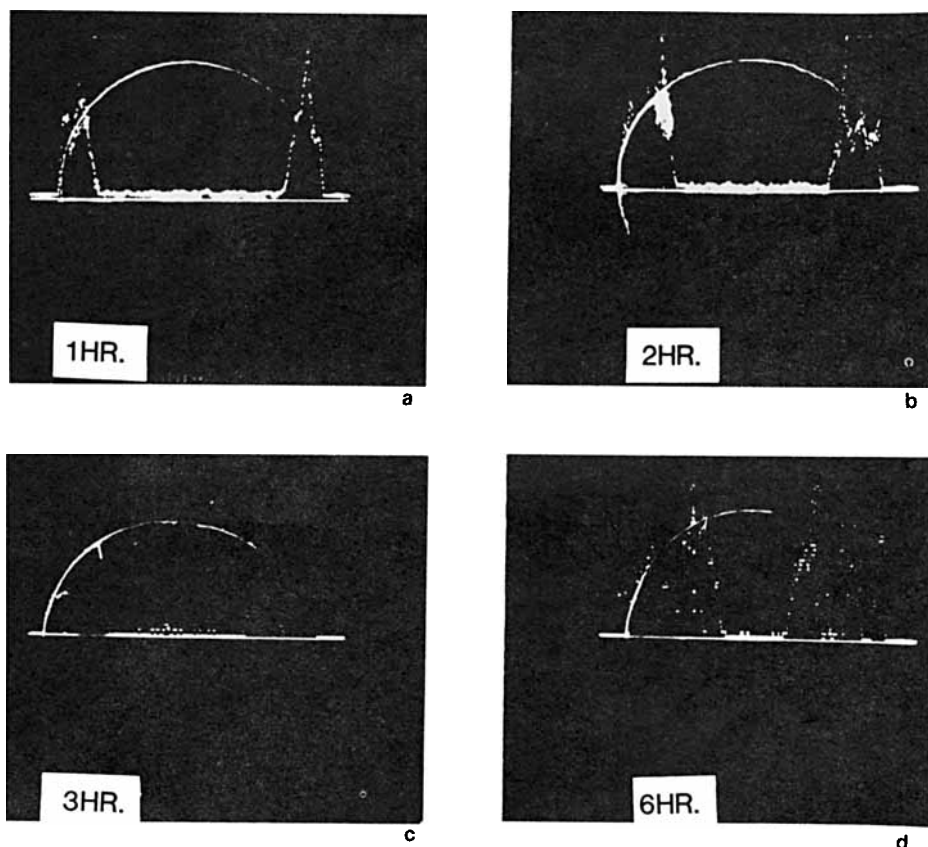


Fig. 2. Photographs of chlorine x-ray intensity profile across the diameter of a LDPE pellet exposed to carbon tetrachloride vapor at 40°C for 1–6 h. The semicircular ring is the outline of pellet circumference; the horizontal line represents the diameter of the pellet across which the profile was measured.

CCl₄ saturated polymer was expected. The loss in intensity on the outside of each region was presumed to be due to diffusion of vapor out of the sample between the time it was removed from the absorption apparatus and deep frozen, and during the time it was taken out of the dry ice for sectioning, carbon coating, and mounting in the SEM. This is consistent with the time calculated (5 min) to lose a similar fraction of CCl₄ (23.4%) from the periphery of a LDPE pellet fully saturated with penetrant, using a desorption diffusion coefficient of 1.4×10^{-7} cm²/s and the standard equation for one-dimensional fickian desorption from a cylindrical rod. The desorption coefficient was estimated by extrapolating to 25°C an Arrhenius-type plot of desorption coefficients determined for the same system at 40–70°C.¹³ This desorption process was presumed to have no effect on the shape of the interior profiles.

The intensity variation seen in the annular ring was presumed to be the result of topographical variations (surface roughness) that prevented the detection of the emitted x-rays, resulting in an apparently reduced chlorine concentration; this artifact was ignored. In fickian sorption, the concentration of penetrant at the polymer surface is normally assumed to be the equilibrium saturation value. It is of interest, then, that the EDAX photographs (Fig. 2) indicate a virtually constant maximum height at all absorption times, in turn indicating a constant maximum penetrant concentration. This maximum concentration was presumed to be the equilibrium value, which was further assumed to represent the concentration at the surface, enabling a correction to be made for the desorption occurring during sample preparation.

The concentration distance curves (Fig. 3) were obtained from these EDAX photographs by measuring the height between the baseline and the points on the interior leading edge (the diffusion front) of the peripheral regions at various positions along the diameter of the pellets. The maximum height

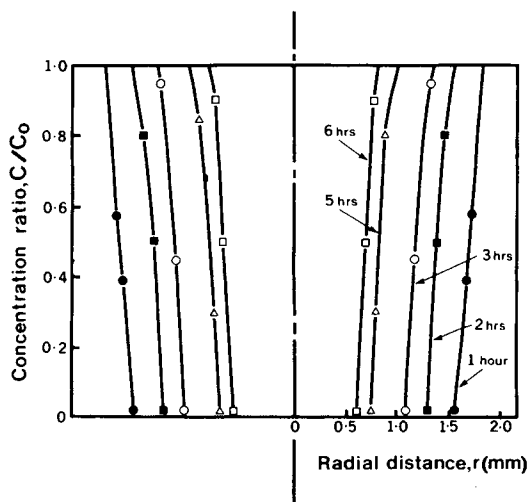


Fig. 3. Concentration profile of CCl₄ in LDPE after absorption at 40°C for 1–6 h, as measured by EDAX. Profiles taken from leading edge of chlorine profiles in Fig. 2.

was assumed to be equal to the equilibrium concentration (and equal to the concentration at the polymer surface). By ratioing the height at each point to the maximum height, the EDAX photographs were used to determine directly the concentration ratio C/C_0 at the corresponding radial distance. The assumption of maximum peak height equal to equilibrium (or surface) concentration eliminated the need to calibrate the system. The concentration ratio was assumed equal to unity everywhere behind the diffusion front (i.e., at radial distances greater than that corresponding to the maximum height), despite the appearance of the EDAX photographs.

Most significantly, it was observed that diffusion took place with a sharp moving boundary (Fig. 3) but that the depth of penetration of the moving diffusion front (at $C/C_0 = 0$) was proportional to the square root of time (Fig. 4). The area under the profile at each sampling time A_t was also proportional to \sqrt{t} , as shown in Fig. 5. Rather than passing through the origin, the plot of A_t against \sqrt{t} was extrapolated through a point on the \sqrt{t} axis corresponding to $t = 8.5$ min.

To check the validity of the EDAX method, the same system was studied by the vapor sorption technique. A comparison of EDAX results (A_t) with M_t/M_∞ measurements obtained from conventional mass uptake (absorption) experiments (Fig. 5) showed that there was reasonable agreement between the two methods. Since A_t is the area under the C/C_0 profile, it is directly comparable with M_t/M_∞ . The slope of the plot of M_t/M_∞ against \sqrt{t} (sorption data) was $\sim 21\%$ lower than the slope of the plot of A_t against \sqrt{t} (EDAX).

DISCUSSION

As a new application, a well-established technique has been used to determine the concentration profile of carbon tetrachloride in low-density poly-

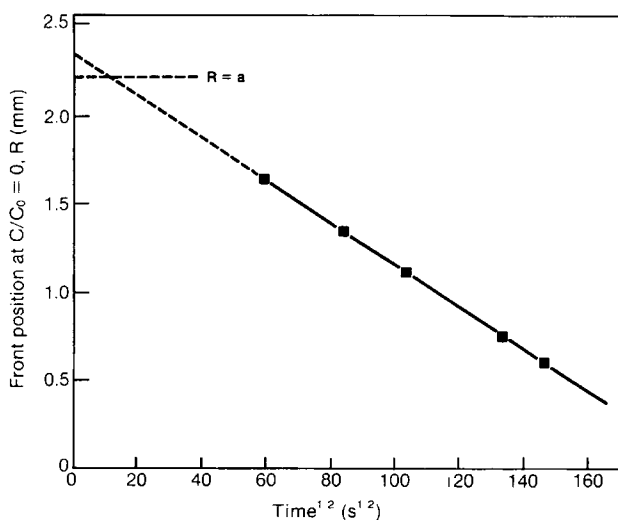


Fig. 4. Position of carbon tetrachloride diffusion front at $C/C_0 = 0$ plotted against the square root of exposure time.

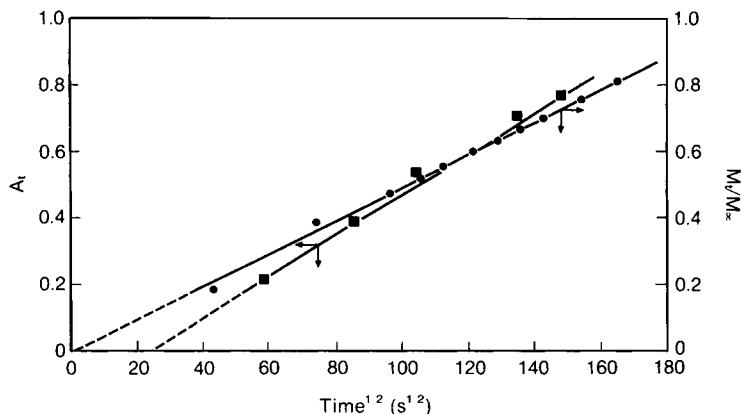


Fig. 5. Integrated absorption curve for carbon tetrachloride in LDPE at 40°C; ● electro-balance data (M_t/M_∞); ■ EDAX data (A_t = area under concentration profile).

ethylene pellets after various periods of absorption. The EDAX method provided distinct and reproducible concentration profiles of the chlorine atoms in carbon tetrachloride (Fig. 2). Desorption of CCl₄ from the periphery of the pellet during sample preparation was presumed to account for the lower than expected chlorine content at the outer edge of the pellet. The interior profile remained sharp, however. Broadening of the diffusion front, as might have been expected during the same sample preparation period was not noticeable, perhaps because of the short time at room temperature. However, the front may have moved a little farther into the pellet during these few minutes, resulting in a slight overestimate of the front position at each time point. Correction for this overestimate has no significant impact on the slope of the A_t against \sqrt{t} plot of Fig. 5.

The concentration profiles, as shown in Fig. 2, were defined by sharp fronts of high concentration gradient, in front of which there was no indication of the presence of penetrant. Unlike the sharp fronts of case II diffusion, which move at constant velocity and which are commonly observed in glassy polymers,¹⁴ the position of the moving front in the CCl₄-LDPE system was proportional to the square root of time (as shown in Fig. 4). Also, the mass of absorbed penetrant and area under the concentration profile increased linearly with the square root of time (Fig. 5). Although a sharp moving boundary is an unfamiliar concept in fickian diffusion, the existence of a sharp boundary is predicted for cases in which the diffusion coefficient is a discontinuous function of concentration.¹⁵ At concentrations less than the discontinuity, the diffusivity is presumed to be near zero; at concentrations greater than the discontinuity, the diffusivity has the normal (exponential) relationship with concentration. With this discontinuous diffusivity-concentration relationship (particularly with the discontinuity at low C/C_0), the leading edge of the advancing diffusion front is sharper than that expected with the more normal exponential relationship. This discontinuous diffusivity-concentration relationship may also account for the absence of front broadening during sample preparation seen in the EDAX photographs since the broadening expected to be seen at the low concentration end of the profile

would be much less with the presumed discontinuous relationship than with the normal exponential relationship. More detailed analysis of the shape of the profile in terms of the concentration dependence of the diffusivity is the subject of another publication.¹⁶

The difference in the results obtained by EDAX compared with that by the standard electrobalance method is relatively small and presumably due to (1) topographical effects on cut surfaces causing variations in x-ray takeoff angles and (2) inaccuracy involved in the plotting of concentration distance curves from measured concentration profiles. Some of the details of the procedure need to be improved to increase the accuracy of the EDAX technique. As an example, the use of an ultrathin microtome can assist in obtaining smoother exposed surfaces for EDAX-SEM scanning. An improvement here could enhance the accuracy by eliminating surface roughness effects. Also, the use of computerized data acquisition profiles could minimize the errors involved in determining concentration profiles from photographs.

Nevertheless, the EDAX method in its present state is capable of following the diffusion process with an accuracy adequate for many purposes. It is limited, however, to compounds containing elements higher than sodium in the periodic table, which for characterization of the diffusion of organic compounds means that this technique is limited to halogenated compounds. In some respects this is not an unworkable limitation, since many of the additives of interest in migration studies are chlorinated or brominated. The EDAX method is relatively simple, does not require special preparation of a penetrant (e.g., radiolabeling), and has the virtue of giving direct information about the concentration gradients without the need for calibration. The use of these concentration gradients to characterize the diffusion of CCl_4 in these LDPE pellets is the subject of another publication.

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