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THE EFFECT OF TEMPERATURE ON THE DIFFISION OF ETHYL ACETATE THROUGH ORIENTED POLYETHYLENE TEREPHTHALATE FILMS OF VARYING THERMOMECHANICAL HISTORY presented by

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# THE EFFECT OF TEMPERATURE ON THE DIFFUSION OF ETHYL ACETATE THROUGH ORIENTED POLYETHYLENE TEREPHTHALATE FILMS OF VARYING THERMOMECHANICAL HISTORY

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By

Akira Shirakura

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### ABSTRACT

# THE EFFECT OF TEMPERATURE ON THE DIFFUSION OF ETHYL ACETATE THROUGH ORIENTED POLYETHYLENE TEREPHTHALATE FILMS OF VARYING THERMOMECHANICAL HISTORY

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By

## Akira Shirakura

The effect of thermomechanical history on the permeation of ethyl acetate vapor through biaxially oriented polyethylene terephthalate (PET) films was studied by a quasi-isostatic procedure. A test system was designed and assembled for this purpose, which allowed permeation to be conducted above ambient temperature. Solubility and sorption profile data for ethyl acetate in PET films was also determined. The results of this study showed a strong temperature dependence for the permeation of ethyl acetate through oriented PET over the temperature range studied, which was well below the glass transition temperature (Tg) for the PET film samples. It was also found that there is a significant effect of crystallinity (i.e. thermomechanical history) on the permeation process.

To my wife and my son.

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#### INTRODUCTION

With the increasing application of plastic materials in the food, beverage and pharmaceutical industries, the importance of studies involving polymer permeability has grown tremendously. Knowledge of the transport of permeants such as oxygen, carbon dioxide and water vapor through polymeric materials has been utilized extensively in selecting barrier polymers for food packaging.

In contrast to the considerable amount of data on the permeability of gases such as oxygen and carbon dioxide, there is a notable lack of experimental data on the permeability of organic vapors through barrier membranes. There is also a paucity of data describing the effect of thermomechanical history on the permeability of organic molecules through polymer films.

The growing importance of polyethylene terephthalate (PET) in food packaging and the general lack of information regarding the aroma barrier properties of PET provided impetus for this study, the general objectives of which are as follows:

 Evaluate the effect of thermomechanical history on the permeability and solubility of ethyl acetate vapor through oriented PET.

2. Evaluate the permeability and sorption of ethyl acetate vapor through PET film of varying percent crystallinity (i.e. varying thermomechanical history) as a function of temperature.

Additional objectives include:

3. Design and assembly of a test apparatus for measuring the effect of temperature on vapor permeability.

4. Determination of percent crystallinity by the density gradient technique.

5. Carry out permeation experiments on the system of ethyl acetate vapor-PET at two temperatures for two films which differ in orientation temperature.

6. Determine the sorption profile on the system of ethyl acetate vapor-PET for each film.

# LITERATURE REVIEW

#### Permeation of Organic Vapors through Polymer Films

Although there is a notable lack of data on the permeability of organic vapors through polymer films, recently this area has been and continues to be the subject of increased investigation.

Pye et al. (1976) reported a continuous or isostatic method for measuring the permeability of polymer membranes that employed gas chromatography analysis with multiple detectors, allowing the authors to study the diffusion of both gases and organic vapors. Zobel (1984, 1985) described a modified isostatic method which combined an adsorption/ desorption cycle for measuring the permeability rates of polymer films to organic vapors. The transport of d-limonene vapor through polymeric packaging materials was studied by DeLassus (1985) using an isostatic procedure. In this study, for quantifying the permeation rate of limonene vapor through the films, a photoionization and an atmospheric pressure ionization procedure were employed (Caldecourt and Tou, 1985). Hernandez (1984) and Baner et al. (1986) also described an isostatic method for determining the permeability of organic vapors through polymer films. Permeated vapor was analyzed by a gas chromatographic technique with flame ionization detection.

An accumulation or quasi-isostatic procedure for determining the permeability of organic vapors through polymeric barrier film was

developed by Hilton and Nee (1978). The film was mounted in a permeability cell above a reservoir of organic liquid. The organic vapor diffused through the barrier film, accumulated in the low concentration chamber of the test cell and was quantified by a gas chromatographic technique. Other workers employed similar methods for determining the permeability of organic vapors through barrier structures (Murray and Dorschner, 1983; Murray, 1985). However, these methods only allow for determination of transmission rates and permeability constant values for one concentration of penetrant, that is the saturation vapor pressure of the liquid at a given temperature.

A quasi-isostatic test procedure with a constant vapor concentration or partial pressure gradient was reported by Gilbert et al. (1983). These authors employed a continuous flow of the organic vapor stream through the high concentration chamber of the test cell. Baner et al. (1986) also described a similar method for determining the diffusion of organic penetrants through polymer membranes. A gas chromatographic method was developed for quantifying the diffused penetrants.

In addition to the permeation methods reviewed above, sorptiondesorption procedures can also be employed for evaluating the transport of organic moieties in polymers (Fujita, 1961). The effect of orientation on the sorption of toluene by high density polyethylene was reported by Bischoff et al. (1984). The sorption and diffusion of toluene vapor in oriented polypropylene (OPP) film of varying draw ratios was studied by Choy et al. (1984). Berens (1978) studied the transport of low molecular weight organics in polyvinyl chloride (PVC) by the sorption procedure. The sorption and diffusion of toluene vapor

in OPP and polyvinylidene chloride films as a function of penetrant concentration, was studied by Baner (1987) by applying the equilibrium vapor pressure and microbalance gravimetric technique.

#### Permeation of Organic Vapors through PET

Polyethylene terephthalate (PET) is a linear polyester, which exhibits a melting point (Tm) of approximately  $255 \, {}^{\circ}C$  and a glass transition temperature (Tg) of approximately  $70^{\circ}C$ . This study was carried out below  $54^{\circ}C$ , therefore the polymer was considered to be below Tg, and in its glassy state. Moreover the PET samples were partially crystalline and biaxially oriented at 90°C and 115°C respectively. A general discussion of permeation properties of glassy semi-crystalline polymers is presented in a later section (see Characterization of the Permeation Process).

Several workers have reported the diffusivity of organic vapors through PET film. Makarewicz and Wilkes (1978) studied the diffusion of acetone, benzene, dioxane, methylene chloride and nitromethane, in both the vapor and liquid phase, through unoriented and amorphous PET. The authors found that an induced crystallization took place while the organic molecules diffused through PET. Misra and Stein (1979) reported the relationship between percent strain and the degree of induced orientation in PET. The authors showed that birefringency, and consequently orientation, varied almost linearly with percent of strain. Hernandez (1984) studied permeation of toluene vapor through glassy biaxially oriented PET films. The author reported that an increasing temperature and previously exposing the film to toluene vapor can affect drastically the permeability properties of PET film to toluene vapor.

#### Permeation Theory

Permeability is often referred to as the ease of transmission of gases or vapors through a resisting material which has no macroscopic pores (i.e. mostly polymeric materials) (Paine, 1983).

The transmission of a gas or vapor through the plastic materials commonly used in packaging is normally of the activated diffusion type. Such a process involves three steps, namely: (1) adsorption of the permeating species, in which the gas or vapor dissolves into the polymer matrix at the high penetrant concentration surface; (2) diffusion through the polymer wall along a concentration gradient; and (3) desorption from the surface at the lower concentration (Stannett and Yasuda, 1965).

The diffusive flux, F, of a permeant in a polymer can be defined as the amount passing through a surface of unit area normal to the direction of flow during unit time, independent of the aggregation of polymer. That is:

$$F = Q / At$$
(1)

Where Q is the total amount of permeant which has passed through area A during time t. By analogy with the transfer of heat by conduction, the transfer of a diffusant through a unit area can be expressed as being proportional to the negative gradient of concentration at any point in the polymer. This can be described by Fick's first law of diffusion

(Crank and Park, 1968).

$$F = -D (dC/Dx)$$
(2)

Where D is the diffusion coefficient with units of  $(length)^2$  time<sup>-1</sup> (e.g. cm<sup>2</sup>s<sup>-1</sup>), x is the length in the direction in which transport of the permeant occurs, and C is the concentration of the permeant in the polymer. As diffusion proceeds, Fick's second law of diffusion describes the non-steady state (Crank, 1975).

$$\frac{dC}{dt} = \frac{d}{dx} \left( D \frac{dC}{dx} \right)$$
(3)

Where t is time. Solutions of Equation (3) depend upon the initial and boundry conditions and on whether or not (D) can be considered a function of penetrant concentration and/or time. In order to obtain analytical solutions, simplifications are normally introduced to yield expressions which are easily solved.

Equation 1 can be integrated, where D is independent of concentration, to give:

$$F = D(C1 - C2)/L$$
 (4)

Where Cl and C2 are the steady state concentration of the permeant at the two surfaces of the film and L is the film thickness.

For experimental and predictive purposes it is convenient to relate the concentration of the permeant at the polymer surface to the concentration of permeant in the surrounding gas phase. For gases and vapors, the permeant concentration is proportional to the partial pressure of the permeant, through the ideal gas law equation. The concentration of the permeant in the polymer, C, can thus be expressed by

$$C = (Sp)(\Delta p)$$
(5)

Where the solubility coefficient (Sp) is a function of temperature and may be a function of the partial pressure ( $\Delta p$ ) or C. When Henry's law is assumed:

$$C = S (\Delta p) \tag{6}$$

Where S is the Henry's law solubility coefficient, which is independent of  $\Delta p$  and C (Crank, 1975). Substitution in Equation (4) yields:

$$F = DS (p1 - p2)/L$$
 (7)

Where pl and p2 are the permeant partial pressures at the two surfaces of the film, and the product D  $\cdot$  S defines the permeability coefficient  $(\overline{P})$ , by the relationship D  $\cdot$  S =  $\overline{P}$  (Barrer, 1939).

When both D and S are independent of penetrant concentration,  $\overline{P}$  is a constant at any given temperature. However, where considerable

interaction between the polymer and the permeant takes place,  $\overline{P}$  is no longer constant but will vary with C and  $\Delta p$  (Zobel, 1982; Hernandez et al., 1986 and references cited therein). For the specific case, where the diffusion coefficient is time-dependent, the transmission process will be anomalous and it is said to be non-Fickian (Fujita, 1961; Meares, 1965; Crank and Park, 1968).

#### Permeability Measurements

Experimental methods and test apparatus for performing permeability measurements have been described by a number of investigators (Barrer, 1951; Rogers, 1956; Zobel, 1982; Hernandez et al., 1986).

One common method for determining permeability is the quasiisostatic method, or the accumulation method. In this method, the permeated gas or vapor is accumulated and monitored as a function of time. A generalized transmission rate profile curve describing the transport of a permeant through a polymer film by the quasi-isostatic method is illustrated in Figure 1.

The permeability coefficient,  $\overline{P}$ , is calculated as:

$$\overline{P} = \frac{QL}{\Delta t A b}$$
(8)

Where Q is the quantity of gas or vapor which has permeated in the time interval  $\Delta t$  in the steady state of flow. A is the area of the film exposed to the permeant. A is the average film thickness and b is the driving force given by the concentration or partial pressure gradient,  $\Delta p$ .



Figure 1. Generalized Transmission Profile Curve for the Quasi-Isostatic Method

For the specific set of experimental conditions, where the film is initially free of permeant and the receiving volume is maintained at essentially zero concentration of penetrant, Barrer (1939) has shown the diffusion coefficient can be calculated by:

$$D = \frac{L^2}{6\Im}$$
(9)

Where  $\odot$  is the intercept on the time axis of the extrapolated linear steady state portion of the curve (see Figure 1) and is called the lag time. Therefore, in theory, all three parameters can be calculated from the quasi-isostatic method;  $\overline{P}$  from the steady state flux; D from the lag time; and S from  $\overline{P}/D$ .

If the diffusion coefficient (D) is a function of permeant concentration, Equation 9 can not be applied and it has been shown that the following inequality holds for the concentration dependent diffusion coefficient (Pollak and Frish, 1959).

$$1/6 \le D/L^2 \le 1/2$$
 (10)

Therefore, D calculated using Equation 9 may be too small when the diffusion coefficient is concentration dependent. An estimate of D from transient state can be made using the equations based on the Holstein relationship (Meares, 1965; Rogers et al., 1954).

$$\ln(t^{1/2} dq/dt) = \ln[(2AS_{\Delta p}/v)(D/\pi)^{1/2}] - (L^2/4Dt)$$
(11)

Hence, a plot of ln  $(t^{1/2} dq/dt)$  vs. l/t should be a straight line of slope  $(L^2/4Dt)$ . The limiting diffusion coefficient,  $D_0$  as  $C \rightarrow 0$ , is obtained from the limiting slope of  $L^2/4Dt$ .

An alternative to the permeation method for determining barrier and sorption characteristics of penetrant/polymer systems is a gravimetric technique, which measures the rate of sorption and desorption. The solubility coefficient and diffusion coefficient values are thus determined by sorption measurements (Hernandez et al., 1986).

When the process is Fickian, the diffusion equation, solved for the sorption of permeant by a polymer film, is given  $b_V$  (Crank, 1975):

$$Mt/M_{\infty} = 1 - 8/\pi^{2} [exp(-D_{\pi}^{2}t/L^{2}) + exp(-9D_{\pi}^{2}t/L^{2})]$$
(12)

Where Mt and  $M_{\infty}$  are the cumulative masses sorbed or desorbed from the film sample of thickness L, at time = t and time =  $\infty$ , respectively. The diffusion coefficient D can be calculated from Equation 13, for which Mt/M $_{\infty}$  = 0.5 (see Figure 2).

 $D = 0.04939 L^2 / t_{0.5}$ (13)

Where  $t_{0.5}$  is equal to the time required to reach a sorption level equal to half of the equilibrium value,  $M_{\infty}$ .

If D is a function of the concentration, the sorption curves and desorption curves do not coincide, and an average diffusion coefficient value can be represented by (Crank, 1975)

$$D = \frac{Dd + D_S}{2}$$
(14)



Figure 2. Generalized Sorption Profile Curve

Solubility coefficient (S) values are readily calculated from sorption experiments by the following equation.

$$S = M_{\infty} / wb$$
(15)

Where S is the solubility coefficient expressed as mass of vapor sorbed at equilibrium per mass of polymer per driving force concentration or permeant activity.  $M_{\infty}$  is the total amount (mass) of vapor absorbed by the polymer at equilibrium for a given temperature, w is the weight of the polymer sample under test and b is a value of the permeant driving force.

#### Temperature Dependence of Permeability

In general, an increase in temperature provides energy for an increase in segmental motion of the polymer chains, which increases the transmission rate of penetrants through the polymer film. The temperature dependence of the diffusion coefficient (D) can be expressed by an Arrhenius-type relationship, when the temperature range is small (Barrer, 1939; Van Amerongen, 1946).

$$D = D_0 \exp(-E_D/RT)$$
(16)

Where  $D_0$  is the pre-exponential diffusion term related to entropy,  $E_D$  is the activation energy of diffusion, T is the absolute temperature and R is the gas constant.

Like the diffusion coefficient, the solubility coefficient (S) is also related to temperature by an Arrhenius-type relationship (Michaels and Parker, 1959):

$$S = S_0 \exp(-H_S/RT)$$
(17)

Where  $S_0$  is the pre-exponential solubility term and  $H_S$  is the heat of solution. Combining Equation 16 and Equation 17 gives:

$$\overline{P} = DS = \overline{P}_{O} \exp(E_{P}/RT)$$
(18)

Where  $\overline{P}_0$  is the pre-exponential term of permeability and  $E_p$  is the apparent activation energy for permeation. It follows that:

$$E_{P} = E_{D} + H_{S}$$
(19)

#### Characterization of the Permeation Process

Permeation properties of glassy crystalline polymers such as PET are generally reviewed as follows.

#### Glassy State

Most polymers have a glass transition temperature (Tg) externally characterized by a change from rubber-like to glass-like properties. Below Tg, the segmental motion of polymer chains is retarded and the chains are more densely packed than above Tg (Buchdahl and Nielsen, 1950). In general, the activation energy for diffusion ( $E_D$ ) is lower, below the glass transition temperature, than above Tg (Meares, 1953). This change in  $E_D$  is related to the increase in thermal expansivity and the increase in excess free volume distribution of the polymer, as the temperature passes through the glass transition (Rogers, 1965).

### Crystallinity

Crystalline polymers, or more specifically semi-crystalline polymers, consist of a crystalline and an amorphous region. An observed bulk property such as density is considered to be additive and is comprised of a weighted contribution from the crystalline and amorphous domains of the polymer. There are two major effects of the degree of crystallinity on the permeability of gases and vapors in polymers. In general, crystalline regions are inaccessible to most permeants (Sobolev et al., 1957) and they act as excluded volumes for the sorption process and impermeable barriers for the diffusion process. The other effect of polymer crystallinity on the diffusion process has been discussed by Michaels et al. (1963a) in terms of the tortuosity arising from the crystalline domains. It has been found that the solubility of gases, such as helium, nitrogen, oxygen, methane and carbon dioxide in polyethylene and polyethylene terephthalate is proportional to the amorphous volume fraction (Michaels et al., 1959; Michaels et al., 1963a):

$$S = S_a I_a \tag{20}$$

Where  $S_a$  is the solubility coefficient for the purely amorphous polymer and  $I_a$  is the amorphous volume fraction. Michaels et al. (1963b) have also found that the effect of crystallinity on the diffusion coefficient of PET for the above gases is expressed as:

$$D = D_a I_a \tag{21}$$

Where  $D_a$  is the diffusion coefficient of a pure amorphous polymer. When the penetrant swells the polymer, the solubility coefficient and the diffusion coefficient are affected by the penetrant concentration, due to a change in crosslinking action (chain immobilization) of the crystalline domains (Rogers, 1965; Michaels et al., 1959). The solubility of solvents which swell the polymer can be expressed as:

$$S = S_a I_a / \beta_1$$
 (22)

Where  $\beta_1$  is a factor relating to chain immobilization. Likewise, the diffusion coefficient can be expressed as:

$$D = D_a / \tau \beta_2$$
 (23)

Where  $\tau$  is a tortuosity factor and  $\beta_2$  is a chain immobilization factor (reference).

# MATERIALS AND METHODS

### Materials

# Film Samples

Commercial grade polyethylene terephthalate (PET) film samples were provided by Eastman Chemical Products, Inc., Division of Eastman Kodak Company. The samples were oriented biaxially at a strain of 350%/sec based on the initial dimension of 4 x 4 inches, which corresponded to an orientation rate of 14 inch/sec, biaxially.

The degree of orientation was 400% based on the initial dimensions. The orientation temperature was 90 and  $115^{\circ}$ C respectively. Table 1 presents values of percent crystallinity and mass-fraction crystallinity calculated from density values of the films at the two orientation temperatures.

Orientation Temperature, <sup>o</sup> C	Density g/cc	% Crystallinity	Mass-Fraction Crystallinity
90	1.360	22	24
115	1.371	31	33

Table 1. Density, percent crystallinity and mass-fraction crystallinity of the PET sample films.

### Permeant

Research grade ethyl acetate (purity greater than 99.5%, boiling point of  $77^{\circ}$ C) was employed throughout, as the permeant molecule.

#### Nitrogen Gas

High purity dry grade nitrogen gas was employed throughout as the carrier of the permeant.

#### Procedure

### Permeability Measurements

<u>Scope</u>. The permeation test system, based on the quasi-isostatic method, was designed, assembled and tested as part of this study. Figure 3 represents a schematic diagram of the permeation test apparatus. It allows for the collection of permeation data at a constant concentration of the organic vapor through a film as a function of temperature.

<u>Description</u>. The film to be tested was mounted in the permeability cell which is comprised of two aluminum cell chambers, each having a volume of 50 cc and a hollow center chamber ring. The assembled permeability cell was placed horizontally in a constant temperature oven (American Scientific Product, N 8630-10) and during permeability studies, a constant concentration and constant flow of permeant vapor was flowed through the center cell chamber, which was separated from the two edge cell chambers by the studied PET films.

A constant concentration of the permeant vapor was generated by bubbling nitrogen gas through the liquid permeant maintained at constant temperature. The vapor generator system, consisting of a gas dispersion



- B Water bath, generation of permeant vapor phase diluted in Nitrogen
- H Oven
- H<sub>c</sub> Heat exchange coil
- N Needle valve



P<sub>c</sub> - Permeability cell R - Rotameter

Vg - Organic vapor generator

T - Nitrogen tank

tube and a 250 cc gas washing bottle containing ethyl acetate liquid, was placed in a Blue-M Magni Whirl water bath maintained to  $23 \pm 0.1^{\circ}$ C. Microflow meters and microvalves had been incorporated into the test apparatus to monitor and maintain constant flow and concentration. The permeant concentration employed in this study was 300 ppm (g/ml) of vapor in nitrogen. As shown in Figure 3, to maintain the permeability cells at constant temperature, the cells were mounted in a constant temperature oven adjusted to the required temperature (i.e.  $30^{\circ}$ ,  $37^{\circ}$  or  $50^{\circ}$ C). Further, the permeant vapor stream was flowed through a heat exchange coil in the oven, prior to passing through the center chamber of the permeability cells, to allow equilibration of the vapor stream to the temperature of test. The vapor permeating through the film into the lower concentration chambers was then quantified by sampling and analysis by gas chromatography, until the permeation rate attained steady state.

<u>Operation</u>. At predetermined time intervals,  $500 \ \mu$ l samples were withdrawn from the low concentration cell chambers with a gas tight syringe (Hamilton, No. 1750) and injected directly into the gas chromatograph (GC). An equal volume of nitrogen was replaced into the cell in order to maintain a constant total pressure (1 atm). The permeability studies were carried out at approximately 0% RH.

# Sorption Measurements

<u>Scope</u>. The sorption measurement system, which is illustrated in Figure 4, was assembled and tested as part of this study. The system allows continuous collection of sorption data until equilibrium is



- B Water bath, generation of permeant
  Vapor phase diluted in Nitrogen
- C<sub>t</sub> Computer terminal
- $C_u Control unit$
- F Gas flow bubble meter
- H<sub>o</sub> Hood
- N Needle valve
- P, Printer
- T Nitrogen tank

- R Rotameter
- R Regulator
- S Sample port
- S<sub>f</sub> Sampling film
- S<sub>c</sub> Strip chart
- S<sub>i</sub> Electrical input/output signal
- $T_v$  Three way value
- W<sub>m</sub>- Cahan electrical balance

Figure 4. Schematic Diagram of Sorption/Desorption Apparatus

reached as a function of penetrant concentration and temperature.

<u>Description</u>. Solubility and solubility profile data were obtained by an equilibrium vapor pressure and microbalance gravimetric technique. A Cahn Electrobalance Model RG (Cahn Instruments Inc., Cerritos, CA) was employed for the gravimetric technique (Hernandez et al., 1986). The sample hang down tube was maintained at a constant temperature of  $37^{\circ}C \pm 0.5^{\circ}C$ . For a sample of approximately 25 mg, the sensitivity of the system was 5 µg. A weighed sample of the polymer film to be tested was suspended directly from one of the arms of the electrobalance and a constant concentration of permeant vapor continually flowed through the sample tube, such that the polymer film was totally surrounded with a low partial pressure of permeant at constant temperature. A constant concentration of permeant vapor (300 ppm wt/v) was produced by using a vapor generator system similar to that described above. Sorption profiles and solubilities were obtained by a continuous recording of weight-gain measurement.

# Analytical

#### Gas Chromatographic Analysis

Analysis of permeant concentration was carried out by a gas chromatographic procedure. A Hewlett-Packard Model 5890A gas chromatograph equipped with flame ionization detection interfaced to a Hewlett-Packard Model 3392A integrator was employed for quantitation. The gas chromatographic conditions are presented in Table 2.

A standard curve of detector response vs. absolute quantity was constructed from standard solutions of known concentration. Figure 5





Figure 5. Standard Curve of Ethyl Acetate

Table 2. Gas chromatographic conditions.

Injection Temperature		200 <sup>0</sup> C
Column Temperature		125 <sup>0</sup> C
FID Temperature		250 <sup>0</sup> C
Area Reject		0
Column	6' x 1/8" O.D. stainless steel,	packed
	with 5% SP2100 on 100/200 mesh	Supelcoport
	(Supelco, Inc., Belefonte, PA)	

shows the standard curve, where response is plotted as a function of ethyl acetate quantity. To elute ethyl acetate at 0.36 min.

## Density Gradient Analysis

The percent crystallinity of the film samples was estimated from density values, which were determined by the density gradient technique. The standard ASTM procedure (Density of Plastics by the Density Gradient Technique, ASTM D1505-68, Revised 1979) was employed for measuring the density of the film samples. The method is based on observing the level to which the sample equilibrates in a gradient, in comparison with the position of standards of known density. The Cole-Palmer Density Gradient Apparatus, which was employed, consists of a graduated glass cylinder containing a mixture of two levels of density of an aqueous solution of calcium chloride dihydrate, prepared in such a way that there is a linearly increasing density gradient existing from the top to bottom. The density of the film specimen was determined by observation of its position and linear interpolation with respect to a set of calibrated glass floats of known density, which were obtained from Lab Glass Inc. (Kingsport, TN).

In operation, two solutions of  $CaCl_2 \cdot 2H_2O$  in water were prepared and introduced into the column using a mixing device which gives a linear density gradient. The calibration curve is shown in Figure 6, where position is plotted as a function of density.

From the density measurements, the percent crystallinity was determined using the following relationship:

% crystallinity = 
$$\frac{(d - da)}{(dc - da)} \times 100$$
 (24)

where d = density of the semicrystalline sample (g/cc)

dc = density of 100% crystalline PET (1.45 g/cc at  $23^{\circ}$ C)

da = density of amorphous PET (1.333 g/cc at  $23^{\circ}$ C)

The mass-fraction crystallinity was also calculated using the following relationship (Choy et al., 1984):

$$Xm = \frac{dc}{d} \left(\frac{d - da}{dc - da}\right)$$
(25)

Where Xm = mass-fraction crystallinity.



**Position of Calibration Weight** 

Figure 6. Calibration Curve of the Density Gradient Tube at 23°C

#### RESULTS AND DISCUSSION

# The Effect of Temperature on the Permeation of Ethyl

Acetate Vapor Through PET Film Oriented at 90°C

Representative transmission rate profile curves for PET film samples oriented at  $90^{\circ}$ C (1.5 mil) are presented in Figure 7, where the total quantity of ethyl acetate permeated (Q) in micrograms is plotted as a function of time, to show the effect of temperature on transmission rates and lag time values. The concentration of ethyl acetate vapor was 300 ppm (g/ml), with a scatter band of 8 ppm throughout all experiments. Since good agreement was observed between replicate runs, the reported data are the average of duplicate studies.

As shown, the general shape of the transmission profile curve indicated typical Fickian behavior, where an initial induction time, a non-steady state and a steady state rate of transmission were observed (Crank, 1975).

The results from Figure 7 clearly illustrate the temperature dependence of the permeability coefficient ( $\overline{P}$ ) and the lag-time diffusion coefficient ( $D_{lag}$ ), with  $\overline{P}$  and  $D_{lag}$  increasing with an increase in temperature. Table 3 summarizes the results. The permeability coefficient ( $\overline{P}$ ) was normalized to unit vapor activity (a), where vapor activity is defined as the ratio of the permeant vapor pressure to saturated vapor pressure at the respective temperature (see Appendix A).



Figure 7. Transmission Profile Curves of Ethyl Acetate Through PET Film Oriented at 90°C (300 ppm, wt/v)

Temperature (°C)	<sub>P</sub> (a,d) Transmission Rate	户(D,d) Permeability Coefficient	θ Lag Time (hr)	(c) D <sub>lag</sub> Diffusion Coefficient
30	2.17 x $10^{-5}$	$1.33 \times 10^{-3}$	363.2	$1.85 \times 10^{-12}$
37	3.97 x 10 <sup>-5</sup>	$3.31 \times 10^{-3}$	230.7	2.91 x $10^{-12}$
54	$1.33 \times 10^{-4}$	2.31 x $10^{-2}$	60.5	1.14 x 10 <sup>-11</sup>

Table 3. The effect of temperature on the permeability of ethyl acetate vapor (300 ppm, wt/v) through PET film oriented at 90°C.

(a) Permeability Rate Units are g/hr·m<sup>2</sup>

(b) Permeability Coefficient Units are g·mil/day·m<sup>2</sup>·a

(c) Diffusion Coefficient Units are  $cm^2/sec$ 

(d) Average of replicate runs.

Lag time  $(\theta)$  was determined by the intersection on the time axis of the extrapolated linear steady state portion of the curve. The lag time diffusion coefficient  $(D_{lag})$  was calculated using Equation 9.

An Arrhenius plot of the permeability constant ( $\overline{P}$ ) of ethyl acetate vapor through PET film oriented at 90°C vs. 1/T is shown in Figure 8. As can be seen, the temperature dependency of the permeability constant ( $\overline{P}$ ), over the temperature range studied (30-54°C), can be represented by Equation 18. From the slope of Figure 8, the activation energy of the permeation process ( $E_p$ ) was determined to be 23.3 kcal/ mole.

The activation energy appeared to be high when compared with the activation energy of a permanent gas, such as oxygen through PET



Figure 8. Temperature Dependence of The Permeability Constant for Ethyl Acetate in PET Film Oriented at 90°C

below  $T_g$  ( $E_p$  = 8 kcal/mole) (Michaels et al., 1963b). A possible explanation for these results is that the molecular size of ethyl acetate is relatively large as compared to oxygen and requires a higher activation energy for diffusion (Meares, 1953) through the PET film sample.

An Arrhenius plot of the diffusion coefficient is shown in Figure 9. The activation energy of diffusion was determined to be 15 kcal/mol, from the slope of Figure 9. When compared to other data of organic vapor-PET systems below  $T_g$ , previous investigators reported a value of  $E_D = 13-14$  kcal/mol for the  $CH_4/PET$  system (Michaels et al., 1963b; Chen, 1974) and 20 kcal/mol for the toluene/PET system (Hernandez, 1984). These are similar in order of magnitude to the activation energy of diffusion determined in this study.

In addition to molecular size, another possible explanation for the strong temperature dependence of ethyl acetate diffusion through PET is the swelling effect by the sorbed permeant. Since all experimental data were obtained well below the  $T_g$  of PET (80.7<sup>o</sup>C), the thermal expansivity due to the increased temperature of test is considered to be limited. Therefore, the results may reflect some measure of the contribution of permeant/polymer interaction which enhances polymer chain conformational mobility and lowers  $T_g$ , resulting in the high degree of temperature dependence observed. The high stress and strain induced in oriented PET may accelerate the relaxation rate which affects the swelling of the polymer.



Figure 9. Temperature Dependence of the Diffusion Coefficient for Ethyl Acetate in PET Film Oriented at 90°C

# Acetate Vapor Through PET Film Oriented at 115°C

Figure 10 shows a plot of the transmission rate profile for ethyl acetate vapor through PET film oriented at  $115^{\circ}$ C, where the permeation studies were carried out at  $54^{\circ}$ C. For studies carried out at  $30^{\circ}$ C, no permeation was observed after 550 hrs. Although no permeation data was obtained at  $30^{\circ}$ C and  $37^{\circ}$ C for the  $115^{\circ}$ C oriented film samples, the level of temperature dependence on permeability and diffusivity values was assumed to be at least equivalent to that of PET film oriented at  $90^{\circ}$ C.

Table 4 summarizes the results of the permeability studies carried out on the PET film oriented at  $115^{\circ}$ C orientation temperature. While no

Temperature ( <sup>O</sup> C)	<del>p</del> (a) Transmission Rate (g/m²∙hr)	₽(b) Permeability Coefficient (g•mil/m2•day•a)	θ Lag Time (hr)	D <sub>lag</sub> (c) Lag time Diffusion Coefficient
30 (d)	3.9 x 10 <sup>-7</sup>	2.4 x 10 <sup>-5</sup>	-	-
54	$3.7 \times 10^{-5}$	5.5 x $10^{-3}$	95.2	$5.3 \times 10^{-12}$

Table 4. The effect of temperature on the permeation of ethyl acetate vapor (300 ppm, wt/v) through PET film oriented at  $115^{\circ}C$ .

(a) Transmission Rate Units are  $g/hr \cdot m^2$ 

(b) Permeability Coefficient Units are  $g^{mil/m^2} \cdot day \cdot a$ 

(c) Diffusion Coefficient Units are  $cm^2/sec$ 

(d) No permeation after 550 hrs. The upper level of the transmission rate was estimated (Appendix B).



Figure 10. Transmission Rate Profile Curve of Ethyl Acetate Through PET Film Oriented at 115°C (300 ppm, wt/v)

measurable permeation was observed at  $30^{\circ}$ C, an upper level of the transmission rate was estimated (see Appendix B).

The effect of thermomechanical history (i.e. % crystallinity) on the relative barrier properties of PET is illustrated graphically in Figure 11, where the transmission rate profile curves for the respective film samples (i.e. 90 and 115°C orientation temperature) evaluated under similar conditions of test are presented.

# Solubility of Ethyl Acetate Vapor in PET Film

A representative plot of  $\frac{Mt}{M\infty}$  vs t<sup>1/2</sup> for sorption of ethyl acetate in the PET film oriented at 90°C, obtained at an ethyl acetate vapor concentration of 300 ppm (wt/V) and a temperature of 37°C, is shown in Figure 12. Superimposed on the experimental data is the calculated curve according to Equation 12, and D<sub>s</sub>, as calculated from Equation 13. A plot similar to that in Figure 12 is shown in Figure 13 for the PET film sample oriented at 115°C. In this case, the calculated curve is also presented for comparison to the Fickian model.

It can be seen that the agreement between experimental and calculated results, following the procedure described above, is quite poor. At the ethyl acetate vapor concentration employed, the polymer structure may be swollen and the mass transfer process becomes concentration dependent, and therefore is not represented well by the theoretical equations that apply only for a constant diffusion coefficient and where the mass transfer process follows a Fickian type behavior and is not concentration dependent.



Figure 11. Influence of Orientation Temperature of PET on Ethyl Acetate Transmission Profile at 54°C (300 ppm, wt/v)



Figure 12: Sorption of Ethyl acetate in PET oriented at 90°C; carried out at 37°C, 300ppm.

![](_page_50_Figure_0.jpeg)

Berens (1977) also observed a much slower approach to equilibrium than predicted by the Fickian uniform-sphere model for the vinylchloride (VCM)/ polyvinyl chloride system, for VCM activities greater than above 0.01. Berens suggested that this behavior involved a "two-stage" sorption process with a non-Fickian, relaxation-controlled mode of sorption superimposed on the Fickian diffusion. This interpretation also seems applicable to the ethyl acetate/PET system; in the early stage of sorption, the ethyl acetate gradient provides the major driving force and the transport process is dominated by Fickian diffusion. When the concentration of penetrant resulting from this process is sufficient to develop a significant swelling stress, the slow response of the glassy PET to this stress produces gradual swelling of the polymer structure and permits additional sorption.

The equilibrium solubility, solubility coefficient values and the diffusion coefficient  $(D_s)$  obtained for ethyl acetate in the PET films are presented in Table 5.

Orientation Temperature (°C)	Se solubility gm vapor/gm pol <i>y</i> mer	S Solubility Coefficient gm/gm/a	D <sub>s</sub> Diffusion Coefficient cm <sup>2</sup> /sec	
90	0.016	0.037	$6.1 \times 10^{-12}$	
115	0.011	0.024	$4.9 \times 10^{-12}$	

Table 5. Solubility of ethyl acetate vapor in PET film at 37°C.

As discussed in the Literature Review section (see page 3), for a semi-crystalline polymer, the sorption of penetrant molecules was thought to occur almost exclusively within the amorphous domains. Recently, Choy et al. (1984) introduced the specific concentration term (Ca) to allow comparison of sorption data between polymer samples of varying percent crystallinity. The specific concentration (Ca) was defined as the amount of penetrant sorbed per unit mass of the amorphous component of the polymer and was expressed by:

$$C_a = S_e / (1 - X_m)$$
 (26)

For the conditions of test (i.e.  $37^{\circ}$ C, 300 ppm vapor concentration) the specific concentration, C<sub>a</sub>, of ethyl acetate in PET film oriented at 90 and  $115^{\circ}$ C is 0.021 and 0.016 gm <u>ethyl acetate</u>, respectively. gm amorphous component These findings intimate that the difference between the solubility of ethyl acetate vapor in PET film oriented at 90 and  $115^{\circ}$ C cannot be attributed solely to the difference in percent crystallinity, but is the result of penetrant induced swelling of the polymer structure, which permits additional sorption. The solubility parameter of ethyl acetate is 9.1 cal<sup>1/2</sup>/cm<sup>3/2</sup> and that for PET is 10.7 cal<sup>1/2</sup>/cm<sup>3/2</sup>. Since the polymer and penetrant are of similar polarity, penetrant/polymer interaction, resulting in the swelling of the polymer structure, is not unexpected (Berens, 1977; Bagley and Long, 1958; Fugita, 1961).

The solubility coefficient (S) determined experimentally at  $37^{\circ}$ C for the PET film sample oriented at  $90^{\circ}$ C ( $\frac{0.037 \text{ gm ethyl acetate}}{\text{gm polymer.a}}$ ) was found to be significantly higher than the value obtained by substitution of permeability data ( $\frac{0.0095 \text{ gm ethyl acetate}}{\text{gm polymer.a}}$ ) into the expression.

$$S = \frac{\overline{P}}{D_{lag}}$$
(27)

Implicit in derivation of this relationship are the following assumptions: (i) the diffusion coefficient (D) of the penetrant molecule through a polymer film is independent of concentration; and (ii) there is a linear relationship between the concentration of penetrant molecule within the polymer film and the vapor pressure of the penetrant in the surrounding gas phase.

However, when permeation involves interacting organic vapors, as with the penetrant/polymer system studied, the relationship between  $\overline{P}$ , D and S is more complex than that indicated by Equation 27. For such cases, concentration as well as time dependent diffusion processes may take place, resulting in swelling of the polymer matrix. In such cases, the diffusion coefficient, solubility coefficient and permeability constant have to be determined independently, in order to describe accurately the mass transfer behavior.

# CONCLUSION

The results of this study showed that a strong temperature dependence of the permeation of ethyl acetate through oriented PET exists over the temperature range investigated, with the temperature range being well below  $T_g$  for the PET samples. It was also found that there is a significant effect of crystallinity on the permeation process.

Since other thermomechanical parameters, i.e. degree of orientation and orientation balance, are constant for the respective films, the structural difference is considered only in the percent crystallinity, which results from the difference in orientation temperature. From the density gradient studies, the percent crystallinity of the PET film oriented at  $115^{\circ}C$  (% crystallinity = 31%) is higher than that of PET film oriented at  $90^{\circ}C$  (% crystallinity = 22%).

The presence of crystalline regions in a polymer has two effects on sorption and diffusion behavior. Firstly, solubility decreases with an increase in percent crystallinity, owing to the insolubility of the penetrant in the crystalline regions. Further, in the diffusion process, an increase in the degree crystallinity of the test film results in a decrease in the diffusion coefficient.

In terms of practical importance, the studies allow for a relative comparison of the barrier properties of a polymer membrane (i.e. PET) over a temperature range below  $T_{\rm c}$  for the test film. The studies also

provide a method for estimating the barrier properties of the test film at ambient temperature, by extrapolation of the Arrhenius plot obtained from higher temperature data. Implicit in this estimation is the assumption that the relationship between log  $\overline{P}$  and temperature (1/T) is linear over the temperature range in question, even though the temperature of test are below the T<sub>g</sub> of the test polymer. The results of this study also provide a means of improving a barrier structure for a specific end use application.

In terms of theoretical importance, this investigation was viewed as a method for studying the phenomenon of diffusion in polymer membranes, for the case of changing temperature and molecular structure.

It is of significant importance to take into consideration the fact that the permeability and solubility data and the resultant relationship developed are all based on data obtained at one vapor concentration (300 ppm, wt/v). Concentration dependency of the diffusion process, when dealing with organic penetrants which exhibit strong penetrant/polymer interaction, must be taken into consideration if the barrier properties over a range of penetrant levels is required.

#### RECOMMENDATIONS

The results of this study, indicated a strong temperature dependence for the permeation of ethyl acetate vapor through oriented PET, over a temperature range significantly below the glass transition temperature (Tg) of the polymer. A possible explanation for the findings may involve penetrant/polymer interaction which effectively acts to plasticize the polymer, resulting in enhanced polymer chain conformational flexibility and a reduction in Tg. The relaxation rate of glassy PET polymer chains may also be effected, leading to enhanced polymer swelling. To verify this hypothesis, the following additional studies are proposed:

1) Conduct additional sorption studies as a function of penetrant vapor concentration and temperature to determine the concentration and temperature dependency of the solubility and diffusion coefficients.

 Evaluate the extent of swelling of the polymer as a result of penetrant sorption.

3) Determine the glass transition temperature (Tg) of the polymer following equilibrium sorption studies.

The studies outlined above will be carried out on PET samples of known thermomechanical history.

APPENDICES

# Appendix A

Calculation of the Vapor Activity of Ethyl Acetate

The vapor activity (a) is defined as:

$$a = p_V/p_0$$

Where  $P_V$  = the permeant vapor pressure (mm Hg)

 $P_0$  = the saturated vapor pressure (mm Hg) at constant temperature. Sample Calculation: The concentration of ethyl acetate is 300 ppm (g/cc).

The molecular weight of ethyl acetate is 88 (g/mol)From the gas law, the vapor activity at  $30^{\circ}$ C is:

$$P_{V} = \frac{300 \times 10^{-6} \text{ g}}{\text{cc}} \times \frac{1}{88 \text{ gm mol. wt}} \times \frac{82 \text{ cc}}{\text{mol. } \circ \text{K}} \times 303^{\circ} \text{K} \times \frac{760 \text{ mm Hg}}{\text{Atm.}}$$

$$P_v = 64.1 \text{ mm Hg}$$

Thus, 
$$a = \frac{P_v}{P_o} = \frac{64.1 \text{ (mm Hg)}}{110.6 \text{ mm Hg}} = 0.59 \text{ at } 30^{\circ}\text{C}$$

At  $37^{\circ}C$ ,  $P_{v} = 65.6$  mm Hg,  $P_{o} = 152.1$  mm Hg, a = 0.43At  $54^{\circ}C$ ,  $P_{v} = 69.2$  mm Hg,  $P_{o} = 330.1$  mm Hg, a = 0.21

### Appendix B

Estimation of the Upper Limit of the Transmission Rates of Ethyl Acetate Through PET Film Oriented at 115<sup>0</sup>C

The lowest area response selected for detecting a permeant with good precision and accuracy was assumed to be 1000 area unit/23 days. Based on the calibration factor (1.08 x  $10^{-11}$  g/a.u.), the total quantity of ethyl acetate after 23 days was calculated as follows:

$$\frac{gm \ ethyl \ acetate}{day} (g/day) = \frac{1000 \ AU}{23 \ days} \times calibration \ factor (\frac{g}{AU})$$
$$\times \frac{1}{.5 \ cc} (injection \ value) \times 50 \ cc \ (total \ cell \ volume)$$

Where gm ethyl acetate = minimum total number of grams of permeant which would have to permeate to get a measurable response from the gas chromatograph, after 23 days continuous testing

Sample Calculation:  $\frac{gm}{day} = \frac{1000 \text{ AU}}{23 \text{ days}} \cdot (1.08 \times 10^{-11} \text{ g/AU}) \cdot (\frac{1}{.5 \text{ cc}}) \cdot (50 \text{ cc}) = 4.7 \times 10^{-8} \text{ g/day}$   $4.7 \times 10^{-8} \text{ g/day} \times \frac{1}{.005 \text{ m}^2} = 9.4 \times 10^{-6} \text{ g/m}^2 \text{ day}$ 

This is an estimated minimum quantity to have permeated and represents an average transmission rate which does not consider lag time. LIST OF REFERENCES

#### LIST OF REFERENCES

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