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PERMEATION OF ETHYL ACETATE VAPOR
THROUGH SILICA DEPOSITED
POLYETHYLENE TEREPHTHALATE FILM
AND COMPOSITE STRUCTURES

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PERMEATION OF ETHYL ACETATE VAPOR THROUGH SILICA DEPOSITED POLYETHYLENE TEREPHTHALATE FILM AND COMPOSITE STRUCTURES

By

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ABSTRACT

PERMEATION OF ETHYL ACETATE VAPOR THROUGH SILICA DEPOSITED POLYETHYLENE TEREPHTHALATE FILM AND COMPOSITE STRUCTURES

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The effect of temperature, relative humidity and retort sterilization conditions on the permeation of ethyl acetate vapor through silica deposited polyethylene terephthalate (SiOx PET) films and laminate structures was studied. The permeability of an ethylene/ vinyl alcohol copolymer (EVOH) and a EVOH laminate structure was also determined.

At 22°C, the SiOx PET film showed excellent barrier properties. It also exhibited relatively high temperature dependence (E_a = 23 kcal/ mol), but was unaffected by sorbed water. For the SiOx PET based retort pouch, an average increase of 260% in the permeation rate was observed following retorting, when the retort temperature was increased from 125 to 130°C. The transmission rate increase was on the order of 30%, in going from 120° to 125°C, retorting temperature. At each temperature, heating times of 20, 40, and 60 minutes were evaluated, and a direct correlation was found between processing time and permeation rate.

Analysis by optical microscopy on the SiOx surface showed a direct relationship between permeability and fracture of the SiOx coating. Further, a direct correlation between retorting conditions and surface damage was found.

To my parents and my lovely wife.

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INTRODUCTION

Ethylene vinyl alcohol copolymer (EVOH), polyvinylidene chloride (PVDC) and meta xylene diamine nylon (MXD-6) are well known plastic high barrier polymeric materials. Recently, development of a new high barrier silica deposited film has been the subject of major interest for various packaging material related manufacturers (Brody, 1988; Sakamaki and Kano, 1989). This film, which is based on silicon oxide deposition onto polyethylene terephthalate (PET), exhibits a number of important characteristics such as:

1) Excellent and stable barrier properties: It has very high barrier properties for water vapor and oxygen. Furthermore, the barrier properties are influenced little by variation of temperature or relative humidity.
2) Transparency: Inside contents are visible through this film.
3) Retortability: It can sustain the retort sterilization process.
4) Microwaveability: Unlike aluminum foil and aluminum metallized film, this film can be safely used in the microwave oven.

This silica deposited film was commercialized as a retort pouch material in lamination with PET and polypropylene in Japan, in 1988 (Sasaki, 1988). This material allows microwave reheating of the pouch contents (e.g. pasta sauces), prior to serving.

Since its introduction in 1988, several reports have been published

on the water vapor and oxygen barrier properties of the silica deposited film, and the barrier data compared to other high barrier films (Toppan, 1988; Brody, 1988; Kaiho, 1990). The articles published indicated that this film also has good aroma and flavor barrier characteristics. However, data on the permeation of organic molecules through this film have not been presented. Since this material shows both excellent water vapor and oxygen barrier properties, packaging designers assumed that this film would also have good organic vapor barrier characteristics. Although this assumption is intuitive, no researcher has engaged in a systematic investigation of this subject.

This study, therefore, focuses specifically on determining the transmission rate of organic vapors through a silica (inorganic) deposited polyethylene terephthalate film (SiOx PET), as compared to other high barrier film structures, under similar conditions of test.

Objectives of the proposed study include:

1) Determination of the vapor transmission rate of ethyl acetate through silica deposited film, as well as through other high barrier films and laminate structures, under varying temperature and relative humidity regimes.
2) Evaluation of the permeation of organic vapor through retort pouch structures which contain a silica deposited film barrier layer, before and after the retort sterilization process.
3) Characterization of processing-induced damage of the SiOx coating layer and its relationship to mass transport property changes.

LITERATURE REVIEW

Silica Deposited Film

Evolution of Silica Deposited film

The vacuum coating of polymer films with transparent metal oxides has been known since 1964 (Krug and Rübsam, 1990a), and was developed to improve the barrier properties of polymeric films to oxygen and water vapor. Processes for the continuous coating of silica oxide (SiOx) onto a polymer web by vacuum deposition had been developed by DuPont de Nemours and Company (DuPont,1964), and also by Unitica Co., Ltd. (Unitica, 1972). However, the lack of a low cost production technology and a low demand from the end user-market's made these products unsuccessful (Sakamaki and Kano, 1988).

Recently, however, the increasing number of microwave ovens in households in both the United States and Japan has resulted in a corresponding increase in the demand for microwaveable food packaging. For example, in United States households, the penetration of microwave ovens reached approximately 80% (Martin, 1988). In 1988, silica oxide deposited film was, for the first time, commercialized as a retort pouch material in lamination with polyethylene terephthalate (PET) and polypropylene by the cooperative work of the following Japanese firms; Toppan Printing Co., Ltd., Ajinomoto Co., Ltd. and Toyo Ink Manufacturing Co., Ltd. (Sasaki, 1988). This material allowed microwave reheating of

the pouch contents (e.g. pasta sauces) prior to serving, with the silica deposited PET layer exhibiting similar functional properties as metallized films, in terms of laminate structure and barrier properties to oxygen and water vapor. The structure of the silica deposited film and its typical pouch structure are shown below (Figure 1 and 2).

Properties of Silica Deposited Films

The efficient coating of metal oxides, such as silica oxide to polymer films required development of new processing techniques, since the physical properties such as vapor pressure and evaporation - not from the liquid but from the solid state - are completely different. To be effective, silicon monoxide (SiO) has to be reactively evaporated to get a SiOx coating with barrier properties. The oxygen content (x) varies from 1.5 to 2, in accordance with the evaporation conditions (SiOx, where $1.5 < x < 2$).

SiOx coatings are generally produced by evaporation of silicon-monoxide (x=1) either by thermal or by electron beam gun evaporation (Krug and Rübsam, 1990a). The thermal process involves vacuum web coaters, using intermetallic boats as point sources across the web width. The web speed is limited, however, by the SiO evaporation rate from the boats, and nonuniformity at the highest evaporation rates (Krug and Rübsam, 1990b).

Electron beam vacuum coating indicates that the power required to enable thermal evaporation of a coating material is supplied by means of an electron beam (Krug and Ludwig, 1990). The power conversion efficiency of an electron beam is better than with conventional sources

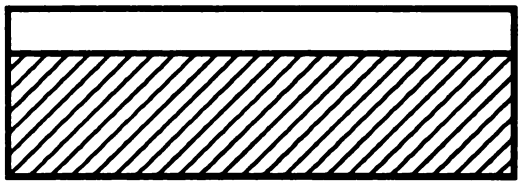


Figure 1. Cross-sectional view of the silica deposited PET film.

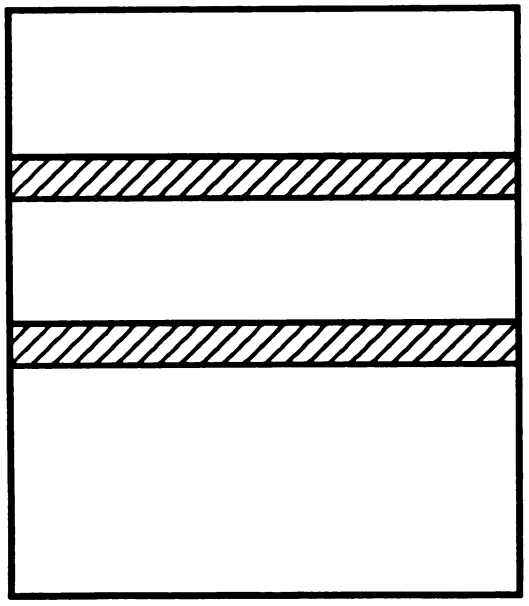


Figure 2. Cross-sectional view of a typical retort pouch structure with silica deposited film.

for thermal evaporation. Furthermore, electron beam guns are applicable to several metals and metal oxides (Krug and Rübsam, 1990b).

Since SiO is sublimed from the solid state and is not simply evaporating from a liquid surface, a special crucible is necessary (Krug and Rübsam, 1990a). For commercial production, a relative web speed of approximately 4 m/s, with an evaporation temperature of approximately 1350°C is observed. The vapor of SiO is oxidized in a controlled reactive atmosphere to achieve a degree of oxidation between x = 1.5 and 1.8 ($SiO_{1.5}$ - $SiO_{1.8}$), with a thickness of 800Å. Generally SiOx-layers are relatively fragile when the coating thickness is less than 1500 Å, and its chemical inertness makes it corrosion resistant. Further, the barrier and mechanical properties of the silica oxide deposited PET based retort pouch are not adversely affected by moisture during retorting (Sakamaki and Kano, 1989). In addition, the surface is printable, and not affected by the inks (Chahroudi, 1989).

Typically the SiOx coating consists of a mixture of SiO (silicon monoxide), Si_2O_3 (disilicon trioxide) and SiO_2 (silicon dioxide), and it, therefore, has a slightly yellowish appearance (Krug and Rübsam, 1990a). In contrast to evaporated aluminum, which has a microcrystalline structure, SiOx is deposited as a glassy network and is therefore totally amorphous. The transparency and the barrier properties are mainly influenced by the coating thickness and chemical composition. The effect of coating thickness, at a fixed chemical composition (i.e. fixed oxygen content), is shown in Figure 3, where oxygen transmission rates are plotted as a function of coating

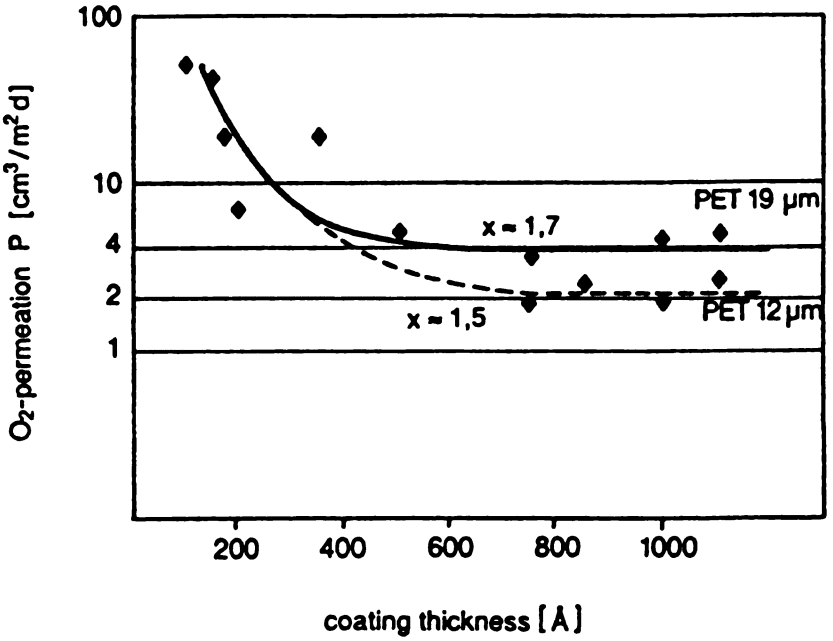


Figure 3. Oxygen permeation through SiOx deposited PET as a function of coating thickness (Krug and Rübsam, 1990b).

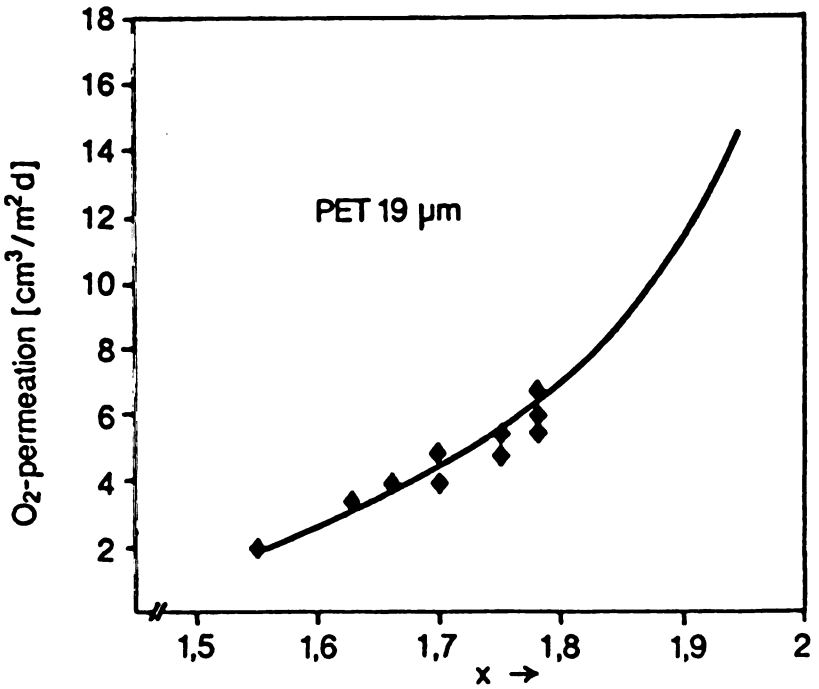


Figure 4. The effect of chemical composition on the oxygen permeation through SiOx deposited PET (Krug and Rübsam, 1990b).

thickness. The general behavior of oxygen permeation as the function of coating thickness is similar to that of metallized films, where with increasing coating thickness the oxygen permeation rate decreases drastically (Krug and Rübsam, 1990a).

However, the mechanism for permeation is different. While aluminum coatings are a microcrystalline structure, the silica coatings are comprised of an amorphous glassy network of SiO, Si_2O_3 and SiO_2. These coatings are nearly free of pin-holes and oxygen permeation takes place through the glassy network itself, as compared to transmission through pinholes, which is the case for aluminum metallized film (Krug and Rübsam, 1990b).

The mechanism of nucleation and growth of the layer is also similar to aluminum metallization. Therefore the general barrier behavior is similar; with increasing coating thickness the O_2 permeation rate decreases until a layer thickness of approximately 600 Å, beyond which no further reductions in oxygen transmission rates observed (Figure 3).

As SiO is a two-element-system, the properties of the coating are generally influenced by the layer thickness and the chemical composition, or degree of oxidation (oxygen content). The effect of chemical composition on the barrier properties of SiOx deposited PET film is shown in Figure 4 (Krug and Rübsam, 1990b).

Oxygen Barrier

The structure of silica deposited film (GL film) consists of a base film and the SiOx coating. GL film is a trademark of the silica deposited PET film produced by the Toppan Printing Co., Ltd. The amount

of oxygen permeating through the SiOx coated structure decreases to 1/100 that of the uncoated base film (biaxially oriented polyethylene terephthalate BOPET 12μ). Further, when silica deposited film is laminated with the other films to provide a multi-layer retortable material, the level of oxygen permeation decreases to 1/300, the rate of the uncoated base film (See Table 1). The oxygen barrier properties of this laminated silica deposited film are better than that of polyvinylidene chloride (PVDC) or polyamide, and slightly higher than that of EVOH, at dry conditions (Table 2). As a transparent, high barrier packaging material, this barrier level, 0.5cc / m^2 day atm allows a long shelf life for most processed foods. Another important property of the silica deposited film is the limited effect of temperature and humidity on the films barrier properties. Kaiho (1987) stated that high humidity conditions have little effect on SiOx film's oxygen permeation rates, and its temperature dependency is also relatively low.

Moisture Barrier

The moisture barrier properties of silica deposited film (GL film) is also excellent. Silica deposited film shows only 1/40 the moisture transmission rate (Water Vapor Transmission Rate, WVTR) of the uncoated base film (PET,12 μ). Lamination with cast polypropylene (CPP) film reduces the WVTR to less than 1/100 (Table 3) of the base film. In comparison to other commonly used barrier films, the silica deposited film's WVTR (0.5 g/ m^2 day) is equivalent to that of a laminated aluminum metallized film, and that of 500μ CPP (Table 4). In production, the 1.0 g/m^2 day WVTR is a difficult target for transparent

Table 1. Oxygen permeance of PET, SiOx PET and SiOx PET laminated structure. [a]

Structure	Oxygen permeance
PET 12μ	155
GL film: PET 12μ /SiOx coating	1.5
PET 12μ / GL film /CPP 60μ	0.5

Units of O_2 permeance = cc/m^2 day atm at 25 °C, 70% RH
(a) from Sakamaki and Kano, 1989

Table 2. Oxygen permeance of SiOx laminated film and other laminated films. [a]

Structure	Oxygen permeance
PET 12μ/ GL film/ CPP 60μ	0.5
ONy 25μ/ PVDC[b]15μ/ CPP 60μ	10.5
PET 12μ/ PVDC[c]15μ/ ONy 15μ/ CPP 60μ	1.8
PET 12μ/ PVDC[c]25μ/ ONy 15μ/ CPP 60μ	1.0
PET 12μ/ EVOH[d]15μ/ CPP 60μ	0.3
OSM[e]15μ/ONy 15μ/ CPP 60μ	3.8
ONy 25μ/ CPP 60μ	15.8

Units of O_2 permeance = cc/m^2 day atm at 25 °C, 70% RH
(a) from Sakamaki and Kano, 1989
(b) KUREHA CO. "K-Flex"
(c) ASAHI KASEI CO. "SARAN UB"
(d) KURARE CO. "EVAL"
(e) TOYOBO "OSM: metaxylen diamine-adipic acid copolymer

Table 3. Water vapor transmission rate of PET, SiOx PET and SiOx laminated structure. [a]

Structure	WVTR
PET 12μ	47
GL film: PET 12μ /SiOx coating	1.2
PET 12μ / GL film /CPP 60μ	0.5

Unit of WVTR = g/m^2 day at 40°C, 100 R.H.

(a) from Sakamaki and Kano, 1989

Table 4. Water vapor transmission rate of SiOx laminated film and other laminated films. [a]

Structure	WVTR
PET 12μ/ GL film/ CPP 60μ	0.5
KOP 25μ/ CPP 25μ	4.0
OPP 25μ/ EVOH 15μ/ CPP 25μ	2.5
ONy 25μ/ CPP 60μ	7.8
PET 12μ/ AL metallizing/ CPP 25μ	0.6
CPP 500μ	0.5

Unit of WVTR = g/m^2 day at 40°C, 100 R.H.

(a) from Sakamaki and Kano, 1989

flexible films of less than 100μ thickness, even though PVDC coated oriented polypropylene (OPP) or high density polyethylene (HDPE) are used (Sakamaki and Kano, 1988).

Retortability

Table 5 lists the oxygen permeance of several laminated barrier films, before and after retort processing (125°C-20 min). As shown, laminated GL film experienced minimum change in oxygen permeance following retort processing, maintaining a permeance of less than 1cc/m^2 day atm.

A comparison between silica deposited film and other barrier materials used in food packaging in terms of oxygen barrier, water vapor barrier, retortability, microwaveability and transparency is presented in Table 6 (Toppan, 1989).

An Alternative Approach

An alternative method to manufacture silica deposited films was developed by The EASTPAC Company, a joint venture between Airco Coating Technology and Eastman Chemical Company (Eastman News, 1990). The commercialization of a chemical plasma deposition system for the application of a high gas barrier transparent coating was announced by the company under the QLF® (Quartz-Like Film) coating trademark.

The plasma enhanced chemical vapor deposition (PECVD) process is

Table 5. Oxygen permeability of SiOx laminated film and other ilms before and after retort process. [a]

Structure	O_2 permeability before retorting	O_2 permeability after retorting
PET 12μ/ GL film/ CPP 60μ	0.5	0.7
ONy 25μ/ PVDC[b] 15μ/ CPP 60μ	10.5	8.2
PET 12μ/PVDC[c] 15μ/ONy 15μ/CPP 60μ	1.8	2.6
PET 12μ/PVDC[c] 25μ/ONy 15μ/CPP 60μ	1.0	1.6
PET 12μ/ EVOH[d] 15μ/ CPP 60μ	0.3	18.8
OSM[e] 15μ/ONy 15μ/ CPP 60μ	3.8	6.0
ONy 25μ/ CPP 60μ	15.8	21.5

(a) from Sakamaki and Kano, 1989

(b) KUREHA CO. "K-Flex"

(c) ASAHI KASEI CO. "SARAN UB"

(d) KURARE CO. "EVAL"

(e) TOYOBO "OSM: metaxylen diamine-adipic acid copolymer

Retort condition: 125 °C - 20 min.

Unit of O_2 permeability = cc/m^2 day atm at 25 °C, 70% RH

Pouched material: water/oil = 1/1 mixed material

Table 6. Comparison among silica deposited film and other barrier materials.[a]

	Silica deposited film	Aluminum foil	Aluminum metallized film	EVOH	PVDC
Oxygen barrier 25°C - Dry	Good	Good	Good	Good	Good
HiTemp-Hi RH	Good	Good	Good	Low-Med	Medium
W.V. barrier	Good	Good	Good	Poor	Medium
Retortability	Good	Good	Poor[b]	Poor-Good	Medium
Microwave-ability	Good	Poor[c]	Poor[d]	Good	Good
Transparency	Good[e]	No	No	Good	Good

(a) from Toppan, 1989

(b) Delamination

(c) Reflection

(d) Spark

(e) Slightly yellowish

a modification of the semiconductor technique. It is a cold temperature process that is non-destructive to plastic, and employs organosillicons as a non-toxic liquid process monomer, rather than silane gas, which is pyrophoric. Plasma-based processing (including QLF) also offers the advantage of being multi-directional, since a coating is deposited on all areas where the plasma contacts a surface. PECVD enables one to obtain uniform coatings on all types of rigid packaging, especially packages of complex shapes, such as bottles, or coating both sides of a surface simultaneously (Felts, 1990).

The gas barrier properties of the PECVD processed film is claimed to be superior to the evaporated films (Felts, 1990). The EASTPAC process also claims recyclability and cost competitiveness (Eastman News, 1990). However, the material has not been used commercially. Therefore its advantageous attributes are yet to be confirmed.

Permeation of Organic Vapors through Polymer Films

Since the transport of organic vapors through packaging materials has been the subject of a number of investigations, various procedures have been developed for quantifying the rate of diffusion of organic vapors through barrier membranes. Pye et al. (1976) described a continuous or isostatic procedure for measuring the diffusivity properties of polymer membranes that used two gas chromatographs connected to a cell. The apparatus developed by Pye et al. and Niebergall

(1978) was designed to allow measurement of transmission rates for mixtures of organic vapors through barrier structures as a function of permeant concentration, temperature, and relative humidity.

Isostatic methods were also reported by Zobel (1982) and DeLassus (1985). Hernandez (1984) and Baner et al. (1986) also employed an isostatic procedure for determining the permeability of organic penetrants through polymer membranes. Analysis of permeated vapor was based on a gas chromatographic technique with flame ionization detection.

Hilton and Nee (1978) developed an accumulation or quasi-isostatic test method for determining the permeability of organic vapors through barrier films. In his 1985 publication, Murray expanded his quasi-isostatic procedure and reported a number of examples for which the test apparatus was employed to determine the relative permeation rates of organic vapors through barrier structures. However these methods are limited to determining the transmission rates and permeability constant values for only saturation vapor pressure of the liquid penetrant, at a given temperature.

Gilbert et al. (1983) evaluated the barrier properties of polymeric films to various organic penetrants by a quasi-isostatic procedure. To provide a constant concentration or partial pressure gradient, the authors continually flowed a penetrant vapor stream through the high concentration chamber of the permeability test cell. In determining the diffusion of organic penetrants through polymer films Baner et al. (1986) also employed the continuous flow of organic vapor through the high concentration cell chamber to assure a constant vapor gradient. A

gas chromatographic method was developed for the permeation rate measurements.

Shirakura (1987) studied the effect of temperature on the diffusion of ethyl acetate through oriented polyethylene terephthalate films of varying thermomechanical history. The effect of relative humidity on the permeability of toluene vapor through a multi-layer coextruded film containing hydrophilic layers was evaluated by Liu et al. (1988)

The transport of small molecules in polymers can also be evaluated by sorption-desorption methods. Fujita (1961) has described the general behavior of sorption and permeability of organic vapors. Other authors employing sorption-desorption methods include Bischoff, et al. (1984) and Choy et al. (1984).

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 (Paine, 1983). The transport of a gas or vapor through polymeric films commonly used in packaging typically involves the activated diffusion process. Such a process involved three steps; (1) absorption of the permeating species, in which 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 diffusion 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:

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

where Q is the total amount of permeant which has passed through area A during time t. 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).

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

where D is the diffusion coefficient with units of $(length)^2$ $time^{-1}$ (e.g. cm^2s^{-1}), 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).

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

$$F=D (C_1 - C_2) / L \quad (3)$$

where C_1 and C_2 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 (Henry's Law). The concentration of the permeant in the polymer, C, can thus be expressed by:

$$C = (Sp)\ (\Delta p) \tag{4}$$

where the solubility (Sp) is a function of temperature and may be a function of the partial pressure (Δp) or C. When Henry's law is assumed:

$$C = S\ (\Delta p) \tag{5}$$

where S is the Henry's law solubility coefficient, which is independent of Δp and C (Crank, 1975). Substitution in equation (3) yields:

$$F=DS\ (p1 - p2) / L \tag{6}$$

where p1 and p2 are the permeant partial pressures at the two surfaces of the film, and the product D*S defines the permeability coefficient (P), by the relationship D*S = P (Barrer, 1939).

When both D and S are independent of penetrant concentration, P is

a constant at any given temperature. However, where considerable interaction between the polymer and the permeant takes place, P is no longer constant but will vary with C and Δp (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 (Rogers, 1956; Zobel, 1982; Hernandez et al., 1986). One common method for determining permeability is the quasi-isostatic 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 5.

The permeability coefficient, P is calculated as:

$$P = \frac{QL}{\Delta t A b} \qquad (7)$$

where Q is the quantity of gas or vapor which has permeated in the

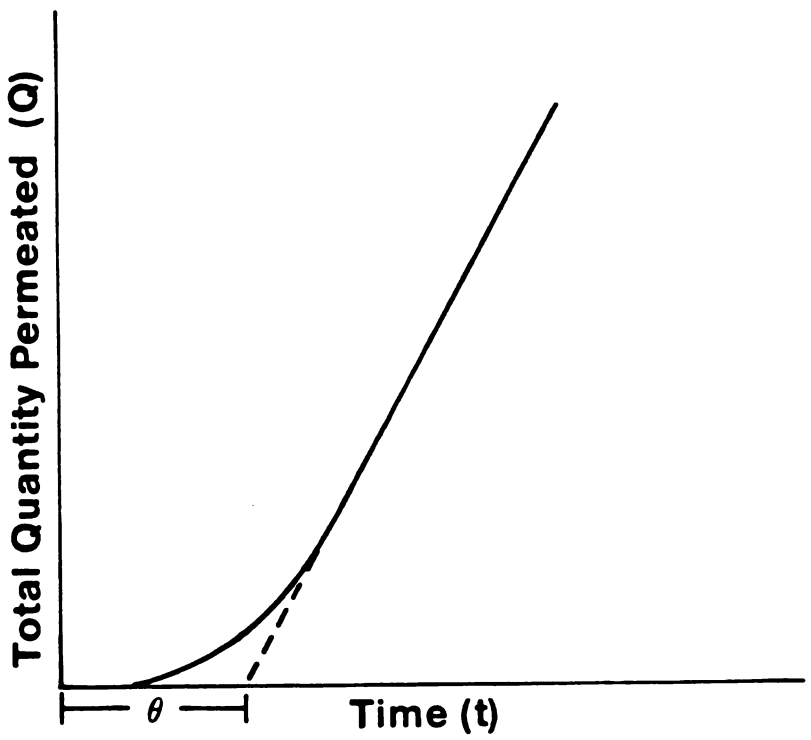


Figure 5. Generalized transmission profile curve for the quasi-isostatic method.

time interval Δt in the steady state of flow. A is the area of the film exposed to the permeant. L is the average film thickness, and b is the driving force given by the concentration or partial pressure gradient.

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 that the diffusion coefficient can be calculated by:

$$D = \frac{L^2}{6\theta} \tag{8}$$

where θ is the intercept of the time axis of the extrapolated linear steady state portion of the curve (Figure 5) and is called the lag time. Therefore, in theory, all three parameters can be calculated from the quasi-isostatic method; P from the steady state flux; D from the lag time; and S from P/D.

MATERIALS AND METHODS

Materials

Film Samples

In this study, three different films and three different laminate film structures were investigated. These films were obtained from Toppan Printing Co., Ltd.(Tokyo, Japan).

1) Films

a. PET,12μm (0.5 mil) Polyethylene Terephthalate [as a base film]

b. SiOx PET, 12μm (0.5 mil) Silica deposited PET.
   Thickness of SiOx : 1200 Å, fixed oxygen content x= 1.7

c. EVOH,15 μm (0.6 mil) Ethylene Vinyl Alcohol Copolymer (EVAL-F)

A cross-sectional view of the silica deposited PET film is depicted in Figure 1.

2) Composite Films

a. PET 12μm / PET 12μm / CPP 60μm [as a base pouch]

b. PET 12μm / SiOx PET 12μm / CPP 60μm

c. PET 12μm / EVOH 15μm / CPP 60μm

A cross-sectional view of the laminated silica deposited PET film is depicted in Figure 2.

PET 12μm:	Degree of Orientation -- 350% based on initial dimensions (biaxially)
	% Crystallinity - 56%
EVOH 15μm:	EVAL - F (E=32%)
SiOx PET 12μm:	PET 12μm described above was coated with silica oxide layer by Toppan Printing Co., Ltd.(Tokyo, Japan)
	Thickness of SiOx : 1200 Å, fixed oxygen content x= 1.7
CPP 60μm:	Retort grade as a heat seal layer
Adhesive:	Urethane type (Retort resistant)

Retort Pouch

Retort pouches were analyzed to evaluate the effect of retort sterilization process on the composite film. The retort pouch structure was identical to the composite film (b).

Structure	PET 12μm/SiOx PET 12μm/CPP 60μm
Size	130mm x 170mm, three sides sealed

Permeant

Ethyl acetate was used as the organic vapor permeant. The selection is based on the ease of analysis and the known contribution of this compound to the aroma profile of food products.

Research grade ethyl acetate was obtained from Aldrich Chemical Co. Inc. (Milwaukee, WI) and was employed throughout, as the permeant vapor.

Carrier Gas

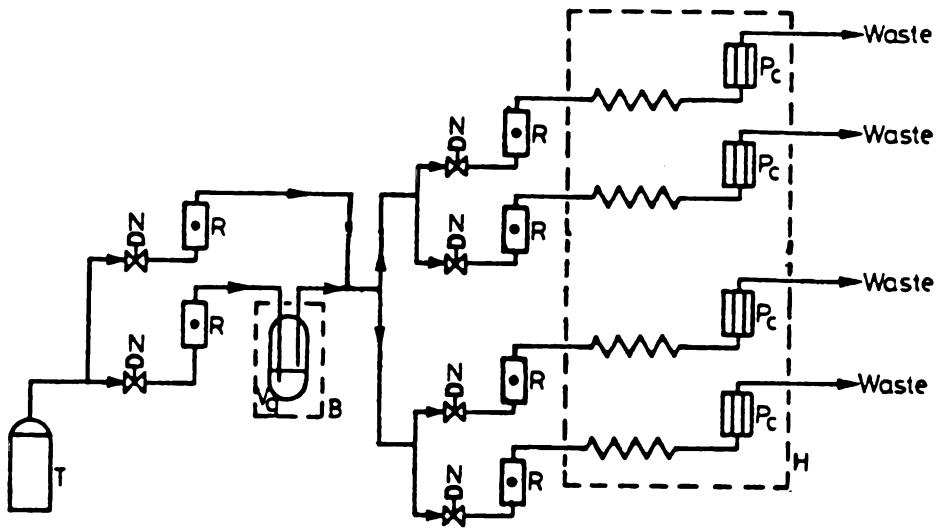
High purity dry grade nitrogen gas produced by AGA Inc. (Cleveland, OH) was employed throughout the experiment as the carrier of the permeant.

Procedure

Permeability Measurements

The permeation test system, based on the quasi-isostatic method, was designed, assembled and tested as part of this study. Figure 6 presents a schematic diagram of the permeation test apparatus. It allows the collection of permeation data as a function of temperature and vapor concentration.

The permeability cell, constructed of aluminum, is composed of two cell chambers and a hollow center ring. The right and left cell chambers each have a volume of 50 cm^3; the volume of the center cavity is approximately 50 cm^3. In operation, the test films are placed in the cell so that the center ring effectively isolates the right and left cell chambers. Hermetic isolation of the chambers from each other and from the atmosphere is achieved by the compression of overlapping Viton O-rings on the film specimen. Viton is a fluorocarbon elastomer that is resistant to attack and swelling by most organic vapors. The cell chambers and the center ring are equipped with an inlet and outlet valve and sampling port. The films to be tested are mounted in the permeability cell and the cell



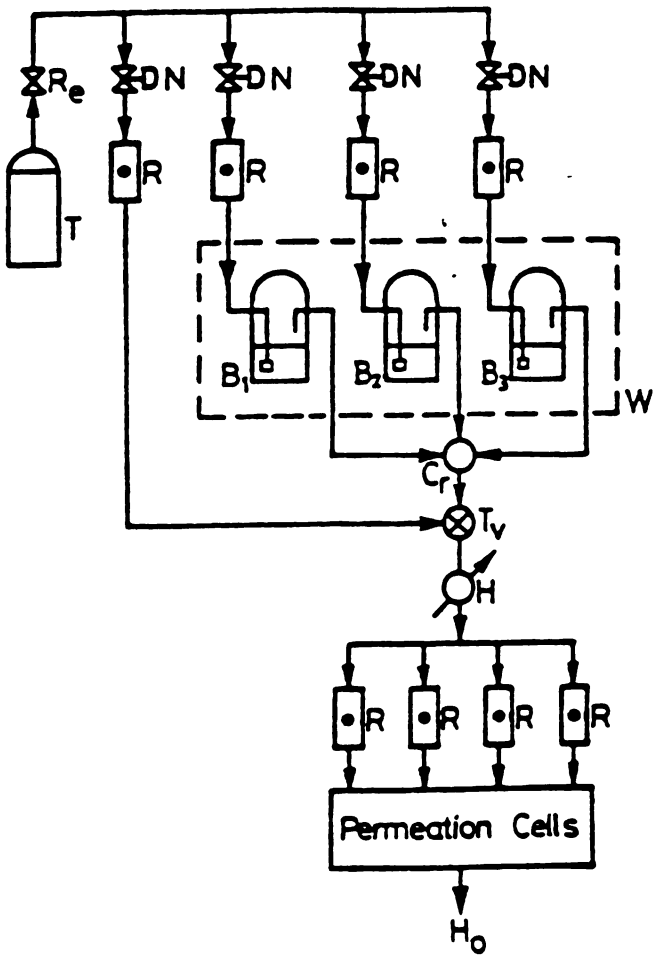
B - Water bath, generation of permeant vapor phase diluted in Nitrogen
H - Oven
N - Needle valve
P_c - Permeability cell
R - Rotameter
T - Nitrogen tank
V_g - Organic vapor generator

Figure 6. Schematic of permeation test apparatus for non-humidified condition.

assembled. A constant, low partial pressure of permeant vapor is then flowed through the center cell chamber at a flow rate in the range of 5 to 10 ml/min. This allows the permeability of two film specimens to be determined concurrently, under identical conditions as reported by Baner et al. (1986).

A constant concentration of permeant vapor is produced by bubbling nitrogen gas through the liquid permeant. This is carried out by assembling a vapor generator consisting of a gas washing bottle, with a fritted dispersion tube, containing the organic liquid. To obtain a lower vapor concentration, the permeant vapor stream is mixed with another stream of pure carrier gas (nitrogen). As shown in Figure 6 flow meters were used to provide a continuous indication that a constant rate of flow was maintained. Gas flow was regulated with NU PRO needle valves, Type B-25G. The vapor generator system was kept at a constant temperature of 21 ± 1°C. The penetrant vapor concentrations are expressed throughout in ppm (mass/volume) vapor in nitrogen, where 1 ppm equals 1μg ethyl acetate per cm^3 of gas mixture al 1 atm and 21°C.

To determine the effect of relative humidity on the permeation of ethyl acetate vapor through barrier films, another test apparatus was assembled. The major difference between the two test apparatus is found in the vapor generator. The vapor generator system of the second apparatus consists of three gas washing bottles with fritted dispersion tubes, connected as shown in Figure 7. One gas washing bottle (B1) contained the liquid penetrant, a second gas washing bottle (B2) was filled with a mixture of distilled water and the



B_1-Organic vapor bubbler
B_2-Organic/water vapor bubbler
B_3-Water bubbler
C_r-Four way valve
H-Hygrometer
H_o-Hood

Figure 7. Schematic of permeation test apparatus for evaluating the effect of relative humidity.

organic liquid penetrant. The third gas washing bottle (B3) contained pure distilled water. Needlevalves and flow meters were used to obtain the desired penetrant concentration and relative humidity. The humidified organic vapor stream was mixed with another stream of nitrogen in order to obtain a lower than saturation concentration of penetrant vapor.

Operation

In the Quasi-Isostatic procedure, the increase in penetrant concentration in the lower concentration cell chambers was determined by gas chromatography with flame ionization detection. At predetermined time intervals, 0.5 ml of headspace gas was removed from the right and left cell chambers with a gas-tight syringe and injected directly into the gas chromatograph. A constant total pressure of 1 atm was maintained throughout the run in both the high and low permeant concentration cell chambers. A constant pressure in the high concentration cell chamber was maintained by continually flowing the vapor stream through the high concentration cell chamber and discharging it at atmospheric pressure. To maintain a constant, total pressure in the low concentration cell chamber, the volume of headspace gas removed for analysis was replaced with an equal volume of nitrogen.

The quantity of vapor permeated with time was monitored until a steady-state rate of diffusion was maintained. In analyzing the resultant data, the total quantity of organic vapor permeated as a function of time was included, up to a level at which the vapor

concentration in the low concentration cell chambers did not exceed 3% of the penetrant concentration in the high concentration cell chamber, that is, the center chamber. The low concentration cell chambers should be purged of residual organic moieties using nitrogen gas (N_2) before the test run was initiated.

The film specimens in non-humidified condition measurements were stored in a desiccator over calcium sulfate ($CaSO_4$) desiccant for two weeks at ambient temperature (23°C) prior to being tested.

As for the film specimens in humidified condition, humidity conditioning was achieved by storing samples at ambient temperature in relative humidity chambers of 57% and 87% R.H., respectively. These humidity conditions were maintained using various standard salt solutions.

Retorting Process

Retort pouches used in this study were provided by Toppan Printing Co., Ltd. (Tokyo, Japan). The specification of the pouches and the conditions of retorting are described below. Retorting was performed at three retorting temperatures, and with three retorting times per temperature, to obtain 9 different samples.

Structure	PET 12μm/SiOx/PET 12μm/CPP 60 μm
Size	130mm x 170mm, three sides sealed
Content	Distilled water (cold fill)
Volume	180 ml
Head Space	Approximately 5cc

Retort Equipment	RCS - 40RTG. N, Hisaka Works, Ltd. (Osaka, Japan)
Retort Conditions	Temperature 120°C, 125°C, 130°C
	Retorting Time 20min, 40min, 60min
	Retorting Pressure 2.0 kg/cm^2 at 120°C
	2.1 kg/cm^2 at 125°C
	2.2 kg/cm^2 at 130°C

Analytical

Gas Chromatographic Analysis

Analysis of permeant concentration was carried out by a gas chromatographic procedure. A Hewlett-Packard Model 5890 gas chromatograph equipped with flame ionization detection interfaced to a Hewlett-Packard Model 3392A integrator was employed for quantification for non-humidified test conditions. A Hewlett-Packard Model 5830A gas chromatograph equipped with dual flame ionization detection, interfaced to a 18850 A GC Hewlett-Packard terminal was used for permeant detection at high relative humidity. The gas chromatographic conditions are presented in Table 7.

The stationary phase of the capillary column (Supelcowax 10) employed with the HP 5890 gas chromatograph was found to degrade upon exposure to water vapor. Therefore, in the studies designed to evaluate the effect of sorbed water on the films barrier characteristics, analyses were carried out on the HP 5830A gas chromatograph where the stationary phase was known to be

Table 7. Gas chromatographic conditions for 5890 and 5830 A.

Model 5890

Column:	60 meter;
	0.25 mm I.D.,
	Fused silica capillary;
	Polar bonded stationary phase;
	Supelcowax 10 (Supelco. Inc., Bellefonte, PA)
Carrier gas:	Helium at 32.6 ml/min.;
Temperature:	Injection temperature -- 180°C;
	Detector temperature -- 250°C;
	Oven temperature -- 150°C;
	Temperature program rate -- 0°C/min.;

Retention time of ethyl acetate: 5.14 min.;

Model 5830A

Column:	10% Cabowax, 20M on 80/100 Supelcoport
	(Supelco. Inc., Bellefonte, PA)
	1/8" o.d. x 6 ft. Stainless steel packed column
Carrier gas:	Helium at 33 ml/min.;
Temperature:	Injection temperature -- 175°C;
	FID temperature -- 350°C;
	Oven max temperature -- 225°C;
	Column temperature -- 165°C;

Retention time of ethyl acetate: 0.98 min.;

unaffected by moisture.

A standard curve of detector response versus absolute quantity was constructed from standard solutions of known concentration for each gas chromatograph (Appendix A).

Standard solutions were prepared by dissolution of known quantities of ethyl acetate in dichlorobenzene.

Analysis of SiOx Surface by Optical Microscopy

Analysis of the SiOx barrier coating on the composite retort pouch structures was carried out with an optical microscope Olympus BH-2, with an exposure control unit. The SiOx surface layer was examined following retort processing, and also following completion of the permeability studies. Approximately 1 cm^2 specimens were cut from the center of the retort pouches, the samples were then mounted on a glass microscope slide and examined at 150 x magnification. The samples were mounted with the cast polypropylene surface in contact with the glass slide, with light transmission from the underside. Photographs of the surface were taken with Polaroid 52 PolaPan 4x5 instant sheet film.

RESULTS AND DISCUSSION

Determination of the Appropriate Conditions for the Permeation of Ethyl Acetate Vapor through SiOx PET Film and Other Test Films

Preliminary Studies

Due to the paucity of data available on the permeation of organic vapor through SiOx PET film, the appropriate conditions of temperature and concentration of the ethyl acetate vapor were determined in a series of preliminary studies prior to performing the proposed permeability tests. As for the base PET film, it is known to have good organic vapor barrier properties, compared to other plastic films. For example, Shirakura (1987) reported that at 37°C, 0% R.H. and 300 ppm (wt/v) of ethyl acetate vapor, no measurable permeation was observed through PET film (31% crystallinity) after 550 hours. The upper level of the transmission rate was estimated to be less than 4×10^{-7} g/m^2 hr.

In accordance with the above data, preliminary studies were carried out at four test conditions, in order to determine the appropriate conditions of temperature and vapor concentration for the analysis of the permeation of ethyl acetate vapor through SiOx PET film. The first condition was 22 ± 1°C, 91ppm vapor concentration, the second condition was set at 50 ± 1°C, 91ppm. The third condition was also set at 50 ± 1°C, but with 237ppm vapor concentration, and the last condition was 65 ±1°C,

288ppm. The relative humidity was set at non-humidified level for all the conditions of test.

The transmission rate profile curves for SiOx PET, PET, EVOH and PET/PET/CPP are presented in Figure 8, where the total quantity of ethyl acetate permeated in micrograms is plotted as a function of time for the respective test regimes. Since good agreement was observed between replicate samples, the reported data are the average of replicate runs, with a confidence limit of ±18% (maximum). Figure 9 presents the permeation data for ethyl acetate vapor through PET film (as a non-coated base film) and SiOx PET to illustrate the effect of the silica oxide deposited layer on the barrier properties of the composite structure.

Figure 10 presents the permeation data for ethyl acetate vapor through SiOx PET and EVOH, to provide a comparison of these two high barrier films. Figure 11 illustrates the stability of the center cell concentration of ethyl acetate vapor. The fluctuation was ±7% throughout all experiments. Scatter band of oven temperature was ±1°C throughout all experiments.

The results from the preliminary studies showed no measurable rate of permeation for SiOx PET film at 50°C - 91ppm and minimal transmission levels at 50°C - 237ppm, although the driving force was increased 2.5 times. As for EVOH, the increase in transmission rate over the same concentration range was also small. However, at 65°C - 288ppm, a significant rate of permeation was observed for both of the high barrier films. Based on the result of these studies, test condition of 65 and 76°C and a vapor concentration at 300 ppm (wt/v) were selected

to evaluate the effect of temperature on the permeation of ethyl acetate vapor through SiOx PET film. These findings further indicate that permeation rate values of SiOx PET and EVOH are more dependent on temperature than on ethyl acetate vapor concentration.

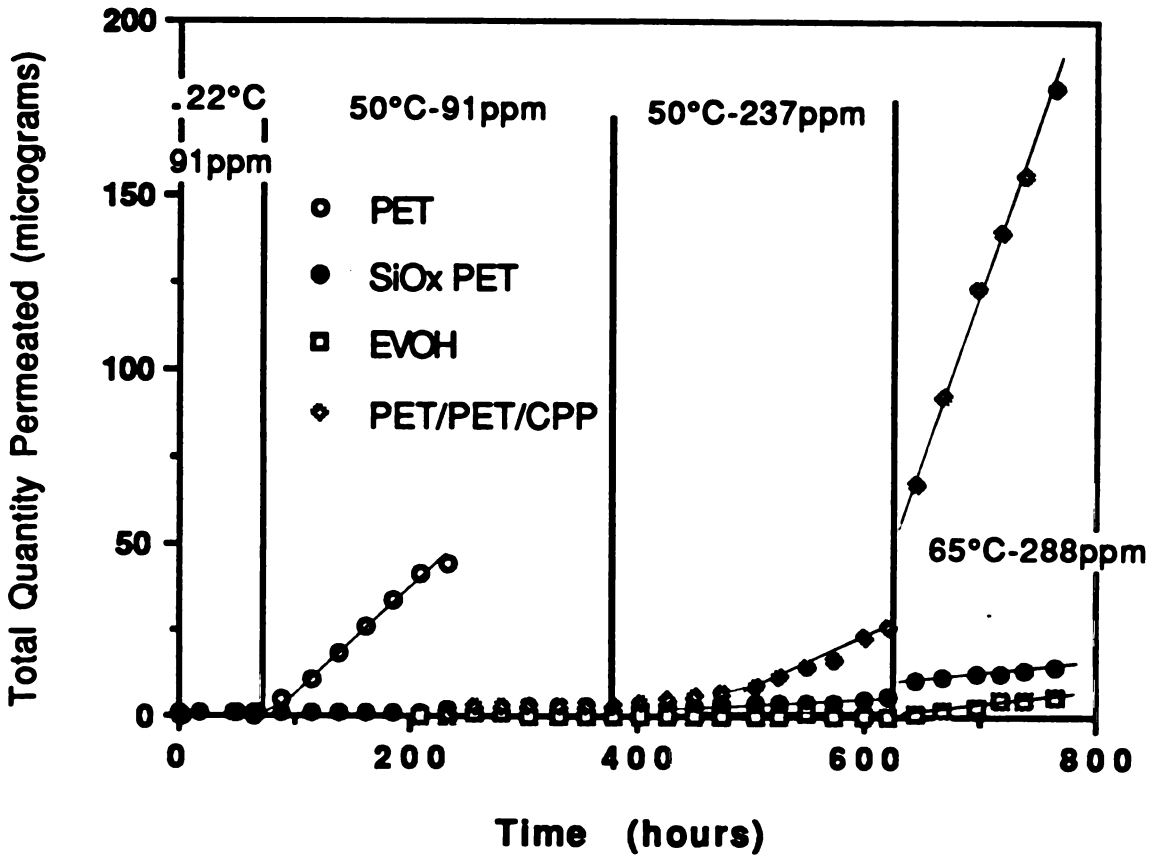


Figure 8. Transmission rate profile curves of ethyl acetate vapor through SiOx PET and other films in the determination of appropriate conditions.

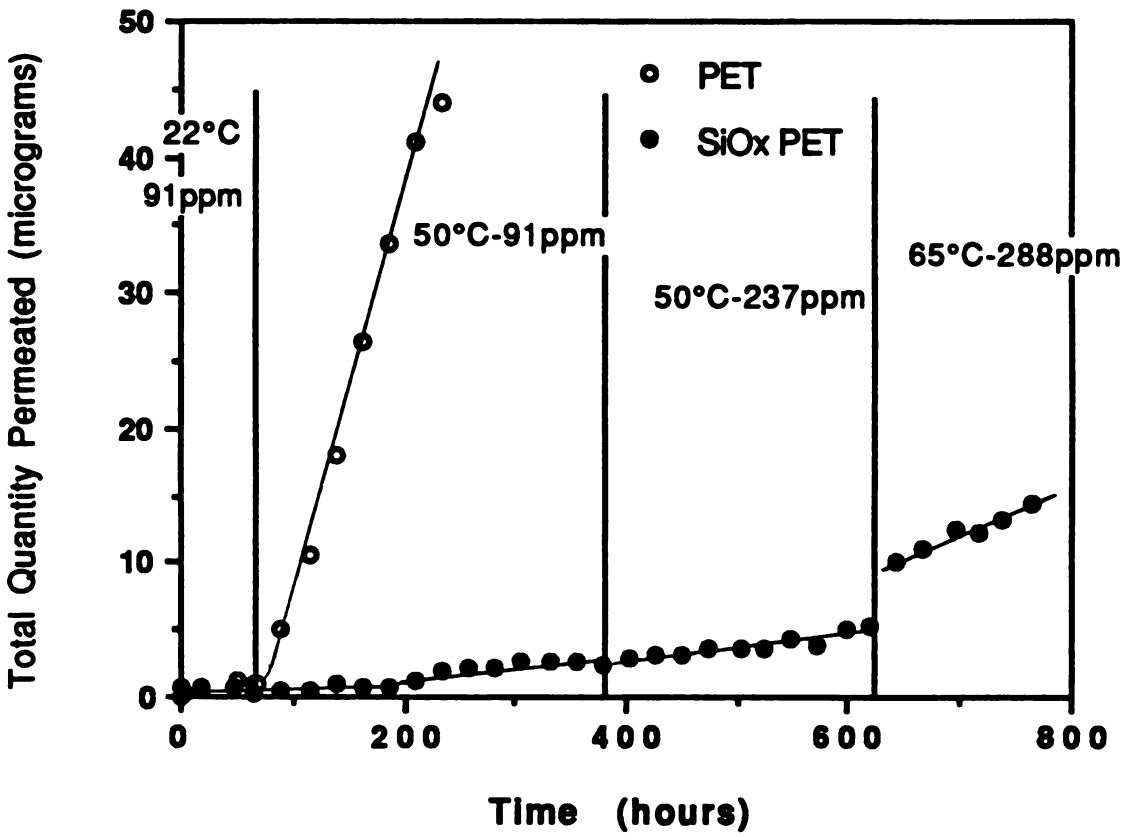


Figure 9. Transmission rate profile curves of ethyl acetate vapor through PET and SiOx PET in the determination of appropriate conditions.

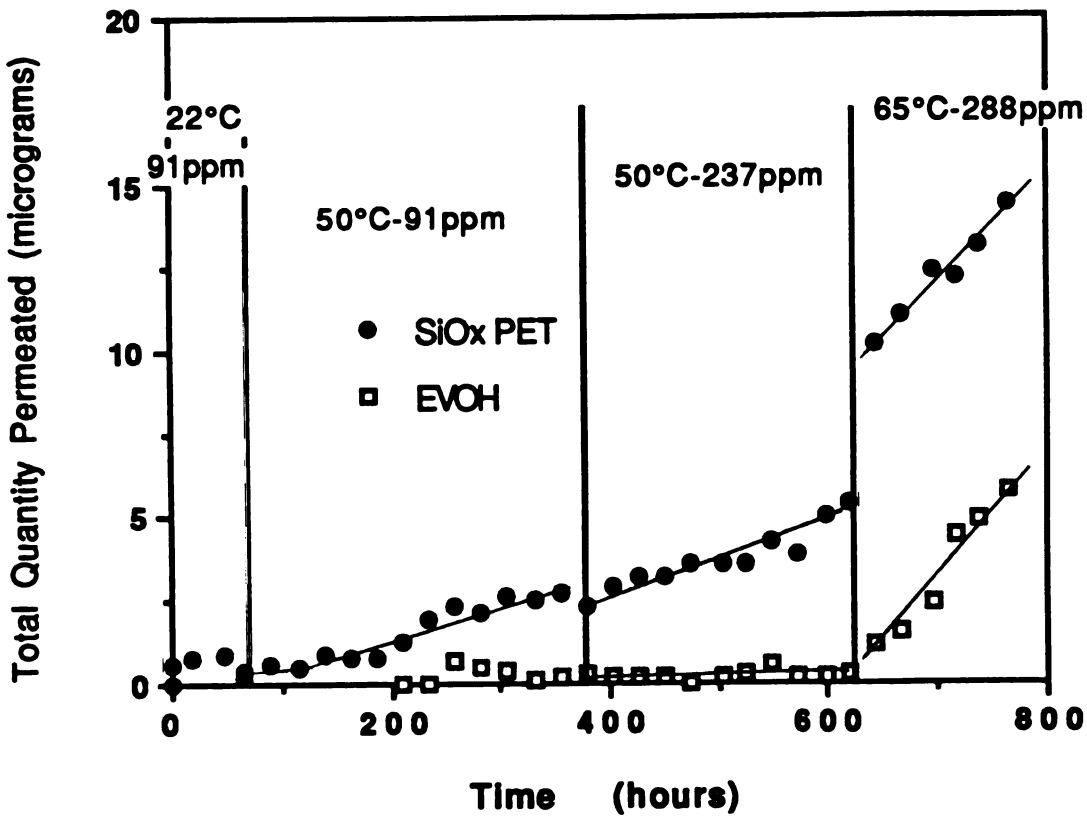


Figure 10. Transmission rate profile curves of ethyl acetate vapor through SiOx PET and EVOH in the determination of appropriate conditions.

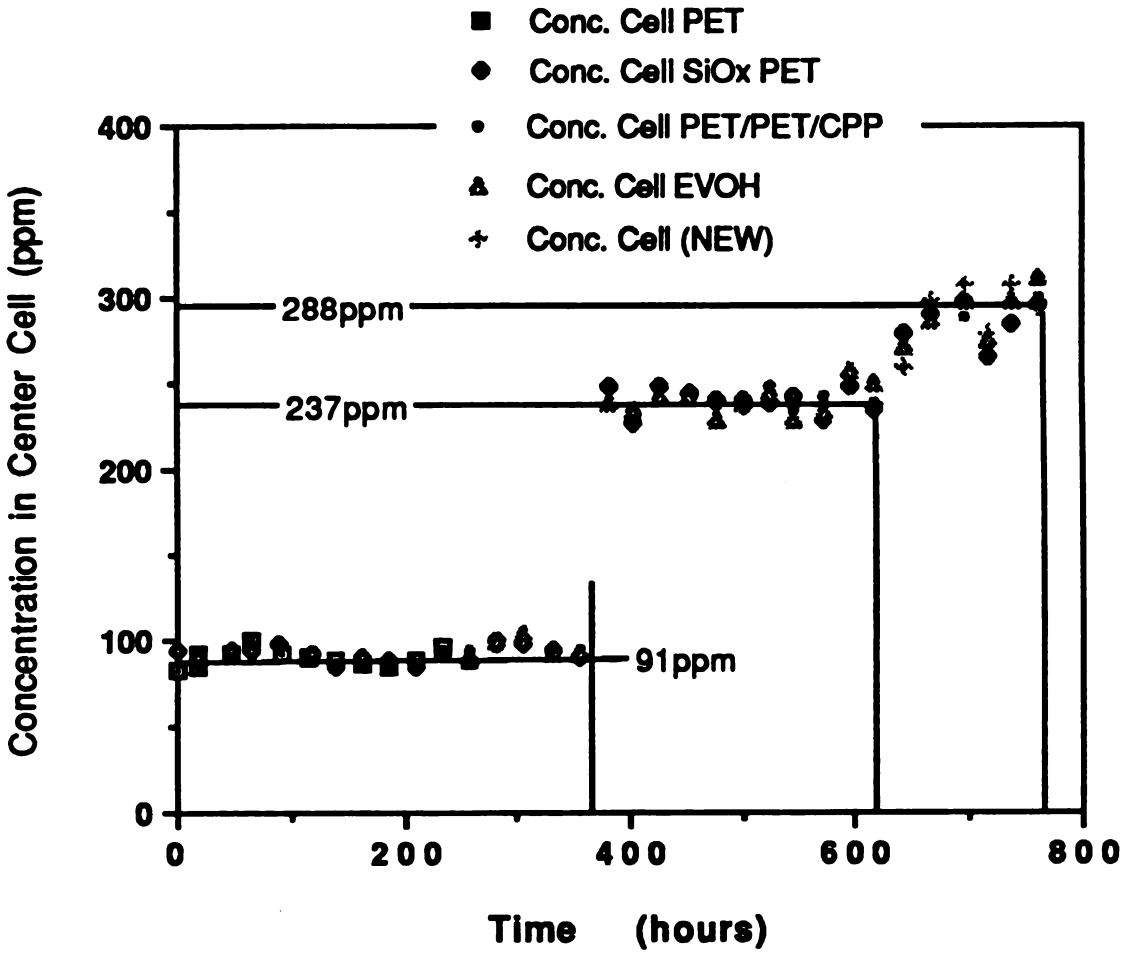


Figure 11. Stability of the center cell concentration of ethyl acetate vapor.

The Effect of Temperature on the Permeation of Ethyl Acetate Vapor through SiOx PET Film

Experiments at 65°C

The transmission rate profile curves for SiOx PET, PET, EVOH, PET/SiOx PET/CPP, PET/PET/CPP and PET/EVOH/CPP are presented in Figure 12, where the total quantity of ethyl acetate permeated in micrograms is plotted as a function of time. The test conditions for all experiments were 65°C - 300ppm - non-humidified condition. Since good agreement was observed between replicate samples tested in the same run, the reported data are the average with a confidence limit of ±3% (maximum). For ease of comparison, Figure 13 presented permeation data for ethyl acetate vapor through films which permeated at a rate less than 0.05×10^{-6} g/hr, that is, films other than PET and PET/PET/CPP.

Figure 14 shows the transmission rate profile of ethyl acetate vapor through PET and PET/PET/CPP, to compare a base film and its composite structure. 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 permeation rate of ethyl acetate vapor through PET was approximately twice that of PET/PET/CPP.

Figure 15 depicts the transmission rate profile curves of ethyl acetate vapor through SiOx PET and EVOH, to compare the two high barrier films. EVOH showed typical Fickian behavior, while the SiOx PET appeared to show atypical behavior during the initial transport period. For the first 24 hours, permeation through the SiOx PET film was not

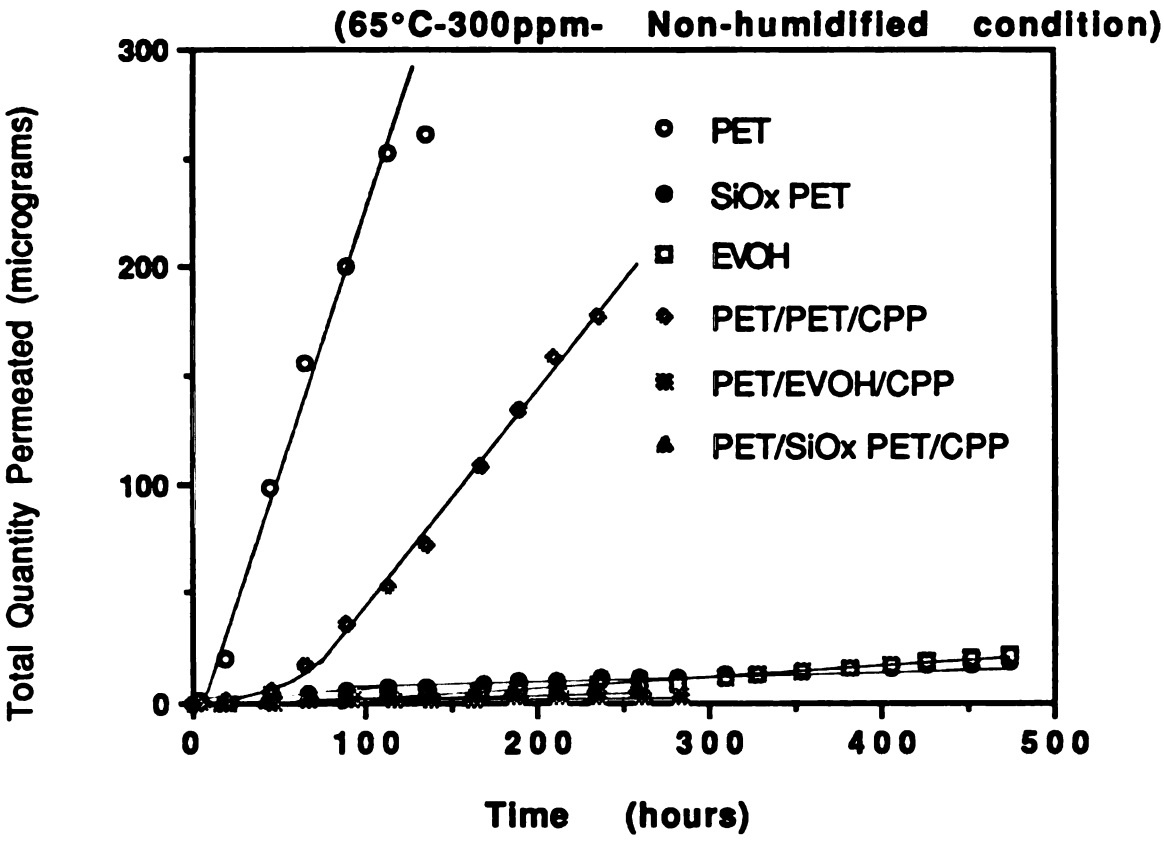


Figure 12. Transmission rate profile curves of ethyl acetate vapor through SiOx PET and other films at 65°C -300ppm - non-humidified condition.

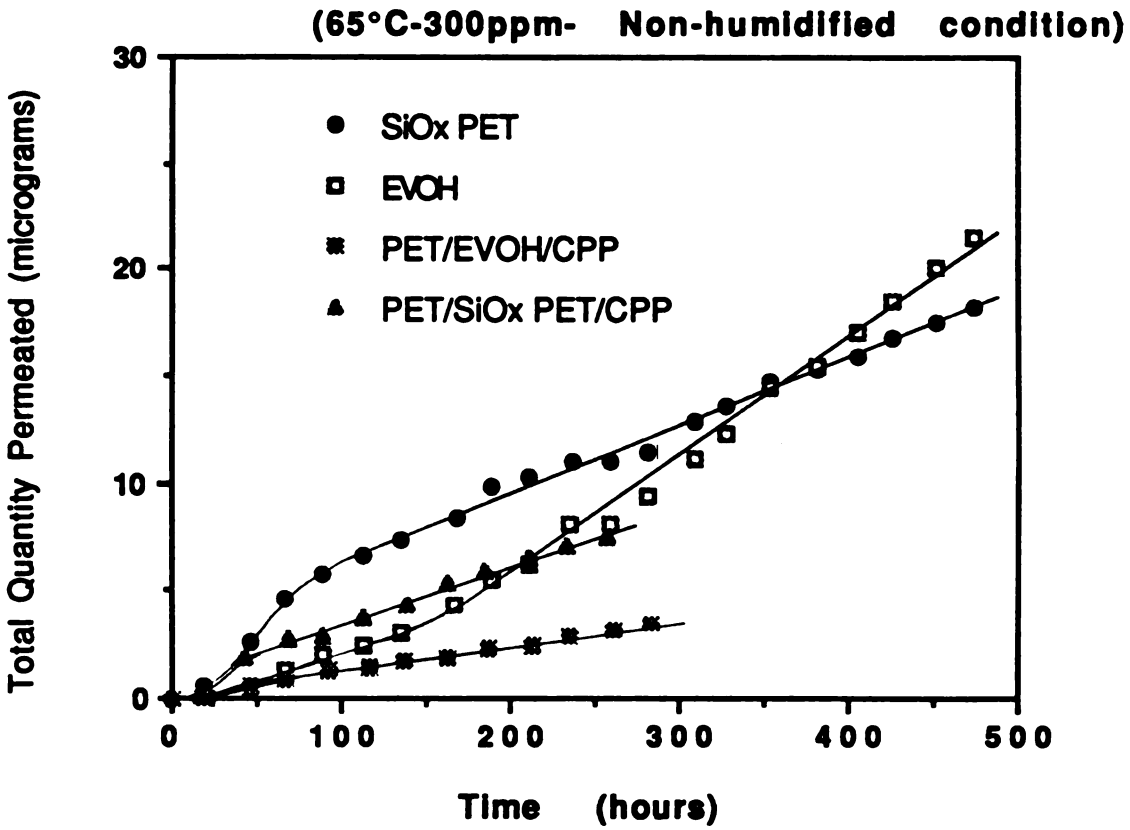


Figure 13. Transmission rate profile curves of ethyl acetate vapor through SiOx PET and other high barrier films at 65°C -300ppm - non-humidified condition.

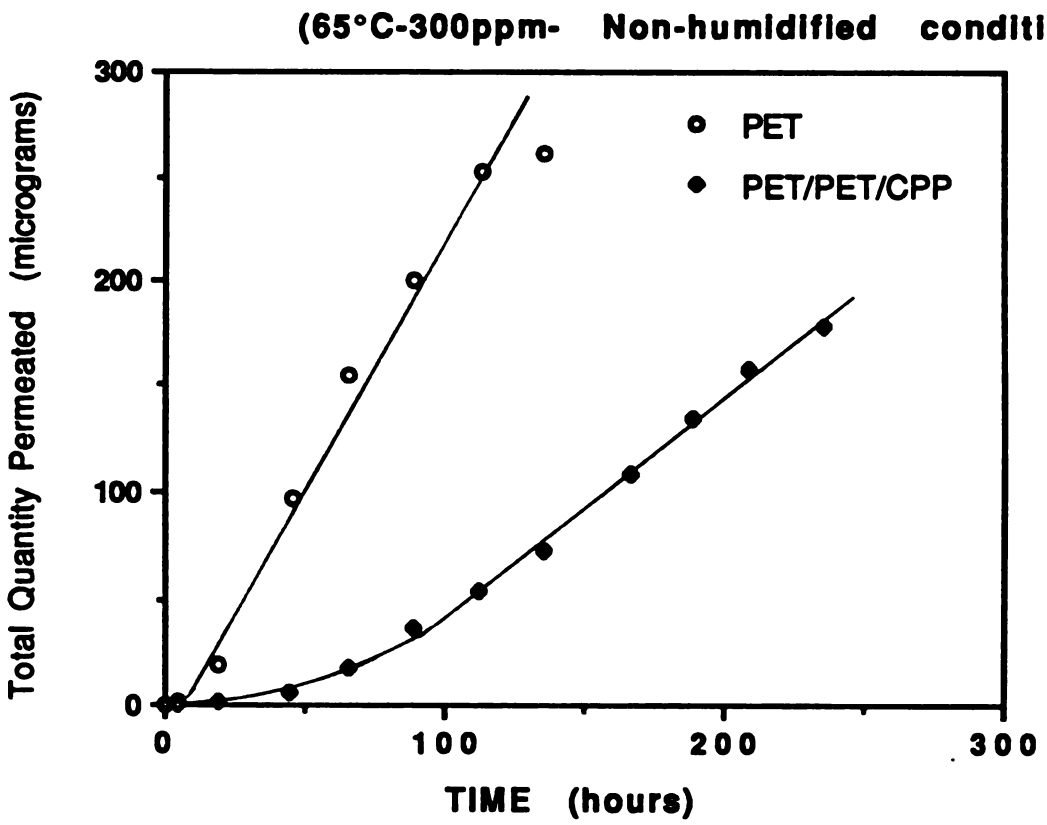


Figure 14. Transmission rate profile curves of ethyl acetate vapor through PET and PET/PET/CPP at 65°C - 300ppm - non-humidified condition.

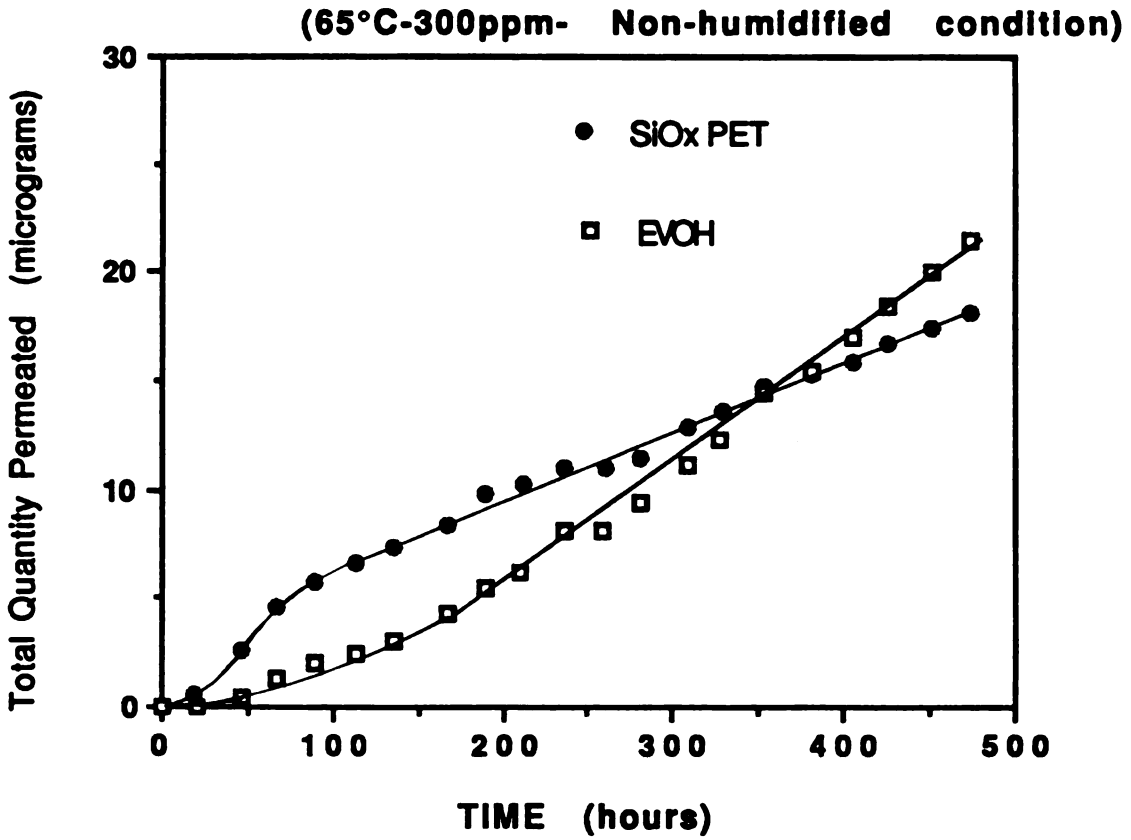


Figure 15. Transmission rate profile curves of ethyl acetate vapor through SiOx PET and EVOH at 65°C -300ppm - non-humidified condition.

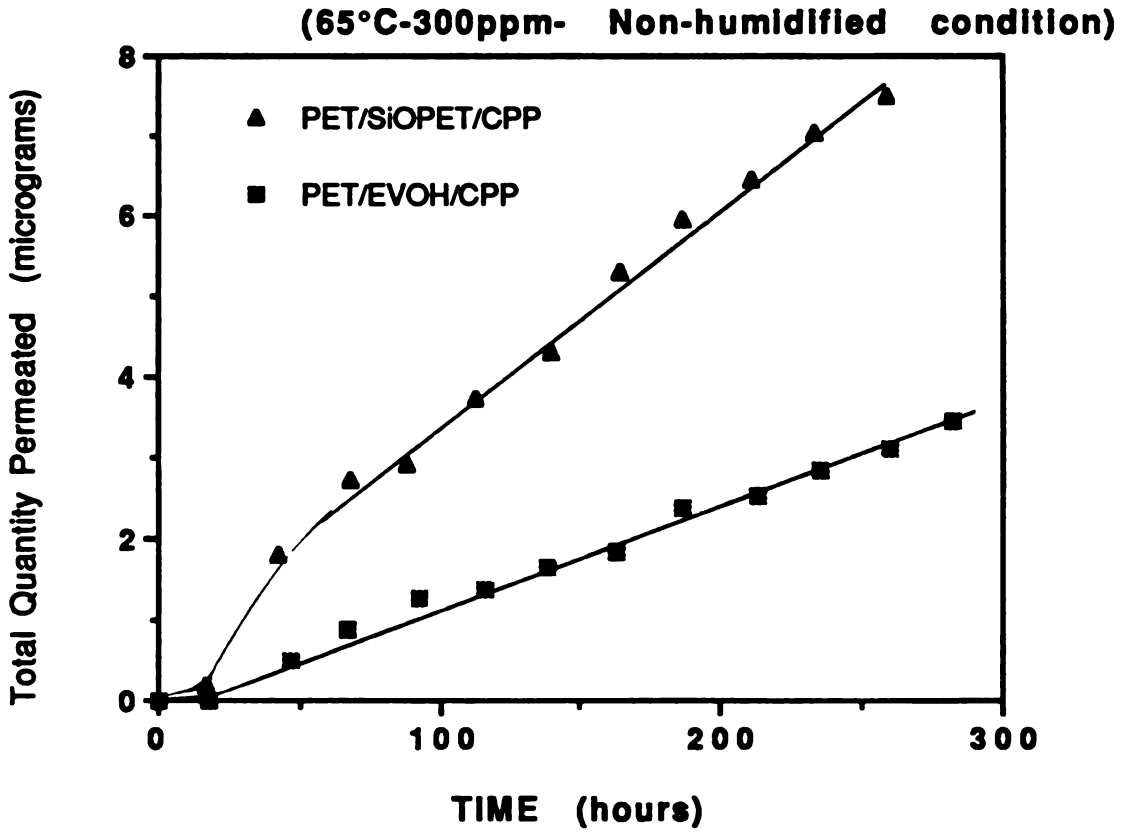


Figure 16. Transmission rate profile curves of ethyl acetate vapor through PET/SiOx PET/CPP and PET/EVOH/CPP at 65°C -300ppm - non-humidified condition.

detectable. Following this initial induction period, a significant increase in the transmission rate was observed, and after 96 hours a steady state rate of transmission was recorded. As shown in Figure 15, at steady state, the rate of permeation through the SiOx PET was lower than that of EVOH.

Figure 16 presents permeation data for ethyl acetate vapor through PET/SiOx PET/CPP and PET/EVOH/CPP, which are high barrier composite structures. PET/SiOx PET/CPP shows the same tendency as the SiOx PET film.

Experiments at 76°C

The transmission rate profile curves for SiOx PET, PET, EVOH, PET/SiOx PET/CPP, PET/PET/CPP and PET/EVOH/CPP at 76°C - 300ppm - non-humidified condition are presented in Figure 17, where the total quantity of ethyl acetate permeated in micrograms is plotted as a function of time. Figure 18 presents the transport data for ethyl acetate vapor through SiOx PET, EVOH, PET/SiOx PET/CPP and PET/EVOH/CPP. These films permeated at a rate less than 0.6×10^{-6}g/hr. Because of the high temperature (76°C), the lag time was short and non-steady state was not clearly observed for any of the films.

Figure 19 shows the permeation data for ethyl acetate vapor through PET and its composite structure, PET/PET/CPP. Figure 20 presents the permeation data for ethyl acetate vapor through SiOx PET and EVOH, to allow comparison of the two high barrier films. The transmission rate of ethyl acetate vapor through EVOH at 76°C was approximately 10 times greater than its transmission rate at 65°C. However, the SiOx PET film

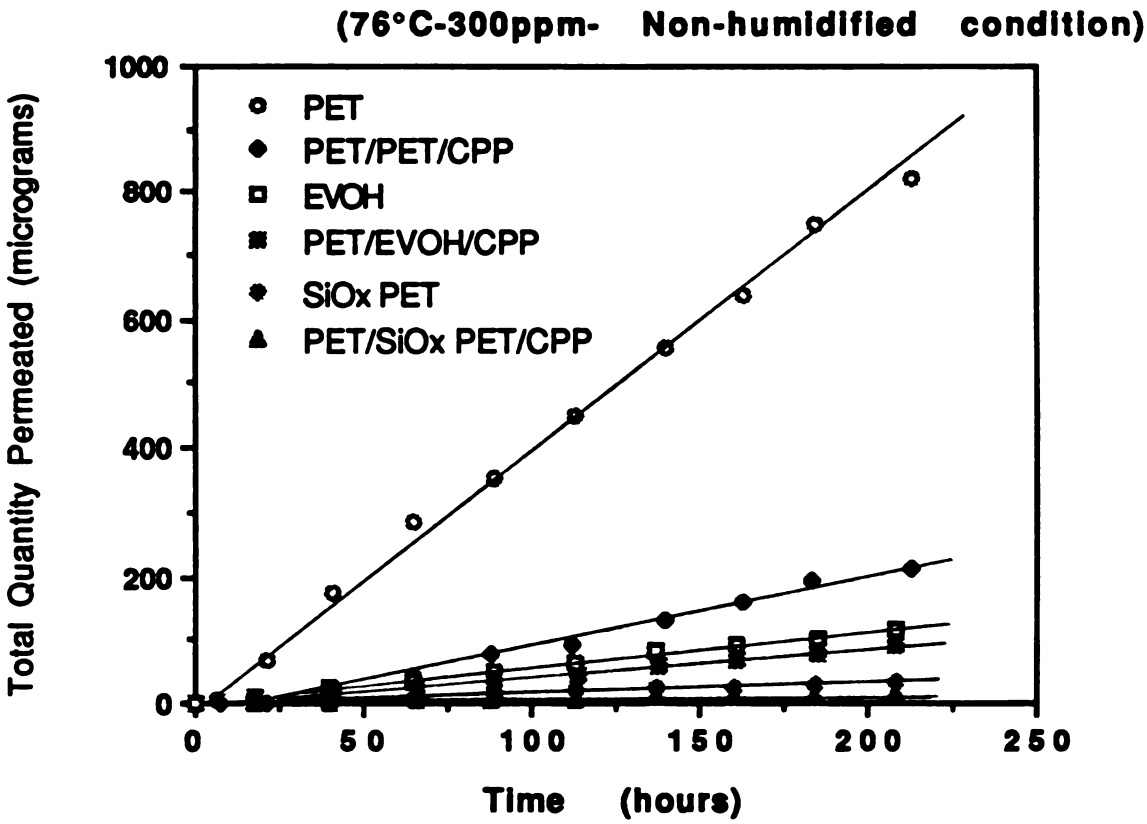


Figure 17. Transmission rate profile curves of ethyl acetate vapor through SiOx PET and other films at 76°C - 300ppm - non-humidified condition.

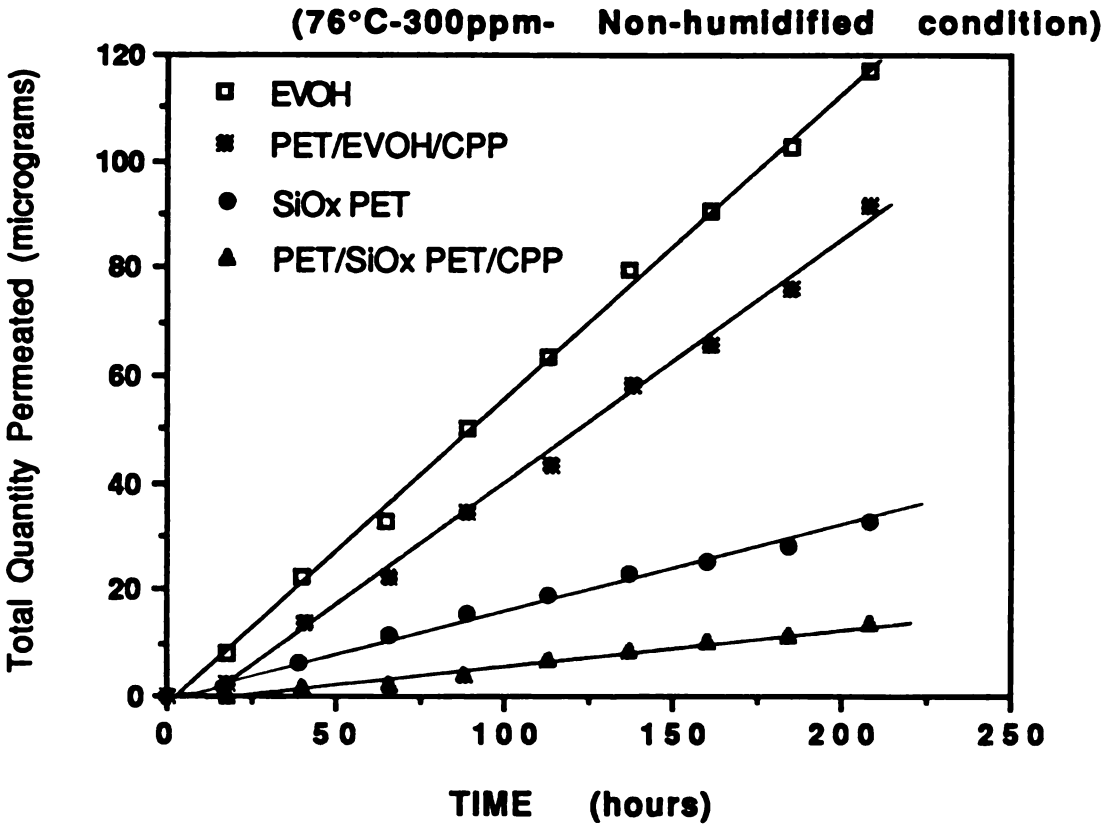


Figure 18. Transmission rate profile curves of ethyl acetate vapor through SiOx PET and other high barrier films at 76°C -300ppm - non-humidified condition.

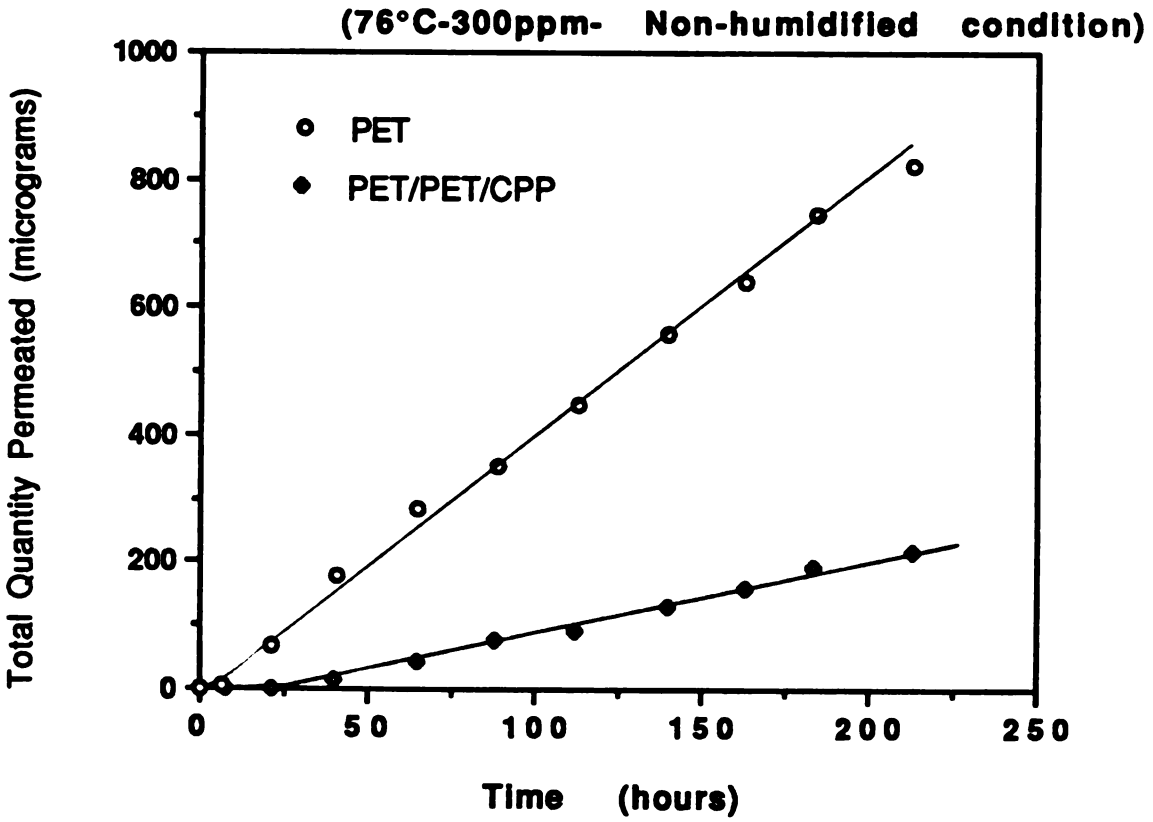


Figure 19. Transmission rate profile curves of ethyl acetate vapor through PET and PET/PET/CPP at 76°C - 300ppm - non-humidified condition.

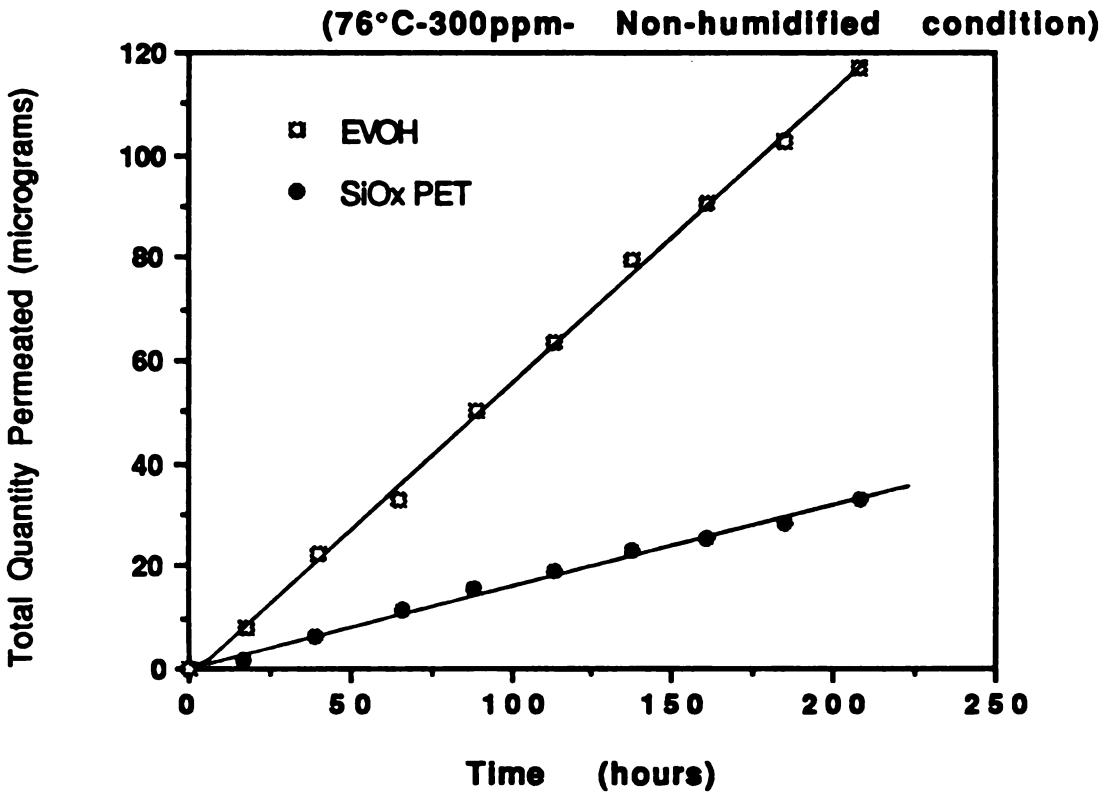


Figure 20. Transmission rate profile curves of ethyl acetate vapor through SiOx PET and EVOH at 76°C -300ppm - non-humidified condition.

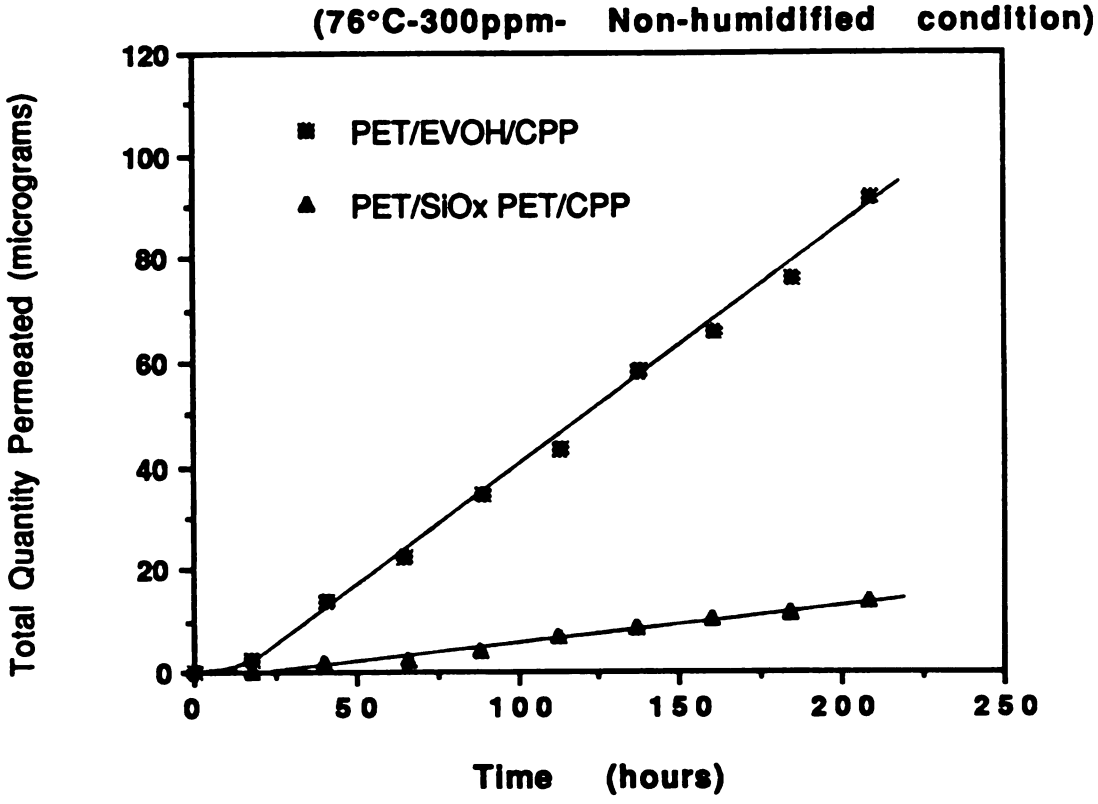


Figure 21. Transmission rate profile curves of ethyl acetate vapor through PET/SiOx PET/CPP and PET/EVOH/CPP at 76°C -300ppm - non-humidified condition.

showed a more modest increase in permeation, which was 4 times greater than its transmission rate at 65°C.

Figure 21 presents permeation data for ethyl acetate vapor through the high barrier pouches; PET/SiOx PET/CPP and PET/EVOH/CPP. As observed for the EVOH film(Figure 20), the EVOH composite structure also exhibited a significant increase in the permeation rate. With respect to the SiOx PET composite structure, the increase in permeation was not as pronounced.

Transmission Rate and Permeance

The transmission rate and permeance were determined from the data obtained in the above experiments. Tables 8 and 9 summarize the results for the three test films, and the three composite structures at 50°C, 65°C and 76°C. The 50°C data was obtained from the results of the pretest. The units for the transmission rate are g/m^2 hr. The permeance units are g/m^2 day 100ppm for MKS units and kg/m^2 sec Pascal for SI units.

In Appendix B, oxygen permeance of test films and the respective composite structures evaluated in this studies are presented. Oxygen permeance was measured under 30°C - 0% R.H. with OX-TRAN 10/50A (Modern Controls, Inc.), with the assistance of Toppan Printing Co., Ltd.

An Arrhenius plot of the transmission rate of ethyl acetate vapor through SiOx PET, PET and EVOH versus 1/T is shown in Figure 22. SiOx PET shows relatively high temperature dependence and a low transmission rate. PET also shows relatively high temperature dependence, but the transmission rate was greater than for SiOx PET and

Table 8. The effect of temperature on transmission rate of ethyl acetate vapor through SiOx PET and other films.

Sample	TRANSMISSION RATE[(a)] Temperature (°C)		
	50	65	76
PET	$5.78 \times 10^{-5} \pm 0.51$	$4.38 \times 10^{-4} \pm 0.16$	$8.20 \times 10^{-4} \pm 0.22$
PET/PET/CPP	$2.01 \times 10^{-5} \pm 0.36$	$1.97 \times 10^{-4} \pm 0.13$	$2.38 \times 10^{-4} \pm 0.40$
SiOx/PET	$2.05 \times 10^{-6} \pm 0.62$	$6.37 \times 10^{-6} \pm 0.85$	$2.86 \times 10^{-5} \pm 0.30$
PET/SiOx PET/CPP	----------	$5.35 \times 10^{-6} \pm 0.22$	$1.57 \times 10^{-5} \pm 0.16$
EVOH	$< 3.19 \times 10^{-7}$	$1.12 \times 10^{-5} \pm 0.13$	$1.14 \times 10^{-4} \pm 0.15$
PET/EVOH/CPP	----------	$2.39 \times 10^{-6} \pm 0.23$	$9.33 \times 10^{-5} \pm 0.11$

(a) Transmission rate values expressed as g/m^2 hr

Table 9. The effect of temperature on permeance of ethyl acetate vapor through SiOx PET and other films g/m^2 hr.

Sample	PERMEANCE[a] Temperature (°C) 50	65	76
PET	4.66 x 10^{-4}±0.41	3.53 x 10^{-3}±0.13	6.60 x 10^{-3}±0.18
PET/PET/CPP	1.62 x 10^{-4}±0.29	1.59 x 10^{-3}±0.10	1.92 x 10^{-3}±0.09
SiOx/PET	1.65 x 10^{-5}±0.50	5.13 x 10^{-5}±0.68	2.30 x 10^{-4}±0.24
PET/SiOx PET/CPP	----------	4.31 x 10^{-5}±0.18	1.26 x 10^{-4}±0.13
EVOH	< 2.57 x 10^{-6}±	9.02 x 10^{-5}±1.05	9.18 x 10^{-4}±1.21
PET/EVOH/CPP	----------	1.92 x 10^{-5}±0.18	7.51 x 10^{-4}±0.09

(a) Permeance values expressed as g/m^2 day 100ppm

Sample	PERMEANCE [b] Temperature (°C) 50	65	76
PET	1.77 x 10^{-15}±0.16	1.28 x 10^{-14}±0.05	2.40 x 10^{-14}±0.06
PET/PET/CPP	6.16 x 10^{-16}±1.10	5.76 x 10^{-15}±0.38	6.95 x 10^{-15}±1.17
SiOx/PET	6.26 x 10^{-17}±2.76	1.86 x 10^{-16}±0.25	8.09 x 10^{-16}±0.85
PET/SiOx PET/CPP	---------	1.56 x 10^{-16}±0.06	4.44 x 10^{-16}±0.45
EVOH	< 9.76 x 10^{-18}	3.27 x 10^{-16}±0.38	3.22 x 10^{-15}±0.42
PET/EVOH/CPP	--------	6.98 x 10^{-17}±0.67	2.64 x 10^{-15}±0.03

(b) Permeance values expressed as g/m^2 sec Pascal

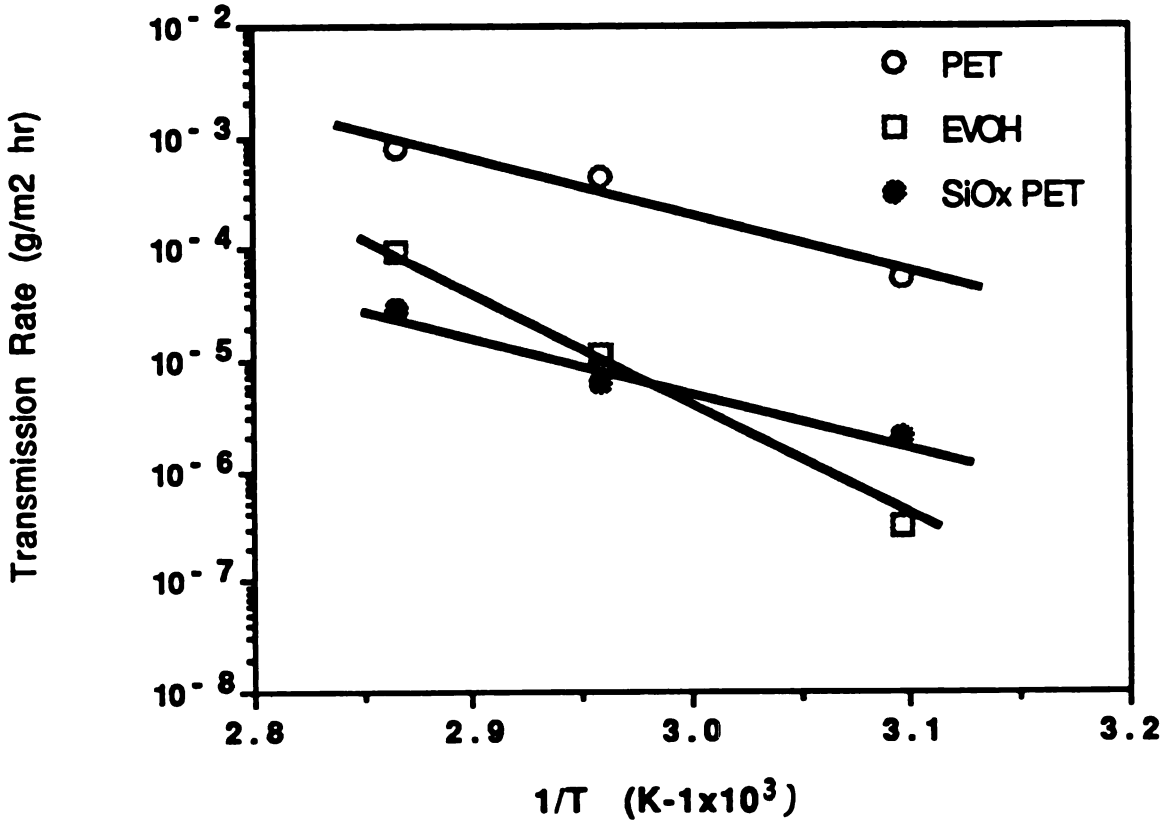


Figure 22. Temperature dependence of permeability rate for ethyl acetate vapor through PET, SiOx PET and EVOH.

EVOH. Based on the activation energy, the EVOH film exhibited very significant temperature dependency (see Table 10).

As can be seen, the temperature dependency of the transmission rate, over the temperature range studied (50 - 76°C), can be represented by the expression:

$$P = DS = P_0 \exp (Ep/RT) \quad (1)$$

From the slope of the Arrhenius plots, the activation energy for the permeation process (Ep) was determined for the respective film samples, and the values summarized in Table 10.

Table 10. Activation energy of permeation of ethyl acetate vapor through SiOx PET, EVOH and PET.

Sample	Activation energy
SiOx PET	22.1 kcal / mol
EVOH	48.8 kcal / mol
PET	23.2 kcal / mol

Shirakura (1987) reported a value for the activation energy of 23.3 kcal / mol for an ethyl acetate /PET system, which is quite similar to the above PET value. The activation energy seemed to be high when compared with the activation energy of oxygen gas through PET below Tg (Ep = 8 kcal/mole) (Michaels et al., 1963). A possible explanation for this is that the molecular size of ethyl acetate is larger than oxygen and requires a higher activation energy for diffusion (Meares, 1953) through

the PET film sample.

The fact that the activation energy values for both the SiOx PET and the PET base film were identical suggests that for the silica coated structures, the temperature dependent process involves the diffusion of ethyl acetate vapor through the PET layer, and nondiffusive transport through the SiOx coating. The latter process appears to be independent of temperature, within the temperature range studied. The permeation process is controlled by diffusion through the PET layer and not by the silica coating on the polyester, although silica coating controlled the overall transmission rate that resulted in an improvement in ethyl acetate barrier properties on 12μm polyester by a factor of 10 times. It is assumed that a perfectly homogeneous SiOx surface layer would exhibit a measurable diffusion rate (Norton, 1953) which would be reflected in the activation energy values obtained.

While the functional role of the silica coating is not fully understood, the following mechanism is proposed. For the silica deposited PET film, the barrier properties of the structure are governed by defects, nonohomogeneity of both the surface coating thickness and composition, or preferential diffusion paths. All of which can contribute to the observed permeability. The diffusion coefficients of the polymer layers immediately adjacent to the silica coating are thus critical in determining the effect of such defects.

The Effect of Relative Humidity on the Permeation of Ethyl Acetate Vapor through SiOx PET and EVOH

Experiments at 87% R.H. and 56% R.H.

The transmission rate profile curves for SiOx PET and EVOH are presented in Figure 23, where the total quantity of ethyl acetate permeated in micrograms is plotted as a function of time. The test conditions were 22°C, 190ppm concentration of ethyl acetate vapor, at 87% and 56% R.H. respectively. Fluctuation of relative humidity was ±2% and fluctuation of concentration was ±5%.

In over 500 hours of continuous testing, there was no measurable permeation at 56% R.H. The results indicate that both test films were excellent ethyl acetate vapor barriers at 56% R.H., and ambient temperature. However, as shown, at 87% R.H. the EVOH film had quite a high transmission rate of ethyl acetate vapor, while the SiOx PET still did not have any permeation.

Table 11 shows transmission rate and permeance data. Also presented in Table 11 are upper limit value estimations for the transmission rates and permeance. The procedure for upper limit estimation is described in Appendix C. As shown, permeation of ethyl acetate vapor through SiOx PET was not influenced by relative humidity. On the other hand, the permeation of ethyl acetate vapor through EVOH was strongly affected by relative humidity. When EVOH is in a dry condition, there is little permeation through the amorphous regions since hydrogen bonding reduces polymer chain segmental mobility, and thus restricts the diffusion of ethyl acetate vapor. When moisture is present,

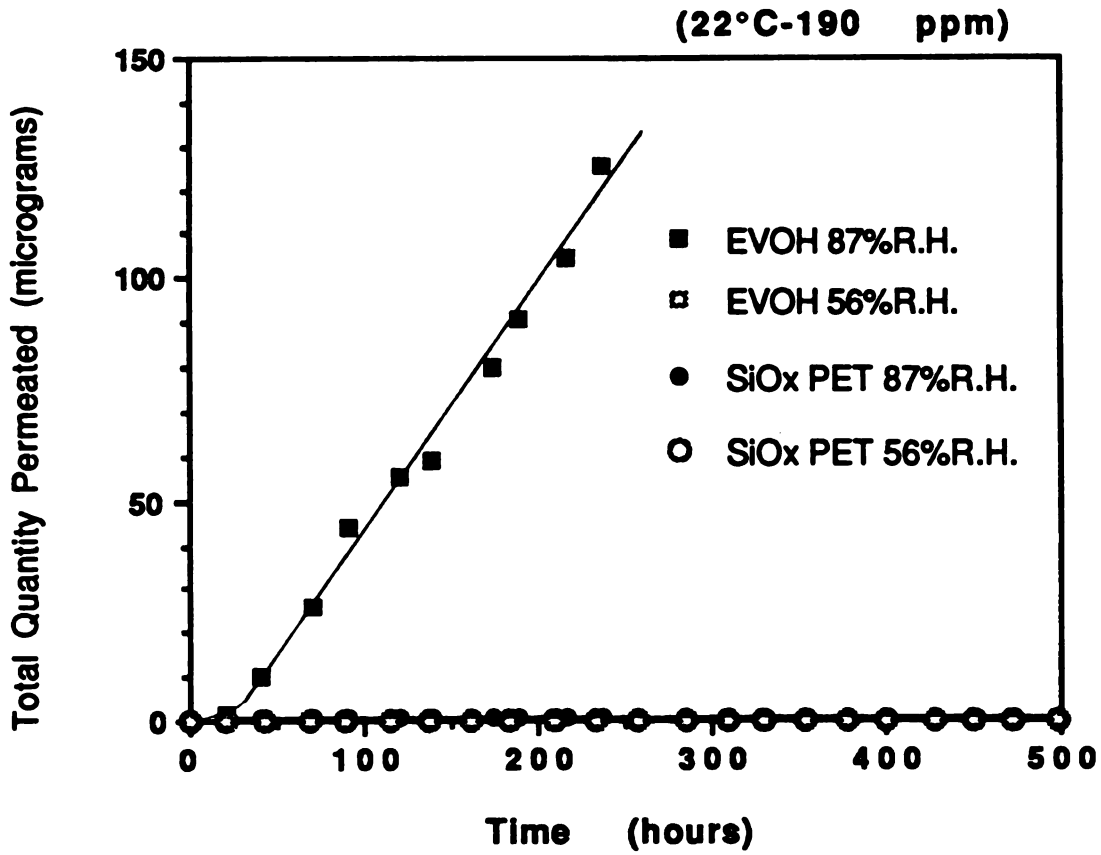


Figure 23. Transmission rate profile curves of ethyl acetate vapor through SiOx PET and EVOH at 22°C -190ppm - 87% and 56% R.H.

sorbed water acts to plasticize the hydrophilic barrier polymer, which decreases the cohesive forces between the polymer chain and increases segmental mobility (Barrie, 1968). The plasticization of the barrier layers will result in a significant increase in ethyl acetate vapor diffusively and accounts for the accelerating effect of relative humidity (Liu et al., 1988).

Table 11. The effect of relative humidity on the permeation of ethyl acetate vapor through SiOx PET and EVOH.

Sample	Transmission rate (g/m^2 hr)	Permeance (g/m^2 day 100ppm)	Permeance (kg/m^2 sec Pa)
(56% R.H.)			
SiOx PET	$< 2.1 \times 10^{-7}$	$< 2.7 \times 10^{-6}$	$< 1.1 \times 10^{-17}$
EVOH	$< 4.2 \times 10^{-7}$	$< 5.4 \times 10^{-6}$	$< 2.2 \times 10^{-17}$
(87% R.H.)			
SiOx PET	$< 4.2 \times 10^{-7}$	$< 5.4 \times 10^{-6}$	$< 2.2 \times 10^{-17}$
EVOH	$1.13 \times 10^{-4} \pm 0.16$	$1.45 \times 10^{-3} \pm 0.21$	$8.39 \times 10^{-15} \pm 0.84$

The Effect of Retort Sterilization on the Permeation of Ethyl Acetate through the PET/SiOx PET/CPP Retort Pouch Structure

Dependency of Retorting Time on Vapor Barrier Characteristics

The permeability studies were carried out at the following conditions; concentration of ethyl acetate vapor 300ppm, non-humidified condition at 67°C. Fluctuation of concentration was ±7%, and fluctuation of temperature was ±1°C. Since good agreement was obtained between replicate samples tested, the reported data are the average of the two. However, one set of the data obtained at 125°C, 20 min. was eliminated because of extremely small values. The reason for the irregular value was likely caused by the leakage of accumulated ethyl acetate vapor at the cell sampling port.

Figures 24, 25 and 26 show the effect of retorting time under specific retorting temperatures of, 120°C, 125°C and 130°C, respectively. The three sets of retorting time/temperature studies were compared to non-retort control samples. Figure 24 shows the permeation of ethyl acetate vapor through SiOx pouches after 120°C retorting process. Figure 25 plots the permeation profile of ethyl acetate vapor through the samples at 125°C retorting temperature, while Figure 26 deals with the SiOx pouches which went through the 130°C retorting process. As shown, a longer retorting time is likely to result in an increase in permeation at each temperature.

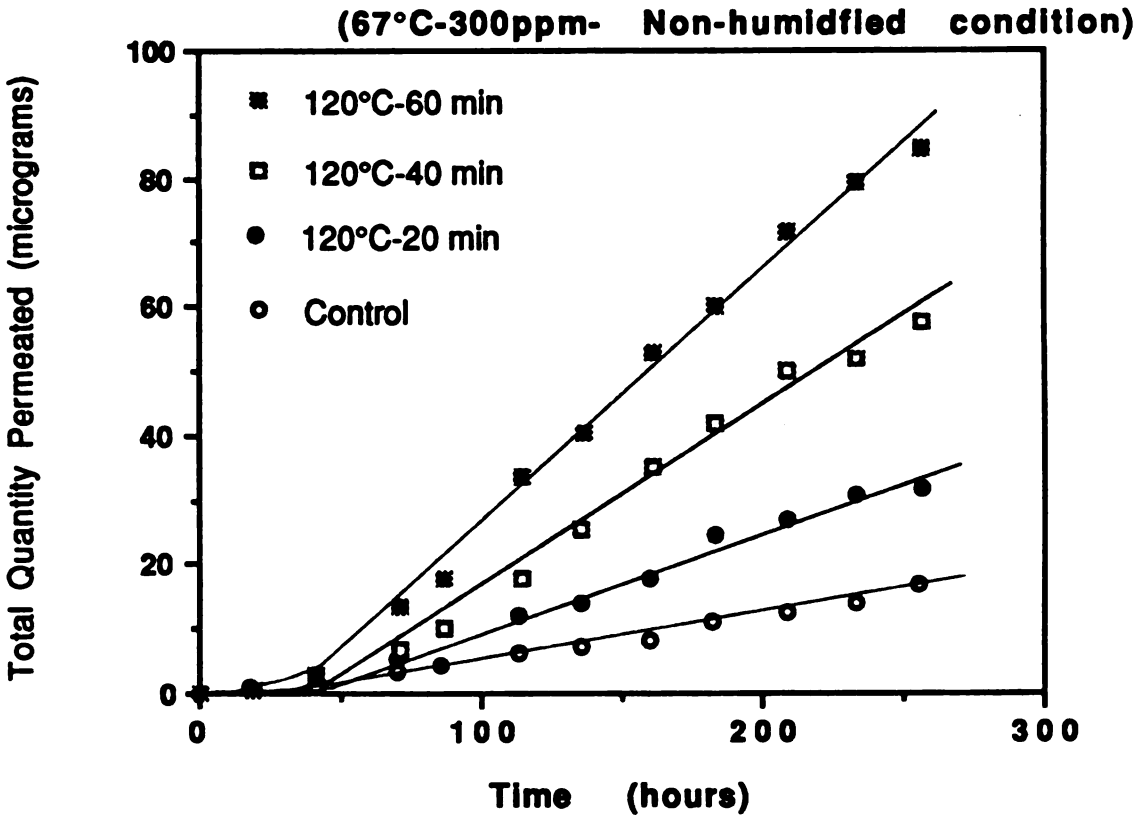


Figure 24. Effect of retorting time on the transmission rate of ethyl acetate vapor through PET/SiOx PET/CPP (Retort temperature 120°C).

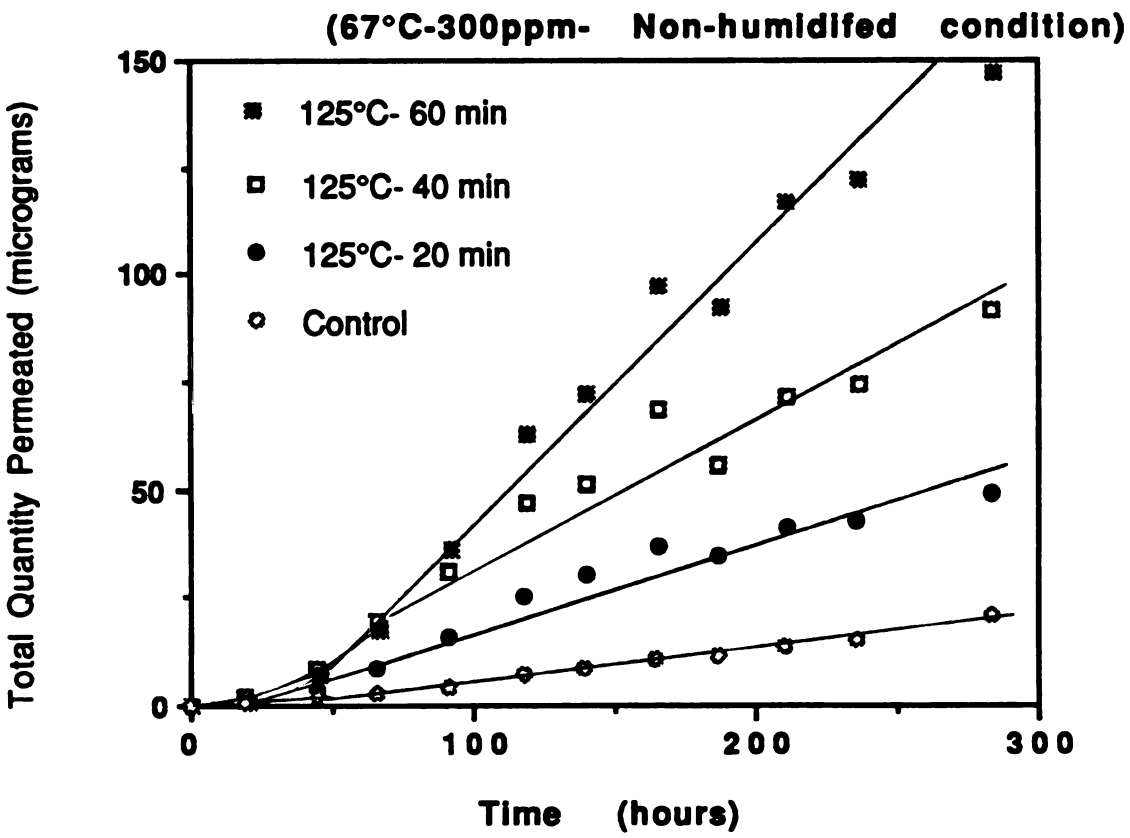


Figure 25. Effect of retorting time on the transmission rate of ethyl acetate vapor through PET/SiOx PET/CPP (Retort temperature 125°C).

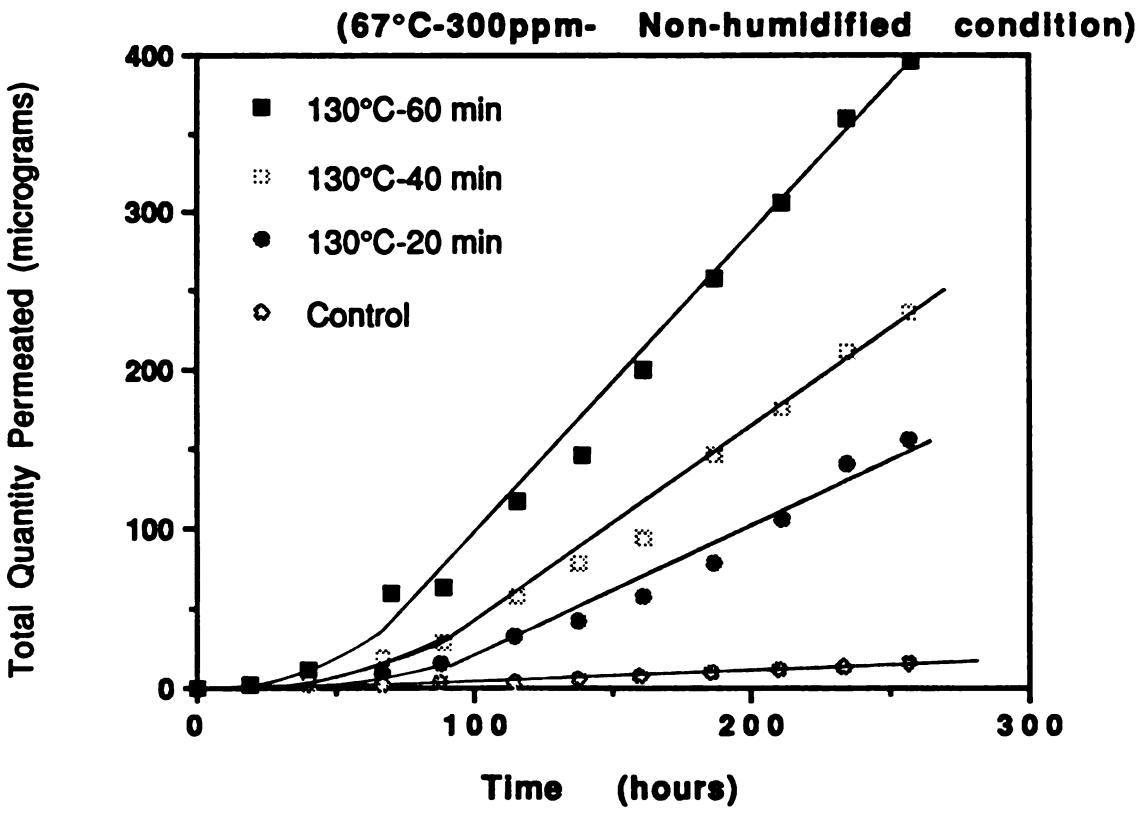


Figure 26. Effect of retorting time on the transmission rate of ethyl acetate vapor through PET/SiOx PET/CPP (Retort temperature 130°C).

Dependency of Retorting Temperature on Vapor Barrier Characteristics

Figures 27, 28, 29 and 30 show the effect of retorting temperature at constant retorting time, 0 (no retort), 20, 40, and 60 min. respectively. Figure 27 represents permeation data for ethyl acetate vapor through the control, non-retorted SiOx pouches, used as a standard film in each experimental cycles. As shown, identical values were obtained for the non-retort samples. In Figure 28 the transmission rate profile curves for ethyl acetate vapor through SiOx pouches after 20 min. retorting time are presented as a function of retort temperatures of 120°C, 125°C and 130°C. Figure 29 shows the permeation data through samples after 40 min. retorting as a function of temperature. Permeation data for the samples which were retorted for 60 min. at 120°C, 125°C and 130°C are shown in Figure 30. As shown, the higher retort temperature resulted in an increase in the transmission rate.

Transmission Rate and Permeance

Tables 12,13 and 14 show the transmission rate and permeance, summarizing the results of the experiments described above. Figures 31 and 32 provide for an overview of permeation characteristics of the pouch following the retorting process. Figure 31 illustrates the dependency of the transmission rate on the retorting temperature. As can be seen, an average 260% increase in the transmission rate occurred when the retort temperature was increased from 125 to 130°C. At 125°C, only an average 30% increase in permeation was observed, as compared to results obtained following retort processing at 120°C for all hold times. Figure 32 describes the dependency of the transmission

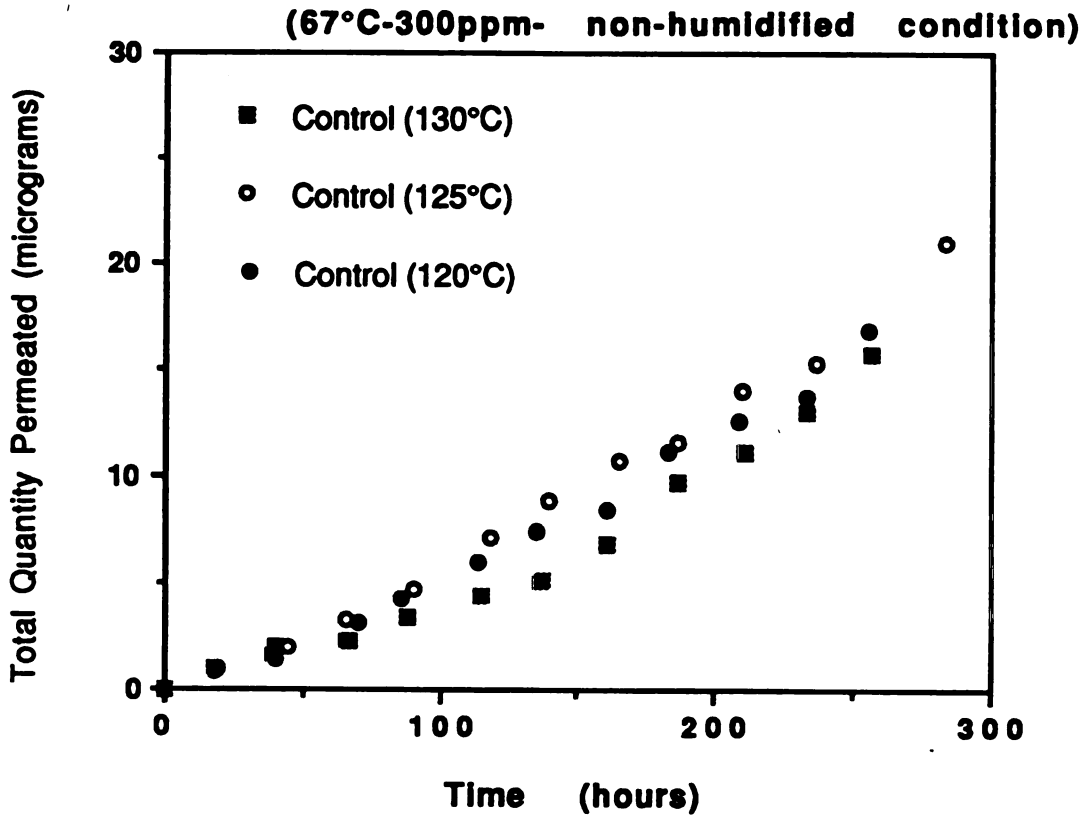


Figure 27. Transmission rate profile curves of ethyl acetate vapor through PET/SiOx PET/CPP (Non retorted pouches).

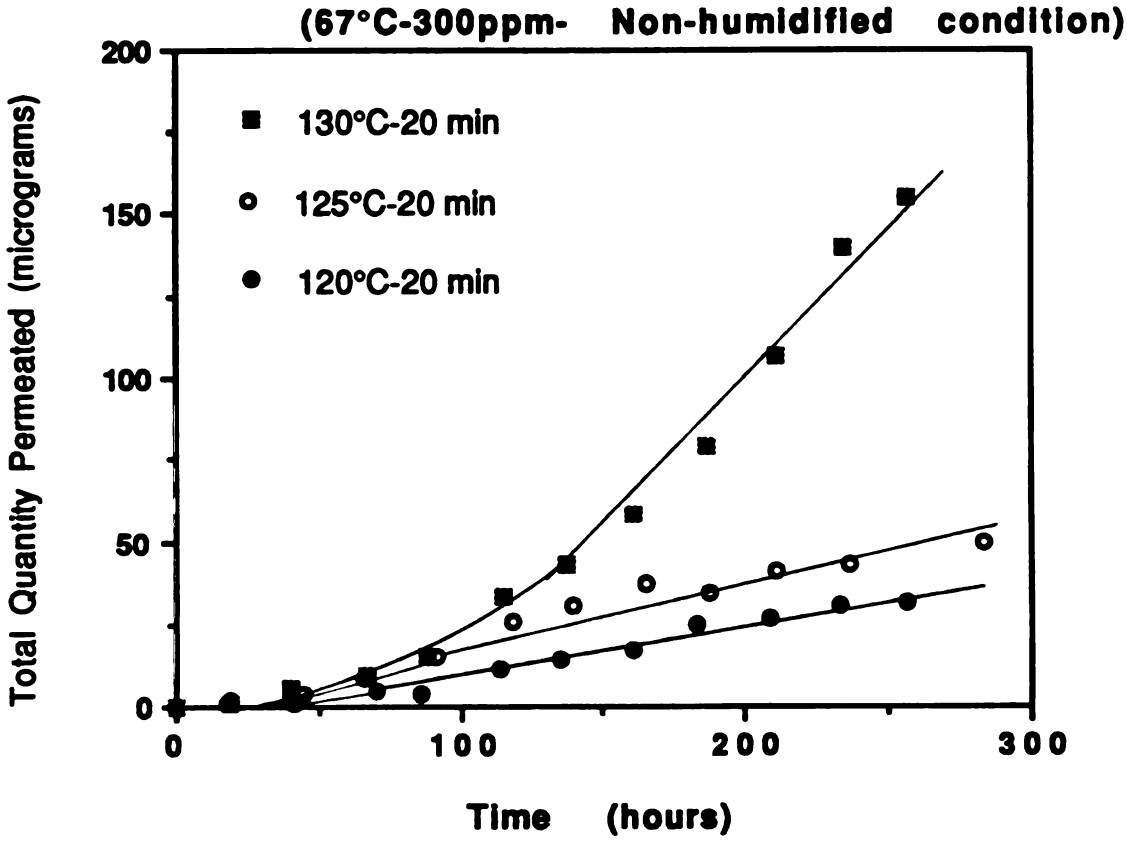


Figure 28. Effect of retorting temperature on the transmission rate of ethyl acetate vapor through PET/SiOx PET/CPP (Retort time 20min).

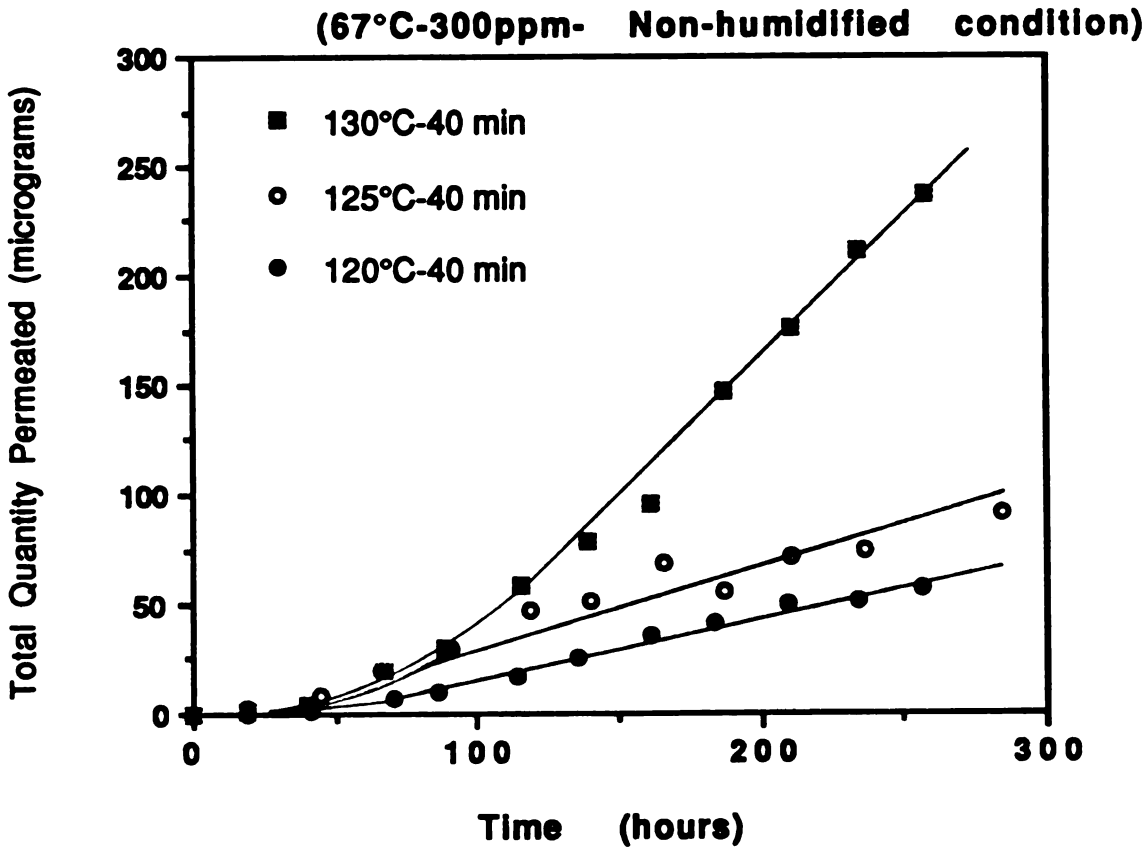


Figure 29. Effect of retorting temperature on the transmission rate of ethyl acetate vapor through PET/SiOx PET/CPP (Retort time 40min).

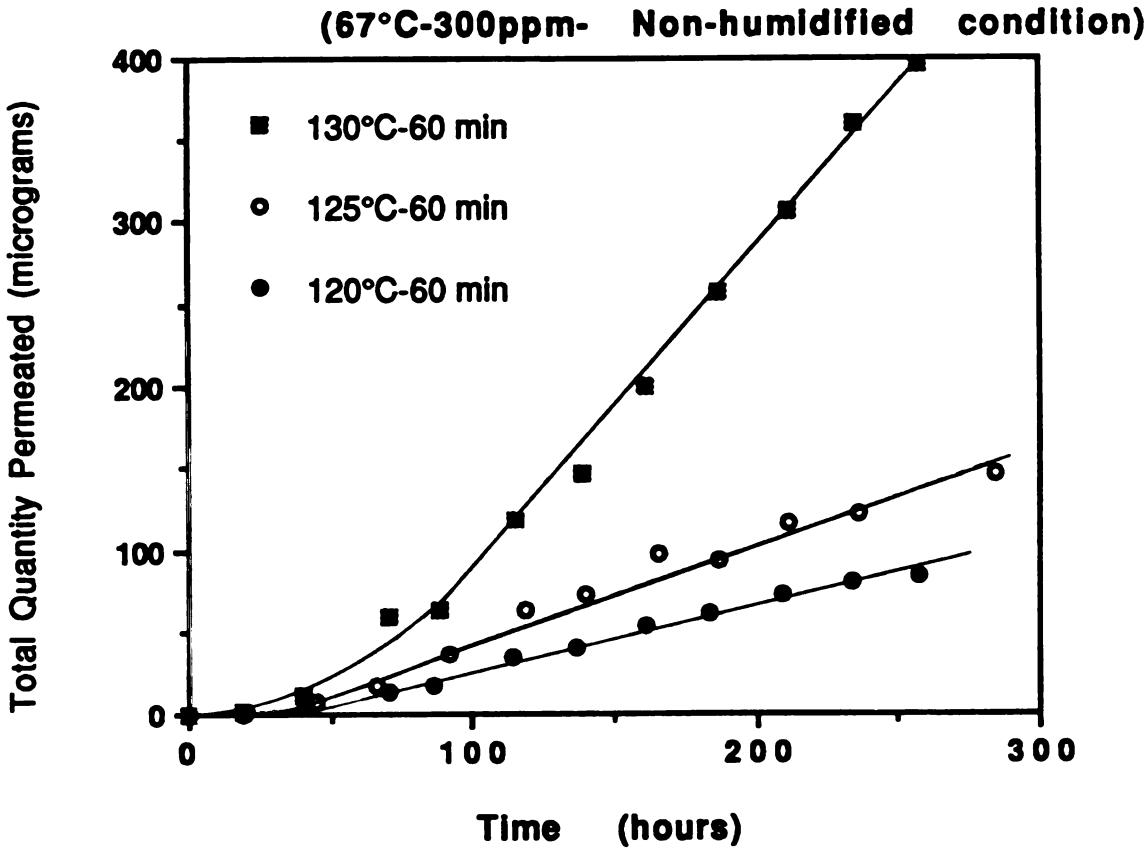


Figure 30. Effect of retorting temperature on the transmission rate of ethyl acetate vapor through PET/SiOx PET/CPP (Retort time 60min).

Table 12. The effect of retort conditions on transmission rate of ethyl acetate vapor through PET/SiOx PET/CPP.

Sample	Transmission rate[a]		
	Upper cell	Lower cell	Average
Control[b]	1.61×10^{-5}	1.22×10^{-5}	$1.22 \times 10^{-5} \pm 0.20$
120°C-20min	2.76×10^{-5}	3.30×10^{-5}	$3.03 \times 10^{-5} \pm 0.27$
120°C-40min	6.04×10^{-5}	5.45×10^{-5}	$5.75 \times 10^{-5} \pm 0.30$
120°C-60min	6.55×10^{-5}	9.31×10^{-5}	$7.93 \times 10^{-5} \pm 1.38$
Control[b]	1.76×10^{-5}	1.37×10^{-5}	$1.57 \times 10^{-5} \pm 0.20$
125°C-20min	-------	4.30×10^{-5}	4.03×10^{-5} - - -
125°C-40min	6.03×10^{-5}	7.77×10^{-5}	$6.90 \times 10^{-5} \pm 0.87$
125°C-60min	9.68×10^{-5}	1.23×10^{-4}	$1.10 \times 10^{-4} \pm 0.13$
Control[b]	1.42×10^{-5}	1.37×10^{-5}	$1.40 \times 10^{-5} \pm 0.03$
130°C-20min	1.53×10^{-4}	1.65×10^{-4}	$1.59 \times 10^{-4} \pm 0.06$
130°C-40min	2.30×10^{-4}	2.48×10^{-4}	$2.39 \times 10^{-4} \pm 0.09$
130°C-60min	3.66×10^{-4}	4.00×10^{-4}	$3.83 \times 10^{-4} \pm 0.17$

(a) Transmission rate values expressed as g/m^2 hr

(b) Not retorted.

Table 13. The effect of retort conditions on permeance of ethyl acetate vapor through PET/SiOx PET/CPP.

Sample	Permeance (a)		
	Upper cell	Lower cell	Average
Control(b)	1.29×10^{-4}	9.76×10^{-5}	$1.14 \times 10^{-4} \pm 0.16$
120°C-20min	2.21×10^{-4}	2.64×10^{-4}	$2.42 \times 10^{-4} \pm 0.22$
120°C-40min	4.83×10^{-4}	4.36×10^{-4}	$4.60 \times 10^{-4} \pm 0.24$
120°C-60min	5.24×10^{-4}	7.45×10^{-4}	$6.34 \times 10^{-4} \pm 1.11$
Control(b)	1.41×10^{-4}	1.10×10^{-4}	$1.26 \times 10^{-4} \pm 0.16$
125°C-20min	-------	3.44×10^{-4}	3.44×10^{-4} - - - -
125°C-40min	4.82×10^{-4}	6.22×10^{-4}	$5.52 \times 10^{-4} \pm 0.70$
125°C-60min	7.74×10^{-4}	9.84×10^{-4}	$8.79 \times 10^{-4} \pm 1.05$
Control(b)	1.14×10^{-4}	1.10×10^{-4}	$1.12 \times 10^{-4} \pm 0.02$
130°C-20min	1.22×10^{-3}	1.32×10^{-3}	$1.27 \times 10^{-3} \pm 0.05$
130°C-40min	1.84×10^{-3}	1.98×10^{-3}	$1.91 \times 10^{-3} \pm 0.07$
130°C-60min	2.93×10^{-3}	3.20×10^{-3}	$3.06 \times 10^{-3} \pm 0.14$

(a) Permeance values expressed as g/m^2 day 100ppm
(b) Not retorted.

Table 14. The effect of retort conditions on permeance of ethyl acetate vapor through PET/SiOx PET/CPP.

Sample	Permeance [c]		
	Upper cell	Lower cell	Average
Control[d]	4.46×10^{-16}	3.52×10^{-16}	4.08×10^{-16} ±0.56
120°C-20min	7.96×10^{-16}	9.52×10^{-16}	8.74×10^{-16} ±0.78
120°C-40min	1.74×10^{-15}	1.57×10^{-15}	1.66×10^{-15} ±0.09
120°C-60min	1.89×10^{-15}	2.68×10^{-15}	2.29×10^{-15} ±0.30
Control[d]	5.08×10^{-16}	3.95×10^{-16}	4.52×10^{-16} ±0.57
125°C-20min	-------	1.24×10^{-15}	1.24×10^{-15} - - - -
125°C-40min	1.74×10^{-15}	2.24×10^{-15}	1.99×10^{-15} ±0.25
125°C-60min	2.79×10^{-15}	3.55×10^{-15}	3.17×10^{-15} ±0.38
Control[d]	4.09×10^{-16}	3.95×10^{-16}	4.02×10^{-16} ±0.07
130°C-20min	4.41×10^{-15}	4.76×10^{-15}	4.59×10^{-15} ±0.17
130°C-40min	6.63×10^{-15}	7.15×10^{-15}	6.89×10^{-15} ±0.26
130°C-60min	1.06×10^{-14}	1.15×10^{-14}	1.10×10^{-14} ±0.05

(c) Permeance values expressed as g/m^2 sec Pascal
(d) Not retorted.

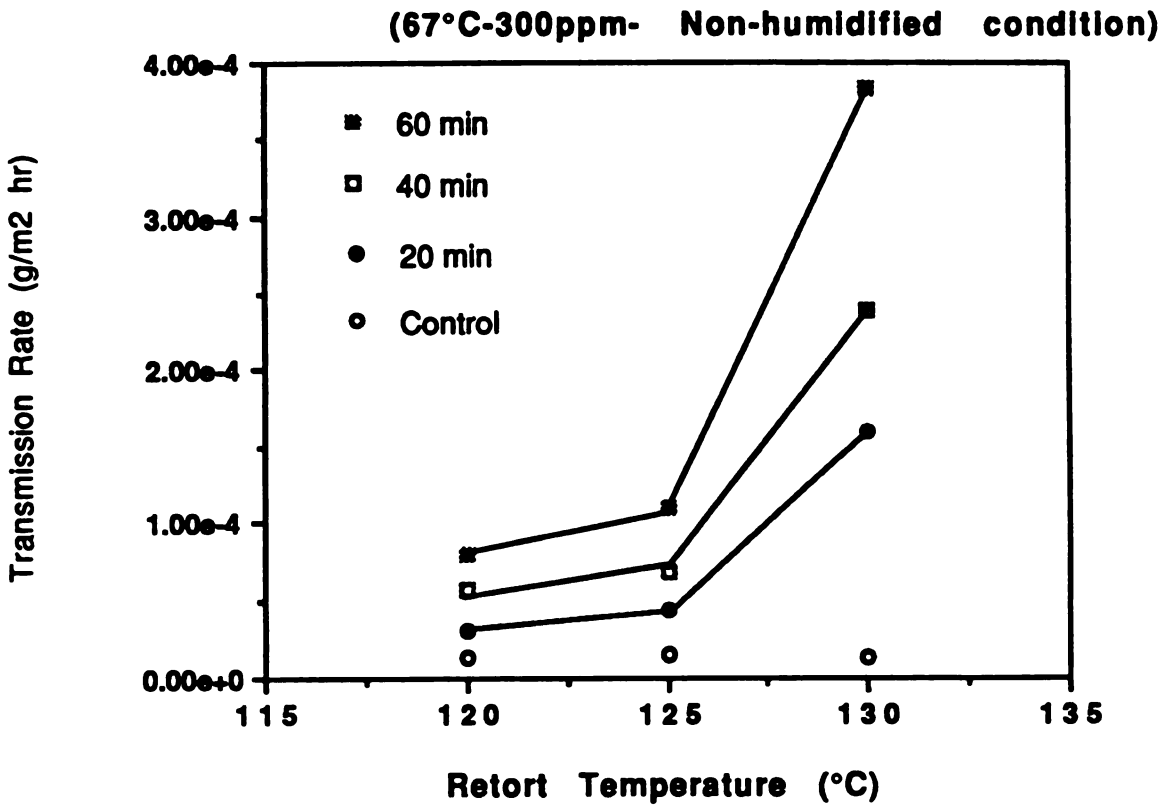


Figure 31. Dependency of transmission rate of ethyl acetate vapor through PET/SiOx PET/CPP on retorting temperature.

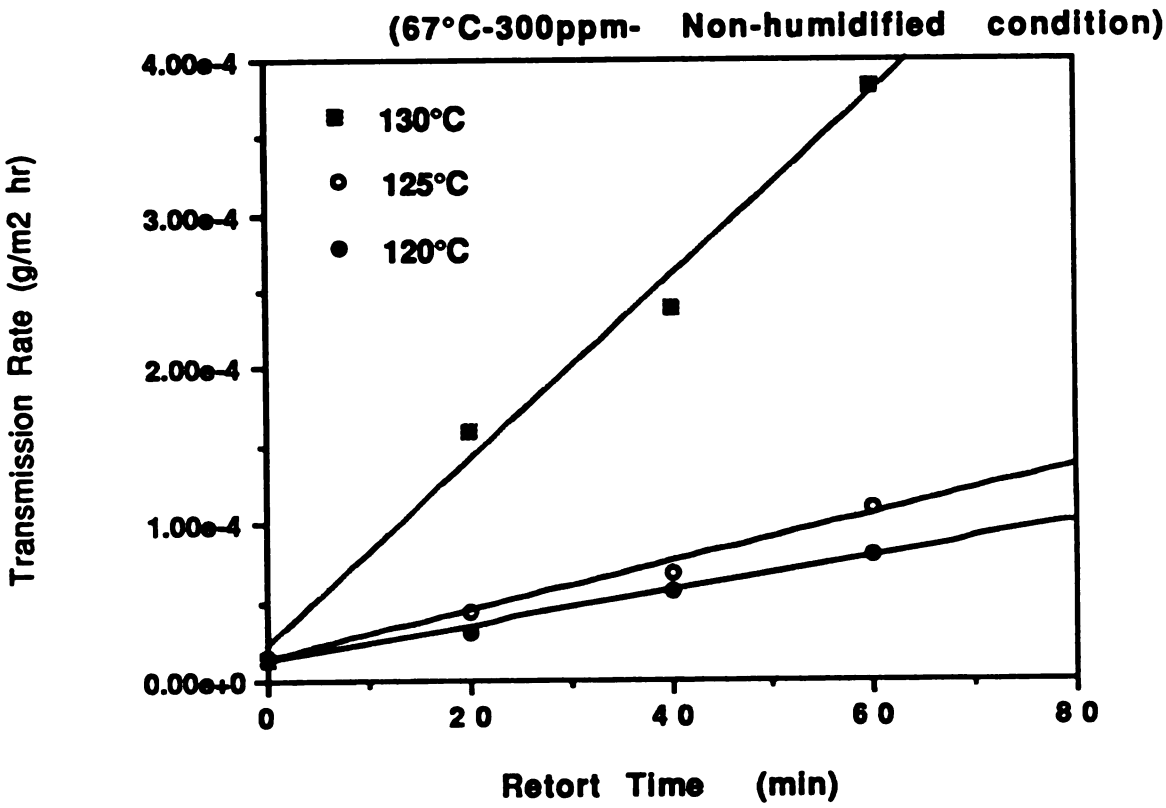


Figure 32. Dependency of transmission rate of ethyl acetate vapor through PET/SiOx PET/CPP on retorting time.

rate on retorting time. As shown, an increase in retorting time resulted in an increased transmission rate for each sample. The increases in the transmission rate at 120°C and 125°C are low. The increase rates per retorting time are 1.12 x 10^{-6}g/m^2 hr/min and 1.60 x 10^{-6}g/m^2 hr/min, respectively. However, at 130°C, the rate increase per minute retorting time increased drastically to 6.15 x 10^{-6}g/m^2 hr/min.

The effect of temperature and hold time on the barrier characteristics of the SiOx PET based retort pouch structure can be attributed to process induced damage to the SiOx barrier coating during the retorting step. This was confirmed by optical microscopy studies which are described below.

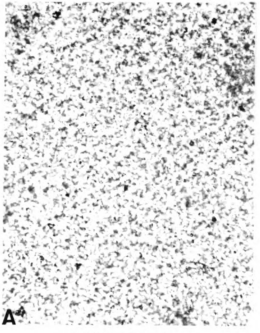
Analysis of SiOx Layer Surface

To evaluate the effect of retort processing conditions on the integrity of the SiOx barrier coating, optical microscopy analyses were carried out, where the SiOx surface layer was examined following retort processing and again following completion of the permeability studies. The results are summarized in Table 15 and presented graphically in Figures 33 - 36 for better illustration. In Figures 33-35, the micrographs of the SiOx surface are shown for pouches retorted at 120, 125 and 130°C, and for hold times of 20, 40 and 60 minutes, respectively at each temperature. As shown, within one temperature regime, as the hold time was increased, there was an increase in the observed cracking and crazing of the SiOx barrier layer. Further, as the retort temperature was increased, and increase in the SiOx surface fracture was observed. These results agreed well with the observed transmission data.

Table 15. Observation of SiOx layer of retort pouches.

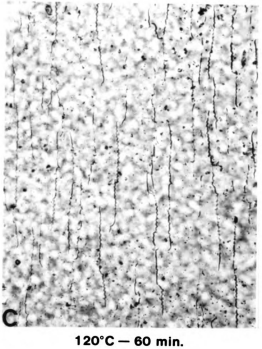
Sample	Description
No Retort	No crack
120°C - 20 min.	No crack
120°C - 40 min.	Tiny, non-continuous crack, one direction
120°C - 60 min.	Non-continuous and continuous crack, one direction
125°C - 20 min.	Tiny non-continuous cracks in some parts
125°C - 40 min.	Crack, one direction
125°C - 60 min.	continuous crack, one direction
130°C - 20 min.	continuous crack, one direction
130°C - 40 min.	Wider, continuous crack, one direction
130°C - 60 min.	Wider, webbed cracks
Temperature only	
125°C - 48 hr.	No crack
135°C - 48 hr.	No crack

Figure 33. Micrographs of SiOx surface - retorted at 120°C.



120°C — 20 min.

120°C — 40 min.



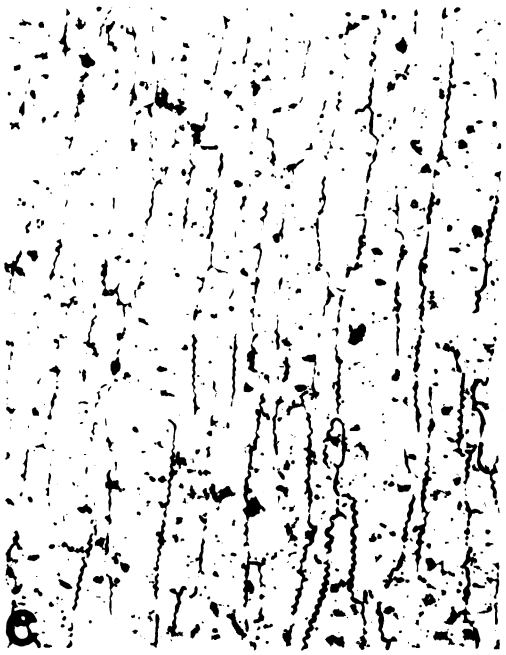
120°C — 60 min.

One smallest scale = 10 μm

Figure 34. Micrographs of SiOx surface - retorted at 125°C.

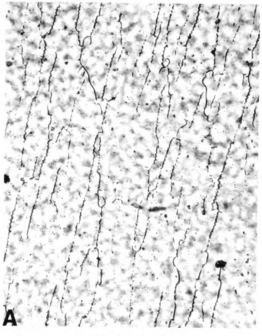
125° — 20 min.

125°C — 40 min.

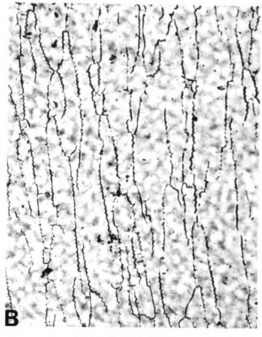


125°C — 60 min.

Figure 35. Micrographs of SiOx surface - retorted at 130°C.



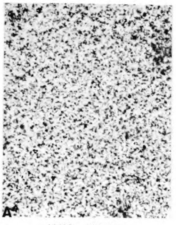
130°C — 20 min.



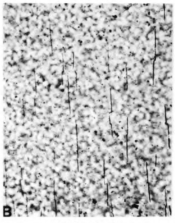
130°C — 40 min.

130°C — 60 min.

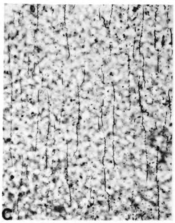
Figure 36. Micrographs of SiOx surface
- retorted at 120, 125 and 130°C



120°C — 20 min.

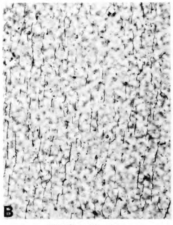


120°C — 40 min.

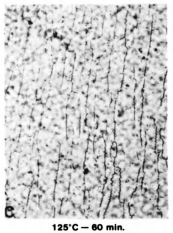


120°C — 60 min.

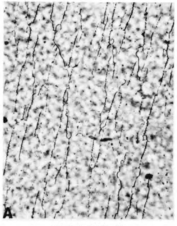
125° — 20 min.



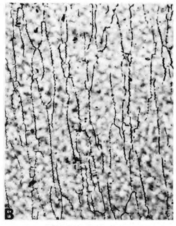
125°C — 40 min.



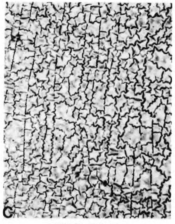
125°C — 60 min.



130°C — 20 min.



130°C — 40 min.



130°C — 60 min.

No significant differences were observed for the SiOx surface following ethyl acetate vapor permeation.

To evaluate the effect of temperature on the integrity of the SiOx coating, retort pouches were exposed to the following conditions, 135°C for 48 hours with 0% R.H. and 125°C for 48 hours with 0% R.H. No damage to the SiOx surface was observed by optical microscope. It was therefore concluded that the observed cracking and crazing of the SiOx layer during retort processing was not caused solely by temperature change. The damage on the surface was likely to be caused by the retorting process, that is, the combination of high temperature, physical stress and water.

SiOx pouches sorb water from both sides of the structure. The inside layer (CPP) is in contact with an aqueous phase, and the outside layer (PET) is exposed to water vapor during steam retorting. Both the inner and outer web of the laminate structure are capable of sorbing larger amounts of water under the conditions of the retort process. The SiOx layer may also sorb water. Kaiho (1987) reports the cast polypropylene layer of the retort pouches should have a small shrinkage rate, as stress will result from such shrinkage.

It is assumed, therefore that the stress and pressure to which the SiOx layer is exposed during the retort process, coupled with the sorption of water, is responsible for the observed damage to the barrier coating.

CONCLUSION

The effect of temperature, relative humidity and retort processing conditions on the permeation of ethyl acetate vapor through silica deposited polyethylene terephthalate film and composite structures were studied by a quasi-isostatic procedure. For comparison, the permeation of ethyl acetate vapor through an ethylene/vinyl alcohol copolymer (EVOH) and a EVOH laminate structure was also determined.

Based on the results of a series of preliminary studies, test conditions of 65 and 76°C, and a vapor concentration at 300 ppm (wt/v) were selected to evaluate the effect of temperature on the permeation of ethyl acetate vapor through SiOx PET film. Lower temperature and lower ethyl acetate vapor concentration levels did not yield measurable permeation rates. The results also suggested that the permeability of SiOx PET is more dependent on temperature than on ethyl acetate vapor concentration.

While the functional role of the silica coating is not fully understood, the following mechanism is proposed. For the silica deposited PET film, the barrier properties of the structure are governed by defects, nonohomogeneity of both the surface coating thickness and composition, or preferential diffusion paths. All of which can contribute to the observed permeability. The diffusion coefficients of the polymer layers immediately adjacent to the silica coating are thus critical in determining the effect of such defects.

During the initial transport period at 65°C, EVOH showed typical Fickian behavior, while the SiOx PET appeared to show atypical behavior. For the first 24 hours, permeation through SiOx PET was not detectable. Following this initial induction period, a significant increase in the transmission rate was observed, and after 96 hours, a steady state rate of transmission was recorded. At steady state, the rate of permeation through the SiOx PET was lower than that of EVOH.

SiOx PET film showed relatively high temperature dependence, and low transmission rates. PET also showed relatively high temperature dependence. However, the transmission rate was much higher than for SiOx PET and EVOH. EVOH showed a very high temperature dependence, based on the activation energy of the process.

In over 500 hours of continuous testing, there was no measurable permeation at 22°C, 56% R.H. The result showed that both SiOx PET and EVOH films were excellent ethyl acetate vapor barrier structures. However, at 22°C, 87% R.H., the EVOH film exhibited a permeation rate of 5.5×10^{-7}g/hr for ethyl acetate vapor, while the SiOx PET film showed no measurable permeation of the organic penetrant. Permeation of ethyl acetate vapor through SiOx PET was not influenced by relative humidity at ambient conditions, and the SiOx PET film showed excellent barrier for ethyl acetate vapor.

With respect to the effect of retort processing variables on the barrier properties of an SiOx PET based retort pouch, an average 260% increase in the transmission rate occurred when the retort temperature was increased from 125 to 130°C, while the transmission rate increase was on the order of 30% in going from 120°C to 125°C for

all hold times. An increase in retorting time was also directly related to higher transmission rates for each temperature.

When the permeation data and SiOx surface analysis by optical microscopy were compared, a direct relationship was obtained between an increase in permeation and wider, more continuous cracks of the SiOx layer.

The effect of temperature on the structural integrity of the SiOx coating of the retort pouch composite was evaluated, and no evidence of cracks or crazing was observed. It was therefore concluded that cracks were not induced solely as a result of temperature change. The damage on the SiOx surface was likely caused by the retorting process, that is, the combination of high temperature, physical stress and moisture sorption. Stress was caused by shrinkage of the CPP film and pressure during retorting process.

FUTURE RESEARCH

The results of this study showed that permeation of ethyl acetate vapor through SiOx PET film had relatively low temperature dependence at 50°C, 65°C and 76°C. No relative humidity dependence was observed in the experiments performed at an ambient condition (22°C). With respect to the effect of relative humidity, however, the examination of SiOx PET film in high temperature and high humidity will be necessary.

Similar studies should be carried out with other organic vapor penetrants, representing a range of polarities and molecular size, to compare their relative behavior. This will contribute for further developments in commercial use of SiOx PET film.

Detailed studies are needed to examine quantitatively the relationship between the cracking of the SiOx layer and the transmission rate. In addition, this study suggests that the combination of temperature, physical stress and water induced cracking of the SiOx layer. Further experiments in this area are of practical interest to determine causes of cracking accurately, and to analyze its mechanism to the full extent.

APPENDICES

Appendix A

Standard Calibration

Two standard calibration factors for ethyl acetate were employed, depending on the gas chromatograph models (5890, 5830A). Concentrations of 5, 8, 16, 20, 50, 100, 1000 and 10000 ppm (v/v) of ethyl acetate in solvent were utilized to create the calibration curves. A 0.5 μl sample was injected directly into the gas chromatograph and the area response was recorded. Area unit response was plotted versus the quantity injected per sample. The reciprocal of the slope equals the calibration factor. Table A1 and Figure A1 show the calibration data and the standard curve of ethyl acetate for the 5890 G.C., respectively. The calibration data and the standard curve of ethyl acetate for the 5830A G.C. is presented in Table A2 and Figure A2.

Ethyl acetate standard calibration factor for 5890 G.C.

$= 1.678 \times 10^{-12}$ (gm/A.U.)

Ethyl acetate standard calibration factor for 5830A G.C.

$= 5.352 \times 10^{-12}$ (gm/A.U.)

Table A1. Ethyl Acetate Calibration Curve Data for 5890 G.C.

PPM(v/v)	Quantity of Ethyl Acetate (gm)	Area Unit First Trial	Area Unit Second Trial	Area Unit Average
5	2.240×10^{-9}	1134	1086	1110
8	3.584×10^{-9}	1899	1802	1851
16	7.168×10^{-9}	3465	3461	3463
20	8.960×10^{-9}	4333	4677	4505
50	2.240×10^{-8}	11309	11123	11216
100	4.480×10^{-8}	24214	25452	24833
1000	4.480×10^{-7}	269530	269190	269360
10000	4.480×10^{-6}	2648100	2685600	2668500

Table A2. Ethyl Acetate Calibration Curve Data for 5830A G.C.

PPM(v/v)	Quantity of Ethyl Acetate (gm)	Area Unit First Trial	Area Unit Second Trial	Area Unit Average
8	7.168×10^{-9}	1328	1339	1334
20	1.792×10^{-8}	3383	3051	3217
50	4.480×10^{-8}	7984	7504	7744
100	8.960×10^{-8}	16280	17120	16700
1000	4.480×10^{-7}	177400	171900	174650
10000	8.960×10^{-6}	1689000	1687000	1688000

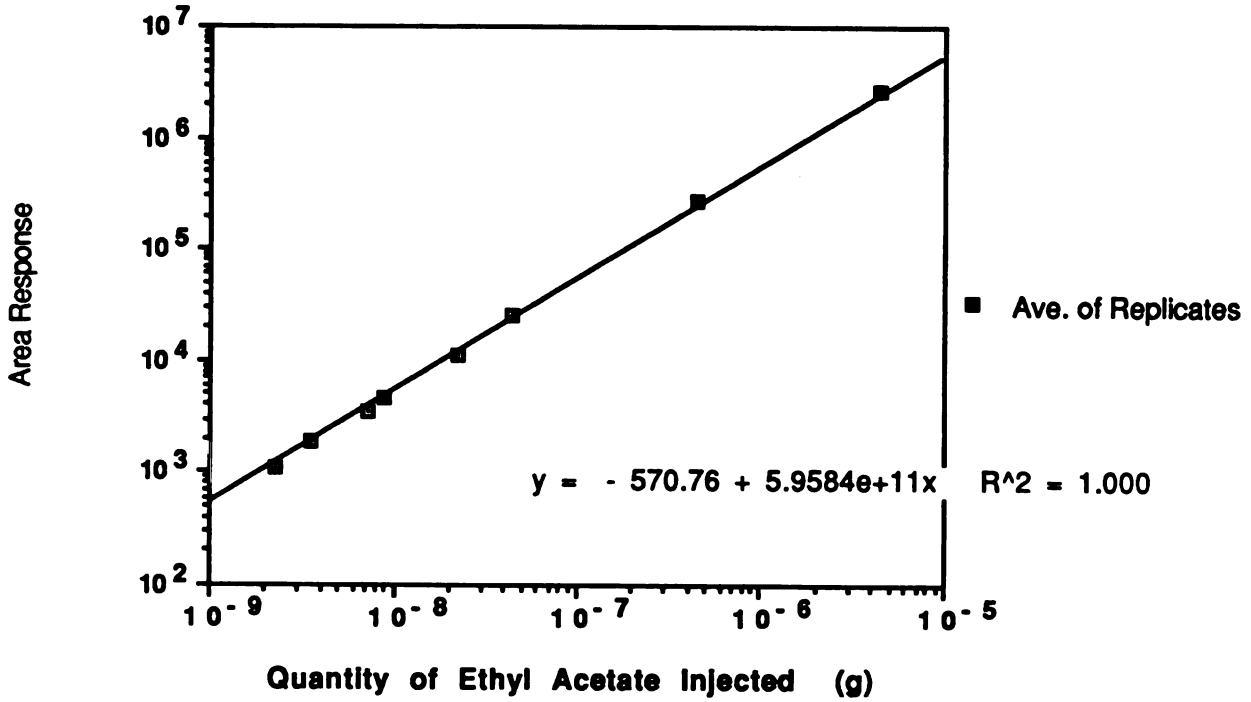


Figure A-1. Ethyl acetate calibration curve for gas chromatograph 5890.

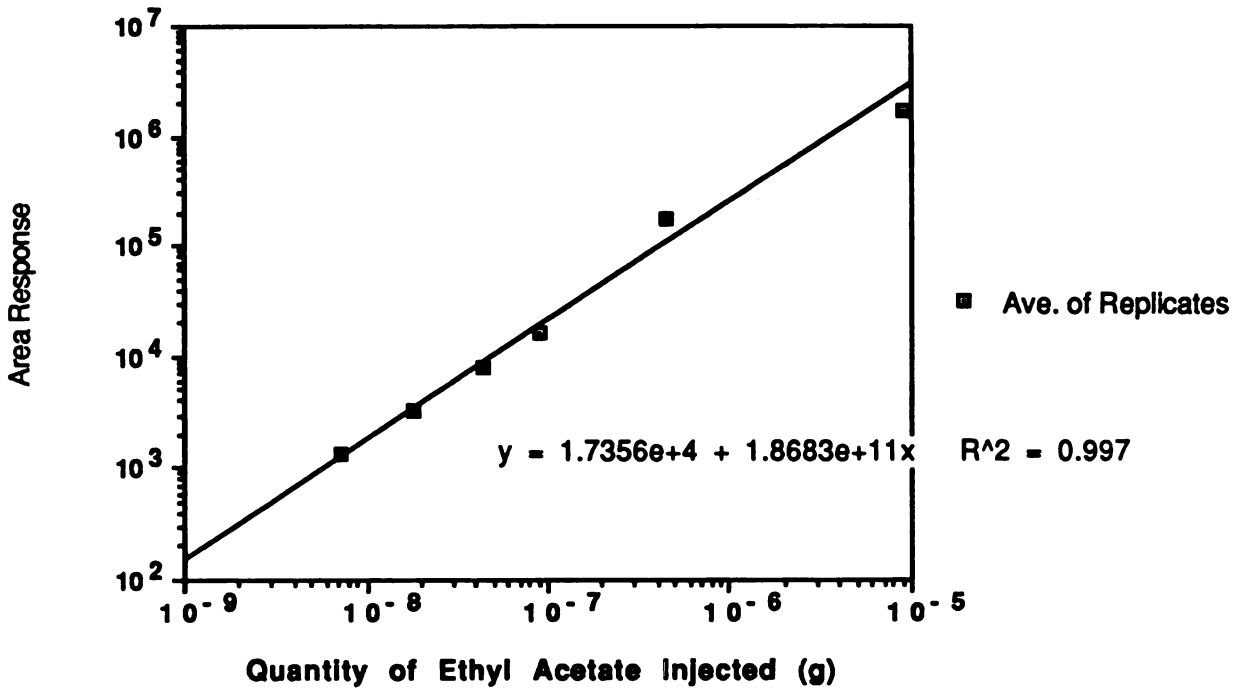


Figure A-2. Ethyl acetate calibration curve for gas chromatograph 5830A.

Appendix B

Table A3. Oxygen Permeance of SiOx PET and Other Films Used in This Study

Structure	Oxygen Permeance
SiOx PET	2.0
PET/ SiOx PET/CPP	0.7
EVOH	0.5
PET/EVOH/CPP	0.4
PET	159.7
PET/PET/CPP	74.9

Units of Oxygen permeance : cc/m^2 day atm

at 30°C-0% R.H.

The values are averages of replicate runs.

Appendix C

Estimation of the Upper Limit of the Transmission Rates of Ethyl Acetate Vapor through SiOx PET Film

Outlined below is the method used to estimate lower limit of permeability rate by the gas chromatograph. The lowest area response selected with 5830A G.C. for detecting ethyl acetate with good precision and accuracy was assumed to be 1000 area unit.

In over 500 hours of continuous testing, the following data were obtained; SiOx PET had less than 1000 AU at 56% R.H., 22°C, and less than 2000 AU at 87% R.H., 22°C. EVOH had less than 2000 AU at 56% R.H., 22°C. These three data was fluctuating and did not show steady state. The calibration factor for 5830A G.C. is 5.352×10^{-12} g/AU for ethyl acetate. The total quantity of ethyl acetate vapor permeated through SiOx PET at 56% R.H. 22°C after 500 hours was calculated as follows:

(Sample Calculation)

$$gm = 1000AU \times (5.352 \times 10^{-12})\ g \times 50cc / 0.5cc = 5.35 \times 10^{-7}$$

50cc : Total cell volume

0.5cc : Injection volume

Permeability Rate for SiOx Film at 56% R.H., 22°C

$$5.35 \times 10^{-7}\ g/500hrs / 0.005m^2 = 2.14 \times 10^{-7}\ g/m^2\ hr$$

This represents an average transmission rate which does not consider lag time.

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