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ORGANIC VAPOR PERMEABILITY OF TRANSPARENT HIGH BARRIER FILMS UTILIZING A HIGH PERFORMANCE THIN Al₂O₃ COATING LAYER

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Hiroshi Suzuki

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ORGANIC VAPOR PERMEABILITY OF TRANSPARENT HIGH BARRIER FILMS UTILIZING A HIGH PERFORMANCE THIN Al₂O₃ COATING LAYER

By

Hiroshi Suzuki

A THESIS

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ABSTRACT

The organic vapor (d-limonene and ethyl acetate) permeability of Al_2O_3 -coated PET films and SiO_x -coated PET films was studied. Evaluation was made utilizing the dynamic purge and trap / thermal desorption procedure.

A comparison of the permeability (and its temperature dependence) of Al_2O_3 coated PET film to various permeants (d-limonene, ethyl acetate, oxygen and water vapor) was made. Results showed that water vapor behaved significantly differently than other permeants, in terms of the mechanism of mass transfer.

There were no major differences observed between the permeability of the Al_2O_3 coated PET film and that of the SiO_x -coated PET film which suggested that the mechanism of mass transfer through both films may be similar.

The effect of physical abuse on gas or vapor permeability was also evaluated for Al_2O_3 -coated PET film. Barrier deterioration, caused by cracks of the ceramic surface, occurred at less than 10 times flexing abuse for both non-polar and polar permeant / Al_2O_3 -coated PET systems. For Al_2O_3 -coated PET / LLDPE laminated film samples, the loss in barrier performance varied for non-polar and polar permeants.

A simple model has been prepared to account for the observed permeability behavior for the Al_2O_3 -coated PET film. This model provides an explanation for the permeability behavior of both normal (non-abused) and abused Al_2O_3 -coated PET films. Dedicated to my daughter and my wife.

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Chapter 1

INTRODUCTION

The importance of polymeric materials for packaging purposes has been increasing because of their unique characteristics (e.g., light weight, high flexibility, high transparency). Moreover, the nature of polymers allows the properties of plastic materials to be controlled at will, utilizing various types of modifications. High barrier plastic films are a very important practical application for modified polymers. Ceramic (e.g., silicon oxide (SiO_x) and aluminum oxide (Al₂O₃)) coating processes for the surface of plastic films have received considerable attention as surface modification techniques.

Silicon oxide (SiO_x) coated polyethylene terephthalate (PET) films were introduced into packaging markets in the early 1980's. These films might be called the "first generation" of SiO_x -coated PET. They were transparent barrier films that afforded good water vapor and oxygen gas barrier properties but were in limited use in the packaging field at that time.

In the high barrier film market, there is no perfect film in terms of the properties and the cost. Even though ceramic-coated films had superior barrier properties, in order to expand the usage of ceramic-coated films, there were three problems to be solved. (1) These films were relatively expensive, compared to other barrier films such as polyvinylidene chloride (PVdC)-coated PET. (2) Because of the nature of ceramics, the ceramic layers on the films were relatively brittle, even though they were less than 200 nm thick. (3) These films were slightly yellow in color, which could negatively influence the visual appearance of the packaged product (Imai, 1998). For example, the films could not be used for the packaging of bonito shavings, which are a traditional Japanese spice. Fresh bonito shavings are pink in color, but when they are oxidized or deteriorated, their color turns amber. The slightly yellow packaging film made the product appear to be amber in color, even though the actual product color was pink.

Recently, however, some significant efforts have resulted in the production of advanced ceramic-coated films. They include not only efforts to improve SiO_x -coated PET (the "second generation" of SiO_x -coated PET) but also to develop new ceramic (i.e. aluminum oxide (Al₂O₃)) coated PET films. The Al₂O₃-coated PET films are less costly than the first generation of SiO_x -coated PET and comparably priced to PVdC coated PET (Hoffmann *et al.*, 1994; Kelly, 1994). In addition, the films are less brittle and very clear. Potentially, therefore, a number of flexible barrier packages can be replaced with Al₂O₃-coated PET based structures.

Although Al_2O_3 -coated PET films exhibit good water vapor and oxygen gas barrier properties (Imai, 1998), the organic vapor (flavor or aroma moieties) permeability of Al_2O_3 -coated PET films has not been determined. For some products, a package system is required which can prevent the loss of volatile organic compounds through the package wall to the external environment. For instance, cosmetics in flexible packages often need to be sealed against the loss of aroma compounds from the product. The primary focus of this study, therefore, was to provide the first data on the barrier properties of Al_2O_3 -coated PET film to organic compounds under varying conditions. The organic permeants selected for this study are d-limonene and ethyl acetate. Ethyl acetate was selected based on its common use as a solvent in the converting industry and its presence as a residual solvent from laminating and printing processes. D-limonene was selected to represent a major flavor volatile for citrus oil and essence (Indou, 1985).

In order to simulate abuses of the packaging film during packing or distribution, this study also evaluated the effect of mechanical stresses, such as flexing stress, on the barrier properties of the Al_2O_3 -coated PET films and Al_2O_3 -coated PET / LLDPE laminated structures.

Another major focus of this study was to investigate the mechanism of mass transfer of gases or vapors through Al_2O_3 -coated PET film. Water vapor exhibits significantly higher permeability through Al_2O_3 -coated PET film than oxygen, even though these permeants have similar molecular sizes. Several investigations have proposed a possible mechanism for permeability of oxygen and water vapor through ceramic-coated films (Barker *et al.*, 1995; Tropsha, 1997), but the studies did not include organic vapors. By using permeants of different characteristics, this study may provide insight into the gas or vapor permeation mechanism of Al_2O_3 -coated PET films.

The specific objectives of this study are:

1) To evaluate the temperature effects on the organic vapor permeability of Al_2O_3 coated PET film using d-limonene and ethyl acetate.

2) To compare the organic vapor permeability of two different types of ceramic-coated PET (SiO_x and Al₂O₃).

3) To evaluate the organic vapor permeability of Al_2O_3 -coated PET, which has been

damaged by flexing at various abuse levels.

4) To evaluate the effect of permeability of a series of permeants of various

characteristics (oxygen, water vapor, d-limonene, and ethyl acetate) through Al₂O₃-

coated PET.

Chapter 2

LITERATURE REVIEW

2-1. Ceramic-Coated Films

2-1-1. Evaporation Processes

The technique to deposit a very thin coating layer on a substrate is one of the key technologies to make modified materials in many industries. The evaporation process is an effective way to manufacture the layer. It consists of two steps: step (1); vaporize the source materials, and step (2); deposit the vaporized materials onto the substrate. There are various evaporation processes, but they can be categorized into two general methods: (i) physical vapor deposition (PVD), which includes vacuum evaporation, sputtering, and molecular beam epitaxy; and (ii) chemical vapor deposition (CVD). The most critical theoretical difference between PVD and CVD is the driving force for the transition from step (1) to step (2) in the evaporation process. PVD uses the physical energy of the evaporated material (e.g., the vapor pressure in the vacuum evaporation process) to form deposits onto the surface of the polymer film substrate. In contrast, CVD uses a chemical reaction as the driving force to deposit the ceramics onto the film surface.

The PVD method (mainly, vacuum evaporation) is most widely employed in the packaging industry to manufacture ceramic-coated films. The schematic model of the process is shown in Figure 2-1. The source materials (i.e. silicon monoxide (SiO) or

aluminum (Al) etc.) are heated in a crucible and then evaporated. The evaporated materials are deposited onto the surface of a film substrate, which is cooled by a chill roll. One of the most important advantages of the PVD method is its very high machine speed, which can reduce production costs through greater efficiency. This method has a potential drawback, however, which is that the film can potentially be damaged in the high temperature environment (Kelly, 1993).

PVD



Figure 2-1 Schematic Model of PVD

The two most common heating systems for the evaporation process involved in PVD method are the boat system and the electron beam gun (EB) system. In the boat system, the crucible is heated by an electric power source, either by a resistor or induction, and the deposition materials are heated by conduction energy. For the EB system, an EB directly heats the material itself. Although the machinery cost for the EB system is higher than that of the boat system, the EB system contains some indispensable advantages, including (i) rapid heating; (ii) higher power; and (iii) precise evaporation rate control (Hoffmann, 1994).

CVD, on the other hand, employs a different mechanism to deposit the ceramic coatings onto the film surface. The schematic model of the process is shown in Figure 2-2. The precursor materials (i.e. organosilicones etc.) are carried as gases, and react with other material such as oxygen in the gas phase.

CVD



Figure 2-2 Schematic Model of CVD

The final reaction products then deposit onto the surface of the film. To promote the gas phase reactions, a plasma state is usually employed. Because CVD does not use a high temperature, the film will not be damaged. Also, CVD does not need an ultra vacuum state (less than 10⁻⁸ torr), which is required in the PVD process. This can contribute to reduced machinery cost. The machine or line speed, however, is not very high, and makes the final cost of the product high. Table 2-1 summarizes the advantages and the disadvantage of these two processes (Charoudi, 1991).

Table 2-1 Tros and cons of evaporation methods			
	PVD	CVD	
Barrier	O	0	
Heat Resistance	\bigtriangleup	\bigcirc	
Flexibility	\bigtriangleup	0	
Transparency	0	\bigcirc	
Speed	\bigcirc	\bigtriangleup	
Machinery Cost	\bigtriangleup	0	
Total Cost	0	×	

 Table 2-1 Pros and cons of evaporation methods

 \bigcirc excellent, \bigcirc good, \triangle fair, \times poor

2-1-2. Development of Ceramic-Coated Film

A ceramic-coated film for packaging purposes was initially developed in 1964 by DuPont de Nemours and Company (Dupont, 1964) as a silicon oxide (SiO_x) -coated PET film. Even though it was an epoch making invention, the product did not succeed in the packaging market because of its high cost. In the mid 1980s, the Toppan, Toyo, and Ajinomoto companies cooperated to create the future for ceramic-coated film (Sakamaki, 1989). The joint venture aimed to develop a new film, which was called by the trade name of GL film, for microwaveable pouches used for retortable foods. GL film and several similar products, however, enjoyed success in a relatively small market, which included retort foods, laminated tubes, and liquid containers. However, because of the negatively perceived yellowish color of the film, the niche market was limited to less than \$100 million per year (Charoudi, 1991).

These films, which can be called the "first generation" of SiO_x -coated films, had some essential problems such as high cost, the yellowish color and inadequate barrier properties. To solve these problems, two major efforts emerged in research and development field. One aim was to reduce the cost by using PVD, and the other was to remove the yellowish color by using CVD (Kelly, 1993). The resultant modified SiO_x coated films can be called the "second generation" of SiO_x -coated films.

2-1-3. SiO_x-Coated Films

Using the PVD method, SiO_x coatings are generally produced by evaporation of silicon monoxide (SiO), either by the boat system or by the EB system. The vapor of SiO is oxidized in a controlled reactive atmosphere to achieve an average degree of oxidation between x = 1.5 and 1.8. The reason the evaporated material has excess Si atoms in the matrix is that if the matrix has been made to be stoichiometrically correct (i.e. silicon dioxide (SiO₂)) by the PVD method, the matrix will have a low packing density (Figure 2-3), which leads to high permeation rates (Hlavac, 1983). The stoichiometrically



Figure 2-3 Matrix of SiO2 and SiOx

insufficient structure results in Si atoms with dangling bonds in the coating structure. The presence of the dangling bonds in the matrix causes the slightly yellowish appearance of the resultant SiO_x -coated structure (Kaihou, 1989).

The properties of the first generation of SiO_x coating are strongly influenced by the layer thickness and the chemical composition (Charoudi, 1991). To maintain good barrier properties, the thickness of the SiO_x -layer needed to be over 1600 Å for a retort grade SiO_x -film.

Second generation SiO_x -coated films have succeeded in providing transparent barrier films for the packaging market. Significant efforts have been made to improve the coating technique, and the thickness of the SiO_x -layer has been reduced to 400 Å or less. This has resulted in a clearer film, and a higher speed operation, which has reduced the cost of producing the SiO_x -coated films.

For the substrate of the PVD SiO_x coatings, PET is preferred, and the resultant SiO_x -coated PET films show excellent barrier characteristics to oxygen and water vapor (Imai, 1998). Nylons and biaxially oriented polypropylene (BOPP) have also been evaluated as substrates, but have not as yet afforded good barrier properties, due to their lower thermal stability compared to PET.

Since the late 1980's, there has been a significant effort to improve the clarity of SiO_x -coated films, especially by using the plasma enhanced chemical vapor deposition (PECVD) process (Nelson, 1993). Organosilicones like 1,1,3,3-tetramethyldisiloxane (TMDSO) or hexamethyldisiloxane (HMDSO), as non-toxic liquid process monomers,

are generally employed as a source material. The monomers are evaporated into an electric field to dissociate and ionize. These reactions result in the deposition of an SiO_2 coating onto the substrate surface, while various gas phase byproducts of the reactions are pumped away.

This method provides a number of advantages over the PVD method. Because chemical reactions are occurring in this process, the deposited materials are packed tightly and are stoichiometrically correct. Because of these factors, the film is clearer than the PVD processed film. The resistance to elongation is also better than that of the PVD processed film (Nelson, 1993). Since PECVD employs a lower temperature process, various substrate films (i.e. PET, BOPP, Nylons, etc.) can be utilized (Yamamoto, 1998). Although this process has these advantages, slow machine speed makes the film expensive and it remains commercially unsuccessful.

During recent years, the second generation of SiO_x -coated films has become established as a high quality, transparent barrier film. However, compared to the entire high barrier packaging market, the market share of SiO_x -coated films is still not very high. There are several reasons for this, but the main problems are that the SiO_x -coated films still have a higher cost than PVdC-coated films and they still have a yellowish color, even though the color is much better than the first generation's (Hoffmann, 1994).

2-1-4. Al₂O₃-Coated Films

One of the latest efforts to improve the barrier characteristics and the clarity of ceramic-coated film is the development of aluminum oxide (alumina = Al_2O_3)-coated film.

 Al_2O_3 -coated film may provide a solution to these problems. Either a direct evaporation system or a reactive evaporation system, which are analogous to PVD methods, can be employed to evaporate the ceramic coating. In Al_2O_3 coating, direct evaporation Al_2O_3 is evaporated from an Al_2O_3 solid source. On the other hand, reactive evaporation uses aluminum and oxygen as source materials and requires their reaction either in the gas phase or at the surface of the substrate (Schiller *et al.*, 1993).

For the direct evaporation method, the EB system is necessary, due to the high vaporizing temperature of Al_2O_3 , which is about 2400 K. The substrate to be coated passes a cooling drum arranged above the evaporator crucible. Although this process appears to simply involve evaporation of Al_2O_3 , the stoichiometry of the deposited material is still a concern, because part of the Al_2O_3 will split up into suboxides, which will make the film darker during the evaporation. To obtain transparent or stoichiometrically correct film, additional admission of oxygen between the crucible and substrate is required.

Because of its relatively low evaporation temperature, aluminum can be evaporated either by the boat system or the EB system for reactive evaporation. The oxygen stream, which reacts with the evaporated aluminum, must remain constant over time and area. It was originally thought that the process involved two sequential reactions, condensation of aluminum on the substrate followed by surface oxidation (Kelly, 1994). Recently, some kinetic and surface topography studies have suggested that the oxidation reaction occurs primarily in the gas phase, and the oxidized particles are then deposited onto the substrate (Kelly, 1994). The stoichiometry of the deposited material (i.e. oxygen : aluminum ratio) can be varied. A small improvement in the oxygen barrier is observed with increasing aluminum content.

2-1-5. Ceramic Mixture-Coated Films

Not only single oxide $(SiO_x, Al_2O_3 \text{ etc.})$ coated film, but also multi-oxide coated films have been prepared to improve barrier properties (Phillips, 1993). PVD evaporated SiO_x coatings have a contradictory issue, which is that if SiO_x -coated film is to maintain high barrier properties, the film will have a yellowish color. On the other hand, if it has a clear appearance, the film will have higher permeation rate, because of the lower density packing formation (Hlvac, 1983).

To solve this contradiction, aluminum oxide, yttrium oxide, tin oxide, and a mixture of SiO_2 and MgO have been proposed as nucleation layers for SiO_2 , whose color is water clear. The idea was to provide a preferable surface for SiO_2 deposition, so it would have a dense formation. These materials have not been launched commercially, but they have a lot of potential for success in the transparent high barrier film market (Charoudi, 1991).

2-2. Properties of Ceramic-Coated Films

2-2-1. Oxygen and Moisture Barrier

Excellent oxygen and moisture barrier characteristics are fundamental properties for clear, high barrier films. PVdC coating onto plastic films has been widely used as a mainstay to increase the barrier properties of plastic films. However, because PVdC coatings contain chlorine, which causes acid rain and dioxin formation when incinerated, there is an ongoing trend in both Europe and Japan to phase out PVdC-coated films (Kelly, 1994). In fact, some supermarkets in Europe have already banned the use of PVdC packaging materials (Kelly, 1993).

With increasing pressure from consumers and government regulations, the foodpackaging industry has been seeking new materials with environmental safety in mind. The most favorable choices for alternative chlorine-free barrier materials are either ceramic-coated films or EVOH film. Both films can provide excellent oxygen barrier properties at low humidity conditions. EVOH, however, loses its barrier properties in a high-humidity environment. Ceramic-coated PET does not show a loss of barrier performance at elevated humidity levels (Imai, 1998).

The oxygen barrier properties of ceramic-coated PET films compare favorably with PVdC-coated PET or EVOH films. As a transparent high barrier packaging material, this barrier level allows a long shelf life for most processed foods.

The existence of a polyolefin sealant layer, which provides a relatively good moisture barrier, with PVdC-coated films or EVOH based barrier structures makes these

flexible packaging structures good moisture barriers (i.e. water vapor transmission rate $(WVTR) < 3 \text{ g/m}^2$.day. However, it is very hard to attain a WVTR of 1 g/m².day or less, which is required for dry food packages using existing clear flexible materials. The ceramic-coated PET structures have a WVTR below this level, at any and all conditions. Oxygen and moisture barrier properties of typical barrier films are summarized in Figure 2-4 (Imai, 1998).

2-2-2. Organic Vapor Barrier

Flavors are complex systems that consist of a number of different classes of volatile organic compounds. These compounds may be sorbed by the packaging material or may permeate through it. These interactions may cause a decrease in flavor components and can result in an unbalanced profile or undesirable flavor (Kail, 1984).

There are three main phenomena which occur between flavor or interactive compounds and packaging materials that may result in a change in the flavor profile: scalping, permeation, and migration. Scalping is the loss of flavor components due to their sorption by the packaging material as a result of those components being soluble in the packaging material. Permeation is the movement of volatile compounds through the packaging material, while migration is the movement of low molecular weight components from the packaging material itself into the product. Among these mass transfer processes, scalping generally plays a major role in flavor deterioration for products in flexible packaging, because a large quantity of aroma compounds can readily dissolve in the sealant material of the flexible package system (Ikegami *et al.*, 1988; Rogers, 1959).



Figure 2-4 Oxygen and water vapor barrier properties of high barrier performance films

Even though scalping has been the primary area of study of flavor changes due to loss of flavor components, losses resulting from permeation cannot be neglected. Moreover, because the ceramic layers of the ceramic-coated PET are very thin (less than 400 Å), scalping by the ceramic layer is not likely to be a major problem. Since the ceramic layers are so vital to barrier properties for ceramic-coated films, studies concerning permeation of organic penetrants through such barrier structures should be given more attention.

Unlike simple gas or moisture vapor barriers measurements, a flavor's intensity is subjective. For this reason, sensory evaluations have been carried out to determine flavor qualities (Kail, 1984; Allison, 1985). These evaluations, however, require well-trained panelists.

Using an objective instrumental approach, there had been no standard test method to measure the organic vapor permeability of polymer membranes, until 1997. In addition, it was difficult to measure the barrier properties of each component of a flavor or aroma profile due to a lack of appropriate instruments and the low level of permeation through the high barrier materials.

For these reasons, the oxygen barrier properties of barrier films have been used to estimate the flavor barrier properties in the packaging field. The general consensus is that films with good oxygen barrier properties will also have good flavor barrier properties, but this statement is not correct in some cases. For example, polystyrene (PS) has a high oxygen transmission rate. In the case of aromas, however, PS shows better barrier properties than even poly-vinilydene chloride (PVdC). Because PS is a highly glassy

polymer, larger permeants, such as organic vapors, tend to be obstructed the permeation by the glassy matrix (DeLassus, 1993). This illustrates the danger of estimating flavor barrier properties on oxygen barrier properties alone. Therefore, it is essential to develop direct methods for measuring flavor barrier properties.

In order to measure organic vapor permeability of high barrier films, improvements in the measuring systems have been necessary. One early study employed a quasi-isostatic procedure to determine the ethyl acetate permeability of SiO_x-coated film (Sajiki, 1991). In this procedure, the lower concentration chamber of the permeation cell is initially filled with a carrier gas and completely closed. After introduced the gas or vapor into the higher concentration chamber, the permeants then accumulates in the lower concentration cell chamber and is monitored at predetermined time intervals by gas chromatography. This early study showed that SiO_x-coated PET exhibited excellent barrier properties (e.g. permeance = $1.9 \times 10^{-19} \text{ kg.m}^2 \text{ sec. Pa}@65^\circ\text{C}$) for ethyl acetate. This barrier level compares favorably with that of ethylene vinyl alcohol copolymer (EVOH) film. In addition, the results suggested that the temperature effect on permeability of SiO_x-coated PET was much less than that of EVOH.

Recently, rapid evaluation of organic compound permeation through polymer membranes was made possible with the introduction of two commercially available systems. These systems are the MAS2000TM Organic Permeation Detection System (Testing Machines Inc., Amityville, NY), and the AROMATRAN TM Permeation Test System (Modern Controls Inc., Minneapolis, MN). Both systems follow a newly
introduced standard (ASTM F1769-97) (ASTM, 1997a) and employ an isostatic test procedure. The details of these systems will be discussed in Sections 2-4-2 and 2-4-3. Using the MAS2000TM, a series of commodity packaging films have been investigated for their organic vapor barrier properties (Huang and Giacin, 1998). Chang (1996) also used the MAS2000TM and studied the permeability of α -pinene through PET / SiO_x-coated PET laminated films. Results showed the SiO_x-coated PET-based laminated films had better barrier properties (e.g. permeance = $1.8 \times 10^{-17} \text{ kg},\text{m}^2.\text{s.Pa}@60^\circ\text{C}$) than EVOHbased laminated films.

2-2-3. Flex Resistance

For most products in flexible packages, the ability of the package to withstand flex cracking is indispensable. Even though the packaging film may have excellent barrier properties as a flat film, if the film has no durability for flex cracking, which can occur during filling, packaging, or distributing, the barrier properties as a flat film are meaningless (Oliveira, 1997). One way of assessing resistance to flex cracking is by the Gelbo flex test (ASTM F392-74) (ASTM, 1987).

As the instrument cycles in the Gelbo flex test, its movable head compresses the sample, while rotating one end 440 °. It can be adjusted to simulate any degree of flex abuse by changing the flex cycles.

The oxygen barrier properties of aluminum metallized films and the first generation of SiO_x -coated films dropped significantly when they were abused by the

Gelbo flex tester. In contrast, the moisture barrier properties did not deteriorate significantly (Marzolf, 1981). These results could be due to the generation of pin-holes during flexure, but the specific cause of barrier property loss has not been resolved.

A number of efforts have been made to improve the flex resistance of ceramiccoated films. For example, using the CVD method, highly flex resistant films have been made (Nelson, 1993). The mechanism of this improvement is still not clear, but one possibility is that the contamination of carbon elements from the gas source may make the ceramic layer flexible. Improvements and developments in new evaporation techniques have also been employed for the PVD method, and the resultant PVDprocessed ceramic-coated layers have shown much better flex durability than the first generation films.

2-3. General Theory Related to the Permeation Process

2-3-1. Permeation Steps

Permeability is often referred to as the ease of transmission of gasses or vapors through a resisting material, which has no macroscopic pores (Rogers, 1985). The transport of a gas or vapor through polymeric films commonly used in packaging typically involves the activated diffusion process. The process involved three steps: (1) absorption 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 (Rogers, 1985).

2-3-2. Sorption Mechanism

The steps of adsorption and desorption can be categorized as having the same mechanism and may be described by the sorption process. Whenever a gas is in contact with a solid, there will be an equilibrium established between the molecules in the gas phase and those which are bound to the surface of the solid. The amount of gas molecules sorbed onto the polymer film surface will depend on the pressure of the gas above the film surface and the temperature of the system. Increasing the gas pressure increases the collision rates of the sorbate molecules into the polymer membrane and also increases the amount sorbed. On the other hand, higher temperatures tend to increase the internal energy of the sorbate molecules, thus decreasing their sorption by the polymer membrane (Rogers, 1965).

2-3-3. Diffusion Mechanism

Some domains of a polymer are a randomly arranged mass of macromolecule chains, which consist of a network containing voids or holes. The diffusion process is the result of polymer molecules having a kinetic agitation or thermal motion. In other words, it will depend on the number, size, and distribution of pre-existing holes, and it also depends on the ease of hole formation (Rogers, 1965). The diffusion of permanent gases (i.e. hydrogen, oxygen, nitrogen), which have a much smaller molecular size than the monomer unit of a given polymer, occurs readily since the rotational oscillation of one or two monomer units will provide sufficient cross sectional area for the diffusant molecule. This mechanism follows both Fick's first law and Henry's law, and the diffusion coefficient is independent of concentration (Barrer, 1939).

On the other hand, the diffusion mechanism for molecules larger in size than the monomer unit of a polymer requires a cooperative movement by the micro-Brownian motion of several monomer units in order to take place. Water vapor or organic vapor, which interact strongly with the polymer, are categorized as this type of permeant molecule. As a result, their diffusion coefficient is primarily controlled by the mobility of the polymer segmental unit, which is directly proportional to the permeant concentration and temperature (Meares, 1965).

2-3-4. Permeation Mechanism of Ceramic-Coated Films

The mechanism of permeation of gases and vapors through ceramic-coated films is not well known. Two different mechanisms, however, have been proposed to explain the permeation process. The basic concept of both mechanisms is "the defects leading permeation" model, where defects in the ceramic coating result in the permeation of gas or vapor. In other words, if there is no defects, the ceramic coating will provide a perfect barrier to permeants. One of the proposed permeation mechanisms requires the existence of macro defects, such as pinholes in the film, which leads permeation. In fact, the permeation path of a permeant through aluminum metallized film is primarily determined by existing pinholes in the aluminum coating (Jamieson and Windel, 1983). The size of the pinholes varies, but most pinholes of 1 to 2 μ m in size which are associated with the presence of dust particles on the film surface. When the film is metallized, dust particles create shadows on the film, thus when the dust particle falls, it creates a un-metallized area (i.e. pinhole) on the film surface. The area of the total pinholes controls the rate of permeation in this mechanism.

For ceramic-coated films, several studies have been carried out to apply the "pinhole theory". Activation energies of transport of oxygen ($\Delta \text{ Ep}(02)$) through SiO_xcoated films were determined to describe the permeation mechanism (Sajiki, 1991; Tropsha, 1997). Tropsha suggested that if the ceramic layer is perfectly defect-free, the $\Delta \text{ Ep}(02)$ between ceramic-coated material and the non-coated substrate should be different. In these studies, however, the $\Delta \text{ Ep}(02)$ of both coated and non-coated materials showed similar values. This result suggested oxygen mainly permeated through the PET matrix via defects or "non-continuous" areas in the oxide layer.

The other route proposed to explain the permeation mechanism for ceramiccoated films is through imperfections in the network of the ceramic coating at the molecular level (micro-defects) (Norton, 1953). For example, the SiO_2 matrix is, in theory, comprised of a crystal lattice structure, which is composed of hexagon type in crystal plane. Since Si atoms and oxygen atoms have atomic radii of 0.41 Å and 1.4 Å, respectively, the size of the voids within the matrix is not large enough to accommodate gases (e.g., oxygen molecules or even helium atoms which have atomic radius of 1.1 Å). In reality, however, the matrix has similar or larger voids or holes (Figure 2-3) than an ideal crystal lattice. To confirm this micro-defect mechanism, the effect of permeant size has been studied (Norton, 1953). The size of the permeant was found to be directly proportional to the permeation rate for a series of inert gases. For instance, the transmission of helium and neon gases through silica glass, which is an amorphous structure and has micro-defects which could be measured. Argon gas, however, did not afford any measurable transmission rate through the silica glass. The atomic diameter of argon is 3.2 Å, which is much smaller than macro-defects which are estimated to be between 1 to 2 μ m in size.

These proposed mechanisms were based on the permeation of simple gases. However, the permeation of moisture vapor or organic vapors may have a more complicated mechanism, due to the polarity of the permeant and the potential interaction of the permeant with the ceramic layers. However, few studies were reported in this field.

2-4. Factors Affecting the Permeation Processes

2-4-1. Nature of Permeants

There are three significant factors, which affect the permeation processes, related to the nature of the permeants. (1) The size of a permeant molecule. In general, an

increase in penetrant size results in a increase in the solubility coefficient (S) value, because larger molecule has higher cohesive force to substrate surface. In same time, however, the diffusion coefficient (D) value tends to decrease with increasing the penetrant size. Kosinowski (1986) studied the effect of n-alkane permeant size on mass transfer processes through low density polyethylene. The diffusion coefficients decreased with increasing numbers of carbon atoms.

Because the permeability is decided by the product of these two parameters (D and S), the effect of permeant size is canceled out and is much less than what its expected. Even though, the effect of permeant size is not significant, the effect still exists in most permeation processes. The uncertainty of molecule diameter by different deciding methods, however, may scatter the effect of permeant size to its permeability.

(2) Shape of the penetrant is other factor which will effect permeability. Berens and Hophenberg (1982) reported that the anisometric molecules may permeate through polymers along their long axes or smallest cross sectional area. Rogers (1985) found a spherical molecule has lower permeability than a straight chain molecule, if they have similar chemical nature.

(3) The third major factor of how the permeant nature can effect permeability is the polarity of the penetrant. In general, if the polymer and the permeant have similar chemical composition or polarity, the permeability is expected to be high. For example, since polyethylene (PE) is a non-polar polymer, the permeation rate of PE to non-polar gases (e.g., oxygen, nitrogen) is high (Rogers, 1985).

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2-4-2. Measuring Temperature

Many factors related with the measuring conditions can contribute to effect the permeation process. The temperature of the test cell, however, can be one of the most important factors.

Since permeability is the product of the solubility coefficient (S) and the diffusion coefficient (D), the effect of measuring temperature on these coefficients have been widely studied (Rogers, 1985; Huang and Giacin, 1998). In general, the solubility coefficient (S) decreases or increases with increasing temperature, depending on the physical state of the permeants. The diffusion coefficient (D), however, increases with increasing temperature, as an increase in temperature provides the energy for the segmental motion and hole formation, which increases the free volume within the polymer bulk phase (Crank, 1956).

The Arrhenius equations can be introduced to explain the temperature dependence of solubility and diffusivity.

$$S(T) = S_0 \times \exp{\frac{(-\Delta H_s)}{RT}}$$
 Eq. 2-1

$$D(T) = R0 \times \exp\left(\frac{(-ED)}{RT}\right)$$
 Eq. 2-2

where Δ Hs and ED are heat of solution and diffusion activation energy, respectively. S₀ and D₀ are pre-exponential terms, R is the gas constant and T is the absolute temperature. The Arrhenius expression can also express the temperature dependence of permeance.

$$R(\tau) = R_0 \times \exp\frac{(-E_R)}{RT} \qquad \qquad \text{Eq. 2-3}$$

where E_R is the activation energy for permeation, R_0 is the pre-exponential term, R is the gas constant and T is the absolute temperature.

The permeation behavior is generally quite different below and above the glass transition temperature (T_g) . Above the T_g of the polymer, enough energy is provided to produce the micro-Brownian motion and the chains can experience segmental motion, while below the T_g , the polymer chains are fixed in a specific conformation. Therefore, in general, at temperatures above T_g , the permeability coefficient is more temperature dependent, but below T_g , it is less temperature dependent.

2-5. Permeability Measurement

2-5-1. Mathematical Approach for Permeation Process

The transmission rate or flux (F) of a permeant through a polymer membrane can be defined as the amount passing through a surface of unit area normal to the direction of flow during unit time (Rogers, 1985).

$$F = Q/At$$
 Eq. 2-4

where Q is the total amount of permeant which has passed through the area (A) during time (t). The transfer of 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, 1956).

$$F = -D (dC/dx) \qquad Eq. 2-5$$

where D is the diffusion coefficient with units of (length)²(time)⁻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. Therefore, dC/dx defines the concentration gradient of the permeant across a thickness dx. This law can be applied to the diffusion in the steady state. Under steady state conditions, a gas or vapor diffuses through a polymer at a constant rate, if a constant concentration or partial pressure difference is maintained across the polymer (Crank, 1956).

Fick's second law describes non-steady state diffusion, where the concentration of the diffusing substance is changing with time. The mathematical treatment of Fick's second law is described by Eq. 2-6 (Crank, 1956).

 $dC/dt = D (d^2c/dx^2)$ Eq. 2-6

There are a number of solutions to this equation, which have been derived for various boundary conditions (Crank, 1956).

The permeation of a gas or vapor through a polymeric material is usually described by the permeability coefficient (P), which can be quantified from knowledge of the diffusion coefficient (D) and solubility coefficient (S), as described by Eq. 2-7.

The diffusion coefficient is a kinetic parameter and is a measurement of how rapidly the transport process will occur and indicates the ease with which a penetrant molecule moves within the polymer matrix. The solubility coefficient is a thermodynamic parameter and is a measurement of the concentration of penetrant molecules sorbed in the polymer matrix. The solubility coefficient is an equilibrium partition coefficient describing the distribution of the penetrant between polymer matrix and vapor phase.

Eq. 2-5 can be integrated, where D is independent of concentration, to give:

F=D(C1-C2)/L Eq. 2-8

where C1 and C2 are the steady state concentrations of the permeant at the two surfaces of the film and L is the thickness of the film.

Eq. 2-8 can also be rewritten by substituting for F, using Eq. 2-4, to give Eq. 2-9.

This enables calculation of the quantity of permeant diffusing through a polymer of area A in time t.

For gases and vapors, the concentration of the permeant in the polymer, at the high concentration surface, is proportional to the concentration or partial pressure of permeant in the surrounding gas phase. This relationship can be expressed by Henry's law:

C = **Sp Eq. 2-10**

where S is the solubility coefficient of the permeant in the polymer and p is the partial pressure of the gas or vapor. By combining Eq. 2-9 and 2-10, it gives:

$$Q=DS(p1-p2)At/L$$
 Eq. 2-11

Since the relationship between P, D and S is expressed as Eq. 2-7, Eq. 2-11 can be rewritten as Eq. 2-12 which enables determination of P from experimental data.

$$\mathbf{P} = \mathbf{QL}/\mathbf{At}(\mathbf{p1}-\mathbf{p2}) \qquad \qquad \mathbf{Eq. 2-12}$$

2-5-2. Isostatic Method

In the isostatic method, a penetrant flows continually through the high concentration cell chamber, and an inert carrier gas flows continually through the low concentration cell chamber. Therefore, the total gas pressure on the two sides of the test film is essentially equal. The partial pressure gradient of the permeant provides a driving force for permeation. The isostatic method allows for the continuous monitoring of the transmission rate of organic vapors through test films from the initial time zero until steady state condition.

The permeability coefficient P is calculated from the transmission rate at steady state by the expression:

$$P = [C]fL/A(p1-p2)$$
 Eq. 2-13

where [C] is the steady state concentration of permeant conveyed to the detector, in mass per unit volume; and f is the rate of carrier gas flow in the low concentration cell, in volume per unit of time.

If the film is essentially free of penetrant, the diffusion coefficient D can be calculated by:

$$D = L^2/7.199.t_{1/2}$$
 Eq. 2-14

where $t_{1/2}$ is the time required to reach a transmission rate value that is equal to half of that at the steady state, in time units.

Using these principles, two commercial instruments, the MAS2000TM and the AROMATRAN TM series, are available for performing organic vapor permeability measurements. Since these units have become commercially available, the ease of measurement of organic vapor permeability has been improved, dramatically.

Both systems employ a flame ionized detector (FID), which provides sensitivity levels in the low parts per billion region, to quantify the level of penetrant which has permeated. Both systems allow rapid evaluation of the diffusion, solubility and permeability coefficients of organic vapors through packaging materials (Huang, 1996).

2-5-3. Dynamic Purge and Trap / Thermal Desorption Technique

The dynamic purge and trap / thermal desorption technique is one of the most effective approaches to determine the permeation rate of high barrier films. The technique involves the use of absorbents to trap and to concentrate the permeant. The vapors concentrated in the sorbent trap are subsequently recovered by a desorption system and transferred directly to a gas chromatograph for analysis. The amount recovered per trapping time is treated as the permeation rate.

The application of a dynamic purge and trap / thermal desorption procedure coupled with the MAS2000TM Permeation Test System was developed and performed (Chang, 1996). The permeance of α -pinene vapor through a series of high barrier composite films, including the first generation of SiO_x-coated PET, which could not be tested by a normal isostatic procedure, was determined. The lowest detection sensitivity

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of the dynamic purge and trap/thermal desorption procedure was found to be 0.2 ng/hr which is three to four orders of magnitude less than the continuous flow isostatic procedure (Chang, 1996). The increased detection sensitivity of the method provides the ability to determine the permeation rate of aroma / flavor permeation rates of high barrier films.

Chapter 3

MATERIALS and METHODS

3-1. Materials and Apparatuses

3-1-1. Films and Laminated Structures

In this study, 2 different films and one laminated structure were prepared to

investigate their permeability. All ceramic-coated films was manufactured by the physical

vapor deposition method (see Section 2-1-1). The laminated structure was manufactured

by a solvent-lamination method using an urethane type adhesive.

1) Films:

a) Al₂O₃-Coated PET film (12 μ m):

GL-AE film (TOPPAN PRINTING Co., Ltd., Tokyo, Japan)

b) SiO_x-Coated PET film (12 µm):

GL-E film (TOPPAN PRINTING Co., Ltd.)

2) Laminated structure:

a) Al₂O₃-Coated PET film (12 μ m) / LLDPE (40 μ m) laminated films:

Al₂O₃-Coated PET; GL-AE film (TOPPAN PRINTING Co., Ltd.)

LLDPE; (Tocelo Co., Ltd., Tokyo, Japan)

Adhesive; Urethane type

3-1-2. Permeants

D-limonene and ethyl acetate were selected as the organic vapor permeants. The basic information of the permeants is summarized in Table 3-1.

d-Limonene (Aldrich Chemical Co., Milwaukee, WI)			
Molecular structure	$(C_{10}H_{16})$		
Density at 25 °C	0.840 g/cc		
Molecular weight	136.24		
Boiling range	175.5 - 176 ℃		
Molar volume	162 cc/mole		
Purity	97%		
Ethyl Acetate (Aldrich Chemical Co., Milwaukee, WI)			
Ethyl Acetate (Aldrich	h Chemical Co., Milwaukee, WI)		
Ethyl Acetate (Aldrich Molecular structure	n Chemical Co., Milwaukee, WI) (CH3CO2C2H5)		
Ethyl Acetate (Aldrich Molecular structure Density at 25 °C	h Chemical Co., Milwaukee, WI) (CH3CO2C2H5) 0.894 g/cc		
Ethyl Acetate (Aldrich Molecular structure Density at 25 °C Molecular weight	h Chemical Co., Milwaukee, WI) (CH3CO2C2H5) 0.894 g/cc 88.11		
Ethyl Acetate (Aldrich Molecular structure Density at 25 °C Molecular weight Boiling range	h Chemical Co., Milwaukee, WI) (CH3CO2C2H5) 0.894 g/cc 88.11 77.1 °C		
Ethyl Acetate (Aldrich Molecular structure Density at 25 °C Molecular weight Boiling range Molar volume	h Chemical Co., Milwaukee, WI) (CH3CO2C2H5) 0.894 g/cc 88.11 77.1 °C 98.56 cc/mole		

Table 3-1 Basic information of the permeants

3-1-3. Solvents

Three different solvents were employed to prepare standard solutions. For the dlimonene standard solution to calibrate both vapor pressure of permeation test and the purge and trap / thermal desorption procedure, carbon tetrachloride was used. For the ethyl acetate standard solutions used to calibrate the vapor pressure of the permeation test, acetonitrile was used. For the ethyl acetate standard solutions used to calibrate the purge and trap / thermal desorption procedure, dichlorobenzene was used. The basic information of the solvents are summarized in Table 3-2.

Carbon Tetrachloride (Mallinckrodt, Inc., Paris, KY)			
Molecular structure	(CCl ₄)		
Density at 25 °C	1.585		
Molecular weight	153.84		
Boiling range	76.3-76.8 °C		
Purity	99.9%		
Acetonitrile (EM Science, Gibbstown, NJ)			
Molecular structure	(CH ₃ CN)		
Density at 20 °C	0.786 g/cc		
Molecular weight	41.05		
Boiling range	81.6 °C		
Purity	99.8%		
Dichlorobenzene (Aldrich Chemical Co., Milwaukee, WI)			
Molecular structure	$(C_6C_4Cl_2)$		
Density at 25 °C	1.551 g/cc		
Molecular weight	147		
Boiling range	179 °C		
Purity	99 %		

Table 3-2 Basic information of the solvents

3-1-4. Apparatuses

In this study, various apparatuses were employed. The types and suppliers of

these apparatuses are listed below:

(1) Thermal Desorption Apparatus:

a) Dynatherm 890/891 thermal desorption unit (Dynatherm, Kelton PA)

b) CarbotrapTM 300 multi-bed thermal desoption tubes; 6 mm O.D. x 4 mm I.D. x 11.5

cm length (Supelco Inc., Bellefonte, PA)

(2) Gas Chromatograph:

Hewlett Packard model 5890A interfaced with a HP 3395 integrator (Avondale, PA)

(3) Gas Chromatography Column (Fused Silica Capillary Column):

a) SPBTM5 (non-polar bounded stationary phase) 30 m long, 0.32 mm I.D., 1.0 µm film

thickness (Supelco Inc., Bellefonte, PA)

b) SupelcowaxTM10 (polar bounded stationary phase) 60 m long, 0.25 mm I.D., 1.0 μ m

film thickness (Supelco Inc., Bellefonte, PA)

(4) Permeation Test Apparatus:

a) For organic vapor; (Measuring system follows ASTM F 1769-97 (ASTM, 1997a))

MAS2000TM Organic Permeation Detection System (Testing Machines Inc., Amityville,

NY)

b) For oxygen; (Measuring system follows ASTM D 3985-81 (ASTM, 1981))

MOCON Ox-Tran 200 Permeability Tester (Modern Controls Inc., Minneapolis, MN)

c) For water vapor; (Measuring system follows ASTM F 1770-97 (ASTM, 1997b))

MOCON Permatran W 3/31 Permeability Tester (Modern Controls Inc.)

(5) Water Bath:

Endocal RTE-100 (NESLAB Instruments, Inc., Portsmouth, NH)

(6) Bubbler:

25 ml Standard Midget Bubbler (ACE Glass Incorporated, Vineland, NJ)

(7) Needle Valves:

Nupro M-Series (Nupro Co., Willoughby, OH)

(8) Fittings:

Swagelok Fitting (Supelco Inc., Bellefonte, PA)

(9) Electronic Mass Flow Meter:

Model Top-Trak 821 (Sierra Instruments, Carmel Valley, CA)

(10) Syringes:

a) 500 ml gas-tight syringe (Hamilton Co., Reno, NV)

b) 5 µl syringe (Hamilton Co., Reno, NV)

(11) Flex tester:

Gelbo Flex Tester Model # 5000 (Research & Testing Co., Inc., Hoboken, NJ)

(12) Optical microscope:

Olympus BH-2 (Olympus Optical Co., Ltd., Tokyo, Japan)

3-2. Methods

3-2-1. Calibration Curve for Vapor Pressure

The concentration of the permeant vapor evaluated with the MAS2000TM Organic Permeation Detection System was determined by gas chromatography analysis. Standard solutions of the compound in solvent (carbon tetrachloride for d-limonene, acetonitrile for ethyl acetate) were prepared and a calibration curve for the permeant was constructed according to the analytical conditions. Initial conditions and temperature programming of gas chromatography are summarized in Table 3-3 and 3-4, respectively.

Compound	d-limonene	ethyl acetate		
Column	SPB [™] 5	Supelcowax TM 10		
Injection temperature(°C)	220	220		
Detector temperature (°C)	250	250		
Head pressure (psi)	10	20		
Total flow port (split vent) (ml/min)	27.8	28.8		
Septum purge (purge vent) (ml/min)	2.76	2.5		
Helium flow rate (ml/min)	1	1		

 Table 3-3 Initial conditions of gas chromatograph

Table 3-4 Temperature programming for gas chromatograph for direct injection procedure.

Compound	d-limonene	ethyl acetate
Initial oven temperature (°C)	50	40
Initial time (min)	2	1
Rate (°C/min)	7	5
Final temperature (°C)	110	200
Final time (min)	0	10
Rate A ^(a) (°C/min)	30	
Final temp A ^(a) (°C)	200	-
Final time A ^(a) (min)	3	_
Total run time (min)	16.58	43.00

(a) the second temperature programming cycle

The above conditions gave a retention time for d-limonene of 8.94 min and for ethyl acetate 8.06 min. The quantity of permeant detected was determined by multiplying the standard concentration (v/v) times the volume injected $(1 \ \mu l)$, which is then multiplied by the density of the permeants. The quantity injected plotted versus the corresponding area response gave the calibration curve, which established the linearity and sensitivity of the analysis for the respective permeant. The calibration profiles obtained for compounds are shown in Appendix A.

3-2-2. Calibration Curves for Dynamic Purge and Trap / Thermal Desorption Procedure

The Carbotrap 300^{TM} adsorbent tube was selected for the present study because its multi-bed adsorbent design allows trapping of various organic compounds of different size and functionality.

The standard calibration curve for the test compound was obtained by the following procedures. A 1 µl sample of a standard solution of the compounds in solvent (carbon tetrachloride for d-limonene, dichlorobenzene for ethyl acetate) was directly injected onto the sorption tube. The sorption tube was then inserted into the heating chamber of the thermal desorption unit, which is directly interfaced to the column of the gas chromatograph. SPB^{TM5} fused silica capillary column was chosen for this analysis. The test compound was thus desorbed by heating and then separated by GC. The test conditions of the thermal desorption procedure and gas chromatography analysis are summarized in Table 3-5 and 3-6, respectively.

370
250
250
350
8
30
9
15

Table 3-5 Conditions of thermal desorption unit.

 Table 3-6 Temperature programming for gas chromatograph for thermal desorption procedure.

Compound	d-limonene	ethyl acetate
Initial oven temperature (°C)	35	40
Initial time (min)	2	5
Rate (°C/min)	20	30
Final temperature (°C)	200	200
Final time (min)	10	10
Total run time (min)	20.25	20.33

The above conditions gave a retention time of 6.75 min for d-limonene and 2.31 min for ethyl acetate. The quantity injected plotted versus the corresponding area response gave the calibration curve, which established the linearity and sensitivity of the analytical procedure. The calibration profiles obtained for the compounds by the thermal desorption procedure are presented in Appendix B. After sample desorption, the sorbant tubes were conditioned at 350 °C for 30 minutes for re-use.

3-2-3. Organic Vapor Permeability Test System

Permeability studies were carried out with the MAS2000TM Organic Permeation Detection System, which was modified with a device for trapping permeated organic vapors. MAS2000TM Organic Permeation Detection System is based on an isostatic permeation test procedure. This system allows for the continuous collection and measurement of the permeation rate of the organic vapor through a polymer membrane. The cell temperature can be accurately controlled from ambient to 200 °C.

Even though the MAS2000TM Organic Permeation Detection System has an incorporated detection system, this study required a sensitivity for the measurements which was significantly greater than that provided by the original isostatic system. In order to obtain higher sensitivity, the test system employed a dynamic purge and trap technique, which allowed accumulation of the permeated vapor. The sensitivity of this system is two orders of magnitude greater than that of the MAS2000TM original isostatic system (Chang, 1996). A bypass line was installed to convey the permeated vapor to the sorption trap. The trapping system ensured that the low concentration cell chamber was continuously flushed with carrier gas and the permeated vapor was conveyed directly to the trapping tube attached. The sorption trap (CarbotrapTM 300) was connected to the exit port of the bypass line, which is incorporated onto the instrument chassis, via a 1/4" thumb wheel Swegelok Fitting for easy removal. Figure 3-1 provides a schematic of the permeation test and trap system.

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Figure 3-1 Schematic diagram of dynamic purge and trap permeability system

3-2-4. Permeability Measurements

The permeability studies were carried out within a temperature range of 55 to 80 °C. Prior to initiating a test run, the test film was conditioned at selected temperatures for at least 6 hours to desorb residual monomer and other volatiles from the film. For each test run, a sample film was cut, mounted on a paperboard film holder with tape. Then the sample was placed in the permeability cell with the PET side facing the sample gas chamber (front cell) side. Therefore, the direction of permeation process was from PET through the ceramic-coated layer (or LLDPE). The area of the test film was 0.0081 m².

A constant concentration of permeant vapor for the high concentration cell chamber was produced by bubbling nitrogen through the liquid permeant. The flow rate of the line was 30 ml/min. The liquid permeant was contained in a 25 ml standard midget bubbler which was placed in a temperature controlled water bath to generate a saturated vapor pressure of desired level. While the organic vapor was generated at the selected temperature (point 1), the film permeability was evaluated with the test cell maintained at a higher temperature (point 2). The parameters of partial pressure, temperature, concentration and volume for the organic vapor generator and test conditions are denoted as p_1 , p_2 , T_1 , T_2 , v_1 and v_2 , respectively (Huang and Giacin, 1998).

Assumptions:

1. At points 1 and 2, the mass flows are equal. Therefore,

$$M_1 = M_2 = M$$
 Eq. 3-1

where M is the mass flow (mass/time).

2. The organic vapor pressure is usually very low, and therefore the mass flow consists primarily of carrier gas (nitrogen). For this case, it can therefore be assumed that the organic vapor behaves as an ideal gas, therefore:

$$F_2 = F_1 \times \frac{T_2}{T_1}$$
 Eq. 3-2

and by definition:

$$c = M/F$$
 Eq. 3-3

where F is the gas flow rate (volume/time).

So, the penetrant vapor concentration at point 1: (c1) is equal to M_1/F_1 and at point 2: (c2) is equal to M_2/F_2 , therefore:

$$c_1/c_2 = T_1/T_2$$
 Eq. 3-4

When expressing c or p by the ideal gas law, at point 1:

$$p_1 = \frac{n \times R \times T_1}{v_1} = \frac{R}{MW} \times \frac{m_1 \times T_1}{v_1} = \frac{R}{MW} \times c_1 \times T_1$$
 Eq. 3-5

and

$$\frac{p_2}{p_1} = \frac{c_2 \times T_2}{c_1 \times T_1}$$
 Eq. 3-6

where c = m/v = mass of permeant vapor per unit volume.

It follows therefore, that:

$$p_2 = p_1 \times \left(\frac{c_1 \times T_1}{T_2} \times T_2 \times \frac{1}{c_1 \times T_1}\right) = p_1$$
 Eq. 3-7

So, at points 1 and 2:

* temperature are different,

- * mass flows (mass/time) are equal,
- * flow rates (volume/time) are different, and
- * partial pressures are equal.

In order to confirm the vapor pressure of a permeant, a gas sampling port was installed between the bubbler and the test cell. To determine the specific vapor concentration, a 50 µl sample was withdrawn from the sampling port and injected directly into the gas chromatograph (GC) for quantification. The GC analysis conditions were the same as that for determining the saturated vapor pressure. The experimentally determined saturated vapor pressures were compared with the interpolated values obtained from Perry's Chemical Handbook (1984) (see appendix C). In this comparison, the following equation was used to calculate the saturated vapor pressure.

$$p = \frac{CF \times AU \times R \times T}{MW \times V}$$
 Eq. 3-8

where:

p = partial pressure (Pa)
CF = calibration factor (g/AU)
AU = area unit response from integrator (AU)
R = gas constant, 6.236x10⁷ (mmHg.µl / mole.K)
T = temperature (K)
MW = molecular weight (g/mole)
V = gas sample volume (µl)

The accuracy of the vapor pressure values between experiment and literature was within 15 % for d-limonene and 40 % for ethyl acetate. (see Appendix C)

3-2-5. Dynamic Purge and Trap / Thermal Desorption Procedure

Once the operational parameters of gas flow rates, temperature, and vapor pressure became stable, the permeation tests were started. After introducing permeant gas into the high concentration cell, the switching valve was activated and the system was operated in the bypass mode. In conducting a permeability run, the test film is initially exposed under isostatic conditions for a period of 72 hours at the required test temperature and vapor pressure, during which time it is assumed that a concentration gradient is established within the film and a steady state transmission rate is attained. Following exposure of the film for a 72 hour period, the level of sorbant accumulated in the sorption tube for a predetermined time interval was determined. For high barrier film like Al₂O₃-coated PET film, a long trapping time was employed (3 hours for d-limonene, and 1 hour for ethyl acetate). The sorbant tube was then removed and replaced by a new trapping tube and permeated vapor again accumulated for quantification. Sampling of the trapping tube was conducted at least twice a day.

The sorbant tube removed from the permeability test system was then immediately transferred to a thermal desoption unit (Dynatherm 890/891 (Dynatherm, Kelton PA)), which thermally desorbs any organic volatiles from the sorbant tube and transfers them to the gas chromatograph for quantification. The sorbed volatiles were desorbed by heating for 8 minutes at 370 °C, with the valve and transfer line held at 250 °C to maintain the desorbed compounds in the vapor phase, while being transferred to the GC. Helium was used as a carrier gas through the thermal desorption unit, at a flow rate of 9 ml/min for 40 psi. After sample desorption, the sorbant tubes were conditioned at 350 °C for 30 minutes to re-use. The trapping and subsequent thermal desorption of volatiles allows their effective release, undiluted, and allows monitoring of otherwise undetectable levels of permeant concentration.

This procedure was repeated for at least 3 continuous days. The results of the detection levels were then compared, to insure the system was at steady state.

After each test run, the permeation cell, switching valve and bypass line of the MAS2000TM were heated for at least 3 days at 100 °C to desorb up any residual volatiles in the system.

3-2-6. Analysis of Test Permeant by Thermal Desorption / Gas Chromatography Procedure

GC analysis was carried out with a Hewlett-Packard Model 5890 gas chromatograph, equipped with a flame ionization detector and interfaced to a Hewlett-Packard Model 3395 integrator, for quantification of permeated vapor. The GC condition were the same as that for determining the calibration curve. The permeance was determined by substitution into the following equation.

$$R = \frac{CF \times AU}{t \times A \times \Delta p}$$
 Eq. 3-9

where;

R = permeance (kg/sec.m².Pa) AU = area unit response from integrator (AU) A = exposed area of the film CF = calibration factor for dynamic purge and trap/thermal desorption (g/AU) t = trapping time (sec) Δp = vapor pressure gradient (Pa)

3-2-7. Analysis of Ceramic Coating Surface by Optical Microscopy

Optical microscopic observations were conducted on the ceramic coating surface to investigate the effect of physical abuse on the integrity of the ceramic coatings, by using an optical microscope (Olympus BH-2 (Olympus Optical Co., Ltd., Tokyo, Japan)). Specimens ($1 \times 2 \text{ cm}$ in size) were cut from the center of the abused film. The samples were mounted with the ceramic coating surface in contact with the glass microscope slide, with light transmission from the underside. Photographs of the ceramic coating surface were taken with Polaroid 52 PolaPan 4 x 5 instant sheet film at 200 and 500 times magnifications.

Chapter 4

RESULTS and DISCUSSIONS

4-1. Estimation of the Detection Sensitivity Limit

The lowest detection limit for the dynamic purge and trap / thermal desorption procedure depends upon the trapping time and the gas chromatographic output signal from the permeant. Applying the dynamic purge and trap / thermal desorption procedure, the lowest signal output from the gas chromatograph was assumed to be around 5,000 area units. In this study, the longest trapping time was 3 hours for d-limonene. Thus, the minimum measurable transmission rate of d-limonene was calculated as follows;

$$\frac{5000AU}{3hr} \times \frac{2.07 \times 10^{-14}g}{AU} = 3.45 \times 10^{-11} \frac{g}{hr} = 9.58 \times 10^{-18} \frac{kg}{sec}$$

. .

The 2.07×10^{-14} g/AU value is the calibration factor for d-limonene, determined by the thermal desorption procedure (Appendix B).

According to previous studies, the minimum measurable transmission rate estimated by operating the MAS2000TM Organic Permeation Detection System in the isostatic mode was 6.86×10^{-14} kg/sec (Laoharavee, 1997). Therefore, the dynamic purge and trap / thermal desorption procedure has a sensitivity 4 orders of magnitude greater than that of the original isostatic procedure.

4-2. Time to Reach Steady State

When the permeation behavior of a gas through a film reaches an equilibrium state, the permeability rate also attains an equilibrium state, which is called the steady state. For conducting typical permeability measurement, Al_2O_3 -coated PET film was initially exposed under isostatic conditions for a period of 72 hours, and then the sorption tube was set to accumulate the penetrants (see Section 3-2-5). The transmission rate was assumed to reach steady state within 72 hours.

In order to verify this assumption, the permeability measurements were conducted at intermediate time periods (less than 72 hours), and the transmission profiles were obtained (Figure 4-1 for d-limonene and ethyl acetate, and Figure 4-2 for water vapor). Utilizing these profiles the time to reach steady state was determined. The results are summarized in Table 4-1.

	Time (hours)
d-Limonene	12*
Ethyl Acetate	20*
Water	38**
* 1 (0.0	

Table 4-1 Time to reach steady state of permeation

* measured at 60 °C

** measured at 37.8 °C

These results indicate that the conditioning period (72 hours) is sufficient to reach steady state transmission rate for these permeant-film systems. Unfortunately, because of the relatively slow permeation behavior and the nature of the purge-trap



Figure 4-1 Transmission profile of d-limonene and ethyl acetate through Al₂O₃-Coated PET Film





system, the diffusion coefficient (D) could not be estimated from these graphs. However, the trend of diffusivity at 60 °C can be expressed in a qualitative manner as:

4-3. Comparison of Permeability of Non-Abused Films

4-3-1. Comparison by Permeants

The permeability of Al_2O_3 -coated PET film (Table 4-2, Figure 4-3), Al_2O_3 coated PET-LLDPE laminated films (Table 4-3, Figure 4-4), and PET (Table 4-4, Figure 4-5), using d-limonene, ethyl acetate, oxygen, and water vapor, were measured. Table 4-5 and Figure 4-6 summarize the permeance values for these respective permeants through the Al_2O_3 -coated PET film.

For d-limonene, ethyl acetate, and oxygen as permeants, the improvement in barrier properties are significant when comparing PET to Al_2O_3 -coated PET. For water vapor, however, the improvements are limited.

		Permeance (kg/m ² .sec.Pa)			
	Oxygen ^(c)	Water ^(d)	d-Limonene ^(e)	Ethyl Acetate ^(f)	
Al ₂ O ₃ PET	1.09 x 10 ⁻¹⁷	7.62×10^{-13}	5.78×10^{-17}	1.21×10^{-16}	
Std.Dev.	2.49×10^{-18}	1.25×10^{-13}	3.23×10^{-17}	8.41×10^{-18}	

Table 4-2 Permeability of Al_2O_3 -coated PET (12µm) to various permeants ^{(a) (b)}

(a) All values are average of replicate runs.

(b) All values were obtained after 72 hours sample conditioning.

(c) Measured at 23 °C (cell temp.),101.3 kPa (vapor pressure).

(d) Measured at 37.8 °C (cell temp.), 6.2 kPa (vapor pressure).

(e) Measured at 60 °C (cell temp.), 0.15 kPa (vapor pressure).

(f) Measured at 60 °C (cell temp.), 2.7 kPa (vapor pressure).



Figure 4-3 Permeability of Al₂O₃-coated PET (12µm) to various permeants

	Permeance (kg/m ² .sec.Pa)			
	Oxygen ^(c)	Water ^(d)	d-Limonene ^(e)	Ethyl Acetate ^(f)
Al ₂ O ₃ PET / LLDPE	1.14 x 10 ⁻¹⁷	5.87 x 10 ⁻¹³	1.11×10^{-16}	5.96 x 10 ⁻¹⁷
Std.Dev.	2.82×10^{-18}	1.22×10^{-13}	1.05×10^{-17}	6.44 x 10 ⁻¹⁹

Table 4-3 Permeability of Al₂O₃-coated PET (12µm) / LLDPE (40µm)

to various permeants (a) (b)

(a) All values are average of replicate runs.

(b) All values were obtained after 72 hours sample conditioning.

(c) Measured at 23 °C (cell temp.), 101.3 kPa (vapor pressure).

(d) Measured at 37.8 °C (cell temp.), 6.2 kPa (vapor pressure).

(e) Measured at 60 °C (cell temp.), 0.15 kPa (vapor pressure).

(f) Measured at 60 °C (cell temp.), 2.7 kPa (vapor pressure).



Figure 4-4 Permeability of Al₂O₃-coated PET (12µm) / LLDPE (40µm) to various permeants
		Permeance (kg/m ² .sec.Pa)						
	Oxygen ^(c)	Water ^(d)	d-Limonene ^(e)	Ethyl Acetate ^(f)				
PET	2.52×10^{-14}	9.27 x 10 ⁻¹¹	2.36×10^{-14}	2.98×10^{-14}				
Std.Dev.	7.47×10^{-16}	1.23×10^{-12}	5.03×10^{-15}	4.02×10^{-15}				

Table 4-4 Permeability of PET (12µm) to various permeants ^{(a) (b)}

(b) All values were obtained after 72 hours sample conditioning.

(c) Measured at 23 °C (cell temp.),101.3 kPa (vapor pressure).

(d) Measured at 37.8 °C (cell temp.), 6.2 kPa (vapor pressure).

(e) Measured at 60 °C (cell temp.), 0.15 kPa (vapor pressure).

(f) Measured at 60 °C (cell temp.), 2.7 kPa (vapor pressure).



Figure 4-5 Permeability of PET (12µm) to various permeants

Table 4-5 Permeability comparison between Al₂O₃ PET (12µm)

and non-coated PET (12µm)

	Permeance (kg/m ² .sec.Pa)					
	Oxygen ^(a)	Water ^(b)	Water ^(b) d-Limonene ^(c) Et			
Al ₂ O ₃ PET	1.09 x 10 ⁻¹⁷	7.62×10^{-13}	5.78 x 10 ⁻¹⁷	1.21 x 10 ⁻¹⁶		
PET	2.52×10^{-14}	9.27 x 10 ⁻¹¹	2.36×10^{-14}	2.98×10^{-14}		

(a) Measured at 23 °C (cell temp.),101.3 kPa (vapor pressure).

(b) Measured at 37.8 $^{\circ}$ C (cell temp.), 6.2 kPa (vapor pressure).

(c) Measured at 60 °C (cell temp.), 0.15 kPa (vapor pressure).

(d) Measured at 60 °C (cell temp.), 2.7 kPa (vapor pressure).



Figure 4-6 Permeability comparison between Al₂O₃ PET (12µm) and and non-coated PET (12µm)

To provide a clear comparison between non-coated PET and Al_2O_3 -coated PET, the theoretical permeability of the PET-LLDPE laminated structure can be estimated by using the conventional equation below (Rogers, 1985):

$$\frac{l_{laminate}}{R_{laminate}} = \frac{l_{PET}}{R_{PET}} + \frac{l_{LLDPE}}{R_{LLDPE}}$$
Eq. 4-1

where; $l_{laminate}$, l_{PET} , and l_{LLDPE} are the thickness of the laminate structure, PET and LLDPE, respectively. $R_{laminate}$, R_{PET} , and R_{LLDPE} are the permeance of the laminate structure, PET and LLDPE, respectively.

Table 4-6 and Figure 4-7 summarize the permeance values for these permeants through Al₂O₃-coated PET / LLDPE laminated films. Because of the higher permeation rate of LLDPE to d-limonene, the contribution of the LLDPE layer was minimized. For ethyl acetate and water vapor, however, the LLDPE layer reduced the overall permeability of the laminated structures.

Because of apparatus limitations, the temperatures of test were varied. However, the permeance values were standardized at a constant temperature (60 $^{\circ}$ C), utilizing the equation below (Rogers, 1985):

$$R_2 = R_1 \times e^{\frac{E_R}{R}(\frac{1}{T_1} - \frac{1}{T_2})}$$
 Eq. 4-2

where R_1 and R_2 are permeance at temperature 1 (T_1) and temperature 2 (T_2), respectively. E_R is an activation energy (for oxygen 9.72 kcal/mole, for water vapor 39.92 kcal/mole (see Section 4-4)), and R is a gas constant. Table 4-7 shows a comparison of

	Permeance (kg/m ² .sec.Pa)						
	Oxygen ^(a)	Water ^(b)	d-Limonene (c)	Ethyl Acetate ^(d)			
Al ₂ O ₃ PET / LLDPE	1.14 x 10 ⁻¹⁷	4.12×10^{-13}	1.11 x 10 ⁻¹⁶	2.45 x 10-17			
LLDPE	$6.52 \times 10^{-13} (e)$	3.00×10^{-11} (f)	2.93 x 10 ^{-9 (g)}	7.75×10^{-11} (h)			
PET/LLDPE ⁽ⁱ⁾	9.65 x 10 ⁻¹⁴	3.55×10^{-11}	1.02×10^{-13}	1.29 x 10 ⁻¹³			

Table 4-6 Permeability comparison between Al₂O₃ PET (12μm) / LLDPE (40μm) and non-coated PET (12μm) / LLDPE (40μm)

(a) Measured at 23 °C (cell temp.),101.3 kPa (vapor pressure).

(b) Measured at 37.8 °C (cell temp.), 6.2 kPa (vapor pressure).

(c) Measured at 60 °C (cell temp.), 0.15 kPa (vapor pressure).

(d) Measured at 60 °C (cell temp.), 2.7 kPa (vapor pressure).

(e) Measured at 24.8 °C (cell temp.), 101.3 kPa (vapor pressure) (Tocelo 1995).

(f) Measured at 37.8 °C (cell temp.), 6.2 kPa (vapor pressure) (Tocelo 1995).

(g) Measured at 45 °C (cell temp.) (Kobayashi 1995).

(h) Measured at 22 °C (cell temp.), 4.11 kPa (vapor pressure) (Barr 1997).

(i) Caluculated by conventional equation (eq. 4-1).



Figure 4-7 Permeability comparison between Al₂O₃ PET (12µm) / LLDPE (40µm) and non-coated PET (12µm) / LLDPE (40µm)

the standardized permeability. The trend of permeability performance through Al_2O_3 -

coated PET film at 60 °C for the respective permeants can be expressed qualitatively as:

(lowest) d-Limonene $< O_2 \le$ Ethyl Acetate $<< H_2O$ (highest).

Table 4-7 Calculated permeance at 60 °C through Al₂O₃-coated PET (12 µm)

	Permeance (kg/m ² .sec.Pa)						
	Oxygen	Water d-Limonene Ethyl A					
Al ₂ O ₃ PET	8.08 x 10 ⁻¹⁷	5.67 x 10 ⁻¹¹	5.78 x 10 ⁻¹⁷	1.21 x 10 ⁻¹⁶			

4-3-2. Comparison of Ceramic Coatings

Two different ceramic-coated PET films were evaluated for both the d-limonene and ethyl acetate permeability. The results are summarized in Table 4-8. and presented graphically in Figure 4-8.

The results showed that even though the ceramic matrices are different, their permeability characteristics were quite similar. These results suggest that the mechanism for mass transfer through both Al_2O_3 -coated PET and SiO_x -coated PET films was similar.

	Permeance (R); $(kg/m^2 \text{ sec. Pa x } 10^{-17})$						
	d-Lim	onene ^(c)	Ethyl Acetate (d)				
	Al ₂ O ₃ PET	SiO _x PET	Al ₂ O ₃ PET	SiO _x PET			
Ave.	5.78	10.20	12.06	12.96			
Std.Dev.	3.23	6.65	0.84	1.86			

Table 4-8 Permeability comparison of ceramic coatings (a) (b)

(b) All values were obtained after 72 hours sample conditioning.

(c) Measured at 60 °C (cell temp.), 0.15 kPa (vapor pressure).

(d) Measured at 60 °C (cell temp.), 2.67 kPa (vapor pressure).



Figure 4-8 Permeability comparison of ceramic coatings

4-4. Dependency of Permeability on Temperature

The effect of test temperature on the organic vapor (d-limonene and ethyl acetate) permeability of Al_2O_3 -coated PET film was evaluated at five permeation cell temperature levels. The results are summarized in Table 4-9 and shown graphically in Figure 4-9 for d-limonene and in Table 4-10 and Figure 4-10 for ethyl acetate.

The results show there was a slight increase in the permeation rates as a function of temperature from 55 to 70 °C in both the d-limonene and ethyl acetate systems. As shown, the permeation rates then increased markedly, this was observed for both systems at around 75 °C, which is the T_g of PET.

Utilizing these permeance values and equation (Eq. 3-2), the activation energy (E_R) was calculated for both the d-limonene (Figure 4-11) and ethyl acetate (Figure 4-12) systems, below T_g . For comparison, E_R values for the oxygen and water vapor permeability of Al₂O₃-coated PET film were also calculated by using literature data (Imai, 1998). A comparison of Arrhenius plots is shown in Figure 4-13. Table 4-11 and Figure 4-14 summarize the activation energy of these permeants through Al₂O₃-coated PET film, below T_g .

For d-limonene, ethyl acetate and oxygen, the E_R values are relatively small, which suggests that the permeation process through Al_2O_3 -coated PET film is not affected much by changing temperature, below the T_g of PET. On the other hand, E_R of water vapor is much higher than the other permeants. This behavior agrees with the Table 4-9

Temperature effect on the permeability of the Al_2O_3 PET / d-limonene system ^{(a). (b), (c)} (Permeance (R) (kg/m².sec.Pa x 10⁻¹⁷))

	Temperature (°C)								
	55	60	65	70	75	80			
Ave.	4.81	5.62	7.34	8.34	24.53	47.47			
Std.Dev.	0.88	1.62	0.60	1.14	2.17	12.65			

(a) All values are average of replicate runs.

(b) All values were obtained after 72 hours sample conditioning.

(c) Measured at 60 °C (cell temp.), 0.15 kPa (vapor pressure).



Figure 4-9 Temperature effect on the permeability of the Al₂O₃ PET / d-limonene system

Table 4-10

Temperature effect on the permeability of the Al2O3 PET / ethyl acetate system $^{(a), (b), (c)}$

	Temperature (°C)							
	55	60	65	70	75	80		
Ave.	1.12	1.21	1.25	1.27	1.95	2.09		
Std.Dev.	0.22	0.08	0.13	0.10	0.37	0.04		

(Permeance $(kg/m^2.sec.Pa \times 10^{-16})$)

(a) All values are average of replicate runs.

(b) All values were obtained after 72 hours sample conditioning.

(c) Measured at 60 °C (cell temp.), 2.7 kPa (vapor pressure).



Figure 4-10 Temperature effect on the permeability of the Al₂O₃ PET / ethyl acetate system



Figure 4-11 Arrhenius plot for the permeance of the Al₂O₃ PET / d-limonene system



Figure 4-12 Arrhenius plot for the permeance of the Al₂O₃ PET / ethyl acetate system



Figure 4-13 Comparison of Arrhenius plots of various permeants through Al₂O₃ PET

	E _R
	kcal/mol
Oxygen	9.72
Water Vapor	39.92
d-Limonene	19.66
Ethyl Acetate	4.25

Table 4-11 Comparison of activation energy for the permeation process through Al₂O₃ PET using various permeants



Figure 4-14 Comparison of activation energy for the permeation process through Al₂O₃ PET using various permeants

significant difference observed between the water vapor permeability and that of the other permeants (d-limonene, ethyl acetate and oxygen). These facts imply that the permeation mechanism (or factors effecting permeation) for water vapor and the other permeants may differ.

4-5. Permeant Factors Affecting Permeation

The mechanism of permeation of gases and vapors through ceramic-coated films is not well known. Two different mechanisms, however, have been proposed to explain the permeation process (see Section 2-3-4). The basic concept of both mechanisms is the "defects leading permeation" model, where defects in the ceramic coating result in permeation of gas or vapor. Since defects may provide the driving force for the permeation through ceramic-coated films, interactions between the defects and the penetrants may effect the mass transfer process.

4-5-1. Permeant Size

Permeant size is, therefore, a major factor effecting the permeability of gases or vapors through Al_2O_3 -coated PET film. Hence the dimensions of the permeants were estimated from atomic radii and bond lengths (Appendix D). These figures represent the smallest cross sectional area of the permeants. Table 4-12 summarized the calculated dimensions of the permeants.

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	Dimensions							
		(10^{-10} m)	10^{-20} m^2					
	w *	wxh	h x d					
Oxygen	2.71	1.48	1.48	4.01	2.19			
Water	2.17	1.64	1.48	3.56	2.43			
d-Limonene	8.73	4.68	4.61	40.86	21.57			
Ethyl Acetate	7.32	3.88	2.53	28 .40	9.82			

Table 4-12 Dimensions of the permeants.

* Longest axis of the permeant

** Second longest axis of the permeant

*** Shortest axis of the permeant

The effect of permeant size was discussed in Section 2-4-1 and as pointed out the smallest cross-sectional area of a permeant may be the crucial factor in determining the effect of penetrant size on permeability. In this study, the same concept was employed and the smallest cross sectional area ($h \times d$) was calculated.

In an attempt to determine a relationship between the size of the permeant and permeability, the smallest cross sectional area was plotted as a function of the log of the permeance for the respective test penetrants (Figure 4-15).

This plot shows no linear relationship between size of permeants and the log of the permeance. Water vapor had a significantly higher permeance value, relative to its size, as compared to the other permeants evaluated. Guttman (1990) suggested water vapor may have a different diffusion mechanism in SiO_x-layer (see Section 4-6-2). The same mechanism may be operating in the Al₂O₃-coated PET film / water vapor system.



Figure 4-15 Relationship between permeability and permeant size

4-5-2. Polarity of Permeant

Another possible contributing factor is the polarity of the permeants. Dielectric constant (ϵ) values can be used to represent the polarity of gases or vapors. Table 4-13 summarizes the dielectric constants for each permeant.

:	ε
Oxygen	1.51
Water	80.37
d-Limonene	2.30
Ethyl Acetate	6.02

Table 4-13 Dielectric constant of permeants (CRC, 1987)

The order is shown below:

(low)
$$O_2 < d$$
-Limonene $<$ Ethyl Acetate $<< H_2O$ (high).

In order to evaluate the relationship between the polarity of the permeant and permeability, permeance values were plotted as a function of permeant dielectric constant (Figure 4-16). This plot shows relatively proportionate relationship between polarity of permeant and permeability. However, because of the broad range of dielectric constant values for the permeants evaluated (from 1.5 (oxygen) to 80.37 (water)), it is difficult to establish a precise relationship without determining the permeability values for a series of other permeants, representing the full range of dielectric constants





4-5-3. Combined Factor by Size and Polarity

The permeation mechanism of gases or vapors through Al_2O_3 -coated PET film is assumed to have complicated process. Therefore, the factors effected the mass transfer mechanism may also be interrelated.

In this study, an attempt to establish a relationship between permeance and permeant characteristics, the reciprocal of the smallest cross-sectional area and dielectric constant were combined, which lead to a new factor ($\varepsilon x (h x d)^{-1}$) (Table 4-14).

	$\varepsilon x (h x d)^{-1}$
	$(m^{-2} \times 10^{20})$
Oxygen	0.69
Water	33.11
d-Limonene	0.11
Ethyl Acetate	0.56

Table 4-14 Combined factor (size and polarity) of permeants.

The order of the combined factors is shown below;

(small) d-Limonene < Ethyl Acetate $\leq O_2 \ll H_2O$ (large).

In order to make a clear comparison, Table 4-15 summarizes the order of permeability and possible permeability deciding factors. The permeability and combined factor showed similar trends, while the size and polarity factor does not show good agreement with the permeability trend.

Permeability	low	Limo	<	O ₂	≤	EA	<<	H ₂ 0	high
Size	large	Limo	>>	EA	>>	H ₂ 0	>	O ₂	small
Polarity	low	O ₂	<	Limo	<	EA	<<	H ₂ 0	high
Size x Polarity	large x low	Limo	<	EA	5	O ₂	<<	H ₂ 0	small x high

Table 4-15 Comparison of the various trends related to permeability.

O₂, Oxygen; H₂O, Water; Limo, d-Limonene; EA, Ethyl Acetate

In Figure 4-17, permeance is plotted as a function of the combined factor. The plot suggests a linear relationship between permeance and the combined factor. However, additional data is necessary, over the entire range of combined factor values, to establish such a linear relationship.

The permeant parameters effecting to permeability may not so simple. However, this introduced factor ($\epsilon x (h x d)^{-1}$) can be used for simple estimation of gases or vapors permeability of Al₂O₃-coated PET film.





4-6. Permeation Mechanism for Non-Abused Films

In order to better understand the permeability behavior of gases or vapors through Al_2O_3 -coated PET film, a simple model is proposed.

4-6-1. Permeation through Defects

Before the modified model is mentioned, a general model (defect leading permeation model) of gas permeation through ceramic-coated films is described below.

The ceramic coating layer may have some micro defects (matrix irregularities) or macro defects (pinholes) by nature. When permeants are supplied, the permeants start to diffuse through the substrate (i.e., PET). After a certain time period, the diffusion reaches an equilibrium state or steady state, and a concentration gradient of the permeant is established within the substrate. Thus, the permeation behavior through defects in the ceramic coating layer will be dependent upon the permeant concentration gradient, permeant characteristics (e.g., size, shape, polarity), and the status of the defects. Figure 4-18 shows a schematic representation of this concept.



Figure 4-18 Defect leading permeation model

4-6-2. Generation of Attractive Defects

Guttman (1990) introduced a model of water vapor permeation through SiO_x layer. He suggested that hydrolysis of the Si-O-Si bond created a pathway for water vapor diffusion through the SiO_x -layer.

In this study, the Guttman (1990) model was applied with the defect leading permeation model, and it lead to a new complex model with the following proposed hypothesis. The hypothesis is: "Water vapor in the atmosphere reacts with Al_2O_3 around the defects, and the defects then become a hydrophilic regions (or polar attractive defects)". The hydrophilic regions can attract polar molecules and may promote increased permeability. This hypothesis (Attractive Defects (AD) model) is schematically shown in Figure 4-19.

4-6-3. Al₂O₃-Coated PET Film

For non-polar permeants, the contribution of attractive defects to increased permeability may be minimized. Moreover, the defects can even obstruct the permeation of non-polar permeants, because the reaction with water vapor may decrease the diameter of the defects. Thus, for non-polar permeants permeability of Al_2O_3 -coated PET film can be expected to be very low (excellent).

For polar permeants, the contribution of attractive defects can be significant. Polar permeants may be attracted to the defects, and the resulting permeability of polar

Mechanism of attractive region generation



Barrier mechanism





permeants through Al_2O_3 -coated PET film can be expected to be significantly higher than that of non-polar permeant.

4-6-4. Al₂O₃-Coated PET / LLDPE Laminated Films

The AD model can apply not only to Al_2O_3 -coated PET film but also Al_2O_3 coated PET / LLDPE laminated films and was fit to the permeability data obtained (Tables 4-5,6 and Figures 4-6,7). Figure 4-20 and 4-21 show schematic expressions for non-polar and polar permeant, respectively.

For non-polar permeants, since LLDPE and the permeants have the same nonpolar nature, the contribution of LLDPE to the permeant barrier is minimized. Therefore, for non-polar permeants (d-limonene and oxygen) permeability of Al_2O_3 -coated PET film and Al_2O_3 -coated PET / LLDPE laminated films may be quite similar.

On the other hand, for polar permeants, the contribution of LLDPE to the permeant barrier may be significant. Therefore, improvements in barrier properties for polar permeants (ethyl acetate and water vapor) can be expected.



Figure 4-20 Barrier mechanism for non-polar permeants through Al2O3 PET



Figure 4-21 Barrier mechanism for polar permeants through Al2O3 PET

4-7. Effect of Physical Damage

Packages meet with various types of physical damage during the packing and distributing processes. In order to simulate this physical damage, Gelbo flex tests were conducted, and the permeability of related gases and vapors was measured through the abused films.

4-7-1. Non-Polar Permeants Permeability

Table 4-16 and Figure 4-22 show the effect of physical damage on oxygen permeability of Al_2O_3 -coated PET film and Al_2O_3 -coated PET/LLDPE laminated films. Significant (greater than 10 times) deterioration in barrier characteristics occurred in both Al_2O_3 -coated PET film and Al_2O_3 -coated PET/LLDPE laminated films after 10 flexures. Catastrophic (greater than 50 times) deterioration in barrier properties occurred in both Al_2O_3 -coated PET film and Al_2O_3 -coated PET/LLDPE laminated films, at less than 100 flexures.

Similar behavior was observed for d-limonene permeability of Al₂O₃-coated PET film and Al₂O₃-coated PET/LLDPE laminated films systems (Table 4-17 and Figure 4-23). Significant deterioration occurred at less than 100 flexures, and catastrophic deterioration occurred at less than 150 flexures for the Al₂O₃-coated PET film and less than 200 flexures for the Al₂O₃-coated PET/LLDPE laminated films.

Sample	Flexing Cycle					
	0	10	100	150	200	
Al ₂ O ₃ PET	1.14 x 10 ⁻¹⁷	7.34 x 10 ⁻¹⁶	1.06 x 10 ⁻¹⁵	1.14 x 10 ⁻¹⁵	2.38×10^{-14} (d)	
Al ₂ O ₃ PET / LLDPE	8.15 x 10 ⁻¹⁸	3.28×10^{-16}	1.12×10^{-15}			

Table 4-16 Flex Resistance for oxygen permeability (permeance (kg/m².sec.Pa)) of Al₂O₃ PET and Al₂O₃ PET / LLDPE ^{(a), (b), (c)}

(b) All values were obtained after 72 hours sample conditioning.

(c) Measured at 23.0 °C (cell temp.), 101.3 kPa (vapor pressure).

(d) Measuring limitation (Some results showed "Not Dated")



Figure 4-22 Flex resistance for oxygen permeability (permeance (kg/m².sec.Pa)) of Al₂O₃ PET and Al₂O₃ PET / LLDPE

Sample	Flexing Cycle						
	0	10	100	150	200		
Al ₂ O ₃ PET	5.78 x 10 ⁻¹⁴	2.10×10^{-16}	1.10×10^{-15}	4.45 x 10 ⁻¹⁵	3.35×10^{-12}		
Al ₂ O ₃ PET / LLDPE	5.21×10^{-17}	1.20×10^{-16}	8.21×10^{-16}		1.25×10^{-13}		

Table 4-17 Flex resistance for d-limonene permeability (permeance (kg/m2.sec.Pa)) of Al₂O₃ PET and Al₂O₃ PET / LLDPE ^{(a), (b), (c)}

(b) All values were obtained after 72 hours sample conditioning.

(c) Measured at 60 °C (cell temp.), 0.15 kPa (vapor pressure).



Figure 4-23 Flex resistance for d-limonene permeability (permeance (kg/m2.sec.Pa)) of Al₂O₃ PET and Al₂O₃ PET / LLDPE

These results indicate that new defects (possibly pinholes) were created in the Al_2O_3 coating layer by flexing abuse on both Al_2O_3 -coated PET film and Al_2O_3 -coated PET/LLDPE laminated films.

4-7-2. Polar Permeants Permeability

In contrast, for water vapor (Table 4-18 and Figure 4-24) or ethyl acetate (Table 4-19 and Figure 4-25), deterioration in barrier properties between Al_2O_3 -coated PET film and Al_2O_3 -coated PET/LLDPE laminated films appeared to be quite different.

For both water vapor and ethyl acetate, Al_2O_3 -coated PET film showed significant deterioration at less than 10 flexures and catastrophic deterioration at less than 200 flexures. However, no catastrophic deterioration was observed at over 200 flexures for both water vapor and ethyl acetate permeation through Al_2O_3 -coated PET / LLDPE laminated films.

These results are summarized in Tables 4-20 to 4-23 and Figure 4-26 to 4-29. Permeability comparisons for Al_2O_3 -coated PET film are shown in Table 4-20 and Figure 4-26. For Al_2O_3 -coated PET / LLDPE laminated films, permeability comparisons are shown in Table 4-21 and Figure 4-27. In order to make clear comparisons, Table 4-22 and Figure 4-28 indicate deterioration rates for Al_2O_3 -coated PET film compared to non-abused film. Also, Table 4-23 and Figure 4-29 indicate deterioration rates for Al_2O_3 -coated PET / LLDPE laminated films deterioration rates for Al_2O_3 -coated PET film compared to non-abused film.

Table 4-18 Flex resistance for water vapor permeability (permeance (kg/m².sec.Pa)) of Al₂O₃ PET and Al₂O₃ PET / LLDPE ^{(a), (b), (c)}

Sample	Flexing Cycle						
	0	10	100	150	200		
Al ₂ O ₃ PET	6.56×10^{-13}	8.28 x 10 ⁻¹²	1.63 x 10 ⁻¹¹	1.99x 10 ⁻¹¹	2.25 x 10 ^{-10 (d)}		
Al ₂ O ₃ PET / LLDPE	4.68×10^{-13}	5.81 x 10 ⁻¹³	1.12 x 10 ⁻¹²	1.31×10^{-12}	1.12×10^{-12}		

(b) All values were obtained after 72 hours sample conditioning.

(c) Measured at 37.8 °C (cell temp.), 6.2 kPa (vapor pressure).

(d) Measuring limitation (Some results showed "Not Dated")



Figure 4-24 Flex resistance for water vapor permeability (permeance (kg/m².sec.Pa)) of Al₂O₃ PET and Al₂O₃ PET / LLDPE

Table 4-19 Flex resistance for ethyl acetate permeability (permeance (kg/m².sec.Pa)) of Al₂O₃ PET and Al₂O₃ PET / LLDPE ^{(a), (b), (c)}

Sample	Flexing Cycle						
	0	10 100		150	200		
Al ₂ O ₃ PET	1.20x 10 ⁻¹⁶	2.57×10^{-15}	2.35×10^{-15}	1.48×10^{-14}	3.14×10^{-14}		
Al ₂ O ₃ PET / LLDPE	5.96 x 10 ⁻¹⁷	7.52 x 10 ⁻¹⁶	8.15 x 10 ⁻¹⁶		6.43 x 10 ⁻¹⁶		

(b) All values were obtained after 72 hours sample conditioning.

(c) Measured at 60 °C (cell temp.), 2.7 kPa (vapor pressure).



Figure 4-25 Flex resistance for ethyl scetate permeability (permeance (kg/m².sec.Pa)) of Al₂O₃ PET and Al₂O₃ PET / LLDPE

Table 4-20 Permeability (Permeance (kg/m².sec.Pa)) comparison of abused Al₂O₃ PET films using various permeants

Permeant	Flex cycles						
	0 10 100 150 200						
Oxygen ^(a)	1.14×10^{-17}	7.34 x 10 ⁻¹⁶	1.06 x 10 ⁻¹⁵	1.14×10^{-15}	2.38×10^{-14} (e)		
Water ^(b)	6.56×10^{-13}	8.28×10^{-12}	1.63 x 10 ⁻¹¹	1.99x 10 ⁻¹¹	2.25×10^{-10} (e)		
d-Limonene ^(c)	5.78 x 10 ⁻¹⁴	2.10×10^{-16}	1.10 x 10 ⁻¹⁵	4.45 x 10 ⁻¹⁵	3.35×10^{-12}		
Ethyl Acetate ^(d)	1.20x 10 ⁻¹⁶	2.57×10^{-15}	2.35×10^{-15}	1.48×10^{-14}	3.14×10^{-14}		

(comparison based on permeance)

(a) Measured at 24.8 °C (cell temp.), 101.3 kPa (vapor pressure).

(b) Measured at 37.8 °C (cell temp.), 6.2 kPa (vapor pressure).

(c) Measured at 60 °C (cell temp.), 0.15 kPa (vapor pressure).

(d) Measured at 60 °C (cell temp.), 2.7 kPa (vapor pressure).

(e) Measuring limitation (Some results showed "Not Dated")



Figure 4-26 Permeability comparison of abused Al₂O₃ PET films using various permeants (comparison based on permeance)

Table 4-21 Permeability (Permeance (kg/m².sec.Pa)) comparison of abusedAl2O3 PET / LLDPE films using various permeants

Permeant	Flex cycles						
	0	10	100	150	200		
Oxygen ^(a)	8.15 x 10 ⁻¹⁸	3.28 x 10 ⁻¹⁶	1.12 x 10 ⁻¹⁵				
Water ^(b)	4.68 x 10 ⁻¹³	5.81 x 10 ⁻¹³	1.12×10^{-12}	1.31 x 10 ⁻¹²	1.12×10^{-12}		
d-Limonene ^(c)	5.21 x 10 ⁻¹⁷	1.20 x 10 ⁻¹⁶	8.21 x 10 ⁻¹⁶		1.25 x 10 ⁻¹³		
Ethyl Acetate ^(d)	5.96 x 10 ⁻¹⁷	7.52 x 10 ⁻¹⁶	8.15 x 10 ⁻¹⁶		6.43 x 10 ⁻¹⁶		

(comparison based on permeance)

(a) Measured at 24.8 °C (cell temp.), 101.3 kPa (vapor pressure).

(b) Measured at 37.8 °C (cell temp.), 6.2 kPa (vapor pressure).

(c) Measured at 60 °C (cell temp.), 0.15 kPa (vapor pressure).

(d) Measured at 60 °C (cell temp.), 2.7 kPa (vapor pressure).





Table 4-22 Permeability (permeance (kg/m².sec.Pa)) comparison of abused

11 O D		•	•	
	h l tilme	nsing v	anous	nermeants
112031		using v	anous	permeants

Permeant	Flex cycles					
	0	10	100	150	200	
Oxygen	1	64	93	100	2086 ^(a)	
Water	1	13	25	30	343 ^(a)	
d-Limonene	1	4	19	72	57899	
Ethyl Acetate	1	22	20	124	263	

(comparison based on deterioration rate ($R_{(abused film)} / R_{(non-abused film)}$))

(a) Measuring limitation (Some results showed more deterioration)




Table 4-23 Permeability (permeance (kg/m².sec.Pa)) comparison of abused Al₂O₃ PET / LLDPE films using various permeants

Permeant	Flex cycles				
	0	10	100	150	200
Oxygen	1	40	137		
Water	1	1	2	3	2
d-Limonene	1	2	16		2396
Ethyl Acetate	1	13	14		11

(comparison based on deterioration rate $(R_{(abused film)} / R_{(non-abused film)})$)





(comparison based on deterioration rate $(R_{(abused film)} / R_{(non-abused film)})$)

These comparisons indicate that deterioration of barrier characteristics for Al_2O_3 coated PET film occurred similarly for both non-polar and polar permeants. However, for the Al_2O_3 -coated PET / LLDPE laminated films, significant loss of barrier properties occurred only for the non-polar permeants. For polar permeants, the laminated structure plays a significant role in preventing deterioration by physical abuse, even though the abuse created new defects on the structures.

4-7-3. Microscopic Observations

Optical microscopic observations were recorded in order to identify morphological differences between the various degrees of abused Al_2O_3 -coated PET films. To make a clear comparison, the surface of a non-abused Al_2O_3 -coated PET film was observed (Figure 4-30). There was no cracks on the non-abused film surface.

The surface of the Al_2O_3 coating induced cracks after 10 flexures (Figure 4-31). After 100 flexures, propagation of the number of cracks was observed (Figure 4-32). After 200 flexures, scattered crystal-like particles were observed (Figure 4-33). These particles may be particles of Al_2O_3 coating peeling from the substrate.

These observations can explain the size dependency for the permeability on different permeants. After 10 flexures, permeability of abused films shows a trend of permeant size dependence (Table 4-22 and Figure 4-28). The barrier performance for smaller permeants (e.g., oxygen) tended to deteriorate significantly, at this point. With increasing flexing cycles, the trend of size dependence is reduced.



Magnification (x 200)



Magnification (x 500)





Magnification (x 500)







Figure 4-32 Surface observation for 100 times flexing Al2O3 PET







With light abuse (10 flexures), the width of cracks may be very small and cause size dependence. Under heavy abuse (200 flexures), the cracks may cause peel-off of Al_2O_3 particles from substrate, and the defects may no longer cause size dependence, because the defects are too large.

4-8. Permeation Mechanism for Abused Films

The same model (AD model) can be applied to both abused Al_2O_3 -coated PET film and Al_2O_3 -coated PET / LLDPE laminated films and was fit to the permeability data obtained (Tables 4-16 to 4-19 and Figures 4-22 to 4-25).

4-8-1. Al₂O₃-Coated PET Film

Figure 4-34 shows schematic expressions, for non-polar permeants through abused Al₂O₃-coated PET film. When the film was abused, new defects could be introduced in the Al₂O₃-layer, and the defects may react with water vapor in the atmosphere. This reaction can make polar attractive defects on the Al₂O₃ coatings. However, since the permeants have a non-polar nature, "attractive" or "non-attractive" defects may not cause significant permeability differences. Therefore, the non-polar permeants permeability of abused film can deteriorate proportionately simply with increasing numbers of pinholes.

The permeation model for polar permeants through abused Al_2O_3 -coated PET film is shown in Figure 4-35. New defects may turn into polar attractive defects on the







Figure 4-35 Barrier mechanism for polar permeants through Al2O3 PET (with Gelbo flexing)

 Al_2O_3 coatings in a manner similar to the non-polar permeants case. These defects may attract polar permeants. Therefore, the polar permeants permeability of abused film can also deteriorate proportionately simply with increasing numbers of pinholes.

4-8-2. Al₂O₃-Coated PET / LLDPE Laminated Films

Figure 4-36 shows a schematic diagram for the proposed mass transfer process, involving non-polar permeants through abused Al_2O_3 -coated PET / LLDPE laminated films. New defects could be introduced by physical damage, but they may not react with water vapor because the LLDPE layer can prevent the penetration of water vapor towards the new defects.

Even though the new defects could not result in attractive defects as defined above, the permeability of non-polar permeants through Al_2O_3 -coated PET / LLDPE laminated films may exhibit increases similar to those observed for the Al_2O_3 -coated PET film. As was discussed in Section 4-8-1, for non-polar permeants, "attractive" or "nonattractive" defects may not result in permeability differences. In addition, the contribution of the sealant layer (LLDPE) to the barrier properties would be minimized, since LLDPE has higher permeation rates for non-polar permeants. Therefore, the permeability of abused films to non-polar permeants may show little or no differences between Al_2O_3 -coated PET film and Al_2O_3 -coated PET / LLDPE laminated films.





The schematic diagram for the proposed mass transfer process of polar permeants through Al_2O_3 -coated PET / LLDPE laminated films is also shown in Figure 4-37. In this system, polar permeants may not be attracted by the non-attractive defects, and the contribution of the sealant layer to the barrier properties may be maximized, because LLDPE has good polar permeants barrier properties. Therefore, the permeability of the laminated films / polar permeant systems do not undergo catastrophic deterioration even under heavy physical damage. In other words, the permeability of abused films to polar permeants may be quite different between Al_2O_3 -coated PET film and Al_2O_3 -coated PET / LLDPE laminated films.





Chapter 5

SUMMARY and CONCLUSIONS

The permeability of Al_2O_3 -coated PET and SiO_x -coated PET films to organic vapors (d-limonene and ethyl acetate) was studied. Permeability data were generated utilizing the highly in sensitive dynamic purge and trap / thermal desorption procedure, with the MAS2000TM Permeation Test System. For both d-limonene and ethyl acetate, the permeability of Al_2O_3 -coated PET film was expectedly low.

A comparison of the permeability of Al₂O₃-coated PET film to a series of permeants (d-limonene, ethyl acetate, oxygen and water vapor) was made. In order to obtain the activation energy for the permeation processes, the temperature dependence of the permeability was also evaluated. Results from these studies showed that water vapor behaved significantly differently than the other permeants evaluated, in terms of the mass transfer process. The trend of permeability could not be explained by either the size or the polarity of the permeants tested. The combined factor of permeant size and polarity, however, was found to provide a better explanation for the trend observed. Smaller and more polar permeants have a greater capacity to permeate through Al₂O₃-coated PET film. Even though the proposed size / polarity hypothesis is simple in principle, this concept may help to estimate the organic vapors permeability of Al₂O₃-coated PET film.

Gas and water vapor permeability measurements were conducted following Gelbo flex testing to evaluate the effect of physical abuse on the barrier characteristics of Al_2O_3 -

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coated PET film. Significant deterioration in barrier properties occurred at less than 10 flexures abuse for oxygen, water vapor, and ethyl acetate / Al_2O_3 -coated PET systems. This deterioration likely resulted from the generation of cracks, the presence of which were confirmed by microscopic observations.

For abused Al₂O₃-coated PET / LLDPE laminated films, however, considerable barrier property difference was observed for polar permeants and non-polar permeants. For non-polar permeants, a similar deterioration trend occurred in both simple Al₂O₃coated PET film and the laminated films. However, for polar permeants, the extent of deterioration of barrier properties observed was different for the two films (i.e., no catastrophic deterioration observed in the films laminated with LLDPE). The laminated structure thus played an important role in preventing barrier deterioration for polar permeants.

The Attractive Defects (AD) model was introduced here to account for the permeability behavior for Al_2O_3 -coated PET film. The model is derived from the hypothesis that is "the defects by nature reacted with water in the environment and thus became hydrophilic (or attractive) regions". The attractive regions (or defects), then, may attract polar permeants and cause barrier deterioration. This model can provide an explanation for the permeability behavior of normal (non-abused) and abused Al_2O_3 -coated PET films. The prevention of the reactions between defects and water in the environment may be one of the keys to improve polar components barrier properties through Al_2O_3 -coated PET film.

Chapter 6

FUTURE STUDIES

In order to improve the level of barrier properties of Al_2O_3 -coated PET to that of aluminum foil, understanding of the permeation mechanism is crucial. The major permeant factors effecting permeability may be the size and polarity of the penetrant. In this study, d-limonene and ethyl acetate were selected as permeants, because of their common usage in related industries. However, determining the permeability using a series of penetrants, which have similar structural characteristics may be useful for evaluating molecular size, polarity, or other factors related to the mass transfer mechanism through ceramic-coated substrates. For example, a series of saturated alcohols (methyl alcohol, ethyl alcohol, etc.) may be a good candidate for study.

In this study, the Attractive Defects (AD) model was proposed to explain permeability behavior through Al_2O_3 -coated PET film. The model proposed that reaction of non-attractive (or normal) surface defects with water vapor may form attractive defects on the Al_2O_3 coatings, with a concomitant deterioration in barrier properties. Thus, the presence of water vapor as a co-permeant may effect permeability of Al_2O_3 coated PET film. The AROMATRANTM can introduce water vapor with a permeant to simulate humid conditions, which may occur in actual distribution and storage conditions. Utilizing this system, studies investigating humidity effects on Al_2O_3 -coated PET film can be carried out to establish the validity of the AD model. **APPENDICES**

Appendix A

Calibration Curve for Setting Vapor Pressure

In order to obtain conversion factors (CF) of vapor pressure for these compounds, calibration curves were plotted by using standard solutions. For d-limonene, 5, 20, 40, 100, and 200 ppm (v/v) standard solutions were prepared by diluting with carbon tetrachloride. For ethyl acetate, 1000, 10000, and 20000 ppm (v/v) standard solutions were prepared by diluting with acetonitrile. A 1 μ l of these solutions was directly injected into the gas chromatograph and the area response was recorded.

Table A-1 and Figure A-1 presents the results for the d-limonene standard solutions. Table A-2 and Figure A-2 presents the results for the ethyl acetate standard solutions.

Table A-1	Calibration data o	f d-limonene f	for setting vapor	pressure
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Concentration	ppm (v/v)	5	20	40	100	200
Mass of Compound	$(g \times 10^{-8})$	0.42	1.68	3.4	8.4	16.8
Area Responce	$(AU \times 10^{5})$	0.4	2.05	3.8	10.59	21.43



Figure A-1 Calibration data of d-limonene for setting vapor pressure

Table A-2 Calibration data of ethyl acetate for setting vapor pressure

Concentration	ppm(v/v)	1000	10000	20000
Mass of Compound	$(g \times 10^{-7})$	9	90	180
Area Responce	$(AU \times 10^4)$	212.56	1679.72	3082.68



Figure A-2 Calibration curve of ethyl acetate for setting vapor pressure

Appendix B

Calibration Curve for Dynamic Purge and Trap / Thermal Desorption Procedure

In order to obtain conversion factors (CF) of dynamic purge and trap / thermal deposition procedure for these compounds, calibration curves were plotted by using standard solutions. For d-limonene, 1, 5, 20, and 100 ppm (v/v) standard solutions were prepared by diluting with carbon tetrachloride. For ethyl acetate, 5, 20 and 100 ppm (v/v) standard solutions were prepared by diluting with dichlorobenzene. A 1 μ l of these solutions was injected into a thermal desorption tube. The tube, then, plugged into a thermal desorption unit, which was directly connected into gas chromatograph and the area response was recorded.

STATISTICS IN STREET

Table A-3 and Figure A-3 shows the result of d-limonene standard solutions. Table A-4 and Figure A-4 shows the result of ethyl acetate standard solutions.

Table A-3 Calibration data of d-limoner

for dynamic purge and trap / thermal desorption procedure

Concentration	ppm (v/v)	1	5	20	100
Mass of Compound	$(g \times 10^{-8})$	0.084	0.42	1.68	8.40
Area Responce	$(AU \times 10^{5})$	0.30	1.61	7.53	40.68



Figure A-3 Calibration curve of d-limonene for dynamic purge and trap / thermal desorption procedure

 Table A-4
 Calibration data of ethyl acetate

for dynamic purge and trap / thermal desorption proce	dure
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Concentration	ppm (v/v)	5	20	100
Mass of Compound	$(g \times 10^{-8})$	0.45	1.8	9.0
Area Responce	$(AU \times 10^4)$	14.73	52.84	158.25



Figure A-4 Calibration curve of ethyl acetate for dynamic purge and trap / thermal desorption procedure

Appendix C

Comparisons of Vapor Pressure of Compounds

Temperature	e (°C)	10	15	20
Area response	e (AU)	3,407,210	5,067,699	8,218,672
Saturated vapor pressure	From experimant	91.66	138.74	228.91
(Pa)	From literature	106.51	147.96	203.95
	% difference	13.9	6.2	-12.2

Table A-5 Comparison of saturated vapor pressure of d-limonene



Figure A-5 Comparison of saturated vapor pressure of d-limonene

Table A-6 Comparison of saturated vapor pressure of ethyl acetate

Temperature (°C)		5	24	
Area response	Area response (AU)		27,676,368	
Saturated vapor pressure	From experimant	2667.77	8887.12	
(Pa)	From literature	4224.28	11638.42	
	% difference	36.8	23.6	



Figure A-6 Comparison of saturated vapor pressure of ethyl acetate

Appendix D



Dimentions ($\text{\AA} = 10^{-10}$ m) of Permeants





Figure A-8 Dimentions of oxygen molecule

d-Limonene (longer axes)



Figure A-9 Dimentions of d-limonene molecule (top view)



Figure A-10 Dimentions of d-limonene molecule (side view)

Ethyl Acetate (longer axes)





Figure A-11 Dimentions of ethyl acetate molecule

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