EVALUATING FUNCTIONAL BARRIERS TO PREVENT MIGRATION OF CONTAMINANTS FROM POST CONSUMER RECYCLED PLASTIC FABRICATED INTO SINGLE LAYER & LAMINATION FILMS

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ABSTRACT

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A study involving the potential migration of contaminant substances from a recycled high density polyethylene (HDPE) film into a selected food simulant was carried out. Isopropanol and tetracosane, which are chemical contaminants recommended by the FDA as representatives of a polar-volatile group and a nonpolar-nonvolatile group, respectively, were selected as the chemical surrogates. For isopropanol, the diffusion coefficient in HDPE film was determined by both isostatic and quasi-isostatic permeation methods with good agreement. The partition distribution of isopropanol between HDPE film and water was also determined from a sorption experiment. For tetracosane, the diffusion coefficient was determined by monitoring the migration of tetracosane from impregnated HDPE film, which was fabricated from a tetracosane spiked HDPE resin by film extrusion, into hexane. The effectiveness of a functional barrier to prevent the migration of both compounds from a laminated film composed of a contaminated HDPE layer and a virgin HDPE layer into food was evaluated by two migration models. Modeling the migration of the two chemical surrogates from a single layer film was also carried out. A comparison of, and optimization of the respective models for estimation of migration rates was also concluded.

To my dear Mom and Dad, big brother and sisters

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INTRODUCTION

The idea of recycling of materials came from our concern with the environment and problems faced in the handling of solid waste (209 million tons in 1994). Plastic packaging materials account for a large percentage of solid waste (19.8 million tons), and at present there is considerable interest in developing a plastics recycling process, especially intended for food packaging applications, where plastics have been significantly employed (EPA, 1994).

For the purpose of using recycled plastics in food packaging applications, it must comply with the Food, Drug and Cosmetic Act and the Food Additive Regulations. In other words, it must be shown that the recycled plastics will not adulterate the food or otherwise compromise its safety. The level of 0.5 *ppb* (*wt/wt*), at which dietary exposures to substances of unknown toxicology can be considered a negligible risk, has been proposed by the Food and Drug Administration (FDA, 1992).

To focus on the use and applicability of recycled plastics, the National Food Processors Association (NFPA) and the Society of Plastics Industry (SPI) have cooperated to develop "The Guidelines for the Safe Use of Recycled Plastics in Food Packaging Applications" (NFPA, SPI, 1994). In achieving this application, three critical aspects of recycled plastics were addressed, namely: (1) the source of recycled material; (2) the nature of the recycling process; and (3) the conditions of use which needed to be considered in order to meet FDA requirements.

A major concern of recycled plastics for food-contact use is remaining contaminants from post-consumer plastic. Unlike metal or glass, which are impervious to contaminants, polymeric materials have the potential to sorb contaminants into their structure, which are difficult to remove. As a result of this, development of analytical methods to evaluate the adequacy of a recycling process, or to measure trace amounts of remaining contaminants and potential contaminant migration into food, has been the focus of considerable interest.

In addition to evaluating the recycling process, the study of migration can be employed to design a multilayer food package, which has recycled material as a non-food contact layer.

Based on these considerations, the present study will focus attention on developing analytical techniques which will allow solution of mathematical expressions, which describe the transfer of contaminants from single and two layer laminate structures, together with migration and sorption studies involving selected migrant/polymer/food simulant systems. Here, two chemical surrogates, based on FDA suggestion, will be used to conduct experiments. One is isopropanol, a representative of a polar-volatile species, which is commonly found in paint strippers, household cleaners and windshield washing fluid etc. The other surrogate is tetracosane, a representative for nonpolar-nonvolatile species, which is an example of an intermediate molecular weight hydrocarbon. High density polyethylene, HDPE, is the polymer sample studied and the food simulants are water and hexane. The systems to be investigated included isopropanol/HDPE/water and tetracosane/HDPE/hexane. The objectives of the present study include:

1. To determine the diffusion coefficient of isopropanol (polar volatile) and tetracosane (nonpolar nonvolatile) in single layer HDPE film as a function of permeant concentration, by permeation and migration techniques, respectively.
2. Carry out actual migration studies on "doped isopropanol" single layer HDPE in contact with water.
3. Carry out sorption studies on virgin single layer HDPE in contact with spiked isopropanol in water as the food simulant, and determine the partition coefficient.
4. Based on the mathematical expression for migration from single layer film, estimate the level of migration to a contact phase.
5. Evaluate mathematical models for a two layer laminate of recycled HDPE / virgin HDPE, where the virgin HDPE layer is the food contact surface, and predict levels of migration to a food contact phase.

A similar study involving two additional chemical surrogates; namely, xylene and 2,4 dichlorophenol, which are representatives of nonpolar-volatile and polar-non volatile substances respectively, has been reported by Sharma (1997).

LITERATURE REVIEW

Recycled Plastics in Food Packaging Applications

In this decade '90, attempts at increasing the amount of post-consumer plastics recycled around the world have continued to grow. For example, in the United States, recycling increased from about 20,000 tons in 1980 to about 680,000 tons in 1993 (Selke, 1996). The main reasons for the growth in plastic recycling are environmental concerns and consideration of handling municipal solid waste (MSW). Plastics were classified as the third largest contributor (19.8%, by volume, of MSW in 1994), but only 4.7% of plastic waste generation was recovered (EPA, 1994). Further, the development of plastic recycling processes which enhance the application of recycled plastic allow the use of tertiary recycled PET, produced via glycolysis and methanolysis processes, in food contact applications (Selke, 1996).

Even though there is a significant effort being directed to recycling plastic, the ratio of recovery to generated plastic waste is still quite low, compared to the ratio of paper and metal materials. To help accelerate the amount of recycled plastic, especially for packaging usage, the applications of recycled plastics need to be expanded. Among the wide range of recycled plastic applications, which vary depending on the nature of each resin type, use of recycled plastics in food packaging applications is one significant possible area. In dealing with food packaging applications, safety issues are of much more concern with plastics than with other packaging materials. This is due to the fact

that the post-consumer recycled plastics have a potential to be contaminated with toxicologically or health dangerous substances.

Like any other material intended for use in food packaging, recycled plastics may only be used in a manner that complies with the Federal Food, Drug and Cosmetic Act and the Food Additive Regulations (21C.F.R. Part 170). In general, basic food packaging materials are regulated by FDA on a " generic basis ", but there are no regulations that deal specifically with the use of recycled material for food packaging. However the existing regulations can work to ensure the safe use of recycled plastic in food packaging in two ways (NFPA, SPI, 1994), namely:

1. Any substance used as a component in a food package must be of a purity suitable for use in contact with food, such that it will not contaminate or adulterate food by, for example, imparting a taste or odor to food (as set forth in 21 CFR part 174.5), the so-called good manufacturing practices section of the regulations dealing with food contact materials); and

2. Any package component made from recycled materials must comply with the food additive regulations applicable to that component, including any specifications for or limitations on the use of the material or any adjuvants in the polymer.

With respect to public health safety concerns, the FDA proposed an upper limit dietary exposure level to chemical contaminants of 0.5 *ppb* (*wt/wt*)as the threshold of regulation for substances used as a food contact article (FDA, 1993). In other words, dietary exposures to contaminants from recycled food contact articles on the order of 0.5 *ppb* or less generally are negligible risk.

Food and Polymeric Packaging Materials Interactions

Polymeric materials have been widely used for food packaging due to benefits derived from their chemical structures, physical properties and economical attraction. These various properties make plastic packaging an excellent protection for food against deterioration factors and for the preservation of food quality. However, material properties are not equivalent for all types of polymers and each type of polymer package is not appropriate for all types of food products. In order to develop an appropriate food packaging design, an indepth understanding of the interaction of food and polymeric packaging materials is required.

There are three fundamental processes related to food packaging interactions, namely: (i) permeation, (ii) sorption, and (iii) migration. Permeation is the process by which molecules are transported from one side of the packaging material to the other as a result of sorption, diffusion and desorption processes. For example, gases and vapors in the external storage environment can permeate through the packaging material into the package internal environment and interact with the packaged food, resulting in the development of off-favor, and off-odor, as well as the deterioration of the food product. The permeation process can also occur in the opposite direction, resulting in the loss of water from the food product, as well as the loss of flavor volatile. Sorption is the process by which a low molecular weight organic moiety is taken up by one medium or phase, from a second contacting phase., the process being driven by a difference in molecular concentration. Flavor scalping, or the sorption of food components by a packaging material, is one such example. Migration is a sorption process in which the transfer of substances proceeds from the packaging material to its contents. Such a case would be

the migration of residual monomer or contaminants from post-consumer recycled plastic into foods.

These three fundamental processes are the result of differential equilibrium between the polymeric packaging, food components or a surrounding environmental phase and introduces a phenomenon of molecular transport that tends to move to the equilibrium state. The molecular transport in polymers is controlled by the diffusivity and solubility of the penetrant molecules. Thus, the process of diffusion and solubility will be reviewed prior to discussing permeation, migration and sorption processes.

Diffusion in Polymers

Small molecules of gases, water vapor or organic vapors can diffuse through a polymer film or sheet to equilibrate their chemical potential or reduce thermodynamic forces. The phenomena of diffusion through polymeric packaging materials occurs via microvoids, which are referred to as the "free volume " or "void volume" of the polymer matrix. The free volume or voids between polymer chains is very dependent on the chemical structure of the polymer and its morphology, which result in differences in polymer chain segmental mobility. The concept of molecular transport regulated by free volume was first introduced by Cohen and Turnball (1959). The development of a number of models based on the free volume concept, such as the theory of Vrentas and Duda (Duda and Zielinski, 1996), have been described in the literature (Kumins et al., 1968, Rudnick et al., 1979).

The diffusion behavior of polymers can be broadly described as "Fickian" or "Non-Fickian". In general, diffusion in rubbery polymers follows Fickian behavior, while glassy polymers show anomalous or non-Fickian behavior (Crank 1975).

For "Fickian" behavior, Fick's first and second laws of diffusion accurately describe the diffusion process. Fick's first law assumes that the rate of transfer of the diffusing substance through a unit area of a section is proportional to the concentration gradient measured normal to the section.

For an isotropic media (structure and diffusion properties at any point are the same relative to all directions), Fick's first law is described by the expression:

$$F = -D\frac{\partial C}{\partial x} \tag{1}$$

where F is the rate of transfer per unit area of section, C is the concentration of diffusing substance, x is the space coordinate measured normal to the section and D is the diffusion coefficient.

Based on the concept of the conservation of substances, the total concentration change across the slab bulk phase with time is directly proportional to the change in concentration gradient with permeant permeation depth (Neogi 1996).

For an isotropic media, therefore:

$$\frac{\partial C}{\partial x} = -\frac{\partial}{\partial x} j_x \tag{2}$$

where C is the concentration of diffusing substance, t is the time and j_x is the flux in x direction, which is along the thickness of a membrane.

From Fick's first and second law and under the boundary condition that the solute is dilute or, when the volume averaged reference velocity is being used or assumed, the flux in x direction can be written as:

$$j_x = -D\frac{\partial C}{\partial x} \tag{3}$$

Thus;

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \tag{4}$$

Equation 4 is therefore the mathematical expression describing Fick's second law of diffusion. When this differential equation is solved under appropriate initial and boundary conditions, for related experimental theory, it describes the measured quantities in terms of diffusivity D, where D can be calculated. Crank (1975) solved and described D in the form of mathematical solutions for a number of experimental situations.

Solubility in Polymers

The solubility coefficient, *S*, is a parameter that describes the equilibrium amount of substances sorbed by the polymer per unit sorbate partial pressure. For organic vapors, the solubility coefficient is normally presented in weight per weight of polymer in equilibrium per unit vapor pressure.

For low partial pressures of gasses, or for dilute concentrations of organic vapors, the solubility follows Henry's law;

$$C = Sp \tag{5}$$

where; C = the concentration of sorbate in polymer

S = the solubility coefficient

p = the vapor pressure of sorbate

In a thermodynamic sense, the solubility coefficient can be described in terms of the heat of solution for the specific sorbate / polymer system and temperature by equation 6.

$$S(T) = S_o \exp\left(\frac{\Delta H_s}{RT}\right) \tag{6}$$

where ΔH_s is the heat of solution, T is temperature in Kelvin degrees, and S_o is a constant which can be derived by measurement of $S(T)$ at different temperatures. The heat of solution, for dissolved gases above their critical point, can be calculated from:

$$\Delta H_s = V_1(\delta_1 - \delta_2)^2 \phi_2^2 \qquad (7)$$

where V_1 is the partial molar volume of the solvent, ϕ_2 is the volume fraction of polymer and δ_i is the solubility parameter of species i (Progelhof and Throne 1993) .

From equation 7, if $\delta_1 = \delta_2$, $\Delta H_s = 0$. It follows therefore, that the penetrant should be soluble in the polymer matrix, due to a negative entropy of mixing, ΔS_s, and a negative free energy of mixing, ΔG_s, ($\Delta G_s = \Delta H_s - T\Delta S_s$). As the difference between δ_1 and δ_2 increases, the tendency towards dissolution decreases.

The solubility parameter, δ, can be calculated either from the cohesive energy density or the molar attraction constant, F, by the method of Hoftyzer and Van Krevelen or Hoy (Van Krevelen, 1990).

Permeation of Gases and Organic Vapor through Polymers.

For the transport of gases or an organic vapor through a homogeneous polymer membrane, permeation in the absence of pores or cracks is considered to occur by these successive processes: (i) absorption of the gas or vapor in the surface layer; (ii) diffusion to the opposite surface under a partial pressure or chemical potential gradient; and (iii) the desorption or evaporation of the penetrant from the surface into the ambient phase.

In the case of an isotropic media, the fundamental differential equations describing unidirectional diffusion, are equation 1 (Fick's first law) and equation 4 (Fick's second law). Here the diffusion coefficient is assumed to be a constant, independent of distance, x, time, t, or concentration, c.

For most experimental and predictive purposes , it is convenient or necessary to relate the sorbed concentration, C, to the ambient permeant concentration, c, in contact with the polymer surface. The distribution of permeant between the ambient and polymer phases is described by the Nernst's distribution function (Rogers, 1985):

$$C = Kc \tag{8}$$

where K is a function of temperature and may also be a function of C. For gases and vapors, c is proportional to pressure, p, through the ideal gas law equation. The equilibrium concentration , C, of permeant in a polymer then can be related to the ambient pressure by :

$$C = Sp \tag{9}$$

where the solubility coefficient, S, is a function of temperature and may be a function of pressure, p, or C. For sufficiently low permeant concentrations, C is directly proportional to p and if the solubility coefficient, S, obeys Henry's Law , then the steady state flux can be expressed from equation 3 as:

$$j_x = \frac{DS(p_1 - p_2)}{l} \tag{10}$$

where p_1 and p_2 are the ambient penetrant partial pressures on two sides of a film of thickness l. The product of D and S is defined as the permeability coefficient, P.

For many organic vapor-polymer systems, both D and S are not constant but rather are a function of concentration, c, spatial coordinate, x, the lapsed time, t, and temperature, T, so that the permeability coefficient will also be dependent on those variables (Roger, 1985).

Migration in Polymers

Similar to virgin plastic packaging materials, recycled plastics may also contain low molecular weight species such as monomer and oligomers, additives such as heat and light stabilizers, antioxidants, antistatic agents, stabilizers, lubricants, and slip agents, as well as being adulterated by low levels of contaminants from post-consumer recycled plastic. When plastics are used to contain foods, the potential for the migration of one or more of the aforementioned chemical moieties, or migrants transferring to the contacting food exists. For migration to occur, migrants have to undergo two processes in succession, namely; diffusion of the migrant to the polymer surface and subsequent dissolution of the migrant accumulated at the surface to the contact phase. The desorption phenomenon of a migrant from a polymer to a contacting phase can be considered a function of the polymer-migrant interaction affinity and diffusion. The affinity or interaction thermodynamics of the polymer-migrant system will determine the equilibrium amount of migrant transferred to a contacting phase. The affinity becomes increasingly important as the migrant concentration decreases.

The transport of a migrant is not only dependent on the nature of the polymer matrix, and the chemical structure of both the contaminants and the food type, but also the conditions of test, such as temperature and storage time.

The amount of contaminant migrating from a plastic film or sheet into a food contact phase can be expressed mathematically by equations that are derived from Fick's first and second laws of diffusion (Crank, 1975). The specific expressions will, however, be dependent upon the assumptions made in their derivation. In order to derive solutions for migration processes, an ideal polymer has to be assumed, which has the following properties(Reid, et al., 1980):

1. It is a flat sheet , infinite thickness, and no edge effect.(The concept of infinite thickness simply imposes the restriction that, during loss of the migrant from the polymer film, the migrant concentration at some depth within the film is essentially unaffected by the diffusion process. Usually, if less than 30-40% of the migrant is extracted, the polymer film may be treated as being infinite in thickness)

2. There is but a single contaminant migrating from the polymer and it is initially homogeneously distributed.

3. The diffusion coefficient of the migrant in the polymer is a function only of temperature and independent of position and time.

4. Swelling or penetration of the polymer by the solvent phase does not occur, or if it does, it does not modify the physical dimensions appreciably, nor does it affect assumption (3) above.

To allow estimation of the amount of contaminant migrating from a single layer structure, there are two general models, one for a well-mixed solvent and the second for an immobilized solvent. Here, only the equations for the well-mixed solvent system will be evaluated and compared to experimental data, which are: (1) semi-infinite

polymer/infinite solvent model; and (2) semi-infinite polymer/finite amount of liquid phase or volume model (Reid, et al., 1980).

1.Semi-infinite polymer/infinite solvent model (This model represents the worse possible scenario to estimate migration from a polymer, and the shortest possible time for migration)

Assumptions: -Diffusion coefficient is independent of migrant concentration.

-Concentration in polymer does not significantly change.

-Product (i.e. food simulant) is an infinite sink for the contaminant (no boundary layer resistant) and is well agitated.

-No concern with partition equilibrium, on the migration of contaminants to the food simulant.

$$M_t = 2C_p^o\left(\frac{D_p t}{\pi}\right)^{1/2} \qquad (11)$$

where; M_t = total quantity of migrant lost from the polymer per unit area of polymer contact phase at time t

C_p° = initial migrant concentration $[g/cm^3]$

D_p = diffusion coefficient of migrant in polymer $[cm^2/s]$

t = time $[s]$

note; This equation does not consider the effect of temperature.

2. Semi-infinite polymer/finite amount of liquid phase or volume

Assumptions: - Product (i.e. food simulant) is an finite sink for contaminant and is well agitated.

- There is no concentration gradient of the migrant into the liquid and no effect of the mass transfer coefficient.
- The partition coefficient is independent of migrant concentration(true for very low concentration of migrant).

$$\frac{M_t}{aKC_p^o} = \left(1 - \exp\left(Z^2\right) erfcZ\right) \qquad (12)$$

where; M_t = total quantity of migrant lost from the polymer, per unit area of polymer contact phase at time t.

$Z = (D_p t)^{1/2}/aK$

K = partition coefficient of migrant between contacting phase and polymer phase (C_s/C_p)

V_L = volume of liquid phase ($V_L = Aa$)

A = contacting area

a = ratio of solvent volume to transfer area (liquid phase thickness)

Role of Partition Coefficient, K in Migration Rate

At the solvent-polymer boundary for either the infinite or finite solvent phase, local equilibrium partitioning of migrant can occur. In general, when an equilibrium partition has developed, the migration rate will decrease. However, the equilibrium partition does not always affect the rate of migration, such that if the dimensionless Z term in equation (12) is a low value, i.e. less than 0.05, the partitioning effects are negligible and the rate of migration of a migrant is determined solely by the diffusion process in the polymer (Reid et al., 1980).

Role of Sample Thickness in Migration Rate

The validity of the mathematical expression for describing the migration rate is strongly affected by the simple assumption of an infinite thickness for the polymer sample. It is severely affected for cases where the contact phase is a polymer-penetrating solvent, such as a fatty food. If the infinite thickness assumption is not valid, the assumption that the initial concentration of the mobile component in the polymeric test material remains unaltered during the entire migration process will no longer exist, resulting in an incorrect estimation.

In order to meet the infinite thickness assumption for a polyolefin film, the limiting thickness, d_g, term was proposed by Figge, which was based on the postulate that the quantities of migrant species migrating reach more constant values from a particular sample thickness onwards(Figge, 1988). The limiting thickness, d_g, is defined as the thickness of the specimen, the value below which the migration rate is proportional to the thickness of the specimen. It can be described by the following equations:

$$d_g = \frac{M(d \to \infty)}{C_p^o} \tag{13}$$

Equation 13 applies to one-sided contact between the polymer specimen and the test solvent, or

$$d_g = \frac{2M(d \to \infty)}{C_p^o} \tag{14}$$

where equation 14 applies to two-sided contact between the polymer specimen and the test solvent.

where: $M(d \to \infty)$ = the constant migration rate for very thick specimens [g/cm^2]

C_p^o = the initial concentration of migrant in the specimen [g/cm^3]

The amount of migrant, migrating from a poleolefin into a contact media can be estimated by the following relationship, which was proposed by Reid et al (1980).

$$M_d(d;t_i) = C_p^o \cdot d \cdot \left[1 - 2 \cdot Z^2 \sum_{n=1}^{\infty} \frac{\exp(-\gamma_n^2 \cdot \psi)}{\gamma_n^2(\gamma_n^2 + Z^2 + Z)}\right] \tag{15}$$

$$Z = \frac{K \cdot k \cdot d}{D_p} \tag{16}$$

$$\gamma_n \cdot \tan\gamma_n - Z = 0 \tag{17}$$

$$\psi = \frac{D_p \cdot t_i}{d^2} \tag{18}$$

where: M_d = the migrating amount of migrant in the solvent

d = thickness of a polymer specimen

C_p^o = initial concentration of a migrant in the polymer specimen

K = partition coefficient of a migrant (C in polymer/C in medium)

k = mass transfer coefficient

γ_n = auxiliary quantity obtained by eqn. 17

t_i = any constant time

The calculated values for M_d obtained from equation 15 agreed with the experimental results obtained for migration of the antioxidant, Irganox 1076, from LDPE, HDPE and PP into the test fat simulant, HB 307, (Figge, 1988). The migration rates, $M(d\rightarrow\infty)$, for the antioxidant and the limiting thickness, d_g, decreased to a large extent in the order of LDPE → HDPE → PP, under the same test conditions.

As previously mentioned, for a well-mixed and finite solvent system the assumption of an infinite thickness would not be seriously in error until about 40% of the migrant has been lost, as shown by Reid, et al., (1980) by the expression:

$$(aK / L)\left(1 - \exp\left(Z^2\right) erfcZ\right) > 0.4 \tag{19}$$

where L is the true polymer sheet thickness, or half of the thickness for two sided contact.

Sorption in Polymers

As discussed above in the review of solubility, the equilibrium amount of penetrant sorbed by a polymer is controlled by the thermodynamics of the system. For example, sorbate solubility is a function of the heat of solution and temperature (eqn. 6). The sorption process of gasses or vapors can be described by the sorption isotherm which is defined as the distribution of the penetrant between the polymer and contact phase. The transport behavior of a penetrant in a polymer could thus be physically interpreted by the sorption isotherm.

The sorption isotherms are presented graphically by a plot of the sorbed amount of penetrant as a function of penetrant vapor pressure or the square root of time. In general, typical sorption isotherms can be described by the Henry's law equation, the Langmiur equation, the Flory-Huggins equation, or the Brunauer-Emmett-Teller (BET) equation (Roger, 1985).

Type 1. Henry's law expression represents the isotherm of a system which can be described as an ideal solution. In this case, the sorbed penetrant is randomly dispersed within the polymer. The solubility coefficient is a constant, independent of sorption concentration levels, at a given temperature and the sorption isotherm is a linear relationship between polymer sorbate concentration and the sorbate vapor pressure or vapor activity. This behavior is found when permanent gases (i.e. O_2, CO_2, N_2) are sorbed by the polymer, provided the gas pressure does not exceed about 1 atmosphere. This is due to the lack of strong polymer-penetrant interaction, resulting in very low solubility coefficient values.

Type 2 or the Langmuir sorption equation: In terms of the molecular pair distribution, it shows a preference for polymer-penetrant pairs to be formed at relatively low pressures, with a smaller level of sorption of more nearly ideal solution behavior at a higher pressure. In physical terms, penetrant molecules will initially be sorbed at some type of specific site within the polymer phase, when these active sites are nearly all occupied, a small amount of penetrant dissolves in the polymer, with more or less a random distribution. An example when the Langmiur expression is applicable is for the sorption of higher pressure gasses in glassy polymer containing voids.

Type 3 or the Flory-Huggins sorption equation: This expression describes a preference for penetrant-penetrant pairs to be formed, such that the solubility coefficient increases continuously with penetrant partial pressure. For a physical interpretation, the first molecule sorbed tends to relax the polymer structure locally, which makes it easier for subsequent molecules to enter into the molecular environment associated with the initially sorbed penetrant molecule rather than be sorbed elsewhere within the polymer bulk phase. This would be expected for a good polymer solvent or a swelling liquid or at a high vapor penetrant level. Another interpretation for systems which follow the Flory-Huggins expression is when penetrant-penetrant interactions are inherently stronger than the corresponding polymer-penetrant interactions, such as for water in relatively hydrophobic polymers. The association or clustering of water molecules within a polymer matrix is the result of hydrogen bonding between water molecules and would lead to stable clusters or aggregates of sorbed penetrant water molecules, which would be less mobile than a non-associated water molecule.

Type 4 or the BET equation is a combination of the Langmiur and Flory-Huggins expressions. It has been used to describe the sorption of water by hydrophilic polymers such as cellulosic materials. The water molecules are initially sorbed to active sites corresponding to polar groups such as amide, carboxyl and hydroxyl groups, while the clustering processes dominate at higher vapor pressure levels.

In practice, the sorption processes may be more complex than the above interpretations and could be a combination or overlap of several isotherm modes occurring simultaneously (Roger, 1985).

For sorption studies, the diffusion equation describing penetrant sorption by a polymer film is also a solution of Fick's second law, as shown by the expression (Crank, 1975):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-D(2n+1)^2\pi^2 t}{l^2}\right) \qquad (20)$$

where: M_t = the amount of penetrant sorbed at time t

M_∞ = the amount of penetrant sorbed at equilibrium

D_p = the diffusion coefficient

l = film thickness

If the weight uptake is controlled by a constant diffusion coefficient process, by setting M_t/M_∞ equal to 0.5, the diffusion coefficient can be calculated within an error of 0.001 per cent from:

$$D_p = \frac{0.049 \cdot l^2}{t_{0.5}} \tag{21}$$

where $t_{0.5}$ is the time when M_t/M_∞ equals to 0.5.

Analytical Techniques for Determining Diffusion, Solubility and Permeability Coefficient Values.

The diffusion coefficient and solubility coefficient are fundamental mass transfer parameters, with the diffusion coefficient used to predict migration and sorption levels by solution of mathematical expressions describing the polymer-contaminant system which are governed by the diffusion process. Diffusion and solubility coefficient values can be determined by permeation, sorption, and migration techniques. For gases, organic vapors, and liquids, permeation and sorption procedures are common measurement techniques. However, they may not be applicable at room temperature for low penetrant vapor pressure levels or for non-volatile organic compounds at temperature conditions of interest. The migration technique may be a solution for such difficult to handle compounds, if they can be included within the polymer matrix and the appropriate mathematical expression describing the migration process can be solved for the diffusion coefficient. In addition to sorption and migration techniques allowing for the determination of diffusion coefficient values, they can also be used to determine the partition coefficient, $K_{L/P}$ *or* $K_{P/L}$, values describing the distribution of organic compounds between the polymer and solvent or food contact phases.

Permeation measurements

There are two general methods for performing permeability measurements, these being the quasi-isostatic and isostatic test methods. The isostatic method is the preferred procedure employed by two commercial analytical instruments designated to measure organic vapor permeability. These instruments are the MAS 2000 by MAS Technologies (Zumbrota, Minnesota) and the Aromatran by MODERN CONTROLS, Inc. (Minneapolis, Minnesota). Both test methods involve a cell consisting of two chambers which are separated by the polymer membrane. There is a flow of permeant vapor across one surface of the membrane, while the permeated vapor is quantified by difference techniques, as described below.

Isostatic or dynamic permeability method.

In this procedure, a flow system is designed to maintain the total pressure of both sides of the polymer membrane at about atmospheric pressure. A constant vapor pressure of permeant is continuously flowed through the high concentration cell chamber, while the permeated vapor is conveyed by N_2 from the low concentration cell chamber to a detector and the transmission rate measured continuously until it reaches a steady-state value. A constant concentration of permeant stream can be generated either by pressure or temperature controlling (Hernandez et al., 1986).

The diffusion coefficient can be calculated from permeability data by the following relationship, which was proposed by Pasternak et al. (1970):

$$\frac{\Delta F}{\Delta F_\infty} = \frac{(\Delta M/\Delta t)_t}{(\Delta M/\Delta t)_\infty} = \left(\frac{4}{\sqrt{\pi}}\right)\left(\frac{l^2}{4Dt}\right)^{1/2} \exp\left(-\frac{l^2}{4Dt}\right) \qquad (22)$$

By plotting ($4Dt/l^2$) as a function of time , the slope of the straight line is related to the diffusion coefficient as shown in equation 23:

$$D = \frac{(slope)\cdot l^2}{4} \qquad (23)$$

An additional equation for calculating the diffusion coefficient was that proposed by Ziegel, et al. (1969). They derived the following simple relationship of D as a function of $t_{0.5}$, the time when $\Delta F = 0.5\Delta F_\infty$, and the thickness of the membrane, as the following:

$$D = \frac{l^2}{7.199 \cdot t_{0.5}}. \qquad (24)$$

At steady-state, the permeability coefficient could be calculated by solution of the following equation (Hernandez et al., 1986):

$$P = \frac{a \cdot G \cdot f \cdot l}{A \cdot b} \qquad (25)$$

where: a = calibration factor to convert detector response to unit of mass of permeant/ unit of volume [(mass/volume)/signal units]

G = response units from detector output at steady state (signal output)

f = flow rate of sweep gas conveying penetrant to detector (volume/time)

A = exposed area to penetrant (area unit)

l = film thickness (length unit)

b = driving force given by partial pressure gradient or concentration (pressure or concentration unit)

Quasi-isostatic permeability method

In the quasi-isostatic procedure, there is a continuous flow of a constant vapor pressure of permeant stream across one surface of membrane, while the penetrated vapor is accumulated into the low concentration cell chamber. Both cell chambers are maintained at one atmosphere total pressure. The partial pressure difference is maintained by sweeping one side continuously with the permeant gas and by replacing the volume withdrawn from the low concentration cell chamber during test with inert gas (i.e. N_2) to maintain a constant partial pressure gradient. Samples of penetrated permeant are withdrawn from the low concentration cell chamber at predetermined time intervals. In practice, the penetrated permeant concentration in the low concentration cell chamber should not exceed 1-2 % of the permeant concentration in the high concentration cell chamber. By plotting total quantity of permeated vapor as a function of time, the diffusivity and permeability coefficients can be determined from the transmission rate profile information. By extending the straight line portion of the transmission rate profile curve at steady-state, to intersect the time axis, the lag time value or θ is obtained and by its substitution into equation 26, the diffusion coefficient is determined.

$$D = \frac{l^2}{6\theta} \tag{26}$$

This relationship is derived from Fick's second law and was proposed by Barrer (1939).The permeability coefficient can be calculated from the following equation (Hernandez et al., 1986):

$$P = \frac{y \cdot l}{A \cdot b} \tag{27}$$

where: y = slope of the straight line portion of the transmission rate profile (mass/ time)

l = thickness of the film (length)

A = exposed area to penetrant (area)

b = driving force given by partial pressure or concentration gradient (pressure or concentration unit)

Analytical Techniques for Sorption and Migration Measurements

The respective analytical techniques for quantitative determination of sorbates in a polymer or migrants in a food contact phase consist mainly of sample preparation, such as solvent extraction, or concentration of the sample and sample analysis. Analysis may be by gas chromatography (GC), high performance liquid chromatography (HPLC) or supercritical fluid chromatography (SFC). The sample preparation step may be carried out by a variety of techniques, which have both advantages and drawbacks, depending upon the specific sorbate and contact phase. Here, the principles of two sample preparation techniques, namely: (i) Thermal stripper-Thermal desorption (TS-TD); and (ii) Solid phase micro extraction (SPME), are described.

Thermal Stripper and Thermal Desorption

The thermal stripper is a sample preparation instrument designed to collect onto an adsorbent packed trap a broad range of low to high molecular weight compounds in gas, liquid or solid states. By heating a sample matrix, a number of compounds may be volatilized and transported by the carrier gas to the absorbent trap at temperatures significantly lower than their actual boiling point. This dynamic purge and trap procedure allows for trace amounts of volatile organic moieties to be collected for analysis. However, it may not be applicable for heat sensitive or very high boiling point compounds. The thermal stripper system and the instrument parameters (i.e. carrier gas flow rate, temperature program and collection time), as well as the composition of the adsorbent trap are major factors contributing to the overall performance of sample collection. In general, the adsorbent tubes are packed with layers of various sorbent materials, so that compounds of difference molecular weight and polarity may be trapped onto an appropriate sorbent layer or layers, but not held so tenaciously that they can not be completely and rapidly desorbed, without thermal degradation during the heating cycle. In doing so, the gas flow during sampling has to enter the adsorbent tube at the least active layer of sorbent material and exit through the most tenacious or active layer (Dynatherm, TD manual, 1989).

The thermal desorption system is an instrument designed to thermally release trapped compounds from the adsorbent tube prepared by the thermal stripper or dynamic purge and trap procedure. It is normally interfaced to an analytical instrument such as a gas chromatograph (GC), so that trapped compounds can be transferred from the sorbent tube for quantification by the carrier gas flow. The optimum temperature of heating and

flow of carrier gas are the heart of good performance in the analytical step. Thus, it is usually preferred to desorb the sample at a high temperature and short time in order to receive a narrow band of released compounds to the GC column.

This sample preparation technique is often used for environmental control, such as for the trapping of low molecular weight hydrocarbons in air, or volatile compounds in the working area. It was also applied to determine the sorbed amount of food flavor in polymer film. Nielsen et al. (1994) analyzed the equilibrium sorbed amount of limonene and ethyl acetate in oriented propylene film by the TS-TD procedure. Lin (1995) developed a purge and trap system for collecting sorbed toluene into product samples and analyzed for the sorbed toluene by gas chromatography- mass spectrometry (GC-MS).

Solid phase microextraction

A solvent free sample preparation procedure is solid phase microextraction, or SPME, which was developed based on the concept of using sorbent material to extract trace amounts of organic compounds from solution. For SPME, a thin layer (10-100 μm) of sorbent material is coated on a fine rod of fused silica fiber or wires made of appropriate materials. The cylindrical geometry of the coated sorbent in SPME creates rapid mass transfer during extraction and desorption, prevents plugging and facilitates sampling and introduction into analytical instruments.

The principle of SPME is the partitioning of analytes between the sample matrix and the extraction medium (Zhang, et al., 1994). If a liquid polymeric coating is used, the amount of analyte sorbed by the coating at equilibrium is related to its concentration in the sample as shown by:

$$n = \frac{K_{fs} V_f C_o V_s}{K_{fs} V_f + V_s} \tag{28}$$

where n is the mass of an analyte absorbed by the coating, V_f and V_s are the volumes of the coating and the sample, K_{fs} is the partition coefficient of the analyte between the coating and sample and C_o is the initial concentration of analyte in the sample. If the volume of the sample is very large ($V_s >> K_{fs}V_f$), the amount of analyte sorbed by the coating at equilibrium is independent of sample volume, thus:

$$n = K_{fs} V_f C_o \tag{29}$$

With proper calibration, SPME can be used to determine the concentration of the analyte in the sample. The speed of extraction is controlled by the mass transfer of analyte from the sample to the coating. Since sorbate diffusion governs the mass transfer rate in polymers for most gaseous samples, extraction equilibrium will be reached in less than 1 *min*, since gases usually have large diffusion coefficient values as compared to coating materials. While for an aqueous sample, the equilibrium time is much longer, since the analytes must diffuse through the aqueous phase, and specifically the static layer of water adjacent to the coating before they can be sorbed by the coating. If SPME needs to be directly applied to extract analytes from an aqueous phase, vigorous agitation of the sample, such as sonication, may improve the equilibrium time.

The SPME device consists of a 1 *cm.* length of fused silica fiber, coated onto the outer surface of the stationary phase and bonded to a stainless steel plunger. The fused silica fiber can be drawn into a hollow needle, which functions to pierce the sampling septum of a GC by using a fiber holder. This needle liked device allows the exposed

fiber to be easily introduced into the injection port of the GC where the sorbed analytes are thermally desorbed and delivered to the GC column.

Presently, there are several commercial coating phases that are claimed to work for compounds ranging from non-polar to polar, such as polydimethysiloxane for non-polar compounds, polydimethylsiloxane/divinylbenzene polymer for polar volatile compounds, and polyacrylate for polar semivolatile compounds.

Boyd-Boland et al. (1995) applied polyacrylate SPME to collect nitrogen-containing herbicides in water samples. Shirey (1997) compared the extraction limits of different coated fiber phases for polar analytes in water samples. The results show that carboxen/polydimethylsiloxane gave superior extraction capability as compared to other coating phases, even a more polar phase such as carboxen/divinylbenzene and polyacrylate fiber, because small pores of the carboxen/polydimethylsiloxane coating, optimized the extraction capacity of the coated fiber phase.

Predictive Models for Migration from Lamination Film

The use of a functional barrier layer, i.e. virgin film layer, to prevent the migration of contaminants from a lamination incorporating recycled film has a potential for food packaging, as long as it is proven that no significant level of contaminants migrate into the food contents. Presently, the use of recycled HDPE resin has been considered by the FDA for application in food packaging, specially for consideration of its compliance with all related regulations for food safety. Due to the fact that migration studies may require a significant time frame and budget to complete, attempts at developing a method for estimating migration rates have been made, based on solution of two basic differential

equations describing diffusion in a polymer matrix (Fick's first and second law). Even though migration models may not be fitted for all food-polymer systems, they can provide an estimation for the migration from representative food packaging systems and a worse case level of migration, which can be employed as a safety factor in film production design. Two predictive models describing migration from laminate films are presented below.

The Laoubi and Vergnaud model

The solution of migrant transfer from film into a food contact phase, described by the Laoubi and Vergnaud model (Laoubi et.al., 1995), was based on the diffusion process for a laminate film containing a recycled layer and a virgin polymer layer and was derived from Fick's second law (eqn 4) under initial and boundary condition corresponding to the following assumptions:

1. The migrant transfer process is controlled by Fickian diffusion with a constant diffusion coefficient.

2. The migrant is initially in the recycled layer and only migrates through the virgin layer into the food contact phase.

3. There is no transfer of food components into the virgin polymer (food contact phase) and no effect of film thickness associated with migrant transfer, due to the very low concentration of migrant.

4. The concentration of migrant in food contacting the virgin polymer layer remains negligible by assuming a large volume of surrounding food contact phase.

For a laminate film (thickness = L) comprised of a recycled layer (thickness = H) and a virgin layer (thickness = L-H) and given the above assumptions, the initial and boundary conditions can be described in mathematical equations as:

Initial conditions: $t = 0$, at $0 < x < H$ $C = C_{in}$ (30)

$H < x < L$ $C = 0$ (31)

Boundary conditions: $t > 0$, at $x = 0$ $\frac{\partial C}{\partial x} = 0$ (32)

$x = L$ $-D\frac{\partial C}{\partial x} = h\left(C_L - C_{ext}\right)$ (33)

where h is the convective coefficient of mass transfer

if $h \to \infty$ $x = L$ $C_L = C_{ext}$ (34)

and for all cases $C_{ext} = 0$ (35)

Using the separation of variables method, the authors solved the expression:

$$\frac{\partial C_{x,t}}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C_{x,t}}{\partial x}\right) \tag{36}$$

The solution for determining the concentration of migrant at position x and time t, $C_{x,t}$ is presented below as a fraction of the initial concentration in the recycled layer :

$$\frac{C_{x,t}}{C_{in}} = \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{1}{(2n+1)}\sin\frac{(2n+1)\pi\ H}{2L}\cos\frac{(2n+1)\pi\ x}{2L}\exp\left(-\frac{(2n+1)^2\pi^2}{4L^2}Dt\right) \qquad (37)$$

By integrating with respect to any position between *0* and *L*, the solution for the amount of migrant remaining in the film at time t, $M_{r,t}$ is expressed as a fraction of the initial amount of migrant in the recycled layer, M_{in} :

$$\frac{M_{r,t}}{M_{in}} = \frac{8L}{\pi^2 H}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)^2}\sin\frac{(2n+1)\pi\ H}{2L}\exp\left(-\frac{(2n+1)^2\pi^2}{4L^2}Dt\right) \qquad (38)$$

By integrating with respect to position between *0* and *H*, the solution for the amount of migrant remaining in the barrier layer at time t, $M_{b,t}$ is expressed as a fraction of the initial amount of migrant in the recycled layer, M_{in} :

$$\frac{M_{b,t}}{M_{in}} = \frac{8L}{\pi^2 H}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\sin^2\frac{(2n+1)\pi\ H}{2L}\exp\left(-\frac{(2n+1)^2\pi^2}{4L^2}Dt\right) \qquad (39)$$

The amount of migrant transferred into food could be calculated from:

$$M_t = M_{in} - M_{r,t} \qquad (40)$$

The Begley and Hollifield model

Begley and Hollifield (1993) applied a solution, which was developed by Crank (1975) for a uniform initial distribution and different constant surface concentration at both sides, to estimate the amount of migrant migrating from a recycled layer through a virgin layer into a food contact phase. The assumptions make by Begley and Hollifield are as follows:

1. The migrant transfer process is controlled by Fickian diffusion with a constant diffusion coefficient.

2. The initial migrant concentration is an infinite source contained only in the recycled layer. In this case, at the surface of the virgin layer adjacent to the recycled layer side, the concentration of migrant remains constant, while the migrant concentration on the surface contacting to the food is always zero.

3. The food is an instantaneous and infinite sink for the contaminant.

For a laminate film made up of a recycled layer (negligible thickness) and a virgin layer (thickness = l), the total amount of migrant, M_t transferring through the membrane at time t can be calculated from the equation :

$$\frac{M_t}{lC_l} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-\frac{Dn^2\pi^2 t}{l^2}\right) \qquad (41)$$

Where C_l is a constant concentration of migrant at the surface of the virgin layer adjacent to the recycled layer, t is time and D is the diffusion coefficient.

MATERIALS AND METHODS

Materials

Polymers

Resin and film samples of high density polyethylene (HDPE) were provided by Tredegar, Inc (Terre Haute, Indiana, USA). The HDPE film, Monax®, was used for permeability, sorption and migration studies with isopropanol as a penetrant, while the HDPE resin samples were spiked with tetracosane and extruded as film to study the migration propensity of tetracosane.

Monax film: Lot # TI-49611, size 43 in. × 1 m., thickness 1.15 mil, and density 0.96 g/ cc. The resin pellets were the resin grade used to produce Monax film.

Solvents

Acetonitrile CH_3CN (HPLC grade) FW 41.05, specific gravity 0.783, bp 81.6 ℃, mp -41 *°C* from EM Industries, Inc (Gibbstown, NJ, USA).

Hexane $CH_3(CH_2)_4CH_3$ (96 %) FW 86.18, specific gravity 0.659, bp 69 *°C*, mp -94 *°C* and Water H_2O (HPLC grade) FW 18 specific gravity 1, bp 100 *°C*, mp 0 *°C* from J.T. Baker (Phillipsburg, NJ, USA).

Solutes

2-propanol $(CH_3)_2CHOH$ (99.5 %) FW 60.1 specific gravity 0.785, bp 82.4 *°C*, mp -89.5 *°C*

Tetracosane $CH_3(CH_2)_{22}CH_3$ (99 %) FW 338.66 specific gravity 0.779, bp391 ℃, mp 49-52 *°C*. Both from Aldrich Chemical Company, Inc (Milwaukee, WI, USA).

Methods

Determination of diffusion coefficient of Isopropanol in HDPE film

The diffusion coefficient of isopropanol in HDPE film was determined by the permeability method, which was based on two different procedures, namely the isostatic and quasi-isostatic (Hernandez, et.al., 1986) techniques. The methodology involved with the respective procedures is presented below.

Isostatic technique

A commercial instrument, the MAS 2000™ organic vapor permeability tester from Testing Machines Inc., (Amityville, NY, USA) was used for measuring the permeability of isopropanol vapor through HDPE film. The MAS 2000 is designed for continuous flow of organic vapor through one permeability cell chamber and the permeated vapor level monitored by N_2 carrier gas continually conveying the vapor from the low concentration cell chamber to a flame ionization detector (FID) for quantification. The test system is equipped with a flow controller, temperature controller and a flame

ionization detector, all of which are connected to and controlled by computer. The instrument software is not only designed for controlling the parameters of the system, but also for determining the permeability, diffusion and solubility coefficient values of the test penetrant/polymer system from permeation rate data. The precision of flow control is within ± 0.1 *ml/min* and temperature control is within ± 0.05 ℃. The instrument sensitivity is at 1 *ppb* (volume by volume) or 120 *picogram/m*^{2}*/sec.*

The isopropanol vapor was generated by bubbling N_2 gas through liquid isopropanol contained within a Pyrex brand gas-washing bottle with fritted cylinder and 29/42 stopper, 250 *ml* (Aldrich Chemical Company, Inc., Milwaukee, WI, USA). The gas washing bottle was placed in a water bath maintained at 23 ± 0.05 *°C* (MW 1110, Blue M Electric Co., Chicago, Illinois, USA) and the vapor activity or concentration of isopropanol was set up by mixing the saturated vapor stream from the gas washing bottle with pure N_2 gas. Both N_2 streams were generated from the same gas cylinder with the regulator pressure set at about 20 *psi* before it was delivered to the MAS 2000 unit. The outlet N_2 from the MAS 2000 was separated into two gas streams for bubbling and mixing. Each N_2 stream flow was controlled by a needle valve (Nupro "M" and "S" series, Swaglok Co., Detroit, MI, USA) with rotameters indicating the flow rate before it was delivered into the gas washing bottle and was mixed with a pure vapor stream. The concentration of the vapor stream was determined by gas chromatography (GC) analysis. A 100 *μl* sample of the vapor stream was injected directly into the GC and the detector response from the GC (area unit) was used to determine the permeant vapor pressure by the following equation:

$$p = \frac{A \times R \times T}{CF \times V_{inj} \times MW} \tag{42}$$

where p = vapor pressure of permeant at T [*mmHg*]

A = area response [*AU*]

R = gas constant (62.36) [*l.mmHg/mol.K*]

T = temperature of vapor stream [*K*]

CF = calibration factor [*AU/g*]

V_{inj} = volume injection [*l*]

MW = molecular weight of permeant [*g/mol*]

$$a = \frac{p}{p_o} \tag{43}$$

where a = vapor activity of permeant

p = vapor pressure of permeant at T [*mmHg*]

p_o = saturated vapor pressure of permeant at T [*mmHg*]

Standard solutions of isopropanol were prepared by a serial dilution of isopropanol in acetronitrile from 1000 *ppm* to 20 *ppm* (volume by volume). A 1 μl sample of each concentration was withdrawn by a 10 μl liquid syringe (801N, Hamilton liquid syringe) and manually injected into the GC. A Hewlett Packard model 5890A gas chromatograph with flame ionization detector interfaced to an integrator, HP-3395, was used (Avondale, PA, USA). The calibration factor was obtained from the slope of the standard calibration curve, which was a plot of area response as a function of sample

weight injected (for each concentration). The calibration curve and calibration factor are presented in Appendix I. The column for this separation was Supelcowax 10 (60 *m* × 0.25 *mm*, 0.25 μm, Supelco, Bellefonte, PA, USA). The gas chromatographic conditions of separation were as follows:

Mode: splitless

Oven: 110 *°C* (10 *min*) to 220 *°C* at 5 *°C/min* and hold for 5 *min*

Carrier: helium 1 *ml/min*

Injection temp.: 220 *°C*

Detector temp.: 250 *°C*

Gases: He 40 psi (1 *ml/min*), H_2 19 psi (20 *ml/min*)

, air 35 psi (300 *ml/min*), N_2 30 psi (30 *ml/min*)

Elution time: 5.60 *min*

The saturated vapor pressure of isopropanol at room temperature was determined by injection of a 100 μl headspace sample from a sample vial (30 *ml*, crimp seal, Supelco, Inc, Bellefonte, PA, USA) to which was added 3 *ml* liquid isopropanol and the sealed vial stored in a constant temperature chamber (23 ± 1 ℃).

Samples of film were prepared by cutting test samples of about 13 *cm* × *13 cm* and mounting the test film on a frame which was designed to have an exposed surface area of 0.0081 m^2 . This was the area assumed for permeation determination. For calibration of the MAS 2000 test system, a clean surface aluminum foil sample was mounted on the mounting frame and placed between the front and back cell chambers. A 100 μl sample of a preset vapor stream was injected directly into the sampling port on the system chassis and the injected vapor sample conveyed by carrier gas directly to the FID detector for

analysis. After the instrument was calibrated, permeability tests were performed on a series of HDPE film samples. During a test run, the amount of isopropanol which had permeated was measured until a steady state rate was attained. Several vapor activity levels (0.1-0.4) were tested to evaluate the effect of penetrant concentration on the permeability, diffusion and solubility coefficient of the isopropanol / HDPE system.

Quasi-isostatic technique

The quasi-isostatic permeation runs were carried out with a system similar to that described by Hernandez, et al. (1986). The test system consists of a gas supply (N_2), a vapor generator system, flow controllers and a permeability cell. The vapor generator system was similar to that described aboves. The N_2 from a cylinder was split into two streams by a T-value and connected directly to flow controllers, one for the gas washing bottle and the other for mixing of pure N_2 with the vapor outlet stream from the gas washing bottle.

The permeability cell is made of stainless steel and consists of three cylindrical shape parts; a bottom and top cell chamber with an inside volume of 50 *cc* and a hollow center ring mounted between the two cell chambers, with a separation volume of 50 *cc*. This permeability cell creates an exposed surface area of the test film of about 50 cm^2. Sampling ports are affixed to each cell chamber and vapor inlet and outlet ports are configured to the center ring. For permeation measurements, a film sample was cut and mounted between the top cell chamber and the center ring, while the bottom chamber and center ring was isolated by an aluminum foil. The vapor stream was allowed to continuous flow through the center cell chamber during test and the quantity of

isopropanol permeated to the low concentration cell chamber was determined at predetermined time intervals by a GC procedure. For this analysis, a 100 μl sample was withdrawn from the low concentration cell chamber (1750 , Hamilton 500 μl gas tight syringe). The conditions of GC separation and the standard calibration factor were the same as previously described for the isostatic technique. Between each sample test, the permeability cell was washed and dried in a vacuum oven. For vapor activity selection, the center cell chamber was isolated from the top and bottom cell chambers with the aluminum foil and the organic vapor stream was flowed through the center cell chamber or high concentration cell chamber. A 100 μl headspace of sample was removed from the center cell chamber with a 500 μl gas tight syringe (1750, Hamilton 500 μl gas tight syringe) and the vapor concentration was determined by GC analysis. The gas flow through the vapor generator and diluant gas were then adjust to provide the desired vapor pressure.

Determination of partition coefficient of Isopropanol in HDPE film and water

The equilibrium partition coefficient of isopropanol between HDPE film and an aqueous solution was determined by a sorption technique. The sorption apparatus was designed based on the description presented in ASTM D4754-87, a standard test method for two-sided liquid extraction of plastic materials using the FDA migration cell.

Sorption was monitored from a a low concentration solution of ispropanol in water (100 *ppm* , volume by volume).

Test specimens were prepared from HDPE film in the form of round disks (OD 21.69 mm) by cutting with a cork borer. A stainless steel wire was formed as a support

stand, next 30 film disks were weighed and alternately threaded with glass beads onto the stainless wire, thus creating two sided contact. Each set of mounted disks were then placed into 40 *ml* precleaned amber vials, filled with 40 *ml* sorption solution (100 ppm , v/v isopropanol in water) and the vials closed with open-top screw cap-teflon / silicon septa (vials and caps from Supelco, Inc, Bellefonte, PA, USA). Four sets of sorption cells and one blank cell (no film disks) were prepared and stored in a constant temperature chamber (23 ± 1 ℃) for a period of 60 days to ensure equilibrium state. This storage time was estimated from a survey of equilibrium sorption times reported by Baner (1993), who reported that equilibrium sorption times for aqueous solutions of a variety of aromas into HDPE and polypropylene (PP) films were reached in about 20 days at 20 ℃.

During the course of the study, each of the sorption cells was shaken by hand every seven days. At the end of the storage time, the quantity of isopropanol remaining in solution and the concentration sorbed by the HDPE film disks were measured by application of a two step process, namely: sample preparation by a thermal stripper (TS) step and analysis with interfaced thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS).

Analysis technique

The thermal stripper and thermal desorption-GC-MS analytical techniques eliminated solvent extraction, which avoids loss of isopropanol during transfer and allowed for sufficient sensitivity for detecting very low levels of isopropanol sorbed by the HDPE film.

For the analytical procedure, the instrument parameters were optimized and a standard calibration curve for the TS and TD-GC-MS procedures was constructed by analysis of a series of standard solutions of known concentration. The optimized conditions for the TS and TD-GC-MS procedures are presented below.

Thermal Stripper

Instrument:	Model 1000 (Dynatherm, Kelton, PA, USA)
Sorbent material:	Carbotrap 302 with glass frit at sample inlet ID 4 *mm* (Supelco Inc, Bellefonte, PA, USA)
Carrier gas:	He 50 *psi*
Flow rate:	Preheat state 50 *ml/min* for 5 *min* Purge state 150 *ml/min* for 2 *min* Dry state turn off
Temperature:	Block 199 ℃, oven 110 *°C*, tube 75 ℃

Thermal Desorption

Instrument:	Model 890 (Dynatherm, Kelton, PA, USA)
Carrier gas:	He 60 *psi*
Flow rate:	Desorption at 7 *ml/min* for 6 *min* Clean at 35 *ml/min* for 30 *min*
Temperature:	Desorption 250 ℃, clean 280 ℃, transfer line 230 ℃.

Gas Chromatography and Mass Spectrometer

Instrument:	GC is a HP 5890A

Detector:	MS 5970 with Chemstation analysis software
	(Hewlett Packard, Avondale, PA, USA)
Column:	Supelcowax 10 (60 *m* × 0.25 *mm*, 0.25 μm)
Carrier gas;	He
Mode:	SIM (Selected Ion Monitoring)
	Selection m/z = 27, 31, 43, 59
Oven:	40 *°C* (5 *min*) to 200 at 5 *°C/min* and hold for 10 *min*
Elution time:	12.30 min

The TD unit was interfaced to the GC-MS unit. Thus, samples were thermally desorbed from the sorbent tube and delivered directly to the GC for separation and detected by MS. The calibration curve and calibration factor are presented in Appendix I.

Following a predetermined storage (equilibrium) time, the amount of isopropanol sorbed by the film disks (polymer phase) and that remaining in solution (liquid phase) were determined. Quantification of isopropanol in the liquid phase of the sorption cell and the analysis of standard solutions of known concentration was carried out by the same procedure. First, the TS unit was preheated until the oven temperature reached 110 °C, next a precleaned sorbent tube was affixed to the sample receiver port. A 3 μl of liquid sample was then withdrawn and injected into the side port of a 10 *ml* hang down tube mounted in the oven of the TD unit.

The isopropanol concentration in the liquid sample was then thermally transferred to the sorbent tube with a He flow of 150 *ml/min* for 2 *min* . The sorbent tube was then removed and transferred to a glass storage tube with screw cap closure. The sample sorbed by the sorbent tube was immediately analyzed by the TD-GC-MS procedure.

Desorption conditions were identical to those described above. The total sorbed amount of isopropanol was conveyed to the GC column which allowed for separation and quantification by MS operated in the SIM mode. The quantity of isopropanol in the liquid phase was further calculated in the form of concentration (*wt/wt*).

For determining the amount of isopropanol sorbed by the HDPE film disks at equilibrium, the stack of film disks was removed from the sorption cell and the film disks were collected and rapidly wiped free of remaining solution on the surface to reduce loss of isopropanol due to volatilization. Next, all of the dry film disks (about 0.35 *g*) were transferred to the sample hangdown tube of the TS unit and the analysis performed as described for the liquid phase. Again, the quantity of isopropanol in the polymer phase was further described in term of concentration (*wt/wt*).

Finally, the equilibrium partition coefficient of isopropanol between HDPE film and water was calculated by taking a ratio of the equilibrium concentration of isopropanol in the water and film, respectively.

Migration study of Isopropanol from HDPE film into water

A preliminary experiment for the migration of isopropanol from film into water was designed and tested by employing a solid phase microextraction (SPME) procedure. The preliminary experiment involved preparation of a spiked film sample followed by a migration experiment. The experimental details are described below.

Spiked film sample preparation

Isopropanol was spiked into cleaned HDPE film samples by a sorption technique. The cleaned HDPE film sample was exposed to a high concentration of isopropanol vapor in a closed chamber until reaching an equilibrium state. First, a stainless steel chamber (H 23 cm × ID 13 cm) equipped with gas inlet and outlet port and sampling port was connected to a vapor generator and a vapor stream of isopropanol was allowed to continuously purge through the assembled chamber. The vapor concentration was determined by sampling 100 *μl* of vapor from the gas outlet port with a 500 *μl* gas tight syringe (1750 , Hamilton 500 *μl* gas tight syringe) and analysis by GC-FID. The vapor generator system was similar to the one described for the permeation experiments. Next, four sets of mounted film disks were prepared as described in the previous section (on page 42) and film disks of each set were weighed. The respective sets of film disks were then hung on a stainless steel frame inside the sorption chamber and the chamber assembled. The samples were maintained in the chamber for more than 70 days to ensure an equilibrium sorption of isopropanol by the HDPE film disks.

Analysis for migration study

The migration apparatus was designed as described in ASTM D4754-87, a standard test method for two-sided liquid extraction of plastic materials using the FDA migration cell. The mounted series of isopropanol spiked film disks was placed into a 40 *ml* precleaned amber vial filled with 40 *ml* water and closed with an open-top screw cap-teflon/silicone septa. At predetermined time intervals, a 1.3 *ml* aliquot of solution was withdrawn and transferred to a 2 *ml* vial which was closed with a screw top hole cap

PTFE/silicone septa (Supelco, Inc, Bellefonte, PA, USA). At the time of sampling, a disk of film was removed from the stack to maintain a constant ratio of contacting surface area and volume of water (1 *ml/in*^{2}). The isopropanol in the liquid sample transferred to the 2 *ml* vial was extracted by SPME and simultaneously stirred with a magnetic stirring bar for 10 *min.*

Following extraction, the amount of isopropanol sorbed by the fiber of the SPME apparatus was analyzed by direct thermal desorption into the GC-FID via the injection port. The fiber type used for the SPME and the GC-FID conditions are shown below.

SPME fiber: 65 μm Polydimethylsiloxane/divinylbenzene polymer
(Supelco, Inc, Bellefonte, PA, USA)

GC-FID conditions

Instrument: GC model HP 6890 with Integrator model HP 3396
(Hewlett Packard, Avondale, PA, USA)

Column: HP-5 (crosslinked 5% PH ME siloxane),
(30 *m* × 0.32 *mm*, 0.25 μ *m*)
(Hewlett Packard, Avondale, PA, USA)

Mode: splitless

Oven: 50 °*C* (5 *min*) to 90 °C at 2 °C/*min*
and to 220 °C at 10 °C/*min* hold for 5 *min*

Carrier: helium 1 *ml/min*

Injection temp: 220 °C

Detector temp: 280 °C

Gases: He 40 psi (1 *ml/ min*), H_2 50 psi (33 *ml/ min*)

, air 60 psi (400 *ml/ min*), N_2 40 psi (25 *ml/ min*)

Desorption: 30 *min*

Elution time: 3.08 min

Between each sample analysis, the fiber of the SPME apparatus was cleaned thermally by maintaining the fiber inside the injection port of the GC for a period of 30 minutes. The migrating amount of isopropanol in water was further calculated. The calibration curve and calibration factor are presented in Appendix I.

Determination diffusion coefficient of Tetracosane in HDPE film

Tetracosane being a solid at room temperature and exhibiting an extremely low vapor pressure negated the ability to determine the diffusion coefficient of tetracosnae throuugh HDPE film by either a permeability method or by the vapor sorption method. The migration method could be applied to determine the diffusion coefficient under an experimental design corresponding to the boundary conditions of the mathematical relationship expressed in equation 11. With further assumptions, an estimation of the diffusion coefficient could be made, based on inclusion of tetracosane into HDPE film and monitoring it migration.

Spiked film making

Tetracosane spiked pellets were prepared by a coating technique, and subsequently used to fabricate tetracosane spiked HDPE film. A level of tetracosane in the pellets was set at about 500 *ppm* by weight. First, the HDPE pellet and tetracosane

were weighed at levels of 150 *g* and 0.075 *g*, respectively. Next, the tetracosane was dissolved in 100 *ml* of hexane and transferred to a 1000 *ml* round bottom flask. The HDPE pellets were then mixed into this solution and the process of coating was started together with solvent evaporation by using a Buchi Evaporator model RE-111A (Fisher Scientific, Pittsburgh, PA, USA). The round bottom flask was immersed in a water bath which was heated to 65 ℃ with a Thermolyne Nuova II hotplate (Fisher Scientific, Pittsburgh, PA, USA) and it was slowly rotated under water asperator pressure, until the solvent was fully evaporated. Three batches of coated pellets were prepared for extrusion to film.

The coated pellets were fabricated to films using a Killion Extruder model KLB-100 (Killion Extruder, Inc., Cedar Grove, NJ, USA). The films were extruded under the following conditions.

Barrel zone temp.:	zone1 355 ℉, zone2 380 ℉, zone3 380 ℉
Die temperature:	385 ℉
Screw speed:	14.5 *rpm*
Chill roll temp.:	65 ℉
Chill roll speed:	9.8 *rpm*

With the above conditions, the thickness of the film was between 0.0015-0.0020 inch.

Migration test

The migration apparatus was designed following the procedure described in ASTM D4754-87, a standard test method for two-sided liquid extraction of plastic

materials using the FDA migration cell. The migration of tetracosane from spiked film into hexane, water and acetonitrile was monitored under the same test conditions. First, the initial concentration of tetracosane in the spiked film was determined; 30 disks of spiked film (about 0.39 g / 0.022 m^2) were weighed and extracted with hexane by soxhlet extraction technique for 24 hours, and the extracted solution analyzed for tetracosane by GC-FID. Eight sets of mounted spiked film disks and three sets of blanks were prepared following the procedure described in the previous section for determination of the partition coefficient of isopropanol. The weight of the spiked film disks for each set was recorded. The stacks of spiked film disks were then placed separately into 40 *ml* precleaned amber vials, filled with 40 *ml* hexane for four cells, water for two cells and acetonitrile for two cells. The remaining three blank cells were separately filled with these solvents. All migration cells were closed with open-top screw cap-teflon/silicone septa. At predetermined time intervals, a 1 μl aliquot of solution was analyzed by GC-FID, under the following conditions.

GC-FID conditions

Instrument:	GC model HP 5890A with Integrator model HP 3395 (Hewlett Packard, Avondale, PA, USA)
Column:	SPB-5 (poly 5%-diphenyl-95%-dimethylsiloxane), (30 m × 0.32 mm, 0.25 μm), (Supelco, Inc, Bellefonte, PA, USA)
Mode:	splitless
Oven:	250 $°C$ hold for 30 min
Carrier:	helium 1 ml/min

Injection temp: 300 ℃

Detector temp: 250 ℃

Gases: He 45 psi (1 *ml/min*), H_2 20 psi (33 *ml/min*)

, air 40 psi (300 *ml/min*), N_2 35 psi (25 *ml/min*)

Elution time: 6.63 min

Standard solutions of tetracosane in hexane were prepared by a serial dilution procedure and used to determine the linearity and sensitivity of the analytical procedure. The calibration curve and calibration factor are presented in Appendix I.

Evaluating the migrating amount of Isopropanol and Tetracosane from single layer HDPE film and lamination HDPE film

By knowing the diffusion coefficient of isopropanol and tetracosane in HDPE film, the migration rate of these compounds into a food contact phase, which is assumed to be controlled by the diffusion process, can be calculated from suitable equations derived for specific boundary conditions. Here, a migration rate of both compounds from a single layer film was estimated by equation 11. In addition, the functional barrier for preventing the transfer of migrants into a food contact phase from a laminate film contaning a contaminated HDPE layer and a virgin HDPE layer was evaluated by computing the migrating amount of both compounds from film into food contact phase with the Laoubi and Vergnaud migration model (Laoubi et al., 1995) and the Begley and Hollifield migration models (Begley et al., 1993). The results of migration from a single layer and a lamination film were compared and the functional barrier was evaluated, based on the capacity of remaining contaminants level inside the film.

RESULTS AND DISCUSSIONS

Permeation Measurements of Isopropanol through HDPE Film

The results of permeation measurements determined by both the isostatic and quasi-isostatic techniques are summarized below.

Diffusion coefficient of isopropanol in HDPE film

The diffusion coefficient of isopropanol in HDPE film was determined from the permeation data for isopropanol vapor through a HDPE film, measured by both the isostatic and quasi-isostatic techniques. Both techniques employ the same concept to determine the diffusion coefficient of vapor in film. The isostatic or dynamic permeation measurement allows the diffusion coefficient to be calculated from the $t_{0.5}$ value, which is related to the fractional change in mass flux from time zero to steady-state flux, where the $t_{0.5}$ value is the time required to reach one-half of the steady state transmission rate, as shown in equation 24. Whereas the diffusion coefficient obtained from the quasi-isostatic procedure is related to the intersection of the linear portion of the transmission rate profile curve with the time axis, where the obtained lag time value (θ) is used to calculate the diffusion coefficient by substitution into equation 26. The permeation measurements were performed at several vapor activity levels, at room temperature (23 ± 1 ℃), to evaluate the effect of vapor concentration on the diffusion coefficient. Since the test temperature was well above T_g for HDPE, about 195-200 K, the HDPE film is in the

rubbery state. Thus, the measured permeation of isopropanol vapor is assumed to be governed only by the diffusion mechanism. The diffusion coefficient values for isopropanol through HDPE film by both isostatic and quasi-isostatic permeation method are presented in Tables1 and 2, respectively. For the isostatic technique, the diffusion coefficient was between 3.6×10^{-14} to 3.9×10^{-14} m^2/s for the vapor activity range between 0.1 and 0.38, while for the quasi-isostatic technique, D values were between 3.6×10^{-14} to 4.5×10^{-14} m^2/s, for the vapor activity levels between 0.15 to 0.5. The quasi-isostatic procedure showed greater scatter in the data as shown in Figure 1, where the diffusion coefficient values are plotted as a function of vapor activity for both the isostatic and quasi-isostatic procedures. The results from the quasi-isostatic permeation method show much more fluctuation of the diffusion coefficient than the values obtained by the isostatic method. This is attributed to the fact that the calculation of diffusion coefficient from the quasi-isostatic procedure requires a very precise linear portion of the steady state transmission rate to define the time lag by extrapolation. The error was not considered due to extrapolation of the steady state portion of the curve to the x axis, but rather that the experimental method required manually sampling and analysis during the permeation experiments. However, in terms of statistical analysis, there was no statistically significant difference in the population mean of diffusion coefficient values observed between either technique, at a significance level of 0.5 (Appendix II). It was also found that there was no statistically significant difference in population mean of the diffusion coefficient between concentrations levels for each technique. This leads to the conclusion that the diffusion coefficient of isopropanol in HDPE film is likely independent of concentration, within the experimental range of activities studied.

Table 1 Diffusion, Permeability and Solubility Coefficient values for Isopropanol in HDPE film by the Isostatic technique[1]

Vapor activity	Diffusion Coefficient (m^2/s)	Permeability Coefficient (μ g.m/m^2.s.Pa)	Solubility Coefficient (g/g.Pa)
0.10	3.6E-14	4.6E-9	1.6E-7
0.21	3.8E-14	4.6E-9	1.5E-7
0.38	3.9E-14	4.6E-9	1.5E-7
Average	3.7E-14	4.6E-9	1.6E-7
SD	±2.9E-15	±4.2E-10	±1.8E-8

[1]. The results are the average of four samples.

Table 2 Diffusion, Permeability and Solubility Coefficient values for Isopropanol in HDPE film by the Quasi-isostatic technique[2]

Vapor activity	Diffusion Coefficient (m^2/s)	Permeability Coefficient (μ g.m/m^2.s.Pa)	Solubility Coefficient (g/g.Pa)
0.15	3.6E-14	3.7E-9	1.3E-7
0.19	4.2E-14	3.9E-9	1.2E-7
0.27	4.5E-14	4.5E-9	1.3E-7
0.41	3.9E-14	4.4E-9	1.4E-7
0.50	3.9E-14	3.8E-9	1.2E-7
Average	4.1E-14	4.1E-9	1.3E-7
SD	±5.7E-15	±8.4E-10	±3.0E-8

[2]. The results are the average of at least two samples.

Permeability coefficient of isopropanol through HDPE film

The permeability coefficient values for isopropanol through HDPE film, determined by the isostatic and quasi-isostatic procedures are summarized in Tables 1 and 2, respectively. For better illustration, the permeability coefficient values determined are plotted on a function of permeant concentration in Figure 2. As shown, the permeability

coefficient values agreed well over the vapor activity range evaluated. Further, there was good agreement between the *P* values determined by the two procedures

Solubility coefficient of isopropanol in HDPE film

In addition to determining the diffusion and permeability coefficients, the permeation measurement also allows for determination of the solubility coefficient from the relationship $P = DS$, assuming the diffusion coefficient is independent of the penetrant concentration and Henry's law is obeyed. Here, the diffusion coefficient was constant and did not vary statistically with concentration and Henry's law was assumed, due to the low vapor activity range studied. Thus, the solubility coefficient values determined from permeability data by both the isostatic and quasi-isostatic techniques were assumed to be acurate (see Tables 1 and 2). As shown, the solubility coefficient values obtained from both techniques were in agreement, with *S* falling between 1.2×10^{-14} and 1.6×10^{-14} *g/g Pa*. The relationship between the solubility coefficient values determined by the respective permeability experiments and vapor activity is shown in Figure 3.

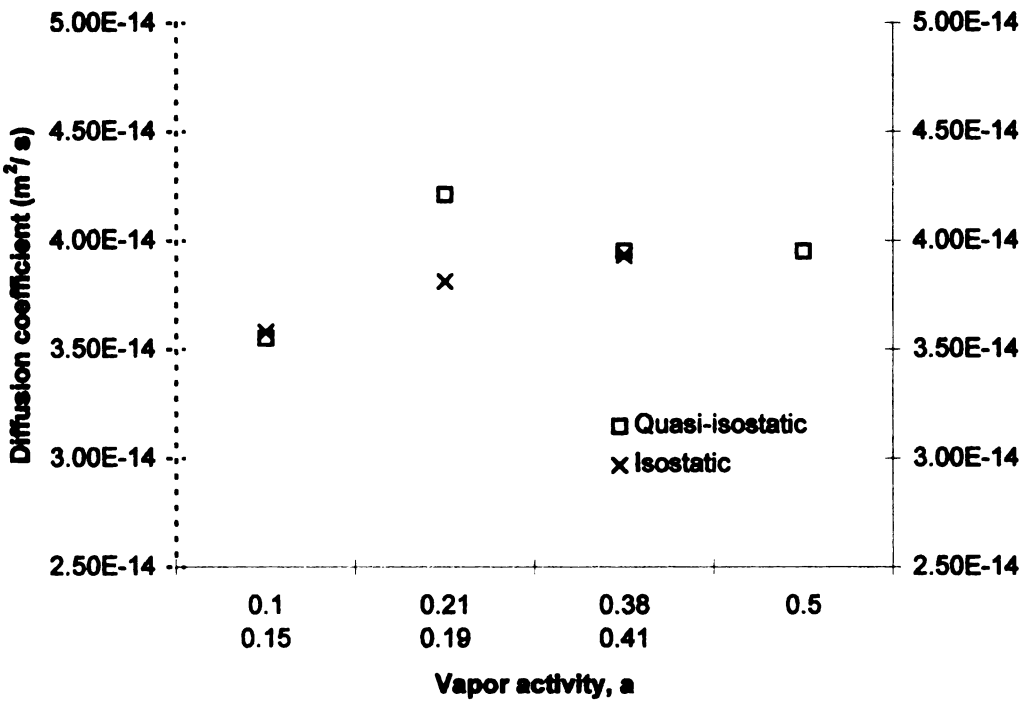

Figure 1 Diffusion coefficient of Isopropanol in HDPE film at 23 °C by Quasi-isostatic and Isostatic permeation techniques.

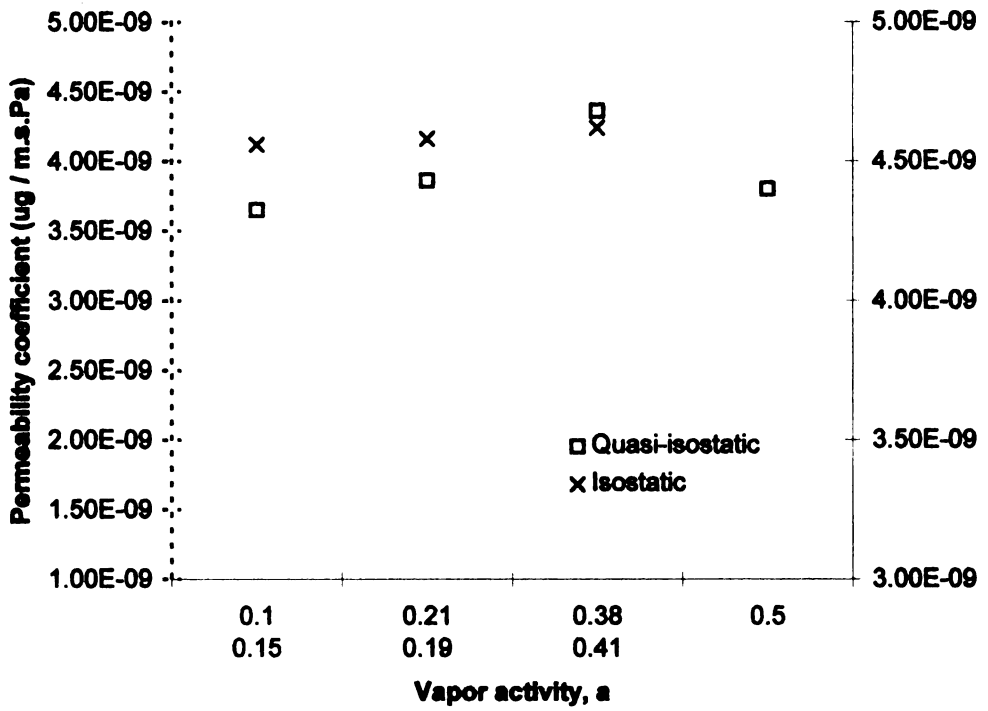

Figure 2 Permeability coefficient of Isopropanol through HDPE film at 23 °C by Quasi-isostatic and Isostatic permeation techniques.

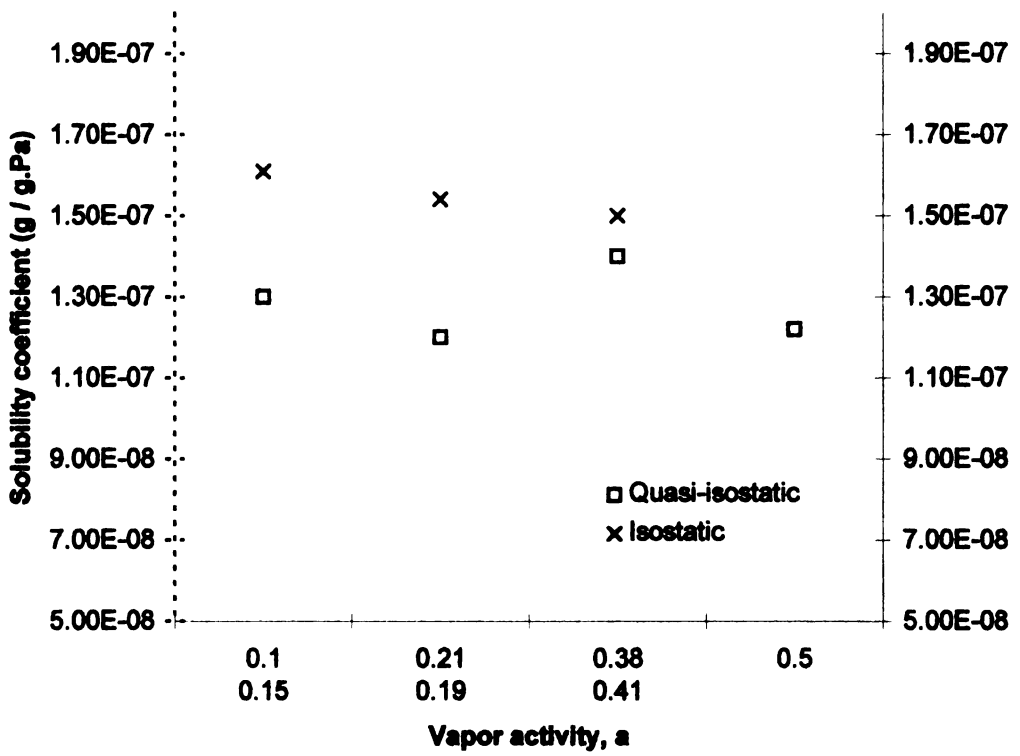

Figure 3 Solubility coefficient of Isopropanol in HDPE film at 23 °C by Quasi-isostatic and Isostatic permeation techniques.

Determination of the Equilibrium Partition Coefficient of Isopropanol between HDPE Film and Water

The equilibrium partition coefficient of isopropanol between HDPE film and water was determined by measuring the equilibrium sorption of isopropanol in HDPE film and the level of isopropanol remaining in the aqueous solution at equilibrium. The equilibrium partition coefficient values determined are reported as a ratio of the equilibrium concentration of isopropanol in the aqueous solution divided by the sorbed concentration of isopropanol in HDPE film at equilibrium ($K_{L/P}$). Three samples and one blank or control were tested and the results are summarized in Table3.

Table 3 Equilibrium partition coefficient of Isopropanol between an aqueous phase and HDPE film by the sorption method at 23 °C

Sample	C_L (wt/wt)[1]	C_P (wt/wt) [2]	$K_{L/P}$[3]
blank	7.5E-5	-	-
1	7.3E-5	1.2E-7	6.0E+2
2	7.5E-5	1.3E-7	5.6E+2
3	7.5E-5	1.2E-7	6.3E+2
average	-	-	6.0E+2
standard deviation	-	-	±36

[1]. C_L is a concentration of isopropanol in aqueous phase.
[2]. C_P is a concentration of isopropanol in HDPE film.
[3]. $K_{L/P}$ is a partition coefficient of isopropanol between aqueous phase and HDPE film.

A partition coefficient value of 600 clearly indicates a very low amount of isopropanol sorbed by the HDPE film from the aqueous solution and supports the expectation of low solubility of isopropanol in HDPE film. Here, the partition coefficient was determined by the equilibrium sorption procedure and was determined at only one sorbate concentration (100 *ppm, wt/wt*). This partition coefficient value was determined

at an initial isopropanol concentration of 100 ppm (*wt/wt*) and it was assumed to be a constant, with no concentration dependence over a wide range of sorbate concentrations. The analytical method developed to determine the concentration levels of isopropanol in the HDPE phase, the TS-TD-GCMS procedure, has a sensitivity at a sufficiently low level for the analysis of relatively low sorbed amounts of isopropanol in the polymer. Gavara et al. (1996) was successful in using TS-TD-GCFID procedure to determine the partition coefficient of toluene in water/polystyrene, as well as for binary mixtures of toluene and d-limonene, toluene and ethyl acetate in water/polystyrene (Gavara, et al., 1996). In this case, partition coefficient ($K_{P/L}$) values ranging between 1.9 and 5100 were determined.

Migration Studies of Isopropanol from HDPE Film into Water

The migrated amount of isopropanol from spiked HDPE film into water was measured as a function of time by the SPME procedure until a constant amount of migration was reached. Next, the actual level of migration in mass per unit area was plotted as a function of time and the predicted migration levels were calculated from equation 12, where the diffusion coefficient was varied until the linear portion of the prediction curve was superposed over the actual migration curve. The results are summarized in Table 4 and presented graphically in Figure 4, where the migrated levels of isopropanol (g/m^2) is plotted as a function of contact time. As shown in Figure 4, the predictive migration levels agreed well with the actual migration levels for the contact time from 0 to 10,800 sec. However, since the initial concentration of migrant in the film was assumed to be constant, for application of equation 12, but in practice the migrant

concentration is gradually decreasing until an equilibrium concentration is obtained, application of equation 12 may not be applicable over the total time range to equilibrium. Since the assumption of a constant migrant concentration is not valid over the total time range. The diffusion coefficient by this superposition method to give the best fit to the test data was 3.0×10^{-14} m^2/s, which the average the diffusion coefficient determined by the isostatic technique was 3.7×10^{-14} m^2/s. A complete calculation of the predictive curve is presented in Appendix III.

The SPME is theoretically excellent for qualitative analysis and good for quantitative analysis, if it is well calibrated. In this experiment, the SPME with PDMS/divinylbenzene fiber was applied to extract isopropanol in water. In this case, the stagnant layer of water around the fiber may interfere with the partitioning of isopropanol between water and fiber, even with the use of magnetic stirring. This can limit the sensitivity of the fiber to extract analyte, particularly small amounts of polar compounds such as isopropanol from the water phase. Theoretically, the SPME affords an alternative, and highly sensitive extraction technique, provided the fiber has a strong affinity for analytes such as isopropanol in water and reduces the chance of loss of isopropanol during analysis. Nevertheless, the SPME could be a fast extraction instrument for survey experiments. In general, analytical methods for determination of very low levels (*ppb*) of volatile polar compounds in aqueous solution are difficult. Many commonly used solvent extraction techniques are not suitable for extraction of polar compounds in water. Even though the purge and trap technique has worked well for some solvents, the sensitivity is limited to part per million, due to their solubility in water (Shirey 1997). Hence, for migration studies, it may be preferable to determine the actual

contaminant levels in the film, which are normally very low, rather than to determine trace levels of migrants in an aqueous contact phase.

Table 4 Migration of Isopropanol from spiked HDPE film into aqueous phase (water) at 23 °C

Time (sec)	Actual Migration (g/m^2)	Predicted Migration [1] (g/m^2)
0.00	0.00	0.00
9.0E+2	0.011	0.012
3.6E+3	0.021	0.024
1.1E+4	0.034	0.041
2.2E+4	0.038	0.058
9.0E+4	0.039	0.12

[1]. The migrated amount are predicted by using equation 12.

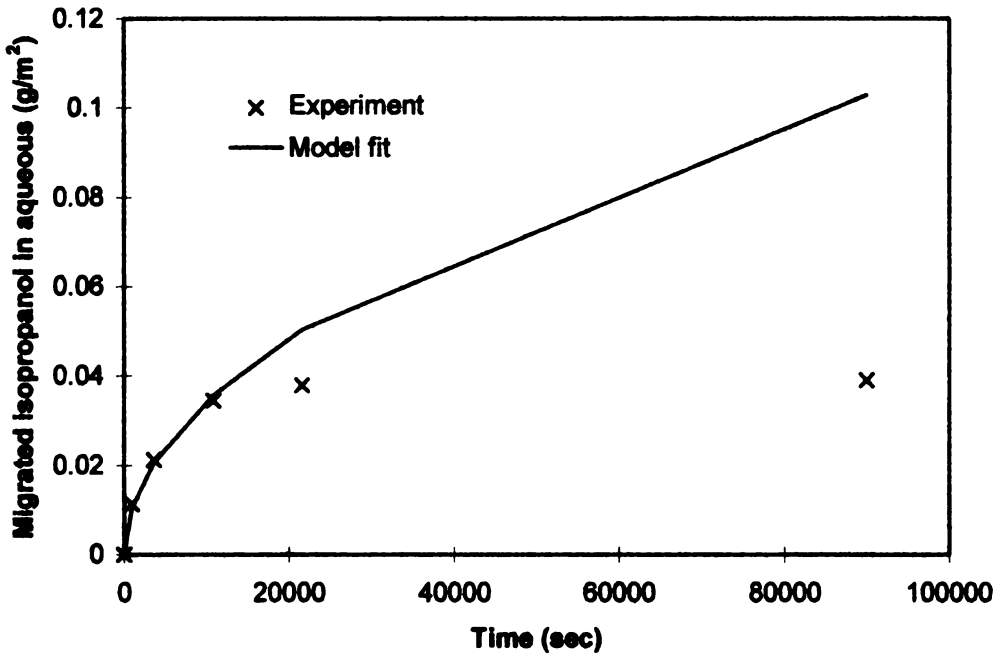

Figure 4 Migrated amount of Isopropanol from spiked HDPE film into aqueous phase (water) at 23 °C

Determination of Diffusion Coefficient of Tetracosane in HDPE Film

The tetracosane spiked HDPE film samples were prepared as described in the materials and methods section and were extracted with hexane by soxhlet extraction to determine the initial concentration of tetracosane present. The extraction solvents were analyzed by GC-FID and the results are summarized in Table 5. The initial tetracosane concentration of coated HDPE resin expected was about 500 *ppm* (*wt/wt*), based on the mixing ratio. As shown in Table 5, the calculated level of tetracosane in the spiked HDPE pellets was in good agreement with the mixing ratio concentration. This verified the validity of the coating method for impregnation of tetracosane onto HDPE resin pellets. As also shown in Table5, the initial amount of tetracosane in the extruded film

appeared to be constant and with minimal losses during the extrusion step, providing further supportive evidence of the validity of using this average initial concentration as the initial concentration for the migration experiments.

Table 5 Initial amount of tetracosane in coated pellet and extruded film

Sample[1]	Weight of sample (g)	Weight of $C_{24}H_{50}$ (g)	Concentration (g/g)
film1	0.3944	0.00016	0.00039
film2	0.4041	0.00016	0.00039
film3	0.4386	0.00018	0.00042
coated pellet	0.4238	0.00021	0.00049

[1]. Sample films were cut from several area of film roll.

The diffusion coefficient of tetracosane in HDPE film was estimated by solving for M_t/M_∞ from equation 12, with varying diffusion coefficient values and comparing the calculated and actual migration data for the best fit. The actual migration experiments were carried out with three selected solvents, namely: hexane, acetonitrile and water. For acetonitrile and water, there was no measurable migration of tetracosane within experimental time, while for hexane, a rapid rate of migration of tetracosane was observed. The actual migration data obtained and the predicted migration values are presented in Appendix IV. The diffusion coefficients estimated for each sample are summarized in Table 6. Also summarized in Table 6 are the determined partition coefficient values. No attempt was made at evaluating the effect of tetracosane concentration on the partition distribution and the diffusion coefficient was assumed to be a constant and independent of sorbate concentration

The average diffusion coefficient for tetracosane in HDPE film was 1.1×10^{-16} m^2/s. This values agreed with the diffusion coefficient values for n-C18 and n-C32 hydrocarbon in HDPE, as determined by Limm and Hollififield (1996) and shown in Table 7. Even though the migrant, the solvent and testing condition were different from these employed in the present study, comparison provided the trend of the diffusion coefficient value. The diffusion coefficient of tetracoane in hexane was less than the n-32 hydrocarbon in corn oil since hexane is a stronger solvent than corn oil and the testing temperature was also lower. It is important to note that since hexane is an polymer swelling solvent for HDPE, the calculated diffusion coefficient value is considered an upper bound value. For a non-interactive contact phase, the diffusion coefficient for tetracosane in HDPE may be several order of magnitude lower.

A potential source of error associated with the above method for determination of the diffusion coefficient is lack of agreement with the assumption that tetracosane migration is a Fickian diffusion controlled process, since the prediction model (equation 12) is a solution for Fick's second law of diffusion. However, by observing the migration curve (a plot of M_t/M_∞ as a function of square root of time as shown in Figure 20-25, Appendix IV), which showed a linear region in the initial stage (but less than 60 % of M_∞) followed by the curve being concave to the abscissa axis, it was assumed that the migration process was well described by equation 12 and the estimated diffusion coefficient would not be in serious error. For a prediction of migration of tetracosane in other food systems, the high value of this diffusion coefficient, compared to food solvent would be considered as a safety factor of the packaging design.

Table 6 Partition coefficient and diffusion coefficient of tetracosane in HDPE/Hexane at 23 °C

Sample	Partition coefficient $K_{L/P}$	Diffusion coefficient m^2 / s
1	0.0048	5.0E-17
2	0.0075	1.5E-16
3	0.0080	1.6E-16
4	0.0069	6.5E-17
5	0.0062	1.9E-16
6	0.0034	2.0E-17
Average	0.0061	1.0E-16
SD	0.0017	±6.9E-17

Table 7 Comparing diffusion coefficient of tetracosane in HDPE/Hexane to n-C18 and n-C32 in HDPE/corn oil

Polymer	Migrant	Temperature (°C)	Solvent	Diffusion coefficient (m^2/s)
HDPE	n-18	30	corn oil	1.3E-14[1]
HDPE	n-24	23	hexane	1.1E-16
HDPE	n-32	30	corn oil	1.2E-16[2]

[1],[2]. The data were from Limm and Hollifield (1996).

Estimating Migration Levels of Isopropanol and Tetracosane from a Single Layer HDPE Film and a Laminated HDPE Film

Based on the assumption that migration of contaminants into a food contact phase (liquid food) is a solely diffusion controlled process, the migration of isopropanol and tetracosane from a polymer film to a fluid contact phase was estimated separately, for a single layer HDPE film and laminated HDPE film by using the diffusion coefficient values determined for the respective migrants in HDPE film. Three migration models, namely: (i) a simple model (Model I) for a single layer film; (ii) the Begley and Hollifield

model (Model II); and (iii) the Lauobi and Vergnaud model (Model III), were evaluated to estimate the amount of migration. The simple model (Model I) was used to estimate migration levels from a single layer structure, while Models II and III were used to estimate migration from a two layer laminate structure. An evaluation of these models was made and the effectiveness of a functional barrier layer (virgin HDPE layer) to prevent the migration of both compounds was also determined.

The three migration models considered are discussed below.

Single layer of HDPE film (Model I):

$$M_t = 2C_p^o\left(\frac{D_p t}{\pi}\right)^{1/2} \qquad \text{from eqn. 11}$$

Double layer lamination model:

Begley and Hollifield model (Model II)

$$\frac{M_t}{lC_l} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-\frac{Dn^2\pi^2 t}{l^2}\right) \qquad \text{from eqn. 41}$$

Lauobi and Vergnaud model (Model III)

$$\frac{M_{r,t}}{M_{in}} = \frac{8L}{\pi^2 H}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)^2}\sin\frac{(2n+1)\pi\ H}{2L}\exp\left(-\frac{(2n+1)^2\pi^2}{4L^2}Dt\right) \quad \text{from eqn. 38}$$

$$\frac{M_{b,t}}{M_{in}} = \frac{8L}{\pi^2 H}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\sin^2\frac{(2n+1)\pi\ H}{2L}\exp\left(-\frac{(2n+1)^2\pi^2}{4L^2}Dt\right) \quad \text{from eqn. 39}$$

$$M_t = M_{in} - M_{r,t} \quad \text{from eqn. 40}$$

It should be noted here that the single layer would be called the recycle layer or contaminated layer and the virgin layer is called the barrier layer. The single layer was a recycled HDPE film, while the laminate was a HDPE/HDPE structure, with the recycled HDPE forming the external surface, and the barrier or virgin HDPE layer providing the food contact layer.

From the Plastics Recycling Task Force document, "Guidelines for the Safe Use of Recycled Plastics for Food Packaging Applications" (NFPA, SPI, 1994), a study of the effectiveness of plastics reclamation processes was made. In these guidelines, seven compounds which are 2,4 dichlorophenol, ethylene glycol, isopropanol, methyl salicylate, methy stearate, 2,2,4-trimethylpentane and xylene were selected to represent possible contaminants present in post consumer recycled plastics. It was stated in the guidelines that "a level of 1% of each surrogate in plastics was an effective contamination rate, which was believed to exaggerate the level of contaminated container that can be found in

the recycled stream." The guidelines involved spiking virgin HDPE flakes with 1 % of each of the contaminants and determining the levels of the respective contaminants remaining in the spiked HDPE flakes after they had been through a cleaning step in the reclamation process. The remaining contaminant levels were then assumed to be representative of the initial concentration levels of contaminants in recycled HDPE plastics. By assuming a 1% level of the contaminant in post consumer HDPE plastic, followed by the cleaning process, the retained isopropanol level was 0.21 $\mu g/cm^3$ which is lower than the minimum initial concentration level of 0.81 $\mu g/cm^3$ required to attain the maximum allowable contaminant level in food. In addition, there was no data report for tetracosane in the guideline. Thus, here, the initial concentration level of isopropanol and tetracosane in HDPE film was calculated based on a threshold of regulation dietary exposure level, 0.5 *ppb* in food, as shown below.

For estimation of migration levels, an initial concentration of migrants in HDPE film was calculated, based upon a threshold of regulation dietary exposure, 0.5 *ppb*, together with a consumption factor of HDPE, 0.33,and a ratio of food weight and contacting package area, 1.55 g/cm^2 , as recommended by the FDA (FDA, 1992). The density of the HDPE film and the thickness of the recycle layer were 0.965 g/cm^3 and 0.002921 *cm* (1.15 *mil*), respectively. From the regulation dietary exposure and the consumption factor, the concentration of migrant in the food contact phase was obtained by the following expression;

$$CF \cdot M = 0.5 ppb \tag{44}$$

where; CF = consumption factor

M = the concentration of migrant in food

Thus, for recycled HDPE plastic, the maximum allowable migrant concentration level in the food was 1.5 *ppb* (*gram migrant/gram food*). Next, the minimum initial concentration in HDPE film yielding 1.5 *ppb* in the food was calculated from the expression;

$$M = \frac{W_p \cdot M_{in}}{FC} \tag{45}$$

where;

M	= the concentration of migrant in food	$[g_m/g_f]$
W_p	= the weight of polymer for 1 cm^2	$[g_p/cm^2]$
M_{in}	= the initial concentration of migrant in polymer	$[g_m/g_p]$
FC	= the ratio of food to contacting package area	$[g_f/cm^2]$

By substituting all variables in equation 45, the minimum initial concentration level of migrant in HDPE film yielding 1.5 *ppb* in the food was 0.84 *ppm* (*wt/wt*) or 8.1×10^{-7} g/cm^3. This minimum initial concentration level of migrant in film represents the lower bound of migrant level that can result in a migrant concentration level of 1.5 *ppb* in food, assuming the migrant completely transfers to the food. Furthermore,

concentration levels of migrant which are above this minimum concentration level in the film would be expected to show higher migration rates, due to the higher concentration gradient and thus exceed the restriction migrant concentration level more rapidly.

Even though using a minimum initial concentration level of migrant of 0.84 *ppm* (*wt/wt*)in the film to estimate migration levels to a food contact phase by Model I, II and III will equal but not exceed the regulation limit of 1.5 *ppb*. (assuming total migration), this minimum initial concentration level of migrant in film was still selected to estimate the migration levels of isopropanol and tetracosane to food migrating from a single layer and a laminated HDPE film, based on the following considerations. First, the migrant level in food will never reach the regulation limit if the migrant concentration level is lower than the selected minimum initial concentration level of migrant in film (0.84 *ppm*). Second, if the estimated migrant levels in the food contact phase, calculated by Model II and III show an 'ineffectiveness' of the functional barrier layer to prevent the migration of contaminant, such that the time for the migrant level in the food to equal or exceed the regulation limit is less than the expected product shelf life, it can be concluded that the migration of higher initial concentration levels of migrant in film can not be prevented by the same functional barrier layer. On the contrary, if the estimated migrant level in the food, calculated by Models II and III, shows an 'effectiveness' of a functional barrier layer to retard the migration of contaminant, such that the time for the migrant level in the food contact phase to approach the regulation limit is much longer than the expected product shelf life, it can not be directly concluded, as to whether it is safe to use the functional barrier to prevent the migration levels from being exceeded at higher initial concentration levels. However, it still demonstrates the potential use of a functional

barrier to restrict migration, by reducing the initial concentration level of contaminant in film to as low a value as possible.

The diffusion coefficient values determined for the respective migrants and used to solve for the levels of migrant transfer with time were an average value for each of migrant, namely: 3.7×10^{-10} cm^2/s and 1.1×10^{-12} cm^2/s for isopropanol and tetracosane respectively.

For both migrants, the estimated migration levels from the recycle layer by Model I were compared to the results obtained from Models II and III. In the latter cases, a functional barrier layer of HDPE was considered. The results of the solution of the respective migration models are summarized in Tables 8 and 9 and presented graphically in Figures 5 and 6. For Models I and II, the presented results which were above 1.5 *ppb* as shown in Tables 8 and 9 and Figures 5 and 6 are invalid numbers and are only used to illustrate the deficiencies of the two Models. As shown in Figures 5 and 6, migration model I gave the fastest time to reach the maximum allowable level in the food, 1.5 *ppb*, since no functional barrier layer was considered. From Tables 8 and 9, it becomes apparent that a barrier layer retards the rate of migration, especially for Model III. Model II also predicted a rate of migration similar to that of Model I, since in Model II, the initial concentration of migrant was assumed to be constant at the surface of the barrier layer located next to the recycle layer and there was no consideration given to the migration rate of migrant within the recycle layer. In Model III, the thickness of the recycle layer and the gradual reduction of the initial migrant concentration are considered, making this model more realistic. Nevertheless, for a very thin barrier thickness such as 1 *mil*, the results from Model III showed a failure of the functional barrier to totally prevent

the migration of isopropanol. The total amount of isopropanol was transferred into the food in less than five days. In contrast to isopropanol, the results from Model III showed an effectiveness of the barrier layer to retard the migration of tetracosane. It would take more than one and a half years to attain about 95% migration at the same initial concentration of migrant.

Table 8 Comparison of the migrated amount of isopropanol from a single layer film and a laminated film based on predictive Models I, II and III[1]

Time (sec)	Model I[2] (ppb)	Model II[3] (ppb)	Model III (ppb)
0.00	0.00	0.00	0.00
3.6E+3	0.68	0.09	0.04
7.2E+3	0.96	0.33	0.16
1.1E+4	1.2	0.60	0.30
1.4E+4	1.4	0.87	0.42
1.8E+4	1.5	1.1	0.53
2.2E+4	1.7	1.4	0.64
2.3E+4	1.7	1.5	0.67
2.9E+4	1.9	2.0	0.81
7.2E+4	3.0	5.2	1.3
8.6E+4	3.3	6.3	1.4
1.8E+5	4.8	13.4	1.5

(1). A single layer film is a 1.15 mil contaminated HDPE film, while a laminated film is a lamination of 1.15 mil contaminated HDPE film and 1 mil virgin HDPE film.

(2),(3). The values above 1.52 are an invalid numbers and just presents the defect of Model I and II.

Table 9 Comparison of the migrated amount of tetracosane from a single layer film and a laminated film based on predictive Models I, II ad III[1]

Time (sec)	Model I[2] (ppb)	Model II[3] (ppb)	Model III (ppb)
0.00	0.00	0.00	0.00
5.0E+6	1.3	0.86	0.41
6.0E+6	1.5	1.1	0.50
8.0E+6	1.7	1.5	0.66
1.0E+7	1.9	1.9	0.80
1.2E+7	2.1	2.4	0.92
2.0E+7	2.7	4.1	1.2
5.0E+7	4.2	10	1.5
8.0E+7	5.4	17	1.5
9.0E+7	5.7	19	1.5
1.0E+8	6.0	21	1.5
1.5E+8	7.4	32	1.5

(1). A single layer film is a 1.15 mil contaminated HDPE film, while a laminated film is a lamination of 1.15 mil contaminated HDPE film and 1 mil virgin HDPE film.

(2),(3). The values above 1.52 are an invalid numbers and just presents the defect of Model I and II.

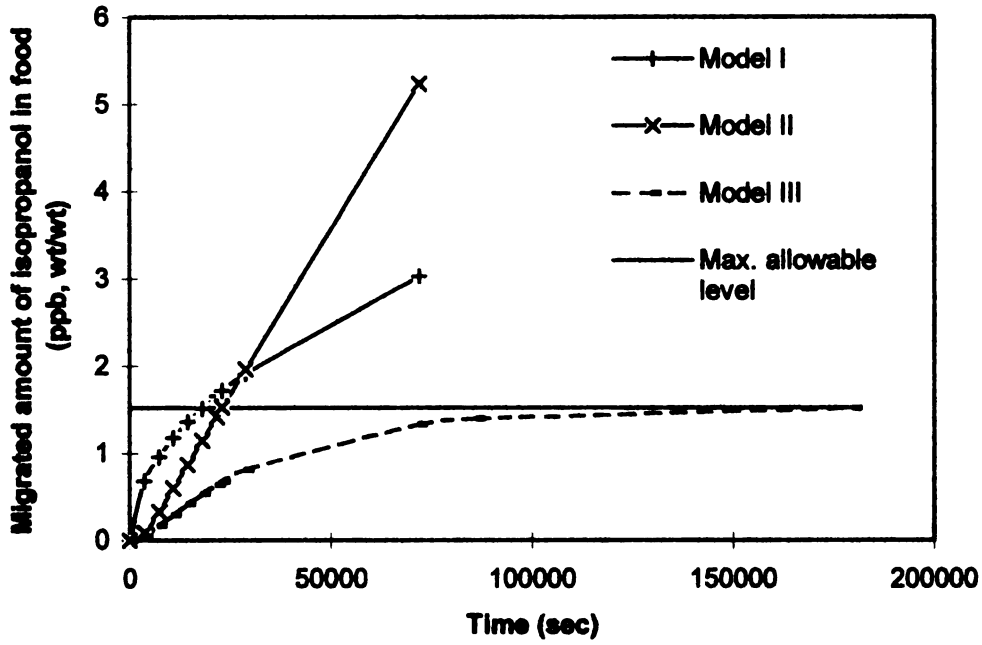

Figure 5 The profiles of the migrated amount of isopropanol from a single layer and a laminated film based on predictive Models I, II and III

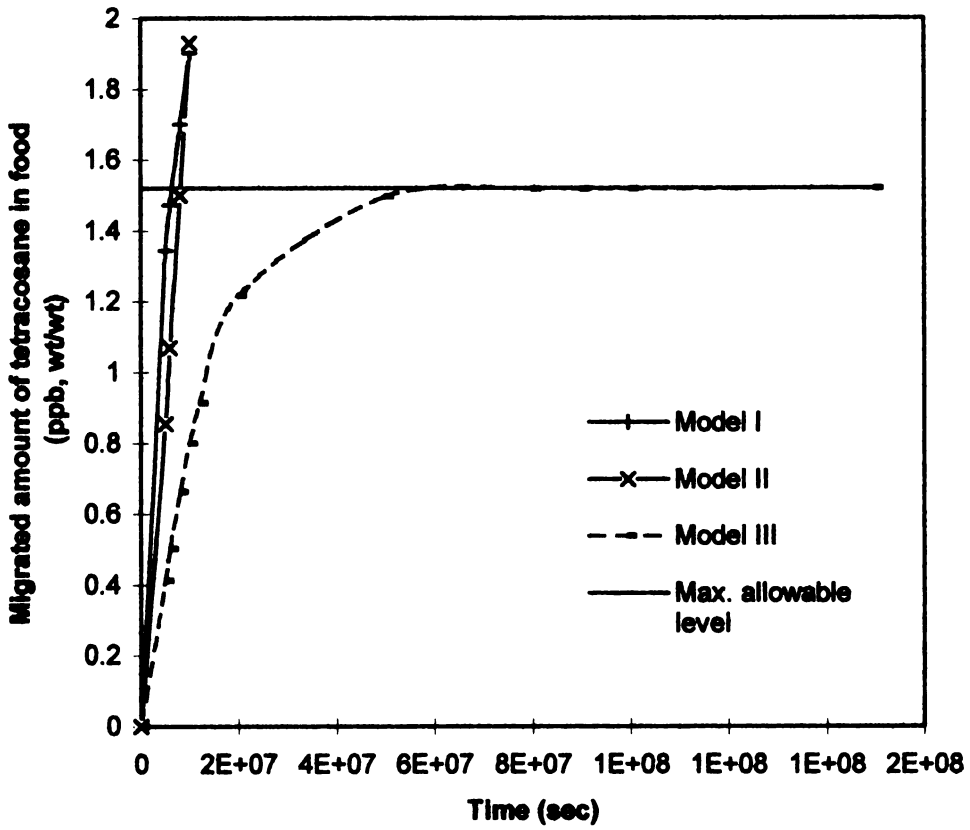

Figure 6 The profiles of the migrated amount of tetracosane from a single layer and a laminated film based on predictive Models I, II and III

A profile of the amount of migrant in each layer was determined, which considered the remaining amount of migrant in the recycle layer, incoming amount of migrant into the barrier layer, and outgoing amount of migrant to the food contact phase as a function of contact time. The results were summarized in Table 10 and presented graphically in Figure 7 for isopropanol and in Table 11 and Figure 8 for tetracosane.

The effect of the functional barrier thickness on the predictive results from Models II and III was determined for the barrier thickness ranging from 1 *mil* to 10 *mil*. The results were summarized in Tables 38-41 (Appendix V) and presented graphically in Figures 9-12 where the migrated amounts of isopropanol and tetracosane were plotted as a function of time for the respective barrier thickness levels. As shown, for the thinner barrier layers (1 and 2 *mil*), the migration levels calculated from Model II were always higher than these obtained from Model III. However, when the barrier thickness was equal or greater than 4 *mil*, the migration levels estimated during the early stages of storage time (i.e. less than 40 % of total migration time) were greater with Model III than for Model II. The time for total transfer of migrant from Model III was still greater than for Model II. This phenomenon was observed for both migrants. Thus, if Model III was used to estimate migration levels for a laminate fabricated with a barrier layer greater than 4 *mil*, during the early stages of migration the result would be an over estimation of transfer levels. By varying the barrier thickness, a relationship between the time to reach maximum allowable migration levels as a function of barrier thickness was determined for both migrants, as shown in Figure 13 and 14, respectively. The relationship between barrier layer thickness and the time to reach the maximum allowable level of migrant can be described by the following polynomial expressions.

For isopropanol:

$$T = (2\times10^{15})t^5 - (1\times10^{14})t^4 + (2\times10^{12})t^3 + (4\times10^{9})t^2 + (9\times10^{7})t + 112381 \quad (46)$$

For tetracosane:

$$T = (3\times10^{17})t^5 - (2\times10^{16})t^4 + (4\times10^{14})t^3 + (2\times10^{12})t^2 + (5\times10^{10})t + 3\times10^{7} \quad (47)$$

where T is the time (*sec*) to reach maximum allowable level and t is the thickness (*cm*) of barrier layer.

These two equations allow the prediction of the time to reach the maximum allowable level of migrant at any barrier thickness above *0*, for the same initial migrant concentration level.

Based on the results discussed, it can be concluded that Model II is not the most appropriate migration model for describing the migration rate from a two layer laminate film. Further, while Model III afforded a certain level of satisfaction as a prediction model, it is important to note that this expression was derived based upon several important assumptions, namely: (i) that the convective coefficient of mass transfer was set as infinite; (ii) that the diffusion coefficient was independent of concentration and time; (iii) and there was no concern of the interaction between food content and polymer. The validity of the application of this model to estimate or predict migration levels should therefore be evaluated on a case by case basis.

Table 10 The migration data of isopropanol for a lamination of 1.15 mil contaminated HDPE layer/ 1 mil HDPE barrier layer by Model III

Time (sec)	Migrant in recycle layer (g/cm^2)	Migrant in barrier layer (g/cm^2)	Migrant in food (g/cm^2)
0.00	2.4E-9	0.00	0.00
3.6E+3	1.8E-9	4.6E-10	6.8E-11
7.2E+3	1.6E-9	4.9E-10	2.6E-10
1.0E+4	1.5E-9	4.8E-10	4.1E-10
2.0E+4	1.1E-9	3.7E-10	9.2E-10
3.0E+4	7.9E-10	2.7E-10	1.3E-9
4.0E+4	5.8E-10	2.0E-10	1.6E-9
5.0E+4	4.3E-10	1.7E-10	1.8E-9
6.0E+4	3.2E-10	1.1E-10	1.9E-9
7.0E+4	2.3E-10	7.9E-11	2.0E-9
8.0E+4	1.7E-10	5.8E-11	2.1E-9

Table 11 The migration data of tetracosane for a lamination of 1.15 mil contaminated HDPE layer/ 1 mil HDPE barrier layer by Model III

Time (sec)	Migrant in recycle layer (g/cm^2)	Migrant in barrier layer (g/cm^2)	Migrant in food (g/cm^2)
0.00	2.4E-9	0.00	0.00
5.0E+6	1.3E-9	4.3E-10	6.4E-10
6.0E+6	1.2E-9	4.0E-10	7.8E-10
8.0E+6	9.9E-10	3.4E-10	1.0E-9
1.0E+7	8.3E-10	2.8E-10	1.2E-9
1.2E+7	7.0E-10	2.4E-10	1.4E-9
2.0E+7	3.5E-10	1.2E-10	1.9E-9
5.0E+7	2.6E-11	8.8E-12	2.3E-9
8.0E+7	1.9E-12	6.5E-13	2.4E-9
9.0E+7	7.9E-12	2.7E-13	2.4E-9
1.0E+8	7.9E-13	1.1E-13	2.4E-9

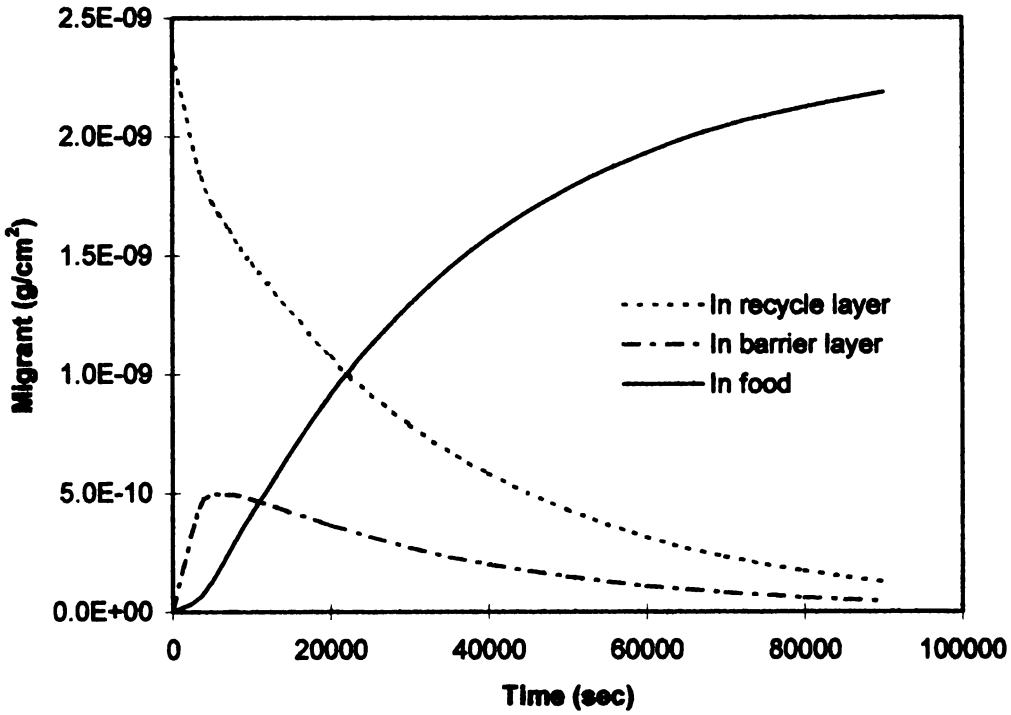

Figure 7 The migration profile of isopropanol for a lamination of 1.15 mil contaminated HDPE layer/1 mil HDPE barrier layer by Model III

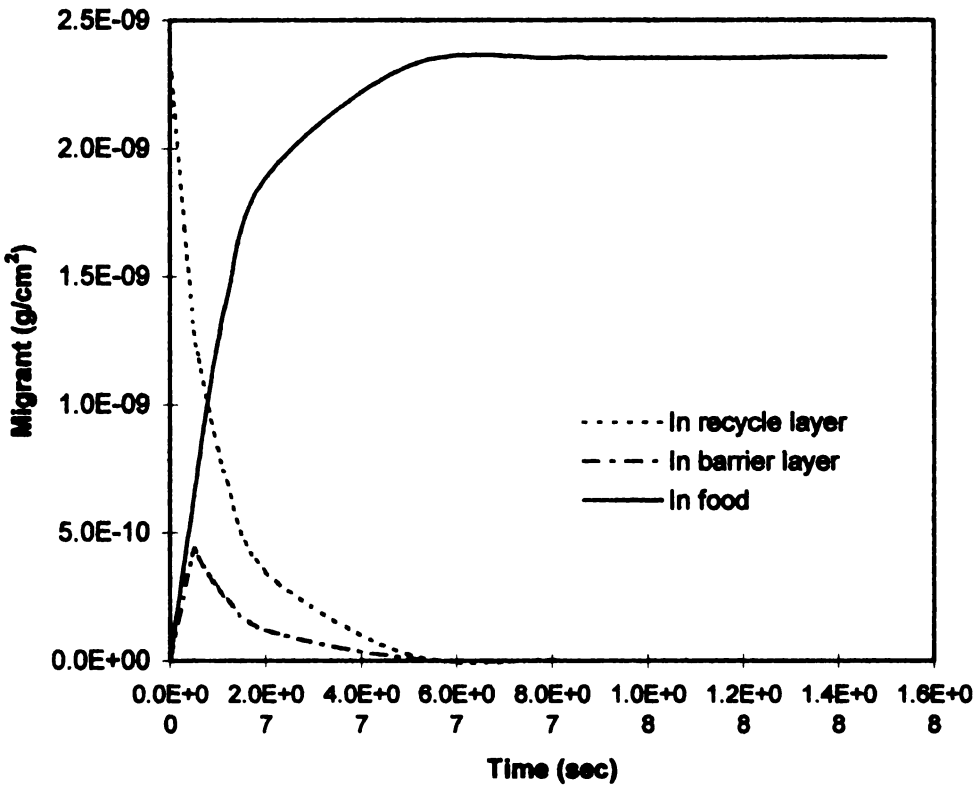

Figure 8 The migration profile of tetracosane for a lamination of 1.15 mil contaminated HDPE layer/1 mil HDPE barrier layer by Model III

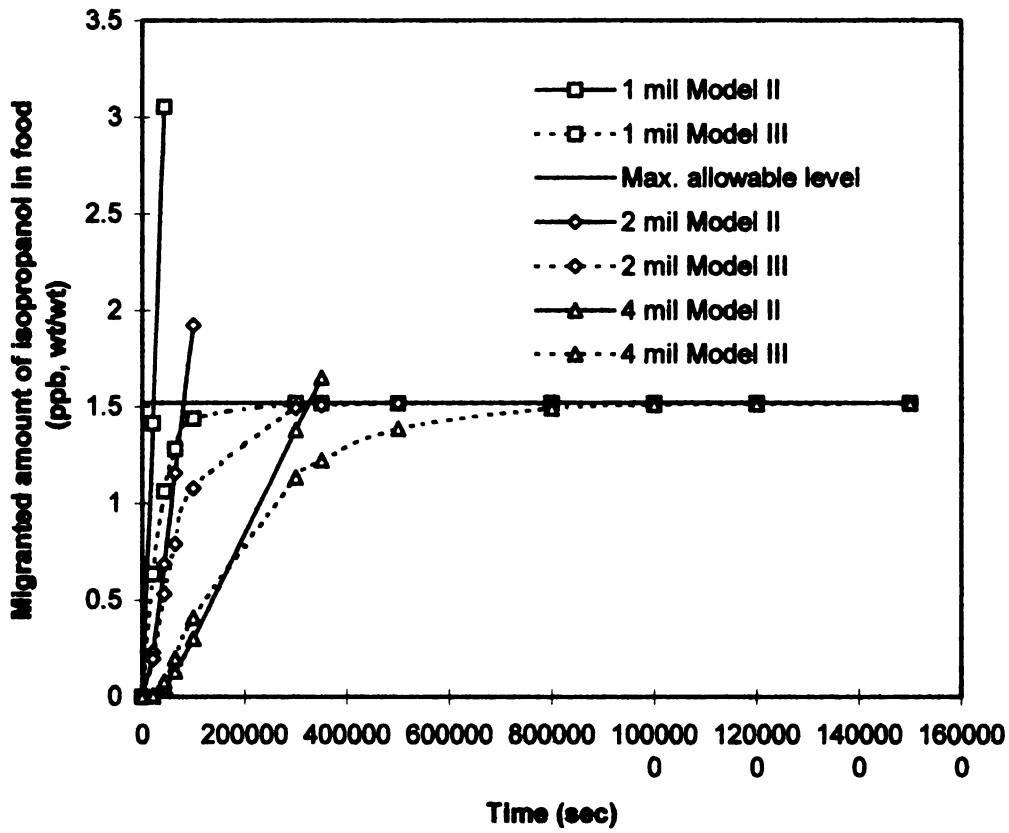

Figure 9 The migration profile of isopropanol for a lamination of 1.15 mil contaminated HDPE layer/1, 2, 4 mil HDPE barrier layer by Models II and III

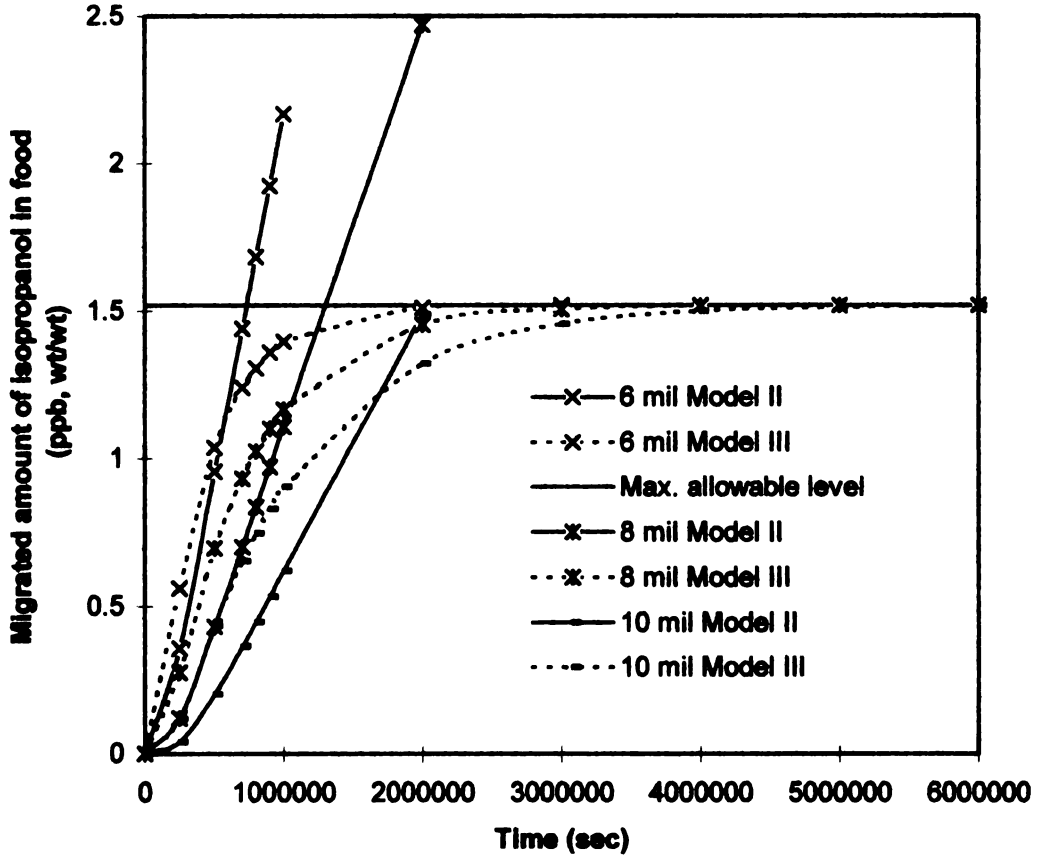

Figure 10 The migration profile of isopropanol for a lamination of 1.15 mil contaminated HDPE layer/ 6,8,10 mil HDPE barrier layer by Models II and III

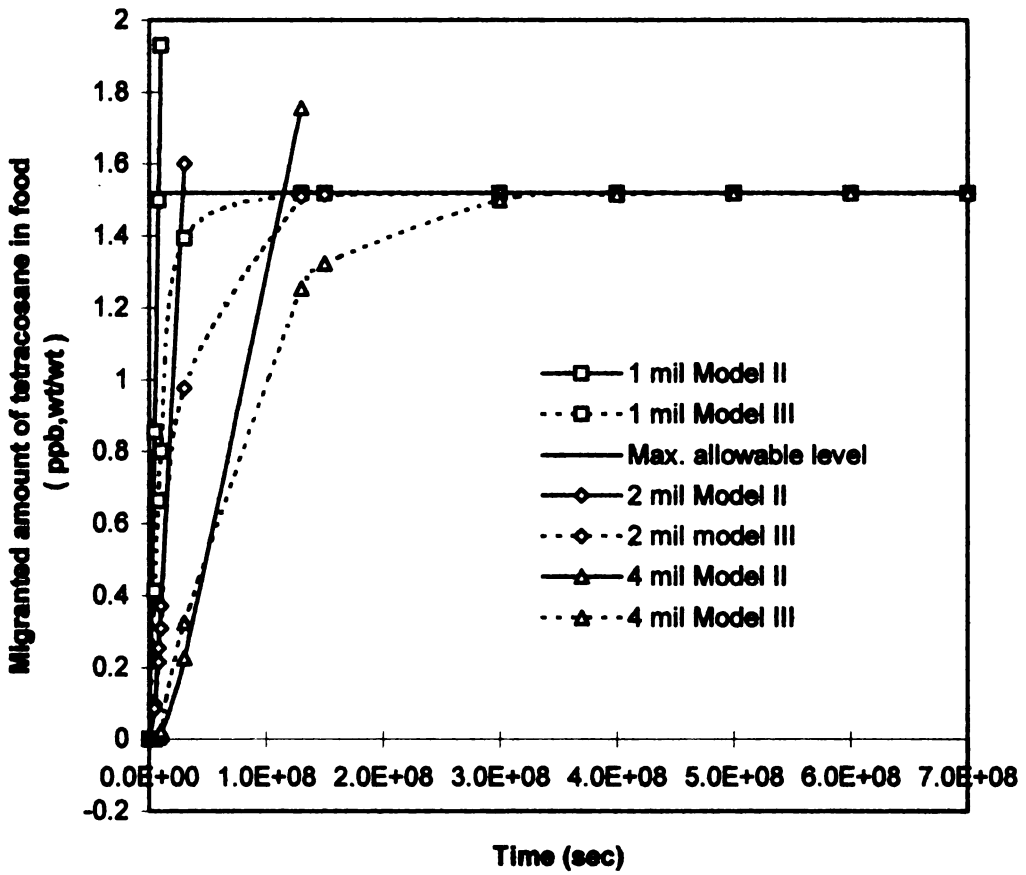

Figure 11 The migration profile of tetracosane for a lamination of 1.15 mil contaminated HDPE layer/ 1, 2, 4 mil HDPE barrier layer by Models II and III

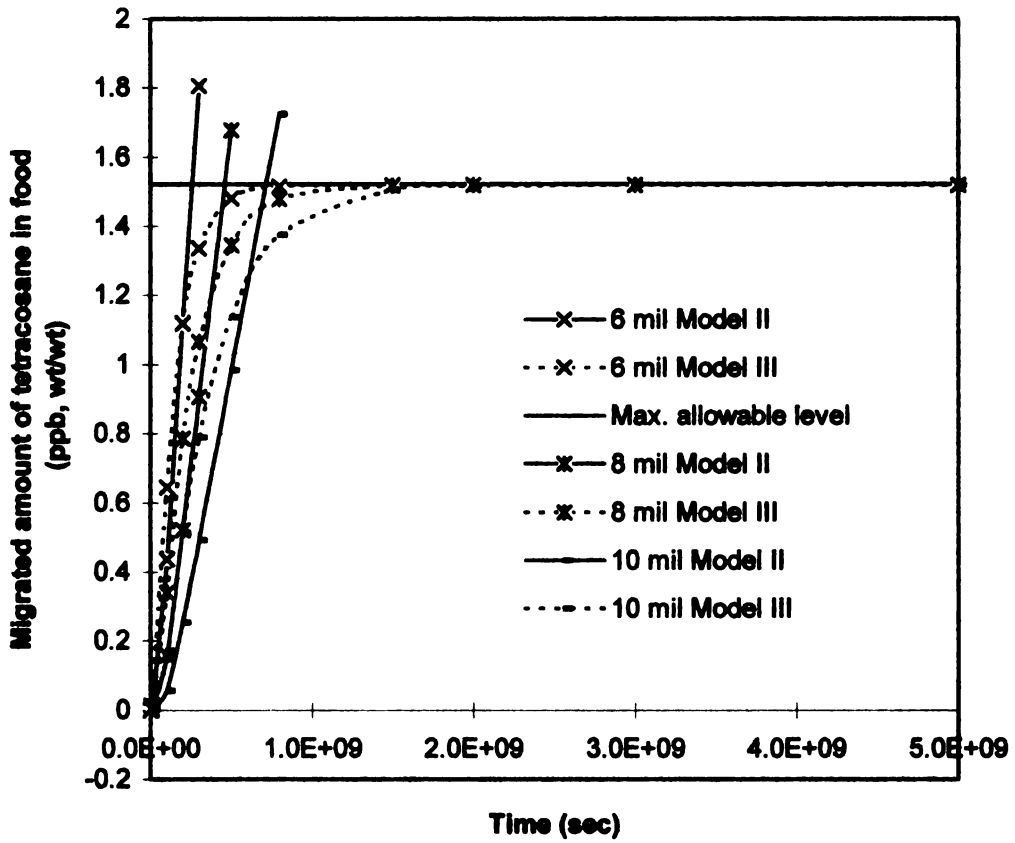

Figure 12 The migration profile of tetracosane for a lamination of1.15mil contaminated HDPE layer/ 6, 8, 10 mil HDPE barrier layer by Models II and III

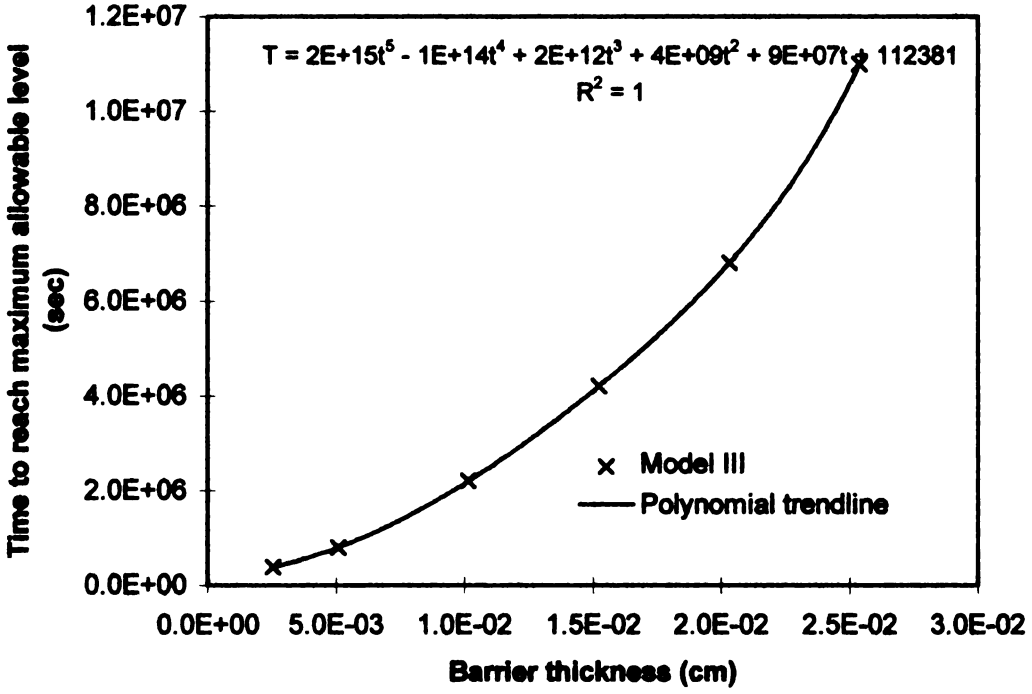

Figure 13 The relation of time to reach maximum allowable level as a function of a barrier thickness for isopropanol as initial concentration of 0.84ppm

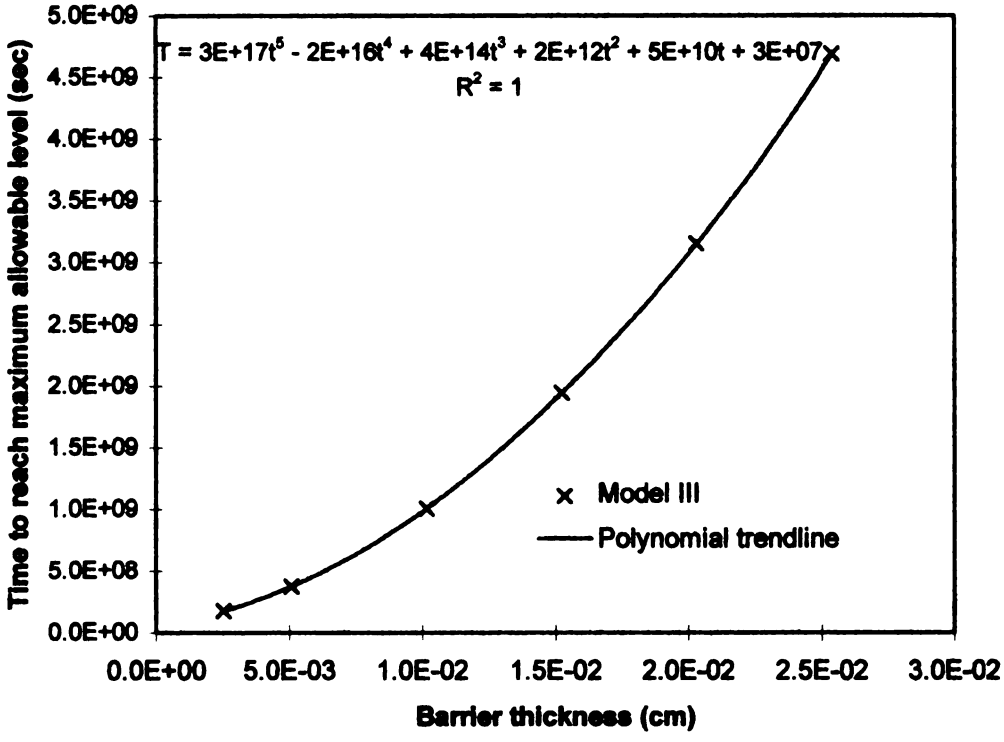

Figure 14 The relation of time to reach maximum allowable level a function of a barrier thickness for tetracosane as initial concentration of 0.84ppm

SUMMARY AND CONCLUSIONS

For isopropanol, the diffusion coefficient in HDPE film was determined by the permeation method as a function of vapor activity. For tetracosane, which is an extremely low vapor pressure solid at room temperature, the diffusion coefficient was determined via the migration method. The diffusion coefficient of isopropanol in HDPE film at room temperature showed a rather constant value within the vapor concentration range evaluated. An assumption of a constant diffusion coefficient, which was defined beforehand, would therefore not be in serious error for use in migration modeling expressions. The partition coefficient of isopropanol between HDPE film and water at room temperature showed a very low level of isopropanol sorbed by HDPE film, giving an equilibrium partition coefficient value of $K_{L/P} = 600$. For the tetracosane, the diffusion coefficient was determined from a migration study rather than from a permeation method. Only one concentration level of tetracosane in HDPE film was used to perform a migration experiment and to estimate the diffusion coefficient. The calculated diffusion coefficient was an estimation value or an integral diffusion coefficient, since it was determined by assuming a constant diffusion coefficient value. In addition, since hexane is a polymer swelling solvent for HDPE, the calculated diffusion coefficient is assumed to be an overestimated value and would be considered an upper bound value. For a non-interactive contact phase such as water, the diffusion coefficient for tetracosane in HDPE may be several order of magnitude lower. By using the migration study to determine the

diffusion coefficient, the partition coefficient was determined simultaneously. Further, the migration study also provided a real condition of food simulant/packaging interaction. For tetracosane, even using a polymer swelling solvent as a food simulant, the partition coefficient still afforded a significant level of migrant distributed to the HDPE film.

By knowing the diffusion coefficient and maximum allowance of contaminants level in food content, the migration amount of isopropanol and tetracosane from HDPE film into a food contact phase was estimated, based upon a diffusion controlled process, by appropriate mathematical expressions for each system. For a single layer of contaminated HDPE film, the total amount of isopropanol in film would migrate out in less than 6 hours, while it would take about 2 months for tetracosane. Thus, this contaminated film would be considered as unacceptable for use direct contact with food. In addition to a simple single layer structure, application of a functional barrier to prevent migration was also evaluated. The laminate considered, was composed of a contaminated HDPE layer and a virgin layer of the same HDPE resin. Based on the assumption that migration of contaminants into a food contact phase (liquid food) is a solely diffusion controlled process, the migration of isopropanol and tetracosane from a polymer film to a fluid contact phase was estimated separately, for a single layer HDPE film and a laminated HDPE film by using the diffusion coefficient values determined for the respective migrants in HDPE film. Three migration models, namely: (i) a simple model (Model I) for a single layer film; (ii) the Begley and Hollifield model (Model II); and (iii) the Lauobi and Vergnaud model (Model III), were evaluated to estimate the amount of migration. The simple model (Model I) was used to estimate migration levels from a single layer structure, while Models II and III were used to estimate migration from a two

layer laminate structure. An evaluation of these models was made and the effectiveness of a functional barrier layer (virgin HDPE layer) to prevent the migration of both compounds was also determined. For the isopropanol, a barrier thickness of 8 *mil* is required to retard complete migration of the minimum initial concentration of 0.84 *ppm* for up to 3 months. Such a thickness would be considered a polymer sheet, rather than a film phase. In contrast, the functional barrier showed an effectiveness to prevent migration. For example, only 1 mil of the barrier thickness could increase the totally migration time to 3 month. Even though, isopropanol showed a rapid migration rate from the laminate containing a functional barrier, the concept of the application of a functional barrier could have validity if the virgin layer was a high barrier resin such as a polyamide.

This study demonstrated the potential of the application of recycled plastic for use as a food packaging material, as a laminate film, if the food contact layer is a good barrier for organic substances. However, the migration of a variety of contaminants to various food systems and end use conditions has to be studied, especially actual migration studies from lamination films, since the interaction of food components with the polymer and severe or abusive storage conditions could accelerate the migration rate. In such cases a highly compatible solvent could swell the polymer matrix, resulting in a change in the mechanism for the migration of contaminants. Further, higher temperature conditions may increase the diffusion coefficient value, which is a major mechanism involved with the migration process. It would be a risk to make a decision regarding the safety of such structures for food contact without a good understanding of such variables.

RECOMMENDATIONS FOR FUTURE STUDIES

In order to investigate whether the use of recycled HDPE plastic, as a food packaging material, is safe, several factors need to be considered. Based on this study, there are a number of questions and concerns related to the migration of dangerous substances from post consumer recycled plastic. One important subject is that the selected chemical surrogates are appropriate or representative of possible contaminant substances in recycled HDPE plastic. This leads to a suspicion of the method for evaluating the use of recycled HDPE plastic, if its safety will be evaluated only from migration studies of selected surrogates. This study also showed that recent migration models can only provide an estimation of the migration rate since there is a limit due to assumptions made in their solution.

Future studies proposed would include actual migration studies involving recycled HDPE obtained from several sources, to a variety of actual food systems. For the application of recycled HDPE plastic in the form of a lamination film, the effectiveness of a barrier layer to prevent the migration should be evaluated based on the migration studies of real laminated film. This actual migration studies will also be used to validate the accuracy of mathematical expressions. The tasks of the actual migration studies will be useful for the future development of mathematical models.

APPENDICES

Table 14 Standard calibration of isopropanol for GC-MS

Concentration (ppm)	Quantity injection[1] (g)	Area response [2] (AU)
0	0.0	0
5	4.4E-09	745908
10	8.7E-09	1555413
50	4.4E-08	7260250
100	8.7E-08	14966860

[1]. For 3 µl volume injection
[2]. Average values

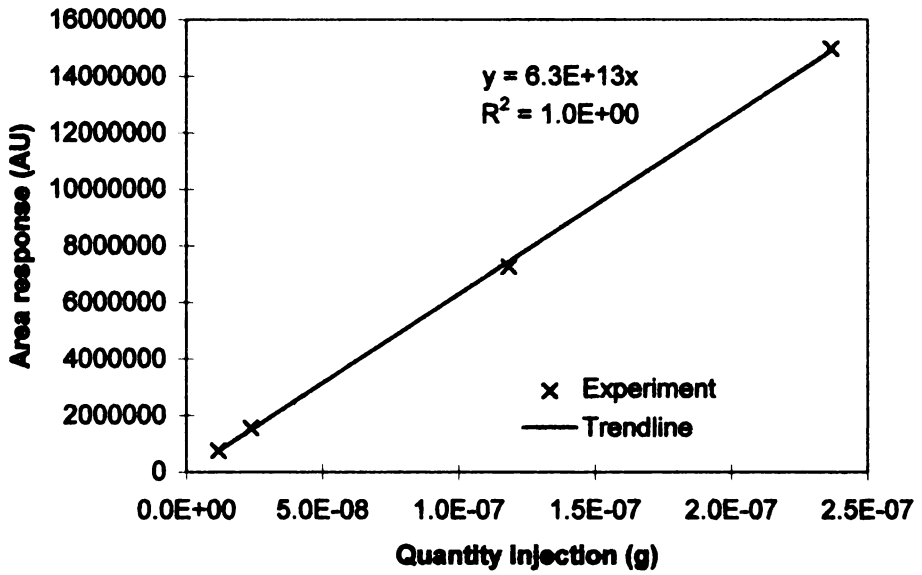

Figure 17 Standard calibration curve of isopropanol for GC-MS

Table 15 Standard calibration of isopropanol for HP 6890 by SPME

Concentration (ppm)	Mass (g)	Area response (AU)
0.5	4.0E-07	471[(1)]
5	4.0E-06	4572[(2)]
50	4.0E-05	45320
100	7.9E-05	92024
200	1.6E-04	182664

[(1)].[(2)]. Estimation values

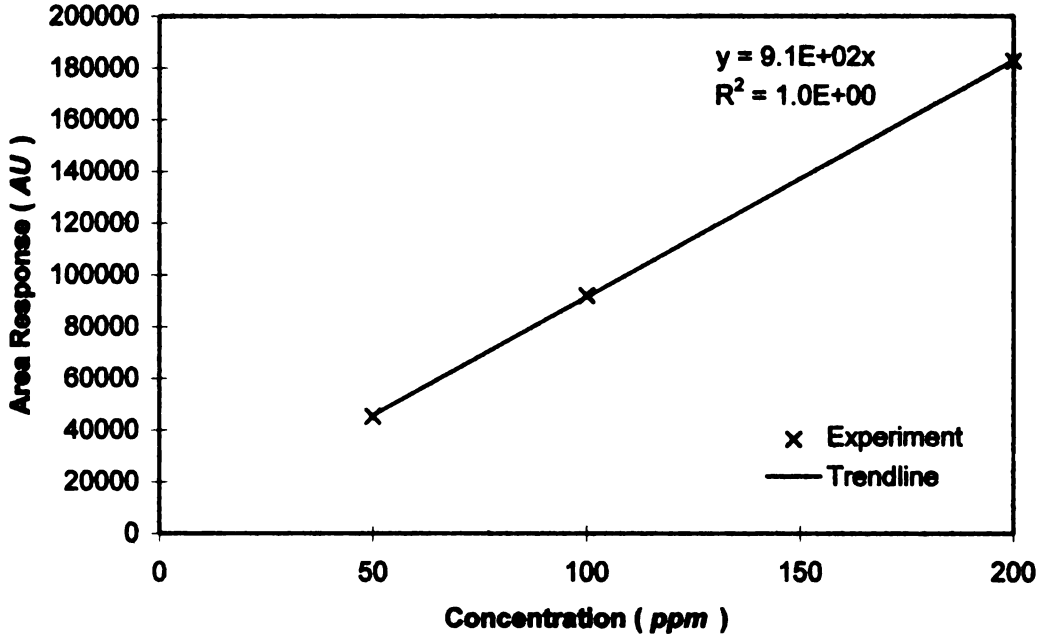

Figure 18 Standard calibration curve of isopropanol for HP 6890 by SPME

Table 16 Standard calibration of hexane for HP 5890A

Concentration (ppm)	Quantity injection[1] (g)	Area response [2] (AU)
0	0.00	0
0.5	3.9E-10	812.5
5	3.9E-09	6186.5
10	7.8E-09	14534.5
25	2.0E-08	32747.5
50	3.9E-08	67102

[1]. For 1 μl volume injection
[2]. Average values

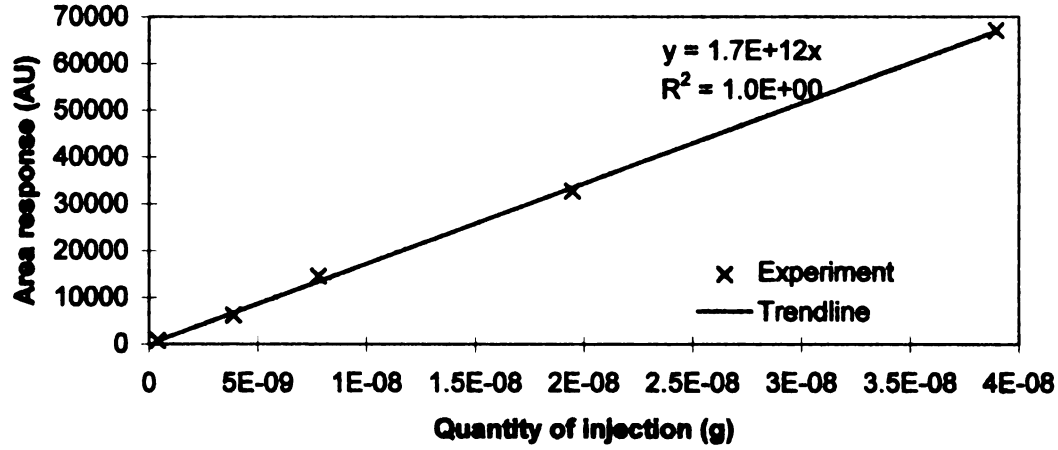

Figure 19 Standard calibration curve of hexane for HP 5890A

APPENDIX II

Statistical Analysis for Permeation Experiments

Statistic descriptive of determined diffusion, permeability and solubility coefficient either by isostatic or quasi-isostatic procedure were presented below.

Table 17 Statistical descriptive of diffusion coefficient determined by isostatic

Concentration	Sample number	Mean	Standard Deviation	Standard Error
0.10	4	3.6E-14	2.7E-15	1.4E-15
0.21	4	3.8E-14	1.7E-15	8.6E-16
0.38	6	3.8E-14	3.6E-15	1.5E-15
Total	14	3.7E-14	2.9E-15	7.7E-16

Table 18 Statistical descriptive of permeability coefficient determined by isostatic

Concentration	Sample number	Mean	Standard Deviation	Standard Error
0.10	4	4.6E-09	6.0E-10	3.0E-10
0.21	4	4.6E-09	4.7E-10	2.3E-10
0.38	4	4.6E-09	2.2E-10	1.1E-10
Total	12	4.6E-09	4.2E-10	1.2E-10

Table 19 Statistical descriptive of solubility coefficient determined by isostatic

Concentration	Sample number	Mean	Standard Deviation	Standard Error
0.10	4	1.6E-07	1.6E-08	8.2E-09
0.21	4	1.5E-07	2.3E-08	1.1E-08
0.38	4	1.5E-07	1.7E-08	8.4E-09
Total	12	1.6E-07	1.8E-08	5.1E-09

Table 20 Statistical descriptive of diffusion coefficient determined by quasi-isostatic

Concentration	Sample number	Mean	Standard Deviation	Standard Error
0.19	3	4.2E-14	4.6E-15	2.6E-15
0.27	2	4.4E-14	1.3E-14	8.9E-15
0.41	4	4.0E-14	1.1E-30	5.3E-31
Total	9	4.1E-14	5.4E-15	1.8E-15

Table 21 Statistical descriptive of permeability coefficient determined by quasi-isostatic

Concentration	Sample number	Mean	Standard Deviation	Standard Error
0.19	3	3.9E-09	1.7E-09	9.7E-10
0.27	2	4.5E-09	3.5E-10	2.5E-10
0.41	4	4.4E-09	2.6E-10	1.3E-10
Total	9	4.2E-09	9.1E-10	3.0E-10

Table 22 Statistical descriptive of solubility coefficient determined by quasi-isostatic

Concentration	Sample number	Mean	Standard Deviation	Standard Error
0.19	3	1.2E-07	6.0E-08	3.4E-09
0.27	2	1.3E-07	3.0E-08	2.2E-08
0.41	4	1.4E-07	8.1E-09	4.0E-09
Total	9	1.3E-07	3.3E-08	1.1E-08

For each test procedure, the analysis of variance method (ANOVA)was used for evaluating whether there was a difference of a mean of determining parameters (diffusion, permeability and solubility coefficient) among each testing concentration or not. The results of ANOVA for each parameter were presented below.

Table 23 The ANOVA for diffusion coefficient determined by isostatic

Group	Sum of squares	Degree of freedom, df	Mean square	F	F table
Between group	1.265E-29	2	6.232E-30	0.724	3.98
Within group	9.473E-29	11	8.612E-30		
Total	1.074E-28	13			

Table 24 The ANOVA for permeability coefficient determined by isostatic

Group	Sum of squares	Degree of freedom, df	Mean square	F	F table
Between group	8.867E-21	2	4.423E-21	0.021	4.26
Within group	1.889E-18	9	2.098E-19		
Total	1.897E-18	11			

Table 25 The ANOVA for solubility coefficient determined by isostatic

Group	Sum of squares	Degree of freedom, df	Mean square	F	F table
Between group	2.462E-16	2	1.231E-16	0.349	4.26
Within group	3.179E-15	9	3.532E-16		
Total	3.425E-15	11			

Table 26 The ANOVA for diffusion coefficient determined by quasi-isostatic

Group	Sum of squares	Degree of freedom, df	Mean square	F	F table
Between group	3.401E-29	2	1.701E-29	0.510	5.14
Within group	2.000E-29	6	3.334E-29		
Total	2.340E-28	8			

Table 27 The ANOVA for permeability coefficient determined by quasi-isostatic

Group	Sum of squares	Degree of freedom, df	Mean square	F	F table
Between group	6.414E-19	2	3.207E-19	0.325	5.14
Within group	5.928E-18	6	9.880E-19		
Total	6.569E-18	8			

Table 28 The ANOVA for solubility coefficient determined by quasi-isostatic

Group	Sum of squares	Degree of freedom, df	Mean square	F	F table
Between group	6.608E-16	2	3.304E-16	0.242	5.14
Within group	8.206E-15	6	1.368E-15		
Total	8.867E-15	8			

A two way analysis of variance method (ANOVA)was also used for evaluating whether there was a difference of a mean of determining parameters (diffusion, permeability and solubility coefficient) due to test procedures and concentration or not. In order to have an analysis, it was assumed that a concentration of quasi-isostatic was similarto the one for isostatic procedure. The results of two way ANOVA were presented below.

Table 29 Two way ANOVA of test techniques and concentration effects for diffusion coefficient

		Sum of Squares	df	Mean Square	F	Sig
Main effects	(Combined)	8.503E-29	3	2.834E-29	4.170	.025
	Concentration	6.805E-29	2	3.403E-29	5.006	.022
	Techniques	8.332E-30	1	8.332E-30	1.226	.286
2-Way Interactions	Concentration * Techniques	1.840E-29	2	9.198E-30	1.353	.288
Model		9.459E-29	5	1.892E-29	2.783	.057
Residual		1.019E-28	15	6.797E-30		
Total		1.965E-28	20	9.827E-30		

Table 30 Two way ANOVA of test techniques and concentration effects for permeability coefficient

		Sum of Squares	df	Mean Square	F	Sig
Main effects	(Combined)	2.254E-18	3	7.513E-19	1.464	.264
	Concentration	5.427E-19	2	2.714E-19	.529	.600
	Techniques	1.962E-18	1	1.962E-18	3.824	.069
2-Way Interactions	Concentration * Techniques	3.765E-19	2	1.883E-19	.367	.699
Model		2.396E-18	5	4.793E-19	.934	.487
Residual		7.697E-18	15	5.131E-19		
Total		1.009E-17	20	5.047E-19		

Table 31 Two way ANOVA of test techniques and concentration effects for solubility coefficient

		Sum of Squares	df	Mean Square	F	Sig
Main effects	(Combined)	3.519E-15	3	1.173e-15	1.682	.213
	Concentration	2.863E-16	2	1.431E-16	.205	.817
	Techniques	3.098E-15	1	3.098E-15	4.443	.052
2-Way Interactions	Concentration * Techniques	6.188e-16	2	3.094E-16	.444	.650
Model		3.881E-15	5	7.761E-16	1.113	.395
Residual		1.046E-14	15	6.974E-16		
Total		1.434E-14	20	7.170E-16		

APPENDIX III

Migration Study of Isopropanol Spiked HDPE Film into Water by the SPME

All parameter for prediction a migration amount of isopropanol from spiked film into water were presented below.

Referring to equation 12

$$M_t^* = \frac{M_t}{aKC_p^o} = \left(1 - \exp\left(Z^2\right) erfcZ\right)$$

Calculation for the thickness of food content *a*:

$$a = \frac{V_L}{A}$$

where:

V_L = Volume of food content (water) 40 cm^3

A = Food / film contacting area (surface area of film 30 disks) 2.217 cm^2

So, a = 0.18 cm

Calculation for an initial concentration of isopropanol in spiked film

$$K = \frac{C_L}{C_p}$$

Where:

K = Partition coefficient (600)

C_L = Concentration of isopropanol in water at equilibrium of migration (1.8×10^{-3} g/cm^3)

So, C_P = Concentration of isopropanol in polymer at equilibrium of migration (2.9×10^{-6} g/cm^3)

The initial concentration of isopropanol in film is a sum of a concentration of isopropanol in liquid and polymer at equilibrium (1.8×10^{-3} g/cm^3).

APPENDIX IV

Migration Study of Tetracosane Spiked HDPE Film into Hexane by the GC-FID

All parameter for prediction a migration amount of tetracosane from spiked film into hexane were presented below.

Referring to equation 12

$$M_t^* = \frac{M_t}{aKC_p^o} = \left(1 - \exp\left(Z^2\right) erfcZ\right)$$

Calculation for the thickness of solvent (hexane), a:

$$a = \frac{V_L}{A}$$

where:

V_L = Volume of solvent (hexane) in migration cell

A = Food / film contacting area (surface area of film disks)

So, a = thickness layer of solvent

The equilibrium partition coefficient of tetracosane for spiked film/hexane system could be determined by equation:

$$K = \frac{C_L}{C_p} = \frac{\left(M_{m,L}/M_L\right)}{\left(M_{m,P}/M_P\right)}$$

Where:

K = Equilibrium Partition coefficient

C_L = Concentration of migrant in liquid phase at equilibrium

C_P = Concentration of migrant in polymer phase at equilibrium

$M_{m,L}$ = Mass of migrant in liquid phase at equilibrium

$M_{m,P}$ = Mass of migrant in polymer phase at equilibrium

M_L = Mass of liquid phase

M_P = Mass of polymer phase

The initial concentration of tetracosane in film is a ratio of a sum of the amount of migrant in liquid phase and polymer phase at equilibrium to a volume of film disks.

A comparison of experiment data of migration and model fit data, by equation 12, have to make to estimate the diffusion coefficient of tetracosane in HDPE film. The results of matching data were presented below.

Table 32 The comparison of migration of tetracosane between the experiment and the model fit for sample 1

Square root of time $sec^{1/2}$	M_t / M_{ini} [1] (experiment data)	M_t / M_{ini} [2] (model fit data)
0	0.00	0.00
37.95	0.042	0.051
55.78	0.070	0.073
70.65	0.093	0.091
100.99	0.13	0.13
110.62	0.15	0.14
148.55	0.21	0.18
248.51	0.25	0.27
324.24	0.29	0.33
785.41	0.34	0.56
993.97	0.36	0.61
1402.42	0.37	0.70
1463.76	0.39	0.69
1525.30	0.40	0.69
1603.34	0.40	0.64

[1], [2]. The ratio of the amount of migration at time t to the initial amount in film.

Table 33 The comparison of migration of tetracosane between the experiment and the model fit for sample 2

Square root of time $sec^{1/2}$	M_t / M_{ini} [1] (experiment data)	M_t / M_{ini} [2] (model fit data)
0	0.00	0.00
40.99	0.038	0.034
75.61	0.063	0.060
89.77	0.069	0.070
101.75	0.074	0.079
115.99	0.085	0.089
143.06	0.094	0.11
185.67	0.14	0.14
195.26	0.21	0.14
202.13	0.22	0.15
282.86	0.24	0.20

[1], [2]. The ratio of the amount of migration at time t to the initial amount in film.

Table 34 The comparison of migration of tetracosane between the experiment and the model fit for sample 3

Square root of time $sec^{1/2}$	M_t / M_{ini} [1] (experiment data)	M_t / M_{ini} [2] (model fit data)
0	0.00	0.00
34.64	0.043	0.03
264.56	0.21	0.21
398.79	0.30	0.29
875.63	0.32	0.49
1010.53	0.33	0.53

[1], [2]. The ratio of the amount of migration at time t to the initial amount in film.

Table 35 The comparison of migration of tetracosane between the experiment and the model fit for sample 4

Square root of time $sec^{1/2}$	M_t / M_{ini} (1) (experiment data)	M_t / M_{ini} (2) (model fit data)
0	0.00	0.00
42.43	0.058	0.041
264.61	0.22	0.22
572.22	0.38	0.39
644.44	0.42	0.42
792.80	0.42	0.48
895.87	0.42	0.51
983.92	0.45	0.53
1028.04	0.45	0.54

(1), (2) The ratio of the amount of migration at time t to the initial amount in film.

Table 36 The comparison of migration of tetracosane between the experiment and the model fit for sample 5

Square root of time $sec^{1/2}$	M_t / M_{ini} (1) (experiment data)	M_t / M_{ini} (2) (model fit data)
0	0.00	0.00
397.95	0.38	0.30
494.34	0.37	0.36
572.29	0.38	0.39
648.48	0.36	0.42
725.99	0.39	0.46
824.58	0.42	0.49

(1), (2) The ratio of the amount of migration at time t to the initial amount in film.

Table 37 The comparison of migration of tetracosane between the experiment and the model fit for sample 6

Square root of time $sec^{1/2}$	M_t / M_{ini} [1] (experiment data)	M_t / M_{ini} [2] (model fit data)
0	0.00	0.00
263.94	0.18	0.17
398.27	0.28	0.24
494.23	0.29	0.28
572.58	0.32	0.32
770.04	0.32	0.39
846.33	0.40	0.41
938.61	0.42	0.44
1355.99	0.42	0.54

[1], [2]. The ratio of the amount of migration at time t to the initial amount in film.

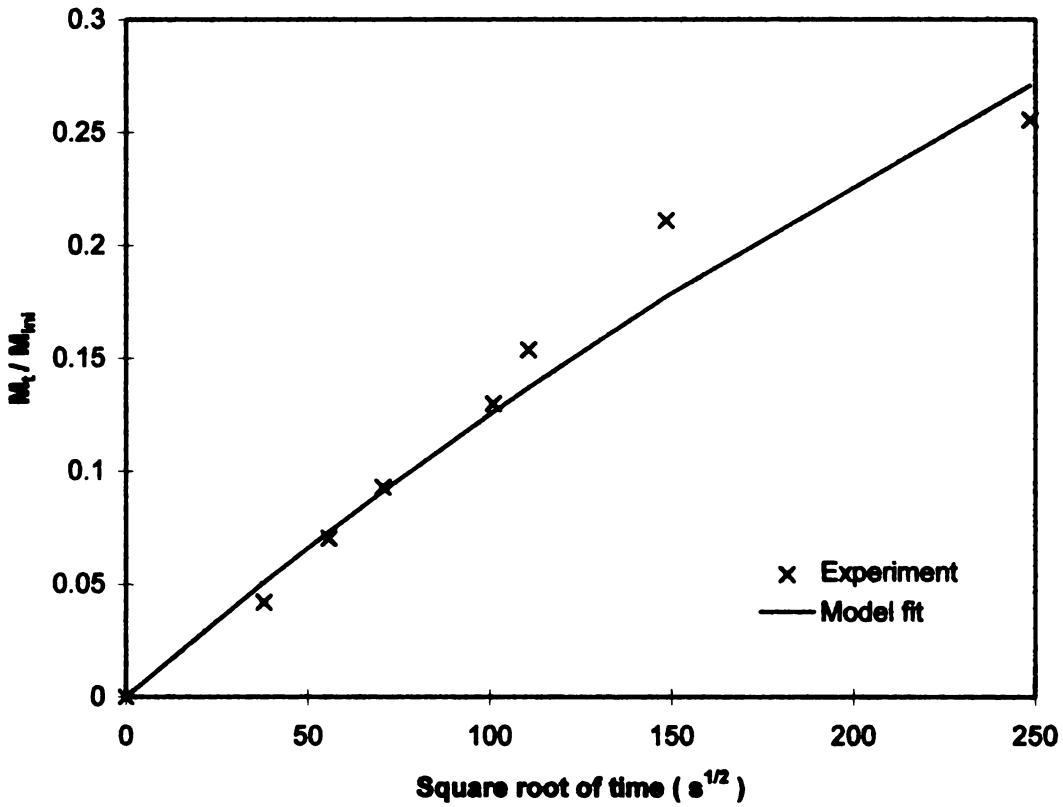

Figure 20 The profile of the comparison of migration of tetracosane between the experiment and the model fit for sample 1

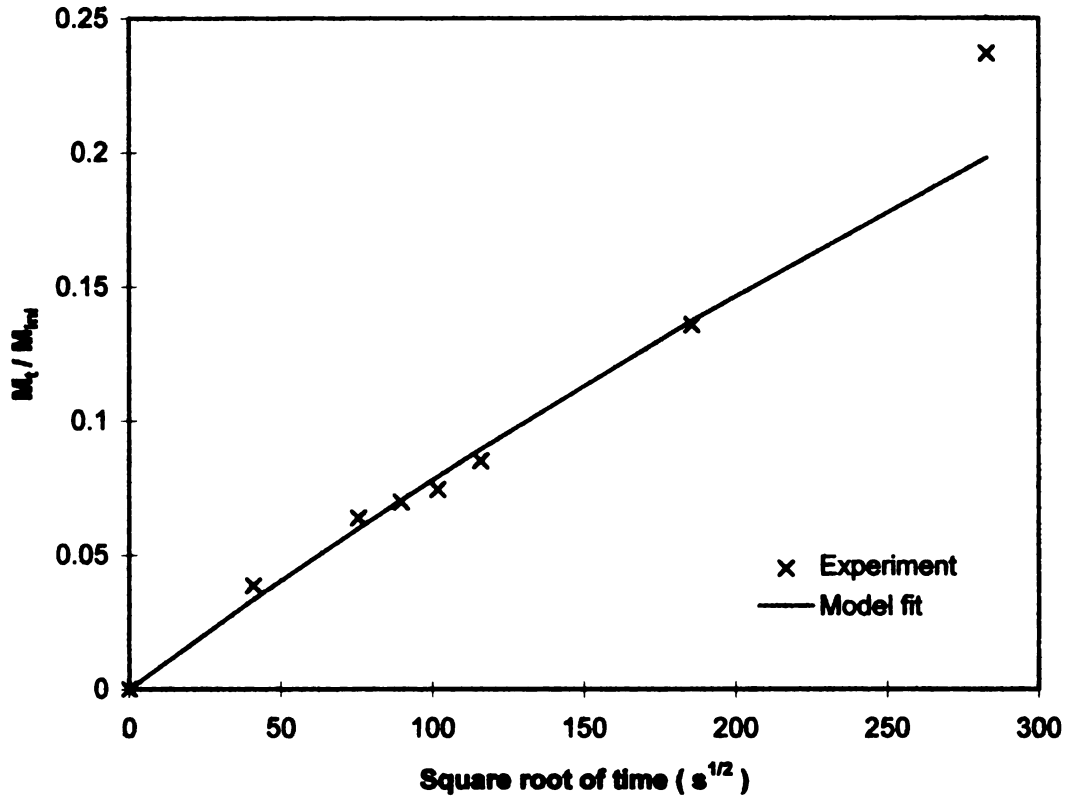

Figure 21 The profile of the comparison of migration of tetracosane between the experiment and the model fit for sample 2

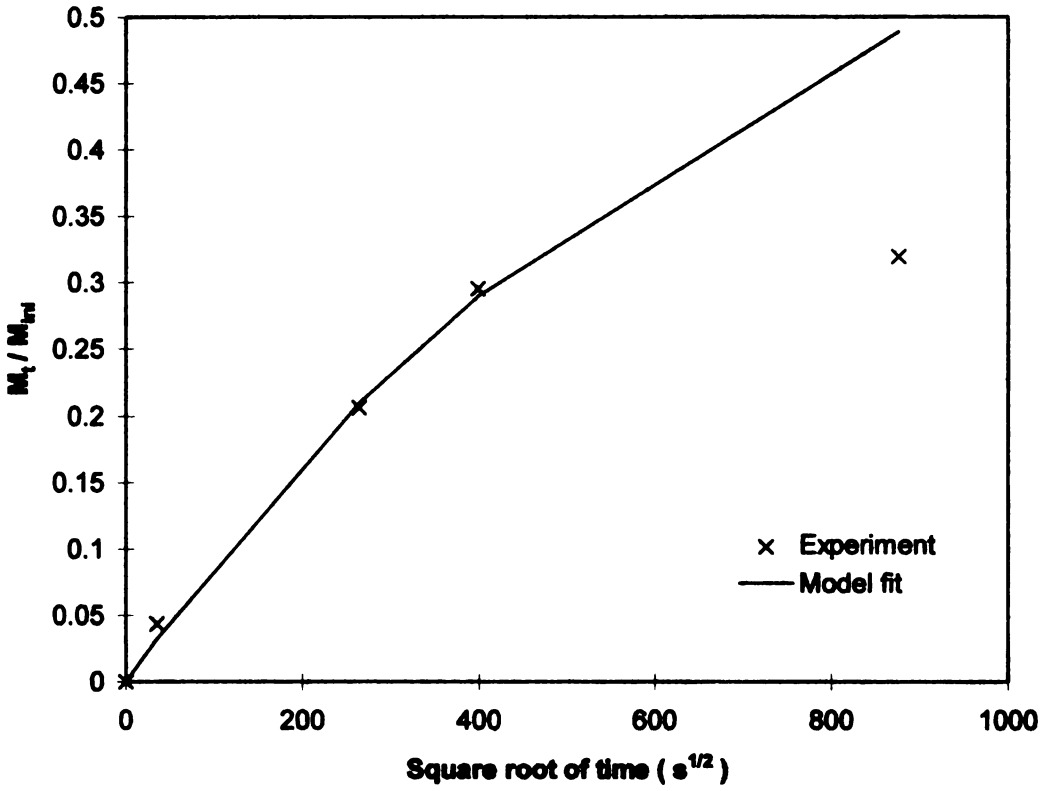

Figure 22 The profile of the comparison of migration of tetracosane between the experiment and the model fit for sample 3

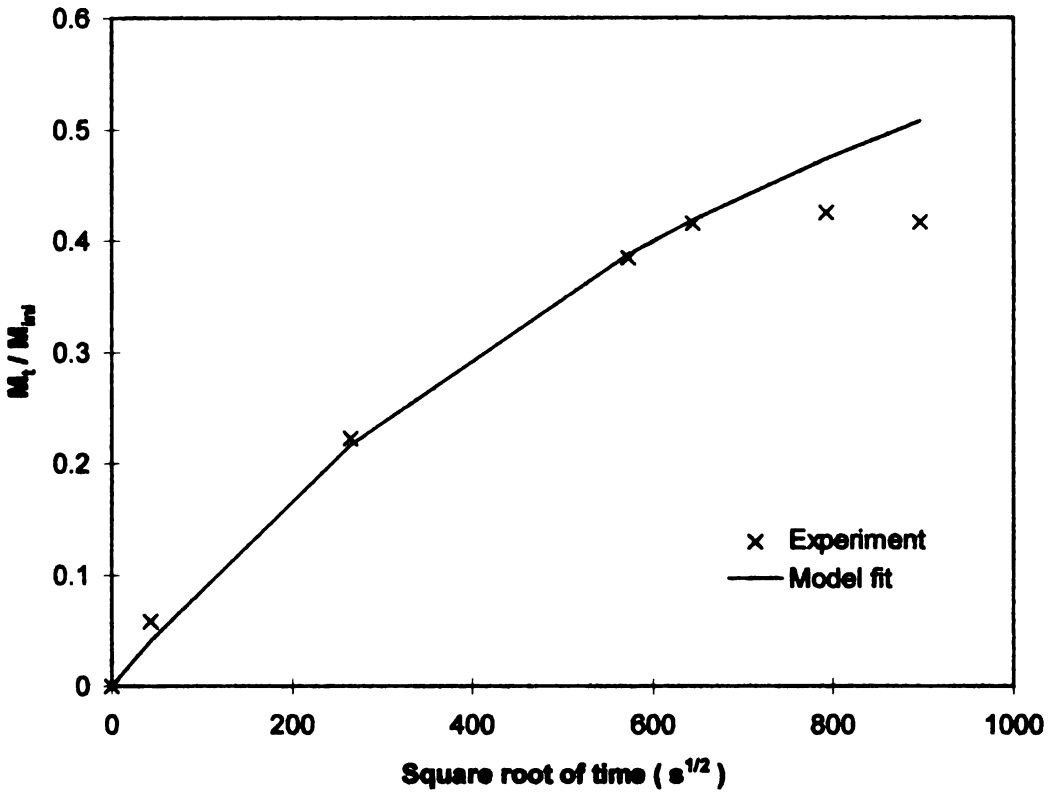

Figure 23 The profile of the comparison of migration of tetracosane between the experiment and the model fit for sample 4

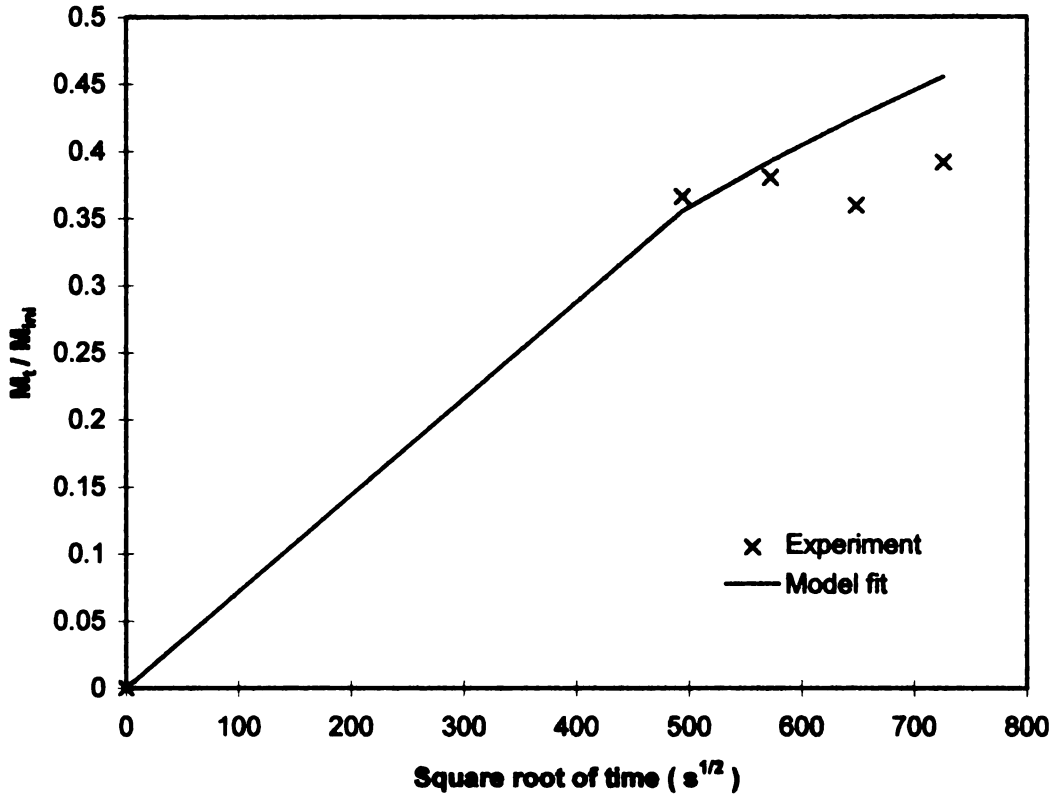

Figure 24 The profile of the comparison of migration of tetracosane between the experiment and the model fit for sample 5

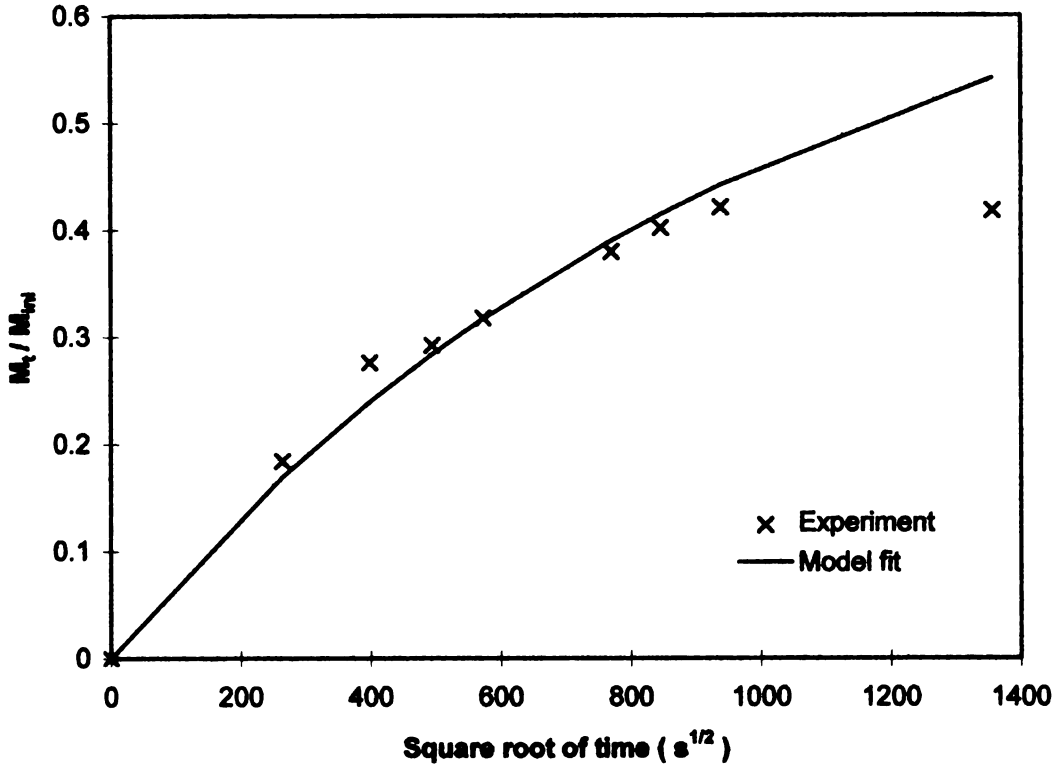

Figure 25 The profile of the comparison of migration of tetracosane between the experiment and the model fit for sample 6

APPENDIX V

The Comparison of the Predictive Migration Levels by Models II and III

The predictive migration levels of isopropanol and tetracosane from a laminated film of a 1.15 *mil* contaminated HDPE film and virgin HDPE films of 1,2,4,6,8 and 10 *mil* were calculated by using Model II and III as shown in the Tables 38-41.

Table 38 The migrated amount of isopropanol from a laminated film with the barrier thickness of 1,2 and 4 mil based on the predictive Models II and III

Time (sec)	Barrier of 1 mil		Barrier of 2 mil		Barrier of 4 mil	
	Model II (ppb)	Model III (ppb)	Model II (ppb)	Model III (ppb)	Model II (ppb)	Model III (ppb)
0.0	0.00	0.00	0.00	0.00	0.00	0.00
2.2E+4	1.4	0.63	0.23	0.20	0.00	0.01
4.3E+4	3.0	1.1	0.69	0.53	0.05	0.08
6.5E+4	4.7	1.3	1.2	0.79	0.13	0.20
1.0E+5	7.4	1.4	1.9	1.1	0.30	0.41
3.0E+5	22	1.5	6.3	1.5	1.4	1.1
3.5E+5	26	1.5	7.3	1.5	1.6	1.2
5.0E+5	38	1.5	11	1.5	2.5	1.4
8.0E+5	60	1.5	17	1.5	4.1	1.5
1.0E+6	76	1.5	21	1.5	5.2	1.5
1.2E+6	91	1.5	26	1.5	6.3	1.5
1.5E+6	1.1E+2	1.5	32	1.5	7.9	1.5

Table 39 The migrated amount of isopropanol from a laminated film with the barrier thickness of 6,8 and 10 mil based on the predictive Models II and III

Time (sec)	Barrier of 6 mil		Barrier of 8 mil		Barrier of 10 mil	
	Model II (ppb)	Model III (ppb)	Model II (ppb)	Model III (ppb)	Model II (ppb)	Model III (ppb)
0.0	0.00	0.00	0.00	0.00	0.00	0.00
2.5E+5	0.36	0.56	0.12	0.27	0.04	0.12
5.0E+5	0.96	1.0	0.43	0.70	0.20	0.43
7.0E+5	1.4	1.2	0.70	0.93	0.36	0.65
8.0E+5	1.7	1.3	0.84	1.0	0.45	0.74
9.0E+5	1.9	1.4	0.97	1.1	0.53	0.83
1.0E+6	2.2	1.4	1.1	1.2	0.62	0.90
2.0E+6	4.6	1.5	2.5	1.5	1.5	1.3
3.0E+6	7.0	1.5	3.8	1.5	2.4	1.5

Table 40 The migrated amount of tetracosane from a laminated film with the barrier thickness of 1,2 and 4 mil based on the predictive Models II and III

Time (sec)	Barrier of 1 mil		Barrier of 2 mil		Barrier of 4 mil	
	Model II (ppb)	Model III (ppb)	Model II (ppb)	Model III (ppb)	Model II (ppb)	Model III (ppb)
0.0	0.00	0.00	0.00	0.00	0.00	0.00
5.0E+6	0.85	0.41	0.10	0.08	0.00	0.00
8.0E+6	1.5	0.66	0.25	0.22	0.00	0.01
1.0E+7	1.9	0.80	0.37	0.31	0.1	0.02
3.0E+7	6.2	1.4	1.6	0.98	0.22	0.32
1.3E+8	28	1.5	7.8	1.5	1.8	1.2
1.5E+8	32	1.5	9.0	1.5	2.1	1.3
3.0E+8	64	1.5	18	1.5	4.4	1.5
4.0E+8	86	1.5	24	1.5	5.9	1.5
5.0E+8	1.0E+2	1.5	31	1.5	7.5	1.5
6.0E+8	1.3E+2	1.5	37	1.5	9.0	1.5
7.0E+8	1.5E+2	1.5	43	1.5	10	1.5

Table 41 The migrated amount of tetracosane from a laminated film with the barrier thickness of 6,8 and 10 mil based on the predictive Models II and III

Time (sec)	Barrier of 6 mil		Barrier of 8 mil		Barrier of 10 mil	
	Model II (ppb)	Model III (ppb)	Model II (ppb)	Model III (ppb)	Model II (ppb)	Model III (ppb)
0.0	0.00	0.00	0.00	0.00	0.00	0.00
5.0E+6	0.00	0.00	0.00	0.01	0.00	0.03
8.0E+6	0.00	0.00	0.00	0.02	0.00	0.08
1.0E+8	0.44	0.64	0.16	0.34	0.05	0.16
2.0E+8	1.1	1.1	0.52	0.78	0.25	0.51
3.0E+8	1.8	1.3	0.90	1.1	0.49	0.79
5.0E+8	3.2	1.5	1.7	1.3	0.98	1.1
8.0E+8	5.2	1.5	2.8	1.5	1.7	1.4
1.5E+9	10	1.5	5.5	1.5	3.4	1.5
2.0E+9	13	1.5	7.5	1.5	4.7	1.5
3.0E+9	20	1.5	11	1.5	7.2	1.5
5.0E+9	34	1.5	19	1.5	12	1.5

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