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thesis entitled DETERMINATION OF DIFFUSION<sup>3</sup> AND PREDICTION OF MIGRATION OF XYLENE AND 2,4-DICHLOROPHENOL THROUGH HIGH DENSITY POLYETHYLENE

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# DETERMINATION OF DIFFUSION AND PREDICTION OF MIGRATION OF XYLENE AND 2,4-DICHLOROPHENOL THROUGH HIGH DENSITY POLYETHYLENE

By

**Richa Sharma** 

# A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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#### ABSTRACT

# DETERMINATION OF DIFFUSION AND PREDICTION OF MIGRATION OF XYLENE AND 2,4-DICHLOROPHENOL THROUGH HIGH DENSITY POLYETHYLENE

By

# **Richa Sharma**

A study was performed to predict migration of two possible contaminants, xylene and 2,4 dichlorophenol into food from a package structure incorporating recycled HDPE and a food contact virgin barrier. The virgin barrier is expected to reduce or delay the migration of the contaminants. The prediction of migration was done using two mathematical models, proposed by Begley and Hollifield and by Laoubi and Vergnaud. On the basis of the prediction, the dietary concentrations of the contaminants in the food were also determined. For the prediction of migration, the models require the diffusion coefficients of the compounds through the polymer. These were obtained experimentally using isostatic and quasi isostatic test procedures.

The results of the models were analyzed and the predicted migration from the two models were compared. The results of the predictions of the models indicated that the virgin barrier is not very effective in controlling the migration into the food. However it was also observed that the simplifying assumptions used by these models lead to a probable over-estimation of the migration of the contaminants from the packaging into the food. To my family

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# **TABLE OF CONTENTS**

LIST OF TABLES	ix
LIST OF FIGURES	x
1. INTRODUCTION	
1.1.1. Background	1
1.1.2 Objectives of the Study	3
2. LITERATURE REVIEW	
Part: I	
2.1.1 The Threshold of Regulations	7
2.1.2 The need For Functional Barriers	9
2.1.3 Description of a Functional Barrier	11
2.1.4 Recent Developments in the Incorporation of Functional	13
Barriers for Recycled Polymers	
Part:II	
2.2.1 Efficiency of Functional Barriers	16
2.2.3 Empirical Determination of Functional Barriers	17
2.2.3 Theoretical Models	18

2.2.4	Model 1 : Begley and Hollifield Model	18		
2.2.5	Model 2 : S. Laoubi and J.M. Vergnaud	26		
2.2.6	Model 3 : L. L. Katan	32		
2.2.7	Prediction of Dietary Concentration	33		
Part I	Part III			
2.3.1	Permeability Theory	35		
2.3.2	Measurement of Permeability	37		
2.3.3	Absolute Pressure Method	38		
2.3.4	Isostatic Method	39		
2.3.5	Quasi Isostatic Procedure	41		

# 3. MATERIALS AND METHODS

•

3.1.1	Film Sample	45
3.1.2	Model Test Contaminants	45
3.1.3	2,4 Dichlorophenol Physical and Chemical Characteristics	47
3.1.4	Xylene : Physical and Chemical Characteristics	48
3.1.5	Permeability Measurements on 2,4 Dichlorophenol	48
3.1.6	Permeability Experiments on Xylene	50
3.1.7	Determination of Vapor Pressure	52

3.1.8	Calibration of the Gas Chromatograph	53
3.1.9	Theoretical Modeling	54

# 4. RESULTS AND DISCUSSION

4.1.1	Calibration Curves for Xylene and 2,4 Dichlorophenol	55
4.1.2	Results of Permeability Experiments of Xylene	55
4.1.3	Results of Permeability Experiments on 2,4 Dichlorophenol	60
4.1.4	Incorporation of the Diffusion Coefficients into the	
	Mathematical Models: Begley and Hollifield	73
4.1.5	The Laoubi and Vergnaud Model	73
4.1.6	Comparison of the Two Models	80

# 5. CONCLUSION

5.1.1.	Summary	86
5.1.2	Recommendations and Future Work	88

# 6. APPENDICES

.

Appendix 1. Gas Chromatograph Conditions	90
Appendix 2. Calibration Curves	92

Appendix 3. Transmission Profile Curve

# 7. BIBLIOGRAPHY

·

94

95

# LIST OF TABLES

Table 1.	Xylene: Results of Isostatic Permeability Experiments	56
Table 2.	2,4 Dichlorophenol: Summary of Permeability and Diffusion Coefficients	56
Table 3.	Xylene: Prediction of Migration Using the Begley and Hollifield Model for Monolayer Recycled Strucure (1 Mil)	63
Table 4.	Xylene: Prediction of Migration Using the Begley and Hollifield Model for Two Layer Barrier Structure (10 mils)	65
Table 5.	2,4 Dichlorophenol: Prediction of Migration Using the Begley and Hollifield Model for a Monolayer Recycled Structure (1 mil)	70
Table 6.	2,4 Dichlorophenol: Prediction of Migration Using the Begley and Hollifield Model for Two Layer Barrier Structure (10 mil)	72
Table 7.	Xylene: Laoubi and Vergnuad Model: Prediction of Migration (1mil)	74
Table 8.	2,4 Dichlorophenol: Laoubi and Vergnuad Model: Prediction of Migration (1 mil)	75
Table 9.	Xylene: Laoubi and Vergnaud Model: Prediction of Migration (10mil)	76
Table 10	. 2,4 Dichlorophenol: Laoubi and Vergnaud Model: Prediction of Migration (10 mil)	77

•

# LIST OF FIGURES

Fig. 1.	Schematic of Begley and Hollifield Model	23
Fig. 2.	Scheme of the Two Layer Packaging	28
Fig. 3.	Typical Transmission Profile Curve	43
Fig. 4.	Plot of Diffusion vs Vapor Activity For Xylene	58
Fig. 5.	Plot of Permeability vs Vapor Activity for Xylene	59
Fig. 6.	2,4 Dichlorophenol: Transmission Profile Curve	61
Fig. 7.	Xylene: Comparison of Migration Through Single Layer and Two Layer Structure	68
Fig. 8.	2,4 Dichlorophenol: Comparison of Migration Through Single Layer and Two Layer Structure	69
Fig. 9	Xylene: Concentration of Contaminant in the Package as a Function of Time.	81
Fig. 10	2,4 Dichlorophenol: Concentration of Contaminant in the Package as a Function of Time	82
Fig. 11.	Xylene: Comparison of Migration Between the Two Models	83
Fig. 12.	2,4 Dichlorophenol : Comparison of Migration Between the Two Models	84

•

#### **1. INTRODUCTION**

#### 1.1.1 Background

The disposal of solid wastes is a major issue that has been faced by most governments during the past few years. Since the existing landfills have already reached, or are rapidly reaching, their capacity, there is a need to turn towards recycling as the solution to the ever increasing problem of solid waste. Packaging, in various forms, is a major component of the solid waste stream in the United States. This includes materials such as paperboard, metal, plastics, glass, etc. as well as various types of composites of these materials. Within these packaging materials, plastics by themselves represent a significant share of the solid waste. It is for this reason that within the last few years, pressures to utilize post consumer recycled content in plastics packaging have increased greatly.

Plastics are used in all kinds of industries to package a wide range of products because of their versatility. They combine properties of all the existing packaging materials to give a product with features such as reasonable barrier properties, ease in processing, light weight, economy, printability and many other advantages. Particularly in the food industry, plastics are rapidly replacing conventional packaging materials such as glass and metals. They are used in a wide variety of applications and

1

may be either in the form of rigid or flexible packages for food products. These packages can be made up of single or multi-layered plastic structures and used either for primary or secondary packaging.

Due to increasing pressures to reduce solid waste, most industries are being pushed towards incorporating recycled plastics into their packaging. Specifically, the food industry, which previously stayed away from using recycled packaging materials in contact with food, is now beginning to utilize post-consumer recycled plastics in packaging.

One of the main concerns in using recycled plastic as a packaging material for food contact applications, is that after its use by the consumer, there is a possibility that the package could come in contact with various substances for which it was not originally intended. Some of these substances could be harmful for human consumption and could even be potential carcinogens. An example of this contact with toxic materials is the possible storage of pesticides, oils, or various other household chemicals in plastic bottles after the original product has been consumed. Because of the relatively poor barrier properties of plastics compared to glass and metal, if the toxic material is stored for a sufficiently long period of time, some of the contaminant may be sorbed into the plastic package wall. When these contaminated packages are taken for reprocessing, there is a strong possibility that the cleaning and processing operations are not efficient enough to

2

remove all of the contaminants from the polymer resin. Finally, after the reprocessed resin is converted to a new packaging material for food contact purposes, there is a danger of these residual contaminants migrating into the food product over its shelf life. This may be may be harmful if the product is consumed by humans, with the extent of damage caused depending on the nature of the contaminant and the amount of contaminant that has migrated into the food product.

This kind of contamination of food products due to contact with postconsumer recycled plastics is a major concern of the FDA for consumer safety. FDA's primary interest is to keep the consumer safe from the possible existence of these toxic materials, and to keep a control on the maximum possible intake of any residual contaminants from post-consumer recycled plastics used in food contact packaging. For this purpose the FDA has recently adopted a policy known as the "threshold of regulation," which limits the amount of contaminant that can be present to a level which it considers safe for repeated human consumption.

# 1.1.2 Objectives of the study

Among the various plastics used for packaging, high density polyethylene, (HDPE) is a polymer that has very wide applications in the food and consumer packaging industry. Large volumes of this polymer are used in food packaging, and due to environmental issues there is an increasing need to incorporate the recycled HDPE back into the food packaging system. It can be risky to have the recycled HDPE in direct contact with the food because of the safety issues surrounding the possible migration of contaminant into the food product. Hence it appears feasible to consider a "safer" alternative of incorporating a food contact barrier made of virgin HDPE separating the recycled HDPE and the food.

The use of "functional barriers," a layer of virgin polymer between the recycled layer and the food product, has been suggested to reduce the amount of migration of contaminants from the recycled layer by acting as a barrier between the recycled layer and the food. However, for the safety of the consumer, it is important to ensure that these "functional barriers" actually prove to be effective in preventing or reducing migration from the recycled layer into the food product.

This study attempts to determine the effectiveness of a virgin HDPE layer as a "functional barrier" in reducing migration of contaminants from a recycled layer into a food to a minimum level that is accepted by the FDA. As an alternative to performing actual migration tests, which can be elaborate and time consuming, mathematical models are used here which predict the migration of compounds through packages incorporating functional barriers. This prediction will help determine if the virgin barrier proves to be effective in reducing or preventing migration.

For the study, two representative compounds, xylene and 2,4 dichlorophenol were chosen from a range of recommended contaminants. The models utilized for the prediction of migration are the Begley and Hollifield model and the model proposed by S. Laoubi and J. Vergnuad. The study aims to determine the predicted migration obtained from these selected models, compare the results between the two, and to judge if either of the models portray what can be expected in the real-life situation of the migration process. For the prediction of migration, these models require the diffusion coefficient of the contaminant through the film and the initial concentration of the contaminant in the recycled layer. The diffusion coefficients for both the selected contaminants were determined through experimental methods using isostatic and quasiisostatic test procedures. The results of the predicted migration of the contaminant can then be used to predict its dietary concentration in the food and hence can determine if this concentration is expected to be within the limits specified by the FDA (i.e. below 0.5ppb).

The specific objectives of this study are as follows:

- To determine the permeability and the diffusion coefficients of 2, 4, dichlorophenol and xylene through high density polyethylene,

- To predict migration using the Begley and Hollifield model and the model suggested by Laoubi and Vergnuad,

- To compare the predicted migration of the two models, both for monolayer packages, and for two layer packages incorporating a functional barrier,

- To determine the dietary concentration based on these predictions and to determine if this level of contamination is below the threshold of regulation and hence determine the effectiveness of the functional barrier, based on the theoretical models.

A similar study is also being performed for HDPE with two other contaminants, namely isopropanol and tetracosane, by W. Lertsiriyothin in the School of Packaging.

#### 2. LITERATURE REVIEW

# PART: I

#### **FUNCTIONAL BARRIERS**

# 2.1.1 The Threshold of Regulation

The law governing the use of food additives in the United States is the Federal Food, Drug and Cosmetic Act. According to this law, a substance is deemed to be a food additive if its "intended use results or may reasonably be expected to result either directly or indirectly in its becoming a component, or otherwise affecting the characteristics of the food unless the substance is generally recognized as safe (GRAS) or is used in accordance with prior sanction of approval". (FDA, Proposed Rules ,1993). Food packaging materials are thus considered indirect food additives and are subject to the regulations concerning indirect food additives.

Currently there do not exist any separate laws for recycled plastics used in direct contact with food, and the FDA regulations apply to recycled plastics the same way as they do for the virgin polymers. Hence this law is applicable to all kinds of packaging materials whether they are made from 100% virgin polymer or have some component of post-consumer recycled material.

Based on the study of the toxicological effects of a large number of potentially hazardous chemicals, the FDA has concluded that the presence of a substance in the daily diet at or below 0.5 ppb (parts per billion) is generally so negligible as to cause no health problems to humans. As a result of this study, the FDA has established a dietary concentration of 0.5 ppb as the threshold of regulation for substances used in food contact articles. This means that the substance must not migrate, and not be expected to migrate into food in amounts that result in dietary concentrations that are above 0.5 ppb. The value of 0.5 ppb is equivalent to dietary exposure of 1.5 micrograms/person/day based on a diet of 1500 grams of solid food and 1500 grams of liquid food/person/day in the United States. (FDA, Proposed Rules, 1993). This value gives the FDA a wide margin of error even if the compound is later found out to be a human carcinogen. This is because a 0.5 ppb threshold is 2000 times lower than the dietary concentration at which the vast majority of studied compounds are likely to cause non-carcinogenic toxic effects and 200 times lower than the chronic exposure level at which potent pesticides induce toxic effects.

In recent times, the analytical methods to detect migration into food have become capable of measuring and detecting small quantities of migrants into food products. This level of 0.5 ppb corresponds to a migratory level that is above the detection limit for many of the analytical methods used to quantify migrants from food contact materials. For example if a consumption factor of 5% is used (minimum value recommended by the FDA in absence of any specific market volume data), it corresponds to a migration level of 10 ppb. The analytical methods used to detect migration of food contact materials can quantify well within this range.

#### 2.1.2. The need for functional barriers

In order to reduce migration from the post-consumer recycled plastic into the food, it is important that the packaging have low concentrations of contaminants to start with. The greatest problem with post-consumer recycled plastics is that the reclamation processes currently used are not very effective in removing contamination completely. Some of these processes also have the added disadvantage of not being economically feasible.

Among the currently used reclamation methods for recycled polymers in contact with food products, the depolymerization process proves to be the most effective in the elimination of possible contaminants. This is because depolymerization breaks down the recycled (contaminated) polymer into basic monomeric and oligomeric units. Due to this process, the resulting polymer has a purity that is quite comparable to the virgin polymer and is generally considered safe for food contact materials. (Franz et. al., 1994). However, a shortcoming of this process is that it is very expensive and is limited in its suitability and application. Currently the only polymer that can be effectively recycled using depolymerization is PET. Recycled PET from this process is being used for soda beverage bottles, but as mentioned, it is not a commercially feasible process because of high costs involved. (Overton, 1994)

Physical reprocessing is the most common recycling method for postconsumer plastics and is generally an economically feasible method too. The high processing temperatures involved help in removing bacterial and surface contamination but the cleaning and processing operations of the recycled polymer may not always be adequate to remove all the contaminants that may have absorbed into the polymer. Hence physical reprocessing is most effective if the recycler has control over the life cycle of the material so that the material does not come in contact with potentially dangerous contaminants. As discussed earlier, these contaminants may migrate into the food products when the polymer resin is processed into a food contact packaging material. (Franz et al., 1994; Overton, 1994)

Reuse of post-consumer plastics (e.g. reuse of plastic bottles after cleaning and washing) is even more economically feasible than the above mentioned recycling processes and is gaining popularity in the beverage industry. The process by itself may not prove to be effective in removing contaminants from the plastic material in the event of 'misuse' of the packages by the consumers. For this reason, a very tight source control must be maintained in order to minimize contamination of the package to reduce risk of migration. This process, however, has proved to be very suitable for certain polymers such as PET which is generally resistant to absorbing extraneous chemicals. (Overton, 1994)

Because of the limitations of the existing reclamation processes, there is a need to look for other options or systems in which recycled polymers may be put to use in food packaging. One such concept, slowly gaining acceptance in the food industry, is the combination of a recycled polymer layer and a virgin polymer layer in the structure of a food contact package, with the virgin polymer in contact with the food to prevent migration of residual contaminants from the recycled layer into the food.

# 2.1.3 Description of a functional barrier

The term "functional barrier" is generally the term used to describe a layer which, when used in combination with recycled plastic in a packaging material, reduces migration from any leftover contaminants in the recycled polymer into the food product to a toxicologically acceptable level. This is so as not to endanger human health caused by the possible consumption of such toxic substances in undesired levels.

Thus a functional barrier essentially incorporates the use of a virgin layer of polymeric material which separates the food from the recycled plastic material. This virgin layer then acts as a barrier to the migration of possible contaminants from the recycled plastic to the food contact layer. Migration of package components is less of a problem with dry food products, but is more likely to occur from the packaging material when the food product contains alcohol, acid or fat. Although the barrier layer may not completely eliminate the migration of contaminants from the recycled plastic to the food product, it can sufficiently slow down the process so that essentially there is negligible migration during the life time of the product. It is important to determine whether this level is below the threshold level specified by the FDA in their regulations.

For making a barrier structure, the post-consumer polymer is first cleaned and re-processed by standard methods. It can then be coextruded or laminated with the virgin resin in such a way that the virgin resin comes in contact with the food product and the recycled layer is on the outside of the package. Most of the functional barriers developed are made of the same polymer as the recycled resin. This is mainly because of the ease of fabrication involved when both the layers are of the same polymer resin. It is also important to use the same polymers in the structure in order to facilitate further recycling of the plastic materials.

12

The package can also be fabricated as a three or more layered structure in which the recycled polymer is sandwiched between two layers of virgin polymers. Development of multilayer coextrusion techniques has enabled recycled polymer to be used in the core layer. These are already being used in quite a widespread manner for detergents and other non-food applications where migration is not really the major issue.

Recently some developments have been made and approvals have been given by the FDA for the incorporation of barrier layers in food packaging containing post consumer recycled plastics. These are discussed in brief below.

2.1.4 Recent developments in the incorporation of functional barriers for recycled polymers.

According to FDA spokespersons, some materials may be safely used as a functional barrier, even under the most severe conditions, without any migration from the recycled layer to the food contact layer. Aluminum foil properly fabricated is one such material that acts as a functional barrier preventing migration from the recycled layer into the food product. Hence a recycled plastic film may be used without any concerns when aluminum foil acts as the food contact layer separating the recycled layer from the food. (PRTF Guidelines, 1994). However the same guarantee cannot be given for plastic

materials acting as functional barriers because of their relatively inferior barrier properties compared to aluminum.

Some structures incorporating a barrier layer in contact with food products have been prepared recently. The FDA has reviewed the use of coextruded laminated structures where a food contact layer of virgin polymer separates the food from the recycled plastic material. Many polyolefins, polyesters, and other polymeric materials of adequate thicknesses have been found to effectively act as functional barriers preventing significant migration from the recycled layers. Experimental analysis and theoretical modeling have shown that in structures of virgin/recycled PET laminates and structures of virgin/recycled PS laminates, a 1 mil layer of virgin PET and a 1 mil layer of virgin PS, respectively, as the food contact layers, act as functional barriers and allow minimum (less than 0.5ppb dietary concentration) migration of contaminants into the food when stored for about 2 weeks at room temperature or lower. (Thorsheim and Armstrong, 1993.)

There have not been many developments on the use of a barrier structure of virgin HDPE/recycled HDPE, which will be used in our study. Only very recently the FDA has given approval to Union Carbide for use of post-consumer recycled HDPE for packaging dry foods with no surface fats. It must be separated from the food by a food-grade HDPE layer at least 4 mils thick. The resin is being offered for use in producing multilayer rigid

containers, and is priced higher than virgin HDPE and recycled HDPE for non-food packaging use.

Approval has already been given to Continental PET Technologies, (Florence, KY), manufacturers of containers for food and beverages, for the use of a multi-layered PET bottle with recycled PET sandwiched between layers of virgin PET. The food contact layer is one mil of virgin PET and separates the recycled PET from the beverage. Migration tests conducted with this package, using the actual product, proved that the virgin layer was an effective barrier, i.e. it reduced the migration of contaminants into the product to a level that was much below the acceptable daily intake. The results of these tests were submitted to the FDA and the bottle was approved for food contact purposes. (Miller, 1993)

Extensive tests on the effectiveness of a functional barrier have been performed on a 3 layered polypropylene cup with recycled PP as the sandwiched layer and virgin resin as the food contact layer. The thickness of this cup was 0.8mm with 50% mass fraction of recycled polymer. The results of these tests showed that the virgin layer of the polymer (in this case PP) functioned as an effective barrier to the migration of contaminants from the recycled surface to the food product. (Franz et al., 1994)

# PART: II

# METHODS FOR DETERMINING THE ADEQUACY OF A FUNCTIONAL BARRIER

# 2.2.1 Effectiveness of a Functional Barrier

Whenever a package incorporating a recycled layer and a functional barrier is introduced, it is very important to determine its effectiveness in preventing migration. The most reliable way to determine if a functional barrier is effective, is by performing migration experiments using actual conditions. But this method may not always be practical because of the long times involved in migration testing. Recently some investigators have developed mathematical models to predict the migration of the contaminants from the recycled layer into the food product without having to perform actual tests. These models require the diffusion coefficient values of the contaminant/polymer system and initial concentrations of the contaminant in the recycled layers in order to make the prediction.

The effectiveness of a functional barrier can be determined by three different methods: 1) empirically, using representative model systems; 2) theoretically, using dimensionless parameters to define general idealized systems and 3) also theoretically, but using quantitatively defined systems relevant to real life.

Various factors contribute to the adequacy of a barrier in preventing migration from the recycled layer to the food. These include the type of the polymer, the initial concentration of the contaminant in the recycled plastic, the nature of the food product, the thickness of the barrier layer, conditions of use such as time, temperature, humidity, etc. Standard testing protocols to evaluate the adequacy of a functional barrier in given situations are followed by the FDA and industrial scientists.

#### 2.2.2 Empirical Determination of Functional Barrier

Empirical work has been done on PET by deliberately contaminating resin with a number of substances considered to represent those which might be found in post consumer recycled (PCR) plastics. An experiment was done using a three layer coextruded PET bottle with the contaminated layer sandwiched between plies of virgin PET. Migration tests were performed using appropriate test procedures. The migration levels were compared with the migration from single layered bottles made from recycled PET. From the experimental data it was found that migration levels from the 3-layered PET bottles with a functional barrier were reduced by more than two orders of magnitude compared to the migration from single-layered bottles. (Franz et.al., 1996)

#### **2.2.3 Theoretical Models**

Theoretical models have been developed recently for the prediction of the migration of a contaminant from a recycled package system into the food product. The models under consideration in this study can predict migration of a contaminant over a period of time. For this prediction, it is necessary to have knowledge of the diffusion coefficients of the contaminant/package system, thickness of the material, and the initial concentration of the contaminant in the polymer. There are also some models that require the determination of the partition coefficient to predict migration. The models that are used in this study to predict migration are explained in brief below.

#### 2.2.4 Model 1: Begley and Hollifield Model

A mathematical model was proposed by Begley and Hollifield (1993) to predict migration into the food from a package structure. The model predicts migration through a monolayer recycled package structure (Case A) as well as migration through a twolayered package structure with a virgin layer separating the recycled polymer from the food. (Case B). These models include many assumptions that simplify the real-life situation of migration through the package structure into the food.

### **CASE A: Migration Through a Monolayer Package**

In the first case involving the prediction of migration through the monolayer package, the package is assumed to be made of 100% recycled polymer and is in direct contact with the food product. This situation represents a worst case scenario. The migration from this type of package into the food is assumed to follow Fickian behaviour and is mathematically expressed by the following equation (Crank, 1975);

$$Mt = 2C_o \sqrt{\frac{Dt}{\pi}}$$
(1)

# Where:

 $M_t$  is the amount of substance migrating from a unit surface area of package, expressed in ug/cm<sup>2</sup>,

 $C_o$  is the concentration of the contaminant in the polymer at time 0, expressed as ug/cc; t is the time, in seconds;

D is the diffusion coefficient of the contaminant through the polymer film, expressed in  $cm^{2}/sec$ 

The initial concentration of both the contaminants in the recycled film, C<sub>o</sub>, was assumed, based on the Plastics Recycling Task Force document (PRTF), "Guidelines for the Safe Use of Recycled Plastics for Food Packaging Applications." The guidelines state the seven compounds that best represent the possible contamination in post consumer recycled plastic. This is discussed in more detail in Chapter 3. The guidelines also give an indication of the maximum level at which each of the seven compounds are expected to remain in the post-consumer HDPE before it undergoes the cleaning and recycling operations. According to the guidelines, each of these seven compounds will have an effective contamination rate of a maximum of 1% in the polymer before it has been cleaned and recycled into new packaging material. This implies a contamination rate of a maximum of 1% each, for both xylene and 2, 4 dichlorophenol in HDPE, which reduces after recycling and cleaning operations. In order to arrive at this contamination in the recycled plastic, the PRTF arranged for the cleaning and reprocessing of the HDPE spiked with 1% of each of the contaminants. The contaminant remaining in the plastic after cleaning and processing gave the maximum concentration likely to remain in the post consumer recycled plastic. This concentration represented the initial concentration  $C_{o}$ , and was determined as 120 ug/cc for xylene and 9.6 ug/cc for 2,4 dichlorophenol.

The prediction by this model is based on the assumption that the contaminant concentration in the polymer does not change during storage, and the food is an infinite sink for the contaminant, providing no resistance to mass transfer. Also the model does not consider the effects of partition equilibrium on the migration of contaminants from food packaging into the product.

Due to over-simplifying assumptions, the values of migration predicted from this expression are expected to be much higher than those obtained from actual migration testing. For example, in real life conditions, the concentration of the contaminant in the recycled layer will reduce with time as the contaminant migrates into the food. In this model, however, the concentration in the recycled layer is assumed to be constant with time. So when applied in the expression it will depict more migration than would be generally expected, especially for longer periods of time. Another assumption of the model is that it does not consider migration of the contaminant out through the outer layer of the recycled polymer which will further reduce the amount of contaminant that will migrate into the food.

#### CASE B: Migration Through a Barrier Structure

The second case considers migration through a two-layered barrier package structure. In this case the package is a laminated package structure made of a layer of

recycled polymer and a layer of virgin polymer where the virgin polymer layer is the food contact layer and separates the food product from the recycled layer. Fig. (1 B) is a schematic illustration of this situation.

In this case, the contaminant will first enter the layer of virgin polymer before it enters the food. The initial concentration of the contaminant in the virgin layer is zero and there is a finite concentration in the recycled layer. For simplification purposes, this type of migration can be treated as a pseudo membrane problem where there is a fixed concentration on one side of the film and a zero concentration on the other side. The solution to this type of problem is expressed by the equation below;

$$Mt = \left[\frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{l=1}^{\infty} \frac{-l^n}{n^2} \exp(-Dn^2 \pi^2 \frac{t}{l^2})\right] C_o l$$
(2)

Where;

*l* is the thickness of the virgin layer in cm.

C<sub>o</sub> is the initial contaminant concentration in the recycled layer.



Schematic of the Begley and Hollifield model with single layer and a two layer structure incorporating a functional barrier.
This equation is also simplified by various assumptions. As in the previous expression for the prediction of migration through a single layer, this expression also assumes that the concentration of the contaminant in the recycled layer is constant which will tend to give a higher prediction of migration than will be normaly expected in real life situations. Also it is likely that the contaminant will not move freely into the virgin layer (as is assumed in the model), but will first diffuse out of the recycled layer before it enters the virgin layer. Because of these assumptions, the prediction of migration is expected to be much more than what is expected in the real-life situation, as is the case in the monolayer package.

The model also describes a variable  $\tau$ , given by:

$$\tau = \frac{Dt}{l^2} \tag{3}$$

which gives a general picture of the rate of mass transfer. The larger the value of  $\tau$ , the more contaminant will have crossed the virgin layer and contaminated the food. Also, at values of  $\tau > 0.6$ , the migration from the two layer package is expected to approach that from a single layer package. The model is not valid for the prediction of migration for a two layer structure for values of  $\tau > 0.6$ . This is due to the fact that at higher values of  $\tau$ ,

either the diffusion coefficient is so high or the thickness of the virgin layer/recycled layer is so low that there will be no effect of a barrier in preventing migration. Also a high value of  $\tau$  could be due to larger time periods which may give the contaminant an opportunity to eventually make its way through the functional barrier into the food. In either of these cases there is practically no use of employing a functional barrier.

These equations have many visible flaws because of the over-simplification of the diffusion process with various assumptions, and consequently, an over-estimation of migration. However, they can still be used as a starting point estimate to predict migration through a single layer and a two layer package system. The results from these models can also be compared with other models or with actual migration tests. The predictions can also be used to determine if the models can be used for a wide range of contaminants and if they are applicable to what is normally expected in real life migration situations.

25

### 2.2.5 MODEL 2 : S. Laoubi and J.M. Vergnaud

Another mathematical expression was developed by S. Laoubi and J.M.Vergnaud (1995), to predict the migration of a contaminant through a two-layer package structure incorporating a functional barrier.

Like the model developed by Begley and Hollifield, this model too makes certain assumptions in order to simplify the complex situation of mass transfer through this system. The assumptions made by this model are as follows :

1) The recycled and the virgin layer are made of the same polymer so that the diffusivity of the contaminant is the same through both the layers.

2) The contaminant is initially present in the recycled polymer in a uniform concentration.

3) The contaminant migrates through the two films and through the surface of the foodcontact virgin polymer but there is assumed to be no migration from the external surface of the recycled polymer.

4) The mass transfer follows Fickian diffusion.

5) The food does not migrate into the polymer.

6) The thickness of the film changes negligibly because of the very small concentrations of the contaminant.

7) The concentration of the contaminant in the food is negligible because of the large volume of the food in contact with the functional barrier.

In order to arrive at the prediction of migration through such a structure, the investigators started by expressing diffusion with the help of Fick's equation with a constant diffusivity, D

$$\frac{\delta C_{x,t}}{\delta t} = D * \frac{\delta C_{x,t}}{\delta x^2}$$
(4)

where  $C_{x,t}$  is the concentration of the contaminant in the package structure at position x and time t.

A scheme of the barrier structure is shown in Fig. (2) .The initial conditions state that at time =0, at any position x in the recycled layer, the concentration of the contaminant C is equal to the initial concentration  $C_o$  or  $C_{in}$ .

Hence the initial boundary conditions can be given by,

at t=0, for 
$$0 \le x \le H$$
, C=Cin;  
and for  $H \le x \le L$ , C=0



Scheme of the two layer packaging, with a recycled film as functional barrier suggested by Laoubi and Vergnaud.- Initial boundary conditions

Fig. (2)

Where L is the total thickness of the package and H is the thickness of the recycled layer.

At the position x = 0 there is no mass transfer. However at position x=L, according to the mathematical prediction, there will be mass transfer with a convective coefficient of mass transfer h. Using these boundary conditions,

when t > 0, x=0  $\delta C/\delta x=0 \rightarrow$  there is no transfer

when 
$$x=L$$
,  $-D \delta C/\delta x = h(C_L-C_{ext})$ 

when h is very large ,  $h \rightarrow \infty$ , and the above equation simplifies to

at 
$$x=L$$
  $C_L=C_{ext}$ 

In both the cases, the concentration in the food is assumed to be negligible and hence  $C_{ext} = 0$ 

The concentration of the contaminant is 0 at the food contact surface at the start of the migration process. For h= $\infty$ , the concentration at position x and time t, C<sub>x,t</sub> is expressed as a fraction of the uniform initial concentration of the contaminant in the recycled polymer.

$$\frac{C_{x,t}}{C_t} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \frac{(2n+1)\pi H}{2L} \cos \frac{(2n+1)\pi x}{2L} \exp(-\frac{(2n+1)^2 \pi^2}{4L^2} Dt)$$
(5)

The amount of contaminant remaining in the packaging at time t,  $M_{r,t}$ , is obtained by integrating the concentration  $C_{x,t}$  with respect to the space between the boundaries 0 and L. It is expressed in terms of time as the fraction of the initial concentration of the contaminant located in the recycled polymer, and is given by the expression;

$$\frac{M_{n}}{M_{i}} = \frac{8}{\pi^{2}} \frac{L}{H} \sum_{n=0}^{\infty} \frac{(-1)^{n}}{(2n+1)^{2}} \sin \frac{(2n+1)\pi H}{2L} \exp(\frac{-(2n+1)^{2}\pi^{2}}{4L^{2}} D_{i}$$
(6)

Where:

The value  $(M_{r,t} / M_i)$  is a dimensionless ratio,

L is the thickness of the entire structure,

H is the thickness of the recycled polymer,

D is the diffusion coefficient of the contaminant through the film, and

t is the time in seconds

The initial concentration of the contaminant in the polymer is determined as discussed in the previous article. With the knowledge of the initial concentration of the

contaminant in the polymer, we can determine the amount that will migrate into the food product knowing the diffusion coefficient of the contaminant/polymer system. While the initial concentration of the contaminant in the polymer is dependent on the original contaminant level in the polymer and the efficiency of the recycling and the cleaning process, the diffusion coefficient through the film depends upon the fundamental characteristics of the polymer film and the contaminant involved, and can be determined experimentally. As is evident from the equation, this model is not specific to any particular polymer and can be applied to any structure where the recycled layer and the virgin layer are both made up of the same polymer.

This model is capable of giving the following results which will help in determining the adequacy of the functional barrier :

- profiles of the concentrations of the contaminant through the structures for different times,

- rates of transfer of contaminant in the functional barrier,

- concentration of the contaminant at the external surface of packaging,

- and rate of transfer of contaminants into the food.

### 2.2.6 Third approach : L.L. Katan

A third approach to this type of problem has been suggested by L.L. Katan (1996) in which the solution to the prediction of the migration through a functional barrier structure is based on the assumption that the virgin layer acts like a "sponge". According to this theory, at a time  $t_b$  which is also called the burst-out time, a substantial portion of the contaminant diffuses into the barrier, and then migrates into the food at an accelerating rate. It states that in this situation the thickness of the barrier layer has more effect on the burst out time than the diffusion coefficient of the compound. That is, the diffusion coefficient does not play as much a role as the thickness of the polymer in reducing the migration. The mathematical treatment gives the concentration of the contaminants in the food contact layer as :

$$c_{\infty} = \frac{C_0 x_r}{x_r + x_b} \tag{7}$$

where  $x_r$  and  $x_b$  are the thickness of the recyclate and barrier layers respectively. From this model it follows that if  $x_r/x_b$  is small (i.e. the barrier layer is small), the barrier effect is insignificant. Co is the initial concentration of the contaminant, and  $C_{-}$  is the concentration of the contaminant in the food contact barrier layer at time t=∞. This model, unlike the above two models, does not take into account the diffusion coefficients of the compound. This system is not incorporated in the study since we are interested in predicting migration for individual specific contaminant/polymer systems. For this type of prediction we need the diffusion values for the contaminant/ polymer system.

### 2.2.7 Prediction of the Dietary Concentration

From the predicted migration of the contaminant into the food, the dietary concentration of the contaminant in the food can be calculated. This can be a guideline to determine how long the virgin layer will act as a functional barrier preventing migration into the food above acceptable levels. In order to predict the dietary concentration, apart from the migration values, the consumption factors and the food type distribution factors also need to be determined. These are discussed below.

The FDA has defined consumption factors as the portion of the diet likely to contact specific packaging materials. It is defined as the ratio of the weight of food contacting a specific packaging material to the weight of all food packaging and varies for different packaging materials. It is obtained from factors such as the types of foods, the ratio of the food to the weight of the package, and the number of food packaging units in each food packaging category. The consumption factors are well defined for different polymers depending on the extent of their use in the market. In the event that they are not expected to have a widespread use in the market, the minimum consumption factor that can be used for any polymer is 0.05. On the basis of these factors, the consumption factor of polyethylene is 0.13, assuming a wide spread use of the polymer. This is the value that is used in our work in calculating the dietary concentration of the contaminant in the food. Also, since the migration of a contaminant into a food depends on the nature of the food, (ie, aqueous, acidic, alcoholic or fatty) food type distribution factors are also considered to account for the variable nature of the food contacting each packaging material. It indicates the fraction of the food contacting each material that is aqueous, acidic, alcoholic and fatty. Another factor that has to be taken into consideration while calculating the concentration of the contaminant migrated into the food, is the amount of food in direct contact with the packaging material. According to the FDA guidelines, on an average 1.55 grams of food contacts one square cm of packaging material. The dietary concentration in the food is calculated by the following expression:

### Dietary concentration = <M>\*CF\*Ft

Where CF is the consumption factor, M is the migration of the contaminant in the food, Ft is the food type distribution factor for the system. In our studies, the food type distribution factor has been taken as 1 since the models assume that there is no restriction to the transfer of the contaminant at the interface of the packaging and the food. Hence

the dietary concentration is calculated on the basis of the predicted migration and consumption factor alone.

The mathematical models can thus be used to predict migration of contaminants over a period of time after determining the diffusion coefficients of the contaminant/ polymer systems by actual experiments. The diffusion coefficients obtained can be incorporated into the equations along with the film thicknesses and the initial concentration of the contaminants. The diffusion experiments are performed using isostatic and quasi-isostatic procedures and a brief description of the theory and the experimental setup is described in the following pages.

### PART III

### **MASS TRANSFER: THEORY**

### 2.3.1 Permeability Theory

Since plastics, unlike glass and metals, are not complete barriers to vapors, the study of permeation and mass transport behavior of vapors through plastic films is necessary to judge its extent of barrier properties. Permeation of organic vapors, water vapor, and gases such as oxygen and carbon dioxide, is experimentally determined using various methods.

Basically permeation is the transport of a substance through a substrate, involving the following stages: adsorption of the permeating species onto the surface of the polymer, solution of the gas or vapor into the polymer matrix, diffusion through the wall along a concentration gradient and desorption on the other surface.

For films, permeability of a gas or vapor through the film is directly proportional to the diffusion coefficient, usually denoted as "D," and to the solubility coefficient, usually denoted as "S."

Mathematically the permeability is expressed as:

$$\mathbf{P} = \mathbf{D}\mathbf{x}\mathbf{S} \tag{8}$$

where the diffusion coefficient 'D' is related to the rate of the advancement of the permeant molecules and the time required for the system to reach steady state. For simplification it is assumed that the concentration/distance relationship through the polymer is linear and that diffusion takes place in one direction only (ie. through the film). For gases and vapors that show no interaction with the polymer, the permeability coefficient is independent of the concentration of the diffusing gas.

The transmission rate is the amount of penetrating substance transferred per unit

time through a package or a specimen of stated dimensions. Transmission rate is generally inversely proportional to the thickness of the morphologically uniform specimens and is also proportional to the driving force. The permeance is the transmission rate normalized for the area and the driving force. This study involves the experimental determination of permeability data such as diffusion, solubility and permeability. Under low concentrations of vapor, the vapor pressure of the penetrant is proportional to its concentration in the polymer. From Henrys Law it follows that,

$$C=S \times dP \tag{9}$$

### where;

C=concentration of the penetrant in the polymer phase S=solubility coefficient dP=partial pressure of the penetrant in the gas phase

### 2.3.2 Measurement of Permeability

The following three methods are generally used to measure gas and vapor permeability for packaging materials:

- (I) the absolute pressure method,
- (ii) the isostatic method, and
- (iii) the quasi- isostatic method.

### 2.3.3 Absolute Pressure Method

The earlier studies of permeability of organic vapor through polymer films were carried out using this method. In the absolute pressure method, only the permeant vapor in question is used and no other carrier gas or vapor is employed. The total pressure gradient between the two chambers provides the driving force for the mass transfer process. (ASTM D3985). The permeated gas or vapor is determined by a manometric or volumetric technique. Steady state is attained when a constant increase in pressure or volume with respect to time is observed in the low pressure chamber. However the problem with using this method for permeability determinations is that the study cannot be done at different relative humidities and co-permeants cannot be used.

### 2.3.4. Isostatic method

In the isostatic test procedure, the total pressure in both the chambers of the permeation cell is kept constant. A constant permeant partial pressure or concentration gradient is maintained between the two cell chambers, by continuously sweeping the desired permeant concentration in an inert carrier gas stream over one side of the film and maintaining the carrier gas flow on the other side concurrently. The permeant diffuses through the film into the lower concentration chamber and is then taken up by the carrier gas to a detector where it is quantified. The steady state permeation rate is the product of the steady state concentration of the permeant in the carrier gas stream and the flow rate of carrier gas. Continuous monitoring of the transmission rate of organic vapors through the polymer film can be obtained using the isostatic test procedure from initial time to the steady state conditions. The permeability of this vapor at different relative humidities can also be determined. There are a number of test systems and equipments used to measure permeation by the isostatic method. Recently, two commercial instruments have been introduced for measuring the organic vapor permeability. MOCON's AROMATRAN Permeation test system (marketed by Modern Controls Inc., MN) is used for measuring the permeation rate of various organic compounds through polymer films. This system is equipped with flame ionization detector (FID) with a high degree of sensitivity.

The other system, which is the one that is used in this study, is the MAS 2000 organic permeation detection system marketed by Testing Machines Inc., NY. This system is also equipped with an FID that provides sensitivity levels in the region of low parts per billion. The determination of permeability, diffusion coefficient and solubility can be obtained rapidly using the MAS 2000 system, which is interfaced with an IBM computer. The computer controls the conditions of the experiment such as temperature, pressure, flow rates and cell parameters such as opening and closing of the cell. The computer is equipped with Lotus 123<sup>™</sup> software that can be used to analyze the data obtained from the permeability experiments.

The amount permeated through the film is plotted against time and the time required to reach a rate of transmission equal to half the steady state is determined. This is then used to calculate the diffusion coefficient as follows:

$$D = \frac{l^2}{7.199t_{0.5}}$$
(10)

Where l is the thickness of the polymer and  $t_{0.5}$  is the time required to reach a rate of transmission equal to half the steady state value. The permeability coefficient P can be determined from the isostatic procedure by substitution into the equation below

$$P = \frac{a * G * f * l}{A * b}$$
(11)

where:

a= calibration factor

G= response units from detector output at steady state.
f= flow rate of sweep gas conveying penetrant to the detector.
A=area of the film exposed to the permeant in the permeation cell *l*= film thickness
b= partial pressure

### 2.3.5 Quasi-Isostatic Procedure

The quasi-isostatic method is an accumulation test method for determining the permeability of organic vapors through barrier films. In this test method, the polymer film is mounted in the permeability cell above a reservoir of the contaminant. The permeant vapor which has diffused through the barrier film accumulates in the low concentration chamber of the permeability cell above the film. The quantity of the permeant accumulated in the low concentration chamber increases as a function of time The vapor is then generally quantified using gas chromatography.

A quasi-isostatic test system was developed for determining the

permeability of organic vapors through packaging films by Hilton and Nee (1978). However this system had the drawback that it was limited to only saturated vapors at a given temperature.

Franz (1993) developed a system that could permit permeability experiments at low vapor pressure. It is a variation of the quasi isostatic procedure and involves an adsorption trap and solvent desorption techniques incorporated with gas chromatographic analysis.

As described above, in the quasi-isostatic method, the quantity of permeant accumulated increases as a function of time. When the quantity accumulated per unit time reaches a constant value, we can say that the steady state of diffusion has been reached. The total quantity of the permeant transmitted is plotted as a function of time and this plot is known as the transmission profile curve. A typical plot of the transmission profile curve is shown in Fig (3). The transmission profile curve gives the lag time  $\theta$ , which is calculated by extrapolating the linear segment of the total quantity of penetrant to have transmitted through the film to the time axis.

The diffusion coefficient for the specific set of experimental conditions is determined from the lag time and the thickness of the film as follows:

$$D = \frac{l^2}{6\Theta} \tag{12}$$



Fig(3)



•

where : l is the thickness of the film

 $\theta$  is the intersection of the projection of the steady state portion of the transmission profile curve with the time axis and denotes the lag time in seconds. Also, the permeability coefficient at the steady state can be calculated by the equation below;

$$P = \frac{y * l}{A * b} \tag{13}$$

Where;

b= slope of the straight line portion of the transmission profile curve.

l= thickness of the film

A=surface area of the film exposed to the permeant in the permeability cell

### **3. MATERIALS AND METHODS**

### 3.1.1 Film Sample

High density polyethylene (HDPE), obtained from Tredegar Film Products (Richmond, Virginia) was used for the permeability experiments. (Trade name: Haute Monax, Lot/S.O.# 49611). It was obtained in the form of a roll 43"x 1 meter. The roll was kept at room temperature and carefully covered to keep it free from any kind of damage. The film samples had thickness ranging from approximately 1.12-to-1.19 mils. The average thickness of the roll was determined as 1.17 mils. The test samples were cut from the roll and it was ensured that the samples did not have any kind of cracks, holes or other types of defects that might lead to erroneous results in the permeability tests. It was also ensured that the samples taken were free of dust particles or any other foreign bodies.

### 3.1.2 Model Test Contaminants

The guidelines given by the Plastic Recycling Task Force has suggested a list of compounds which were selected to best represent the entire range of likely contamination

in the recycled polymers in the post-consumer recycled stream. These contaminants have been chosen so that they cover the range of polar, volatile and non-volatile; non polar, volatile and non-volatile; and heavy metal. Polar and non polar compounds are chosen since the extent of polarity will affect the solubility of a substance in another. Volatile and non-volatile compounds are chosen because the volatility of a compound is a function of its vapor pressure and will affect migration. The model compounds and their representation are as follows:

Isopropanol - polar-volatile - representative of paint strippers, household cleaners etc.

2,4, dichlorophenol - polar non- volatile - representative of pesticides
Xylene - non polar-volatile - aromatic fraction of gasolene, paint thinners etc.
Tetracosane - non- polar, non- volatile
Heavy Metal - Copper-2-ethylhexanoate - crab grass killer
Methyl Stearate- Fats and oils, Motor Oils, Brake fluids.
Ethylene Glycol- Antifreeze

As discussed, the two contaminants selected to study in these initial permeability experiments were:

(I) 2,4 dichlorophenol and

(ii) Xylene

The physical and chemical properties of the compounds are discussed in brief below.

### 3.1.3 2,4, Dichlorophenol : Physical and Chemical Characteristics:

This compound is a solid at room temperature. It was obtained from Aldrich (Milwaukee, USA) and had a purity of 99%. It is a polar non -volatile compound possessing the following chemical characteristics. (Aldrich Catalog)

Chemical Formula - Cl<sub>2</sub> C<sub>6</sub> H<sub>3</sub> OH

Molecular Weight - 163.00

Boiling range - 209 to 210 deg C

The saturation vapor pressure of 2, 4 dichlorophenol is very low at room temperatures. Due to the difficulties of generating vapor at low pressures, and because of the safety concerns surrounding the use of the compound, the permeability tests had to be limited to the quasi-isostatic method. The determination of the diffusion coefficients was done at saturation vapor pressure of the compound.

### 3.1.4 Xylene : Physical and Chemical Characteristics:

Xylene is a liquid at room temperature. The chemical was obtained from Aldrich (Milwaukee, USA) and was 98 % pure HPLC grade. It is non polar, volatile with the following chemical characteristics.(Aldrich Catalog, 1996)

Chemical Formula - C<sub>6</sub> H<sub>4</sub> (CH<sub>3</sub>)<sub>2</sub>

Molecular weight - 106.17

Boiling range - 143 to145 deg C

### 3.1.5 Experimental Methods

# 1. Permeability Measurements on 2,4, Dichlorophenol Using Quasi-isostatic Methods:

As mentioned above, permeability studies for 2,4 dichlorophenol were carried out using the quasi-isostatic method because of the limitations in operating with this chemical due to its physical properties and health safety concerns.

For the studies, a small quantity of, 2,4 dichlorophenol was placed in a

glass petri dish and placed in the lower chamber of the permeability cell. The sample test film of high density polyethylene was placed between the lower chamber and the upper chamber of the cell. Thus a partial pressure gradient was created between the upper chamber and the lower chamber causing the vapor to permeate from the higher concentration chamber to the lower concentration chamber through the HDPE film.

This kind of experimental set up limited the study to the determination of diffusion for only the saturated vapor pressure of the contaminant. The amount of contaminant permeated through the film to the upper chamber of the cell was determined over a period of time. This was done by taking a fixed quantity (50 microliter) of the headspace in a gas tight syringe and injecting it into the gas chromatograph which was coupled with an FID detector. The gas chromatograph gives the corresponding area response to the injected sample from which the quantity permeated can be calculated using the calibration factor for the compound. The calibration of the gas chromatograph is discussed in detail in section 3.1.7. The sampling of the headspace in the upper chamber was done at regular intervals of time until steady state was reached and there was no increase in the quantity permeated. The quantity permeated with respect to time was plotted, which gave the transmission profile curve of the contaminant through the film. A plot of a transmission profile curve obtained by the experiment is shown in Fig (1). The experiment was repeated 3 times in order to obtain consistency of the results

### 3.1.6 Permeability Experiments for Xylene Using Isostatic Method:

The determination of the diffusion and the permeability coefficients of xylene was carried out by the isostatic method using the Mas 2000 vapor permeability tester as described earlier. The tests were conducted at four different vapor activities, 0.1, 0.2, 0.3, and 0.4 corresponding to partial vapor pressures of 0.5, 1.0, 1.5, and 2.0 mmHg of the contaminant. The tests were conducted in triplicate in order to ensure validity of the results. At the start of the test, the test parameters and measurements and other relevant information about the test sample and the conditions of the test were entered into the computer interfaced with the Mas 2000.

For a test run, the vapor activity was calculated from the following equation;

$$VaporActivity = \frac{P}{Psat}$$
(14)

Where;

Psat is the saturation vapor pressure of the contaminant and

P is the partial pressure of the permeant.

The vapor was generated by bubbling nitrogen through the liquid permeant in a

glass vapor generator. The permeant vapor stream was then diluted with another stream of nitrogen in order to obtain a low vapor pressure, and hence desired low vapor activity. The area response of the gas chromatograph corresponding to the required vapor activity was calculated using the gas law and the calibration factor. The determination of the calibration factor is discussed in detail in section 3.1.7. The settings of the gas chromatograph are shown in Appendix 1. The flow meters were adjusted correspondingly to get the required area response when a sample of the permeant flow was taken from the sampling port and injected into the column of the gas chromatograph.

After the vapor pressure, and consequently the vapor activity, was adjusted and the signal base line reached a steady state, the Mass 2000 was calibrated for the permeant by injecting the vapor from the sampling port into the calibration port of the Mass 2000. This was done in the non-test mode. The detector response is indicated by pico amps. The Mass 2000 calculates the calibration factor automatically. The consistency of the vapor activity was verified periodically by injecting a sample of the vapor from the sampling port into the gas chromatograph and ensuring a constant area response. The machine was then run on the test mode and the quantity permeated was calculated over a period of time. A sample of the raw data obtained for a specific vapor activity, from the Mas 2000, is shown in Appendix 4. This gives the increase in the signal as a function of time. The quantity permeated was calculated from the signal and the calibration factor that was obtained from the Mas 2000. The diffusion coefficient for the vapor activity was calculated by determining the  $t_{0.5}$  from the raw data and using it in Equation (10) as discussed in Chapter 2. The permeability coefficient was calculated from Equation (11) discussed in Chapter 2.

### 3.1.7 Calibration of the Gas Chromatograph

The gas chromatograph was calibrated using standard solutions of the contaminants in appropriate solvents. The conditions of the gas chromatograph are shown in Appendix 1. A standard solution of 2,4, dichlorophenol was prepared using dichloromethanol and a standard solution of xylene was prepared using methanol. The solutions were prepared by varying the concentrations of the contaminants in their solvents, quantified in parts per million. A master batch of 1000ppm of the contaminant in the solution was prepared which was further diluted to the required concentrations for the compounds. The concentrations used for the calibrations can be seen in Appendix 2. A 1 ul sample was removed from each of the standard solutions and injected into the gas chromatograph. The response in area units was recorded for each concentration. A standard curve of the area response vs the permeant quantity was constructed and the calibration factor was determined from the slope of this plot. The standard calibration

curve for 2,4, dichlorophenol and xylene and the conditions used are shown in the Appendix 2.

### 3.1.8 Determination of Saturation Vapor Pressure

The saturated vapor pressure was determined for both the compounds using the headspace technique. Using this method, a small quantity of each of the compounds was placed in a glass vial and sealed. The vials were allowed to stand for 2 days at room temperature to ensure that the headspace was saturated with the vapor of the compound. After two days, a 100ml sample of the head space was taken with the help of an air tight syringe and injected into the column of the gas chromatograph. The area response corresponding to the injected volume was recorded and the saturation vapor pressure was calculated using the standard gas law equation and the calibration factor determined for the compound. The saturated vapor pressure for 2,4 dichlophenol was determined as 0.24 mmHg and the saturation vapor pressure of xylene was 4.5 mmHg.

### 3.1.9 Theoretical Modeling:

The diffusion coefficients obtained for both the contaminants in high density polyethylene were incorporated into the models for the prediction of migration. The results obtained from these models are described in detail in Chapter 4. Prediction of the dietary concentration was done by using the predicted migration values and the consumption factors and these results are also discussed in the following Chapter.

### 4. RESULTS AND DISCUSSION

### 4.1.1 Calibration Curves for Xylene and 2,4 Dichlorophenol

The calibration factors were determined for xylene and 2,4 dichlorophenol as discussed in Chapter 3. The calibration curves, a plot of the quantity injected vs the area response, are shown in Appendix 2. The calibration factor for xylene was determined as 5.6E-13(g/Au) and the calibration factor for 2,4 dichlorophenol was determined as 2.3E-13 (g/Au). The saturation vapor pressures for both the compounds at room temperature were calculated from the calibration factor and the gas law, and were determined as 0.24mmHg and 4.5 mmHg for 2,4 dichlorophenol and xylene respectively.

### 4.1.2 Results of Permeability Experiments on Xylene

The permeability results obtained from isostatic experiments for xylene are illustrated in Table (1). The table shows the experimentally determined diffusion coefficients for various vapor activities ranging from 0.1 to 0.4. It can be seen that the relationship between the diffusion coefficient and the vapor activity is quite linear and that the diffusion coefficients remain almost constant over the range of vapor

# Table (1)

# Xylene

# **Results of the Isostatic Permeability Experiments**

Vapor Activity	Vapor Pressure mmHg	D m2/sec	Permeability coefficient gmil/cm2.sec mmHg	Solubility Coefficient g/cc.mmHg
0	0	0	0	0
0.4	2	1.1E-14	4.1E-10	0.009
0.3	1.5	9.2E-15	3.8E-10	0.019
0.2	1	8.3E-15	3.4E-10	016
0.1	0.5	8.1E-15	3.2E-10	0.01

# Average Diffusion = 9.2E-15 m2/sec

.

## Table (2)

# 2,4 Dichlorophenol

# Results of Permeability and Diffusion Coefficients Using the Quasi-isostatic procedure

Test No.	Transmissio rate (g/sec)	Permeability (g.mil/sqcm. sec.mmHg)	Diffusion Coefficient sqm/sec	Lag time (secs)
-	1 4.9E-10	3.2E-11	2.0E-14	7000
	2 4.9E-10	3.2E-11	2.0E-14	7100
	3 4.9E-10	2.8E-11	2.1E-14	7200

activities indicating that the diffusion follows Fick's law. A plot of the diffusion coefficients as a function of the vapor activity is shown in Fig. (4). The diffusion coefficient is measured in  $m^2/sec$ .

The permeability coefficients were also calculated from the steady state data of the isostatic experiment and the plot of the permeability coefficient and the vapor activity is shown in Fig. (5). The plots indicate that the permeability coefficients remain constant over a range of vapor activities.

Table (1) also gives the values of the solubility coefficients of the compound at these vapor activities. The solubility coefficients were calculated using the relation P=D\*S described in Chapter 2.

Data mentioning the diffusion coefficients of these two compounds was not found in literature and hence an accurate confirmation of the results could not be made. However, a comparison was made with the diffusion coefficients obtained for compounds with almost similar structures. The diffusion coefficient obtained for BHT ( which is similar in structure to 2,4 Dichlorophenol ) was 4.7x 10<sup>-14</sup> m<sup>2</sup>/sec (Hoojat et. al. 1987) This is close to the diffusion coefficient obtained for dichlorophenol in our study (2.0 E-14 m<sup>2</sup>/sec<sup>3</sup>). Similarly the diffusion coefficient of toluene ( which is similar in structure to xylene) was 1.6 E-13 m<sup>2</sup>/sec. ( Shu Jung Huang, 1996). This is somewhat close to the diffusion coefficient of xylene in our study (0.92E-14m2/sec). Fig (4)

Xylene

Plot of Diffusion Vs Vapor Activity for Xylene



Fig. (5)

Xylene

Plot of Permeabilty Vs Vapor Activity for Xylene


#### 4.1.3 Results of Permeability Experiments on 2,4 Dichlorophenol

As discussed earlier, the permeability experiments for 2,4 dichlorophenol were performed using the quasi-isostatic procedure at the saturation vapor pressure of the compound. The experiments were performed in triplicate and the results of these experiments are shown in Table (2). The diffusion coefficients were obtained experimentally using equation (12) described in Chapter 2. An example of the transmission profile curve obtained, which is a plot of the quantity permeated vs the time, is shown in Fig (6). The transmission profile curves for the other two experiments are shown in Appendix (3). The lag time  $\theta$ , in seconds, was calculated from the x-intercept of the straight line (steady state) portion of the curve and is shown in the table. The permeability coefficient was also calculated for the steady state using Equation (13) and can be seen in the table.

# Fig. (6)

# 2,4 Dichlorophenol

# Transmission Profile Curve Obtained from the Quasi-isostatic Test Procedure



Regression Output:		
Constant		-4.8E-06
Std Err of Y Est		4.8E-07
R Squared		0.977815
No. of Observations		4
Degrees of Freedom		2
X Coefficient(s)	7.1E-10	
Std Err of Coef.	7.5E-11	
Lag Time	7100	

# 4.1.4 Incorporation of the Diffusion Coefficients into the Mathematical Models : Begley and Hollifield model

#### a) Xylene

The experimentally obtained diffusion coefficient for xylene using the isostatic method was incorporated into the Begley and Hollifield model for the prediction of migration. The results of the prediction of migration using this model are depicted in Table (3). The column "Mtr" denotes the prediction of migration of xylene through unit surface area of packaging (ug/cm<sup>2</sup>) through a single layer recycled HDPE film using Equation (1). This is denoted as a function of time. The initial concentration of xylene was assumed to be 120ug/cc which is the value obtained from the PRTF Guidelines, 1993 as discussed in Chapter 2. The thickness of the recycled layer is assumed to be 1 mil. The values of the variable " $\tau$ " are also depicted in the table. The model states that at values of  $\tau > 0.6$ , the predicted migration from the two layer structure approaches that from a single layer structure and exceeds that of the single layer at higher values. As discussed in Chapter 2, the predicted migration results from this model for a barrier structure incorporating a food contact virgin layer are not applicable at values of  $\tau > 0.6$ . Since in this situation, the value of  $\tau$  is greater than 0.6 on the first day itself, for these conditions, the expression will not be valid for the two layered barrier structure.

Table (3)

**Xylene** 

### Prediction of Migration Using the Begley and Hollifield Model For a Monolayer Recycled Structure Thickness of recycled layer=1mil

Time	Mtr	Tau
(days)	(ug/sqcm)	(dt/l2)
0	0.00	0.00
+	0.38	1.23
2	0.54	2.46
3	0.66	3.70
4	0.76	4.93
5	0.85	6.16
10	1.21	12.32
15	1.48	18.48
20	1.71	24.64
25	1.91	30.80
30	2.09	36.96
35	2.26	43.12
40	2.41	49.28
45	2.56	55.44
50	2.70	61.60

Mtr=Migration through recycled layer into the food.

Initial Concentration = 120ug/cc

\* All the available contaminant migrates after the first day. Prediction of

subsequent migration is invalid.

In order to reduce  $\tau$ , and to consequently make the model work for the prediction of migration for a barrier structure, either the diffusion coefficient has to be decreased or the thickness of the polymer has to be increased. D is characteristic of the contaminant/ polymer system and hence is a constant for this system, and we are interested in a minimum shelf life of the food of at least 30 days for the prediction of migration. Therefore in order to bring the value of  $\tau$  lower, so that the equation is valid for a two layer structure, the thickness of the structure will have to be increased substantially. Table (4) illustrates this, showing a reduced value of  $\tau$  corresponding to an increased thickness of the virgin layer by 10 times the original thickness (i.e. 10 mils). This model does not consider the thickness of the recycled layer in the prediction of migration. According to this model, the migration of a compound in a barrier structure containing virgin layer is assumed to be dependent only on the thickness of the virgin layer and is independent on the thickness of the recycled layer. The results of the predicted migration from the two layer structure and the monolayer structure is illustrated in Table (4). The predicted migration from the two layer structure was calculated using Equation 2. described in Chapter 2. Though the equation involves a summation of terms from 1 to $\infty$ , the calculations were done for the first 6 terms only, since the contribution from the successive terms were almost negligible. If fewer terms are used, the predictions of migration for the initial few days will not be accurate as per the equation. The predicted

# Table (4)

#### Xylene

#### Prediction of Migration Using the Begley and Hollifield Model Two Layer Barrier Structure Thickness of the Virgin Layer = 10 mils

Time	Mtr	Mtv	Tau	Dietary
(days)	(ug/sqcm)	(ug/sqcm)		Conc. (ppb)
0	0.00	0.00	0.00	0.00
1	0.38	0.00	0.01	0.00
2	0.54	0.00	0.02	0.00
3	0.66	9.5E-05	0.04	0.02
4	0.76	0.0007	0.05	0.15
*5	0.85	0.002	0.06	*0.55
10	1.21	0.05	0.12	9.88
15	1.48	0.15	0.18	30.97
20	1.71	0.30	0.25	59.47
25	1.91	0.46	0.31	92.08
30	2.09	0.63	0.37	126.94
35	2.26	0.82	0.43	163.03
40	2.41	1.00	0.49	199.78
45	2.56	1.18	0.55	236.90
50	2.70	1.37	0.62	274.22

Mtr = Migration through Food Contact Layer in mono-layer structure Mtv = Migration through virgin layer in a two -layered structure Initial Concentration =120ug/cc Dietary Concentration in ppb

\* Dietary Concentration

dietary concentration was also calculated from the expression in Chapter 2, which involves multiplying the migration values by the consumption factors corresponding to HDPE. It can be seen from the table that even though the thickness is increased to 10 mil. the barrier will not prevent the migration of the contaminant to a value that is below the threshold level as specified by the FDA. Part of the explanation for this could be due to the assumption of the model that the concentration of the compound in the package is constant even though it is obvious that in real life the concentration will decrease with time as the compound migrates into the food. For example, the amount of contaminant available to migrate from this barrier structure is 120ug/cc. This amount has already migrated at approximately 100 days as can be derived from Table 4. Hence there must be no more contaminant remaining in the polymer to migrate into the food. However, because of the assumption that the concentration in the polymer is a constant, there is continued predicted migration in this model which is contrary to what is possible in real life situations. As discussed in Chapter 2, this will give unrealistically high prediction of migration, especially as the time increases. Also the predictions of migration in this case after a period of 100 days are totally invalid. The same justification will also apply to the single layer package structure in Table (3) where all the contaminant would have migrated out of the structure at the first day itself. This situation will aggravate even further with compounds with high diffusion coefficients such as xylene and 2,4

dichlorophenol.

On the other hand, if the assumptions of this model are utilized to predict the dietary concentration, it indicates that the virgin layer will have to be very thick in order to prevent substantial migration from the recycled layer into the food. This will not be very useful from the economic, as well as environmental aspect because in such a situation we are likely to end up using more polymer in order to make the barrier more effective. This will not only increase the cost involved but will also defeat the purpose of the environmental concerns of using more polymer.

But as discussed, we have to consider the fact that the prediction is not at all accurate because of the assumption of constant concentration.

Fig. (7) shows a comparison of the predicted migration through a monolayer and two layer package structure for a thickness of 10 mils.

#### b) 2,4, Dichlorophenol

For 2,4, dichlorophenol, which has a slightly higher diffusion coefficient, the results of the prediction of the model are similar to that of the prediction of xylene obtained above. Table (5) illustrates the results obtained for predicted migration from the monolayer recycled HDPE structure. Here again, the initial concentration of the

# Fig (7)

# Xylene

# Comparison of Migration Through a Single Layer and Two layer Structure



# Fig (8)

# 2,4 Dichlorophenol

Comparison of Migration Through a Single Layer and Two layer Structure



### Table (5)

#### 2,4, Dichlorophenol

Prediction of Migration Using the Begley and Hollifield Model For a Monolayer Recycled Structure Thickness of the Recycled Layer =1mil

Time	Mtr	Tau
(days)	(ug/cc)	
0.00	0.00	0.00
*	0.05	2.68
2.00	0.06	5.36
3.00	0.08	8.04
5.00	0.10	13.39
10.00	0.14	26.78
15.00	0.17	40.18
20.00	0.20	53.57
25.00	0.23	66.96
30.00	0.25	80.35
35.00	0.27	93.74
40.00	0.28	107.14
45.00	0.30	120.53
50.00	0.32	133.92

Mtr = Migration Through Food Contact Layer Initial Concentration = 9.6ug/cc \* All the available contaminant migrates after the first day. Prediction of subsequent migration is invalid. contaminant was assumed from the PRTF guidelines as mentioned above. The initial concentration of 2,4 dichlorophenol in the polymer was assumed as 9.6 ug/cc. Also for this situation, the thickness of the recycled layer was assumed to be one mil. In this case, again, assuming a thickness of one mil, the value of  $\tau$  is very high and the model is not valid for the prediction of migration through a two layered structure at this thickness. Also at a thickness of 1 mil, all the available contaminant would have migrated in the first day, but because of the assumption of constant concentration, the model keeps showing migration even after all the contaminant has left the polymer. When the thickness of the virgin layer is increased to 10 mil, the value of  $\tau$  decreases, and the model can be used to predict the migration from the two layer barrier structure incorporating a functional barrier. Table (6) illustrates the prediction of migration through a two-layer structure with a functional barrier of thickness of mil. Again, all the available contaminant would have migrated out of the structure in 50 days making the model totally invalid after that period. Though the equation involves a summation from 0 to  $\infty$ , only the first six terms are used since the contribution from the remaining terms is negligible. Here again we can see that the assumption of constant concentration is not very accurate, leading to an over estimation in migration. If this model is followed then it demonstrates that increasing the thickness of the virgin layer does not help reducing the dietary concentration of the contaminant below the threshold value. Fig. (8) shows a comparison of the predicted

# Table (6)

# 2,4, Dichlorophenol

## Prediction of Migration Using the Begley and Hollifield Model Two Layer Barrier Structure Tickness of the Virgin Layer = 10 mils

Time	Mtr	Mtv	Tau	Dietary
(days)	(ug/sqcm)	(ug/sqcm)		Conc. (ppb)
0.00	0.00	0.00	0.00	0.00
1.00	0.05	0.00	0.03	0.00
2.00	0.06	4.8E-05	0.05	0.01
3.00	0.08	0.00079	0.08	0.16
5.00	0.10	0.01	0.13	1.03
10.00	0.14	0.03	0.27	5.64
15.00	0.17	0.06	0.40	11.65
20.00	0.20	0.09	0.54	18.05
25.00	0.23	0.12	0.67	24.54
30.00	0.25	0.16	0.80	31.06
35.00	0.27	0.19	0.94	37.59
40.00	0.28	0.22	1.07	44.12
45.00	0.30	0.25	1.21	50.65
50.00	0.32	0.29	1.34	57.18

Mtr = Migration through Food Contact Layer in mono-layer structure Mtv = Migration through virgin layer in a two -layered structure Initial Concentration =9.6 ug/cc Dietary Concentration in ppb migration through a monolayer and two layer package structure with a 10 mil thick recycled layer and a 10 mil thick virgin layer.

From these results we can conclude that the functional barrier for HDPE would be effective in substantially controlling migration only if the thickness of the barrier layer is very high. Since the prediction of migration from the model is a gross over estimation of the actual migration due to the assumption of constant concentration, it is obvious that in real life, the migration would not be as high as is predicted and using the results from this model may be very erroneous. Actual migration studies have to be done in order to confirm this. However it is very likely that the results obtained from this oversimplified model will not be applicable to real life migration studies and it would either have to be modified further or other models would have to be considered.

#### 4.1.5 The Laoubi and Vergnaud Model

The predicted migration for both the compounds were also calculated using the model proposed by Laoubi and Vergnuard. This model takes into account only a two layered structure incorporating the virgin barrier. The thickness of the recycled layer and the barrier layer is taken as one mil respectively. The predicted migration results for xylene are shown in Table (7), and the predicted migration results for 2,4, dichlorophenol

#### Table (7)

#### **Xylene**

## Laoubi and Vergnuad Model

# **Prediction of Migration Through a Two Layer Structure Incorporating a Functional Barrier**

Time (Days)	Sum (Mt/Mi)	Mt (ug/cm3)	Mtr (ug/cm3)	Mtv (ug/cm3)	Mtf (ug/cm3)
0	1.00	420.00	442.94	6.20	0.00
0	1.00	120.20	113.01	0.39	0.00
1	0.54	64.56	45.64	18.93	55.44
5	0.03	3.13	2.21	0.92	116.87
10	0.00	0.07	0.05	0.02	119.93
15	0.00	0.00	0.00	0.00	120.00

Thickness of Recycled Layer=1mil, Thickness of Virgin Barrier=1mil

Mt=Concentration of the contaminant in the entire packaging

Mtr=Concentration of the contaminant in the recycled layer.

Mtv=Concentration of the contaminant in the virgin layer.

Mtf= Concentration of the contaminant leaving the virgin layer into the fo Initial concentration =120 ug/cc

#### Table (8)

#### 2,4 Dichlorophenol

#### Laoubi and Vergnuad Model

# Prediction of Migration Through a Two Layer Structure Incorporating a Functional Barrier

Time		Sum	Mt	Mtr	Mtv	Mtf
(Days)		(Mt/Mi)	(ug/cm3)	(ug/cm3)	(ug/cm3)	(ug/cm3)
	0	0.97	9.35	9.75	0.00	0.25
	1	0.22	2.11	1.63	0.48	7.49
	2	0.04	0.41	0.31	0.09	9.19
	3	0.01	0.08	0.06	0.02	9.52
	4	0.00	0.01	0.01	0.00	9.59
	5	0.00	0.00	0.00	0.00	9.60

Mt=Concentration of the contaminant in the entire packaging.

Mtr=Concentration of the contaminant in the recycled layer.

Mtv=Concentration of the contaminant in the virgin layer.

Mtf= Concentration of the contaminant migrating from the polymer into th Initial concentration =9.6 ug/cc

# Table (9)

#### Xylene

### Laoubi and Vergnaud Model

# Prediction of Migration Through a Two Layer Structure Incorporating a Functional Barrier (10 mil recycled layer; 10 mil virgin layer)

Time	Mt/Mi	Mt	Mtr	Mtv	Mtf	Dietary
(days)		ug/cc	ug/cc	ug/cc	ug/cc	Conc.(ppb)
0	1.00	120.48	113.81	6.39	0.00	0.00
1	1.00	120.09	111.10	9.05	0.00	0.00
5	1.00	120.01	103.10	16.91	0.01	0.07
10	0.99	119.10	96.24	22.86	0.90	8.97
15	0.98	117.05	90.92	26.12	2.95	29.53
20	0.95	114.26	86.43	27.83	5.74	57.36
25	0.93	111.08	82.48	28.60	8.92	89.22
30	0.90	107.68	78.90	28.78	12.32	123.17
35	0.87	104.20	75.61	28.58	15.80	158.05
40	0.84	100.69	72.55	28.13	19.31	193.14
50	0.78	93.77	66.96	26.81	26.23	262.27
60	0.73	87.15	61.93	25.22	32.85	328.47
100	0.54	64.56	45.64	18.93	55.44	554.37
150	0.37	44.24	31.25	12.98	75.76	757.65
200	0.25	30.30	21.41	8.89	89.70	897.00
365	0.07	8.69	6.14	2.55	111.31	1113.07

Mt=Concentration of the contaminant in the entire packaging.

Mtr=Concentration of the contaminant in the recycled layer.

Mtv=Concentration of the contaminant in the virgin layer.

Mtf= Concentration of the contaminant in the polymer migrating into the food. Initial concentration =120 ug/cc

# Table (10)

#### 2,4 dichlorophenol

### Laoubi and Vergnaud Model

# Prediction of Migration Through aTwo Layer Structure Incorporating a Functional Barrier (10 mil recycled layer; 10 mil virgin layer)

Time	Mt/Mi	Mt	Mtr	Mtv	Mtf	Dietary
(days)		ug/cc	ug/cc	ug/cc	ug/cc	Conc.(ppb)
0.00	1.00	9.60	9.10	0.50	0.00	0.00
1.00	1.00	9.60	8.67	0.94	0.00	0.00
2.00	1.00	9.60	8.33	1.27	0.00	0.03
3.00	1.00	9.59	8.06	1.53	0.01	0.11
4.00	1.00	9.56	7.82	1.73	0.04	0.43
5.00	0.99	9.50	7.62	1.89	0.10	0.96
10.00	0.94	9.05	6.80	2.26	0.55	5.48
11.00	0.93	8.94	6.66	2.28	0.66	6.61
15.00	0.88	8.46	6.17	2.30	1.14	11.36
20.00	0.82	7.85	5.64	2.22	1.75	17.47
25.00	0.76	7.26	5.17	2.09	2.34	23.41
30.00	0.70	6.70	4.75	1.95	2.90	29.03
35.00	0.64	6.17	4.37	1.80	3.43	34.27
40.00	0.59	5.69	4.02	1.66	3.91	39.13
50.00	0.50	4.82	3.41	1.41	4.78	47.76
60.00	0.43	4.09	2.89	1.20	5.51	55.10
70.00	0.36	3.47	2.45	1.02	6.13	61.32
100.00	0.22	2.11	1.49	0.62	7.49	74.86
150.00	0.10	0.93	0.65	0.27	8.67	86.74

**Mt=Concentration of the contaminant in the entire packaging.** 

Mtr=Concentration of the contaminant in the recycled layer.

Mtv=Concentration of the contaminant in the virgin layer.

Mtf= Concentration of the contaminant in the polymer migrating into the food. Initial concentration =9.6 ug/cc

are shown in Table (8). For the prediction of migration, Equation (6), described in Chapter 2, as used. As seen from the equation, a summation of terms is used. We used only the first 6 terms in the expression since the contribution made by the consecutive terms is almost negligible.

Here again we can see that the virgin polymer does not act as a functional barrier at a thickness of one mil of recycled polymer and one mil of virgin polymer. For both the compounds, almost the entire contaminant migrates out of the polymer in less than 10 days. Unlike the Begley and Hollifield model, this model does take into account the decreasing concentration in the recycled layer and does not predict any further migration once all the contaminant has left the polymer. To observe the effect of the migration with an increase in the thickness of the barrier layer, the thickness of the barrier layer was increased by 10 times (i.e.10 mils ) as done in the previous model. Tables (9) and (10) are predictions of migration when the thickness of the recycled layer and the functional barrier is increased to 10 mils each.

From the tables we can see that though the migration into the food reduces substantially with an increase in the thickness, the dietary concentration is still much above the threshold of regulation specified by the FDA even at 10 days. Hence even according to this model, the functional barrier does not prove to be effective even at a 10 mil thick virgin layer in spite of the fact that the predicted migration from this model is much lower compared to the Begley and Hollifield model. This is mainly because it does not assume constant concentration of the contaminant throughout, but takes into account that the concentration in the package will decrease as a function of time. Hence it is more likely to give results that will be closer to real life situations. Still, it does not act as a functional barrier in keeping the dietary concentration at levels below the threshold value even at higher thicknesses. The Laoubi and Vergnaud model also gives the concentration of the contaminant through the entire package structure. It gives the concentration of the contaminant in the recycled layer, virgin layer, and food as a function of time. Tables (9) and (10) show the concentration of the contaminant in the different layers as a function of time. Mtr, Mtv, and Mtf are the concentration of the contaminant in the recycled layer, functional barrier and in the food. Fig (9) and Fig (10) are plots of the profiles of the concentration of the contaminant with respect to time, through the two layers in the structure, and into the food. As is expected, it is seen that for both the compounds, the concentration of the contaminant reduces gradually over a period of time in the recycled layer as the contaminant diffuses into the virgin layer. In this case, as against the Begley and Hollifield model, the concentration in the recycled layer is not constant and decreases over a period of time. The concentration in the virgin layer first increases and then decreases as the contaminant migrates from the virgin layer into the food. The concentration of the contaminant in the food increases gradually with

time as the contaminant migrates from the functional barrier into the food. These profiles of the contaminant transfer in the system are similar to the profiles obtained by the researchers, Laoubi and Vergnaud, by inserting theoretical values of diffusion coefficients into the mathematical model.

#### 4.1.6 Comparison of the Two Models

The Begley and Hollifield model assumes that the concentration does not change with time, whereas the Laoubi and Vergnuad model takes into account that the concentration in the recycled layer will reduce with time. Hence, the predicted migration from the Begley and Hollifield model is expected to be higher than that of the former as discussed earlier. This is also the kind of observation that has been made in this study and a comparison of the predicted migration between the two models can be seen in Fig. (9) and Fig. (10) for both xylene and 2,4 dichlorophenol respectively. Also, the Begley and Hollifield model does not take into account the thickness of the recycled layer for the prediction of migration and assumes that the migration depends only on the thickness of the barrier layer. In order to predict the amount of the contaminant that will migrate through the polymer, it is also important to take into consideration the thickness of the recycled layer as is done in the Laoubi and Vergnaud model. For the above two reasons **Xylene** 

Fig (9)

Concentration of the Contaminant in the Package System as Function of Time Thickness of the Recycled Layer =10 mil, Thickness of Virgin Layer=10 mil



# Fig (10)

# 2,4 Dichlorophenol

Concentration of the Contaminant in the Package System as Function of Time



Fig	(1	1	)
0	•	-	

# Xylene

Comparison Of Predicted Migration Between the Two Models for a two layer Barrier Structure with a Virgin Layer of 10 mil



# Fig (12)

## 2,4 Dichlorophenol

## Comparison Of Predicted Migration Between the Two Models for a two layer Barrier Structure with a Virgin Layer of 10 mil



the Begley and Hollifield model will predict more migration than the Laoubi and Vergnuad model.

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#### 5. CONCLUSION

#### 5.1.1 Summary

The study involved determining the permeability experiments of the selected compounds, xylene and 2,4 dichlorophenol using the isostatic and quasi-isotatic test methods. The diffusion coefficients were obtained from these tests using the steady state permeation data.

Mathematical models were used to predict migration of both the compounds through a post consumer recycled HDPE film using the experimental values of the diffusion coefficients. The initial concentration of the compounds were taken from the PRTF Guidelines, on the basis of the contamination most likely to occur in post consumer recycled plastics. The mathematical models were employed for single layer recycled HDPE structures, and two layer package structures involving a recycled HDPE layer and a food contact layer of virgin HDPE acting as a 'functional barrier.' The models used follow simplified assumptions which predict more migration than is likely to occur in real life situations.

The prediction of migration obtained from the Begley and Hollifield model was observed to be higher than that from the Laoubi and Vergnuad model. This result was expected because of the difference in assumptions used by the models.

The results of the predicted migration were compared for the two layer and single layer package structures. The study also used the results of the predicted migration to determine the dietary concentration in the food based on the parameters set up by the FDA. Based on the results of the models alone, and not considering the simplifications made by them, we find that the functional barrier does not prove to be very effective in keeping migration below the threshold level. In order for the barrier to be effective, its thickness will have to be increased substantially. This will in turn increase both the cost, as well as the consumption of the recycled polymer thus defeating the objective of reducing recycling waste.

However, as discussed earlier, we have to also take into consideration the fact that both these models tend to over- estimate migration. This is more evident in the Begley and Hollifield model. Due to this over-estimation, there will also be a subsequent overestimation in the prediction of the dietary concentration of the contaminant. The increase in the predicted dietary concentration of the contaminant is also compounded by the incorporation of safety factors in determining the consumption factors which are used to predict dietary concentration of the contaminant.

#### 5.1.2 Recommendations and Future Work:

The likelyhood of the over estimation of predicted migration makes it important to perform actual migration studies with these compounds. The next step in this project would be to perform actual migration studies using doped films with the compounds at the recommended initial concentrations used. The migration studies can be done using the standard food simulating solvents. An attempt should also be made to try to modify the models so that they represent a more real life situation.

The models also assume that there is no resistance to the transfer of the contaminant into the food once it reaches the food contact surface. This generally represents a worst case situation and may be true for fatty products but may not be true for types of food such as dry foods. In such a situation there will once again be an over-estimation of migration.

Also another point that has to be taken into account is that the compound will be able to diffuse through the non food contact end of the package, thus reducing the available concentration of the compound that can move into the food product, leading to lower migration of the compound into the food. Another important factor to be considered is the time intervals between the manufacture of the package and filling it with food. These time intervals may be large, up to many months, or very short, up to a few minutes. In the first case the migration may start out of the package even before it is filled with food. Hence it would not be right to assume that migration of the compound starts when the package is filled with the food as this might lead to an under-estimation of migration. The temperature of storage or use is also going to play a large part in the migration of the contaminant into the food and also has to be considered while predicting migration.

Though the over estimation of migration of the models gives a "safety factor", a gross over -estimation will most definately lead to increased use of polymer and hence increased cost. Hence it is important to determine the extent of overestimation with actual migration studies. If the results of the migration studies are close to the predicted migration by the models, then it will be possible to use these models as a rough estimate in cases where there is not enough time to perform the actual tests. However an agreement of the migration tests with the predictions also mean that for these particular compounds, though the models are good for predictions, there is no advantage of incorporating a functional barrier since it does not help in reducing the migration even at high thicknesses of the polymer film. Using a higher thickness of the polymer film will only lead to the use of more volumes of polymer which is against our aim of reducing plastic waste.

89

### **APPENDIX (1)**

**(A)** 

#### 1. Xylene

#### **1.Gas Chromatograph Conditions**

HP 5890A Gas Chromatograph Column : Supelcowax Carrier Gas : Helium Detector : Flame Ionization Detector Temperature : 280 deg C Injector Temperature : 220 deg C Injection Volume : 1ul

### 2. Temperature cycle

Initial temperature - 45deg C Initial Time - 5 min Final Temperature- 200 deg C Final Time - 5 min Rate- 12 deg C/ min

## **APPENDIX (1)**

# **(B)**

#### 2,4 Dichlorophenol

### **1.Gas Chromatograph Conditions**

HP 5890A Gas Chromatograph Column : SPB-5 Carrier Gas : Helium Detector : Flame Ionization Detector Temperature : 280 deg C Injector Temperature : 220 deg C Injection Volume : 1ul

### 2. Temperature cycle

Initial temperature - 45deg C Initial Time - 5 min Final Temperature- 200 deg C Final Time - 5 min Rate- 12 deg C/ min

## **Appendix 2**

# Fig.(1)

# **Calibration Curve For Xylene**



Conc		Area	Quantity
(ppm)		Response	Injected
		(Au)	(g)
	10	36620	1.674E-08
	20	65671	3.348E-08
	40	123781	6.698E-08
	80	246782	1.339E-07

# **Regression Output:**

Constant		-3.0E-09
Std Err of Y Est		9.4E-10
R Squared		0.999779
No. of Observations		4
Degrees of Freedom		2
X Coefficient(s)	5.6E-13	
Std Err of Coef.	5.9E-15	92

# Appendix 2





Conc.	Area	Quantity
(ppm)	Response	Injected
	(Au)	(g)
200	1160.2	3.8E-10
400	2409	7.6E-10
800	5769	1.5E-09
1600	12256	3.0E-09

# **Regression Output:**

Constant	1.5E-10
Std Err of Y Est	4.5E-11
R Squared	0.998994
No. of Observations	4
Degrees of Freedom	2

X Coefficient(s)	2.3E-13
Std Err of Coef.	5.2E-15
CALIBRATION FAC	TOR = 2.3 E-13 (g/Au)

# Appendix 3

# 2,4 dichlorophenol

# Transmission Profile Curve Obtained From Quasi Isostatic Test Procedure



Regression Output:	
Constant	-9.4E-06
Std Err of Y Est	8.8E-07
R Squared	0.942331
No. of Observations	4
Degrees of Freedom	2
•	

X Coefficient(s)	1.0E-09
Std Err of Coef.	1.8E-10

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