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OXYGEN PERMEATION OF VIRGIN HDPE FILMS VERSUS RECYCLED HDPE FILMS

By

Tareq Al-Ati

A THESIS

Submitted to
Rochester Institute of Technology
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Packaging Science Department

1994

COLLEGE OF APPLIED SCIENCE AND TECHNOLOGY
ROCHESTER INSTITUTE OF TECHNOLOGY
ROCHESTER, NEW YORK

CERTIFICATE OF APPROVAL

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MASTER OF SCIENCE DEGREE

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11/8/94

Date

ABSTRACT

Oxygen Permeability of Virgin HDPE Films versus Recycled HDPE Films

By

Tareq Al-Ati

In an attempt to confront consequences of the growing municipal solid waste stream, recycling has become one of the logical, successful, and practical solutions. With the expanding food and plastics industries, the proposition of using post-consumer materials in food-contact applications may be justifiable. However, for the recycling "cause" to succeed, its technologies and products have to fulfill the standards and requirements set forth by the parties involved: food and plastics industries, recyclers, FDA, to name few. In this study, 100% post-consumer HDPE films are found to have the same oxygen permeability as virgin HDPE films. Gas chromatography has been used in monitoring the permeability of oxygen of both materials. The finding of equal oxygen permeation rates for both recycled and virgin HDPE films may indicate that the recycling process in itself does not effect the oxygen permeation of the HDPE resins. The recommendation of this project is that recycled polymers should undergo further analysis to examine their safety before they are proposed for food-contact applications.

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ACKNOWLEDGMENTS

I am grateful to my thesis advisor, Professor Fritz Yambrach, for advising and reviewing this work. I wish to thank Dr. Dan Goodwin and Dr. Carol Whitlock for their assistance with this endeavor. Also, I extend my gratitude to Kuwait Institute for Scientific Research for sponsoring my scholarship. I am thankful to my superiors and colleagues in the Food Technology Group for their support and attention when I needed them. To the faculty and staff of the packaging science department, Ms. Beverly Clark, and friends, thank you for easing my assimilation into the RIT community.

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CHAPTER ONE

PLASTICS FOR FOOD PACKAGING

INTRODUCTION

In order to establish a successful approach towards food preservation technologies, clear understanding of the requirements needed to maintain, and to aid in maintaining, nutritive components and organoleptic properties of food products has deemed essential. The complexity and advances in the food industry have created sophisticated technologies aimed at producing wholesome foods. These sophisticated technologies require the food industry to have many essential and peripheral relations and involvements with various industries. Packaging industries are considered a complementing party to the food's, because of the interactive functions that packaging materials are able to convey to the food products.

There have been many recent advances in the plastics industries. As a result, plastic products can be manufactured with properties superior to the conventional packaging materials of glass and metal. In addition, these materials are capable of meeting functional standards required by packaging materials and are favorable for the economics of the packaging industry. The increased dependence on plastics is evidenced by the considerable demand from the food industry, among many others. However, when used as food packaging materials, the chemical and physical properties of plastics and the nature of their morphologies must be suitable and compatible with properties and characteristics of the food they contain. One of the key properties of plastics in this respect, and one that directly effects food products and their shelf-life, is their permeability profiles to oxygen, moisture, and organic vapors. Hence, the permeability characteristics of plastics may be one of the important determinants of food products' shelf life, especially when the degradative reactions are oxygen or moisture dependent.

FACTORS OF FOOD SPOILAGE

Factors that result in limiting food's shelf life must be taken into account when designing a plastics package. Deterioration of foods results from direct and indirect causes. Direct causes are a leading factor in food spoilage. They result in off-taste or color, which usually terminates the product's shelf-life. Some examples of this are the physical, biochemical, and microbiological changes that always make food products unsaleable. Indirect causes, on the other hand, are those which do not affect foods' shelf life from the microbial or organoleptic aspects, but would result in such changes as softening or cracking of the products. Examples of indirect causes include light, pressure, gasses, moisture, and temperature. In order for a package to protect and maintain the quality of the food contained inside, it has to minimize the effect of the outside environmental hazards and to successfully act as a barrier between the micro-environment inside the package and the exterior environment. (Ashley, 1986, p. 270). Therefore, these causes must be considered when selecting a packaging material for a particular food product. For more on food packaging, refer to Palling (1980), Kadoya (1990), and Henyon (1990).

SHELF LIFE OF FOOD

The United Nations International Trade Center recently conducted a survey showing that losses amounting to 30% of export revenues in developed countries may be attributable to inadequate packaging. The food losses in less developed countries can reach 50%, and is also a result of inadequate packaging. (Nagel, 1991. p. 98). However, because the shelf life of foods is the ultimate concern of parties participating in all phases of the food industry (food engineering, production, processing, and logistical operations as transportation and storage, etc.), permeability characteristics of the packaging material has become one of the key considerations in this regard.

As a major parameter of shelf life, food quality depends on many factors, including moisture content, degree of oxidation, concentration of the active flavors, aromas, and others. In order to keep these factors under control at optimal levels, the logistical conditions (including complete cycles food products undergo: transportation, distribution, and storage), and the permeability of the packaging materials must be appropriately maintained and designed. Foods inside packages constitute dynamic systems. A container of a food product, while affected by the external environment, exposes the packaged food to the components of the headspace. This results in making the stability of the internal environment dependent upon the initial processing and packaging conditions, external environmental hazards (mechanical, temperature and humidity abuses, etc.), seal quality, and permeation rate of the packaging materials. However, an optimum packaging system must also fall in the parameters of economic considerations. (Ashley, 1986, pp. 300-302).

Nonetheless, beside permeation effects, there are other interactions occurring to the food-polymer pair that can limit the shelf life. Examples of these interactions may include chemical and physical interactions between foods and polymers, polymers scalping of foods' key flavors onto their surfaces, and the migration of polymer components and/or additives into the food products. There are also essential components to the quality of food products whose maintenance at appropriate levels is among the primary functions of the packaging materials. They include, for instance, the loss of carbon dioxide (in carbonated beverages), moisture loss (water based foods and beverages), moisture gain (dry foods and oil based foods), ethanol loss (alcoholic beverages), oil migration (oil-based products), and flavor loss (or losses of other volatile organic vapors). (Salame, 1974, pp. 276-279). The literature is rich on the subject of shelf life. Recent works on shelf life and on testing methods can be found in Mathlouthi (1986), Speigel (1992, chapter 9), and Robertson (1993, chapter 12).

Finally, packaging materials are expected to maintain the nutritive value of food products. The oxygen permeability of packaging materials can play an important role in limiting vitamin C loss, for example, in fruit juices and in other food products which are kept under controlled conditions. The degradation of vitamin C in fruits can be reduced when fruits are stored under low temperatures and kept away from air and light, given the utilization of an appropriate packaging system, (Paine and Paine, 1983, p. 250).

PACKAGING FUNCTIONS NEEDED FOR FOOD PRODUCTS

In the US, about half of all packaged products are foodstuffs (Osborn and Jenkins, 1992, p. 185). Probably this has contributed to the fact that food spoilage in the US is less than 3% for processed food and 10-15% for fresh foods (Nagle, 1991, p. 97). The protection needed for food products imposes several properties and functions on the packaging materials.

The primary function of a package is to keep, present, and dispense the product inside it. But for food products, the package is designed also to provide protection against physical and chemical changes that may occur during transportation, storage, and other logistic steps. Physical changes include mechanical damages (caused by abusive shocks and vibrations of the logistic equipments and vehicles), loss of crispness or consistency, loss of appearance, and others which make the product unsaleable. Chemical changes are related to the organoleptic degradation which results from losses of taste, color, and/or odor. (Ashley, 1986, p. 270). For a more in-depth discussion of the use of plastic packaging for food products, refer to Jenkins & Harrington (1991) and Finch (1992).

EFFECTS OF OXYGEN PERMEABILITY ON FOOD PRODUCTS

The organoleptic degradation of food products is dependent on, among other factors, the oxygen barrier properties of the packaging materials. The degree to which oxidative reactions occur is directly related to the limited amount of oxygen trapped inside the package once it is sealed and to the amount of oxygen permeating through the packaging materials. Glass and metal packages limit such reaction on foodstuffs, but, due to increasing costs of transportation and manufacturing of metal and glass packaging materials, the food industry has started to look at an alternative material, plastics.

During the 1950s and 1960s, plastic materials were used to package microbiologically stable foods, dry foods, and those which utilized preservatives, to name a few. Oxygen has very limited negative effects on these products. But to package oxygen-sensitive foods, each of the following sources of oxygen must be considered: air entrapped during blending operations, air in the head space at the time of sealing, and oxygen in air that can permeate through packaging materials during products' shelf life. (Bourque, 1989, pp. 33-40).

In addition, oxygen tolerance differs from one type of food to another. For example, salad dressing, peanut butter, most soft drinks, and high alcohol drinks are very sensitive to oxygen, and therefore are expected to have a very low oxygen tolerance. However their oxygen tolerance is higher than such foods as beer, low acid foods, wine, coffee, and food baby, etc. (Salame, 1989, p. 124). Refer to Appendix A for examples of foods and their corresponding oxygen tolerance.

FLEXIBLE-PACKAGING INDUSTRY

There are five industries involved in flexible packaging: plastic resin and film producers, flexible packaging converters, packaging machinery manufacturers, product manufacturers, and contract packagers. In addition, there are industries which are peripheral, but important, to flexible packaging, such as manufacturers of cellophane, paper products, adhesives, aluminum foil, and printing inks. (Osborn and Jenkins, 1992, p. 229).

Food and non-food flexible and rigid packagings have a market of about 40 billion pounds, worth 24 billion US dollars, 78% of which is dedicated to food and beverage packaging markets. But close examination of the worldwide production of food packaging materials reveals the following trend: 51% for liquid foods, 19% for snack food packaging, 7% for meet and cheese packaging, and 1% for convenience (e.g., microwaveable) foods. (Rice, 1991, p. 50). The food packaging industry consumes about 90% of such films as OPP, PP, PVC, nylon, and PS, and about 15% of the HDPE film, 25% of the LDPE (including LLDPE) and EVA (Osborn and Jenkins, 1992, p. 185). For more on the use of plastics in the food industry, Layman (1991) gives a practical overview on this subject.

However, because this work pertains to oxygen permeability studies of a plastic packaging material (HDPE), it is important to introduce some basic definitions, processes, properties and other related subjects to plastics.

PLASTICS

The word plastic is derived from PLASTIKOS, a Greek word meaning formable or deformable (Robertson, 1993, p. 10). Plastics can be shaped and manipulated to satisfy specific applications. They can be molded, extruded, fabricated, etc., in order to meet particular requirements of an end product. It was not until the 1920's that the various industries used the word plastics. (Dubois, 1974, p. 1). However, the invention of plastics started in the 1860s with the synthesis of cellulose nitrate. The second synthesized plastic was phenol-formaldehyde (Bakelite) around 1905 (Patton,1976, p. 6) and (Dubois, 1974, p. 28). Since then, the development of plastics has been increasing until they become strong packaging competitors with the traditional glass and metal materials.

As hydrocarbons, plastics are obtained from natural resources of oil, natural gas, and coal. In lay use the word "resin" generally stands for a naturally occurring substance used in coatings. But according to the plastics industry, the term "resins" technically stands for a disorganized or amorphous liquid or solid with high viscosity and high molecular weight. (Patton. 1976, p. 51). The plastic resins are by-products of refining gasoline, a process which utilizes coal, air, petroleum, natural gases, limestone, salt, and sulfur as its raw materials. From these materials other substances called "intermediates" produce the plastics resins. (Dubois, 1974, p. 11). However, olefins are one of the principle raw materials for the plastics industry, from which a wide range of plastic resins are manufactured. Olefins, (C_nH_{2n-2}), are chemically reactive substances because they are unsaturated chemicals. Although olefins are normally not found in crude oil, they are formed during the oil refinery processes (Patton, 1976, p. 47), when the large molecules are "cracked" into smaller units.

Generally, plastics are divided into two different categories, thermoplastics and thermosets. Thermoplastics are distinctive in that they can be repeatedly softened (at high temperatures) and hardened (at low temperatures). But thermosets, once they are hardened, cannot be resoftened. The former is made by the process of additional polymerization, whereby the monomers, plastics' building blocks, are added to a growing chain. The later, however, is produced by condensation polymerization, in which an active chemical reacts to release (condense) another small molecule (i.e., water). An example of thermoplastics is asphalt, a natural substance that can be softened by heat. Naturally occurring thermosets includes wood, cotton, wool, hair, feathers, etc. (Patton, 1976, p. 51). One of the attractive features of thermosets is their stability under high pressure and high temperature, which is not true in the case of thermoplastics (Dubois, 1974, p. 27). Hence, a majority of the plastics used in food packaging are thermoplastics.

Plastics are composed of long compounds called polymers which are synthesized by polymerization. The word polymer is derived from the Greek POLY meaning many, and MEROS meaning parts (Robertson, 1993, p. 11). In the process of polymerization, the structural units of polymers, namely monomers, are joined together to make a chain whose length depends on the desired functions of a specific plastic product. Thus, the chain length is considered to be the most important factor determining the characteristics of any particular polymer. (Osborn and Jenkins 1992, p. 1). In general, most monomers exist in the gaseous form, and liquid polymers would be in a short chain with low molecular weight. But the polymer has to be of a large enough molecular weight in order to be solid. Most synthetic thermoplastics have chains of 500 or more carbon atoms, with a distance of about 1.5×10^{-8} cm between any two carbon atoms. (Patton, 1976, pp. 53-54). The length of a PE chain, for example, is in the range of 1000 to 2000 monomers units (Osborn and Jenkins 1992, p. 1), and the commercial grades of PE have a molecular weight in the range of 50,000-300,000 (Brydson, 1982, p. 217). Wendroff (1985) has investigated this subject.

Polyethylene (PE)

Ethylene is a gas, but a polymer of 16 ethylene monomers is a liquid. A polymer of 35 monomers makes grease, 140 is wax, and 500 is the commonly used plastic (Patton, 1976, pp. 55-61). The early polymerizations of PE were under high temperatures and very high pressures. But during the 1950s, the German Professor Ziegler developed catalysts that can polymerize the PE at near atmospheric pressure and at 50-70°C. (Briston, 1980, p. 42).

However, when PE is produced with high molecular weight, the mechanical properties of PE increase, although polymers with a very large molecular weight are very difficult to make. Generally, PE polymers are produced in three different grades: low density, intermediate density, and high density. The difference between any two can be shown with the measure of the specific gravity, which is the ratio of the polymer weight to the same volume of water. The specific gravity of the three grades is:

LDPE	0.912-0.925
Intermediate	0.925-0.940
HDPE	0.940-0.965

The specific gravity is strongly related to crystallinity. Low density polymers have more branched molecules and lower crystallinity. High density polymers are less branched and thus are more crystalline than the low density ones. (Patton, 1976, pp. 55-61).

The molecular weight (M.W.) of one PE monomer (CH2-Ch2) is 28. Because the PE is usually produced to contain 5,000 monomers, typical PE has a M.W. of 140,000. However, the effect of making long chains is to increase the number and degree of entanglements and the intermolecular attraction within the polymer network. As PE's M.W. increases, the following properties are also found to increase: melt viscosity, tensile strength, impact strength, abrasion resistance, and shrinkage at elevated temperatures. Very high M.W. polymers are costly to produce and more difficult to convert into films. Most of the commercial polymers used in packaging are of the intermediate grades. (Osborn and Jenkins, 1992, pp. 3-7).

Polymerization

As mentioned earlier, plastics are manufactured in the process of polymerization. In this process, a PE molecule (obtained from the ethylene gas), for example, is attacked by a free radical which makes the molecule acquire the free radical and so becomes reactive at one site. Then another PE molecule joins the first molecule at the reactive site, resulting in two molecules with one reactive site at which a third molecule will be added. The process continues with free radical site propagating to each newly added molecule of PE, until two ends of the PE chain meet to cancel each other's free radical effect. At this point, the PE chains cease to grow and, therefore, the polymerization process terminates. (Osborn and Jenkins, 1992, p. 1).

Crystalline and Amorphous Regions

Polymers behave the way they do, because of the specific composition of their crystalline and amorphous regions. It is important to understand what they are. When polymer melt is slowly cooled, its molecules are aligned in parallel arrangement that enhance intermolecular forces and create symmetry. As the polymer melt approaches solidification, crystallites form. However, either because there are some molecules that are very entangled with each other, or due to the presence of branches, the symmetry formation ceases and less organized (amorphous) areas occur between the crystalline ones. For this reason, polymers, especially those with high molecular weight, are never completely crystalline; they are in the range of 20-90% crystallinity. (Osborn and Jenkins, 1992, p. 13).

Plastics can be visualized as a network containing crystalline region, in which long parallel polymer chains entangled closely in an organized fashion, surrounded by loosely organized amorphous regions (Robertson, 1993, p. 21). It has been found that it is only through these amorphous regions that permeation takes place, since crystalline regions are very tightly arranged and impermeable (Ashley, 1986, p. 281). Crystallinity, and other factors that have a direct effect on permeation, will be discussed later.

Curing Agents and Additives

Plastics are manufactured with the aid of many different agents whose function is important not only to start the process of polymerization, but also to make plastics gain some of the desired properties. These agents are normally non-volatile organic compounds, and are commonly called curing agents or additives. For the polymerization to begin, specific agents must be used to provide the process with the required free radicals. These agents are called initiators. The most commonly used additives for initiating the process of polymerization are peroxides. This class of additives includes such compounds as BPO, methyl ethyl keton peroxide (MEKP), peresters, dialkyl peroxide, and AIBN. In addition, activators or promoters, and those which resist ultraviolet radiation, can be used to cure polyester, for instance, during polymerization. (Seymour, 1991, p.21).

Plasticizers, another important group of additives, are used during the process of thermoplastics' manufacturing. Plasticizers are utilized in order to facilitate the processibility and flexibility of the end product. Beside coloring, flame-retardant and antistatic agents, additives also have the effect of preventing plastics' deterioration caused generally by heat, light, and oxidation. Because plastics can be used in food-contact applications, however, the selection of plasticizers or any additives is very important. Because of their potential migration into foods, some health hazard issues arise. (Dubois, 1974, p. 55). More information on plastics' characteristics can be found in the work of Lox (1986, b).

MASS TRANSPORT

Before examining the main phenomenon under examination, i.e. permeation, it should be realized that it belongs to yet another more general phenomenon called mass transport. In general, mass transport refers to either permeability, sorption, or migration, although in the literature one may easily notice that these terms are often used interchangeably. To better serve the purpose of this research paper, it is important to clearly define each process of mass transport. Permeability stands for the transfer of components from the internal environment of the packaged product to the atmosphere via the packaging material(s), or vise versa. Sorption refers to the process by which the packaging material takes up molecules of the packaged product, without escaping into the atmosphere. Finally migration occurs when the package allows some of its own components to pass into the packaged product. It is, thus, obvious to realize how crucial are the effects of mass transport phenomena on food products. (Gavare, Hernandez, and Giacin, 1993, p. 846). For more information on mass transport and migration processes and the interaction between packaging materials and foods, refer to the following: Bruck, Bieber, & Figge (1986), Gray, Harte & Miltz (1987), Hotchkiss (1988), and Risch & Hotchkiss (1991).

Moreover, the disadvantages of the transport mechanisms could be added to such shortcomings of some plastics as: high gas and water permeability, absorption of food/beverage flavor, low heat resistance (many foods require retort or pasteurization), brittle, poor appearance, high cost (especially in small packages), and migration of monomers which concerns FDA, (Salame, 1989, p. 132). For more on this subject, see Lox (1992). Nevertheless, it is this transport phenomenon which can certainly reduce the package integrity, reduce the product's shelf life, and raise quality and health hazards issues.

PERMEABILITY

Plastics are used as food packaging materials due to several attractive properties found in them. For many applications, plastics are more successful than either metal or glass for food packaging for several reasons. Plastics resist breaking; they do not change the taste of the food with which they come in contact; they require less energy for fabrication and transportation, and therefore are better for the environment; they are light weight, flexible, transparent, and they cost less to produce, (Salame, 1989, p. 132).

However, probably one of the important properties that is increasingly attracting considerable scientific and industrial attention, at least in the area of the food industry, is the range of permeabilities in plastic packaging materials. A thorough understanding of the polymers' microstructure and the effect of thermal, mechanical, and solvent treatment on them can help in developing permeation properties that are suitable for a specific application. At this step it is important to introduce the permeation process, its nature, and its components.

PERMEATION

The word permeation has the connotation of the movement of a molecule across a membrane, due to a difference in permeant concentration. Gases, vapors, and liquids are transported differently depending on the membrane structure they are crossing. (Vieth, 1991, p. 73). When a gas or an organic vapor is in contact with a polymer surface, the permeation process is likely to occur. Under this condition, the flow of the penetrant (gas or vapor) takes place from the site with a high concentration of the permeant to another with a lower one, via the polymer. (Murray, 1989, p. 22). Here the movement of the penetrant can be visualized as a sequence of steps or jumps to cross the polymer barrier and reach the site with the lower concentration level. (Rogers, 1986, p. 19) and (Robertson, 1993, p. 74).

When a molecule permeates through a polymeric film, it has to go through the following steps. First, the surface of the film absorbs the permeating molecule. Second, solution (condensation and mixing) of the molecule occurs into the film matrix. Third, under the influence of the concentration gradient, the molecule diffuses through the film. Fourth and finally, the molecule is desorped (evaporates) from the film matrix to the external environment. (Ashely, 1986, p. 281), (Bonis, 1989, p. 86) and (Rogers, 1986, p. 19). Because the molecule has to go through these stages, the permeation involves both processes of solution and diffusion in such a way that satisfies the equation: $P=S \times D$; where P is the permeability coefficient, S is the solubility coefficient, and D is the diffusion coefficient, (Ashley, 1989, p. 281). Vieth (1991, chapter 2 & 4), Robertson (1993, chapter 4) and Finch (1992, chapter 8) provide elaborate work on the calculations of permeability.

Solubility

The amount of penetrants that is actually dissolved by the packaging materials depends on the solubility coefficient. The solubility coefficient is a thermodynamic parameter. It is a measure of the concentration of penetrant molecules that will be in position to migrate through the polymer. The solubility coefficient is dependent on many variables. Of primary importance is the condensability (i.e., concentration) of the penetrant with the polymer. (Strandburg, Delassus, & Howell, 1991, p. 134). The magnitude of the solubility coefficient is determined by the chemical nature and the morphology of the packaging material and the permeating substance itself. Units commonly used to express the solubility coefficients are:

mass or volume of solute per unit mass;
volume of solvent.pressure;
$g.g^{-1}.atm^{-1}$;
$g.cm^{-3}.Pa^{-1}$; or
$Kg.cm^{-3}.atm^{-1}$. (Finch, 1992, p. 297).

However, the solubility parameter has been found to be strongly dependent on crystallinity. This finding is based on the fact that solubility is confined almost exclusively to the amorphous regions. Also, because plasticization, an interaction between penetrant and the polymer (to be discussed later), results in loss of crystallinity, it is therefore closely related to solubility. Moreover, because polar groups tend to develop strong bonding, increasing polymer polarity will reduce solubility. In turn this will decrease permeability mainly due to the high activation energy that result from polar polymer. (Billmeyer, 1984, p. 334).

Diffusion

The diffusion of gases through amorphous polymers has initiated the first theories attempting to explain the diffusion phenomenon. The activated zone theory, for instance, considers the following relationship: the diffusion coefficient is a function of the squared diameter of the diffusing molecule. Another early theory, proposed by Pace and Datyner, is the diffusion through semicrystalline polymers which states that the diffusing molecules are influenced by the macromolecular chains which are scattered throughout the polymer matrix in a parallel fashion. (Moisan, 1986, p. 150).

Hole Theory

One of the earliest efforts to describe the diffusion process was the theory of Barrer (1951), and it is called the hole theory. In the hole theory, the polymer matrix, full of both amorphous and crystalline regions, encompasses cavities or holes that can be either fixed or mobile. The Brownian movement of the molecular segments of the polymer chains was found to be the reason behind the formation of holes throughout the matrix. A molecule can only permeate when there is enough space for its passage, i.e., a hole. (Vieth, 1991, p. 25) and (Murray, 1989, p. 22). Therefore, diffusive motion depends on segmental chain motion and the nature of penetrating molecules (Rogers, 1986, p. 19).

For the formation of a hole, certain van der Walls, and probably other bonds holding the molecular structure and chain segments, must be broken. However, in reality, there is no need for actual holes to be physically formed. What actually happens is that before and after any two points the permeating molecule moves (jumps), the penetrating molecules share a volume with its surrounding chain segments of the host polymer matrix. The energy needed for this rearrangement increases, apparently as the size of the penetrant increases. It is very likely that several jumps are needed before a molecule moves a distance equal to its size within the polymer matrix. (Rogers, 1986, p. 19).

Free Volume

Holes of polymers' matrices are also commonly referred to as free volume, which is considered to be voids entrapped in the matrix whereby penetrants find an easy path. The voids are the result of the segmental motion of the polymer chain. (Murray, 1989, p. 22). Free volume is found to increase as bulky side chains increase in number and size, or when a polymer is made with a poor symmetry, which has an effect of increasing the permeability, as illustrated in Appendix B.

Polymers become brittle and glassy at a cool enough temperature called the glassy transition temperature Tg (to be discussed later). At the glassy state, polymers contain a distribution of microvoids frozen in the polymer structure. Also, in this state free segmental rotations are restricted, leading to the formation of fixed microvoids "holes" throughout the polymer. These microvoids act to immobilize the penetrant molecules by entrapping them. (Vieth, 1991, p. 29).

However, there are some important factors that relate to penetrant characteristics and which can influence their permeability through polymer. These factors include, among others, volatility, size, and shape of the penetrant. The volatility of a penetrant controls the maximum concentration, whereas size and shape strongly effect the molecule's movement through the holes. For example, linear molecules permeate more rapidly than cyclic ones. (Murray, 1989, p. 22).

Activated and Non-Activated Diffusion

When a defected polymer film (with pores) is in contact with a gas, for instance, then diffusion may take place either by the pressure difference across the pores (viscous diffusion), or by concentration difference across the pores (ordinary or Fickian diffusion). But, when the pore's diameter is smaller than the gas molecules', then Knudsen diffusion occurs, whereby surface-diffusion and ordinary diffusion, or others combined, dominate the diffusion process. This is called activated diffusion. However, when the size of pores is similar to the penetrating molecule's, and when there is no reaction between the gas molecules and the polymer, then non-activated diffusion is more likely to occur. (Vieth, 1991, p. 73).

PLASTICIZATION OF POLYMERS

One of the major considerations and effects that mass transport has on polymer barriers is the interaction between the penetrant molecules and the polymer. In this case, the penetrant is expected to create more segmental motion and larger voids, a process referred to as plasticization or swelling of polymers. (Murray, 1989, p. 22).

Polymers with hydroxyl groups (--OH) or amide groups (CN=OH), for example, are held with H-bond which makes them very sensitive to water. When water is in contact with a polymer, it enters and interrupts the H-bond, weakening the forces holding polymer chains together. The polymer thus becomes plasticized, leading to a greater segmental mobility. This facilitates gas diffusion, and the end result is a higher gas permeability (refer to Appendix C). Hydrophobic polymers (hydrocarbons, olefins, etc.), polymers with low polarity (esters and halogens), and polymers with dipole interacting groups are not strongly affected by water. Nonetheless, polymers with less free volume void are inaccessible to the diffusing gas, and water plasticizes them only slightly. (Salame, 1989, P. 137).

Plasticization has also a physical effect on polymers. Sorption of the ambient vapors and liquids may plasticize the polymers involved, resulting in weakening a variety of mechanical properties (Rogers, 1986, p. 12). In addition, swelling of polymers may double the original volume, and the once hard or glassy polymers become rubbers or gels (Windle, 1986, p. 75). Refer to Vieth (1991) and Finch (1992) for more details on plasticization and the overall phenomenon of permeability.

FACTORS AFFECTING PERMEABILITY

Polarity and Cohesive Energy Density

Some factors that are crucial to permeability rates are the composition and molecular structure of the polymer. However, because permeation involves the movement of a permeating molecule, its molecular structure is also an important factor. Therefore, the solubility of penetrants is affected by the similarity between the penetrant and the polymer. But, in general, non-polar molecules diffuse more readily than polar ones, and the effect is more profound in polar polymers. (Ashley, 1986, p. 289).

Polymer polarity can be measured by the cohesive energy density (e_{coh}), which is the amount of energy holding the polymer chains together. Because a permeating molecule needs the chains to open up in order to enable its passage, it follows that the higher the e_{coh} is, the lower the permeability of the polymer. (Salame, 1989, p. 136). This relationship is depicted in Appendix D.

There are cases where a polymer with excellent gas barrier is a poor moisture barrier, and this has been attributed to the polarity factor. For instance, those polymers containing hydroxyl groups, which are very polar, have a very low gas permeability but high moisture permeability, as demonstrated in Appendix E. When plasticized, their permeability against gas is highly increased and thus they become a weak gas barrier. Non-polar hydrocarbons, such as PE and PP, make excellent moisture but poor gas barriers. (Robertson, 1993, p. 90) and (Ashley, 1986, p. 284). This phenomenon can be explained by the fact that gas permeation is mainly controlled by the diffusion parameter, whereas moisture permeation is controlled by the interaction between water and the polymer. (Salame, 1989, p. 141).

Chain Packing

The polymer's ability to have a close chain-to-chain packing is a direct result of increasing molecular symmetry, and can be achieved by the orientation process or by a polymer having higher crystallinity. Due to their simple molecular structure, linear polymers are more likely to have a good packing property. They would have lower permeabilities than polymers with bulky side groups. Bulky groups result in a poor chain packing, thus increasing polymers' permeabilities (see Appendix F). Orientation is found to reduce the permeability of amorphous polymers by 10-15% and to reduce the permeability of crystalline ones by 50%. (Robertson, 1993, p. 91). However, orientation is effective only when the polymer has some crystallinity, so that the crystallites can be lined up and cause the penetrating molecule to undergo a more tortuous path. (Salame, 1989, p. 134). Information on orientation effects on the chain packing can be found on the paper written by Jasse (1986).

Crystallinity

The crystalline region of a polymer is where there is almost no permeation, not even by the smallest gas molecule. Although non-existent, 100% crystalline polymers would have a permeability approaching zero, (Salame, 1989, P. 134), and (Ashley, 1986, P. 286). Because crystallinity causes closer packing of molecules in the crystalline regions, higher crystallinity results in increasing the density of the polymer; the end result is thus lower permeability. (Patton, 1976, P. 56). See Appendix G.

At temperatures well below the melting point, crystalline regions would be inaccessible to most penetrants; therefore they act as excluded areas for sorption process and as impermeable domains for the diffusion process, (Rogers, 1986, p. 65). In addition to this, crystallinity has direct effects on other physical properties of polymers. Because the crystallite decreases the mobility in a polymer's network, it makes it more resistant to an applied force. It follows that increasing crystallinity increases stiffness and tensile strength. (Osborn and Jenkines, 1992, 16). Stien has presented some of the crystallization characteristics of some recycled polymers in his publication (1992).

Bonding Between Chains

Chain bonding can be achieved by several processes. The process of cross linking, for example, can be used to initiate chain bonding. Cross linking chemically bonds chains together and reduces the chain mobility. This results in decreasing the permeability mainly due to decreasing the diffusion coefficient. (Robertson, 1993, p. 91).

Glass Transition Temperature (Tg)

The concept and effects of the Tg are very important to the permeability performances of polymers because it is a very accurate measure of the molecular motion, the lack of which prevents the formation of holes and voids. An understanding of this property is a good tool in manipulating polymers' properties to meet some desired functions. To appreciate the effects of the Tg, a further discussion of it follows.

Changes of states in polymers are loosely defined. At high enough temperatures, a semicrystalline or a amorphous polymer exhibits a liquid state, with wriggled molecular chains occupying amorphous regions. As the polymer is cooled, it starts to crystallize at a temperature termed the crystalline melting point, relevant to the freezing point. At this temperature molecules become aligned and packed in organized crystalline regions. But due to the entangled molecules, crystallization is not complete at this point. If cooling is continued, the polymer becomes supercooled, yet still remains liquid. At a low enough temperature, the supercooled polymer start to vitrify. This temperature is called the glassy transition temperature, Tg. At this temperature the polymer becomes brittle, glassy, and has the physical properties of crystalline solids, but its molecules are still disorganized as in the liquid state. (Robertson, 1993, p. 23). In other words, Tg stands for the transition from a glassy to a rubbery state (Boyer, 1985, p. 136). In the case of highly crystalline polymers, the Tg is difficult to determine because the properties below and above Tg are very similar. (Patton, 1976, p. 37) and (Robertson, 1993, p. 24). For further information on the transition phase of polymer melts, the paper of Kruger and Pietralla (1985) is a good reference.

It is known that the greater the chain segments' motion, the easier the gas can permeate the film. At temperatures below Tg, the crystalline regions and regions of order in the amorphous regions decrease the freedom of the segmental motion (Culter, 1989, p. 52). The decreased segmental motion leads to fewer voids and less free volume, and tortuous paths are also created along the matrix. Hence, permeability is reduced because it would be more difficult for a molecule to permeate through or within the polymer. (Robertson, 1993, p. 91). Appendix H shows different oxygen permeabilities of different polymers as an effect of the Tg.

As gas permeation can be lowered by reducing Tg, water permeability is dependent on the polarity factor. But researchers have found that for any two polymers of the same degree of polarity, higher Tg will lower both water and gas permeability. (Salame, 1989, p. 135). In addition, it was found that fast cooling results in polymers with less density and in polymers with more amounts of free volume than slower cooling, (Windle, 1992, p. 111). For more details about the Tg and the changes it creates, refer to Maxwell (1985).

Temperature and Pressure

The permeation rate of a gas through a polymer is a function of the partial pressure differential of this particular gas, and not of the total pressure difference between the two sides of the polymer (Robertson, 1993, p. 102). The permeability of penetrating molecules that exhibit no interaction with the polymer is dependent on the partial pressure of the molecule. When a strong interaction occurs between the two, the permeability also occurs in a direct relationship with the pressure. This can be explained by the fact that the diffusion constant (D) increases due to the plasticization of the sorbed molecule, which also increases the solubility coefficient (S) as well. (Ashley, 1986, p. 286).

It is found that the diffusion constant always increases as temperature increases, thus causing the permeability to increase as well (Ashely, 1986, p. 290), as depicted in Appendix I. The increase of permeability is a direct effect of temperature on the motion of the segmental chains primarily in the amorphous regions. This occurs because movements are restricted in the crystalline regions (Osborn and Jenkins, 1992, P. 14). More about these and other factors that have some effects on the permeability are presented on the paper of Pascat (1986).

MEASUREMENT METHODS OF GAS PERMEABILITY

Robertson (1993) describes some of the common methods of measuring gas permeability, pressure increase method, concentration increase method, volume increase method, and detector film method.

Pressure Increase Method

The pressure increase method is called manometric technique, and is designed according to the ASTM D-1434. In this method, the film, whose permeation is under investigation, is mounted and sealed in an O-ring gas transmission cell. The permeability coefficient can be calculated by maintaining the pressure between the chamber of a very high pressure with the one of a very low pressure.

Concentration Increase Method

Although this method keeps the total pressure between both sides of the film equal (hence the term isostatic is also used), a partial pressure difference across both sides must be created. The partial pressure difference is created by continuously sweeping one side with the test gas, and

maintaining a flow of an inert gas on the other side (where the test gas diffuses). The concentration of the test gas can be measured by the use of gas chromatography, thermal conductivity detectors, or others means (ASTM D 3985).
One major advantage of this method over the former one (applicable to flat films only) is that different forms of packages can be tested (bottles, pouches, containers, etc.).

Volume Increase Method

In this method the change in volume is measured at constant pressure. This method is designed so that the change in volume is caused by permeation of a gas through a film. It is also called volumetric method (ASTM D 1434). It is simpler but less sensitive than the pressure increase method, and therefore, is less frequently used than either pressure or concentration increase methods.

Detector Film Method

This is a relatively recent method to measure permeabilities of films. It utilizes principles of the spectrophotometric technique. A plastic detector film is impregnated with a reagent that is sensitive to a gas whose permeation through the film is expected, and so can be measured. The film has a distinct absorption spectrum that changes as the gas is absorbed. (Robertson, 1993, pp. 101-104). The detector method requires less equipment and is more rapid than the rest. Also, because it can detect less minimum quantities of oxygen than other methods, smaller film samples can used and permeability tests are can be done in shorter time.

CHAPTER TWO

POST-CONSUMER POLYMERS IN FOOD-CONTACT APPLICATIONS

INTRODUCTION

Many studies have focused on the mechanical properties of recycled materials. To name few, Cao, Ramer, & Beatty (1992) and Blatz (1992) have looked at this issue, among many others. However, no papers have been found in the literature that pertain to permeability studies of these materials. It seems that little is known about permeability profiles of post-consumer polymers. Therefore, this research project is dedicated to investigate this subject, more specifically the oxygen permeability of 100% post-consumer HDPE.

Recycling technologies, however, have been developed as a response to the dire need to recycle post-consumer materials. Although hard to prove or disprove, this demand probably has contributed to a glut of available recycled materials. For this reason, finding new applications for the recycled products may aid in allocating these recycled resources to different end use markets.

The food industry is growing and expanding its demands of the packaging industry. Therefore, the food industry may be looked at as promising market for the massive amounts of the post-consumer plastics created by the same industry. Regarding the health related implications raised by using recycled polymers in food-contact and other food packaging materials, it is important to understand the responsibilities and roles of the involved agencies (e.g., EPA and FDA, etc.). These agencies have a mandate to monitor and regulate the use of not only recycled materials, but any materials used to package food products. Their concerns are the adulteration and contamination of recycled materials during the recovery and recycling processes. Once a thorough examination of the interaction between recycled polymers and food systems is achieved, the recycling technologies may be able to respond satisfactorily to the requirements set forth by the food industry and regulating agencies. These requirement are mainly related to such issues as food safety and quality, food-packaging functions, and marketing demands. It is highly recommended that cooperative efforts of the above agencies, food industry, and recyclers be directed at achieving this goal.

WORLD AND U.S. PRODUCTION OF PLASTICS AND HDPE

The world production of plastics in 1940 was about 1 million tons; in 1990 it leaped to be in excess of 100 million tons (Boone, Lox, and Pottie, 1993, p. 277). Currently, the estimated world production of plastics is about 600 million tons (Andrews, and Subramanian, 1992, p. xi).

These numbers represent a massive global growth in the production of plastics, of which the US is a major share holder. In the US alone, the plastics sold in 1989 were about 26 MM t which amounts to about 1/3 of world sales. Out of this huge volume, three types, PE, PP, and PVC, comprise 60%. (Boettcher, 1992, p. 16). In the same year, the US reached a consumption rate of about 8.1 billion pounds/year of PE films (Leaversuch, 1993, p. 64) and over 8 billion pounds of HDPE (Bennett, 1992, p. 33).

The US consumption of plastics resins has increased from 1991 to 1992 by 6.8%. Another indication of the tremendous growth of plastics production is the shipments of injection molding machines which have increased by 36% between 1991 and 1992. (Smok, 1993, p. 7).

Clearly, the world has experienced an unprecedented growth in the plastic's industry during the past half century, and that growth is very likely to continue into the future. This has some inevitable negative effects on the depleted natural resources and the environment, but its harshest impacts are on the municipal solid waste stream. One scheme of waste management, landfills, has not proved to be a successful solution for every post-consumer material.

PLASTICS WASTE IN THE U.S.

During the 1980's, the US produced an average of 180 million tons of municipal solid waste a year. More specifically, in 1988 the amount of plastics entering the waste stream was about 29 billion pounds, representing 56% of what was produced that year. (Pearson, 1992, p. 1). Dominated by packaging materials, currently, out of the 160 million tons of municipal solid waste annually produced in the US, 7% by weight (about 18% by volume) are plastics. This trend is expected to grow in the next 10 years. (Boettcher, 1992, p. 16) and (Osborn and Jenkins, 1992, p. 217). For practical insight into the issue of the solid waste management refer to Guarino (1991), and Rotruck (1991).

Economics and market shares aside, this increasing amount of plastics entering the landfilles has raised the issue of recycling technologies as a sound remedy for the dilemma of this growing component of municipal solid waste stream. The recycling of plastics has become an even more pressing issue due to the many facts surrounding disposal of municipal solid waste, recycling technologies and their products, and components and trends of the solid waste stream. Some states in the US will use up all of their landfills before the year

2000, raising the possibility of shipping their waste to landfills of neighboring states. Also, it is getting extremely difficult and expensive to allocate new sites for building new landfills. In addition, legislators are passing more laws that require the use of recycled contents in packaging materials.

Moreover, It was found that if plastics were only recycled once, the amount of the plastics waste would be reduced by 50% (Boettcher, 1992, p. 16). This is true since plastic beverage containers, according to a paper written in June 1992, constitute about 1/3 of the recyclables' volume (Pearson, 1992, p.1). After compaction in the landfills, rigid plastics containers such as HDPE milk jugs, PET beverage bottles, and EPS fast food take-out-trays, are found to constitute over 80% of the plastics packaging waste by volume, and 60% by weight. (Osborn and Jenkins, 1992, p.217). In addition, transporting products packaged with PET, as apposed to glass, reduces energy in the form of fuel by 50%. Finally, due to their high stability, plastics do not react in the landfills, and therefore have no negative impact on the environment. (Boettcher, 1992, p. 16). The advantages of recycling plastics, when added to the positive characteristics of plastics, are regarded as attractive incentives in promoting the recycling of post-consumer plastics.

PLASTICS AND RECYCLING

Currently, less than 0.5 million tons of plastics are recycled, out of approximately 600 million tons produced worldwide (Andrews and Subramanian, 1992, p. xi). Whereas, Western Europe (12 EC countries plus Austria, Finland, Norway, Sweden and Switzerland) had a plastics production of about 26 million tons in 1980, of which only 7.4% were mechanically recycled. (Leaversuch, 1993, p. 64). The US alone recycled roughly 150,000 tons in 1989 (from the 26 MM t. produced that year), and only 140,000 tons in 1988 (Andrews and Subramanian, 1992, p. xi). In 1991 the US recycled about 600,000 tons of its industrial plastics waste (Boettcher, 1992, p. 18). Last year, about 6.9% of all plastic packaging was recycled, according to the American Plastics Council. (Anonymous, 1994, p. 16). An expert view on the subject of recycling management and programs is available; refer to Teasley (1991).

RECYCLING OF HIGH DENSITY POLYETHYLENE

A national survey, conducted in the US, indicates that potential demand for the recycled resins is much greater than the supply. In 1988 the plastics materials that were recycled were approximately: 190 million pounds of PET, 145 million pounds of HDPE, 20 million pounds of PS, 60 million pounds PP, 5 million pounds of PVC and 30 million pounds of commingled plastics. Currently, PE and PS are the dominant recycled plastics. Such handling of thermoplastics will reduce the cost of raw materials to manufacturers and reduce the burden caused by post-consumer plastics on the solid waste stream. (Bennett, 1992, p. 26).

Out of the 1989' sales of virgin HDPE (8.1 billion pounds), only 145 million pounds were recycled. This is a 25% increase compared to the year 1988, when only 93 million pounds of HDPE were recycled. While the potential capacity of the HDPE market is about 442 million pounds, only less than a third of the market's need for the recycled HDPE is met by recycling 145 million pounds. (Bennett, 1992, p. 26). Now, the market is experiencing an unprecedented demand for the recycled HDPE. The surge in demand is attributed to the enactment of the "rates and dates" laws in California and Oregon which take effect in the year of 1995. These laws requires manufacturers to include about 25% of reused material in packaging materials in order to do business locally. This results in increasing the price of the recycled HDPE to be 34 cents/pound, from the 28 cents/pound at the end of 1993, while the virgin is only 37 cents/pound compared to the 30 cents of last year. (Anonymous, 1994, p. 16). The recycled HDPE is marketed for the following applications: soft drink base cup, plastic pipes, plastic lumber, household chemical containers, etc. (Bennett, 1992, p. 26).

As illustrated in Table 1, the waste management practice of HDPE is directed more towards recycling than either landfills or incineration. Therefore, studying the permeation characteristics of recycled HDPE would probably help in not only identifying the proper food applications and exploring new markets for the recycled HDPE, but also help in alleviate the impacts the problem of municipal solid waste.

Table 1. Disposal Goals for HDPE

Method	Currently	1992 Goal
Landfill	80%	55%
Incinerate	9%	20%
Recycling	11%	25%

(Bennett, 1992, p. 27).

Before introducing the role of FDA and other agencies in the area of regulating and controlling the use of recycled polymers for food-contact application purposes, it would be appropriate to examine the different recycling technologies that are currently used. The following description of the recycling technologies will include a brief discussion of the effects and possibilities of using the products of these technologies in food-contact applications.

RECYCLING TECHNOLOGIES OF PLASTICS

Plastics can be recycled by several different processes. The Environmental Protection Agency named these processes Primary, Secondary, and Tertiary recycling. Primary recycling (also referred to as 1°) is the recycling of in-house scrap and trim that are produced at the production line in plastics plants. Secondary recycling (2°) is the process by which the plastics are physically reprocessed first by grinding, washing, peelerizing, flaking, and then by remelting the newly formed resins to finally make new polymeric materials. Finally, Tertiary recycling (3°) is the chemical process that breaks down the plastics into their corresponding structural units, monomers or oligomers, which are then cleaned and used to design new plastics. (Thorsheim and Armstrong, 1993, p. 55).

Primary Recycling (Scrap Reprocessing)

Primary recycling is the use of uncontaminated manufacturing scrap polymers for instant regrinding (Oblah, 1993, p. 543). For food-contact applications, post-consumer polymers made by the primary recycling do not raise any health hazard concerns. The EPA has stated, in article 56 FR 49992, that this process is acceptable in the production of polymers used in contact with foods, if appropriate Good Manufacturing Practice (GMP) guidelines are followed. (FDA, 1992, p. 2).

Because industrial plastic waste has a high likelihood of containing single polymer type, it is therefore considered a relatively contaminants-free waste. Also, because of their high stability, the quality of industrial polymer waste is not usually impacted during recycling. Regrinding is often the only operation needed to melt-make the new product. In addition, recycled polymers are often melt-blended with virgin polymers without negatively changing their properties. (Boettcher, 1992, p. 28). However, if the scrap is collected from different manufacturers, then there is a concern about the ability of different adjuvants with different concentration levels to meet the existing regulations. (FDA, 1992, p. 2).

Secondary Recycling (Physical Reprocessing)

This is the physical conversion of post-consumer plastics into new products (Oblah, 1993, p. 543). In this method the fundamental polymer is not altered. The secondary recycling involves the following: regrinding, melting, and reforming the plastic packaging materials. But, before regrinding, the pelletized resins must be contaminants' free.

In order to guarantee that the recycled polymer will not adulterate the packaged foods, recyclers must prove that the method used will produce polymeric materials with concentrations of contaminants that are low enough to be acceptable for human consumption. In order to reach a certain material quality, some additives, antioxidants, processing aids, adjuvants, etc., may be needed, but their levels and types must comply with corresponding regulations. (FDA, 1992, p. 2).

Tertiary Recycling (Chemical Reprocessing)

This refers to the reversal process of the chemical reaction that produced the original virgin polymer, in order to yield the same raw materials needed for producing the new polymer. Hence, it is also called closing-the-loop process. One very successful polymer that has been recycled with this process is the PET bottles. (Oblah, 1993, p. 543). It involves the depolymerization of post-consumer packaging materials to produce the original monomers or oligomers, which are then repolymerized into new polymeric materials. To produce the final new packaging materials, the regenerated monomers are often mixed with virgin materials. This process also involves several purification and washing steps, such as distillation, crystallization, and additional chemical reaction. (FDA, 1992, p. 4).

The recycling methods are not the same in terms of efforts needed for recycling or the value of the reclaimed products. In addition to the reuse of polymers, by remelting in modified or unmodified form, it is also possible to recover pure monomers from highly contaminated polymers by chemical degradation. Several companies have succeeded in PET recycling by methanolysis, a process that produces high quality PET. This recycling method seems promising for food-contact applications. (Boettcher, 1992, p. 28).

Tertiary recycling, however, is a complex, energy intense, and time consuming method. An easier method would be Secondary recycling, even though it involves collecting, sorting, chipping, washing, remelting, and converting the new polymer into a food packaging material. (Begley and Hollifield, 1993, p. 109). Tertiary recycling has a few advantages over the Secondary method. The first is that the quality of the raw materials produced is as high as the virgin ones. In addition, Tertiary recycling can consume more quantities of post-consumer polymers than Secondary recycling. Also, polymers produced by Secondary recycling processes always experience some degree of degradation. (Mapleston, 1993, p. 58). However, it is believed that Tertiary recycling takes much more energy than the other two systems.

POTENTIAL SAFETY PROBLEMS OF RECYCLING TECHNOLOGIES

If commingled plastics find a way to the recycling facilities, Secondary recycling may result in producing packaging materials that are not suitable for food-contact applications. This problem arises mainly due to the limited control of the source of the post consumer material before going to the recycling facilities. Therefore, recyclers involved in the Secondary recycling must demonstrate to FDA the ability of practicing an adequate control over the source of the recycled resins, submit information on the appropriate conditions under which the recycled materials may be used (e.g. frozen or refrigerated products), and determine whether the recycled materials are restricted to particular types of foods. (FDA, 1992, p. 2).

Therefore, in order to establish a successful recycling program for plastics, information about the following must be obtained: collection, separation, reprocessing technology, and markets for recycled plastics (Bennett, 1992, p. 26).

RECYCLING RESPONSIBILITIES OF FDA

The Federal Food, Drug and Cosmetic Act (FD&C) has determined the primary responsibility of FDA. FDA is expected to ensure that products under its supervision are wholesome and safe. The agency actually started regulating materials that are used in food-contact applications since the 1958's Food Additives Amendment. In addition, in 1968 the National Environmental Policy Act (NEPA) delineated even more roles for FDA to carry out, and FDA is required to review the impact of new food packaging materials on the environment. This role is explicitly defined by section 101 (b)(6) of NEPA. It demands that all federal agencies, including FDA, have a statutory responsibility to help the nation approach the maximum attainable recycling of depletable resources. (Thorsheim and Armstrong, 1993, p. 55). More on these roles can be found on the paper of Gamber (1991).

Under the FD&C Act, FDA's involvement in the recycling of packaging materials is mainly aimed at the assurance that food- contact materials do not adulterate foods. FDA therefore conducts pre-market studies to prove the suitability of any food-contact material which meets the "statutory food additive" definition and which are not "otherwise exempt", and this includes the recycled plastics. (Heckman and Foley, 1993, p.76). It is, therefore, important for successful applications of recycled materials in food packaging that NEPA, FDA, recyclers, and other related parties establish a cooperative approach for this end. For a review on the worldwide recycling standards refer to: Miki and Oki (1993), Bakker and Gigliotti

(1993), and Johnson (1993).

Premarket Tests

The section 210(s) of the FD&C Act clearly defines what a food additive is. The food additive is any substance "...the intended use of which results or may reasonably be expected to result, directly or indirectly, in its becoming a component or otherwise affecting the characteristics of any food." This is a very important piece of legislation from the food packaging point of view because it captures the essence of what is considered a packaging material and what is not, and then regulates its use. In addition, due to the potential health hazard of additive materials in foods, Congress established a petition process which aids in evaluating the safety of any new food additive pending for a premarket approval (Machuga, Pauli, and Rulis, 1992, p. 180).

FDA is required to conduct a premarket study for any material that meets the definition of the food additive. The definition considers the packaging materials as indirect food additives, and they are therefore subjected to the premarket regulation. The use of direct food additives, which are those materials with technical effects on food, are also regulated by this definition. (Schwartz, 1991, p. 232).

Good Manufacturing Practice (GMP)

In general, the manufacture of any polymer, regardless of its application, is strictly regulated by the US Environmental Protection Agency (EPA). In fact, EPA has the authority to regulate the entire life-cycle of any chemical from its manufacture to its ultimate disposal. Polymers, according to EPA, "... can not be manufactured ... if the polymer is designed or reasonably anticipated to substantially degrade, decompose, or depolymerize." (Carg, 1993, p. 915). This regulation considers the expected functions of the polymers' end products, and whether they can be used as packaging materials or not. However, for food-contact applications, the polymers used are regulated by FDA.

A key regulation which specifies the minimum requirements for any material proposed for use as a food-contact material is the general regulation under Part 174.5(a)(2). It states that "Any substance used as a component of articles that contact food shall be of a purity suitable for its intended use.", (FDA, 1992, p. 1).

This regulation is called "Good Manufacturing Practices" and is also referred to as (21 CFR 174.5). It does not eliminate recycling materials from being food-contact materials, as long as they are of suitable purity (Thorsheim and Armstrong, 1993, p. 56). The regulation dictates that **purity** is the determining factor upon which a decision of approval or disapproval can be made regarding a use of **any material** for food- contact application.

From the above, it would be reasonable to deduce that, in order for recycled polymers to be food-contact materials, they must meet the specifications set forth for the virgin polymers and, most importantly, for the purity requirement (Heckman, 1992, p. 416).

Moreover, FDA has proposed a general approach suggesting that in addition to meeting the same specifications applicable to the virgin polymer, the recycled polymers must assure, with chemical analysis, that secondary and tertiary recycling programs will not produce chemical contaminants beyond the acceptable levels. Therefore, an acceptable recycling scheme is one that is able to satisfy the GMP requirement of producing materials with dietary exposure of 1 ppb or less of any contaminant. (FDA, 1992, p. 9).

ABSENCE OF REGULATIONS FOR RECYCLED FOOD-CONTACT MATERIALS

To be approved by FDA, recycled materials, per se, do not have to meet any legal requirements in order to be used in food packaging. FDA's approval/disapproval of food-contact materials is based solely on the composition of the materials, and neither on the manufacturing process used to produce them, nor on the source of the raw materials, virgin or recycled. As with any food packaging materials (glass, aluminum, etc.), recycled polymeric materials have to meet the safety requirement, specifications, and limitations of FDA's food additive regulation. Consequently, the main concern of FDA's regulations are the safety issues. FDA approval decision is based on a determination of whether or not food-contact materials (virgin and recycled alike) will make food products injurious to health. (Heckman and Foley, 1993, p. 76).

As Schwartz (1991) states, the lack of regulations that authorize, explicitly, the use of recycled polymers in food-contact applications "should not be interpreted" as if FDA intended or intends to ban their use. There are two explanations for the absence of such regulations. First of all, FDA did not expect the recycling technology involvement in food packaging at the time of writing the regulation (Part 177). Secondly, no one petitioned the agency to write such a regulation. (Schwartz, 1991, p. 237). Therefore, there are no sound reasons to believe that FDA is against the use of recycling materials in food-contact and other food packaging applications.

Nonetheless, the absence of such laws is not going to continue. FDA is developing protocols, for the industry's use, which require manufacturers to ensure the production of recycle materials with suitable purity for food-contact use. The major concern for compliance with a legal regulation for using recycled polymers is the demonstration that they are free of contaminants. Provided that they meet the Food Additive Regulation and they are pure enough, there is "absolutely no legal reason precluding the recycled polymer" from use in food application. (Heckman, 1992, p. 418).

Currently, the use of recycled polymers in food-contact applications is not explicitly regulated by specific law (Thorsheim and Armstrong, 1993, p. 55). However, the use of recycled polymers is governed by the same regulations applicable to all food packaging materials. FDA's regulations pertinent to food additives, including those which govern the process of clearing packaging materials to be used in contact with foods, declare no limits on the source of the raw materials making up the packaging materials. Rather, the regulations require the materials to fulfill particular specifications and to pass certain tests. Therefore, FDA's regulations do not prohibit properly recycled materials for food- contact applications, as long as they meet the appropriate standards. (Heckman and Foley, 1993, p. 76).

IMPORTANT CONSIDERATIONS ABOUT THE USE OF RECYCLED POLYMERS

Based on FDA's past handling of the already approved recycled materials, it is clear that the agency is particularly alert and cautious about: 1) the source of the polymers, which should ensure a clean feedstock; 2) recycling processes, which must not result in any contaminants and must be able to remove any existing ones; and 3) the products' uses. Therefore, important considerations for the use of recycled materials for food packaging include the polymer type, additive levels, and cleanliness. The feedstock should be of known history, and which materials would be also suitable for contacting foods if in its virgin form. The additives, which are added during or after recycling processes, must comply with the Food Additive Regulation, and their concentrations must be in accordance with the corresponding specifications. The main concern with the cleanliness of the recycled materials is the possibility of chemical and microbial contamination. The thermal treatments during recycling processes, however, are high enough to limit the impact of such contamination. (Thorsheim and Armostrong, 1993, p. 56).

Manufacturers of recycled resins for food-contact packaging are asked by FDA to address some specific issues.

FDA will not allow high concentrations of adjuvants, commonly used in recycled polymers, and the process of recycling must demonstrate that adjuvant extractive procedures are included. Also, suppliers of recycled polymers must provide clean polymers, i.e., free from microorganisms and filth. Recycled polymers should be free of contaminants that might be added during the course of recycling, and which have the potential to migrate to foods. The above considerations are actually what the Food Additives Regulation stresses, i.e., safety and purity of the recycled polymers. (Heckman, 1992, p. 417).

In addition, and more importantly, FDA recognizes that no further food additive clearance for the recycled polymers is required as long as they comply with existing clearance governing the intended use of the polymer in the virgin form and is properly cleaned, (Heckman, 1992, p. 418).

RECYCLING MATERIALS AND POSSIBLE HEALTH HAZARDS

The health concerns raised by using packaging materials are generally based on the possibility of contamination and not necessarily the presence of a specific contaminant (Thorsheim and Armstrong, 1993, p. 55). The recycling process is not without potential threat to health. There is a possibility that traces of carcinogens, or other substances that constitute a health hazard, become part of the packaging material, and, hence, raise the likelihood of migrating into food products. The sources of these low-concentration contaminants are introduced in the processes of the Secondary and Tertiary recycling. Even though successive recycling processes result in diluting the contaminants, in the long run a very low concentration of contaminants may conceivably find its way to the packaging materials. Therefore, over a long period of time, it is possible that a consumer may be exposed to low concentrations of a certain contaminant. (FDA, 1992, p. 4).

To ensure the safety of this practice and to avoid contaminants, the Food Additives Regulation has stipulated conditions that guarantee safe levels of exposure to contaminants. The permitted conditions include temperature, types of food, adjuvants' levels in polymers, and predicted usage, either one-time or multiple, of the food-contact materials. These conditions are important because they have direct effects on human exposure to polymer additives. (Schwartz, 1991, p. 232). Therefore, the key requirement for a satisfactory recycled polymer for the food-contact application is its freedom from contaminants, or the minimal acceptable level of them. (Heckman, 1992, p. 418).

For this reason, FDA is developing a Threshold Regulation Policy which estimates the maximum levels of contaminants in the recycled polymers. This policy is designed especially for chemicals that are known to present in the food packaging materials. (Thorsheim and Armstrong, 1993, p. 56). More specifically, FDA considers that dietary intake levels of 0.5 to 1 ppb constitute a negligible risk for any chemical known to be present in the packaging materials. FDA considers a recycling process that proves to remove contaminants to levels less than 0.5 ppb as safe and an adequate health safety standard. (FDA, 1992, p. 5) and (Thorsheim and Armstrong, 1993, p. 56).

Levels of contamination between 0.5 to 1 ppb are considered to be insignificant (Schwartz, 1991, p. 238) and (FDA, 1992, p. 9), and such dietary exposures do not compromise the public health. Therefore, recycled materials that fall in this range of contamination level do not require an actual oral feeding study or any unnecessary animal testing (Machuga, Pauli, and Rulis, 1992, p. 182).

In addition to the roles taken by FDA, the Coalition of North Eastern Governors (CONEG) is involved in the issue of packaging contamination too. CONEG has developed a Model Toxic Legislation, and it became law in Connecticut, Maine, New Hampshire, Rhode Island, Vermont, New York, and New Jersey. The main concern of this legislation is to reduce the amount of lead, cadmium, mercury, and hexavalent chromium in the packaging materials. The manufacturers and distributors are expected to comply with this law within a two year period. The legislation, however, provides an exemption process for packages made from recycled materials. (Carg, 1993, p. 916).

CHAPTER THREE

HYPOTHESIS AND METHODOLOGY

INTRODUCTION

The last two chapters reviewed important properties and functions of polymeric food packaging materials and explained how the recycled polymers are evaluated from legal and technical perspectives. In this chapter, empirical data demonstrates that post-consumer polymers can be made to perform certain functions as well as their virgin counterparts. Because oxygen permeation has a direct effect on food quality, it is a key factor in assessing materials for food packaging. For this reason, the comparison of virgin and recycled polymers must include an evaluation of oxygen permeation; equal levels would suggest the appropriateness of either material.

When considering the use of recycling materials in food applications, many parameters need to be evaluated in addition to the permeability studies. Simply having an identical oxygen permeability profile with virgin materials does not prove that other functions of recycled materials are adequate for food packaging purposes. At the same time, recycled materials do not have to be perfectly identical to the virgin ones in order to be considered for food applications. Food products can tolerate minimal variations between the two materials. To address their potential applications in food packaging, recycled polymers have to meet the following conditions:

1- They must be reproduced, with the appropriate technologies, to perform adequately in protecting and maintaining the integrity and safety of the food products; and

2- They must comply with the same FDA standards applicable to the virgin materials.

This research project attempts to compare oxygen permeabilities of virgin HDPE resins with post-consumer HDPE resins. Identical data for the two materials would indicate that recycled plastics could have potential applicability in the food industry after meeting and passing the safety requirements and testings. This is true simply because the permeability is a material-specific parameter. This means that if two materials have permeabilities that are not significantly different, then their properties (chemical, physical, mechanical, etc.) may not be significantly different either. If this happens then the two materials are not significantly different, and, therefore, it is very likely that one material can replace the other in an application. The ultimate purpose of this comparison is to establish whether or not a significant difference exists between the means of both materials' permeation rates.

The results of the gas chromatography analysis are drawn from two sample groups. The oxygen percentages (concentration) of both materials are obtained to make two sets of data. The means of the data are statistically evaluated; if the evaluation determines a significant difference between the means, the conclusion is that both materials have different permeability rates. In this case recycled materials may not be suggested for food packaging because their use may compromise food quality. But, when the means are not significantly different, then both materials have the same permeation rates, and the recycled materials may be required to undergo further safety evaluations in order to justify their use in food applications. This way the recycled materials are shown to be safe and to be protective of the integrity and quality of the product.

HYPOTHESIS

In order to make a valid decision about the difference between the means, a hypothesis must be formed and then tested. Testing a hypothesis leads to the acceptance of only one of the two statements, the null hypothesis or alternative hypothesis. If the test results in rejecting the null hypothesis, then the alternative hypothesis is accepted.

Null Hypothesis

The statement of the null hypothesis that satisfies the purpose of this experiment is as follows:

"On a significance level of 0.05, there is no significant difference between the oxygen permeation rate of virgin HDPE and the oxygen permeation rate of recycled HDPE."

Alternative Hypothesis

Hence, the alternative hypothesis is:

"On a significance level of 0.05, the oxygen permeation rate of virgin HDPE is significanly different from the oxygen permeation rate of recycled HDPE."

Therefore, the null hypothesis is accepted if the means of the oxygen permeation rates of the virgin HDPE films equal the means of the oxygen permeation rates of the recycled HDPE films. On the other hand, if the means are not equal, the null hypothesis is rejected and the alternative hypothesis is accepted instead.

In order to test the null hypothesis, the analysis of variance (ANOVA) and two-sample t-test have been used. ANOVA can statistically analyze two sets of data and determine their means. The t-test was used to evaluate the means of the data. So, the ANOVA was used to calculate the means, and the t-test was used to test whether these mean values are significantly different or not.

METHODOLOGY

Samples Properties

The obtained samples (recycled and virgin HDPE films) are produced on a water-quenched cast film line. The recommended applications of virgin HDPE resins include water, milk, and juice bottles. For this reason, the virgin HDPE materials are made with properties and processing techniques that meet FDA regulation 21CFR (Section 177.15220) which allows polymers to be used in articles, or components of articles, intended for use in contact with food.

The recycled HDPE resins, on the other hand, have been manufactured with the Secondary recycling method, by the same company which produces the virgin samples, with a 100% post consumer "homopolymer" resin. This is important because it tells that the material is produced with great consistency. This quality may be adequate enough to consider the recycled HDPE for food applications. Perhaps that is why the company is implying its interest of developing food related applications from its recycled materials by stating that its recycled HDPE is "not sanctioned" by FDA's regulation 21CFR. The company recommends that its recycled materials be used in straight (as blend), or in coextruded structures, making them suitable for the following processes: blow molding, injection molding, film extrusion, and thermoforming. However, the company did not suggest any food applications.

The manufacturer has tested the essential physical properties of both the recycled and virgin HDPE. The comparison is shown in Appendix J (a). This comparison does not include the permeabilities of these materials, which indicates that the parties involved in utilizing post-consumer polymers in packaging food products are neglecting an important functional property needed in this industry. The lack of information has created a need for more research on the area of permeability characteristics of recycled materials, especially when their virgin forms are used in food-contact applications. And that is the purpose of this research.

The Experiment Procedure

Introduction

The following pieces of equipment and materials are used:

- Gas Chromatograph Hewlett Packard 5890A (Serial No. 2429802858);
- 3392A Integrator Hewlett Packard (chart recorder);
- Syringe 1 ml., with press lock, by Precision Sampling Corp.;
- Thermal Impulse Heat Sealing Machinery, Vertrod Corp., (Serial No. V-42057, Model 24 PCS);
- Helium Gas, High Purity (99.997%); and
- Nitrogen Gas.

The goal of the experiment is to establish permeation rates, from which slopes are generated from the daily oxygen ingress into the tested samples. The experiment takes into consideration the variability in the test procedure, by having very large sample groups. The recycled and virgin materials are made into pouches, which in turn are compartmentalized in a grid fashion. Permeation rates for one material's compartments are the same in theory, but, due to the inconsistencies in sample fabrication, compartments may have different permeation rates from their adjacent compartments (same material). Slight variations among one material's compartments are expected especially when using very sensitive equipment like the GC to read the oxygen concentration. To overcome the variability problem, the entities where permeation takes place (compartments) are significantly increased in number. Hence, the data collected has a relatively large size- 420 numbers representing the oxygen make-up of the compartments for both materials.

The experiment is set up to monitor the trend of the daily change in the amount of oxygen permeating through the virgin and recycled HDPE materials. With the aid of the GC, comparison of the rates of this oxygen change inside the compartments is achieved. Typically, permeation rates initially increase progressively as the oxygen starts to permeate until a steady-state rate is reached, indicating a maximum permeation rate has been achieved (Amini, 1986, p. 651). HDPE is a poor gas barrier and therefore the oxygen permeation in this experiment is expected to reach the steady-state fairly quickly. Therefore, a seven-day period for this experiment is chosen. This procedure has been frequently and successfully used in the packaging science laboratory for permeability testing of various materials. However, this procedure does not follow the ASTM standards because these standards cite relatively expensive and particular equipment that is not available.

Materials and Samples Preparation

After receiving the materials from the manufacturer, the sizes and thicknesses are measured. Both the recycled and virgin HDPE samples have the same thickness of 3.5 mils. It is very important that both materials have the same consistent thickness, a parameter that has a direct effect on permeability. The samples are turned into pouches with similar but slightly different areas. See Appendix J (b). However, since the focus of this project is to compare the rate at which oxygen concentration changes inside compartments of both materials, then oxygen permeability coefficient is not affected by slight sample size differences. The area factor has no effect on the GC readings nor on the results of the experiment. Six pouches are made from virgin HDPE films and another six pouches are made from the recycled films. Each of the two groups is labeled with the letters A, B, C, D, E, and F.

Each of the twelve pouches is flushed very carefully with a just enough amount of the inert gas, nitrogen. The flushing is cautiously done, so that high pressure inside the compartments of the pouches can be avoided. High pressure inside over-flushed compartments may under-estimate the oxygen ingress into compartments. If this happens, inconsistent permeabilities may result, creating an error in the readings.

After flushing, each pouch is left with a very small opening, through which the excess of the nitrogen is forced out after pouches are completely compartmentalized in a grid fashion with the sealing equipment. Each pouch has seven rows and each row has five compartments. Each pouch, therefore, has 35 compartments, resulting in 210 compartments (for all 6 pouches) of virgin HDPE and 210 compartments (for all 6 pouches) of recycled HDPE.

Data Acquisition Procedure

1- On each day, before analyzing the type and quantity of gases in each compartment, the GC's syringe is cleaned by flushing it three times with air inside the lab (where the test is performed and pouches are kept). Then a 1/10 ml. of air is injected into the GC in order to obtain the amount of oxygen in air. This piece of data serves as the base line (on permeation graphs) for the oxygen found in the compartments for that day. The amount of the permeating oxygen into the compartments, therefore, shouldn't exceed the values of the base line.

2- Every day only one row (5 compartments) from each pouch is analyzed with the GC. Since each pouch has seven rows of compartments, all pouches are tested in seven days.

3- For each pouch, the time between one row testing and the next is a period of 24 hours. For example the, GC is run for the first row of pouch A at 8:00 pm, so the next row of the same pouch must be examined at 8:00 pm on the next day.

4- On each day, each compartment is injected with a syringe and a 1 ml. sample from the inside gases is withdrawn.

5- The GC is set at the following conditions:

- Oven temperature at 60 °C;
- Detector temperature at 60 °C;
- The carrier gas (He) had a flow rate of 25-28 ml./minute.

On each day, these conditions are reset and a new baseline is determined. Each test sample day gives the same baseline gas composition.

6- A 0.10 ml. sample is injected into the GC, and the rest is kept inside the syringe as a reservoir. Once the curve of the graph (generated by the chart recorder) reaches the base line, the GC is considered to have completed its analysis. The syringe can then be emptied from its content, and preparation for the next reading can begin.

7- The GC's analysis is generated in a chart depicting the percentage of each component inside the syringe (gases of a compartment) with a percentage values of each type of gas (oxygen, carbon dioxide, and nitrogen). Before the next reading is taken, the curve of the chart recorder has to reach the base line, which indicates that the GC has completed its analysis. (Due to the presence of some experimental noise, an irregular graph may be generated. Although this happens only infrequently, when it does the reading is repeated with another 1/10 ml of the sample from the reservoir that is locked inside the syringe.)

8- Before taking a second sample from the next compartment, the syringe's content is emptied into the air, and air is forced in and out of the syringe at least three times. This ensures that no residues from the previous sample are kept inside the syringe.

9- After cleaning the syringe with air, a new sample is taken from the next compartment, and the above steps are repeated again- one compartment at a time. The procedure continues until all compartments are analyzed with the GC.

RESULTS

The first peak generated in each of the GC's chart represents the oxygen peak. Each oxygen peak indicates the concentration of oxygen inside the compartment being analyzed. The charts show these concentrations in percent figures. The area under the peak is calculated as a percentage of the sample by the integrator and recorded below the chart. These figures representing the oxygen percentages inside compartments are used to make the key body of the data needed for this study. The following Tables (2.a and 2.b) contain the oxygen percentage inside all the compartments. These tables are the original data obtained from the experiment.

Table 2.a Oxygen Concentrations of Virgin HDPE Samples
(Percent of Sample)

VIRG. A		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	1.019	4.777	7.738	9.796	9.833	10.884	11.149
	2	0.836	6.243	12.4915	5.962	8.996	10.159	9.83925
	3	8.289	6.513	6.6535	5.823	9.266	10.988	11.042
	4	1.007	11.818	8.729	9.067	7.543	11.262	10.396
	5	2.178	3.12	10.379	6.908	8.371	11.067	10.605

VIRG. B		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	1.016	3.713	11.993	6.994	9.163	11.15	7.938
	2	1.562	4.297	10.951	8.62	10.254	10.334	9.44
	3	1.713	6.763	12.604	11.171	10.236	10.776	9.899
	4	8.083	5.843	12.172	11.064	10.751	11.672	11.001
	5	2.702	8.017	13.349	11.155	11.242	11.402	11.524

VIRG. C		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	6.567	10.378	11.319	11.482	13.352	14.033	10.579
	2	3.85	11.34	13.673	10.607	11.315	11.704	11.17
	3	5.507	13.19933	13.062	11.026	10.982	11.003	11.438
	4	2.403	5.149	7.772	7.6855	10.263	10.905	11.461
	5	2.61	5.418	7.904	9.551	11.389	11.313	11.429

Table 2.a (cont'd)

VIRG. D		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	1.478	3.558	10.658	5.749	10.545	9.375	8.764
	2	2.492	3.099	11.879	5.4505	7.551	8.373	8.786
	3	0.531	3.027	6.846	7.896	10.709	11.526	10.9
	4	0.759	11.697	12.707	10.3975	11.299	11.699	11.522
	5	2.257	6.947	12.588	10.71	12.85	11.26	11.284

VIRG. E		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	11.396	5.212	11.258	11.467	11.31	9.912	10.471
	2	0.975	5.504	8.03	8.3855	11.124	11.265	9.596
	3	1.457	4.418	6.724	9.465	11.175	11.548	11.304
	4	1.483	3.517	7.597	9.904	10.683	9.812	11.847
	5	3.127	9.86	10.406	10.99	11.419	10.27	10.736

VIRG. F		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	3.767	5.85	8.508	7.128	9.196	9.379	9.411
	2	1.188	3.904	7.555	7.943	10.501	10.302	8.236
	3	12.228	8.609	8.432	8.358	8.634	9.909	10.501
	4	1.034	3.713	6.668	10.349	10.584	11.062	10.413
	5	1.285	3.201	5.852	11.428	10.83	11.712	10.833

Table 2.b Oxygen Concentrations of Recycled HDPE Samples
(Percent of Sample)

RECY. A		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	0.534	6.671	14.076	10.089	11.497	11.134	10.969
	2	0	3.961	11.708	10.162	10.956	10.916	11.002
	3	0	4.863	12.612	11.20367	11.98267	13.20875	10.969
	4	0	3.816	8.013	10.207	10.868	10.684	10.721
	5	0	6.787	10.261	10.15	10.73	11.297	11.088

RECY. B		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	1.672	6.034	6.333	9.376	10.715	11.586	11.264
	2	0.507	8.658	6.689	9.516	10.879	11.044	10.704
	3	15.373	5.199	5.543	9.161	10.123	9.928	10.516
	4	2.487	7.264	14.63767	12.108	12.47067	11.132	10.952
	5	0.923	4.513	7.855	10.333	11.227	11.539	11.149

RECY. C		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	2.608	6.057	11.621	9.958	11.476	11.743	10.931
	2	0.526	13.13233	9.116	9.291	10.483	11.063	11.105
	3	2.354	4.271	8.613	9.512	10.58	11.478	11.217
	4	2.112	5.042	8.481	10.3	11.12	11.359	11.065
	5	0	2.928	8.328	9.03	10.314	11.245	10.537

Table 2.b (cont'd)

RECY. D		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	2.288	6.469	9.288	10.439	10.869	10.409	10.22
	2	2.596	9.036	9.937	11.026	11.281	11.158	11.57
	3	12.023	6.546	8.815	11.11	11.913	10.781	11.521
	4	1.125	3.008	7.205	11.433	11.459	11.193	11.815
	5	1.509	3.305	7.887	11.253	11.013	11.039	10.885

RECY. E		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	2.529	5.128	8.12	10.992	11.559	11.821	11.744
	2	0.95	5.306	9.943	10.027	10.936	10.749	10.882
	3	0.946	4.038	10.462	9.702	9.68	10.682	10.836
	4	0.495	2.616	8.169	9.857	10.657	8.909	10.876
	5	0.912	5.20525	7.795	9.309	11.047	11.23	11.083

RECY. F		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	2.921	12.382	11.386	10.939	11.656	10.896	9.337
	2	1.296	12.4755	10.968	11.266	10.892	10.512	9.499
	3	5.096	12.134	10.873	11.461	11.176	9.995	8.618
	4	2.777	6.849	10.682	11.345	10.657	10.478	10.002
	5	5.1915	7.622	10.684	11.225	10.73	10.453	11.176

EXPERIMENTAL ERROR

The original data show that there are some numbers that can not be equivalent to the actual oxygen concentration inside the compartments. Some of these unreasonable values are extremely high on the first day, when the oxygen percentage is expected to be almost zero. These values are a result of the experimental noise or error, which might be due to the following factors and reasons:

1- The GC's port of entry was not functioning perfectly. This may result because the septa (the part that the syringe penetrants at each injection, and whose function is to keep the ambient air from getting into the GC) has developed a hole after a number of injections. Therefore air may be permitted into the GC and, therefore, may be analyzed as a part of the injected sample.

2- The subsequent injections may be done, inadvertently, prior to the complete stabilization of the GC after the last injection.

3- Sometimes when injecting a hard material with a smooth surface, like HDPE, it is not easy to apply the right amount of pressure on the syringe to penetrate the compartment and withdraw a gas sample. Incorrect injection may result making the syringe to slide on the surface of the compartment (creating a long opening instead of a hole) or to penetrate both walls of the compartment. When this happens for a compartment, no reading is taken for that compartment. Such readings must be avoided, because air has more chance to get mixed with the sample withdrawn into the syringe.

4- The hole generated by the penetrating syringe may enlarge while the syringe is flushed three times inside the compartment. A small amount of air may get into the compartment. If this happens, the GC will read more oxygen than what is actually inside the compartment.

5- There may be small amounts of the previous sample left in the GC. This portion of the last sample gets mixed with the next injection. The next GC reading, therefore, would reflect higher oxygen values than the actual concentration.

6- The sealing quality may deteriorate after a period of time, especially in over-flushed compartments. Also, the sealing at some points, where wrinkles occur, is weaker. In both cases, the permeability process takes place faster than usual.

7- Some of the sample materials have air bubbles trapped in the material. This would clearly alter the consistency of the material's chemical make-up and its permeability rate.

8- Samples of air are taken from the same place where the pouches are kept (the lab, in this case), in order to determine the base line of oxygen in permeation graphs. However, it is found that when several persons are in the lab while air samples are collected, the percentage of oxygen in air becomes considerably lower than if only one person is in the lab. Breathing lowers the air oxygen, especially in a limited area. Therefore, when possible, readings of air oxygen are taken when either one person or when a few people are in the lab.

DATA MANIPULATION AND ANALYSIS

Introduction

In order to test the null hypothesis, the original data are manipulated is such away to satisfy the applications of the statistical tests, ANOVA and t-test, and their conditions. For the analysis to be carried out, both the ANOVA and t-test require normally distributed samples (Devore, 1987, pp. 266). This means that the compartments must be randomly chosen for the GC to analyze. In other words, selection of compartments can be viewed as if they are cut and separated in two boxes: one for the virgin samples and the other for recycled samples. Every day, 30 compartments are chosen at random to be analyzed with the GC. This way the statistical conditions of the t-test and ANOVA are met.

However, due to the nature of the experiment and its procedure (discussed earlier), some readings can not be considered in our analysis. There are readings from the GC (see Tables 2.a and 2.b) that are extremely high or extremely low. Some oxygen values are even higher than the oxygen in air. For this reason, such unreasonable readings have been deleted. An important advantage of the ANOVA and t-test is that these deletions neither effect nor interfere with the results of these tests. So the data analysis and hypothesis testings will be based on the data with the deletions, which will be referred to as the adjusted data.

Data Manipulation Procedure

First, the original data is plotted (see Figures 1.a, 1.b, 2.a, 2.b) in order to observe the variability of the data. With these figures it is possible to identify the values around which oxygen percentages lie and cluster, and to determine how far some values diverge from these clusters. This way, it is possible to identify the unreasonable values which had resulted from the experimental noise, and then to delete them. As a result, two additional sets of data, adjusted data, are created (see Tables 3.a and 3.b). The adjusted data is the main data upon which the hypothesis tests are performed. Testing the means of the adjusted data will determine whether the materials have equal permeation rates or not.

The MINITAB is the statistical software used to perform the oneway ANOVA test on the adjusted data. The ANOVA test is used to calculate the means of oxygen percentages on a day-by-day basis. The software is used to generate one mean value for all the oxygen percentages for all compartment for every day. Therefore, there are seven mean values for seven days (see the Minitab printout in Appendix K). Table 4 shows two sets of means obtained from the ANOVA, one for the virgin HDPE and one for the recycled HDPE. When the two-sample t-test is used with a significance level of 0.05 to examine the means of the two sets, the result shows that the P-value = 0.92, (see Minitab's printout in Appendix L).

The P-value is the smallest significance level at which the null hypothesis can be rejected. It is important to note that if the P-value is smaller than or equal to the significance level (0.05 in this case), the null hypothesis is rejected; and if the P-value is larger than the significance level used, then the null hypothesis is not rejected. (Minitab Mini-Manual, 1992, pp. 4-12) and (Devore, 1987, p. 311). Because the P-value shown by the results of the t-test (P= 0.92) is larger than the significance level (0.05), then the null hypothesis is accepted.

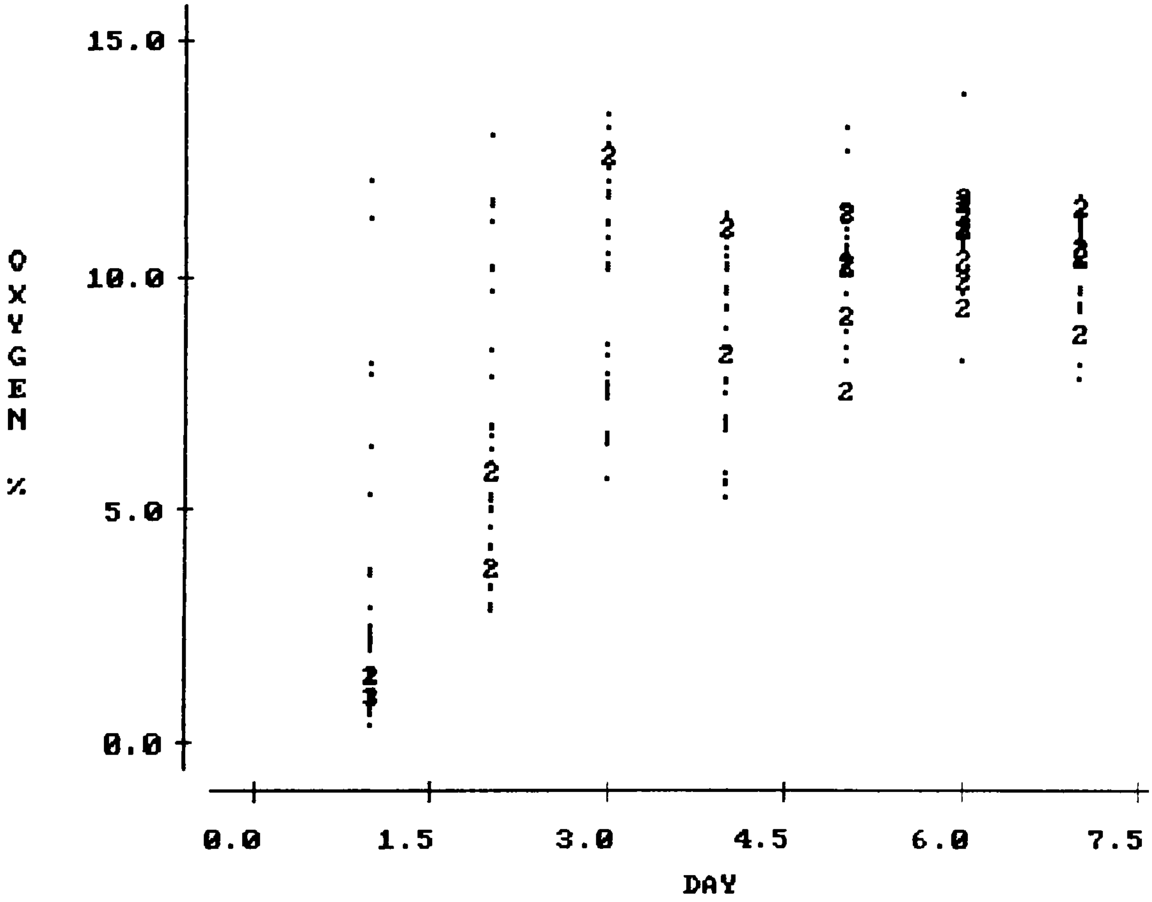


Figure (1.a) Oxygen Concentrations in Virgin HDPE Samples

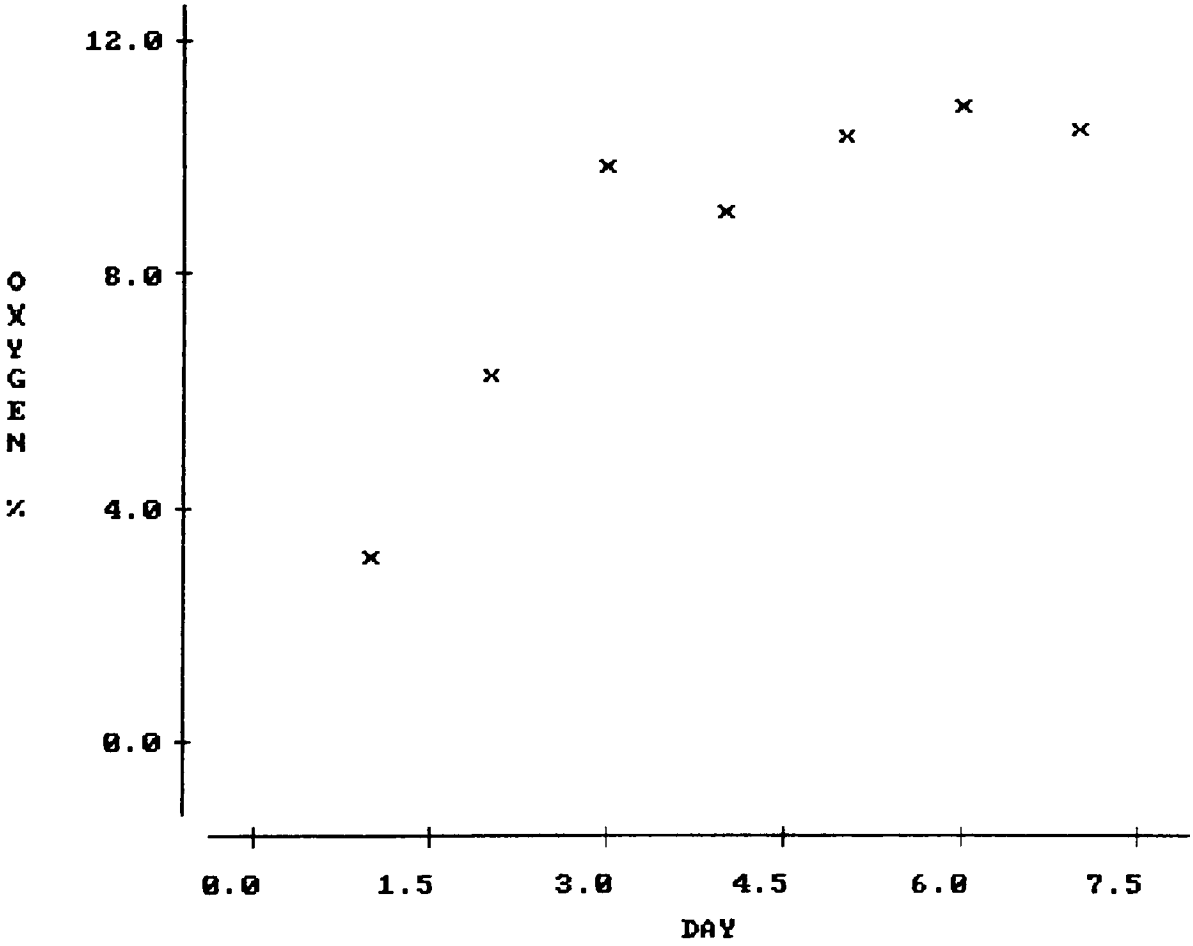


Figure (1.b) Mean Values of Oxygen Concentrations of Virgin HDPE Samples

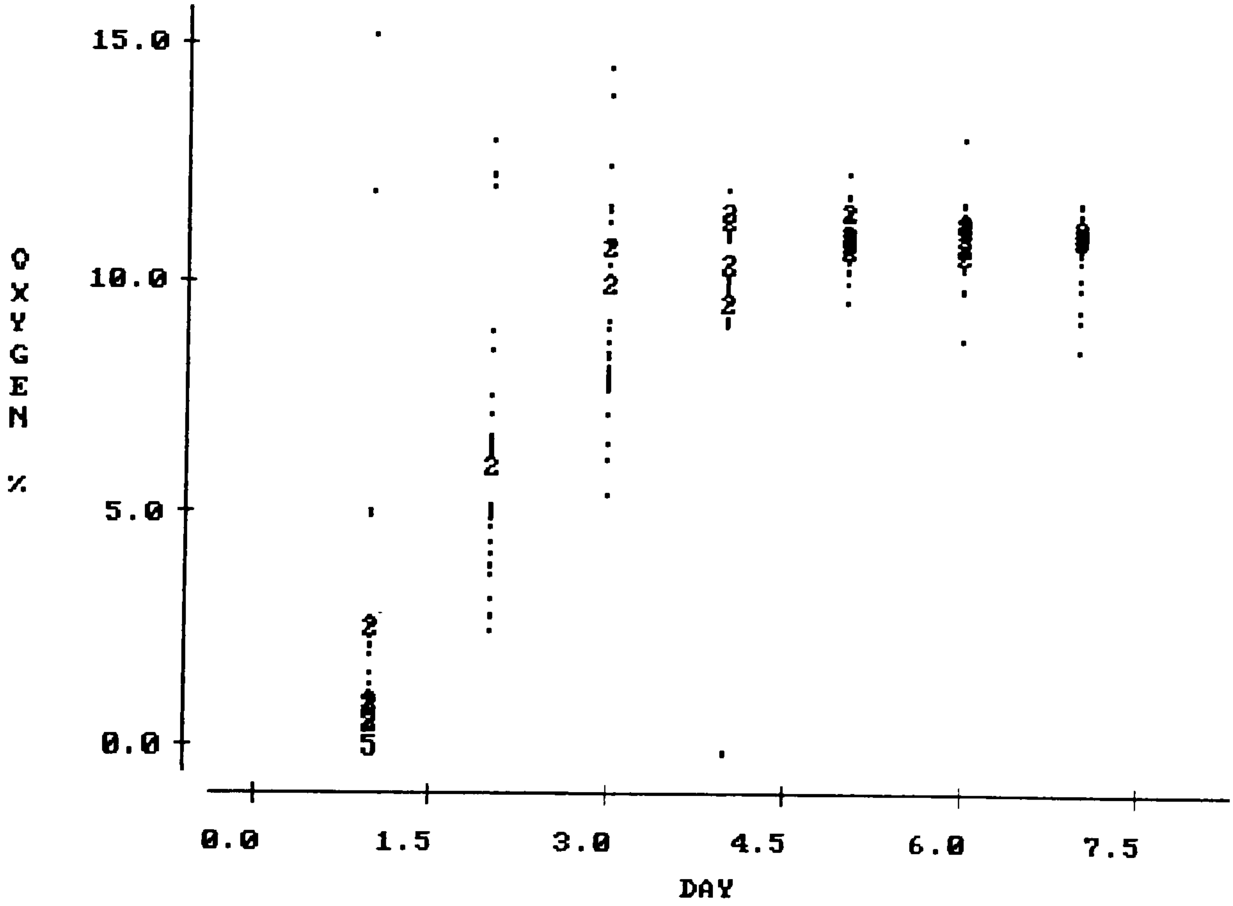


Figure (2.a) Oxygen Concentrations in Recycled HDPE Samples

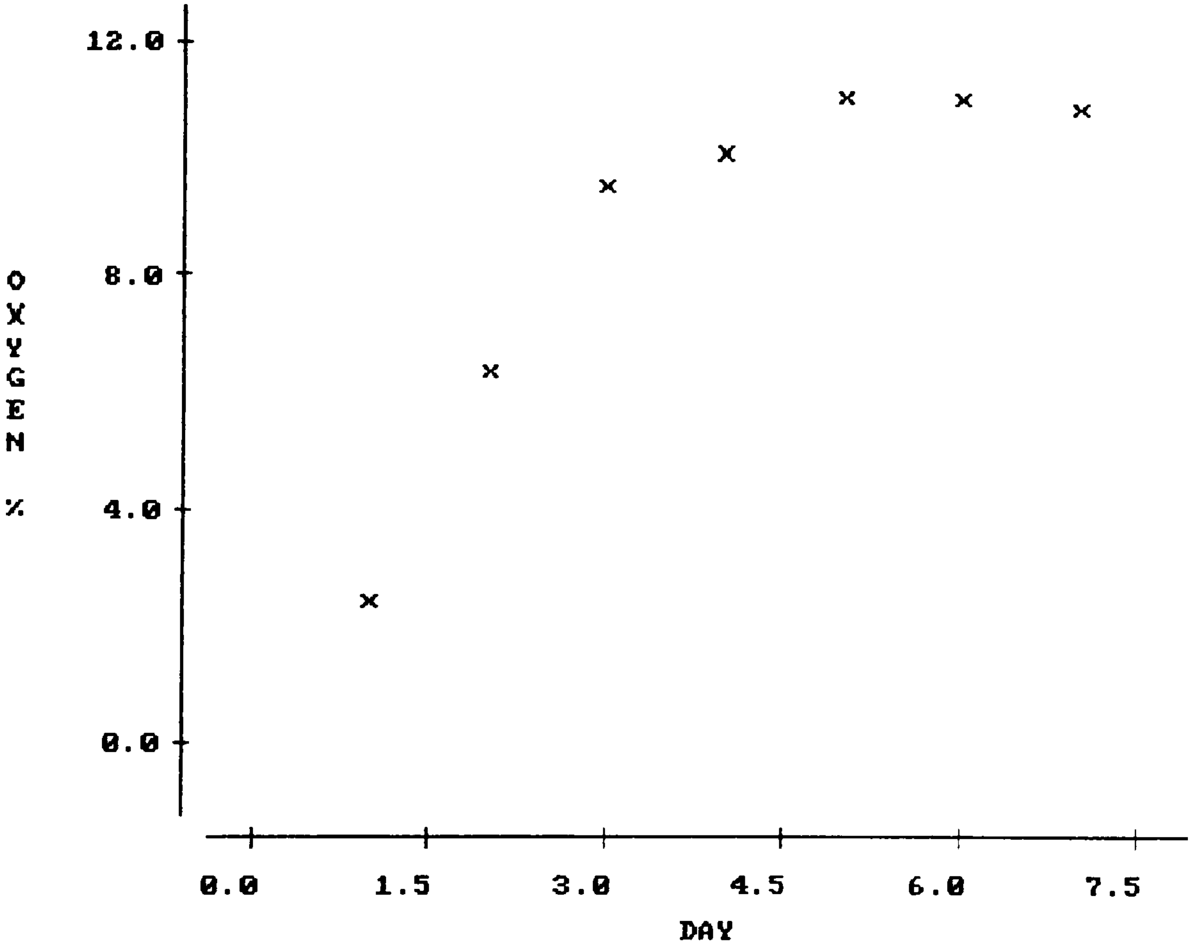


Figure (2.b) Mean Values of Oxygen Concentrations of Recycled HDPE Samples

Table 3.a Oxygen Concentrations of Virgin HDPE Samples
(Adjusted Percent of Sample)

VIRG. A		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	1.019	4.777	7.738	9.796	9.833	10.884	11.149
	2	0.836	6.243	12.4915	*	8.996	10.159	9.83925
	3	*	6.513	6.6535	*	9.266	10.988	11.042
	4	1.007	*	8.729	9.067	7.543	11.262	10.396
	5	2.178	3.12	10.379	*	8.371	11.067	10.605

VIRG. B		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	1.016	3.713	11.993	*	9.163	11.15	*
	2	1.562	4.297	10.951	8.62	10.254	10.334	*
	3	1.713	6.763	12.604	11.171	10.236	10.776	9.899
	4	*	5.843	12.172	11.064	10.751	11.672	11.001
	5	2.702	8.017	*	11.155	11.242	11.402	11.524

VIRG. C		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	*	10.378	11.319	11.482	*	*	10.579
	2	3.85	*	*	10.607	11.315	11.704	11.17
	3	5.507	*	*	11.026	10.982	11.003	11.438
	4	2.403	5.149	7.772	7.6855	10.263	10.905	11.461
	5	2.61	5.418	7.904	9.551	11.389	11.313	11.429

Table 3.a (cont'd)

VIRG. D		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	1.478	3.558	10.658	*	10.545	9.375	*
	2	2.492	3.099	11.879	*	7.551	*	*
	3	0.531	3.027	6.846	7.896	10.709	11.526	10.9
	4	0.759	*	12.707	10.3975	11.299	11.699	11.522
	5	2.257	6.947	12.588	10.71	*	11.26	11.284

VIRG. E		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	*	5.212	11.258	11.467	11.31	9.912	10.471
	2	0.975	5.504	8.03	8.3855	11.124	11.265	*
	3	1.457	4.418	6.724	9.465	11.175	11.548	11.304
	4	1.483	3.517	7.597	9.904	10.683	9.812	11.847
	5	3.127	9.86	10.406	10.99	11.419	10.27	10.736

VIRG. F		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	3.767	5.85	8.508	7.128	9.196	9.379	*
	2	1.188	3.904	7.555	7.943	10.501	10.302	*
	3	*	8.609	8.432	8.358	8.634	9.909	10.501
	4	1.034	3.713	6.668	10.349	10.584	11.062	10.413
	5	1.285	3.201	*	11.428	10.83	11.712	10.833

Table 3.b Oxygen Concentrations of Recycled HDPE Samples
(Adjusted Percent of Sample)

RECY. A		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	0.534	6.671	*	10.089	11.497	11.134	10.969
	2	0	*	11.708	10.162	10.956	10.916	11.002
	3	0	4.863	*	11.20367	*	*	10.969
	4	0	*	8.013	10.207	10.868	10.684	10.721
	5	0	6.787	10.261	10.15	10.73	11.297	11.088

RECY. B		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	1.672	6.034	*	9.376	10.715	11.586	11.264
	2	0.507	*	*	9.516	10.879	11.044	10.704
	3	*	5.199	*	9.161	10.123	*	*
	4	2.487	7.264	*	*	*	11.132	10.952
	5	0.923	4.513	7.855	10.333	11.227	11.539	11.149

RECY. C		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	2.608	6.057	11.621	9.958	11.476	11.743	10.931
	2	0.526	*	9.116	9.291	10.483	11.063	11.105
	3	2.354	4.271	8.613	9.512	10.58	11.478	11.217
	4	2.112	5.042	8.481	10.3	11.12	11.359	11.065
	5	0	*	8.328	*	10.314	11.245	10.537

Table 3.b (cont'd)

RECY. D		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	2.288	6.469	9.288	10.439	10.869	10.409	*
	2	2.596	*	9.937	11.026	11.281	11.158	11.57
	3	*	6.546	8.815	11.11	*	10.781	11.521
	4	1.125	*	*	11.433	11.459	11.193	11.815
	5	1.509	*	7.887	11.253	11.013	11.039	10.885

RECY. E		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	2.529	5.128	8.12	10.992	11.559	11.821	11.744
	2	0.95	5.306	9.943	10.027	10.936	10.749	10.882
	3	0.946	4.038	10.462	9.702	*	10.682	10.836
	4	0.495	*	8.169	9.857	10.657	*	10.876
	5	0.912	5.20525	7.795	9.309	11.047	11.23	11.083

RECY. F		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Base Line		12.463	12.841	12.633	11.314	11.79	13.273	14.16775
Sample	1	2.921	*	11.386	10.939	11.656	10.896	*
	2	1.296	*	10.968	11.266	10.892	10.512	*
	3	*	*	10.873	11.461	11.176	*	*
	4	2.777	6.849	10.682	11.345	10.657	10.478	*
	5	*	7.622	10.684	11.225	10.73	10.453	11.176

Table 4. Means of the Oxygen Concentrations Permeated through Virgin and Recycled HDPE Samples

Day	Virgin HDPE	Recycled HDPE
1	1.929	1.310
2	5.410	5.770
3	9.637	9.522
4	9.819	10.380
5	10.149	10.958
6	10.845	11.062
7	10.928	11.086

In addition, the means of both materials are plotted against time, in days (see Figures 3, 4, and 5). A best fitted straight line is drawn on each permeation graph. This step is achieved, with the help of the Minitab, in order to compare the slopes of both curves. As shown in Appendix M, the regression equation for the oxygen permeation graphs of the virgin material is:

2.89 + **1.38** X Days.

The equation shows that the slope is 1.38. On the other hand, the recycled permeation graph has a slope of 1.51, from the equation:

2.54 + **1.51** X Days.

It can be observed that both materials have very close slopes, indicating very similar permeation profiles (see Figure 5). However, it is worth noting that small differences are expected even among the slopes of the permeation curves that belong to one particular material. Such a difference between slopes (1.38 and 1.51) in this case does not mean necessarily that both materials have different permeation rates, and, therefore, should not be used to discredit the null hypothesis.

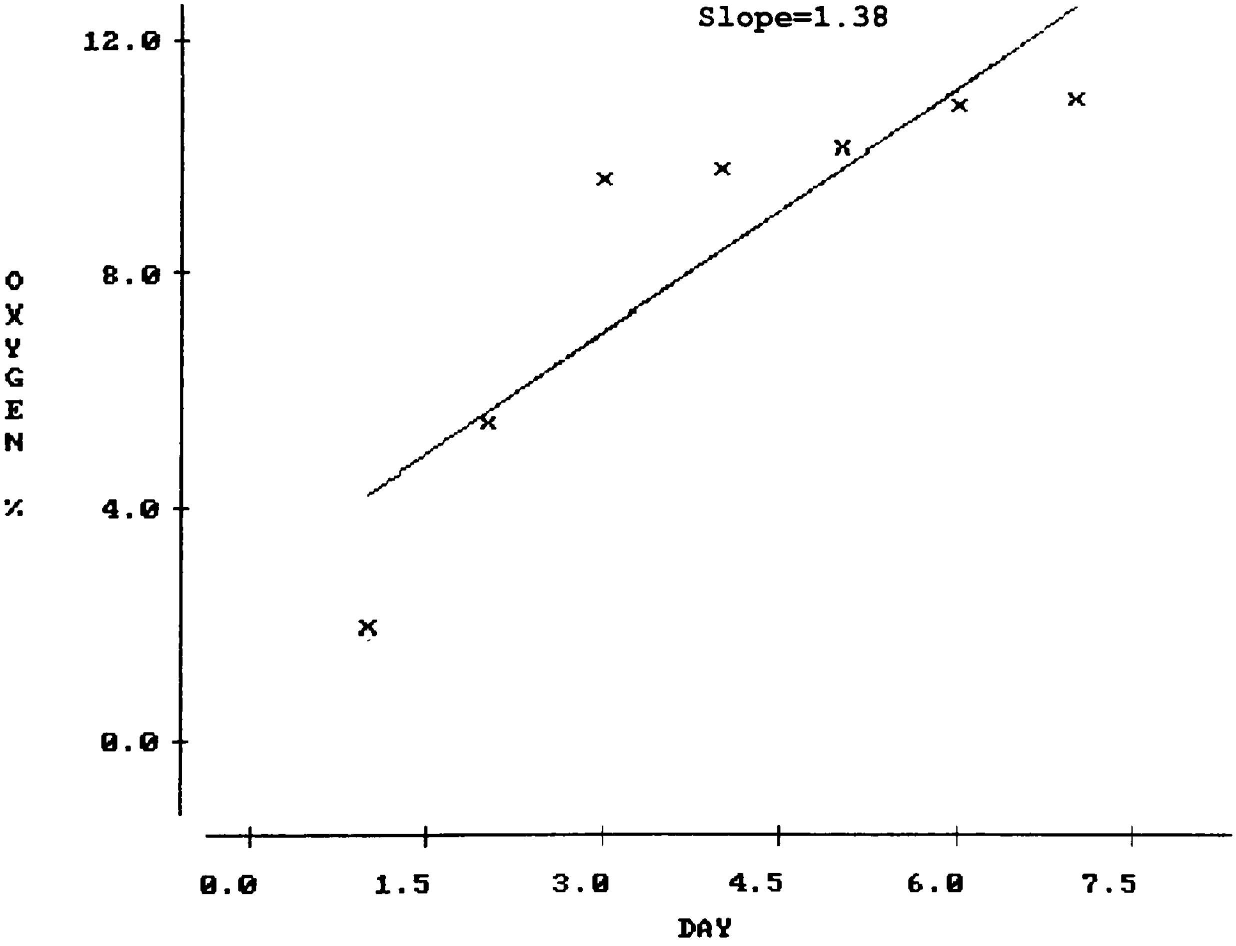


Figure (3) Mean Values of Oxygen Concentrations of Virgin HDPE Samples with the Slope

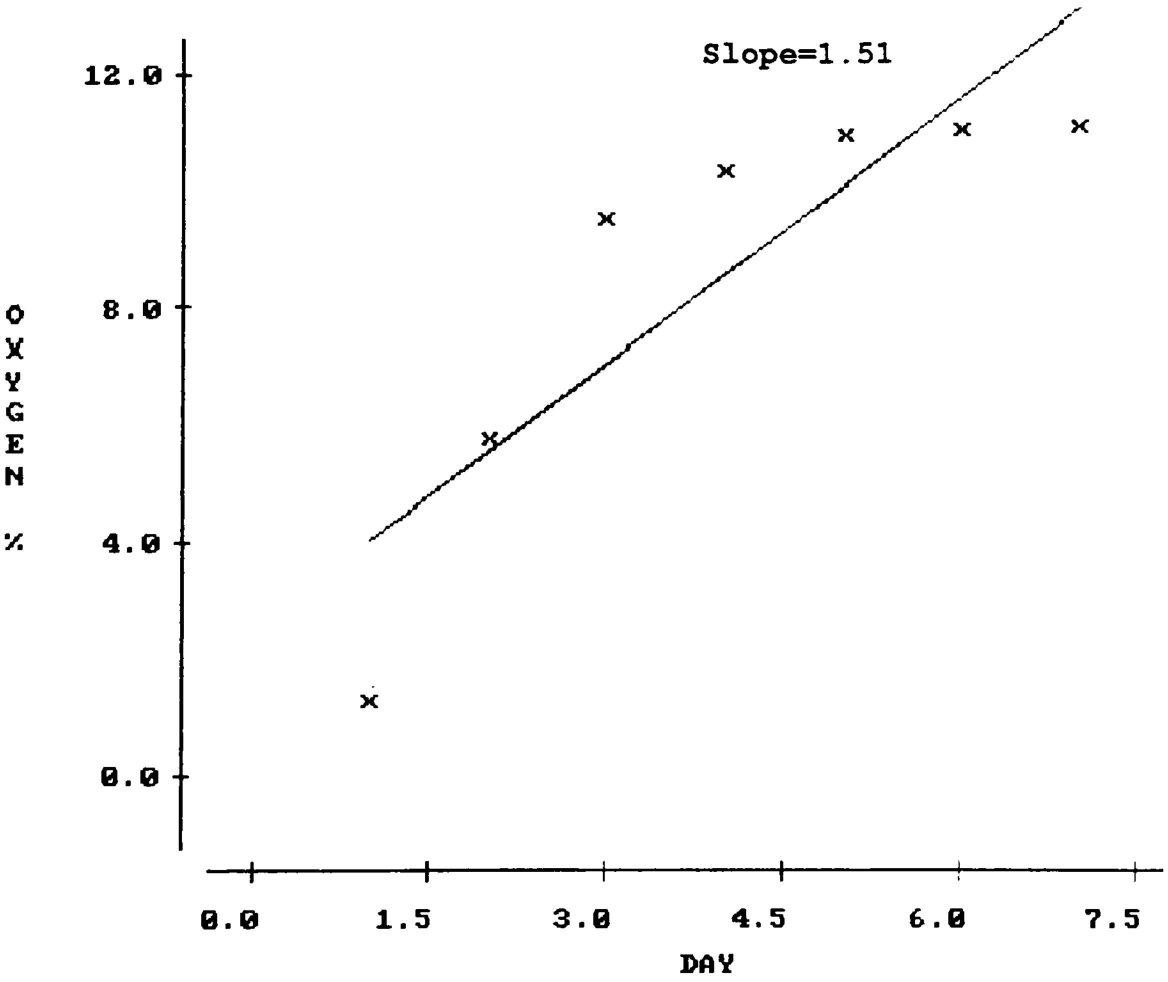


Figure (4) Mean Values of Oxygen Concentrations of Recycled HDPE Samples with the Slope

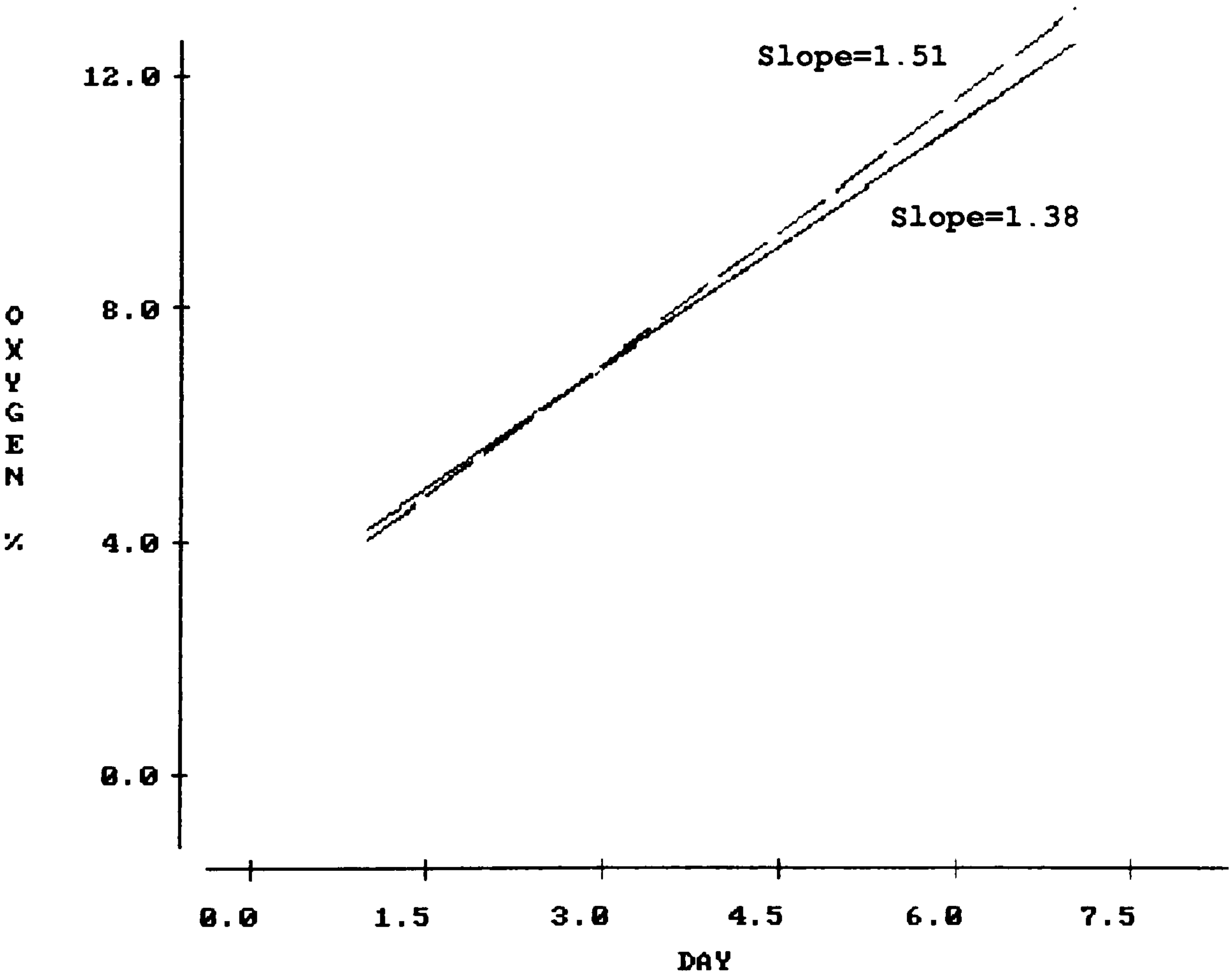


Figure (5) Comparison of the Slope of Virgin HDPE Samples and Recycled HDPE Samples

A more reliable testing of the differences between the oxygen permeability of both materials is to obtain every slope of each and every seven-day-set of data, for the two materials, and then to evaluate them using the t-test. The step of generating 60 permeation curves seems unnecessary and therefore is avoided, but regression analysis is necessary to obtain the slope of these sets of data. Appendix N shows the regression analysis of all sets of data with their corresponding straight-line equations.

Slopes are provided by the regression analysis and, from that analysis, Table 5 is made to lists 30 slopes for the virgin HDPE resins and another 30 slopes for the recycled HDPE resins. When Table 5 is tested, with the two-sample t-test, the results on Appendix O are obtained. The t-test indicates the means of the two sets of slopes are equal, on the significance level of 0.05, with a P-value of 0.21.

Table 5. Slopes Generated from the Regression Analysis in Appendix N

Sample Group	Slopes of Virgin HDPE	Slopes of Recycled HDPE
1)	1.60	1.61
2)	1.12	1.54
3)	1.05	1.75
4)	1.44	1.70
5)	1.40	1.53
6)	1.81	1.57
7)	1.70	1.79
8)	1.08	1.69
9)	0.685	1.27
10)	1.28	1.72
11)	0.024	1.29
12)	1.30	1.63
13)	0.981	1.53
14)	1.47	1.50
15)	1.49	1.72
16)	1.65	1.57
17)	1.52	1.35
18)	1.86	0.855
19)	1.49	1.78
20)	1.20	1.52
21)	0.631	1.59
22)	1.96	1.49
23)	1.72	1.50
24)	1.67	1.68
25)	0.881	1.64
26)	1.05	1.54
27)	1.88	1.76
28)	0.405	0.151
29)	1.67	1.45
30)	2.02	0.474

CONCLUSION AND RECOMMENDATIONS

The research project attempts to establish a link between the effects of recycling technologies on plastics' properties with what regulating agencies (especially FDA) view as essential requirements for the approval of using post-consumer polymers in food-contact applications. Insignificant difference of the oxygen permeation rates between the recycled and virgin HDPE is established and supported by empirical data.

In the evaluation of recycled and virgin HDPE films, the oxygen permeation rates of both appear to be the same. The data analysis performed on the experiment supports the null hypothesis. It shows that the means of the oxygen permeation rates of the virgin and 100% post-consumer HDPE films are not significantly different, on the significance level of 0.05.

The support of the null hypothesis is basically provided by two P-values which are generated from testing the data with the two-sample t-test. The first P-value (0.92) is the result of evaluating the daily means of the adjusted oxygen concentration (which are the daily percentages minus the extreme values). The second P-value (0.21) is generated by comparing the means of the slopes of all permeation curves obtained in this experiment. All of the P-values (0.92 and 0.21) are higher than the significance level (0.05) upon which the null hypothesis is established.

Therefore, the data doesn't provide sufficient evidence to prove the means of both materials are significantly different. Hence, since the means are equal, on the significance level of (0.05), it follows that the permeation rates of both materials are not significantly different. This indicates that post-consumer polymers can maintain an important requirement for food quality by exhibiting similar oxygen permeability profiles as their virgin counterparts. It is thus the recommendation of this study to address and promote the use of recycled materials in food packaging with more concrete analytical, technical, economical, and legal evaluations.

It is not the intention of this study to propose the use of any recycled materials in any particular food packaging applications. But this study tries to reveal the possibility that recycled materials may be almost identical in their properties to the virgin ones, a finding which may suggest that recycling technologies may have no significant effects on the permeability of the post-consumer polymers they produce. This also calls for further scientific investigation.

However, the empirical data presented in this project is the result of analyzing only two materials. It is plausible that other materials perform differently when recycled than in their virgin forms. It must be emphasized, therefore, that thorough examinations of the chemical, microbiological, and safety aspects of post-consumer polymeric materials and the technologies producing them must be completed before even attempting to carry out any permeability testings.

Identical permeability profiles of the recycled and virgin materials does not present adequate reasoning, by itself, to suggest the use of recycled plastics in food applications. In this regard, the permeability considerations should not supersede the safety factor of the recycled polymers. It is understandable that the agencies involved, especially FDA, have not explicitly stated that recycled materials can be used in food-contact or in food packaging application.

Despite the seemingly over-protective image of FDA, the agency is trying to establish some protocols (as mentioned in chapter two), that would help to resolve this issue. FDA's main concern is the public's safety around the issues of appropriate utilizations of recycled polymers in food-contact applications. The agency must be given credit for executing its obligations, and, at the same time, be given a chance to establish their long-awaited protocols.

However, it is of great importance that scientific research continues in examining the safety and microbiological profiles of recycled materials. Scientific research must identify the characteristic properties and impacts of these materials on food systems and on the interactions of the recycled-polymer and food pair.

Permeation studies of recycled materials beyond the seven-days period used in this experiment are strongly recommended. Such studies would help in examining any changes recycled materials may undergo as a function of long periods of time. These studies would also indicate the suitability of recycled materials for particular food products. They would show how recycled materials perform under different shelf life of one week, three months, or six months, etc. As a result, the shelf life of perspective food products may be estimated more precisely. In addition, examining the permeability of different recycled polymers to carbon dioxide, moisture, and organic vapors would aid in understanding the various facets of the performance of recycled polymers. Hopefully then, exact food products may be identified and suggested for specific recycled materials.

A final remark on this study is that food preservations technology comprise the applications of various basic and applied aspects of many scientific fields. Food packaging can be viewed as an integrating arena for many technologies and sciences to interact and complement each other for one cause, preservation of nutritive foods. This project is a step toward this goal. It does not propose the use of a new material or a new technology, but it does propose that recycled polymeric materials may contribute to the food preservation cause. Although the safety aspect can be precisely examined, it raises some controversial implications. Nonetheless, the fact remains that recycling technologies are able to produce functional materials that have limited applications in the food industry. It is, therefore, the obligation of scientific research to identify these applications and their risk factor.

Appendices

Appendix A:

The Estimated Maximum Oxygen Tolerance of Selected Food Products

The Estimated Maximum Oxygen Tolerance of Selected Food Products

Food/Beverage	Oxygen Sensitivity maximum O_2 tolerance (ppm)
1- Beer(pasteurized)	1-2
2- Typical Autoclaved Low-Acid Foods:	
canned milk	1-3
canned meats and vegetables	1-3
canned soups	1-3
baby foods	1-3
3- Fine Wine	2-5
4- Coffee (fresh ground)	2-5
5- Tomato-based products	3-8
6- High-acid fruit juices	8-20
7- Carbonate soft drinks	10-40
8- Oils and shortenings	20-50
9- Salad dressings, peanut butter	30-100
10-Liquor, jams, jellies	50-200 +

Source: Salame, M. (1989), p. 143.

Appendix B:

The Effect of Free Volume on Oxygen Permeability

The Effect of Free Volume on Oxygen Permeability

Polymer	Fractional Free volume	O_2 Permeability @ 25°C*
Poly 4-methyl pentene-1	0.204	24
Polystyrene	0.176	2.6
Polycarbonate	0.168	1.5
Polymethyl methacrylate	0.132	0.10
Nylon 6	0.120	0.045 (dry)
Polyvinylidene fluoride	0.098	0.030
Polyacrylonitrile	0.080	0.00060
Polyacrylonitrile (annealed)	0.050	0.00025
Polyvinyl alcohol (dry)	0.030	0.000025

*Units are $[(\mathrm{cc.cm})/(\mathrm{cm}^2.\mathrm{sec.cmHg})]$ X $10x^{10}$

Source: Salame, M. (1989), p. 136.

Appendix C:

A- The Effect of Humidity on Oxygen Permeability

B- The Swelling Effect on Oxygen Permeability

A- The Effect of Humidity on Oxygen Permeability

Polymer	P O_2 (cm^3/(mil day 100 in^2 atm)	
	Dry, at 0% r.h.	At 100% r.h.
HDPE	110.0	110.0
Polyvinyl alcohol	0.01	25.0
Uncoated cellulose	0.13	200.0
Nylon 6	1.0	5.0
Polyvinylacetate	55.0	150.0
Acrylonitrile-styrene copolymer	1.0	1.0
Polyester	7.0	6.0

Source: Ashley, R.J. (1986), p. 288

B- The Swelling Effect on Oxygen Permeability

Polymer	Condition	O_2 Permeation @ 25°C*
PE	dry	2.9
PE	100% RH	2.9
Polyacrylonitrile	dry	0.00060
Polyacrylonitrile	100% RH	0.00065
PET (oriented bottle)	dry	0.031
PET	100% RH	0.028
Polyvinyl alcohol	dry	0.000025
Polyvinyl alcohol	95% RH	0.012
Cellophane (uncoated)	dry	0.0008
Cellophane (uncoated)	100% RH	1.2
Nylon 6	dry	0.0070
Nylon 6	100% RH	0.030

*Units are [(cc.cm)/(cm^2.sec.cmHg)] X $10x^{10}$

Source: Salame, M. (1989), p. 137.

Appendix D:

The Effect of the Cohesive Energy Density on Permeability

The Effect of the Cohesive Energy Density on Permeability

Polymer	e_{coh} (cal/cc)	Permeation @ 25°C	
		O_2	H_2O
PE	66	2.9	100
Polystyrene	85	2.6	1,100
Polyvinylacetate	88	0.35	8,500
Polyvinylchloride	94	0.055	250
Polyacrylonitrile (unannealed film)	180	0.00060	300
Polyvinyl alcohol	220	0.000025 dry	water-soluble

*Units are [(cc.cm)/(cm^2.sec.cmHg)] X 10x^{10}

Source: Salame, M. (1989), p. 136.

Appendix E:

The Effect of Functional Groups on Oxygen Permeability

The Effect of Functional Groups on Oxygen Permeability

Nature of X in $-(CH_2-CHX-)-_n$	P O_2 (cm^3/(mil day 100 in^2 atm)
$-OH$	0.01
$-CN$	0.04
$-Cl$	8.0
$-F$	15.0
$-COOCH_3$	17.0
$-CH_3$	150.0
$-C_6H_5$	420.0
$-H$	480.0

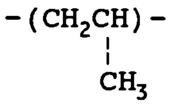
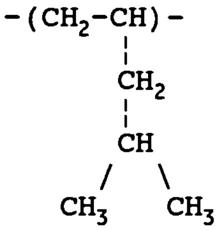
The unit of film thickness is mil., 1 mil=25 micro m.

Sources: Ashley, R.J. (1986), p. 285.

Appendix F:

The Effect of Chain Packing on Oxygen Permeability

The Effect of Chain Packing on Oxygen Permeability

Polymer	Structure	Packing Ability	**P** O_2 (cm^3/(mil day 100 in^2 atm)
HDPE	$-(CH_2-CH_2)-$	Good	110
PP	 $-(CH_2CH(CH_3))-$	Fair, hindrance of CH3 group	150
Poly-4-methyl penten-1	 $-(CH_2-CH(CH_2CH(CH_3)_2))-$	Poor, bulky side groups	400

Source: Ashley, R.J. (1986), p. 258.

Appendix G:

A: The Effect of Crystallinity on Permeability

B: The Effect of Crystallinity on Oxygen Permeability

A. The Effect of Crystallinity on Permeability.

Polymer	% Crystallinity	Permeability @25°C*	
		O_2	H_2O
PE (d=0.92)	43	2.9	100
PE (d=0.955)	74	0.58	18
PET	<10	0.075	500
PET	30	0.037	280
PET	45	0.022	190

*Units are [(cc.cm)/(cm^2.sec.cmHg)] X $10x^{10}$

Source: Salame, M. (1989), p. 134.

B. The Effect of Crystallinity on Oxygen Permeability

Polymer	% Crystallinity	P O_2 (cm^3/(mil day 100 in^2 atm)
LDPE	50	480
HDPE	80	110
Nylon 66, quenched	20	8.0
Nylon 66, annealed	40	1.5

Sources: Ashley, R.J. (1986), p. 286; and Osbron, K. R. and Jenkins, W. A. (1992), p. 91.

Appendix H:

The Affect of Glass Transition Temperature on Oxygen Permeability

The Affect of Glass Transition Temperature on Oxygen Permeability

Polymer	Tg (°C)	O_2 Permeability @ 25°C*
PE	-113	2.9
PP	-13	1.6
Polyvinyl acetate	28	0.35
PET	75	0.037
Polymethyl-acrylonitrile	120	0.0030

*Units are $[(cc.cm)/(cm^2.sec.cmHg)]$ X $10x^{10}$.

Source: Salame, M. (1989), p. 135.

Appendix I:

The Effect of Temperature on Oxygen Permeability

The Effect of Temperature on Oxygen Permeability

Polymer	Ep (kcal/mole)	O_2 Permeability* 25°C	 40°C	 Ratio
PETG	7	0.16	0.28	1.75
PET (bottle)	8.5	0.030	0.060	2.00
AN Copolymer (70% AN)	12	0.0060	0.016	2.67
PVDC Copolymer	19	0.0015	0.0070	4.67

*Units are [(cc.cm)/(cm^2.sec.cmHg)] X $10x^{10}$.

Source: Salame, M. (1989), p. 139.

Appendix J

A: Physical Properties of Virgin and Recycled HDPE Samples

B: Dimensions and Number of Compartments of All Samples

A: Physical Properties of Virgin and Recycled HDPE Samples

Physical Properties	Recycled HDPE	Virgin HDPE	Units	ASTM Test Method
Density	0.960+	0.960+	g/cm^3	D 1505
Melt Index	0.70	0.7	g/10 min.	D 1238
Tensile strength	4,100	4,400 @ break	psi	D 638
Elongation	400	>600 @ break	%	D 638
Flexural modulus	202,500	220,000	psi	D 790
Vicat softening point	125	125	°C	D 1525
Tensile impact	-	100	ft-Ib/in.	D 1822
Low temperature brittleness	< -76	< -76 (F_{50})	°C	D 746
Hardness, shore D	68	68		D 2240
Heat deflection temp.@ 66 psi	78	78	°C	D 648

B. Dimensions and Numbers of Compartments of All Samples

Pouches:	Rows	Compartments/ raw	Compartments/ pouch	Area in. X in.
Virgin A	7	5	35	12.00 X 10.00
Virgin B	7	5	35	10.75 X 10.50
Virgin C	7	5	35	12.40 X 10.50
Virgin D	7	5	35	12.00 X 10.50
Virgin E	7	5	35	12.42 X 10.00
Virgin F	7	5	35	11.60 X 10.00
Recycled A	7	5	35	11.00 X 11.00
Recycled B	7	5	35	10.75 X 10.75
Recycled C	7	5	35	10.75 X 10.75
Recycled D	7	5	35	11.00 X 10.75
Recycled E	7	5	35	10.50 X 10.50
Recycled F	7	5	35	10.75 X 10.75

Appendix K

A: ANOVA Test Showing the Means of the Oxygen Concentrations in Virgin Samples

B: ANOVA Test Showing the Means of the Oxygen Concnetrations in Recycled Samples

A: ANOVA Test Showing the Means of the Oxygen Concentrations in Virgin Samples

```
MTB > Oneway 'Virgin' 'Days'.

ANALYSIS OF VARIANCE ON Virgin
SOURCE      DF          SS          MS         F          p
Days         6     1767.20      294.53    141.97      0.000
ERROR      173      358.91        2.07
TOTAL      179     2126.11
                                    INDIVIDUAL 95 PCT CI'S FOR MEAN
                                        BASED ON POOLED STDEV

 LEVEL    N     MEAN  STDEV ----+---------+---------+---------+
   1     25    1.929  1.183    (*-)
   2     26    5.410  2.068               (-*-)
   3     26    9.637  2.192                              (-*-)
   4     24    9.819  1.375                              (-*-)
   5     28   10.149  1.137                              (-*-)
   6     28   10.845  0.711                              (-*-)
   7     23   10.928  0.531                               (-*-)

                              ----+---------+---------+---------+
POOLED STDEV =  1.440            3.0       6.0       9.0      12.0
```

B: ANOVA Test Showing the Means of the Oxygen Concnetrations in Recycled Samples

```
MTB > Oneway 'Recycled' 'Days'.

ANALYSIS OF VARIANCE ON Recycled
SOURCE     DF        SS        MS        F        p
Days        6  2083.118   347.186    518.27    0.000
ERROR     164   109.862     0.670
TOTAL     170  2192.980
                               INDIVIDUAL 95 PCT CI'S FOR MEAN
                                   BASED ON POOLED STDEV
LEVEL   N     MEAN STDEV ----+---------+---------+---------
   1    26    1.310  1.011  (*)
   2    18    5.770  1.067                 (*-)
   3    23    9.522  1.342                              (*)
   4    28   10.380  0.755                              (*)
   5    26   10.958  0.388                             (-*)
   6    26   11.062  0.396                              (*)
   7    24   11.086  0.316                               (*)

                          ----+---------+---------+---------
POOLED STDEV =  0.818        3.0       6.0       9.0
```

Appendix L

The Result of the TwoSample t-Test on the Means of the Oxygen Concentrations of Virgin and Recycled Samples

The Result of the TwoSample t-Test on the Means of the Oxygen Concentrations of Virgin and Recycled Samples

```
MTB > twosample 95.0 'VIR' 'Recy";
SUBC> alternative 0.

TWOSAMPLE T FOR VIR.Adj VS RECY.Adj
          N      MEAN     STDEV   SE MEAN
VIR.Adj   7      8.39      3.41       1.3
RECY.Adj  7      8.58      3.72       1.4

95 PCT CI FOR MU VIR.Adj - MU RECY.Adj: (-4.4, 4.0)

TTEST MU VIR.Adj = MU RECY.Adj (VS NE): T= -0.10  P=0.92
     DF=  11
```

Appendix M

A: The Regression Analysis Showing the Straight Line Equations for the Oxygen Permeation of Virgin Samples

B: The Regression Analysis Showing the Straight Line Equations for the Oxygen Permeation of Recyceld Samples

A: The Regression Analysis Showing the Straight Line Equation for the Oxygen Permeation of Virgin Samples

```
MTB > regress 'virgin' 1 'days'.

The regression equation is
Virgin = 2.89 + 1.38 Days

180 cases used 30 cases contain missing values
Predictor       Coef       Stdev    t-ratio        p
Constant      2.8916      0.3544       8.16    0.000
Days         1.38023     0.07945      17.37    0.000
s = 2.105       R-sq = 62.9%     R-sq(adj) = 62.7%

Analysis of Variance

SOURCE        DF          SS          MS         F         p
Regression     1      1337.3      1337.3    301.79     0.000
Error        178       788.8         4.4
Total        179      2126.1

Unusual Observations
Obs.   Days   Virgin      Fit   Stdev.Fit   Residual   St.Resid
 12    3.00   12.491     7.032      0.176      5.459      2.60R

 46    3.00    11.993    7.032      0.176      4.961      2.36R

 48    3.00    12.604    7.032      0.176      5.572      2.66R

 49    3.00    12.172    7.032      0.176      5.140      2.45R

 76    2.00    10.378    5.652      0.223      4.726      2.26R

 81    3.00    11.319    7.032      0.176      4.287      2.04R

117    3.00    11.879    7.032      0.176      4.847      2.31R

119    3.00    12.707    7.032      0.176      5.675      2.71R

120    3.00    12.588    7.032      0.176      5.556      2.65R

150    2.00     9.860    5.652      0.223      4.208      2.01R

151    3.00    11.258    7.032      0.176      4.226      2.01R

R denotes an obs. with a large st. resid.
```

B: The Regression Analysis Showing the Straight Line Equation for the Oxygen Permeation of Recyceld Samples

```
MTB > regress 'recycled' 1 'days'.

The regression equation is
Recycled = 2.54 + 1.51 Days

171 cases used 39 cases contain missing values

Predictor        Coef        Stdev    t-ratio        p
Constant       2.5444       0.3452       7.37    0.000
Days          1.50800      0.07613      19.81    0.000

s = 1.977       R-sq = 69.9%     R-sq(adj) = 69.7%

Analysis of Variance

SOURCE         DF          SS          MS         F         p
Regression      1      1532.7      1532.7    392.33     0.000
Error         169       660.2         3.9
Total         170      2193.0

Unusual Observations
Obs.  Days   Recycled  Fit     Stdev.Fit  Residual   St.Resid

  2    1.00   0.000      4.052      0.279    -4.052     -2.07R

  3    1.00   0.000      4.052      0.279    -4.052     -2.07R

  4    1.00   0.000      4.052      0.279    -4.052     -2.07R

  5    1.00   0.000      4.052      0.279    -4.052     -2.07R

 12    3.00   11.708     7.068      0.172     4.640      2.36R

 75    1.00    0.000     4.052      0.279    -4.052     -2.07R

 81    3.00   11.621     7.068      0.172     4.553      2.31R

186    3.00   11.386     7.068      0.172     4.318      2.19R

R denotes an obs. with a large st. resid.
MTB > nooutfile
```

Appendix N

A: Slopes and Straight Line Equations for the Virgin Samples

B: Slopes and Straight Line Equations for the Recycled Samples

A: Slopes and Straight Line Equations for the Virgin Samples

```
MTB > regress c20 1 c50

The regression equation is
Virg-A1 = 1.50 + 1.60 Day

Predictor        Coef       Stdev    t-ratio        p
Constant        1.500       1.340       1.12    0.314
Day            1.5964      0.2995       5.33    0.003

s = 1.585       R-sq = 85.0%     R-sq(adj) = 82.0%

Analysis of Variance

SOURCE       DF          SS          MS         F         p
Regression    1      71.357      71.357     28.41     0.003
Error         5      12.560       2.512
Total         6      83.918


MTB > regress c21 1 c50

The regression equation is
Virg_A2 = 3.62 + 1.12 Day

6 cases used 1 cases contain missing values

Predictor        Coef       Stdev    t-ratio        p
Constant        3.616       2.991       1.21    0.293
Day            1.1195      0.6579       1.70    0.164
s = 3.481       R-sq = 42.0%     R-sq(adj) = 27.5%

Analysis of Variance

SOURCE       DF          SS          MS         F         p
Regression    1       35.09       35.09      2.90     0.164
Error         4       48.47       12.12
Total         5       83.57

MTB > regress c22 1 c50

The regression equation is
Virg_A3 = 4.08 + 1.05 Day

5 cases used 2 cases contain missing values
Predictor        Coef       Stdev    t-ratio        p
Constant       4.0756      0.6786       6.01    0.009
Day            1.0472      0.1368       7.65    0.005
s = 0.5674      R-sq = 95.1%     R-sq(adj) = 93.5%
```

```
Analysis of Variance

SOURCE         DF          SS          MS         F         p
Regression      1      18.860      18.860     58.58     0.005
Error           3       0.966       0.322
Total           4      19.826


MTB > regress c23 1 c50

The regression equation is
Virg_A4 = 1.78 + 1.44 Day

6 cases used 1 cases contain missing values

Predictor        Coef        Stdev    t-ratio        p
Constant        1.779        2.151       0.83    0.455
Day            1.4359       0.4518       3.18    0.034

s = 2.183       R-sq = 71.6%     R-sq(adj) = 64.5%

Analysis of Variance

SOURCE         DF          SS          MS         F         p
Regression      1      48.107      48.107     10.10     0.034
Error           4      19.055       4.764
Total           5      67.162


MTB > regress c24 1 c50

The regression equation is
Virg_A5 = 2.02 + 1.40 Day

6 cases used 1 cases contain missing values

Predictor        Coef        Stdev    t-ratio        p
Constant        2.025        2.106       0.96    0.391
Day            1.3988       0.4634       3.02    0.039
s = 2.452       R-sq = 69.5%     R-sq(adj) = 61.9%

Analysis of Variance

SOURCE         DF          SS          MS         F         p
Regression      1      54.788      54.788      9.11     0.039
Error           4      24.046       6.011
Total           5      78.833

MTB > regress c25 1 c50

The regression equation is
Virg_B1 = 1.24 + 1.81 Day
```

```
5 cases used 2 cases contain missing values
Predictor       Coef       Stdev    t-ratio        p
Constant       1.236       3.233       0.38    0.728
Day           1.8149      0.8348       2.17    0.118
s = 3.462       R-sq = 61.2%     R-sq(adj) = 48.2%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1       56.66       56.66      4.73    0.118
Error         3       35.96       11.99
Total         4       92.62

MTB > regress c26 1 c50

The regression equation is
Virg_B2 = 1.73 + 1.70 Day

6 cases used 1 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant       1.730       2.267       0.76    0.488
Day           1.6971      0.5821       2.92    0.043
s = 2.435       R-sq = 68.0%     R-sq(adj) = 60.0%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      50.405      50.405      8.50    0.043
Error         4      23.721       5.930
Total         5      74.126


MTB > regress c27 1 c50

The regression equation is
Virg_B3 = 4.71 + 1.08 Day

Predictor       Coef       Stdev    t-ratio        p
Constant       4.707       2.637       1.78    0.134
Day           1.0791      0.5897       1.83    0.127

s = 3.120       R-sq = 40.1%     R-sq(adj) = 28.1%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      32.607      32.607      3.35    0.127
Error         5      48.686       9.737
Total         6      81.293
```

```
MTB > regress c28 1 c50

The regression equation is
Virg_B4 = 7.33 + 0.685 Day

6 cases used 1 cases contain missing values

Predictor         Coef         Stdev    t-ratio        p
Constant         7.334         2.457       2.99    0.041
Day             0.6851        0.5104       1.34    0.251

s = 2.135        R-sq = 31.1%     R-sq(adj) = 13.8%

Analysis of Variance

SOURCE       DF          SS          MS          F        p
Regression    1       8.213       8.213       1.80    0.251
Error         4      18.235       4.559
Total         5      26.448


MTB > regress c29 1 c50

The regression equation is
Virg_B5 = 3.85 + 1.28 Day

6 cases used 1 cases contain missing values

Predictor         Coef         Stdev    t-ratio        p
Constant         3.847         1.742       2.21    0.092
Day             1.2784        0.3729       3.43    0.027
s = 1.931        R-sq = 74.6%     R-sq(adj) = 68.3%

Analysis of Variance

SOURCE       DF          SS          MS          F        p
Regression    1      43.855      43.855      11.76    0.027
Error         4      14.921       3.730
Total         5      58.777


MTB > regress c30 1 c50

The regression equation is
Virg_C1 = 11.0 - 0.024 Day

4 cases used 3 cases contain missing values

Predictor         Coef         Stdev    t-ratio        p
Constant       11.0361        0.7808      14.13    0.005
Day            -0.0241        0.1768      -0.14    0.904
s = 0.6616       R-sq = 0.9%      R-sq(adj) = 0.0%
```

```
Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      0.0082      0.0082      0.02    0.904
Error         2      0.8754      0.4377
Total         3      0.8836


MTB > regress c31 1 c50

The regression equation is
Virg_C2 = 3.76 + 1.30 Day

5 cases used 2 cases contain missing values

Predictor        Coef       Stdev    t-ratio        p
Constant        3.763       1.806       2.08    0.129
Day            1.2970      0.3583       3.62    0.036

s = 1.650       R-sq = 81.4%     R-sq(adj) = 75.2%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      35.660      35.660     13.10    0.036
Error         3       8.166       2.722
Total         4      43.826


MTB > regress c32 1 c50

The regression equation is
Virg_C3 = 5.48 + 0.981 Day

5 cases used 2 cases contain missing values

Predictor        Coef       Stdev    t-ratio        p
Constant        5.476       1.393       3.93    0.029
Day            0.9815      0.2763       3.55    0.038
s = 1.272       R-sq = 80.8%     R-sq(adj) = 74.4%
Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      20.422      20.422     12.62    0.038
Error         3       4.855       1.618
Total         4      25.278


MTB > regress c33 1 c50

The regression equation is
Virg_C4 = 2.07 + 1.47 Day
```

```
Predictor       Coef       Stdev    t-ratio        p
Constant      2.0659      0.8080       2.56    0.051
Day           1.4706      0.1807       8.14    0.000

s = 0.9561      R-sq = 93.0%     R-sq(adj) = 91.6%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      60.555      60.555     66.25    0.000
Error         5       4.570       0.914
Total         6      65.126


MTB > regress c34 1 c50

The regression equation is
Virg_C5 = 2.55 + 1.49 Day

Predictor       Coef       Stdev    t-ratio        p
Constant       2.555       1.088       2.35    0.066
Day           1.4904      0.2433       6.13    0.002

s = 1.288       R-sq = 88.2%     R-sq(adj) = 85.9%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      62.199      62.199     37.52    0.002
Error         5       8.289       1.658
Total         6      70.487


MTB > regress c35 1 c50

The regression equation is
Virg_D1 = 1.50 + 1.65 Day

5 cases used 2 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant       1.498       2.790       0.54    0.629
Day           1.6544      0.7204       2.30    0.105

s = 2.988       R-sq = 63.7%     R-sq(adj) = 51.7%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      47.076      47.076      5.27    0.105
Error         3      26.777       8.926
Total         4      73.853
```

```
MTB > regress c36 1 c50

The regression equation is
Virg_D2 = 2.08 + 1.52 Day

4 cases used 3 cases contain missing values

Predictor        Coef        Stdev    t-ratio        p
Constant        2.083        4.558       0.46    0.692
Day             1.517        1.460       1.04    0.408

s = 4.318       R-sq = 35.1%     R-sq(adj) = 2.6%

Analysis of Variance

SOURCE       DF          SS          MS          F        p
Regression    1       20.14       20.14       1.08    0.408
Error         2       37.29       18.65
Total         3       57.43

Unusual Observations
Obs.   Day    Virg_D2     Fit   Stdev.Fit  Residual    St.Resid
  6    6.00       *     11.19     5.21         *           * X
  7    7.00       *     12.70     6.57         *           * X

X denotes an obs. whose X value gives it large influence.


MTB > regress c37 1 c50
The regression equation is
Virg_D3 = - 0.08 + 1.86 Day

Predictor        Coef        Stdev    t-ratio        p
Constant       -0.076        1.231      -0.06    0.953
Day            1.8560       0.2753       6.74    0.001

s = 1.457       R-sq = 90.1%     R-sq(adj) = 88.1%

Analysis of Variance

SOURCE       DF          SS          MS          F        p
Regression    1      96.453      96.453      45.45    0.001
Error         5      10.611       2.122
Total         6     107.064


MTB > regress c38 1 c50

The regression equation is
Virg_D4 = 3.26 + 1.49 Day
```

```
6 cases used 1 cases contain missing values
Predictor        Coef        Stdev    t-ratio        p
Constant        3.264        3.392       0.96    0.390
Day            1.4922       0.7125       2.09    0.104
s = 3.442       R-sq = 52.3%     R-sq(adj) = 40.4%

Analysis of Variance

SOURCE        DF         SS          MS          F        p
Regression     1      51.95       51.95       4.39    0.104
Error          4      47.38       11.85
Total          5      99.34


MTB > regress c39 1 c50

The regression equation is
Virg_D5 = 4.56 + 1.20 Day

6 cases used 1 cases contain missing values

Predictor        Coef        Stdev    t-ratio        p
Constant        4.561        2.562       1.78    0.150
Day            1.2035       0.5852       2.06    0.109

s = 3.031       R-sq = 51.4%     R-sq(adj) = 39.2%

Analysis of Variance

SOURCE        DF         SS          MS          F        p
Regression     1     38.864      38.864       4.23    0.109
Error          4     36.758       9.190
Total          5     75.623

MTB > regress c40 1 c50

The regression equation is
Virg_E1 = 7.10 + 0.631 Day
6 cases used 1 cases contain missing values

Predictor        Coef        Stdev    t-ratio        p
Constant        7.097        2.674       2.65    0.057
Day            0.6314       0.5556       1.14    0.319

s = 2.324       R-sq = 24.4%     R-sq(adj) = 5.5%

Analysis of Variance

SOURCE        DF         SS          MS          F        p
Regression     1      6.977       6.977       1.29    0.319
Error          4     21.605       5.401
Total          5     28.582
```

```
MTB > regress c41 1 c50

The regression equation is
Virg_E2 = 0.68 + 1.96 Day

6 cases used 1 cases contain missing values

Predictor        Coef       Stdev    t-ratio        p
Constant        0.681       1.280       0.53    0.623
Day            1.9619      0.3287       5.97    0.004

s = 1.375       R-sq = 89.9%     R-sq(adj) = 87.4%

Analysis of Variance

SOURCE        DF          SS          MS         F        p
Regression     1      67.356      67.356     35.62    0.004
Error          4       7.563       1.891
Total          5      74.920

MTB > regress c42 1 c50

The regression equation is
Virg_E3 = 1.12 + 1.72 Day

Predictor        Coef       Stdev    t-ratio        p
Constant        1.120       1.186       0.94    0.388
Day            1.7233      0.2652       6.50    0.001

s = 1.403       R-sq = 89.4%     R-sq(adj) = 87.3%

Analysis of Variance

SOURCE        DF          SS          MS         F        p
Regression     1      83.152      83.152     42.22    0.001
Error          5       9.848       1.970
Total          6      93.000

MTB > regress c43 1 c50

The regression equation is
Virg_E4 = 1.15 + 1.67 Day

Predictor        Coef       Stdev    t-ratio        p
Constant        1.154       1.380       0.84    0.441
Day            1.6703      0.3086       5.41    0.003

s = 1.633       R-sq = 85.4%     R-sq(adj) = 82.5%
```

```
Analysis of Variance
SOURCE       DF          SS          MS         F        p
Regression    1      78.116      78.116     29.30    0.003
Error         5      13.330       2.666
Total         6      91.446


MTB > regress c44 1 c50

The regression equation is
Virg_E5 = 6.02 + 0.881 Day

Predictor       Coef       Stdev    t-ratio        p
Constant       6.021       1.995       3.02    0.029
Day           0.8807      0.4461       1.97    0.105

s = 2.360       R-sq = 43.8%     R-sq(adj) = 32.6%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      21.718      21.718      3.90    0.105
Error         5      27.857       5.571
Total         6      49.575

Unusual Observations
Obs.    Day  Virg_E5    Fit    Stdev.Fit  Residual   St.Resid
  1    1.00    3.127    6.902      1.608    -3.775     -2.19R


R denotes an obs. with a large st. resid.


MTB > regress c45 1 c50

The regression equation is
Virg_F1 = 3.63 + 1.05 Day

6 cases used 1 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant       3.633       1.012       3.59    0.023
Day           1.0491      0.2600       4.04    0.016

s = 1.087       R-sq = 80.3%     R-sq(adj) = 75.4%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      19.260      19.260     16.29    0.016
Error         4       4.730       1.183
Total         5      23.990
```

```
MTB > regress c46 1 c50

The regression equation is
Virg_F2 = 0.32 + 1.88 Day

6 cases used 1 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant       0.324       1.131       0.29    0.789
Day           1.8785      0.2904       6.47    0.003

s = 1.215       R-sq = 91.3%     R-sq(adj) = 89.1%

Analysis of Variance

SOURCE       DF          SS          MS         F         p
Regression    1      61.756      61.756     41.84     0.003
Error         4       5.904       1.476
Total         5      67.661


MTB > regress c47 1 c50

The regression equation is
Virg_F3 = 7.25 + 0.405 Day

6 cases used 1 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant      7.2524      0.6305      11.50    0.000
Day           0.4048      0.1310       3.09    0.037
s = 0.5480      R-sq = 70.5%     R-sq(adj) = 63.1%

Analysis of Variance
SOURCE       DF          SS          MS         F         p
Regression    1      2.8672      2.8672      9.55     0.037
Error         4      1.2010      0.3003
Total         5      4.0682

MTB > regress c48 1 c50

The regression equation is
Virg_F4 = 1.01 + 1.67 Day

Predictor       Coef       Stdev    t-ratio        p
Constant       1.010       1.574       0.64    0.549
Day           1.6697      0.3519       4.75    0.005

s = 1.862       R-sq = 81.8%     R-sq(adj) = 78.2%
```

```
Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      78.059      78.059     22.52    0.005
Error         5      17.335       3.467
Total         6      95.394


MTB > regress c49 1 c50

The regression equation is
Virg_F5 = - 1.03 + 2.02 Day

Predictor       Coef       Stdev    t-ratio        p
Constant      -1.030       2.758      -0.37    0.724
Day           2.0177      0.6168       3.27    0.022

s = 3.264       R-sq = 68.2%     R-sq(adj) = 61.8%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      113.99      113.99     10.70    0.022
Error         5       53.26       10.65
Total         6      167.25
```

B: Slopes and Straight Line Equations for the Recycled Samples

```
MTB > regress c60 1 c50

The regression equation is
Recy_A1 = 1.77 + 1.61 Day

6 cases used 1 cases contain missing values

Predictor        Coef        Stdev    t-ratio        p
Constant        1.767        2.098       0.84    0.447
Day            1.6116       0.4491       3.59    0.023

s = 2.326        R-sq = 76.3%     R-sq(adj) = 70.4%

Analysis of Variance

SOURCE        DF           SS           MS          F         p
Regression     1       69.696       69.696      12.88     0.023
Error          4       21.645        5.411
Total          5       91.341


MTB > regress c61 1 c50

The regression equation is
Recy_A2 = 2.47 + 1.54 Day

6 cases used 1 cases contain missing values

Predictor        Coef        Stdev    t-ratio        p
Constant        2.468        3.344       0.74    0.501
Day            1.5359       0.7024       2.19    0.094

s = 3.393        R-sq = 54.4%     R-sq(adj) = 43.1%

Analysis of Variance

SOURCE        DF           SS           MS          F         p
Regression     1        55.04        55.04       4.78     0.094
Error          4        46.05        11.51
Total          5       101.10


MTB > regress c62 1 c50

The regression equation is
Recy_A3 = 0.64 + 1.75 Day
```

```
4 cases used 3 cases contain missing values
Predictor        Coef        Stdev    t-ratio        p
Constant        0.642        3.070       0.21    0.854
Day            1.7476       0.7339       2.38    0.140

s = 3.363       R-sq = 73.9%     R-sq(adj) = 60.9%

Analysis of Variance

SOURCE        DF          SS          MS          F        p
Regression     1       64.13       64.13       5.67    0.140
Error          2       22.62       11.31
Total          3       86.76


MTB > regress c63 1 c50

The regression equation is
Recy_A4 = 1.07 + 1.70 Day

6 cases used 1 cases contain missing values

Predictor        Coef        Stdev    t-ratio        p
Constant        1.070        2.395       0.45    0.678
Day            1.6952       0.5030       3.37    0.028
s = 2.430       R-sq = 74.0%     R-sq(adj) = 67.4%

Analysis of Variance

SOURCE        DF          SS          MS          F        p
Regression     1      67.054      67.054      11.36    0.028
Error          4      23.614       5.904
Total          5      90.668


MTB > regress c64 1 c50

The regression equation is
Recy_A5 = 2.51 + 1.53 Day

Predictor        Coef        Stdev    t-ratio        p
Constant        2.509        2.240       1.12    0.314
Day            1.5269       0.5009       3.05    0.028

s = 2.651       R-sq = 65.0%     R-sq(adj) = 58.0%

Analysis of Variance

SOURCE        DF          SS          MS          F        p
Regression     1      65.279      65.279       9.29    0.028
Error          5      35.128       7.026
Total          6     100.407
```

```
Unusual Observations
Obs.       Day    Recy_A5           Fit  Stdev.Fit   Residual
St.Resid
  1      1.00        0.00        4.04        1.81       -4.04
-2.08R

R denotes an obs. with a large st. resid.


MTB > regress c65 1 c50

The regression equation is
Recy_B1 = 1.90 + 1.57 Day

6 cases used 1 cases contain missing values

Predictor         Coef         Stdev    t-ratio        p
Constant         1.896         1.375       1.38    0.240
Day             1.5710        0.2943       5.34    0.006

s = 1.525       R-sq = 87.7%     R-sq(adj) = 84.6%

Analysis of Variance

SOURCE        DF          SS          MS         F         p
Regression     1      66.222      66.222     28.49     0.006
Error          4       9.297       2.324
Total          5      75.519


MTB > regress c66 1 c50

The regression equation is
Recy_B2 = 0.29 + 1.79 Day

5 cases used 2 cases contain missing values

Predictor         Coef         Stdev    t-ratio        p
Constant         0.292         2.357       0.12    0.909
Day             1.7909        0.4676       3.83    0.031

s = 2.153       R-sq = 83.0%     R-sq(adj) = 77.4%

Analysis of Variance

SOURCE        DF          SS          MS         F         p
Regression     1      67.999      67.999     14.67     0.031
Error          3      13.906       4.635
Total          4      81.905
```

```
MTB > regress c67 1 c50

The regression equation is
Recy_B3 = 1.96 + 1.69 Day
3 cases used 4 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant      1.9649      0.9765       2.01    0.294
Day           1.6899      0.2521       6.70    0.094
s = 0.5447      R-sq = 97.8%     R-sq(adj) = 95.6%

Analysis of Variance

SOURCE       DF          SS          MS         F         p
Regression    1      13.326      13.326     44.92     0.094
Error         1       0.297       0.297
Total         2      13.623

Unusual Observations
Obs.  Day  Recy_B3     Fit    Stdev.Fit  Residual    St.Resid
  1   1.00       *     3.655     0.742         *          * X
  6   6.00       *    12.104     0.667         *          * X
  7   7.00       *    13.794     0.897         *          * X

X denotes an obs. whose X value gives it large influence.


MTB > regress c68 1 c50

The regression equation is
Recy_B4 = 2.86 + 1.27 Day

4 cases used 3 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant       2.862       1.769       1.62    0.247
Day           1.2743      0.3730       3.42    0.076

s = 1.902       R-sq = 85.4%     R-sq(adj) = 78.1%

Analysis of Variance

SOURCE       DF          SS          MS         F         p
Regression    1      42.218      42.218     11.67     0.076
Error         2       7.234       3.617
Total         3      49.452

MTB > regress c69 1 c50

The regression equation is
Recy_B5 = 1.35 + 1.72 Day
```

```
Predictor        Coef        Stdev    t-ratio        p
Constant        1.348        1.585       0.85    0.434
Day            1.7179       0.3544       4.85    0.005

s = 1.875       R-sq = 82.5%     R-sq(adj) = 78.9%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      82.636      82.636     23.49    0.005
Error         5      17.587       3.517
Total         6     100.223


MTB > regress c70 1 c50

The regression equation is
Recy_C1 = 4.03 + 1.29 Day

Predictor        Coef        Stdev    t-ratio        p
Constant        4.028        1.986       2.03    0.098
Day            1.2927       0.4442       2.91    0.033

s = 2.350       R-sq = 62.9%     R-sq(adj) = 55.5%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      46.791      46.791      8.47    0.033
Error         5      27.621       5.524
Total         6      74.412


MTB > regress c71 1 c50

The regression equation is
Recy_C2 = 1.53 + 1.63 Day

6 cases used 1 cases contain missing values

Predictor        Coef        Stdev    t-ratio        p
Constant        1.534        2.194       0.70    0.523
Day            1.6301       0.4608       3.54    0.024

s = 2.226       R-sq = 75.8%     R-sq(adj) = 69.7%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      62.001      62.001     12.51    0.024
Error         4      19.819       4.955
Total         5      81.820
```

```
MTB > regress c72 1 c50

The regression equation is
Recy_C3 = 2.15 + 1.53 Day


Predictor       Coef       Stdev    t-ratio        p
Constant       2.151       1.255       1.71    0.147
Day           1.5346      0.2805       5.47    0.003

s = 1.484       R-sq = 85.7%     R-sq(adj) = 82.8%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      65.944      65.944     29.93    0.003
Error         5      11.017       2.203
Total         6      76.961


MTB > regress c73 1 c50

The regression equation is
Recy_C4 = 2.48 + 1.50 Day

Predictor       Coef       Stdev    t-ratio        p
Constant       2.478       1.426       1.74    0.143
Day           1.5047      0.3188       4.72    0.005

s = 1.687       R-sq = 81.7%     R-sq(adj) = 78.0%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      63.397      63.397     22.28    0.005
Error         5      14.225       2.845
Total         6      77.622


MTB > regress c74 1 c50

The regression equation is
Recy_C5 = 0.51 + 1.72 Day

5 cases used 2 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant       0.514       2.471       0.21    0.848
Day           1.7206      0.5045       3.41    0.042

s = 2.430       R-sq = 79.5%     R-sq(adj) = 72.7%
```

```
Analysis of Variance

SOURCE        DF          SS          MS         F         p
Regression     1      68.681      68.681     11.63     0.042
Error          3      17.712       5.904
Total          4      86.393


MTB > regress c75 1 c50

The regression equation is
Recy_D1 = 2.80 + 1.57 Day

6 cases used 1 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant       2.798       1.675       1.67    0.170
Day           1.5702      0.4301       3.65    0.022

s = 1.799       R-sq = 76.9%     R-sq(adj) = 71.1%

Analysis of Variance

SOURCE        DF          SS          MS         F         p
Regression     1      43.145      43.145     13.33     0.022
Error          4      12.950       3.238
Total          5      56.096


MTB > regress c76 1 c50

The regression equation is
Recy_D2 = 3.76 + 1.35 Day

6 cases used 1 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant       3.765       2.097       1.80    0.147
Day           1.3454      0.4404       3.06    0.038

s = 2.127       R-sq = 70.0%     R-sq(adj) = 62.5%

Analysis of Variance

SOURCE        DF          SS          MS         F         p
Regression     1      42.236      42.236      9.33     0.038
Error          4      18.101       4.525
Total          5      60.337
```

```
MTB > regress c77 1 c50

The regression equation is
Recy_D3 = 5.99 + 0.855 Day
5 cases used 2 cases contain missing values

Predictor        Coef        Stdev    t-ratio        p
Constant        5.992        1.427       4.20    0.025
Day            0.8552       0.2989       2.86    0.065
s = 1.240       R-sq = 73.2%     R-sq(adj) = 64.2%
Analysis of Variance

SOURCE        DF          SS          MS         F         p
Regression     1      12.578      12.578      8.18     0.065
Error          3       4.610       1.537
Total          4      17.189


MTB > regress c78 1 c50

The regression equation is
Recy_D4 = 1.22 + 1.78 Day

5 cases used 2 cases contain missing values

Predictor        Coef        Stdev    t-ratio        p
Constant        1.225        2.744       0.45    0.686
Day            1.7783       0.5445       3.27    0.047

s = 2.507       R-sq = 78.1%     R-sq(adj) = 70.7%

Analysis of Variance

SOURCE        DF          SS          MS         F         p
Regression     1      67.042      67.042     10.67     0.047
Error          3      18.853       6.284
Total          4      85.895


MTB > regress c79 1 c50

The regression equation is
Recy_D5 = 2.34 + 1.52 Day

6 cases used 1 cases contain missing values

Predictor        Coef        Stdev    t-ratio        p
Constant        2.344        2.217       1.06    0.350
Day            1.5201       0.4657       3.26    0.031

s = 2.250       R-sq = 72.7%     R-sq(adj) = 65.9%
```

```
Analysis of Variance

SOURCE        DF          SS          MS         F         p
Regression     1      53.919      53.919     10.65     0.031
Error          4      20.245       5.061
Total          5      74.164


MTB > regress c80 1 c50

The regression equation is
Recy_E1 = 2.49 + 1.59 Day
Predictor        Coef       Stdev    t-ratio        p
Constant        2.489       1.354       1.84    0.126
Day            1.5882      0.3029       5.24    0.003

s = 1.603       R-sq = 84.6%     R-sq(adj) = 81.5%

Analysis of Variance

SOURCE        DF          SS          MS         F         p
Regression     1      70.628      70.628     27.50     0.003
Error          5      12.842       2.568
Total          6      83.470


MTB > regress c81 1 c50

The regression equation is
Recy_E2 = 2.45 + 1.49 Day

Predictor        Coef       Stdev    t-ratio        p
Constant        2.445       1.934       1.26    0.262
Day            1.4884      0.4325       3.44    0.018

s = 2.288       R-sq = 70.3%     R-sq(adj) = 64.4%

Analysis of Variance

SOURCE        DF          SS          MS         F         p
Regression     1      62.029      62.029     11.84     0.018
Error          5      26.184       5.237
Total          6      88.213


MTB > regress c82 1 c50

The regression equation is
Recy_E3 = 2.02 + 1.50 Day
```

```
6 cases used 1 cases contain missing values

Predictor        Coef       Stdev    t-ratio        p
Constant        2.024       2.272       0.89    0.423
Day            1.5009      0.5190       2.89    0.044

s = 2.688       R-sq = 67.6%     R-sq(adj) = 59.6%

Analysis of Variance
SOURCE       DF          SS          MS         F         p
Regression    1      60.446      60.446      8.36     0.044
Error         4      28.908       7.227
Total         5      89.354


MTB > regress c83 1 c50

The regression equation is
Recy_E4 = 1.28 + 1.68 Day

5 cases used 2 cases contain missing values

Predictor        Coef       Stdev    t-ratio        p
Constant        1.285       2.489       0.52    0.641
Day            1.6816      0.5565       3.02    0.057

s = 2.489       R-sq = 75.3%     R-sq(adj) = 67.0%

Analysis of Variance

SOURCE       DF          SS          MS         F         p
Regression    1      56.552      56.552      9.13     0.057
Error         3      18.580       6.193
Total         4      75.132


MTB > regress c84 1 c50

The regression equation is
Recy_E5 = 1.54 + 1.64 Day

Predictor        Coef       Stdev    t-ratio        p
Constant        1.538       1.415       1.09    0.327
Day            1.6362      0.3164       5.17    0.004
s = 1.674       R-sq = 84.2%     R-sq(adj) = 81.1%

Analysis of Variance

SOURCE       DF          SS          MS         F         p
Regression    1      74.963      74.963     26.74     0.004
Error         5      14.016       2.803
Total         6      88.980
```

```
MTB > regress c85 1 c50

The regression equation is
Recy_F1 = 3.69 + 1.54 Day

5 cases used 2 cases contain missing values
Predictor       Coef       Stdev    t-ratio        p
Constant       3.691       2.813       1.31    0.281
Day           1.5445      0.6743       2.29    0.106

s = 2.594       R-sq = 63.6%     R-sq(adj) = 51.5%

Analysis of Variance

SOURCE       DF          SS          MS          F        p
Regression    1      35.305      35.305       5.25    0.106
Error         3      20.185       6.728
Total         4      55.490


MTB > regress c86 1 c50

The regression equation is
Recy_F2 = 2.30 + 1.76 Day

5 cases used 2 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant       2.299       3.335       0.69    0.540
Day           1.7599      0.7996       2.20    0.115
 s = 3.076       R-sq = 61.8%     R-sq(adj) = 49.0%

Analysis of Variance

SOURCE       DF          SS          MS          F        p
Regression    1      45.840      45.840       4.84    0.115
Error         3      28.384       9.461
Total         4      74.224

MTB > regress c87 1 c50

The regression equation is
Recy_F3 = 10.6 + 0.151 Day

3 cases used 4 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant      10.564       1.029      10.27    0.062
Day           0.1515      0.2520       0.60    0.655

s = 0.3564      R-sq = 26.5%     R-sq(adj) = 0.0%
```

```
Analysis of Variance
SOURCE        DF          SS            MS          F        p
Regression     1      0.0459        0.0459       0.36    0.655
Error          1      0.1270        0.1270
Total          2      0.1729

Unusual Observations
Obs.   Day    Recy_F3    Fit      Stdev.Fit  Residual    St.Resid
  1    1.00      *      10.716     0.784        *           * X
  2    2.00      *      10.867     0.544        *           * X
  6    6.00      *      11.473     0.544        *           * X
  7    7.00      *      11.624     0.784        *           * X

X denotes an obs. whose X value gives it large influence.


MTB > regress c88 1 c50

The regression equation is
Recy_F4 = 3.74 + 1.45 Day

6 cases used 1 cases contain missing values

Predictor         Coef         Stdev     t-ratio         p
Constant         3.739         2.071        1.81     0.145
Day             1.4455        0.5319        2.72     0.053
s = 2.225        R-sq = 64.9%     R-sq(adj) = 56.1%

Analysis of Variance
SOURCE        DF          SS            MS          F        p
Regression     1      36.565        36.565       7.39    0.053
Error          4      19.801         4.950
Total          5      56.366


MTB > regress c89 1 c50

The regression equation is
Recy_F5 = 8.18 + 0.474 Day

6 cases used 1 cases contain missing values

Predictor         Coef         Stdev     t-ratio         p
Constant         8.183         1.315        6.23     0.003
Day             0.4738        0.2731        1.73     0.158

s = 1.142        R-sq = 42.9%     R-sq(adj) = 28.7%
Analysis of Variance
SOURCE        DF          SS            MS          F        p
Regression     1       3.928         3.928       3.01    0.158
Error          4       5.221         1.305
Total          5       9.149
```

Appendix O

TwoSample t-Test on the Slopes of the Virgin and Recycled Samples

TwoSample t-Test on the Slopes of the Virgin and Recycled Samples

```
MTB > print c91 c92

 ROW   V_slope  R_Slope

   1     1.600    1.610
   2     1.120    1.540
   3     1.050    1.750
   4     1.440    1.700
   5     1.400    1.530
   6     1.810    1.570
   7     1.700    1.790
   8     1.080    1.690
   9     0.685    1.270
  10     1.280    1.720
  11     0.024    1.290
  12     1.300    1.630
  13     0.981    1.530
  14     1.470    1.500
  15     1.490    1.720
  16     1.650    1.570
  17     1.520    1.350
  18     1.860    0.855
  19     1.490    1.780
  20     1.200    1.520
  21     0.631    1.590
  22     1.960    1.490
  23     1.720    1.500
  24     1.670    1.680
  25     0.881    1.640
  26     1.050    1.540
  27     1.880    1.760
  28     0.405    0.151
  29     1.670    1.450
  30     2.020    0.474

MTB > twosample 95.0 c91 c92;
SUBC> alternative 0.

TWOSAMPLE T FOR V_slope VS R_Slope
           N       MEAN      STDEV   SE MEAN
V_slope   30      1.335      0.476     0.087
R_Slope   30      1.473      0.369     0.067

95 PCT CI FOR MU V_slope - MU R_Slope: (-0.359, 0.082)

TTEST MU V_slope = MU R_Slope (VS NE): T= -1.26 P=0.21  DF=54

MTB > nooutfile
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BIBLIOGRAPHY

Anonymous. (1994, October). New packaging regulations boost demand for recycled HDPE. Chemicalweek, p. 16.

Amini, A. Mary. (1986). Testing, permeation and leakage. In Marilyn Backer and David Eckroth (Eds.), The Wiley Encyclopedia of Packaging Technology (pp. 650-654). New York: John Wiley & Sons.

Ashley, R. J. (1986). Permeability and plastics packaging. In J. Comyn (Ed.), Polymer permeability (pp. 269-308). London: Elsevier Applied Science.

Backer, M., & Gigliotti. M. (1993). Worldwide environmental contrasts- North America. In Geoffrey M. Levy (Ed.), Packaging in the Environment (pp. 212-244). London: Blackie Academia & Professional.

Begley, Timothy H., & Hollifield, Henry C. (1993, November). Recycled polymers in food packaging: Migration considerations. Food Technology, pp. 109-112.

Bennett, Robert A. (1992). Recycling plastics: Product application and potential. In G. D. Andrews, & P. Subramanian (Eds.), Emerging technology in plastics recycling (pp. 26-38). Washington, DC: American Chemical Society.

Billmeyer, Fred W. (1984). Textbook of polymer science (pp. 344-347). Singapore: A Wiley-Interscience Publication, John Wiley & Sons.

Blatz, Philip S. (1992). Properties of high-density polyethylene from postconsumer recycled containers. In G. D. Andrews, & P. Subramanian (Eds.), Emerging technology in plastics recycling (pp. 258-265). Washington, DC: American Chemical Society.

Boettcher, Peter F. (1992). Environmental compatibility of polymers. In G. D. Andrews, & P. Subramanian (Eds.), Emerging technology in plastics recycling (pp. 16-25). Washington, DC: American Chemical Society.

Bonis, Laszlo J. (1989). Correlation of coextruded barrier sheet properties with packaged food quality. In Kier M. Finlayson (Ed.), Plastic film technology: High barrier plastic films for packaging (pp. 80-94). Lancaster, PA. USA: Technomic.

Boone, J., Lox, F., & Pottie, S. (1993). Deficiencies of polypropylene in its use as a food-packaging materials: A review. Packaging Technology and Science, 6(5), 277-281.

Bourque, Raymond A. (1989). Shelf life of fruit juices in oxygen permeable packages. In Kier M. Finlayson (Ed.), *Plastic film technology: High barrier plastic films for packaging* (pp. 32-40). Lancaster, PA. USA: Technomic.

Boyer, Raymond F. (1985). Evidence from T_{ll} and related phenomena from local structure in the amorphous state of polymers. In S. E. Keinath, R. L. Miller, & J. K. Rieke (Eds.), *Order in the amorphous state of polymers* (pp. 135-185). New York: Plenum Press.

Briston, J. H. (1980). Rigid Plastics Packaging. In S. J. Palling (Ed.), *Developments in food packaging-1* (pp. 27-53). London: Applied Science.

Bruck, C., Bieber, W., & Figge, K. (1986). Interaction between food and packaging materials and its consequence on migration. In M. Mathlouthi (Ed.), *Food packaging and preservation: Theory and practice* (pp. 39-66). London: Elsevier Applied Science.

Brydson, J. A. (1982). *Plastics Materials.* London: Butterworth Scientific.

Cao, L., Ramer, R. M., & Beatty, C. L. (1992). Evaluation of mechanical properties of recycled commingled post materials. In G. D. Andrews, & P. Subramanian (Eds.), *Emerging technology in plastics recycling* (pp. 88-112). Washington, DC: American Chemical Society.

Carg, Sunil K. (1993, March). Plastics in packaging- an environmental law perspective. Paper presented at Denver, Colorado Meeting. *Polymer Preprints*, *34*(1), 915-916. The Division of Polymer Chemistry, American Chemical Society.

Culter, John D. (1989). Improving barrier through orientation in processing. In Kier M. Finlayson (Ed.), *Plastic film technology: High barrier plastic films for packaging* (pp. 51-61). Lancaster, PA. USA: Technomic.

Devore, Jay, L. (1987). *Probability and Statistics for Engineering and The Science*. Montery, California: Brooks/Cole.

Dubois, Harry J., & John, Frederick W. (1974). *Plastics*. New York: Van Nostrand Reinhold.

FDA. (1992, December). *Points to consider for the use of recycled plastics in food packaging: Chemistry consideration*. Chemistry Review Branch, Indirect Additives Branch, HFS-216. Food and Drug Admin., 200 C Street, S.W., Washington, DC 20204.

Finch, Charles. (1992, a). Properties of plastics used in food packaging: Barrier design. In William E. Brown, Plastics in food packaging (chapter 4). New York: Marcel Decker.

Finch, Charles. (1992, b). Barrier design. In William E. Brown, Plastics in food packaging (chapter 8). New York: Marcel Decker.

Gamber, Glenn. (1991). Current regulatory initiatives on plastic packages: Industry's stake in the market as regulator. Proceedings from The Eighth Annual FoodPlas Conference March 5-7, 1991 Orlando, Florida (pp. 241-250). Lancaster, PA. USA: Technomic.

Gavare, R., Hernandez, R. J. & Giacin, J. (1993, June). Comparative study of experimental methods to determine the partition of organic components in water/polymer system. Proceedings of the IAPRI 8th World Conference on Packaging, 20-23 June 1993 (p. 846). Anhembi Convention Center: SAO Paulo, Brazil: Food Packaging Technology Center.

Gray, J. Ian, Harte, Bruce R., & Miltz, Joseph (Eds.). (1987). Food product-package compatibility. Lancaster, PA. USA: Technomic.

Guarino, Elizabeth. (1991). The regulations of plastics packaging: What's coming. Proceedings from The Eighth Annual FoodPlas Conference March 5-7, 1991 Orlando, Florida (pp. 190-203). Lancaster, PA. USA: Technomic.

Heckman, Jerome, and Foley, John. (1993). Review of environmental legislation- North America. In Geoffrey M. Levy (Ed.), Packaging in the Environment (pp. 73-86). London: Blackie Academia & Professional.

Henyon, Debra (Ed.). (1991). Food packaging technology. STP 1113. Philadelphia, PA.: ASTM.

Hotchkiss, Joseph H. (Ed.). (1988). Food and packaging interactions. ACS Symposium Series 365. Washington, DC: American Chemical Society.

Jasse, B. (1986). Orientation and properties of some polymers used in the foodstuffs packaging industry. In M. Mathlouthi (Ed.), Food packaging and preservation: Theory and practice (pp. 283-324). London: Elsevier Applied Science.

Jenkins, Wilmer A., & Harrington, James P. (1991). Packaging foods with plastics. Lancaster, PA. USA: Technomic.

Johnson, E. (1993). Worldwide environmental contrasts- Europe. In Geoffrey M. Levy (Ed.), Packaging in the Environment (pp. 187-211). London: Blackie Academia & Professional.

Kadoya, Takashi (Ed.). (1990). Food packaging. San Diego, USA: Academic Press.

Kruger, J. K., & Pietralla, M. (1985). Evidence for the transition-like phenomena in oligomers and polymers above their melt transition. In S. E. Keinath, R. L. Miller, & J. K. Rieke (Eds.), Order in the amorphous state of polymers (pp. 281-304). New York: Plenum Press.

Layman, Bill. (1991). What's it going to be: Flexible, rigid, microwaveable, dual ovenable, or what? Proceedings from The Eighth Annual FoodPlas Conference March 5-7, 1991 Orlando, Florida (pp. 161-173). Lancaster, PA. USA: Technomic.

Leaversuch, Robert D. (1993, July). Recycling. Modern Plastic, p. 64.

Lox, Frans. (1992, a). Safety and toxicity of packaging. Packaging and ecology, (chapter 6). UK: Pira International.

Lox, Frans. (1992, b). Packaging materials. Packaging and ecology (pp. 125-152). UK: Pira International.

Machuga, Edward J., Pauli, George H., & Rulis, Alan M. (1992). A threshold of regulation policy for food-contact articles. Food Control, 3(4), 180-182.

Mapleston, Peeter. (1993, November). Chemical recycling may be an option to meet mandated reclaim levels. Modern Plastics, p. 58.

Mathlouthi, M. (Ed.). (1986). Food packaging and preservation: Theory and practice. London: Elsevier Applied Science.

Maxwell, Bryce. (1985). Rheological studies of amorphous polystyrene above Tg. In S. E. Keinath, R. L. Miller, & J. K. Rieke (Eds.), Order in the amorphous state of polymers (pp. 395-414). New York: Plenum Press.

Miki, H., & Oki, Y. (1993). Worldwide environmental contrasts- Japan. In Geoffrey M. Levy (Ed.), Packaging in the Environment (pp. 245-265). London: Blackie Academia & Professional.

Minitab (mini-manual). (1992). A beginner's guide to minitab. Lebanon, PA. USA: Minitab.

Moisan, J. Y. (1986). Effects of oxygen permeation and stabilizer migration on polymer degradation. In J. Comyn (Ed.), Polymer permeability (pp. 119-176). London: Elsevier Applied Science.

Murray, Lee. (1989). An organic vapor permeation rate determination for flexible packaging materials. In Kier M. Finlayson (Ed.), Plastic film technology: High barrier plastic films for packaging (pp. 21-31). Lancaster, PA. USA: Technomic.

Nagel, Jaye M. (1991). Food packaging: Implications and considerations for recycled plastics. Proceedings from The Eighth Annual FoodPlas Conference March 5-7, 1991 Orlando, Florida (pp. 92-115). Lancaster, PA. USA: Technomic.

Oblah, Richard M. (1993, June). The use of recycling polyester in packaging. Proceedings of the IAPRI 8th World Conference on Packaging, 20-23 June 1993 (p. 543). Anhembi Convention Center: SAO Paulo, Brazil: Food Packaging Technology Center.

Osborn, Kenton R., & Jenkins, Wilmer A. (1992). Plastic films: Technology and packaging applications. Lancaster, PA. USA: Technomic.

Paine, Frank A., & Paine, Heather H. (1983). A handbook of food packaging. Glasgow: Leonard Hill.

Palling, S. J. (Ed.). (1980). Developments in food packaging-1. London: Applied Science.

Pascat, B. (1986). Study of some factors affecting permeability. In M. Mathlouthi (Ed.), Food packaging and preservation: Theory and practice (pp. 7-24). London: Elsevier Applied Science.

Patton, William J. (1976). Plastics technology: Theory, design, and manufacture. Reston, VA.: Reston.

Pearson, Wayne. (1992). Recycling plastics from municipal solid waste: An overview. In G. D. Andrews, & P. Subramanian (Eds.), Emerging technology in plastics recycling (p. 1). Washington, DC: American Chemical Society.

Rice, Judy. (1991). Teaming up plastics packaging with food products: A 10-year retrospective & an assessment of the challenges ahead. Proceedings from The Eighth Annual FoodPlas Conference March 5-7, 1991 Orlando, Florida (pp. 47-64). Lancaster, PA. USA: Technomic.

Risch, Sara J. & Hotchkiss, Joseph H. (Eds.). (1991). Food and packaging interactions II. ACS Symposium Series 473. Washington, DC: American Chemical Society.

Robertson, Gordon L. (1993). Food packaging: Principles and practice. New York: Marcel Dekker.

Rogers, C. E. (1986). Permeation of gases and vapours in polymers. In J. Comyn (Ed.), Polymer permeability (pp. 11-73). London: Elsevier Applied Science.

Rotruck, John. (1991). Solid waste solutions for food and beverage packages. Proceedings from The Eighth Annual FoodPlas Conference March 5-7, 1991 Orlando, Florida (pp. 180-186). Lancaster, PA. USA: Technomic.

Salame, M. (1989). The use of barrier polymers in food and beverage packaging. In Kier M. Finlayson (Ed.), Plastic film technology: High barrier plastic films for packaging (pp. 132-145). Lancaster, PA. USA: Technomic.

Salame, Morris. (1974). The use of low permeation thermoplastics in food and beverage packaging. In Harold B. Hopfenberg (Ed.), Permeability of plastic films and coatings, to gases, vapors, and liquids (275-284). New York: Plenum Press.

Schwartz, Patricia S. (1991, March). Regulations for plastics packaging: What's coming? An FDA perspective of regulations for food packaging. Proceedings from The Eighth Annual FoodPlas Conference March 5-7, 1991 Orlando, Florida (pp. 231-238). Lancaster, PA. USA: Technomic.

Seymour, Raymond B. (1991). Reinforced Plastics: Properties and applications. Ohio: ASM International.

Smok, Douglas. (1993, September). Plastics: Sales grow and so does pain. Plastics World, p. 7.

Speigel, Alan. (1992). Shelf life testing. In William E. Brown, Plastics in food packaging (chapter 9). New York: Marcel Decker.

Stein, Richard S. (1992). Miscibility in polymer recycling. In G. D. Andrews, & P. Subramanian (Eds.), Emerging technology in plastics recycling (pp. 39-48). Washington, DC: American Chemical Society.

Strandburg, G., DeLassus, P. T., & Howell, B. A. (1991). Thermodynamics of permeation of flavors in polymers: Prediction of solubility coefficients. In Sara J. Risch &

Joseph H. Hotchkiss (Eds.), Food packaging interactions II (pp. 133-160). Washington, DC: American Chemical Society.

Teasley, Harry. (1991). Thinking about packaging, the environment, and public policy. Proceedings from The Eighth Annual FoodPlas Conference March 5-7, 1991 Orlando, Florida (pp. 121-155). Lancaster, PA. USA: Technomic.

Thorsheim, Helen R., & Armstrong, David J. (1993, August). Recycled plastics for food packaging. Chemtech, 23(8), pp. 55-58.

Vieth, Wolf R. (1991). Diffusion in and through polymer: Principles and applications. Munich: Hanser.

Windle, A. H. (1986). Case II sorption. In J. Comyn (Ed.), Polymer permeability (pp. 75-118). London: Elsevier Applied Science.

Wendorff, J. H. (1985). Studies on the nature of order in amorphous polymers. In S. E. Keinath, R. L. Miller, & J. K. Rieke (Eds.), Order in the amorphous state of polymers (pp. 53-70). New York: Plenum Press.