This is to certify that the

thesis entitled

THE EFFECT OF SURFACE SULFONATION ON
BARRIER PROPERTIES OF POLYMER FILMS

presented by

KITTI WANGWIWATSILP

has been accepted towards fulfillment
of the requirements for

MASTER degree in PACKAGING

Jack R. Giacin
Major professor

Date OCTOBER 13, 1993

THE EFFECT OF SURFACE SULFONATION ON BARRIER PROPERTIES OF POLYMER FILMS

By

Kitti Wangwiwatsilp

A THESIS

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

MASTER OF SCIENCE

School of Packaging

1993

ABSTRACT

THE EFFECT OF SURFACE SULFONATION ON BARRIER PROPERTIES OF POLYMER FILMS

By

Kitti Wangwiwatsilp

The effect of surface sulfonation on the mass transport characteristics of polypropylene (PP) and polyethylene terephthalate (PET) was investigated for the penetrants, ethyl acetate and toluene. Surface sulfonation of PP was found to reduce the permeability coefficient (P) of ethyl acetate vapor through the treated film, with (P) decreasing with an increase in sulfonation time. Sorption studies showed a one order of magnitude reduction in the effective diffusion coefficient for the 2 minute sulfonated PP film. The solubility coefficient, however, remained fairly constant. For toluene, no detectable level of permeation was observed for the PP film sulfonated for 3 minutes. The observed reduction in the permeability of ethyl acetate and toluene through the sulfonated PP film is attributed to a reduction in the mobility term D, and to the solubility and diffusivity of the organic penetrants within the sulfonated surface layer being significantly different than those parameters within the bulk phase.

Surface analysis (ESCA) showed that sulfonation of PET was ineffective under the treatment conditions employed and had no evident effect on the ethyl acetate barrier properties of PET.

To my parents and family

ACKNOWLEDGEMENTS

Firstly, I would like to express a great deal of thanks and respect to Dr. Jack Giacin for his great guidance, support, encouragement and patience while serving as my major advisor.

I would also like to express my appreciation to Dr. Ruben Hernandez and Dr. Eric Grulke for serving on my committees and for their useful guidance and assistance.

An acknowledgement must be given to Coalition Technologies, Ltd./ Environmental Protection Agency (EPA) for the financial support of this project.

I am very grateful to Dr. Heidi Hoojjat for teaching and guiding me how to operate the laboratory instrument and to solve the problems.

I would like to thank Brian Ericson for his help, advice on sulfonation process over Composite Materials and Structures Center. Also, I have to thank Dan Hook for his help on the surface analysis.

Next, I would like to thank Takashi Urata and Koichi Haraguchi for their assistance on graph preparation. And, I would like to express a lot of thanks to Wimol Taoklam, Prapassara Nilagupta, Nat Pinitpongskul and Kittipong Sithiyavanich for their impressive help and encouragement.

Finally, I will not be able to stand at this point without my parents' support and understanding. So I would like to express thanks and respect, from my heart, to my parents and all of my family.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

In recent years, much attention has been focused on chemical modification of the surface of polymers, and the effect of such a treatment on the polymers barrier properties. For example, surface fluorination during blow-molding can impart excellent organic vapor barrier properties to polyolefins. Here, the surface layer of the polymer is chemically modified, and is inert to the attack of most organic compounds (Metah, 1988). Surface sulfonation is also considered as a method to provide barrier properties to the polymers. Polyethylene can also be sulfonated by treatment with gaseous SO_3, with fuming sulfuric acid, or with SO_3 in chlorinated hydrocarbons, to provide useful industrial materials (Ihata, 1988).

Recently Walles (1989) described the effect of surface sulfonation on the barrier properties of a high density polyethylene (HDPE) article and showed that sulfonation, followed by air purging and neutralization with NH_3 gas, resulted in an excellent organic vapor barrier, at a surface concentration of between 0.75 - 2.0 g S/m^2 surface area. Further, the sulfonation process was readily adapted to both post-mold (Walles, 1971 and 1973) and in-mold sulfonation (Walles).

Kinetic studies showed that sulfonation of a polymer film or sheet is a diffusion controlled process, with reactive gases penetrating the polymer surface up to depths of a micron or more. Thus, modification of the surface as well as the surface region is possible (Walles, 1989).

The oxygen barrier properties of sulfonated polyethylene were found to be strongly dependent upon the nature of the neutralizing counterion, M^+. For example, Walles (1989) reported that Na^+ as a counterion was 6 times as effective as was NH_4^+ in providing a barrier to oxygen diffusion. Lithium ion (Li^+) was 12 times better than NH_4^+, all at a surface concentration of about 0.7 g S/m^2 surface area, which for a 25 μm film equals about 1 % bulk sulfur.

Further, to obtain an extremely high barrier structure, an ultra thin, very regular metallic layer can be created, by combining sulfonation with reductive metallization. In one procedure, the sulfonate courterion is silver (Ag^+), which can be reduced to a colloidal metallic silver layer with a thickness of 10 - 600 atoms. About 80 - 120 atoms were found to provide a total, metallic-type barrier to the transport of air (Walles, 1989). This would be comparable to the barrier characteristics of vacuum metallized structures.

Sulfonation thus offers a new approach to chemically modify the surface of polymeric films and sheets, resulting in modification of the barrier and physico-chemical properties of the polymer membrane.
The objectives of this study include:

1. To evaluate the effect of different levels of surface sulfonation on the organic vapor barrier properties of polypropylene (PP), polyethylene terephthalate (PET) and Nylon 6.

2. To determine permeability, effective diffusion and solubility coefficients by permeation and sorption procedures for the penetrants, ethyl acetate and toluene.

LITERATURE REVIEW

1. SURFACE MODIFICATION

Over the past decade a significant interest has been directed to developing procedures for the surface modification of polymers. The purpose of these studies was to modify the surface properties of the original polymeric materials by changing the molecular structure of the surface, or by coating the surface with some other materials. The modification of a polymer surface can be conducted either by chemical or physical methods. For example, plasma surface modification impedes the electrical conduction of polymeric materials. For example, it was found that the current conduction was lower for hydrogen-plasma treated low density polyethylene (LDPE) samples and for samples exposed to oxygen or ozone after hydrogen-plasma treatment, than for the untreated LDPE samples (Hayashi et al.,1991). The authors proposed that the treated surface layer traps electrons and reduces the field strength at the electrode surface, thus suppressing further injection of electrons. Similar findings were reported by Hayashi et al. (1990) for hydrogen-plasma treated high density polyethylene (HDPE). Recently development of a new high barrier silica deposited film has been the subject of major interest for various packaging material related manufacturers (Sajiki, 1991). The film is based on silicon oxide deposition onto polyethylene terephthalate (SiOx-PET). Surface fluorination provides another technology as a barrier treatment (Naude, 1992 and Kreisher, 1992). For example, this treatment markedly reduces hydrocarbon permeation through plastic vehicle fuel tanks. In addition, Du Pont's Sealer Technology, which has been licensed to major fuel tank manufactures, is a modified nylon product that forms pellets on the tank's interior, significantly reducing hydrocarbon emission (Naude, 1992 and Kreisher, 1992). The corona-discharge technique also provides for polymer surface modification, and is used to improve the adhesion of printing inks, coating and labels to plastic films and containers by oxidation (Amini, 1986). A multi-discharge corona technique has also been applied to remove the rolling oils from aluminum foil (Amini, 1986). Like corona discharge, a flaming technique can also be used to improve the adhesion properties of polymer film, as a result of surface flame oxidization (Amini,1986). A summary of the various methods developed for surface modification of polymers to improve adhesion and hydrocarbon-barrier properties is presented in Table 1 (Amini, 1986).

Ion implantation is a process which can also result in the improvement of various material properties to include: (i) resistance to wear; (ii) corrosion; and (iii) fatigue. It can also modify such physical properties as the index of refraction, magnetic parameters and conductivity. This methodology has found its major application in fabricating semiconductor devices (Smidt, 1989). A recent attractive technique for modifying the surface properties of polymer membranes involves the immobilization of enzymes within a polymer matrix (Toensmeier, 1990). Three major commercial applications of this technology include: (i) lactose removal from milk, in which the enzyme breaks down lactose into digestible glucose and galactose; (ii) cholesterol removal from milk; and (iii) oxygen scavenging from liquids and dry foods. The likely uses of this technology could be for commodity products. Further, this will not impair recyclability (Toensmeier, 1990).

Table 1. Summary of Methods Used for Improvement of Adhesion and Hydrocarbon-Barrier Properties (Amini, 1986).

Methods	Improves	Comments
Corona discharge	adhesion	sophisticated, high treat levels possible
Gas plasma	adhesion	sophisticated, high treat levels possible
Flaming	adhesion	commonly used for plastic bottles
Fluorination	hydrocarbon-barrier	post-treat or in-mold treat possible
Sulfonation	hydrocarbon-barrier	post-treat, some surface yellowing
Polymer blend	hydrocarbon-barrier	PE-Nylon, water barrier decreases
Coextrusion	hydrocarbon-barrier	films, sheets, bottles, generally containing EVOH, PVDC or Nylon
Coating	hydrocarbon-barrier	films, sheets, bottles, generally coated with PVDC

2. SULFONATION

2.1 Sulfonation Process

The sulfonation process typically involves exposing the polymeric material to gaseous SO_3 or fuming sulfuric acid for certain periods of treatment time, to form sulfonic acid groups. Neutralization with ammonium hydroxide (NH_4OH) follows in order to stabilize the sulfonate groups. To improve some properties, ammonium ion can be replaced by certain monovalent and divalent cations (e.g. Na^+, Ca^{++}, Ag^{++}) via ion exchange (Walles, 1989). The sulfonating agents include fluorosulfonic acid, chlorosulfonic acid, salts of chlorosulfonic acid, chlorosulfonic anhydride (pyrosulfuryl chloride), sulfamic acid (aminosulfonic acid), sulfur trioxide or its addition product with a slightly basic substance such as pyridine or dioxane, and acid salts of sulfuric acid. The reagent chosen in a particular case depends upon the compound to be sulfonated and the number of sulfonate groups to be introduced (Suter, 1944). Furthermore, the reaction mechanisms are different depending on the sulfonating reagents and the substrates used.

Sulfonation with compounds of sulfur trioxide is considered as the simplest and most direct method. It has, therefore, been the one most commonly employed, both in the laboratory and in commercial practice, for the manufacture of detergents, dye intermediates, ion-exchange resins, sulfonated oils, and other sulfonates of industrial interest. There have been reports describing the reaction of SO_3 and its adducts with organic compounds for sulfonating alkenes, aliphatic compounds containing carbonyl groups, polycyclic aromatics, and acid sensitive heterocyclic compounds (Gilbert, 1965). With aromatic compounds, the use of SO_3 and other strong reagents has prompted theoretical and empirical studies of the factors involved in the resulting undesired side-reaction of sulfone formation (Suter, 1944 and Gilbert, 1965). Since sulfone formation has prohibited its commercial use, the addition of acetic acid, propionic acid, acetic anhydride or sodium sulfate, has been found to inhibit sulfone formation (Gilbert, 1965).

Salts of sulfonic acids can be obtained by neutralizing with calcium or barium carbonate. A simpler procedure, which is particularly useful in preparing an alkali metal salt, involves pouring the sulfonation mixture into a strong solution of an alkali chloride (Suter, 1944).

2.1.1 Sulfonation Reaction

Surface sulfonation of high density polyethylene (HDPE) with gaseous SO_3 was reported by Ihata (1988a) to lead to the formation of sulfonic acid, with highly conjugated C=C unsaturated bonds. The reaction of HDPE film with SO_3 was suggested to be initiated by the abstraction of a hydrogen atom by SO_3 to give a free radical, which could either react with SO_3 to give a sulfonic acid group, or eliminate a hydrogen atom to form an unsaturated bond. The reaction scheme is shown in Figure 1. Spectrophotometric analyses indicated an increase in the latter mechanism as the sulfonation reaction proceeded. In addition, yellowing and browning on the film surfaces were noticed with the extent of sulfonation (Ihata, 1988a). These findings were also supported by Tardiff (1993), who observed diffusion and reaction of sulfonate groups within the polymer matrix of sulfonated polymeric films. The author indicated that neutralization was important for sulfonation process to stabilize the sulfonic acid groups within the polymer film.

Ihata (1988b) extended the earlier study and reported that conjugated polyene sulfonic acids were sensitive to UV and visible light. The photoreaction induced desulfonation by cleavage of C-S bonds to eliminate sulfonic acid groups adjacent to conjugated double bonds.

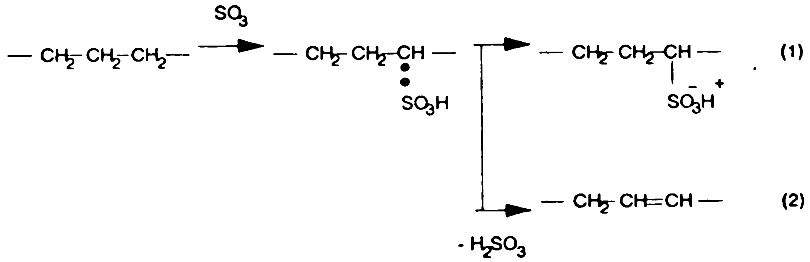


Figure 1: Sulfonation Reaction Scheme of HDPE

Asthana (1993) has recently investigated surface sulfonation on polypropylene and polystyrene. The author described that sulfonation was a highly electrophilic reaction in which SO_3 tended to react at centers of high electron density. It was found, for polypropylene, that the presence of tertiary carbons in the molecules provided active sites for SO_3 substitution. Like polyethylene, the formation of conjugated C=C unsaturated bonds was also found following sulfonation of polypropylene. For polystyrene, the active sites of reaction were confirmed at the para position of the aromatic rings. The reaction schemes are demonstrated in Figure 2 and 3, respectively (Asthana, 1993 and Tardiff, 1993).

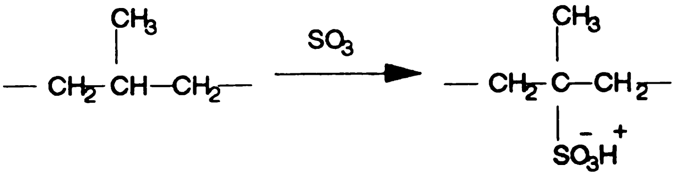


Figure 2: Sulfonation Reaction Scheme of Polypropylene

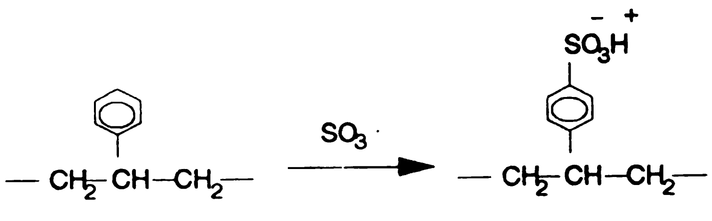


Figure 3: Sulfonation Reaction Scheme of Polystyrene

2.1.2 Neutralization Reaction

Neutralization following the sulfonation step was found to be important for stabilizing the SO_3 groups. Although it can be carried out with various bases, the traditional neutralizing agent is ammonia gas (NH_3) or aqueous ammonium hydroxide (NH_4OH). There is a finding that up to two thirds of C-SO_3H groups cannot be neutralized by aqueous NaOH, while NH_3 gas can diffuse and neutralize all acid groups (Walles, 1989). During neutralization, the hydrogen from the sulfonic acid is replaced with the ammonium ion (NH_4^+) to form a stabilized ion pair. The reaction scheme is shown in Figure 4.

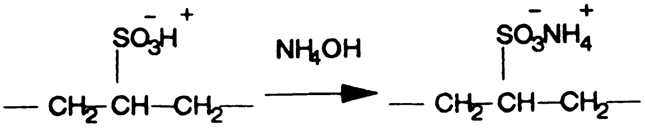


Figure 4: Neutralization of Sulfonated PE with NH_4^+

Selected polymer properties, for example, the barrier property of the sulfonated polymer, were found to be strongly dependent on the nature of the neutralizing counterions. For example, an ion exchange in aqueous solution can be employed to exchange various metal cations to the sulfonate groups. Those metal ions include Li^+, Na^+, Cu^{++}, Mg^{++}, Sr^{++}, V^{++}, Mn^{++}, Co^{++} and Ni^{++} (Walles, 1989).

2.2 Application

Presently, there is an increase in the use of plastic fuel tanks for automobiles because of their light weight and good safety features including, impact resistance, recyclability and no corrosion problem (Naude, 1992). Currently, about 25% of all automobile fuel tanks in North America are plastic, compared to 70% in Europe and 5% in Japan (Kreisher, 1992). However, the new U.S. Environmental Protection Agency (EPA) regulations, led by the California Air Resource Board, will lower or tighten the allowable limit for hydrocarbon fuel vapor loss for the whole vehicle from 2 g per 2 hr to 2 g per 24 hr (Naude, 1992 and Kreisher, 1992). Therefore, automakers have been enthusiastically trying to develop improved barrier properties for the plastic fuel tanks, with various techniques.

A surface sulfonation process, developed by Coalition Technologies Ltd., Midland, MI., was found to be successful in improving the hydrocarbon barrier properties of a high-density polyethylene (HPDE) gasoline tank. It can even reduce flex fuel emissions from the tank to virtually zero (Miller, 1992), particularly the methanol-gas blends.

The process is a two-step process following blow molding. First, the tank interior is exposed to a 10-20% concentration of sulfur trioxide gas (SO_3) to attach sulfonate groups along the HDPE molecular chain. The second step involves reaction with a neutralizing agent to make the sulfonate groups chemically inert. Consequently, the barrier layer is formed by the nesting of the sulfur, oxygen and neutralizing atoms. Sulfonation is compared with surface halogenation (i.e., fluorination, chlorination). Surface sulfonation has an advantage over the halogenation processes, in that fluorination results in brittleness causing loss of barrier upon repeated flexing. This brittleness is due to the high energy of C-F formation (Walles, 1989). For surface chlorination, it imparts barrier layers with flexibility, but its reaction is too slow to be practical. Even with UV-light activation, chlorination is not practical for treatment of interior surfaces of containers. It is reported that about 90% of all plastic tanks for automobiles have been sulfonated for barrier (Walles, 1989). With the barrier ability improvement, this process therefore also has potential application for organic-solvent containers (Amini, 1986).

In addition to the commercial application of surface sulfonation for plastic fuel tanks, this technology has also been employed to modify polymers for biomaterial or medical usage. For example, Dow Plastics has recently licensed this process for fabricating a plastic thromboresistant by grafting anticoagulant heparin onto the sulfonated surface of the plastic (Rogers, 1990). In addition, the technology is compatible with both ethylene oxide (EtO) and gamma radiation sterilization. It also has potential applications for other medical materials by grafting other substrates, including albumin, amino acids and select pharmaceuticals onto the surface of sulfonated plastics (Rogers, 1990). Walles (1989) further proposed that the sulfonate groups could be used to graft ethylene oxide and other epoxides to a polymer surface, thus providing a hydrophilic barrier layer. Sulfonation followed by reductive metallization permits construction of thermos bottles and a high thermal insulator for refrigerators (Walles, 1989). Rogers (1990) proposed that metallization with a silver coating can impart antimicrobial properties to medical devices. The sulfonation treatment is found to improve wettability properties, or increase the hydrophilic nature of a polymer surface. This can provide a solution to the medical industry, since it can result in a reduction of air bubble formation in critical fluid systems. Since a common problem is adhesion of air bubbles to medical devices that contain blood or other fluids. It has also been shown that sulfonation imparts flame resistance to sulfonated polycarbonates (Yates et al. 1987 and Mark, 1975).

Brenner and Lundberg (1977) described applications of lightly sulfonated ethylene-propylene-diene terpolymer (EPDM) foam for shoe soles and thin sheets for textile backing. The authors found that lightly sulfonated EPDM foam could be produced at a high production rate due to two reasons. Firstly, it does not require a curing step and secondly, it can be extruded at high shear rates without melt fracture. This is attributed to the ability of the lightly sulfonated EPDM foams, to form a network of physical crosslinks. Since they are not covalently crosslinked, the product provides reprocessability. However, containers that are manufactured by surface sulfonation have not yet been cleared by the FDA for use with foods and pharmaceuticals (Amini, 1986).

2.3 Previous Studies

It has been reported by Roger (1990) that surface sulfonation of a polymer can result in an improvement in the physical and mechanical properties of the untreated polymer structure to include: water wettability, adhesion, vapor barrier, lubricity, electrical conductivity, antistatic qualities, metallizability and abrasion resistance. Further, a broad range of polymers, including aliphatics, aromatics, cellulosic and silicone, are readily sulfonated. Fluorocarbon-based materials provide an exception and cannot be sulfonated (Rogers, 1990). Typically, polymer films as well as other polymer configurations having CH or NH groups are reported to be sulfonatable (Walles, 1989). By employing Frustrated Multiple Internal Reflection (FMIR) Infrared Spectroscopy, it was confirmed that the surface sulfonation process occurs by inserting sulfonic groups onto a polyethylene (PE) surface, without any extent of oxidation (Olsen and Osteraas, 1969 and Foseca et al., 1985).

2.3.1 Effect on Electrical and Physical Properties.

Fonseca et al. (1985) found that the superficial resistances and resistivities for linear polyethylene (PE) decreased with an increase in the treatment time with fuming sulfuric acid. It was proposed by the authors that the surface conductivity of PE was improved as a result of introducing polar functionality onto the polymer surface. Further, the critical surface tension of the sulfonated PE was also increased. It should be noted that the critical surface tension is a parameter used to characterize the wettability of a surface. It is the maximum surface tension of a liquid capable of spreading on a solid surface and is related to several characteristics of biomaterials, to include: (i) the amount of thrombosis in vivo; (ii) the clotting time for blood; and (iii) the adhesion of living tissues to biomaterials (Fonseca et al., 1985). In some cases, surface yellowing can occur with this surface modification (Amini, 1986). Inagaki and Hirao (1987) studied the electrical properties of sulfonated plasma-polymers prepared from phenylsilane and found that the plasma-polymers containing negatively charged sulfonate groups were electrically conductive. The conductivity properties of the sulfonated plasma-polymers depended highly on relative humidity, as shown by a decrease in the impedance of the sulfonated plasma-polymers with an increase in the relative humidity. In addition, like quarternized plasma polymers (i.e., plasma-polymers containing positively charged, quarternary nitrogen groups), the sulfonated plasma-polymers can be used as a material for moisture sensor devices.

2.3.2 Effect on Mechanical Properties.

Calleja (1984) investigated the effect of sulfuric acid exposure on surface hardening of HDPE and found that the exposure of HDPE to a sulfuric acid atmosphere improved the mechanical properties of the sulfonated polymer. The surface microhardness of HDPE was found to increase with sulfonation exposure time, resulting in hardness values that were equivalent to those of some metals. This was attributed by Fonseca et al. (1985) to the formation of crystal surface linkages. However, for sulfonated polystyrene (PS) films, the tensile properties exhibited no evident correlation with the valance of the neutralizing cation, nor with the atomic radii or atomic number of the cation (Esbensen, 1991).

2.3.3 Effect on Barrier Properties.

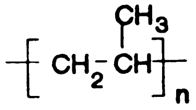
Walles (1989) has reported that surface sulfonation of the inside of HDPE automotive gas tanks with about 20% sulfur trioxide (SO_3) in air, followed by air purging and neutralization with ammonia (NH_3) gas resulted in excellent gasoline barrier properties. The author found that surface sulfonation could reduce gasoline permeance at 75 °F from a one-pint, 25-mil thick, HDPE container from 0.759 g/day to 0.002 g/day. Recently, Miller (1992) reported that Ca^{++} as the neutralizing cation resulted in a reduction in fuel vapor transport through a surface sulfonated HDPE container. It was proposed that Ca^{++} ion resulted in an enhanced barrier layer due to its ability to act as a crosslinking agent between the HDPE molecular chains. This crosslinking resulted in a barrier layer more resistance to swelling, and therefore less permeable to the fuel. Further, to achieve a super barrier, an ultra thin, very regular metallic layer can be created by combining sulfonation with reductive metallization of copper or silver (Walles, 1989). In addition, the barrier properties obtained by surface sulfonation were found strongly dependent upon the nature of the neutralizing counterion. For example, when the neutralizing counterion, NH_4^+, was substituted by a series of monovalent or divalent cations via an ion exchange reaction, an enhancement in oxygen barrier properties was observed for a surface sulfonated polyethylene film. Walles (1989) found that Na^+ ion was 6 times as effective as NH_4^+ ion with respect to oxygen diffusion through the sulfonated membrane, while Li^+ was 12 times more effective than NH_4^+, all at a surface concentration of about 0.7 g S/m^2 (Walles, 1989).

Esbensen (1991) reported that no improvement in the barrier characteristics for oxygen and water vapor was found for a sulfonated polystyrene (PS) film. The author proposed that the barrier properties of the PS film were not improved by surface sulfonation due to the polymer's highly amorphous morphology, which would allow an easily accessible pathway for permeation through the film layer. Also, the author indicated that different neutralizing counterions showed no effect on oxygen and water vapor barrier properties of PS films at the level of sulfonation investigated (Esbensen, 1991). Recently, Ericson (1993) has investigated the effect of surface sulfonation on the adhesion of polymers to an epoxy type adhesive. It was found that surface sulfonation significantly increased the lap-shear strength to polypropylene and was more effective than other surface treatments, to include, chromic acid etching and flame treatment. However, the increase in seal strength was limited, since the lap-shear strength tended to decrease with further extent of sulfonation. This could be attributed by degradation of the polymer. In contrast, sulfonation of polystyrene was found to be ineffective in improving the lap-shear strength of the polymer.

3. POLYMER CHARACTERISTICS

3.1 Polypropylene (PP)

Polypropylene is a linear polymer, containing a large number of propylene monomer units linking to build up long polymer chains. The basic structural unit of PP is shown in Figure 5.



$$\left[-CH_2-CH(CH_3)- \right]_n$$

Figure 5: Monomer Unit of Polypropylene

Early attempts to polymerize propylene using the high pressure process were not successful, giving only oily liquids or rubbery solids of no commercial value. Work by Natta in Italy using Ziegler-type catalysts lead to the development of a stereospecific catalyst that controlled the position of each monomer unit as it was added to the growing chain, thus giving a regular structure polymer (Robertson, 1992).

The most regular crystalline PP is known as the isotactic form. It has many applications in packaging as a result of a series of useful properties to include: low water vapor transmission, medium gas permeability, good resistance to greases and chemicals, good abrasion resistance, high temperature stability, good gloss and high clarity. Whereas the amorphous PP, so called atactic form, is used in hot-melt adhesives (Miller,1986 and Robertson, 1992).

In addition to the sheet form, the use of PP in film is also very significant. Oriented films typically have high toughness and excellent clarity. The first two OPP films produced were homopolymer shrink film, and heat-stabilized film that could not be heat sealed. The later attained wide acceptance as a laminating substance when combined with heat-sealing polymers. It contributed strength, moisture barrier and high surface gloss to the lamination (Hasenauer, 1986). Compared to oriented film, non-oriented film has a number of growing markets. It is available in thicker gauges and is softer at the same thickness. Some applications for the non-oriented polypropylene include release sheets, sanitary products, disposable-diaper layers, bandages and apparel packaging. It is also used in combination with various materials to improve barrier properties, temperature and chemical resistance (Miller, 1986). In addition, its use for health-care packaging is growing rapidly due to increasing use of medical disposables. With the relatively high temperature resistance, nonoriented PP film is used in autoclave equipment, steam sterilizable and retortable pouches (Miglaw, 1986). However, it is claimed not to be suitable for ethylene oxide (EtO) and radiation sterilization (Hirsch, 1986).

3.2 Polyethylene Terephthalate (PET)

PET can be produced by reacting ethylene glycol with either terephthalic acid (TPA) or dimethyl terephthalate (DMT), giving a polymer structure as shown in Figure 6. PET exhibits a melting point (Tm) of approximately 267 °C and a glass transition temperature (Tg) between 67° and 80 °C (Robertson, 1992).

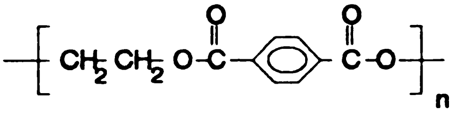


Figure 6: Monomer Unit of PET

Most PET resins are modified homopolymers and are used in the manufacture of containers. About 70-80% of the resin consumption is used for soft-drink bottles. Homopolymers cannot be processed by extrusion blow molding due to insufficient melt strength (Neumann, 1986). Whereas PET films are most widely used in the biaxially oriented, heat stabilized form, there are almost no applications in its unoriented form. If the PET is semi-crystalline, it is brittle and opaque, and if amorphous, it is clear but not tough (Robertson, 1992).

PET film's outstanding properties include its tensile strength, moisture resistance, clarity, barrier properties, excellent chemical resistance, light weight, elasticity and stability over a wide range of temperatures (-60° to 220°C). The latter property has led to the use of PET for boil-in-bag products which are frozen before use. To improve the barrier properties of PET, coatings of either LDPE, PVDC copolymer or PVDC co AN have been made. Metallization also results in a considerable improvement in barrier properties (Kindberg et al.,1986 and Robertson, 1992). PET film may be corona or chemically treated to promote improved adhesion to a variety of inks, coatings and adhesives (Kindberg et al., 1986).

Other applications of biaxially oriented PET film include magnetic-tape products, floppy disks, microfilm, graphic arts, labels, solar-control window films and pressure sensitive tape (Kindberg et al., 1986). There are also some uses in health-care packing since the PET film can withstand all the major modes of sterilization. Nevertheless, the use of PVDC-coated polyester should be avoided due to unfavorable reaction under sterilization (Hirsch, 1986).

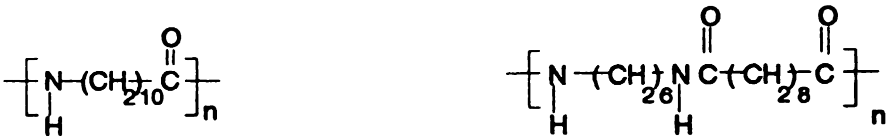
3.3 Polyamides

Polyamides, so called nylons, are thermoplastics characterized by repeating amide groups (-CONH-) in the main polymer chain (Tubridy and Sibilia, 1986). The early development of the nylons were in textile fibers application. Nylons have become commercial for packaging film applications since the late 1950s (Robertson, 1992). In general, they offer clarity, thermoformability, high strength and toughness over a broad temperature range, chemical resistance as well as barrier to gases, oils, fats and aromas. Biaxial orientation of nylon films is believed to improve flex-crack resistance, mechanical and barrier properties (Tubridy and Sibilia, 1986).

The various types of nylons differ structurally by the chain length of the aliphatic segments separating adjacent amide groups (Tubridy and Sibilia, 1986). Thus, there are two different types of nylons films available based on their resin manufacture. One type is made by a condensation of mixtures of diamines and dibasic acids. The products are identified by the number of carbon atoms in the diamine, followed by the number of carbon atoms in the diacids, these structures are also known as omega or ω-amino acids since the amino and carboxyl groups are at opposite ends of the polyamides. Identification of the second type of polyamide is made by a single number, signifying the total number of carbon atoms in the amino acid (Robertson, 1992). Some examples of molecular structure of nylons are shown in Figure 7.

$-\!\left[\mathrm{N(H)}-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right]_n\!-$ $\quad -\!\left[\mathrm{N(H)}-(CH_2)_6-\mathrm{N(H)}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n\!-$

Nylon 6 Nylon 6,6



$-\!\left[\mathrm{N(H)}-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}\right]_n\!-$ $\quad -\!\left[\mathrm{N(H)}-(CH_2)_6-\mathrm{N(H)}-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}\right]_n\!-$

Nylon 11 Nylon 6,10

Figure 7: Monomer Units of Some Polyamides

Since the repeating amide groups have =O and -N, nylons, therefore, can form inter- and intramolecular hydrogen bonds in the molecules. The combination of hydrogen bonding of amide groups and crystallinity yields tough, high-melting thermoplastic materials. The flexibility of aliphatic chains permits film orientation to further enhance strength. As the length of the aliphatic segment increases, there is a reduction in melting point, tensile strength, and water absorption, and an increase in elongation and impact strength (Turbridy and SIbilia, 1986 and Robertson, 1992). However, nylons are considered as a moisture sensitive material, like polyvinyl alcohol (PVOH), due to susceptible formation of hydrogen bonds. The moisture will be absorbed and act as a plasticizer in the polymer matrix. As a result, barrier properties are markedly decreased. Practically, barrier properties of nylons can be improved by such various methods as orientation, coating, lamination and surface modification.

For most packaging applications, nylons are combined with other materials that add moisture barrier and heat sealability, such as LDPE, ionomer, ethylene vinyl acetate (EVA) and ethylene-acrylic acid (EAA). Nylon films have been used mostly in food packaging such as vacuum packaging, boil-in-bag packs and the packaging of surgical equipment for steam sterilization (Briston, 1986 and Turbridy and Sibilia, 1986).

Nylon 6, a polymer obtained from ϵ-caprolactam, is the nylon resin used most frequently in the USA for packaging applications, due to the balance of cost, physical properties and process adaptability. It possesses high temperature, grease and oil resistance. For blown or cast extrusion, as well as cast coextrusion, nylon 6 resins are favored by most converters (Turbridy and Sibilia, 1986 and Robertson, 1992).

Medical packaging applications, such as packaging of hypodermics and other medical devices, are a relatively new and expanding area for the nylons. Their toughness, puncture resistance, impact strength, abrasion resistance and temperature stability make nylons suitable for protecting sterile devices during shipping and storage. Modified-nylon resins have recently been introduced that permit radiation sterilization (Turbridy and Sibilia, 1986).

4. PERMEATION THEORY

4.1 Definition

Permeability is defined as the transmission of gasses or vapors through a resisting material with no macroscopic pores (Paine, 1983). The transport of a gas or vapor through polymeric films commonly used in packaging typically involves the activated diffusion process, of which three steps are involved (Stannett and Yasuda, 1965):

1) Absorption of permeating species, in which gas or vapor dissolves into the polymer matrix at the high penetrant concentration surface.

2) Diffusion through the polymer wall along a concentration gradient.

3) Desorption from the surface at the lower concentration.

Permeation of polymers, in general, is a function of two variables, one relating to diffusion between molecular chains and the other to the solubility of the permeant in the polymer. Diffusion is driven by a concentration gradient for liquids and a partial pressure gradient for gasses. Whereas, solubility involves the affinity of the permeant for the polymer (Imbalzane et al., 1991).

Under steady state conditions, a gas or vapor will diffuse through a polymer at a constant rate, if a constant pressure difference is maintained across the polymer. The diffusive flux (J) of a permeant in a polymer can be defined as the amount passing through a plane or surface of unit area normal to the direction of flow during unit time, That is:

$$J = Q/(A*t) \qquad (1)$$

where Q is the total amount of permeant passing through area A during time t.

The relationship between the rate of permeation and the concentration gradient is of direct proportionality and is described by Fick's first law:

$$J = -D \frac{d(c)}{dx} \qquad (2)$$

where:

J: the flux, rate of transmission per unit area of permeant through the polymer.

D: the diffusion coefficient.

dc/dx: the concentration gradient of the permeant across a thickness dx.

It is referred that the amount of permeant retained per unit volume of the polymer (dJ/dx) is equal to the rate of change of concentration with time:

$$\frac{d(J)}{dx} = -\frac{dc}{dt} \qquad (3)$$

If Eq.(2) is substituted into Eq.(3) then:

$$\frac{d(J)}{dx} = \frac{d}{dx}\left[-D\frac{dc}{dx}\right] = -\frac{dc}{dt} \qquad (4)$$

and with rearrangement of the terms:

$$\frac{dc}{dt} = \frac{d}{dx}\left[D\frac{dc}{dx}\right] \qquad (5)$$

and

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \qquad (6)$$

Eq.(6) is a simplified form of Fick's second law of diffusion and applies under circumstances where diffusion is limited to the cross-direction and D is independent of concentration (Robertson, G.L., 1992).

When the steady state of diffusion has been reached, J is constant and Eq.(2) can be integrated across the total thickness of the polymer l, and between the two concentrations, assuming D to be constant and independent of c, then:

$$J = \frac{D(c_1-c_2)}{l} \qquad (7)$$

By substituting for J using Eq.(1):

$$Q = \frac{D(c_1-c_2)A*t}{l} \qquad (8)$$

When the permeant is a gas, it is easier to measure the vapor pressure (p), which is at equilibrium with the polymer, rather than the actual concentration. At sufficiently low concentrations, Henry's law applies and c can be expressed as:

$$c = S*p \tag{9}$$

Where S is the solubility coefficient of the permeant in the polymer. Consequently,

$$Q = \frac{D*S(p_1-p_2)A*t}{l} \tag{10}$$

By definition, the product D*S is defined as the permeability coefficient or constant (P). Thus:

$$P = \frac{Q*l}{A*t(p_1-p_2)} \tag{11}$$

There are four assumptions made in the above simple treatment of permeation (Robertson, G.L., 1992).

1) Diffusion is in a steady state condition.

2) The concentration-distance relationship through the polymer is linear.

3) Diffusion takes place in one direction only.

4) Both D and S are independent of the penetrant concentration.

Unlike the transport properties of non-reacting gases (e.g. oxygen and carbon dioxide), many organic liquids and vapors create non-ideal diffusion and solubility conditions (so called concentration-dependent). This behavior is due to the ability of the organic vapors to swell the polymer matrix and thus change the configuration of the polymer chains, which increases the rate of permeation (Baner et al.,1986). This results in the observed concentration dependency of the permeability coefficient.

4.2 Effect of Some Properties on Permeation

A broad range of chemical and physicochemical properties that affect permeation are as follows (Imbalzano et al.,1991):

4.2.1 Ease of Condensation of Permeants

Chemicals that readily condense will, therefore, permeate at higher rates.

4.2.2 Intermolecular Chain Forces of the Polymer

With higher intermolecular forces, the permeants may not be able to overcome the inter-chain forces of attraction. As a result, rates of permeation decrease.

4.2.3 Crystallinity

Higher levels of crystallinity possess a greater barrier to permeants, because these crystalline regions diminish the molecular void volume available for passage.

4.2.4 Chemical Similarity Between Permeant and Polymer

A given permeant will be most soluble in a polymer having a similar degree of polarity. This increases not only the permeation rate but also the void space between molecular chains.

4.2.5 Molecular size

For an identical barrier layer, the smaller the permeants, the faster the permeation.

4.3 Permeability Measurement

There are various methods for measuring permeability, which differ in terms of procedure and apparatus. In general, there are two basic test methods developed, which are referred to as the isostatic and quasi-isostatic techniques. The former involves a constant and low concentration of permeant flowing through the high concentration cell chamber of a permeability cell. At the same time, carrier gas of a known flow rate is continually passed through the low concentration cell chamber, and is conveyed to a detector for quantification of the permeant. The quasi-isostatic procedure typically utilizes gas chromatography analysis for quantifying the accumulative amount of organic vapor that has permeated through the membrane (Baner et al.,1986).

4.3.1 Isostatic Method

Though the specific experimental design may vary among investigators, the basic concepts and equations describing the permeation phenomenon are similar. By this procedure, the measurement technique is focused on determining changes in the ratio of $\{(\Delta M/\Delta t)_t/(\Delta M/\Delta t)_\infty\}$, as a function of time. A typical transmission rate profile curve for the isostatic procedure is shown in Figure 8. From the permeability data, diffusion coefficient (D) and permeability coefficient (P) values are determined.

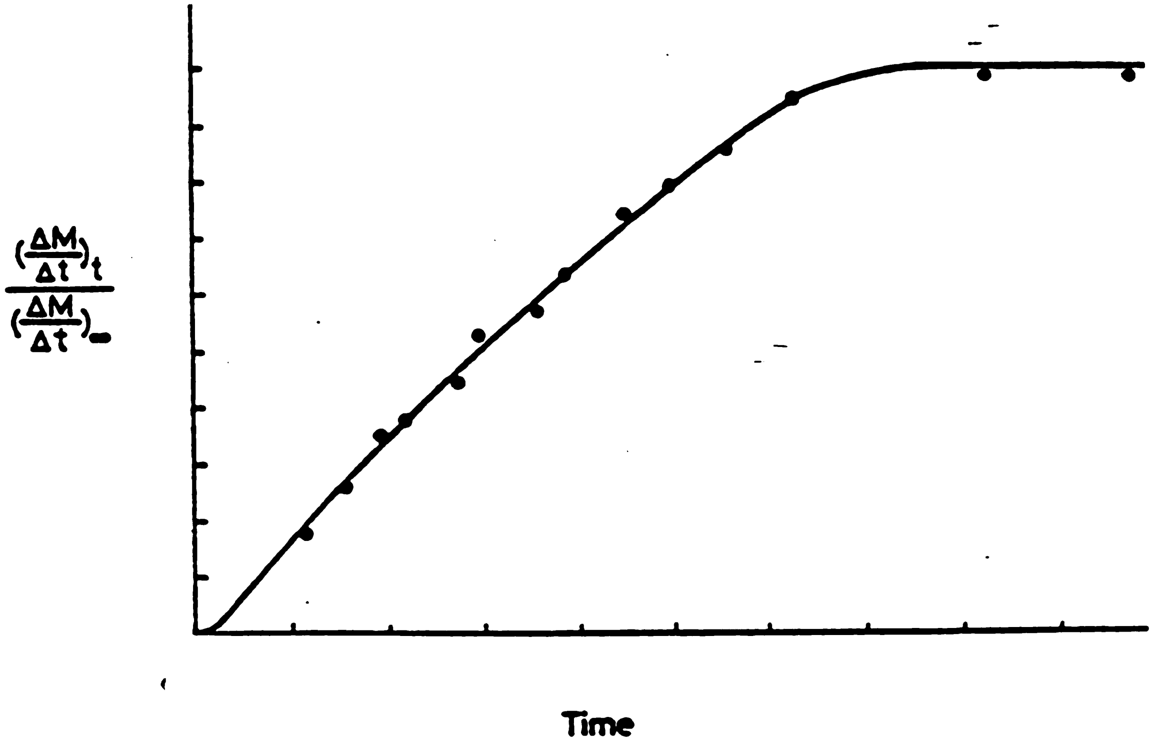


Figure 8: Typical Transmission Rate Profile Curve for Isostatic Procedure

Pasternak et al. (1970) developed an approximation which described the transmission rate profile curve as given in Eq.(12) (Hernandez et al.,1986).

$$\frac{(\Delta M/\Delta t)_t}{(\Delta M/\Delta t)_\infty} = \frac{4}{\sqrt{\pi}} * \left(\frac{l^2}{4Dt}\right)^{1/2} \exp\left(\frac{-l^2}{4Dt}\right) \qquad (12)$$

Where:

$(\Delta M/\Delta t)_t$ & $(\Delta M/\Delta t)_\infty$: the transmission rates of the penetrant at time (t) and at steady state, respectively.

t: time

l: thickness of the film

D: Diffusion coefficient

For each value of $(\Delta M/\Delta t)_t/(\Delta M/\Delta t)_\infty$, a value of $l^2/4Dt$ can be calculated, and by plotting $4Dt/l^2$ as a function of time, a straight line is obtained. Then:

$$D = \frac{(\text{slope})*l^2}{4} \qquad (13)$$

Ziegel et al. (1969) derived Eq.(14) to solve for D (Hernandez et al.,1986):

$$D = \frac{l^2}{7.199*t_{0.5}} \qquad (14)$$

Where $t_{0.5}$ is the time required to reach a rate of transmission $(\Delta M/\Delta t)_t$ equal to half the steady state $(\Delta M/\Delta t)_\infty$ value.

As a result, the permeability coefficient (P) can be determined from the isostatic method by Eq.(15).

$$P = \frac{a*G*f*l}{A*b} \qquad (15)$$

Where:

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

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

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

A: area of the film exposed to permeant in the permeability cell

(area units)

l: film thickness (thickness units)

b: driving force given by the concentration or partial pressure gradient (pressure or concentration units)

4.3.2 Quasi-isostatic Method

For such a method, the permeated gas or vapor is accumulated and monitored as a function of time. A generalized transmission rate profile curve is presented in Figure 9.

According to Fick's second law, Barrer (1939) illustrated the determination of D by Eq.(16) (Hernandez et al.,1986).

$$D = \frac{l^2}{6\theta} \qquad (16)$$

Where:

θ: the intersection of the projection of the steady state portion of the transmission curve, this is referred to as the lag time.

The steady state permeability coefficient can then be determined by Eq.(17) (Hernandez et al., 1986).

$$P = \frac{y*l}{A*b} \qquad (17)$$

Where:

y: the slope of the straight line portion of the transmission rate curve (mass/time)

l: thickness of the film

A: area of the film exposed to the permeant in the permeability cell

b: driving force given by the concentration or partial pressure gradient

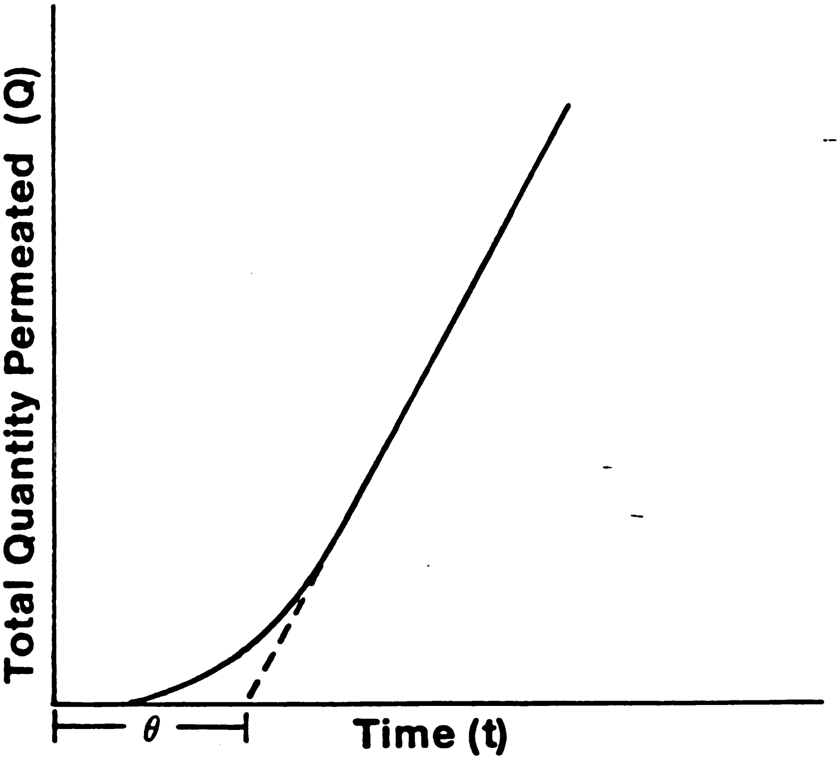


Figure 9: Typical Transmission Rate Profile Curve for Quasi-isostatic Procedure

5. Sorption Measurement

There are several approaches to determine sorption in polymeric films or sheets (Crank, 1975). Usually, sorption experiments are carried out at constant vapor pressure, using a gravimetric technique to record continually the weight gain of organic vapor sorbed by a test film as a function of time (Hernandez, 1986). Baner (1986) employed the equilibrium vapor pressure and gravimetric technique to observe the sorption and diffusion of toluene vapor in OPP and Saran film samples as a function of penetrant concentration, using a Cahn-RG Electrobalance (Cahn Instruments Inc., Cerritos, CA). In such a method, a test film sample was suspended in the sample tube of the electrobalance with constant temperature and concentration of penetrant vapor flow. The gain in weight of the sample due to penetrant sorption was monitored continually, until the equilibrium sorption level was attained.

The solubility coefficient can be calculated from Eq.(18) (Hernandez, 1986).

$$S = \frac{M\infty}{w.b} \tag{18}$$

where:

S: the solubility coefficient (kg/kg-Pa or Kg/m^3-Pa)

M_∞: the total amount of vapor absorbed by the polymer at equilibrium for a given temperature (kg)

w: the weight (or volume) of the polymer sample under test (kg or m^3)

b: the penetrant driving force in units of concentration or pressure (ppm or Pa)

The appropriate solution of the diffusion equation is described by Crank (1975) as:

$$\frac{Mt}{M\infty} = 1-\frac{8}{\pi^2}\left[\exp\left(\frac{-D.\pi^2.t}{l^2}\right)+\frac{1}{9}\exp\left(\frac{-9D.\pi^2.t}{l^2}\right)\right] \tag{19}$$

where:

M_t & M_∞: the amount of penetrant sorbed by the polymer film sample at time (t) and the equilibrium sorption level after infinite time

t: the time to attain M_t

l: the thickness of the film sample

The sorption diffusion coefficient (D_s) can then be calculated from Eq.(20), which is derived from Eq.(19) by setting M_t/M_∞ equal to 0.5.

$$D_s = \frac{0.049l^2}{t_{0.5}} \tag{20}$$

where:

$t_{0.5}$: the time required to attain the value, M_t/M_∞=0.5, which is obtained from the plot of M_t/M_∞ versus the square root of time ($t^{1/2}$) as shown in Figure 10.

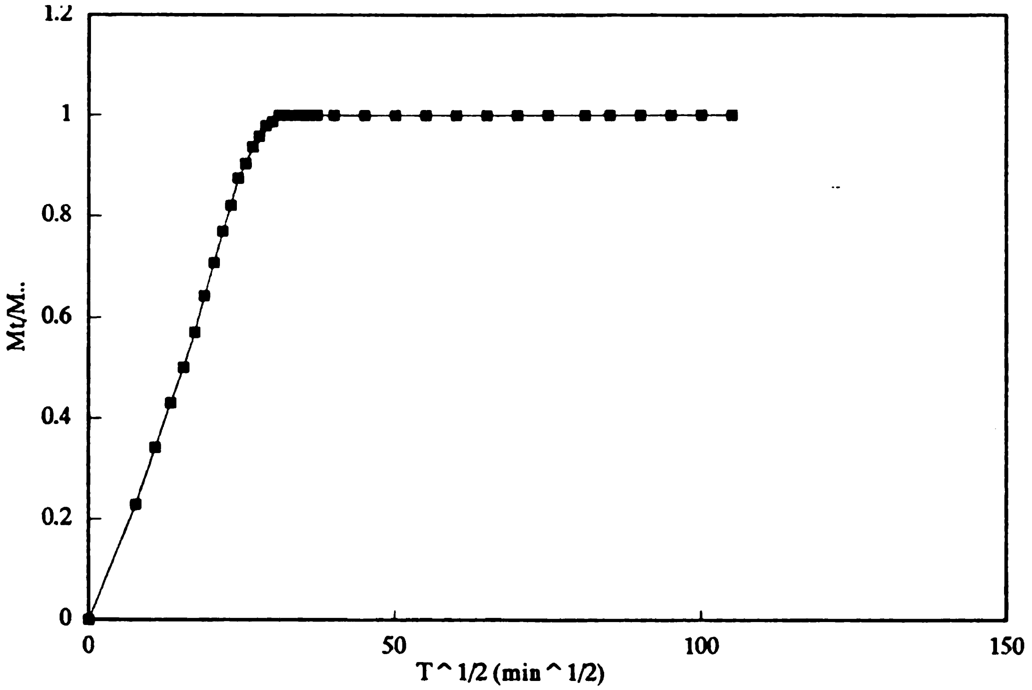


Figure 10: Typical Plot of M_t/M_∞ vs. $t^{1/2}$ for Sorption Procedure

MATERIALS AND METHODOLOGY

MATERIALS

1. Film Samples

In this study, three polymer films were investigated. They are:

1.1 Oriented Polypropylene (OPP)

A 2 mil biaxially oriented polypropylene film, provided by the Mobil Company, was used in these studies. The level of elongation was 420% (machine direction) and 800% (cross direction), based on the initial film dimensions. The percent crystallinity, calculated from heat of fusion, was 45.7%. The calculation is presented in Appendix A.

1.2 Polyethylene Terephthalate (PET)

A 0.5 mil PET film used in the studies was supplied from DuPont Company. The percent crystallinity was 31%. The calculation is also presented in Appendix A. Some typical properties provided by the company are shown in Table 2.

1.3 Nylon 6

A 1.5 mil Nylon 6 film (CAPRAN 77C) provided by Allied-Signal Inc., was used in the studies. Since the sulfonation of Nylon 6 was unsuccessful due to additional reaction occurring during the sulfonation process, no permeability and sorption studies were performed on sulfonated Nylon 6 film samples.

Table 2: Typical Properties of PET Film

Property	Test	Units	Values
Tensile Strength	ASTM D882	kpsi, MD	27
		TD	34
Elongation at	ASTM D882	%, MD	110
Break		TD	80
Modulus	ASTM D882	kpsi	550
Haze	ASTM D1003	%	4.5
Clarity	ASTM D1746	%	76

2. Sulfonating Agent

Oleum ($H_2S_2O_7$), or fuming sulfonic acid, was used as the working fluid of sulfonation. It is sulfuric acid saturated with free sulfur trioxide. The concentration used in the studies was 30% (wt/wt).

3. Cleaning Agent

2% Micro™, a commercially available laboratory grade liquid detergent, was used to clean all film samples prior to sulfonation. Micro™ was obtained from Cole-Parmer Instrument Company (Niles, IL).

4. Neutralizing Agent

Ammonium hydroxide (NH_4OH) solution (5% wt/v) was used to neutralize all the sulfonated film samples. To be consistant, all treated films were immersed in the solution for 5 minutes.

5. Organic Vapor Permeants

Ethyl acetate and toluene were selected as penetrants for the permeation study. The selection was based on the ease of chemical composition analysis, and volatility of the compounds. Research grade ethyl acetate and toluene was purchased from Aldrich Chemical Co.Inc. (Milwaukee, WI). Selected properties of ethyl acetate and toluene are shown below.

Ethyl Acetate

Density	0.894 g/ml
Molecular Weight	88.11
Boiling Range	76.5-77.5 °C

Refractive Index	1.37
Purity	99.9%

Toluene

Density	0.867 g/ml
Molecular Weight	92.14
Boiling Range	110.2-110.6 °C
Purity	99.9%

6. Carrier Gas

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

7. Gas Chromatograph

A Hewlett-Packard Model 5890A gas chromatograph, equipped with dual flame ionization detection and interfaced to a Hewlett-Packard Model 3392A integrator, was employed for all quantitative analyses of organic compounds in this study.

METHODOLOGY

1. Sulfonation Process

The sulfonation process was conducted at the Composite Materials and Structures Center (CMSC), Michigan State University. The schematic diagram of sulfonation system is shown in Figure 11. The method was based on the standard procedure which has been described in detail by Ericson (1993). A brief description of the sulfonation process is presented below.

Four clean, dry film samples (6"x13") were mounted to a film holder and placed in the sulfonating chamber. The lid to the sulfonating chamber was fixed in place using C-clamps to form a vacuum tight seal with the chamber. A nitrogen purge/vacuum/nitrogen purge cycle was developed to eliminate any active gas and water vapor that might be present in the chamber, which could react with SO_3 gas and interfere with the sulfonation reaction.

The sulfonator lines and chamber were flushed with dry nitrogen at a rate of 32 l/min for 3 minutes. A vacuum of about 300 μmHg was then applied to the chamber, followed by another 3 minute purge with nitrogen gas at a flow rate of 32 l/min.

Sulfur trioxide gas from the SO_3 generator was circulated through the sulfonating chamber. The reactor temperature was adjusted at 85±1 °F to obtain the desired concentration of SO_3 of 1±0.2 % (v/v). The gas was continuously circulated through the chamber for a predetermined time interval (1, 1.5, 2 and 3 minutes for OPP and 3, 5 and 7 minutes for PET). The concentration of the SO_3 gas was determined by a titration method (Ericson, 1993). During circulation, a 100 ml SO_3 sample was taken from a sampling port and injected into a flask containing 25 ml deionized water. The mixture was shaken well and its pH was measured. The SO_3 concentration (v/v) was then determined by solution of the standardized expression (Ericson, 1993).

$$\%SO_3 = 209.9436*\{\exp[-2.0649(pH)]\} \qquad (21)$$

After a predetermined exposure time, the system was immediately flushed with nitrogen gas at a flow rate of 32 l/min for 5 minutes to remove the excessive SO_3 from the chamber. The film samples were removed and immediately neutralized with 5% (wt/v) ammonium hydroxide solution. Thereafter, the samples were rinsed with deionized water to eliminate the excessive NH_4OH. After the films were dried, they were placed separately between aluminum foil sheets and stored at ambient temperature.

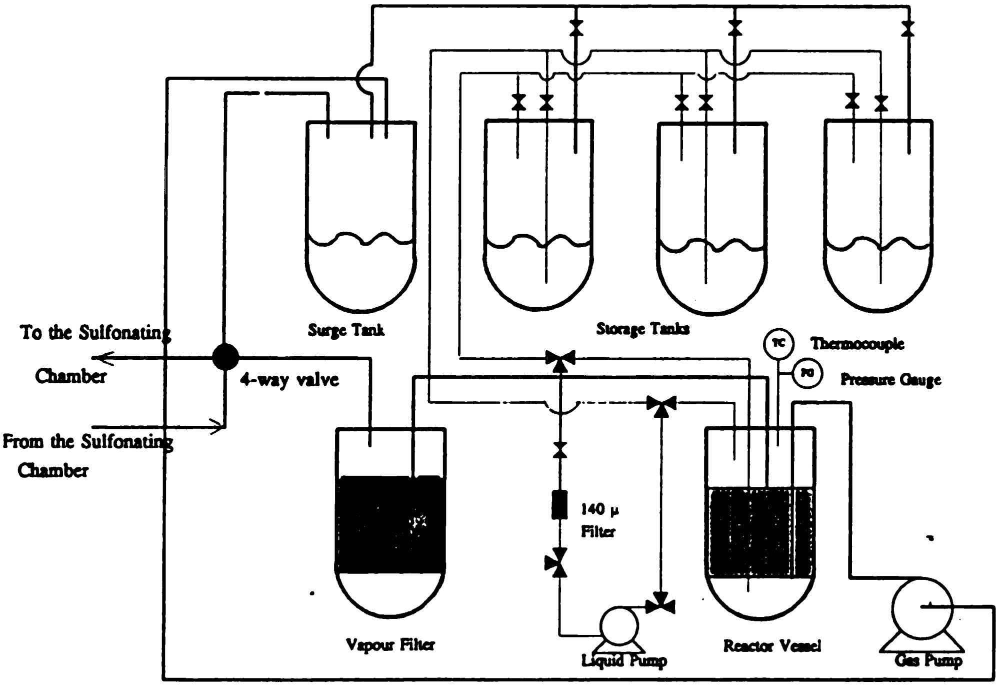


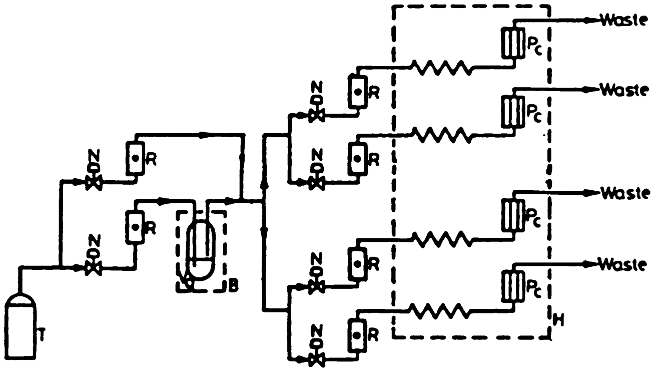
Figure 11: Schematic Diagram of Sulfonation System

2. Permeation Measurement

The permeation test system, employed in this study, was based on the quasi-isostatic method. Figure 12 presents a schematic diagram of the permeation test system. The test procedure is based on collecting permeation data as a function of time, at a specific temperature and permeant vapor activity.

The permeability cell, was composed of two aluminum cell chamber and a hollow center ring. Each chamber was fitted with an inlet and outlet valve and a gas sampling port. The upper and lower cell chambers each had a volume of 50 ml. In operation, film samples were mounted in the cell such that the center ring effectively isolated the upper and lower cell chambers. A constant, low partial pressure of permeant vapor was then flowed continuously through the center cell chamber at a fixed and constant flow rate. Based on this design, the permeability of two film specimens could be determined, concurrently.

A constant concentration of permeant vapor was produced by bubbling nitrogen gas through the liquid permeant. This was carried out by assembling a vapor generator consisting of a gas washing bottle, with a fritted dispersion tube, containing the organic liquid. To obtain a lower vapor concentration, the permeant vapor stream was diluted with another stream of pure nitrogen. Flow meters were used to indicate constant rates of flow. For OPP, permeability studies with ethyl acetate were carried out at 25±1 °C with an average constant vapor concentration of 19 μg/ml, which was equivalent to 0.04 vapor activity. The consistency of the vapor driving force is shown in Figure 13. For the OPP film, the studies with toluene were carried at the same



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

Figure 12: Schematic Diagram of Permeation Test System

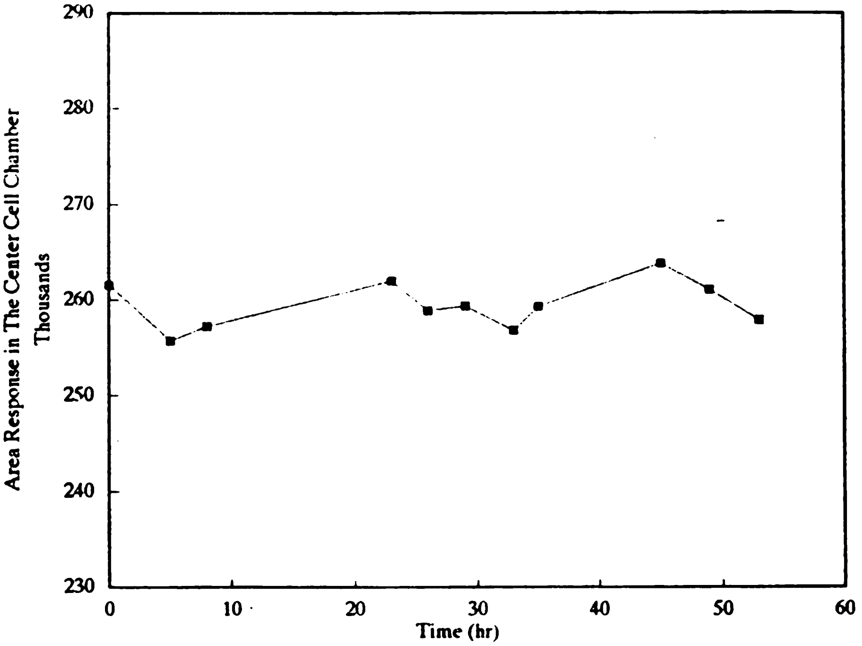


Figure 13: Consistency of the Ethyl Acetate Vapor Driving Force During Permeation Test

temperature (25±1 °C) with an average vapor concentration of 16 μg/ml, which was equal to 0.1 vapor activety. For PET, the permeability studies with ethyl acetate were carried out at 50±1 °C with an average constant vapor concentration of 187 μg/ml (0.15 vapor activity). The saturated vapor pressure values of ethyl acetate and toluene at the test conditions are presented in Appendix B.

In the quasi-isostatic method, the increase in penetrant concentration in the cell chambers is determined by gas chromatography with flame ionization detector. At predetermined time intervals, 100 μl (0.1 ml) of headspace gas was removed from each cell chamber with a gas-tight syringe and injected directly into the gas chromatograph. After each injection, a similar volume of pure nitrogen gas was introduced into the cell chamber to insure that the total pressure in each chamber remained constant.

The quantity of vapor permeated with time was monitored until a steady state rate of diffusion was reached. In analyzing the resultant data, the total quantity of organic vapor permeated as a function of time was included, up to a level at which the vapor concentration in the upper and lower cell chambers did not exceed 4% of the penetrant concentration in the center cell.

3. Sorption Measurements

Sorption measurements were carried out on a Cahn 2000 Electrobalance by the continuous flow method (Cahn Instruments Inc., Cerritos, CA). The electrobalance and sample tube were maintained at a constant temperature of 25±1 °C. A schematic diagram of the test apparatus is shown in Figure 14.

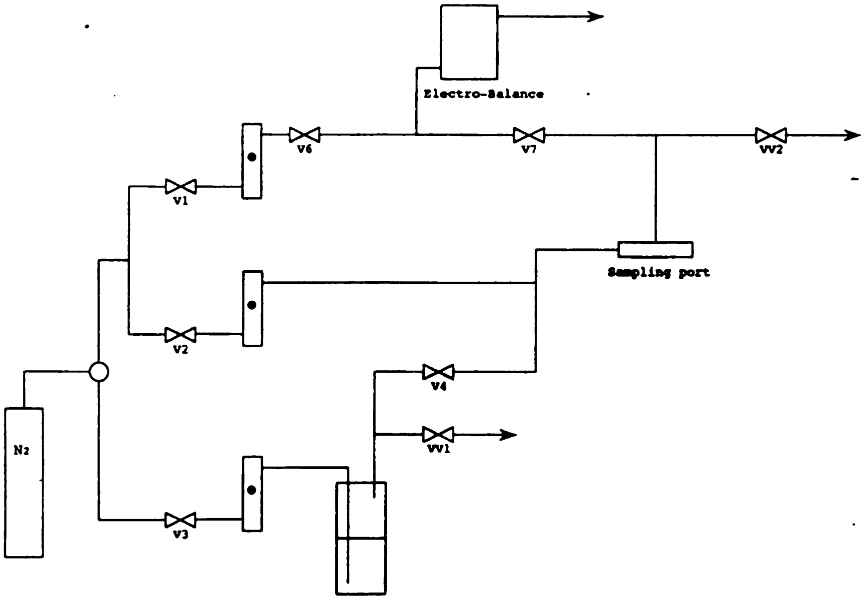


Figure 14: Schematic Diagram of Sorption Test System

As shown, the polymer film sample was suspended directly from the arm of the electrobalance and a constant concentration of penetrant vapor was flowed continuously through the sample tube. The constant concentration of penetrant vapor was produced by employing a vapor generator system similar to that described above. The concentration of ethyl acetate vapor was controlled by the amount of nitrogen gas flowing over the liquid phase, together with the amount of nitrogen gas selected for mixing. The sorption studies were carried out at an average vapor concentration of 47 μg/ml, which was equivalent to 0.1 vapor activity. The organic vapor concentration was quantitated by Gas Chromatography. The analytical conditions are described in the following section.

The test system allows for the continuous collection of sorption data, and the weight gain of film sample, from the initial time (t=0) up to the time that steady state has been reached.

4. Analytical Method

4.1 Gas Chromatographic Analysis

Analysis of permeant concentrations was carried out by a gas chromatographic procedure. A Hewlett-Packard Model 5890A gas chromatograph, equipped with dual flame ionization detectors and interfaced to a Hewlett-Packard Model 3392A integrator was used. A setting of 1 minute purge on was utilized for all analyses. The gas chromatographic conditions are presented below:

<u>GC Model 5890A</u>

Column : Supelcowax 10 (Supelco Inc., Bellefonte,PA)
Fused silica capillary
Polar bonded stationary phase
60 meter in length
0.25 mm I.D.

Carrier gas : Helium at 27 ml/min

Temperature : Injection temperature - 200 °C
Detector temperature - 250 °C
Oven temperature - 150 °C
Temperature programme rate - isothermal run

Range : 4

Attenuation : 0

Zero : 10

<u>Integrator Model 3392A</u>

Zero : 0,-1.1

Attenuation : 6

Chart speed : 0.5 cm/min

Peak width : 0.04

Threshold : 0

Retention time of ethyl acetate: 5.0 minutes
toluene: 5.5 minutes

The standard calibration curves for ethyl acetate and toluene are shown in Appendix C.

4.2 ESCA Analysis

All film samples were submitted to the Composite Materials & Structures Center, M.S.U., for determining the extent of sulfonation by X-ray Photoelectron Spectroscopy or Electron Spectroscopy for Chemical

Analysis (ESCA). This technique is used to determine all compositions except H atom on a film surface, at a depth of 50 angstroms. Each composition is reported as atomic percentage. An example of the results obtained by this procedure is presented in Appendix D.

RESULT AND DISCUSSION

1. SULFONATION OF ORIENTED POLYPROPYLENE (OPP) FILM

1.1 Characteristics

1.1.1 ESCA and Elemental Analyses

The surface composition of the untreated OPP film and the sulfonated samples was determined by X-Ray Photoelectron Spectroscopic analysis (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA). The results obtained are summarized in Table 3, Table 4 and presented graphically in Figure 15.

Summarized in Table 3 are the atomic concentrations for carbon, oxygen, nitrogen and sulfur determined for the respective film samples. The oxygen detected in the non-sulfonated film is assumed to be the result of a surface treatment such as Corona, which is a typical reaction for polypropylene. As shown in Table 4, the atomic ratios obtained for the respective sulfonated films were in agreement with the theoretical molecular structure of the sulfonate group. For the ammonium sulfonate group ($-SO_3^-NH_4^+$), the atomic ratios for S/O and O/C reported were based on corrected values for the oxygen atomic concentration level, where the initial oxygen atomic concentration was subtracted from the total atomic concentration to yield a corrected value. The respective atomic concentration ratios, as a function of reaction or exposure time, are presented graphically in Figure 15. From Figure 15, it can be seen that the respective atomic concentration values approach constant levels following a one minute exposure time, under the reaction conditions employed. Recently, Asthana (1993) reported that the surface of polymers, to include polypropylene, could not be sulfonated beyond a limit. The author also proposed that there was chain movement within the polymer at the molecular level, that did not allow insertion of additional sulfonate groups after a sulfonation limit. For polypropylene the sulfonation limit was reported by Asthana (1993) to be one sulfonate group per three repeat monomer units, on average, which is in good agreement with the results obtained in the present studies. Asthana (1993) confirmed that the site of reaction in polypropylene would be at the tertiary carbon, as described previously. From the present study, the ratio of C/S is about 10 which means there is 1 atom of sulfur present for every 10 atoms of carbon. Each repeating unit of polypropylene contains 3 carbons; therefore, on average, one sulfonate group is present for at least 3 repeating monomer units. The proposed repeat structure is presented below (Figure 16).

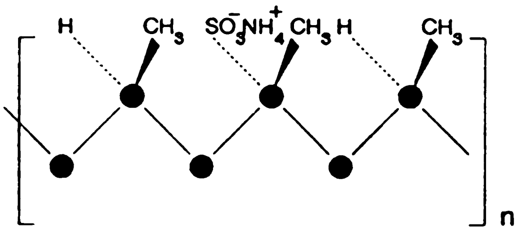


Figure 16: The Molecular Structure of Sulfonated Polypropylene

In addition to ESCA analysis, elemental analyses were also performed on the respective film samples to determine the total percent sulfur per gram of polymer. The comparison of sulfur content measured by ESCA analysis and elemental analysis, as a function of sulfonation time, are summarized in Table 5 and Figure 17, respectively. As shown by the results of ESCA analysis, the atomic percent sulfur approaches a constant value within the first minute of treatment. It should be noted that ESCA is a surface technique which can determine the composition on the material surface within 50-60 angstroms. As shown in Figure 17, while the atomic percent sulfur determined by ESCA seems to approach a constant value, the total weight percent sulfur, as determined by elemental analysis, increases in a linear fashion with sulfonation time.

This is assumed to be the result of SO_3 diffusion and subsequent reaction beyond the surface and within the film bulk phase, with extended treatment times.

1.1.2 Total Surface Free Energy

Contact angle analyses were also carried out to evaluate the effect of sulfonation on the surface free energy of the polymer film. These analyses provided an alternative technique for surface property characterization and were reported by Park (1993). The results of contact angle analyses carried out on the oriented polypropylene film and the respective sulfonated polypropylene film samples are tabulated in Table 6, where the surface free energy as well as the dispersive and non-dispersive components of the total surface free energy are presented (Park, 1993). The change in the total surface free energy, as well as the effect of sulfonation time on the dispersive and polar energy components of the surface free energy are shown by the histogram presented in Figure 18. The effect of sulfonation time on the polar, dispersive and total surface free energy values is also shown graphically in Figure 19, where the respective surface energy values are plotted as a function of sulfonation time. From Table 6 and the graphical analyses of the surface energy parameters, it becomes evident that the maximum level of surface sulfonation is approached within the first minute of reaction for the polypropylene film treated and the reaction conditions employed. Further reaction times resulted in little or no changes in the total surface free energy values or the respective polar and dispersive force contributions. These findings are in agreement with the results of Electron Spectroscopy for Chemical Analysis (ESCA), and provide further supportive evidence for the proposal that the maximum level of surface sulfonation was approached within the first minute of reaction, under the reaction conditions employed.

1.2 Permeation and Sorption Study

Permeability and Sorption studies were carried out with toluene and ethyl acetate, which are penetrants which varied with respect to both functionality and polar characteristics.

The quasi-isostatic procedure was employed to determine permeation rates and permeability coefficients. Also, effective diffusion coefficient values were determined by the lag time method, as previously discussed. Sorption studies were carried out by a gravimetric procedure, by which solubility and effective diffusion coefficient values were determined.

Table 3: Atomic Concentration for Untreated and Sulfonated OPP Films by ESCA Analysis

Sample	Sample Percentage Atomic Concentration				
	C	O	N	S	Total
OPP	93.1	6.9	0	0	100
1-min	66.5	23.1	5.9	4.5	100
1.5-min	65.5	24.3	5.2	5.1	100
2-min	58.0	28.9	6.6	6.5	100
3-min	60.4	27.9	5.4	6.3	100

Table 4: Relative Atomic Ratios of Sulfonated OPP Films

Sample	C/S	S/O	N/S
OPP	-	-	-
1-min	10	3	0.8
1.5-min	10	3	1.0
2-min	10	3	1.0
3-min	10	3	1.1

Table 5: Comparison of Sulfur Content Measured by ESCA Analysis and Elemental Analysis, as A Function of Sulfonation Time

Sample	Atomic % Sulfur (ESCA)	Total % Sulfur Per Gram of Film Sample (Elemental)
OPP	0	0
1-min	4.5	0.062
1.5-min	5.1	0.11
2-min	6.5	0.15
3-min	6.4	0.24

Table 6: The Variations of Solid Surface Energy for Untreated and Sulfonated OPP Films

Sample	Dispersive Energy Component (γ_s^d; dyne/cm)	Polar Energy Component (γ_s^p; dyne/cm)	Solid Total Surface Energy (γ_s; dyne/cm)
OPP	32.61	5.11	37.72
1-min	22.69	35.94	58.63
1.5-min	22.75	41.22	63.96
2-min	22.66	41.67	64.33
3-min	22.86	42.22	65.08

(Observed by I. Park)

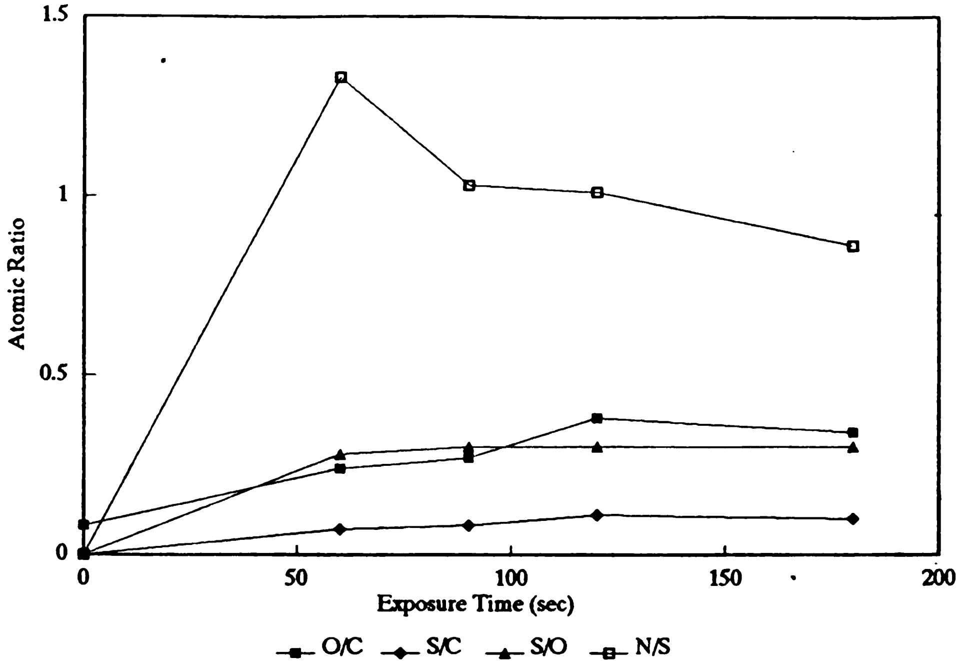


Figure 15: Atomic Ratio of Polypropylene Films As A Function of Sulfonation Time (at 1% SO_3 Concentration)

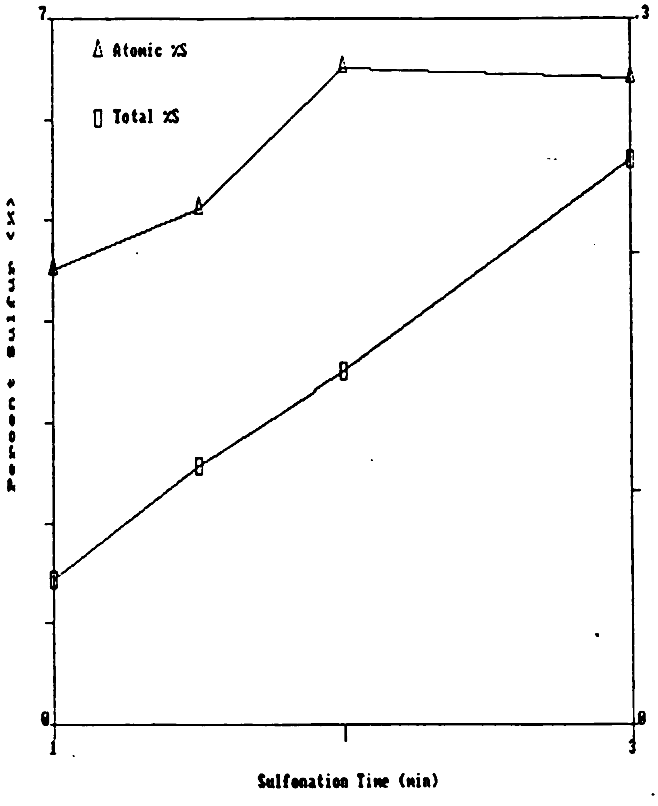


Figure 17: Comparison of Sulfur Content Measured by ESCA and Elemental Analyses in Sulfonated Polypropylene Films

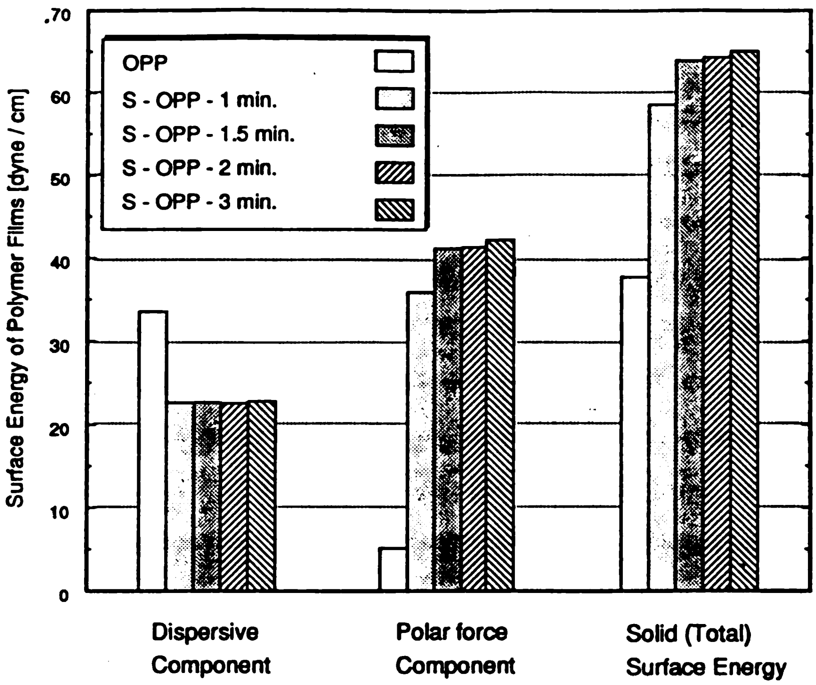


Figure 18: Variation of Solid Surface Energy, Dispersive and Polar Energy Components for Untreated and Sulfonated OPP Samples

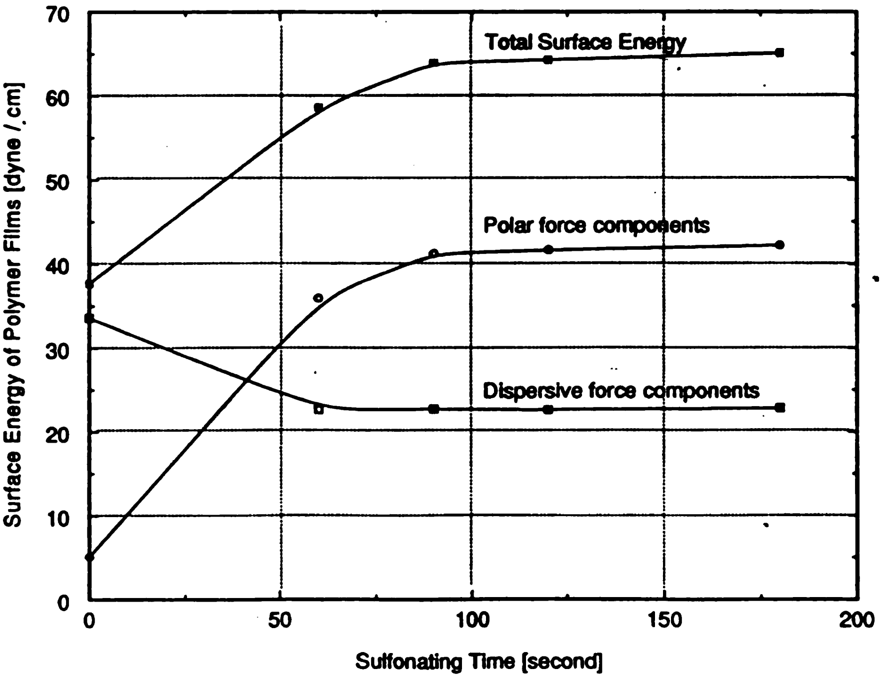


Figure 19: Variation of Solid Surface Energy, Dispersive and Palar Energy Components As A Function of Sulfonation Time

1.2.1 Permeation and Sorption of Ethyl Acetate

Permeation

Permeability studies with ethyl acetate were carried out at a constant vapor activity of a=0.04, at 25°C. The film samples were 2-mil untreated OPP film together with film samples sulfonated for 1, 1.5, 2 and 3 minutes, respectively. The results of the permeability studies are presented graphically in Figure 20, where the transmission rate curves for the respective film samples are plotted as a function of time. The permeability parameters calculated from these data are summarized in Table 7. The atomic percent sulfur and total percent sulfur for the respective film samples are also summarized in Table 7 to provide a comparison. It is evident from these results that sulfonation reduced the permeation rate of ethyl acetate vapor through the sulfonated film with the permeability coefficient (P) values decreasing with an increase in sulfonation time. This is illustrated graphically in Figure 21, where the permeability coefficient (P) is plotted as a function of sulfonation time.

Statistical analysis of the permeability data showed a statistically significant difference at the 95 % confidence ($\alpha = 0.05$) level, between the control and films sulfonated for 1.5, 2 and 3 minutes, respectively. From a least square fit, the following expression was derived to describe the relationship between the permeability constant (P) and sulfonation time (T), at a constant ethyl acetate concentration of 4 mmHg (a=0.04).

$$P = 6.98 - 0.0403(T) \tag{22}$$

$$R^2 = 69\ \%$$

ANOVA tables are illustrated in Appendix E.

Sorption

A representative plot of weight uptake per gram of film for the sorption of ethyl acetate by the OPP film obtained at a penetrant vapor activity of a=0.1 is shown in Figure 22. Superimposed on the curve is the weight uptake per gram of film for the OPP structure sulfonated for

1 and 2 minutes, respectively. The solubility coefficient and the effective diffusion coefficient values calculated from these data are summarized in Table 8. The total thickness of the sulfonated film structures was used in the calculation, although the respective sorption profile plots suggest that the barrier properties of the sulfonated surface layer may be significantly different from the polypropylene bulk phase and therefore will affect the mass transport properties of the sulfonated polypropylene films studied.

It can be seen that, for the respective film samples evaluated, the initial portion of the curve is approximated by a straight line. It was therefore assumed that at this relatively low permeant concentration, mass transport follows a Fickian type behavior.

The relationship between the solubility coefficient and the effective diffusion coefficient, as a function of the extent of sulfonation, expressed as contact time, is presented graphically in Figure 23. As shown in Figure 23 and Table 8, one order of magnitude reduction in the effective diffusion coefficient was obtained for the 2 minute sulfonated polypropylene film, as compared to the untreated control. Whereas the solubility coefficient of the respective sulfonated structure and control remained fairly constant.

Table 7: Permeability Parameters for Sulfonated OPP Film Samples with Ethyl Acetate vapor from Permeation Studies[a]

Sample	Average Values			
	P x 10^{18} ($Kg\text{-}m/m^2\text{-}s\text{-}Pa$)	Effective D x 10^{14} (m^2/s)	Atomic %S Content	% Sulfur Per Gram of Sample
OPP	7.2±2.2[b]	2.3±0.5	0	0
1-min	5.5±2.1[b]	1.6±0.4	4.5	0.062
1.5-min	2.0±0.8[c]	1.1±0.5	5.1	0.11
2-min	1.2±0.3[b]	1.1±0.3	6.5	0.15
3-min	0.8±0.1[c]	1.4±0.5	6.4	0.24

[a] Ethyl acetate partial pressure gradient = 4 mmHg (0.04 vapor activity) at 25°C

[b] Average of four replicates ± S.D.

[c] Average of three replicates ± S.D.

Table 8: Permeability Parameters for Sulfonated OPP Film Samples with Ethyl Acetate vapor from Sorption Studies[a]

Sample	Effective D x 10^{14} (m^2/s)	S x 10^3 ($Kg/m^3\text{-}Pa$)
OPP	0.8±0.1	3.3±0.2[b]
1-min	0.9±0.2	3.3±0.8[b]
2-min	0.04	2.20 [c]

[a] Ethyl acetate partial pressure gradient = 10 mmHg (0.1 vapor activity) at 25°C

[b] Average of two replicates

[c] No replicates

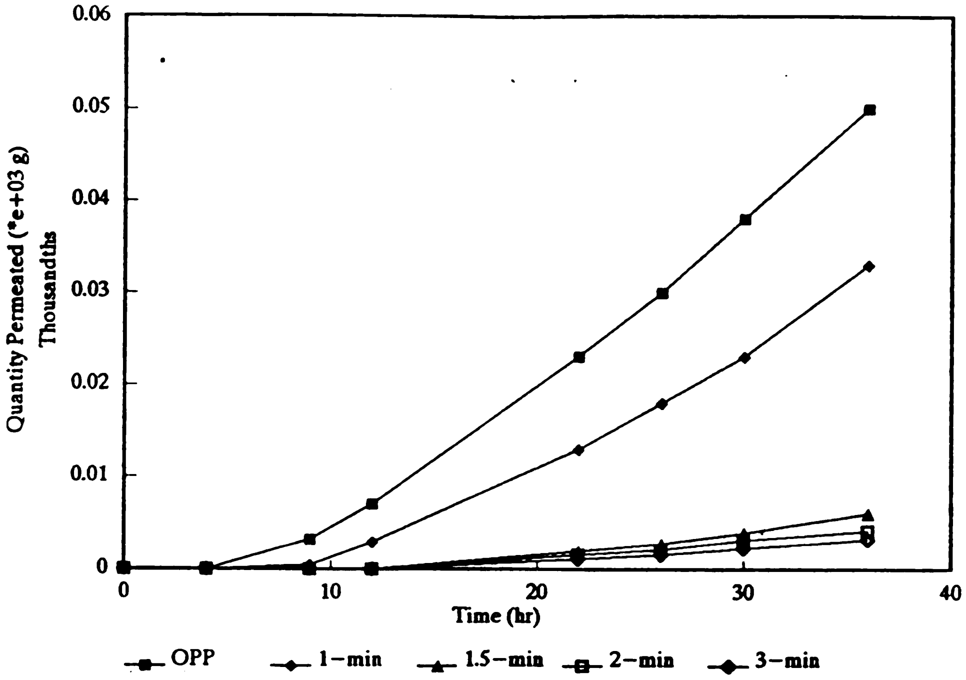


Figure 20: Comparison of Ethyl Acetate Permeation Among OPP and Sulfonated OPP Film Samples (25 °C, a=0.04)

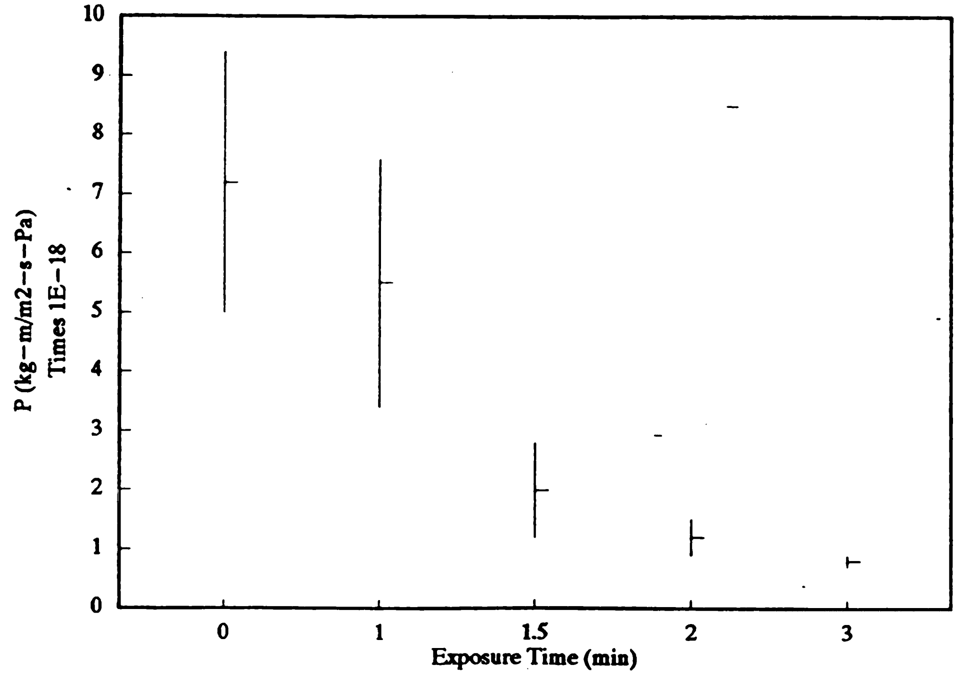


Figure 21: Relation Between Permeability Coefficient of Ethyl Acetate in Polypropylene Films AS A Function of Sulfonation Time

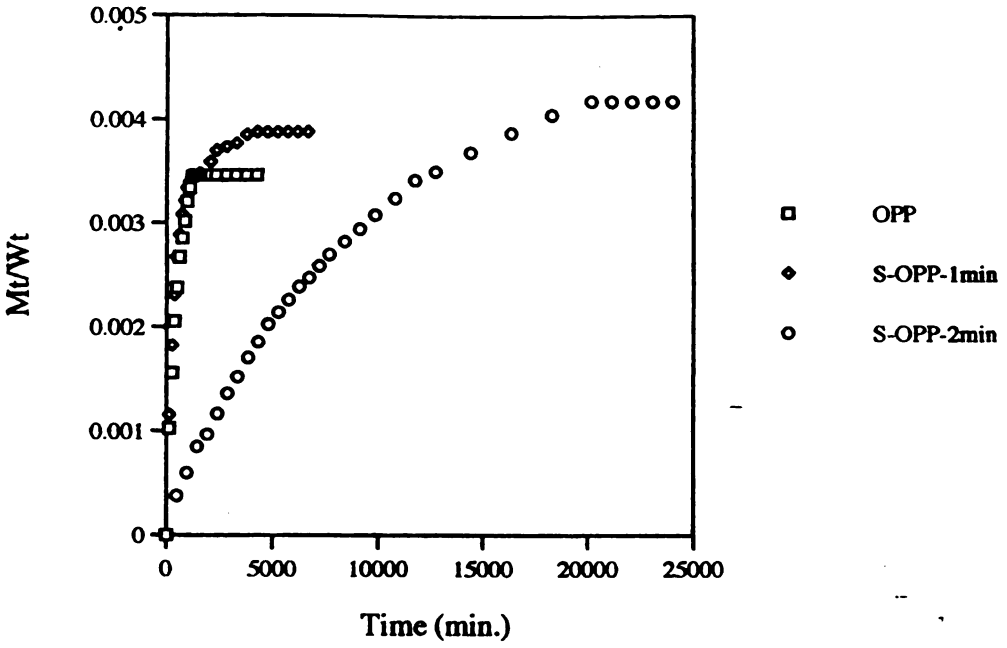


Figure 22: Weight Uptake Per Gram of Film for Ethyl Acetate Sorption in Untreated and Sulfonated OPP Samples (a=0.1)

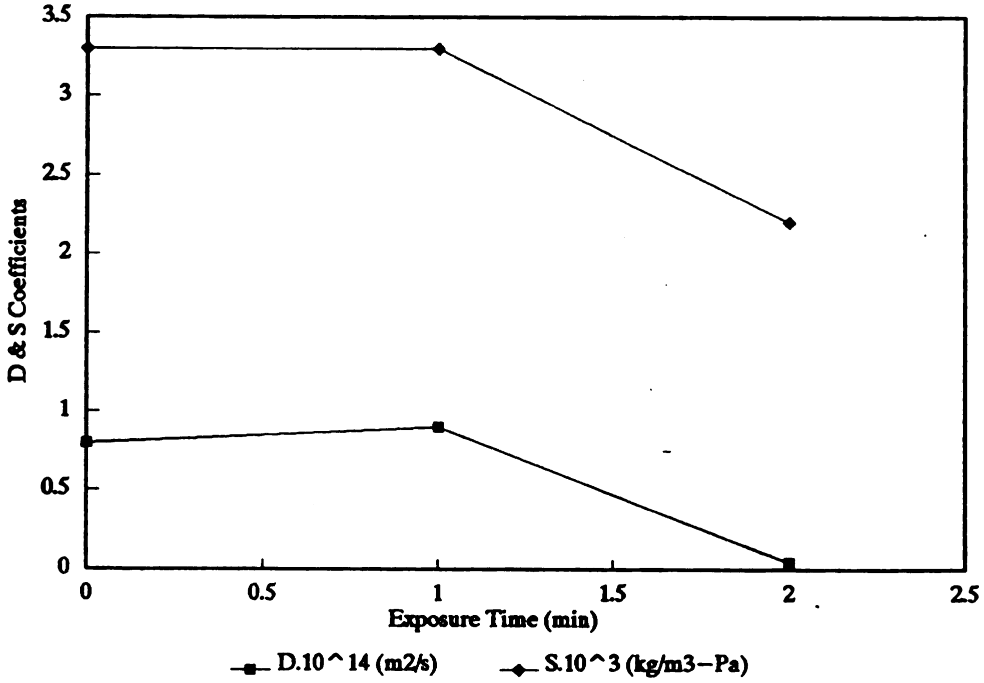


Figure 23: Relation Between D, S Coefficients and Sulfonation Time for Ethyl Acetate Sorption of Polypropylene Films

1.2.2 Permeation and Sorption of Toluene

Toluene permeation studies were carried out at a constant vapor activity of a=0.1 at 25°C. For these studies, toluene permeation rates through the 3 minute sulfonated polypropylene film were determined and compared to the untreated control. Representative transmission rate profile curves for the respective film samples are presented in Figure 24. The resultant mass transport parameters are summarized in Table 9. As shown in Figure 24, toluene vapor permeated rapidly through the OPP film and attained a steady state level within 2 days. In contrast, no detectable level of permeation was observed for the surface sulfonated film sample, after 2 weeks of continuous testing.

In a related study, Gavara (1993) determined the sorption of toluene by polypropylene and polypropylene film samples sulfonated for 1, 1.5 and 2 minutes, respectively. A plot of weight uptake per gram of film for the sorption of toluene by the OPP film and respective sulfonated OPP film samples, obtained at a penetrant vapor activity of a=0.034, is presented in Figure 25. The solubility coefficient and the effective diffusion coefficient values calculated from these data are tabulated in Table 10. The total thickness of the sulfonated film structures was used in the calculation, as discussed above.

The relationship between the solubility coefficient and the effective diffusion coefficient as a function of sulfonation time is presented graphically in Figure 26. As shown in Table 10 and Figure 26, a two order of magnitude reduction in the effective diffusion coefficient was obtained for the 1.5 and 2 minute sulfonated polypropylene films, as compared to the untreated control, at similar test conditions. Whereas the solubility coefficient remained fairly constant following sulfonation. The observed reduction in the permeability coefficient for toluene vapor as a function of sulfonation time can thus be attributed to a reduction in the mobility term, D.

The results of these studies have shown the effectiveness of the sulfonated surface layer in reducing the rates of transmission and the effective diffusion coefficient values of ethyl acetate and toluene through the sulfonated polypropylene films. While this behavior is not totally understood, it can be attributed, in part, to the solubility and diffusivity of the organic penetrants within the sulfonated surface layer being significantly different than these parameters within the bulk phase. In this case, the concentration profile or gradient would drop rapidly across the sulfonated surface layer. Further, since the outer sulfonated surface layer is expected to have a lower diffusion coefficient, it would also take a significant period of time to reach a steady state rate of diffusion through the barrier layer, prior to penetrating the polypropylene bulk phase.

Table 9: Permeability Parameters for Sulfonated OPP Film Samples with Toluene vapor from Permeation Studies(a)

Sample	Average Values			
	P ($Kg-m/m^2-s-Pa$) x 10^{-17}	Effective D (m^2/s x 10^{-15})	Atomic %S Content	% Sulfur Per Gram of Sample
OPP	1.8±0.4(b)	7.3±0.2	0	0
3-min	N/D (c)	N/D	6.4	0.24

(a) Toluene partial pressure gradient = 3 mmHg (0.1 vapor activity) at 25°C

(b) Average of four replicates

(c) N/D: No detectable permeation following 2 week of continuous testing

Table 10: Permeability Parameters for Sulfonated OPP Film Samples with Toluene vapor from Sorption Studies(a)

Sample	Effective D x 10^{14} (m^2/s)	S x 10 (Kg/m^3-Pa)
OPP	2.3	0.8
1-min	1.0	0.68
1.5-min	0.063	0.60(b)
2-min	0.014	0.43(b)

(a) Average toluene vapor activity a=0.034 at 25°C

(b) Estimated from non-steady portion of Sorption Curve (Observed by R. Gavara)

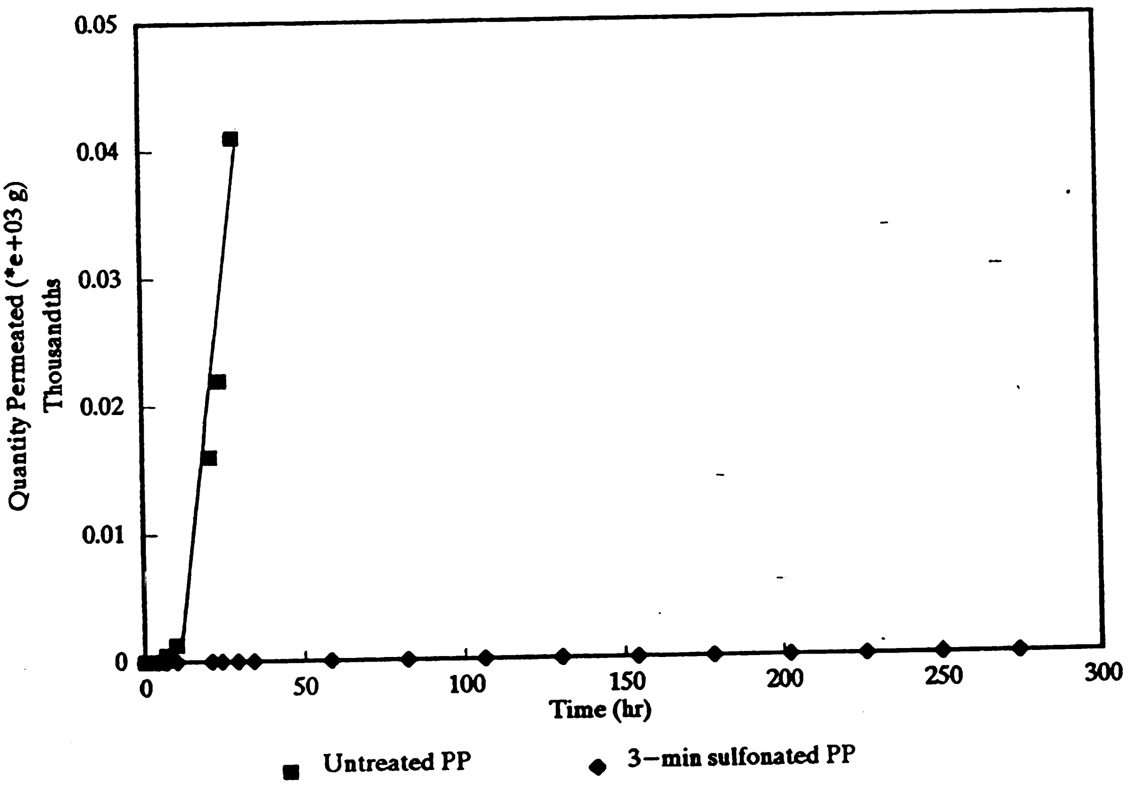


Figure 24: Comparison of Toluene Permeation Between Untreated and Sulfonated Polypropylene (25 °C, a=0.1)

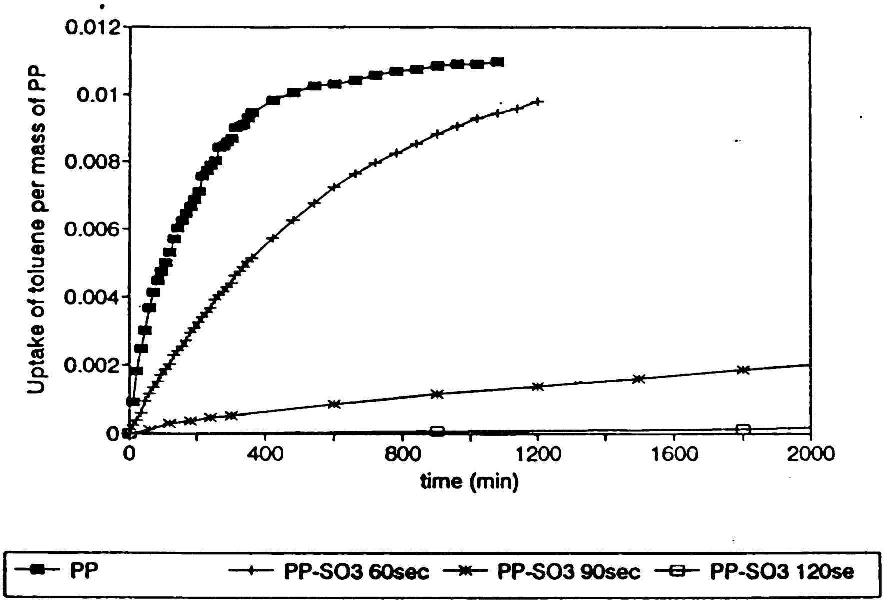


Figure 25: Weight Uptake Per Gram of Film for Toluene Sorption in Untreated and Sulfonated OPP Samples (a=0.034)

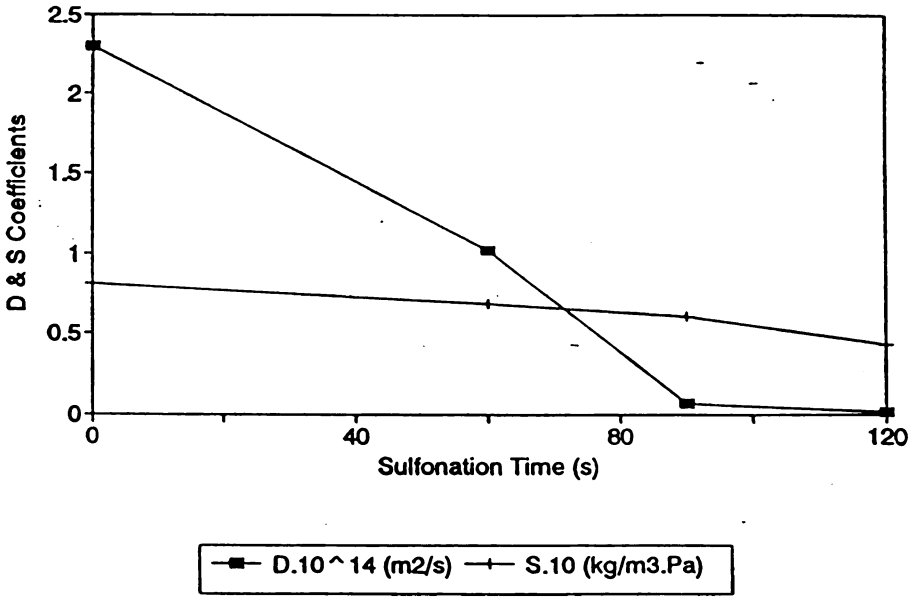


Figure 26: Relation Between D, S Coefficients and Sulfonation Time for Toluene Sorption of Polypropylene Films

2. SULFONATION OF POLYETHYLENE TEREPHTHALATE (PET)

2.1 Characteristics

2.1.1 ESCA Analysis

The surface composition of the untreated PET film and the sulfonated PET samples determined by ESCA analysis is presented in Table 11. For PET, sulfonation was found to be ineffective and only a limited number of sulfonate groups can be substituted onto the film surface. With an average atomic ratio for S/C being 0.005, it implies that there is 1 atom of sulfur present for every 200 atoms of carbon. Each repeating unit of PET contains 10 atoms of carbon. Consequently, 1 sulfonate group is present for every 20 repeating monomer units. These findings are also in a good agreement with the results of contact angle analysis, in that there was little or no change in the total surface free energy for sulfonated PET, as compared to the untreated control (Park, 1993).

The sulfonation of a polymer surface is a highly electrophilic reaction in which SO_3 tends to react at centers of high electron density (Asthana, 1993). For the terephthalate group of the polyethylene terephthate polymer, this would be the respective ortho positions of the aromatic ring. Substitution of these sites, however, would be restricted by steric hindrance of the carbonyl groups.

2.1.2 Total Surface Free Energy

The results of the total surface free energy, as well as the dispersive and polar energy components, are provided in Table 12 (Park, 1993). The effect of sulfonation time on the change in total surface free energy and the respective energy components is shown in Figure 27. From Table 12 and the graphical analysis of the surface energy parameters, it becomes evident that sulfonation of PET is ineffective under the treatment conditions employed. This is attributed to the steric hindrance of SO_3 substitution at the ortho position of the aromatic ring of the terephthalate group, which is the expected site for substitution.

2.2 Permeation Study

For the PET film samples only the permeability of ethyl acetate was considered. Permeation studies were performed at 50 °C under a constant vapor activity of $a=0.15$. The PET samples were sulfonated for 0, 3, 5 and 7 minutes, respectively. A comparison of the transmission rate profile curves for the untreated and sulfonated PET film samples is presented in Figure 28. The permeability parameters determined are summarized in Table 13. From Table 13, it is evident that sulfonation had little effect on the permeability of ethyl acetate through PET film, at the levels of sulfonation achieved.

A statistical analysis of the obtained data for ethyl acetate barrier characteristics was carried out. In order to determine whether a statistically significant difference exists between ethyl acetate barrier property values for an untreated and a surface sulfonated PET, ethyl acetate diffusion coefficient and permeability coefficient values for the untreated PET film were compared with the various surface sulfonated PET film samples. The ANOVA data are presented in Appendix E.

No statistically significant difference was found to exist for the diffusion coefficient values at a confidence level of 95% ($\alpha=0.05$), Statistical analysis showed no significant difference for the permeability coefficient values at a confidence level of 95% ($\alpha=0.05$) except for the 7 minute treated film sample. However, if the permeability coefficient values for treated PET films are compared to the upper and lower bound limits for the permeability coefficient values of replicate analyses carried out on the untreated control, all permeability coefficient values fall within the upper and lower bound limits. The difference in ethyl acetate permeability values between the treated and untreated film samples may be simply the result of inadequate replications to provide for good statistical analysis.

Thus, polymer surface modification at the level of sulfonation achieved has no evident effect on the ethyl acetate barrier properties of PET. This is not surprising, when considering the limited level of sulfonation achieved.

Table 11: Atomic Concentration for Untreated and Sulfonated PET Films by ESCA Analysis

Sample	Percentage Atomic Concentration			
	C	O	N	S
PET	69.6	30.4	0	0
3-min	78.1	21.1	0	0.4
5-min	70.2	29.4	0	0.4
7-min	70.4	29.2	0	0.4

3. SULFONATION OF NYLON 6

The study of the sulfonation of Nylon 6 was unsuccessful, apparently due to additional reactions occurring during the sulfonation treatment. Immediately after sulfonation, the film was found to be tacky and extremely difficult to handle. Consequently, with a batch process, it was very difficult to remove the sulfonated film samples from the sulfonation chamber and neutralize the treated films without considerable physical damage. Further, the sulfonated nylon film was quite opaque, which could have resulted from reaction between SO_3 and moisture in the film itself to yield sulfuric acid. As a result, the film could be damaged or degraded by the acid. Due to the aforementioned problems experienced with sulfonating the polyamide, no permeability or sorption studies were performed on sulfonated Nylon 6 film samples.

Table 12: The Variations of Solid Surface Energy for Untreated and Sulfonated PET Films

Sample	Dispersive Energy Component (γ_s^d; dyne/cm)	Poalr Energy Component (γ_s^p; dyne/cm)	Solid Toatal Surface Energy (γ_s; dyne/cm)
PET	40.85	6.94	47.79
1-min	38.84	14.83	53.67
3-min	37.38	15.86	53.24

(Observed by I. Park)

Table 13: Permeability Parameters for Sulfonated PET Film Samples with Ethyl Acetate Vapor from Permeation Studies[a]

Sample	Average Values		
	P x 10^{20} (Kg-m/m^2-s-Pa)	Effective D x 10^{16} (m^2/s)	Atomic %S Content
PET	5.6±1.7[b]	2.4±0.6	0
3-min	3.4±0.1[c]	2.9±0.5	0.4
5-min	7.2±1.3[c]	1.8±0.02	0.4
7-min	9.2±0.4[d]	2.3±1.0	0.4

[a] Ethyl Acetate partial pressure gradient = 40 mmHg (0.15 vapor activity) at 50°C

[b] Average of four replicates

[c] Average of two replicates

[d] Average of three replicates

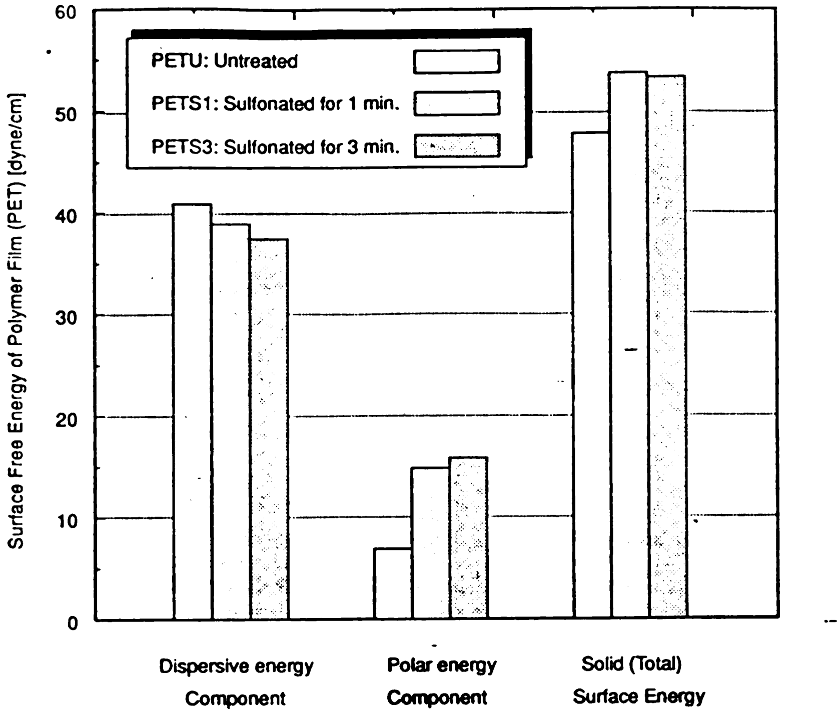


Figure 27: Variations of Solid Surface Energy, Dispersive and Polar Energy Components for Untreated and Sulfonated PET Samples

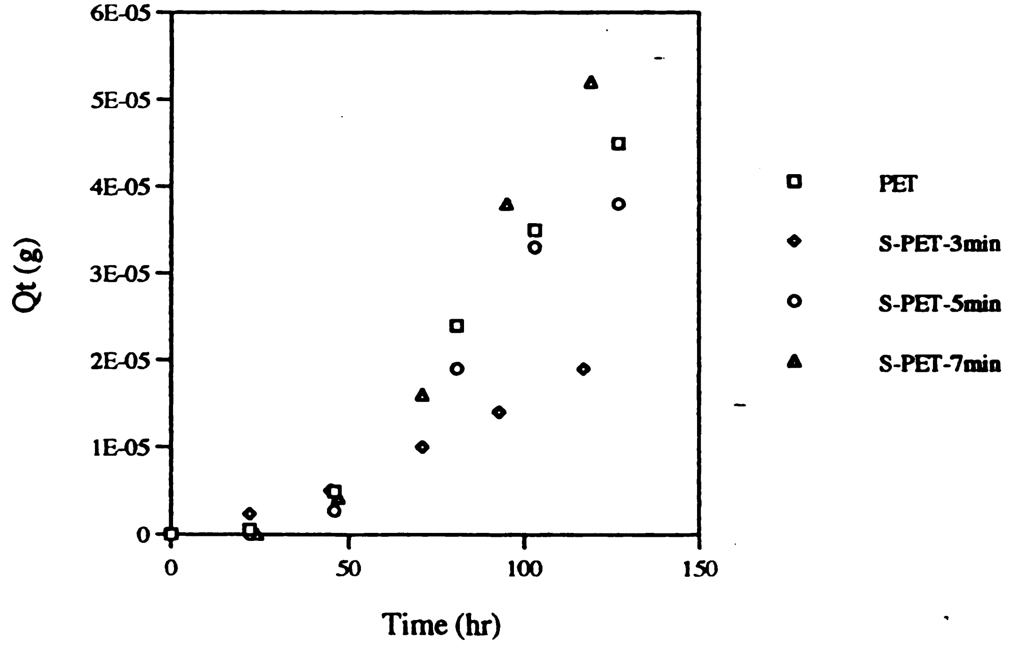


Figure 28: Comparison of Ethyl Acetate Permeation Among PET and Sulfonated PET Film Samples (50 °C, a=0.15)

EXPERIMENTAL ERRORS

Sulfonation

1. Consistency of the process

Since the sulfonation procedure employed in the study is a batch process, it can be lacking consistency compared with a continuous process. It is not certain how uniform the sulfonation can be performed within a run and between the replicate runs. Non-uniformity of sulfur content, could therefore result in variation in observed permeation rates.

2. Stability of oleum

This factor is very important for if the dissolved SO_3 level is reduced, this would result in a deviation in SO_3 vapor concentration generated. In the study, the oleum concentration used was found to be weaker after several months of operation. It could not generate a consistent SO_3 concentration at a particular reactor temperature. The reactor temperature was therefore raised to obtain the required concentration. To diminish this problem, the oleum has to be replaced periodically or when it is found inactive.

3. A presence of moisture in the sulfonation system

Trace levels of moisture present in the system can react with SO_3 to form sulfuric acid. Therefore, it is necessary to eliminate available moisture from the system as much as possible. Otherwise, the SO_3 concentration will be reduced due to the above reaction. For the SO_3 generator system employed, a vacuum pump was used to withdraw the moisture from the sulfonation chamber, prior to the sulfonation reaction. Also, all the connecting valves and hoses were cleaned and baked in an oven over night after each day of operation.

Permeation

1. Consistency of film samples

Film consistency, to include thickness and percent orientation will be dependent on how uniform the film is made by the manufacturer. These parameters as well as uniformity of the sulfonation process will contribute to a standard deviation between replicate runs.

2. Instrument sensitivity

The gas chromatograph has to be checked with a calibration standard to insure reproducable sensitivity, prior to each run. There are several factors that contribute to variations in detector response, to include cleanness of the capillary column, consistent gas flow in the system, consistent head pressure and the amount of compound injected. In addition, each syringe also has its own measurement error. Thus, it is important to use one syringe to withdraw a particular sample for quantitative analysis throughout the experiment.

3. Temperature

Since the permeation process is temperature dependent, the temperature must be controlled to avoid fluctuation.

4. Vapor Activity

For organic vapor permeation, the mass transport process is also concentration dependent. Since the organic vapor can swell the polymer matrix and act as a plasticizer, which results in a decrease in barrier properties of the polymer. Thus, one specific vapor activity has to be employed for all experiments carried out on the same type of polymer film to avoid the variations in transmission rate as a result of variation in vapor concentration.

Sorption

1. Sensitivity of electro-balance

Since the electro-balance is very sensitive, it must be placed where the least potential impact of vibration may occur. Otherwise, it can cause fluctuation of the equipment sensitivity.

2. Gas flow regulator

Due to the sensitivity of the electro-balance and the apparatus design, the vapor concentration cannot be easily checked during the course of the experiment. It can be checked only before and after the test. Consequently, the flow regulators used must be accurate and precise to generate an identical flow rate during the test and between replicate runs. In addition, the nitrogen gas used to generate proper vapor concentration has to be checked to maintain a constant pressure throughout the experiment.

SUMMARY AND CONCLUSIONS

1. Mild Surface sulfonation was found to be very effective in modifying the barrier properties on OPP film. This is attributed to the presence of tertiary carbons in the molecule which provide active sites for SO_3 insertion. Sulfonation reactions were carried out for up to 3 minutes. At longer contact time, the higher extent of sulfonation resulted in degradation of the polymer.

2. For the oriented polypropylene film, sulfonation was found to reduce the permeation rate of ethyl acetate vapor, with a one order of magnitude reduction in P being observed for the 3 minute sulfonated film, as compared to the untreated control.

3. For the toluene/OPP, penetrant/barrier film combination, no detectable level of permeation was observed for the 3 minute sulfonated film, after 2 week of continuous testing.

4. Sorption studies showed that a one order of magnitude reduction in the effective diffusion coefficient was obtained for ethyl acetate sorption by the 2 minute surface sulfonated polypropylene film.

5. Sorption studies involving toluene vapor indicated a two order of magnitude reduction in the effective diffusion coefficient for the 1.5 and 2 minute sulfonated polypropylene films, as compared to the untreated control.

6. The observed reduction in the permeability of ethyl acetate and toluene through the sulfonated polypropylene films is attributed to a reduction in the mobility term D within the sulfonated surface layer.

7. Sulfonation of PET film was found to have little or no effect on ethyl acetate permeability rates. This was attributed to steric hindrance to SO_3 reaction at the ortho positions of the aromatic ring of

the terephthalate group, which is the expected site for substitution.Statistical analysis of the permeability parameter data for ethyl acetate permeability through an untreated and surface sulfonated PET film samples showed no statistically significant difference for the diffusion coefficient values at a confidence level of 95%. With respect to the permeability coefficient values, all coefficients for sulfonated film samples fell within the upper and lower bound limits for replicate analyses carried out on untreated PET film.

The results of these studies have shown the effectiveness of the sulfonated surface layer in reducing the rates of transmission and the effective diffusion coefficient values of ethyl acetate and toluene through the sulfonated polypropylene films. While this behavior is not totally understood, it can be attributed, mostly, to the solubility and diffusivity of the organic penetrants within the sulfonated surface layer being significantly different than these parameters within the bulk phase. In this case, the concentration profile or gradient would drop rapidly across the sulfonated surface layer. Further, since the outer sulfonated surface layer is expected to have a lower diffusion coefficient, it would also take a significant period of time to reach a steady state rate of diffusion through the barrier layer, prior to penetrating the polypropylene bulk phase.

POSSIBLE FUTURE STUDIES

Based on the results obtained in the present study, a number of additional area of investigation can be proposed. Some potential future areas of study are as follows:

1. For the sulfonation of OPP, the effect of different types of counterions can be further investigated. As mentioned previously, several researchers found that exchanging the counterion (e.g., Ca^{++}, Li^{+}) can improve barrier properties of the polymer when compared to the ammonium (NH_4^{+}) counterion.

2. The results of the present studies have shown that the surface sulfonation increases the barrier properties of OPP film to organic penetrants by means of increasing the polar component of the polymer surface free energy. It would be interesting to evaluate the effect of relative humidity on the barrier properties of sulfonated polymeric films. Since water, a polar molecule, may easily sorb into the sulfonated polymer surface and act as a plasticizer.

3. In this research, the sulfonation of a polyamide was not successful. A study of the chemical changes on the polyamide film surface following sulfonation, and the effect of surface sulfonation on its barrier properties is proposed.

4. Physical properties, such as tensile strength, seal strength, peel strength, and puncture resistance, of the sulfonated films should also be determined. These parameters are important for packaging fabrication.

It is also essential to determine how the sulfonated polymeric films can be applied to packaging use. It is questionable if it is safe to use the sulfonated polymer as a direct food contact package or if it can be used in conjunction with other materials as a laminate structure. This has to be studied in significant detail. A potential non-food packaging use of sulfonated films can be the pouch-typed package for automobile lubrication. Especially at this time, where there is great concern about the environment, and thus the wide use of refillable packages may reduce the land-fill problems.

APPENDICES

APPENDIX A

Crystallinity

The percent crystallinity of OPP and PET films were estimated by determining the heats of fusion of the polymers by the Differential Scanning Calorimetry technique (DSC). The crystallinity was then calculated by the expression in Eq.(23). The thermograms obtained for the OPP and PET film samples by DSC analysis are shown in Figures A-1 and A-2, respectively.

$$\text{\% Crystallinity} = \frac{H_f}{H_f^*} \times 100 \qquad (23)$$

where:

H_f : heat of fusion of the polymer examined (J/g)

H_f^* : heat of fusion of the polymer having 100% crystallinity (J/g)

H_f^* for PP (isotactic, Form I) = 209 J/g

for PET = 129.7 J/g

(Polymer Handbook, 2nd edition, John Wiley & Sons)

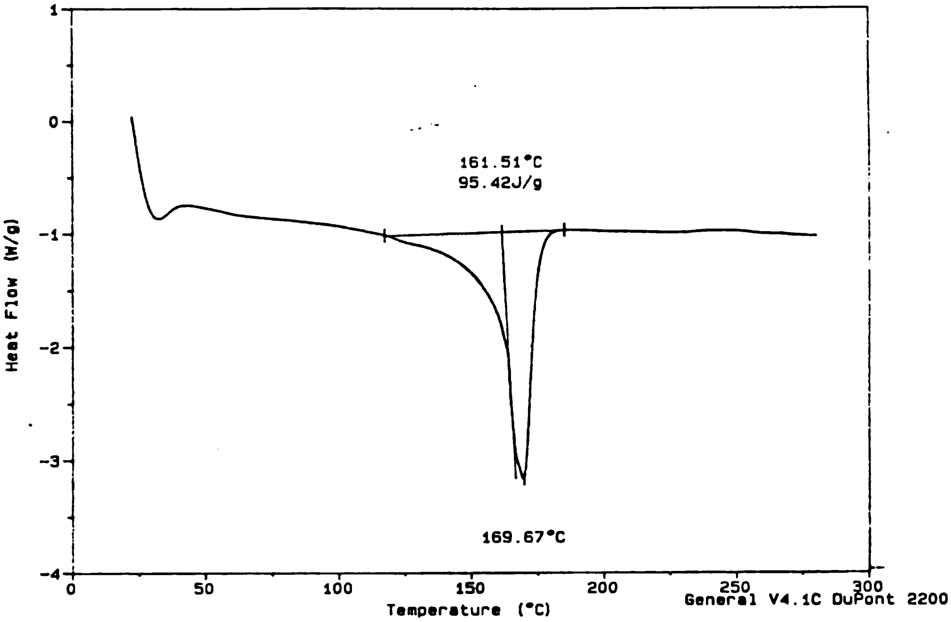


Figure A-1: DSC Scan for OPP

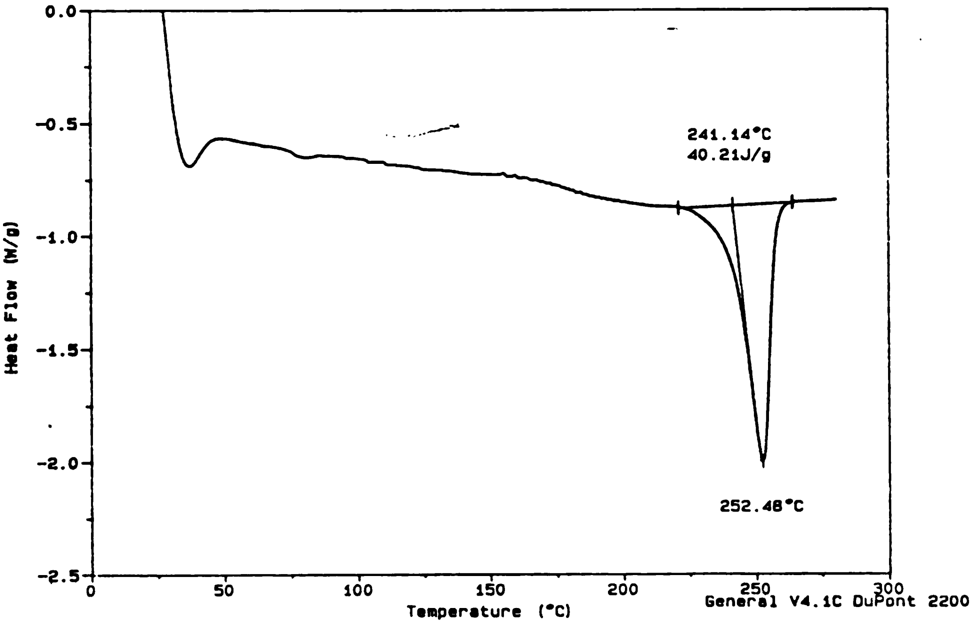


Figure A-2: DSC Scan for PET

APPENDIX B

Saturated Vapor Pressure

The saturated vapor pressure was used to determine the vapor activity of the organic penetrants at the test conditions of the permeation studies, as well as for the sorption studies. The saturated vapor pressure values of ethyl acetate and toluene as a function of temperature are presented in Figure B-1 and B-2, respectively (Perry's Chemical Engineers' Handbook, 6th edition, McGraw-Hill Book Company).

The vapor activity is expressed by the ratio of vapor pressure and saturated vapor pressure at the temperature observed, as in Eq.(24).

$$a = \frac{P}{P^*} \tag{24}$$

where a : vapor activity

P : vapor pressure of organic vapor (mmHg)

P^* : saturated vapor pressure of organic vapor (mmHg)

While the vapor pressure of the organic penetrant is calculated from the ideal gas law:

$$P = \frac{nRT}{V} = \frac{WRT}{MV} \tag{25}$$

where P : vapor pressure (mmHg)

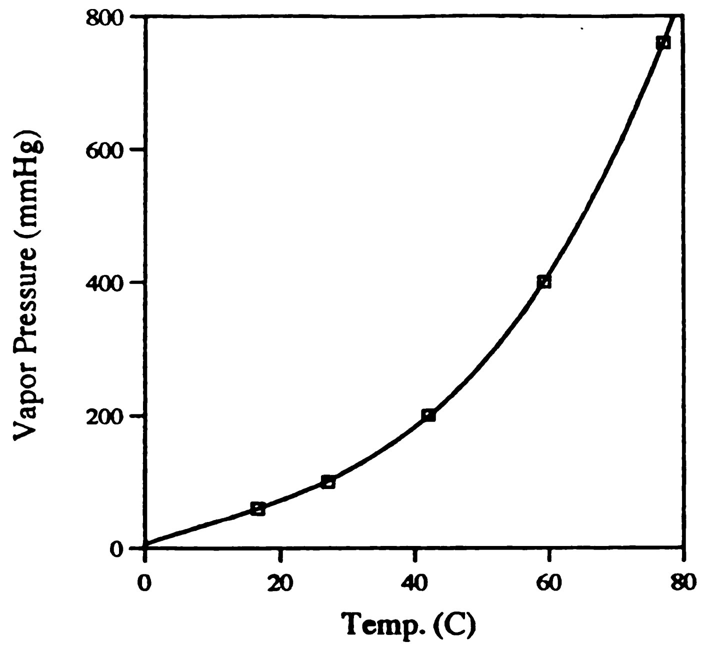
W : weight of organic penetrant (g)

M : molecular weight of organic penetrant ; n = W/M (mol)

R : gas constant (34663.6 mmHg-ml/mol-°R)

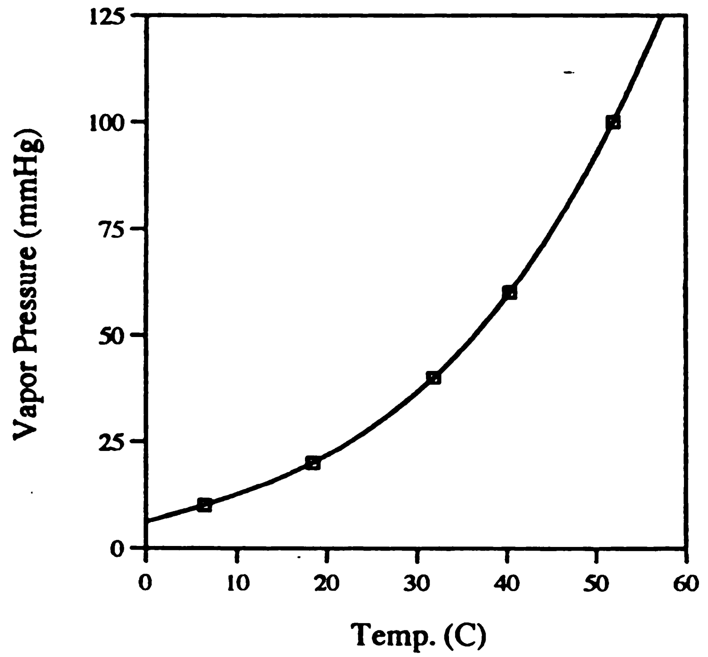
T : Temperature (°R) (°R = °F+460)

V : injection volume (ml)



y = 5.5242 + 3.4658x - 3.9143e-2x^2 + 1.5704e-3x^3 R^2 = 1.000

Figure B-1: Saturated Vapor Pressure of Ethyl Acetate



y = 6.1068 + 0.57757x + 2.0043e-3x^2 + 4.1855e-4x^3 R^2 = 1.000

Figure B-2: Saturated Vapor Pressure of Toluene

APPENDIX C

Standard Calibration

Standard calibration curves for ethyl acetate and toluene were established. Concentrations of 10, 20, 40, 60, 80 and 100 ppm (v/v) of ethyl acetate and toluene in o-dichlorobenzene were prepared to create the calibration curves. A 1 μl sample was injected directly into the gas chromatograph, under specific instrument conditions and the area response was recorded. The conditions were the follows:

Column:

Supelcowax 10: 0.25 mm i.d. x 60 m capillary column

Conditions:

Range	4
He carrier gas	27 ml/min
Column temperature	150 °C
Detector temperature	250 °C
Injection temperature	220 °C

The calibration factors (C.F.) were then determined which is equal to the reciprocal of the slope of the calibration Curve. The calibration data and the standard curve for ethyl acetate are shown in Table C-1 and Figure C-1, respectively. For toluene, the calibration data and the standard curve are presented in Table C-2 and Figure C-2.

C.F. for ethyl acetate = 7.2516 x 10^{-12} g/A.U.

C.F. for toluene = 2.9412 x 10^{-12} g/A.U.

Table C-1: Ethyl Acetate Calibration Data

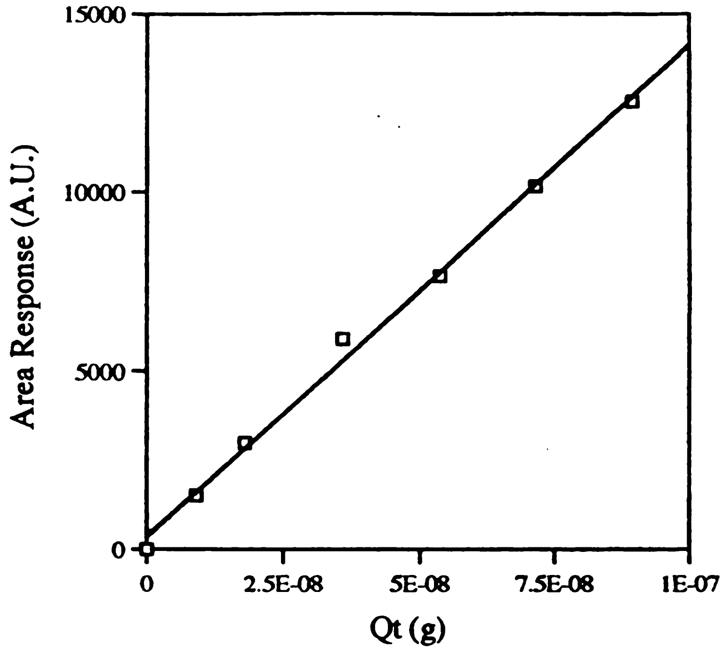
Concentration (ppm,v/v)	Quantity of EtAc Injected x 10^9 (g)	Average Area Response [a]
0	0	0
10	8.94	1495
20	17.88	2977
40	35.76	5885
60	53.64	7648
80	71.52	10155
100	89.40	12529

[a] Retention time = 5.0 min
Ethyl acetate: Molecular weight = 88.11
Density = 0.894 g/ml

Table C-2: Toluene Calibration Data

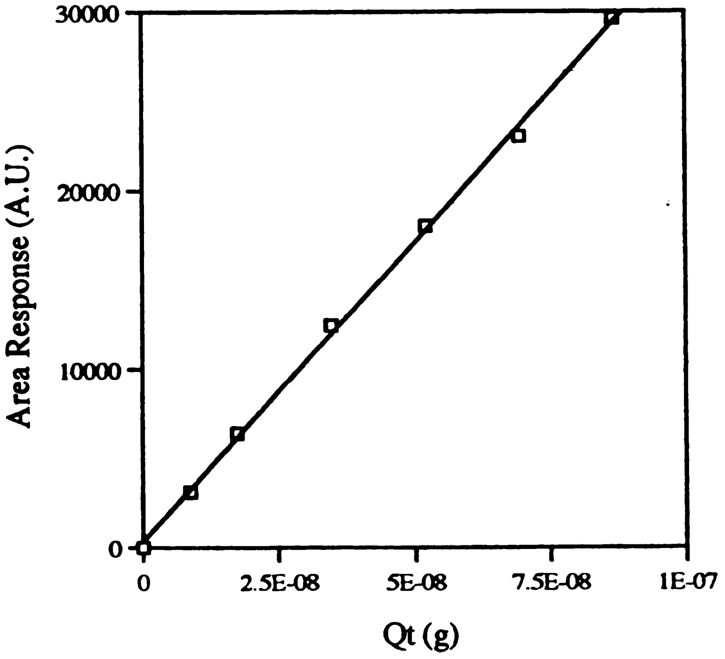
Concentration (ppm,v/v)	Quantity of Toluene Injected x 10^9 (g)	Average Area Response [a]
0	0	0
10	8.67	3088
20	17.34	6386
40	34.68	12434
60	52.02	18012
80	69.36	23036
100	86.70	29591

[a] Retention time = 5.5 min
Toluene: Molecular weight = 92.14
Density = 0.867 g/ml



y = 352.65 + 1.3791e+11x R^2 = 0.996

Figure C-1: Standard Calibration Curve for Ethyl Acetate



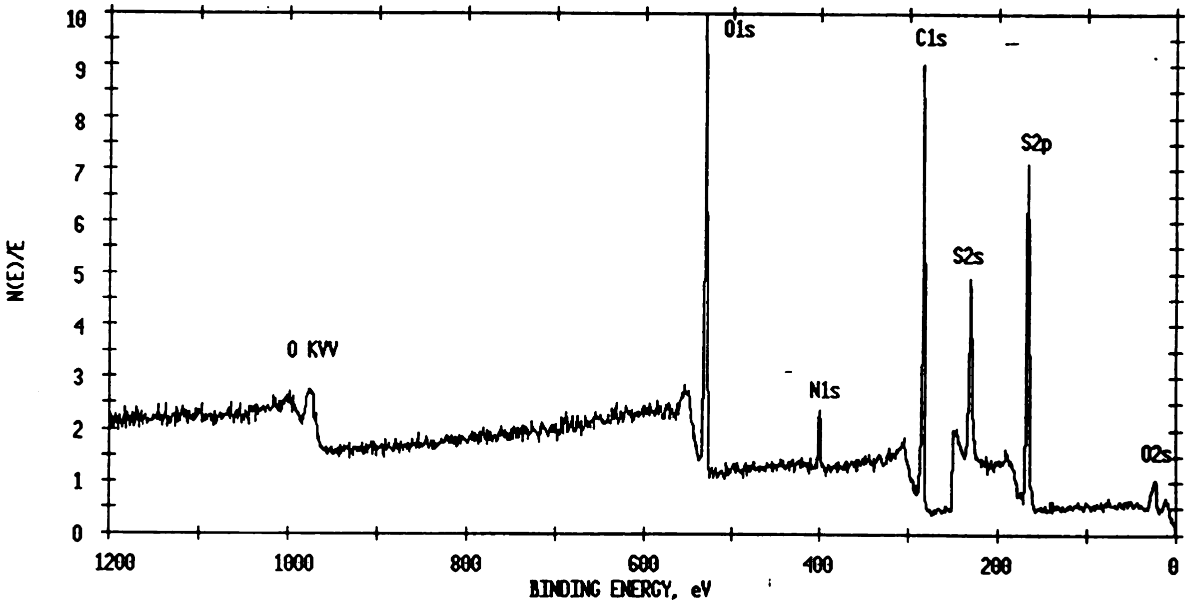
y = 312.36 + 3.3620e+11x R^2 = 0.999

Figure C-2: Standard Calibration Curve for Toluene

APPENDIX D

ESCA Analysis

ESCA SURVEY 5/11/93 ANGLE= 65 deg ACQ TIME=6.51 min
FILE: PP148 SS-PP-180 #1 (Sample B)
SCAN 1: SCALE FACTOR= 1.305 k c/s, OFFSET= 0.060 k c/s PASS ENERGY= 89.450 eV
SCAN 2: SCALE FACTOR= 0.326 k c/s, OFFSET= 0.015 k c/s Al 600 W



Element	Area (cts-eV/s)	Sensitivity Factor	Concentration (%)
C1s	30795	0.296	59.51
O1s	35035	0.711	28.18
N1s	5105	0.477	6.12
S2p	6165	0.570	6.19

Figure D-1: ESCA Analysis for A 3 Minute Sulfonated OPP Film

APPENDIX E

Statistical Analysis

Analysis of variance (ANOVA) was employed to determine statistically significant differences between the P and the effective D values of untreated control and sulfonated samples. The confidence level used in the analysis was 95% (α=0.05). The trend of P and effective D values were then predicted by regression analysis. All of the statistical analyses are shown on the following pages.

```
MTB > oneway c2 c31

ANALYSIS OF VARIANCE ON PERMEABILITY COEFFICIENT OF OPP
SOURCE     DF          SS          MS         F        p
Time        4      119.94       29.99     13.21    0.000
ERROR      13       29.52        2.27
TOTAL      17      149.46
                                   INDIVIDUAL 95 PCT CI'S FOR MEAN
                                   BASED ON POOLED STDEV
 LEVEL      N      MEAN    STDEV  ----+---------+---------+---------+--
     0      4     7.177    2.170                         (-----*----)
    60      4     5.515    2.139                    (----*-----)
    90      3     1.950    0.800       (-----*------)
   120      4     1.202    0.342      (----*----)
   180      3     0.833    0.142    (-----*-----)
                                  ----+---------+---------+---------+--
POOLED STDEV =    1.507              0.0       3.0       6.0       9.0
MTB > regr c2 1 c31

The regression equation is
p-pp = 6.98 - 0.0403 time

18 cases used 2 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant      6.9768      0.7012       9.95    0.000
atimepp    -0.040296    0.006763      -5.96    0.000

s = 1.704       R-sq = 68.9%     R-sq(adj) = 67.0%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    1      103.03      103.03     35.50    0.000
Error        16       46.44        2.90
Total        17      149.46

Unusual Observations
Obs.    time      p-pp        Fit Stdev.Fit   Residual    St.Resid
  8       60     7.950      4.559     0.436      3.391       2.06R

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

```
MTB > plot c2 c31

          -
          - *
       9.0+
          -
  p-pp    - *                *
          -
          -                  *
       6.0+ *
          - *
          -
          -                  *
          -                  *
       3.0+                           *
          -
          -                           *       *
          -                           *       3                *
          -                                                    2

+---------+---------+---------+---------+---------+------time
            0        35        70       105       140       175
         N* = 2

 MTB > regr c2 2 c31 c33

 The regression equation is
 p-pp = 7.54 - 0.0649 time +0.000142 time²

 18 cases used 2 cases contain missing values

 Predictor       Coef      Stdev    t-ratio        p
 Constant      7.5447     0.8118       9.29    0.000
 time        -0.06493    0.01995      -3.25    0.005
 time^2     0.0001419  0.0001084       1.31    0.210

 s = 1.667       R-sq = 72.1%     R-sq(adj) = 68.4%

 Analysis of Variance

 SOURCE       DF          SS          MS        F        p
 Regression    2     107.784      53.892    19.40    0.000
 Error        15      41.679       2.779
 Total        17     149.463

 SOURCE       DF      SEQ SS
 time          1     103.026
 time^2        1       4.759
 Unusual Observations
 Obs. atimepp      p-pp       Fit Stdev.Fit  Residual   St.Resid
   8        60     7.950     4.160     0.524     3.790      2.40R

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

```
MTB > oneway c5 c31

ANALYSIS OF VARIANCE ON DIFFUSION COEFFICIENT OF OPP
SOURCE      DF        SS        MS        F        p
time         4     3.861     0.965     5.08    0.011
ERROR       13     2.471     0.190
TOTAL       17     6.332
                                    INDIVIDUAL 95 PCT CI'S FOR MEAN
                                    BASED ON POOLED STDEV
 LEVEL       N      MEAN     STDEV ---+---------+---------+---------+---
     0       4    2.2900    0.5436                     (------*-----)
    60       4    1.6425    0.3805            (-----*------)
    90       3    1.0700    0.4513  (------*-------)
   120       4    1.0825    0.3161   (-----*------)
   180       3    1.3833    0.4709      (-------*-------)
                                   ---+---------+---------+---------+---
POOLED STDEV =    0.4360             0.70      1.40      2.10      2.80
MTB > regr c5 1 c31

The regression equation is
d-pp = 2.03 - 0.00600 time

18 cases used 2 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant      2.0337      0.2069       9.83    0.000
time       -0.006005    0.001996      -3.01    0.008

s = 0.5027      R-sq = 36.1%     R-sq(adj) = 32.1%

Analysis of Variance

SOURCE       DF          SS          MS          F        p
Regression    1      2.2878      2.2878       9.05    0.008
Error        16      4.0440      0.2527
Total        17      6.3318

Unusual Observations
Obs. atimepp      d-pp       Fit Stdev.Fit  Residual   St.Resid
 17     180      1.870     0.953     0.224     0.917      2.04R

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

```
MTB > plot c5 c31

          - *
      2.80+
          - *
  d-pp    -
          -
          -
      2.10+                  *
          -                  *
          - 2                                                  *
          -
          -                           *       *
      1.40+                  *                                 *
          -                  *
          -
          -                                   2                *
          -                           2       *
      0.70+

+---------+---------+---------+---------+---------+---------+------atimepp
            0        35        70       105       140       175
         N* = 2
```

```
MTB > regr c5 2 c31 c33

The regression equation is
D-pp = 2.34 - 0.0191 time +0.000075 time²

18 cases used 2 cases contain missing values

Predictor       Coef       Stdev    t-ratio        p
Constant      2.3356      0.2066      11.30    0.000
time       -0.019095    0.005077      -3.76    0.002
time^2    0.00007543  0.00002760       2.73    0.015

s = 0.4242      R-sq = 57.4%     R-sq(adj) = 51.7%

Analysis of Variance

SOURCE       DF          SS          MS         F        p
Regression    2      3.6320      1.8160     10.09    0.002
Error        15      2.6998      0.1800
Total        17      6.3318

SOURCE       DF      SEQ SS
time          1      2.2878
time^2        1      1.3442
```

```
MTB > oneway c3 c32

 ANALYSIS OF VARIANCE ON PERMEABILITY COEFFICIENT OF PET
 SOURCE      DF          SS          MS         F        p
 time         3  0.004568  0.001523     10.27     0.006
 ERROR        7  0.001038  0.000148
 TOTAL       10  0.005606
                                    INDIVIDUAL 95 PCT CI'S FOR MEAN
                                    BASED ON POOLED STDEV
  LEVEL       N      MEAN      STDEV  ------+---------+---------+---------+
      0       4   0.05605   0.01673            (----*---)
    180       2   0.03430   0.00141   (-----*-------)
    300       2   0.07205   0.01280               (------*------)
    420       3   0.09247   0.00405                       (-----*----)
                                      ------+---------+---------+---------+
 POOLED STDEV =   0.01218                  0.03      0.06      0.09      0.12
 MTB > regr c3 1 c32

 The regression equation is
 p-pet = 0.0476 +0.000086 time

 11 cases used 5 cases contain missing values

 Predictor       Coef        Stdev    t-ratio        p
 Constant    0.047645     0.008779       5.43    0.000
 time      0.00008568   0.00003310       2.59    0.029

 s = 0.01890     R-sq = 42.7%     R-sq(adj) = 36.3%

 Analysis of Variance

 SOURCE         DF          SS           MS          F        p
 Regression      1   0.0023927    0.0023927       6.70    0.029
 Error           9   0.0032134    0.0003570
 Total          10   0.0056061
```

```
MTB > plot c3 c32

          -
     0.100+
          -                                                      *
  p-pet   -                                                      2
          -
          -                                       *
     0.075+ *
          - *
          -                                       *
          -
          -
     0.050+
          -
          - 2
          -                        2
          -
     0.025+

+---------+---------+---------+---------+---------+------atimepet
            0        80       160       240       320       400
         N* = 5

 MTB > regr c3 2 c32 c34

 The regression equation is
 p-pet = 0.0549 -0.000177 time +0.000001 time²

 11 cases used 5 cases contain missing values

 Predictor       Coef       Stdev    t-ratio        p
 Constant    0.054931    0.006889       7.97    0.000
 time     -0.00017742  0.00009217      -1.92    0.090
 time^2    0.00000065  0.00000022       2.96    0.018

 s = 0.01385     R-sq = 72.6%     R-sq(adj) = 65.8%

 Analysis of Variance

 SOURCE       DF          SS          MS          F        p
 Regression    2   0.0040718   0.0020359      10.62    0.006
 Error         8   0.0015343   0.0001918
 Total        10   0.0056061

 SOURCE       DF      SEQ SS
 time          1   0.0023927
 time^2        1   0.0016791
```

```
MTB > oneway c6 c32

 ANALYSIS OF VARIANCE ON DIFFUSION OF PET
 SOURCE     DF        SS        MS        F        p
 time        3 0.0001352 0.0000451     0.89    0.492
 ERROR       7 0.0003547 0.0000507
 TOTAL      10 0.0004898
                                    INDIVIDUAL 95 PCT CI'S FOR MEAN
                                    BASED ON POOLED STDEV
  LEVEL      N      MEAN     STDEV -----+---------+---------+---------+-
      0      4  0.024200  0.006158             (-------*--------)
    180      2  0.029300  0.005374             (-----------*-----------)
    300      2  0.017750  0.000212   (-----------*-----------)
    420      3  0.023233  0.010294           (--------*---------)
                                   -----+---------+---------+---------+-
 POOLED STDEV = 0.007118              0.01      0.02      0.03      0.04
 MTB > regr c6 1 c32

 The regression equation is
 D-pet = 0.0250 -0.000007 T

 11 cases used 5 cases contain missing values

 Predictor       Coef       Stdev    t-ratio        p
 Constant    0.025005    0.003379       7.40    0.000
 time     -0.00000651  0.00001274      -0.51    0.622

 s = 0.007273    R-sq = 2.8%      R-sq(adj) = 0.0%

 Analysis of Variance

 SOURCE       DF          SS          MS         F        p
 Regression    1  0.00001381  0.00001381      0.26    0.622
 Error         9  0.00047602  0.00005289
 Total        10  0.00048983

 Unusual Observations
 Obs.atimepet     d-pet       Fit Stdev.Fit  Residual   St.Resid
  13       420   0.03510   0.02227   0.00354   0.01283      2.02R

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

```
MTB > plot c6 c32

          -
    0.0350+                                                      *
          -                         *
  d-pet   -
          - *
          -
    0.0280+
          - *
          -                         *
          -
          - *
    0.0210+
          -
          -                                       2              *
          - *                                                    *
          -
    0.0140+

+---------+---------+---------+---------+---------+------atimepet
            0        80       160       240       320       400
         N* = 5

 MTB > regr c6 2 c32 c34

 The regression equation is
 D-pet = 0.0247 +0.000003 time -0.000000 time²

 11 cases used 5 cases contain missing values

 Predictor         Coef        Stdev    t-ratio        p
 Constant      0.024749     0.003829       6.46    0.000
 time        0.00000274   0.00005123       0.05    0.959
 time^2     -0.00000002   0.00000012      -0.19    0.856

 s = 0.007697    R-sq = 3.2%      R-sq(adj) = 0.0%

 Analysis of Variance

 SOURCE       DF          SS          MS         F        p
 Regression    2  0.00001589  0.00000794      0.13    0.876
 Error         8  0.00047394  0.00005924
 Total        10  0.00048983
 SOURCE       DF      SEQ SS
 time          1  0.00001381
 time^2        1  0.00000207

 Unusual Observations
 Obs.atimepet     d-pet       Fit Stdev.Fit  Residual   St.Resid
  13      420   0.03510   0.02186   0.00434   0.01324      2.08R
 R denotes an obs. with a large st. resid.
```

BIBLIOGRAPHY

BIBLIOGRAPHY

Amini, M. A. "Surface and hydrocarbon-Barrier Modification." The Wiley Encyclopedia of packaging Technology, 1986, 620-622.

Asthana, H. "Chemical Modification of Polymer Surfaces Using Sulfonation to Improve Adhesion Properties." Master Thesis, Department of Chemical Engineering, Michigan State University, East Lansing, MI, 1993.

Balta Calleja, F. J. "Surface Hardening of PE Through Sulphuric Acid Exposure." Journal of Material Science Letter 3, 1984, 509-511.

Baner, A. L.(III) "The Measurement and Analysis of the Diffusion of Toluene in Polymeric Films." Master Thesis, School of Packaging, Michigan State University, East Lansing, MI, 1987.

Baner, A. L.(III); Hernandez, R. J.; Krishnamurthy, J.; Giacin, J. R. "Isostatic and Quasi-Isostatic Methods for Determining the Permeability of Organic Vapors Through Barrier Membranes." Current Technologies in Flexible Packaging, ASTM STP 912, M. L. Troedel, Ed., American Society for Testing and Materials, Philadelphia, 1986, 49-62.

Blais, P.; Carlsson, D. J.; Csullog, G. W.; Wiles, D. M. "The Chromic Acid Etching of Polyolefin Surfaces and Adhesive Bonding." Journal of Colloid and Interface Science, June 1974, 47(3):636-649.

Brenner, D.; Lundberg, R. D. "Crosslink Ionically." Chemtech, December 1977, 7(12):748-752.

Briston, J. H. "Films, Plastic." The Wiley Encyclopedia of Packaging Technology, 1986, 330.

Crank, J. "The Definition and Measurement of Diffusion Coefficients." The Mathematics of Diffusion, 2nd edition, 1975, 238-239.

Ericson, B. L. "On The Enhancement of Adhesive Bonding to Polymer and Composite Surfaces Through Gas Phase Sulfonation." Master Thesis, Department of Chemical Engineering, Michigan State University, East Lansing, MI, 1993.

Esbensen, L. "The Effect of Neutralizing Cations on The Barrier Characteristics of A Surface Sulfonated Polystyrene Film." Master Thesis, School of Packaging, Michigan State University, East Lansing, MI, 1991.

Fonseca, C.; Perena, J. M.; Fatou, J. G.; Bello, A. "Sulphuric Acid Etching of Polyethylene Surfaces." Journal of Materials Science, 1985, 20(9):3283-3288.

Gilbert, E. E. "Sulfonation with Compounds of Sulfur Trioxide." Sulfonation and Related Reactions, 1965, 31 and 69.

Hasenauer, R. J. "Film, Oriented Polypropylene." The Wiley Encyclopedia of Packaging Technology, 1986, 320-325.

Hayashi, H.; Nakano, T.; Ishii, K.; Ohki, Y. "Effect of Plasma Surface Modification on the Electrical Conduction in High-Density Polyethylene." Annual Report: Conference on Electrical Insulation and Dielectric Phenomena, 1990, 190-195.

Hayashi, H.; Nakano, T.; Ohki, Y. " Effect of Plasma Surface Modification on Electrical Conduction in Polyethylene." Electrical Engineering in Japan, 1991, 111(6):17-24.

Hernandez, R. J.; Giacin, J. R.; Baner, A. L.(III) "The Evaluation of The Aroma Barrier Properties of Polymer Films." Journal of Plastic Film & Sheeting, July 1986, 2(3):187-211.

Hirsch, A. A. "Health-Care Packaging." The Wiley Encyclopedia of Packaging Technology, 1986, 391-398.

Ihata, J. "Formation and Reaction of polyenesulfonic Acid I. Reaction of Polyethylene Films with SO_3." Journal of Polymer science: Part A: Polymer Chemistry, 1988, 26:167-176.

Ihata, J. "Formation and Reaction of polyenesulfonic Acid II. Photoreaction of Polyenesulfonic Acids." Journal of Polymer science: Part A: Polymer Chemistry, 1988, 26:177-185.

Inagaki, N.; Hiraa, H. "Plasma Polymers Containing Sulfonate Groups." Journal of Polymer science: Part A: Polymer Chemistry, 1987, 25:1803-1809.

Imbalzano, J. F.; Washburn, D. N.; Mehta, P. M. "Permeation and Stress Cracking of Fluoropolymers." Chemical Engineering, January 1991, 105-108.

Kindberg, B. L.; Oldaker, R. L.; Rounsville, S. H. "Films, Oriented Polyester." The Wiley Encyclopedia of Packaging Technology, 1986, 317-320.

Kreisher, K. R. "Proposed Rules on Emissions Give Fuel Tank Molders Cause for Worry." Modern Plastic, March 1992, 69(3):17-18.

Mark, V. "Flame-Resisting Polycarbonate Composition." Ger. Offen., July 1975.

Metah, R. K.; Bush, D. M. "Fluorinated HDPE Protects Flavors." Packaging, August, 100.

Miglaw, I. "Film, Non-oriented Polypropylene." The Wiley Encyclopedia of Packaging Technology, 1986, 315-317.

Miller, B. "New Gas-Tank Process Targets Tighter Emissions." Plastic World, Febuary 1992, 50(3):10-11.

Miller, R. C. "Polypropylene." The Wiley Encyclopedia of Packaging Technology, 1986, 536-540.

Naude, A. "Automotive Chemicals '92: In The Balance-Fuel Tanks." Chemical Marketing Reporter, Febuary 1992, 241(7).

Neumann, E. H. "Polyester, Thermoplastic." The Wiley Encyclopedia of Packaging Technology, 1986, 512-514.

Olsen, D. A.; Osteraas, A. J. "Sulfur Modification of Polyethylene

Surfaces III. Frustrated Multiple Internal Reflection Spectroscopy of Sulfonated Polyethylene Surfaces." Journal of Polymer Science: Part A-1, 1969, 7:1927-1932.

Paine, F. A.; Pain H. Y. A Handbook of Food Packaging, London; Leonard Hill, 1983.

Park, I. "The Effect of Surface Sulfonation of Polymer Films on Dispersion and Non-Dispersion Components of Surface Energy and Peel Adhesion Strength." Master Thesis, School of Packaging, Michigan State University, East Lansing, MI, 1993.

Robertson, G. L. "Permeability of Thermoplastic polymers." Food Packaging: Principal and Practice, 1992, 75-79.

Robertson, G. L. "Structural Properties of Plastic Polymers." Food Packaging: Principal and Practice, 1992, 42-44.

Robertson, G. L. "Structural Properties of Plastic Polymers." Food Packaging: Principal and Practice, 1992, 46-48.

Robertson, G. L. "Structural Properties of Plastic Polymers." Food Packaging: Principal and Practice, 1992, Chapter 2, 31-33.

Rogers, J. K. "Medical Show Discloses Many Plastics Innovations." Modern Plastics, August 1990, 67(8):8-9.

Sajiki, T. "Permeation of Ethyl Acetate Vapor Through Silica Deposited Polyethylene Terephthalate Film and Composite Structures." Master Thesis, School of Packaging, Michigan State University, East Lansing, MI, 1991.

Smidt, F. A. "Surface Modification by Ion Implantation." Chemtech, May 1989, 309-314.

Stannett, V.; Yasuda H. "The Measurement of Gas and Vapor Permeation and Diffusion in Polymer." Testing of Polymers, 1965, Volume 1, Chapter 13, John Wiley and Sons, Inc.

Suter, C. M. "The Preparation of Aromatic Sulfuric Acid." The Organic Chemistry of Sulfur, 1944, 196.

Suter, C. M. "The Properties and Reactions of Aromatic Sulfuric Acid." The Organic Chemistry of Sulfur, 1944, 382.

Tardiff, J. L. "Diffusion and Reaction of Small Molecules in Thin Polymer Films." Master Thesis, Department of Chemical Engineering, Michigan State University, East Lansing, MI, 1993.

Toensmeier, P. A. "High Value Packaging Is Target for Imaginative Innovation." Modern Plastics, July 1990, 67(7):10-11.

Tubridy, M. F.; Sibilia, J. P. "Nylon." The Wiley Encyclopedia of Packaging Technology, 1986, 477-482.

Walles, W. E. "Resinous Enclosure Members Rendered Impermeable by Sulfonation and Neutralization." USP, 1971, 3,613,957.

Walles, W. E. "Resinous Enclosure Members Rendered Impermeable by Sulfonation." USP, 1973, 3,740,258.

Walles, W. E. "Barrier Properties Added to Plastics via Sulfonation and Reductive Metallization." American Chemical Society Meeting, Dallas, TX, April 1989.

Walles, W. E. "In Mold Sulfonation System." USP applied.

Yates, J. B.(III); Smith, D. J.; Campbell, J. R. "Sulfonated Polycarbonate as Flame Retardants." European Patent Application, March 1987.