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SURFACE SULFONATION OF POLYMERS
TO IMPART SELECTED BARRIER
PROPERTIES

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JING Y. ZHU

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**SURFACE SULFONATION OF POLYMERS TO IMPART SELECTED
BARRIER PROPERTIES**

BY

Jing Y. Zhu

A THESIS

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

Master of Science

School of Packaging

1995

ABSTRACT

**SURFACE SULFONATION OF POLYMERS TO IMPART
SELECTED BARRIER PROPERTIES**

BY

Jing Y. Zhu

The PP films were sulfonated at three different time. The two counterions, ammonium (NH_4^+) and sodium (Na^+), were used to neutralized the sulfonated PP at different sulfonation time. ESCA was used to determine the surface compositions of the films. The permeation of oxygen, carbon dioxide and water vapor into the sulfonated PP films were studied in this research. There are there different temperature and two relative humidity were used to determine the oxygen permeation. Unmodified PP specimens were evaluated through the study for comparison purpose.

To My Parents

ACKNOWLEDGEMENTS

There are many people who I wish to thank for both their help and support in completing this project. Firstly, I would like to thank my advisor, Dr. Hernandez, for his patience and helpful advice. Through his guidance I have learned observe, not see.

I must say a very big thank you to the staff at the Composite Materials and Structures Center. Brian Erickson spent an incredible amount of time working with me to sulfonate films. Dan Hook help me to do the ESCA analysis. I also like to thank Dr. Jack Gaicin and Dr. Pinnavaia for your support and suggestion.

Finally, I must thank my parents, Yi and Qi-Xio Zhu, for their love and support.

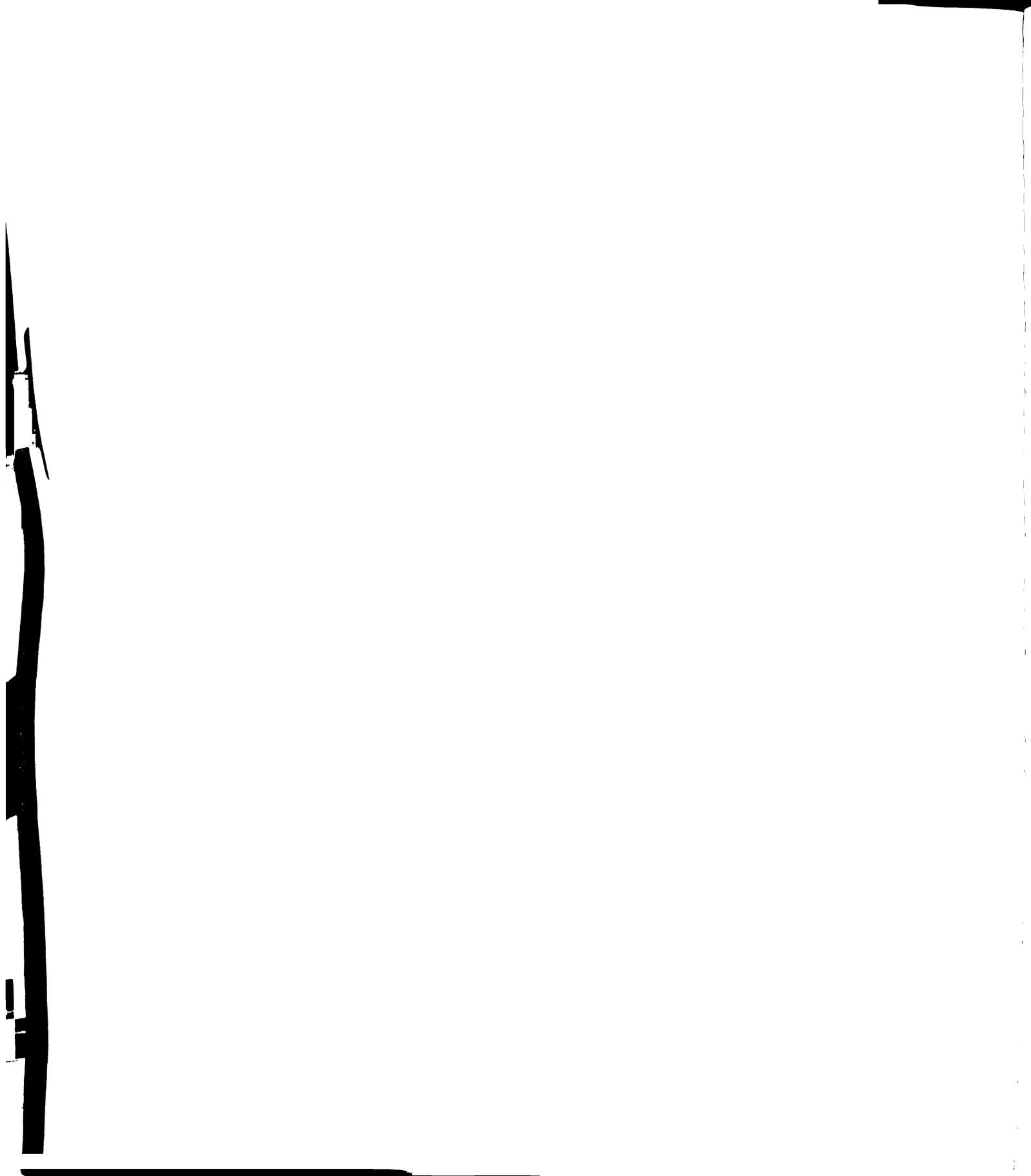


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INTRODUCTION

Over the past decades, the importance of high barrier polymers in the areas of food and pharmaceutical packaging has grown at a very accelerated rate due to considerations of convenience and economy. Most synthetic polymers are used in packaging materials for food, pharmaceutical, and related products. Polyolefin, such as PE and PP, has excellent water barrier, but has a high oxygen permeability so that foods and medicines packaged in these materials suffer oxidation, discoloration, loss of taste aroma, etc. Conversely, some polar polymers, containing hydrophilic groups, have an excellent gas barrier when dry but have very poor water or gas barrier when containing water.

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.

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 75-200 $\mu\text{g SO}_3/\text{cm}^2$ surface area. The oxygen barrier properties of sulfonated PE were found to be strongly dependent upon the nature of the counterion, M^+ . For example, Walles (1989) reported that Na^+ as the counterion

was 6 times as effective as 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 $70 \mu\text{g SO}_3/\text{cm}^2$ surface area, which for a $25 \mu\text{m}$ film equals about 1% bulk sulfur.

This study focuses specifically on determining the barrier properties of oxygen and water vapor of sulfonated polymer films neutralized with NH_4^+ and Na^+ . The study included the effect of relative humidity on the permeability.

The objectives of this study were:

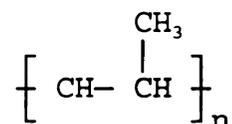
1. To determine the permeation of oxygen, carbon dioxide and water vapor into the sulfonated PP films. Unmodified PP specimens were evaluated throughout the study for comparison purpose.
2. To determine the effect on the oxygen permeability value between ammonium (NH_4^+) and sodium (Na^+) counterions, at different sulfonation time.
3. To determine the oxygen permeation of the sulfonated PP films at high relative humidity, compared with dry condition.

LITERATURE REVIEW

POLYPROPYLENE CHARACTERISTICS

Polypropylene (PP), a thermoplastic material, was first commercialized in 1950s. PP is a versatile material, with major applications in automobile parts, textiles, appliances, films and packaging. By 1992, the production of PP rose 36% to 9.4 billion lb. Despite the estimates of slow demand, analysts predicted that PP would continue to grow on the order of 6% per year.

Polypropylene is made by the catalytic polymerization of propylene monomer under heat and pressure. The chemical structure of polypropylene is as follows:



Monomer Unit of Polypropylene

There are three possible stereo-figuration of PP, isotactic, syndiotactic and atactic, depending upon the disposition of the pendant methyl group with respect to the main chain (Miller, 1986). In the isotactic configuration, all the methyl groups are on the same side of the chain; in the syndiotactic, they alternate regularly; in the atactic, the

disposition is random. The properties of these configurations differ greatly. Atactic PP is amorphous, while the isotactic and syndiotactic are semi-crystalline. Commercially available polypropylenes are partially crystalline products. The polypropylene films are widely used in the food packaging. Initially, Polypropylene films were laminated with cellophane to overcome flex-cracking and to provide toughness. Polypropylene eventually replaced many other films, particularly barrier-coated cellophane, as its economy and excellent physical properties became fully recognized. The density of PP ranges between 0.88 and 0.91 g/cc - one of the lowest among polymers, and their melting temperature range between 160 and 178 °C. This allows foods and pharmaceutical products packaged in polypropylene to be heat-sterilized inside the package which is not the case with PE (Giacin, 1992). Table 1.1 summarizes the properties of the polypropylene produced by cast extrusion and biaxially oriented.

**Table 1.1 Major properties of polypropylene (Modern
Plastics, Encyclopedia'94)**

	Extrusion (cast)	Biaxially Oriented
Specific Gravity (g/cc)	0.885-0.905	0.902-0.907
Tensile Strength (p.s.i.)	4500-10,000	7500-40,000
Elongation %	550-1000	35-475
Rate of water vapor transmission (g.mil/100 sq.in. 24 h) at 37.8°C	0.7	0.25-0.4
O ₂ trans. rate (cc.mil/100 sq.in. 24 h) at 25°C	150-240	100-160
CO ₂ trans. rate (cc.mil/100 sq.in.24 h) at 25°C	500-800	540
Dielectric constant 1 Khz	2.2	2.2

SULFONATION

A method used to modify the surface of polymeric films include exposing the films to a reactive gas. This method has been used with fluorine gas, chlorine gas, and sulfur trioxide to obtain fluorinated, chlorinated, and sulfonated films, respectively. The main goal of this thesis was to sulfonate PP films and to study the barrier properties of the sulfonated films as compared to the non-sulfonated PP. Sulfonation process which modified the surface properties did not alter the properties of the bulk polymer, but rather the surface of the film.

2.1 SULFONATING REAGENT

A sulfonating reagent is a compound which is able to replace a carbon-bonded hydrogen atom in a polymeric molecule by a sulfonic group (SO_3). Sulfur trioxide is a powerful sulfonation agent.

The sulfur trioxide molecule is planar, triangular, and symmetrical (Gilbert, 1965). It is a resonance hybrid in which the oxygen atoms are equivalent. The S-O bond is unusually short, indicating considerable double bond character. Although the exact distribution of electrons between sulfur and oxygen is uncertain, the behavior of SO_3 in chemical reactions indicates that the sulfur atom is

strongly electron-deficient. At the same time, the oxygen atoms are electron-rich. The SO_3 molecule has been described as a "Lewis acid on one side (i.e., the sulfur), and a Lewis base on the other (oxygen)." When SO_3 reacts with polymer films, the acidic sulfur atom attacks electron-rich (basic) systems, and the basic oxygen atoms accepts acidic protons (Gilbert, 1965).

There are three forms of sulfur trioxide, solid, liquid and gas. Although solid SO_3 has been used to a minor extent in the laboratory for making complexes, and for conversion to SO_3 vapor by heating, it has not been considered a commercially practical compound because of its variability, difficulty in handling, and the high increase in vapor pressure occurring during vaporization. Liquid SO_3 could be stabilized satisfactorily against polymerization to solids by addition of a small quantity (as low as 0.1 %) of various compounds - especially derivatives of boron, phosphorus, or sulfur, - resulted in its commercial introduction. For laboratory purposes, the use of SO_3 in liquid form may involve the freshly distilled, or the stabilized commercial material. Vaporization of the SO_3 , and dilution with dry air to about 10% strength, is more commonly used as a standard laboratory procedure. Vaporized SO_3 is a much milder reagent than the pure liquid SO_3 . On a commercial scale, sulfonation is carried out with liquid SO_3 stabilized by mixing it with

a solvent, such as liquid SO_2 , or, more commonly, is in gas phase mixed with dry air. Vapor SO_3 is also obtained commercially by distillation of oleum, from sulfuric acid plant-converter gas or by burning sulfur to obtain SO_2 and then continuing the oxidation process of SO_2 to SO_3 .

The major advantages cited for the use of SO_3 are rapid and complete reaction, with no energy requirement for completing sulfonation. The major problem is that sulfur trioxide has a strong affinity for water. Therefore, it is necessary to find practical procedures for preventing that water get in and contact with SO_3 so that the SO_3 becomes available to react with the polymer films. Recent Raman spectral studies and other studies of sulfonation kinetics indicated that monomeric SO_3 is the true reactive species in oleum and sulfuric acid, as well as in liquid SO_3 , and that the water present in the hydrates functions merely as a complex agent and solvent (Miller, 1986).

2.2 SULFONATION REACTION

It is generally accepted that during sulfonation by either liquid or gas phase, the hydrogen either in a C-H or N-H bond is replaced by an SO_3 molecule which is then hydrogenated to form a sulfonic acid at the site of attachment.

These findings were also confirmed by J. Tardiff (1993), who studied diffusion and reaction of sulfonate groups within the polymer matrix of sulfonated polymeric films. H. Asthans (1993) studied chemical modification of polymer surfaces using sulfonation to improve adhesion properties. Asthans indicated that desulfonation (which results in formation of H_2SO_3) occurs easily in case of polymers containing only aliphatic carbon as compared to a polymer containing aromatic carbon.

2.3 Neutralization

The sulfonic acid groups generated during sulfonation can be neutralized to create a more stable group. Neutralization can be carried out with a variety of bases, e.g. ammonia gas (NH_3) or aqueous ammonium hydroxide (NH_4OH). Neutralization with ammonium hydroxide will extract the hydrogen from the sulfonic acid and form a stabilized ion pair ($-\text{C}-\text{SO}_3^-\text{NH}_4^+$). The reaction scheme is shown in Figure 2.2.

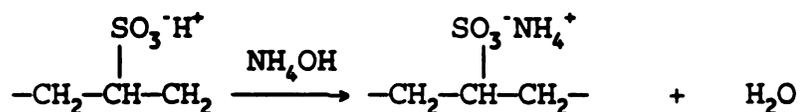


Figure 2.2. Neutralization Reaction Scheme of PE

Neutralization can also be accomplished by depositing metal ions via ion exchange from water solution. Various metal ions can be used, for example, lithium, sodium, copper, magnesium, nickel, cobalt, manganese, vanadium, and strontium. Also the barrier and physical properties of sulfonated polymers are strongly dependent upon the counterion utilized. W. Walles (1989) found that Na^+ ion was 6 times more effective than NH_4^+ ion in regarding the diffusion of oxygen through a sulfonated membrane, Li^+ was 12 times more effective than NH_4^+ , all at a surface concentration of about 0.7 g S/m^2 .

2.4 Previous Studies

2.4.1 Reaction of the sulfonation polymer surface

Olsen and Osteras (1969) used fluorescent multiple internal reflection (FMIR) spectroscopy to obtain direct evidence of the nature of the surface groups of the sulfonated polyethylene. J. Ihata (1988) reported on a study of the photoreaction of polyenesulfonic acids by ESR, where the desulfonation reaction took place. It was found that conjugated polyenesulfonic acids formed by the reaction between PE films and SO_3 were sensitive to visible and UV radiation that cleavage the C-S bonds of the sulfonic acid groups adjacent to polyenes. The resulting polyene radicals either reacted with oxygen in the air to form ketone

compounds or released hydrogen atom to give more conjugated polyenes on the average under reduced pressure.

Cameron (1985) have proposed that the most significant chemical changes on the surface is olefinic conjugation leading ultimately to carbonization. Recently, H. Asthana (1994) studied on the sulfonated polypropylene and polystyrene. He found that sulfonation of PP leads to a mixture of various kinds of compounds besides sulfonic acids by contact angle and XPSA. There are no signs of degradation or desulfonation in polystyrene as was seen in polypropylene.

2.4.2 Effect on Electrical and Physical Properties

C. Fonseca (1985) proposed that the bulk electrical properties of the inert polymers (as polyethylene) can be modified by sulfonation to dope or introduce polar molecules. From the critical surface tension and platelet adhesion tests, they also found that the microindentation hardness and the critical surface tension of this polymer increased.

N. Inagaki (1987) found that the sulfonation of phenyl groups in the plasma-polymers occurred rapidly within 1 min when exposed to SO_3 gas. The sulfonation made the plasma-polymer electrically conductive and showed a strong dependence of the impedance on the relative humidity.

2.4.3 Effect on Mechanical Properties

F. Calleja (1984) investigated the surface hardening of polyethylene through sulfuric acid exposure. He found that exposure of PE to a sulfuric acid atmosphere substantially improves the mechanical properties of the thin sulfonated surface of the polymer, yielding hardness values which are in the vicinity of some metals. In addition, it is shown that microindentation hardness proves to be an extremely sensitive technique which enables a fine detection of the local surface hardening of polymer, developed at very low levels of sulfonation.

However, In L. Esbensen (1991) study of the effect of neutralizing cation of a surface sulfonated polystyrene film, 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.

2.4.4 Effect on the Barrier Properties

Walles (1973) studied on the resinous enclosure members (HDPE bottles, LDPE bottles, tank, PP bottle & PVDC bottle) to rendered impermeable by sulfonation. The sulfonated enclosure members are rendered substantially impervious to the penetration of various solvents and vapors by degrees from about 0.015 to about 50.0 milligrams on a square centimeter of surface sulfonation. In 1973, Walles reported on the surface sulfonation-epoxidation of polyethylene and polystyrene, too. He found that these polymers were rendered

adhesive, antistatic and highly impermeable to oleophilic materials and low molecular weight gas such as oxygen and carbon dioxide by initially surface sulfonating these polymers and subsequently reacting the substitute sulfonic acid groups with alkylene oxide or similar epoxide to form the corresponding ester of sulfonic acid. Further, Walles (1984) studied on the metallized plastic articles. Metallized plastic article which can optionally be treated with an additional amount of an aqueous colloidal dispersion of an organic polymer or metal provides essentially impermeable to atmospheric gases and other vapors. In addition, the barrier properties obtained by surface sulfonation were found strongly dependent upon the nature of the neutralizing counterion. Walles (1989) found that Na^+ ion which substituted NH_4^+ via an ion exchange reaction of a sulfonated polyethylene film was 6 times as effective as NH_4^+ ion with respect to oxygen diffusion through the sulfonated membrane. Li^+ was 12 times more effective than NH_4^+ , all at a surface concentration of about 0.7 g S/m^2 . Chiao (1988) investigated on gas separations using membranes comprising sulfonated polyether sulfone. He found that sulfonated of polyether sulfones have good separation factors for oxygen, nitrogen and carbon dioxide methane separations from a mixture gases.

However, Esbensen (1991) reported that exchange of the neutralizing cation ammonium with the following cations: Li^+ , Na^+ , K^+ , Mg^{++} , Ca^{++} and Ba^{++} had no effect on the barrier characteristics of the surface sulfonated polystyrene film for the penetrants, oxygen and water vapor, at the $0.8 \mu\text{g S/cm}^2$ and 50 \AA , respectively sulfonation level.

PERMEABILITY**3.1 Introduction**

The study of the permeability of plastic packaging films of gases, water vapor and organic vapors is both practically and theoretically important. Properly design packaging system can prevent product deterioration by controlling excessive gain or loss of gases and vapor during product storage. The permeability P of a film or sheet specimen is given as following equation:

$$P = \frac{Ql}{At\Delta p} \quad (1)$$

where: Q = mass or volume rate of permanent gas or vapor.

l = thickness of the film.

t = time

Δp = partial pressure differential.

The permeation mechanism actually involves three steps :

(i) sorption and solution of the penetrant into the polymer

(ii) diffusion of the penetrant through the polymer matrix

(iii) desorption of the penetrant from the surface of the polymer.

Diffusion coefficient (D) and permeability (P) values are obtained from permeability studies, isostatic procedure or quasi-isostatic procedure.

The basic equations for describing the diffusion process are Fick's first and second laws of diffusion (Hernandez, et al, 1986)

$$F = -D \frac{dc}{dx} \quad (2)$$

and

$$\frac{dc}{dt} = \frac{d}{dx} \left(D \frac{dc}{dx} \right) \quad (3)$$

where:

F = the flux or mass of diffusion per unit area per time

c = the concentration of the penetrant in the film

D = the mutual diffusion coefficient, in (length)²/time;

According to Henry's Law, the concentration of the penetrant (c) in the polymer and the penetrant concentration in the gas or vapor phase in the equilibrium with the polymer is:

$$C = Sp \quad (4)$$

where:

S = the solubility coefficient.

By substituting equation (3) and (4) into equation (1) :

$$P=DS$$

3.2 Permeability Measurements

A permeability cell consists of two half cells which hold a film sample tightly. One of the half cell hold the gas or vapor to be used as the permeant. The permeant diffusing through the film goes into the other half cell, where is accumulated or conveyed to a detector measurement. Three methods can be utilized measuring permeability of a film :

- (i) Isostatic Method
- (ii) Quasi-isostatic Method
- (iii) Absolute Pressure Method

3.2.1 Isostatic Method

In the isostatic method, the total pressure in both chambers of the permeation cell is constant. This is achieved by keeping both chambers of the permeation cell at atmospheric pressure. In the permeability measurement, there must be a difference in permeant partial pressure across the film. The permeant at the lower concentration chamber is conveyed to specific detector by a carrier gas for quantitation.

Isostatic method is commercially available for measuring CO₂

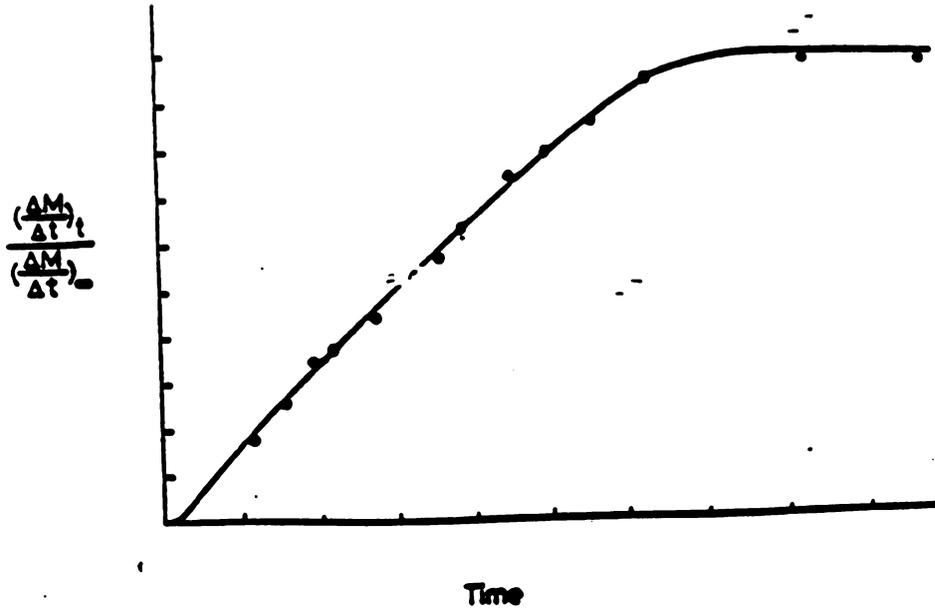


Figure 3.1 Typical Transmission Rate Profile Curve for Isostatic Procedure (Take from Henandez et al)

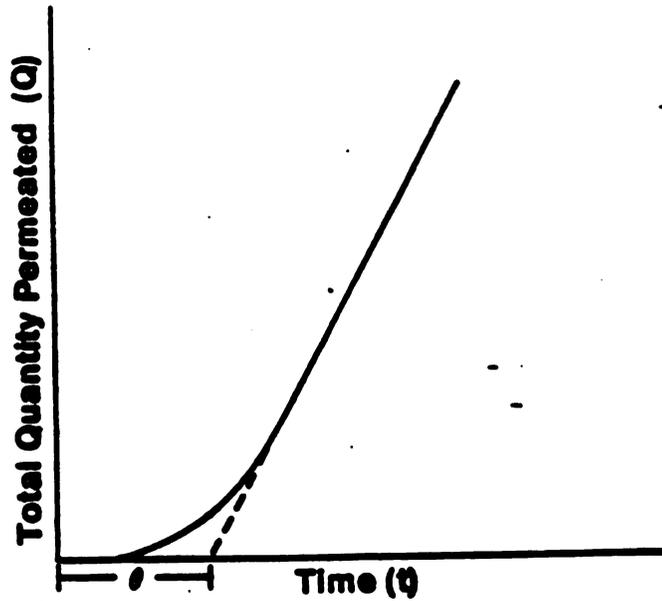


Figure 3.2 Typical Transmission Rate Profile Curve for Quasi-Isostatic Procedure

and O₂ permeability of both plastics films and fabricated packaging articles. A representative transmission rate curve describing the transport of a permeant through a polymer membrane in an isostatic method is shown in Figure 3.1. A First approximate solution to the Fick's second law is given in Equation (5) (Hernandez, 1986)

$$\frac{(\Delta M/\Delta t)_t}{(\Delta M/\Delta t)_\infty} = \left(\frac{4}{\pi}\right) \left(\frac{l^2}{4Dt}\right)^{1/2} \exp\left(\frac{-l^2}{4Dt}\right) \quad (5)$$

Where:

$(\Delta M/\Delta t)_t$ = the transmission rates of the penetrant at time
(t)

$(\Delta M/\Delta t)_\infty$ = the transmission rates of the penetrant at
steady state.

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 time, a straight line is obtained. From the slope of this graph, D is calculated by substitution in Equation (6)

$$D = \frac{(\text{slope}) l^2}{4} \quad (6)$$

Equation (6) can be derived as following: (Hernandez, 1986)

$$D = \frac{l^2}{7.199 t_{0.5}} \quad (7)$$

where:

$t_{0.5}$ = half of the time required to reach a rate of transmission $(\Delta M / \Delta t)_{\infty}$ value.

The permeability coefficient (P) can be determined from the isostatic method by substitution into Equation (8)

$$P = \frac{aGfl}{Ab} \quad (8)$$

where:

- a = calibration factor to convert detector response to units of mass of permeant/unit of volume [(mass/volume)/signal units]
- G = response units 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)
- b = driving force given by the concentration or partial pressure gradient (pressure or concentration units)

3.2.2 Quasi-Isostatic Method

The quasi-isostatic method is different from the isostatic method of measuring permeability. In this case, the lower concentrated chamber is completely closed as it collects the permeant. However, the difference in penetrant partial pressure or a concentration gradient between the two chambers must be maintained constantly. The concentration of permeant gas or vapor that has permeated through into lower concentration chamber can be quantified by gas chromatography, using a sampling syringe.

In this method, the permeated gas or vapor is accumulated and monitored as a function of time. A generalized transmission rate profile curve describing the transport of a permeant through a polymer membrane by the quasi-isostatic method is shown in Figure 3.2.

The diffusion coefficient can be calculated as following (Hernandez, 1986).

$$D = \frac{l^2}{6\theta} \quad (9)$$

Where:

θ = the intersection of the projection of the steady-state portion of the transmission curve (see figure 5), called the lag time.

The steady state permeability coefficient (P) can be determined from the quasi-isostatic method by substitution into Equation (10)

$$P = \frac{y l}{a b} \quad (10)$$

where:

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

3.2.3 Absolute Pressure Method

With the absolute pressure method, the sample is mounted in a gas transmission cell forming a sealed semi-barrier between two chambers. One chamber contains the test gas at a specific high pressure and the other chamber, at lower pressure, receives the permeating gas. There are two methods:

1. Pressure Differential Method
2. Volume Differential Method

MATERIALS AND METHODS

SULFONATION

4.1 Materials

Film Sample

Oriented Polypropylene (OPP)

2 mil biaxially oriented polypropylene film, provided by Mobil Company, was used in these studies. The level of orientation was 420 % (machine direction) and 800 % (cross direction), based on the initial film dimensions. The percent crystallinity was 45.7 %.

Sulfonating Agent

Oleum ($H_2S_2O_7$), also called fuming sulfonic acid, was the sulfonation agent. Oleum was prepared by mixing 100% sulfuric acid with free sulfur trioxide. The concentration of oleum we used was 30% (wt/wt). Therefore, a 100 gram sample of 30% oleum consisted of 70 grams of sulfuric acid and 30 grams of free sulfur trioxide.

Cleaning Agent

Before sulfonation, the films were cleaned with a laboratory grade liquid detergent, called Micro™, obtained from Cole-Parmer Instrument Company. The concentration of Micro™ used in cleaning was 2% (v/v).

Neutralizing Agent

After sulfonation, films were neutralized with solution of 5% Ammonium Hydroxide in water. Films were immersed in the NH_4OH solution for 5 min.

Salt Solution

Sodium Chloride, Analytical Reagent, obtained from Mallinckrodt, Inc. (Tray, Michigan) was used to make 5% salt solution for ion exchanged with NH_4^+ .

Water

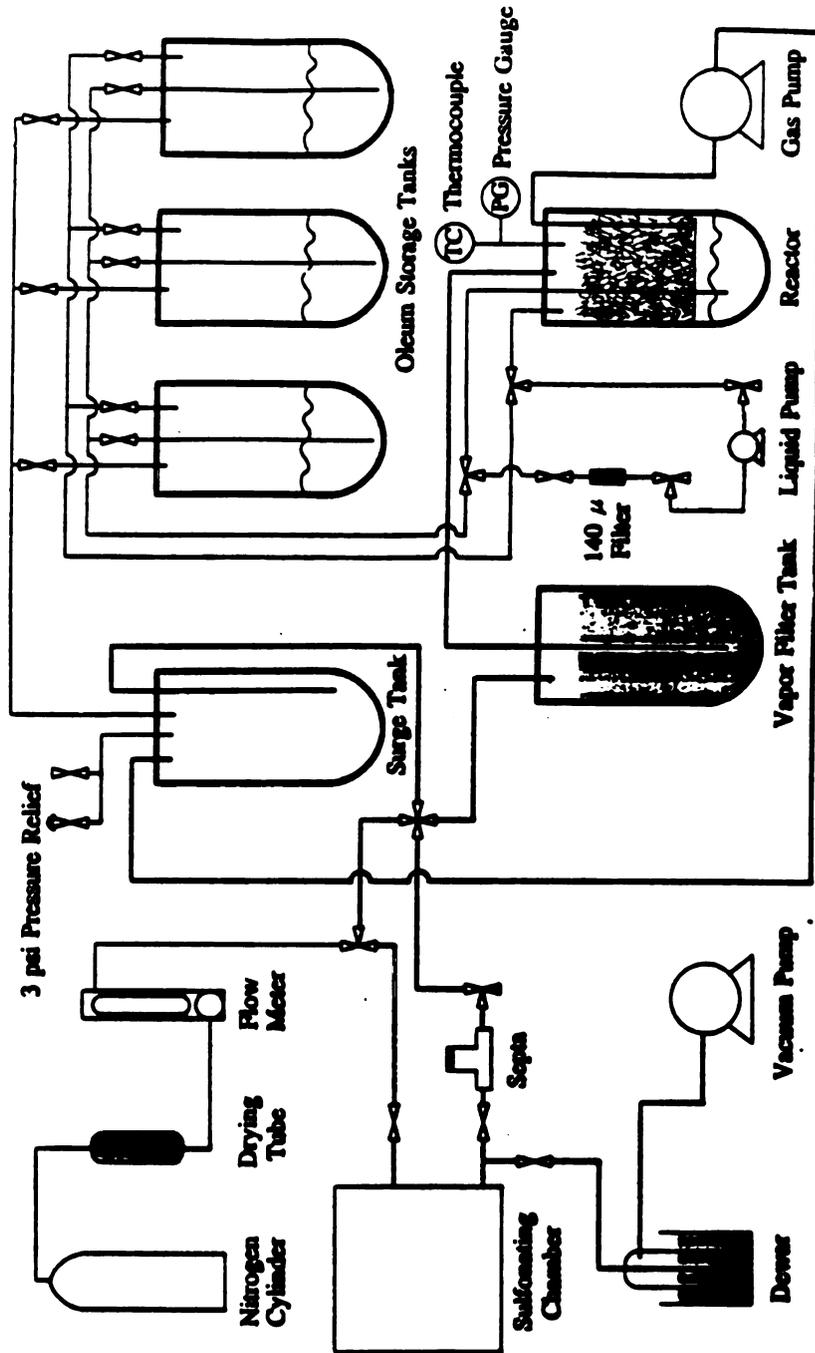
Deionized water was used to prepare the solution and wash the films.

Nitrogen Gas

99% nitrogen gas was used as carrier gas supplied by AGA Gas, Inc. (Cleveland, OH). It was connected to a desiccant filter with the outlet tube to dry the N_2 gas.

4.2 Sulfonation Unit

A schematic of the sulfonation unit is shown in Figure 4.1 (Erickson, 1993). The system is to produce a controllable gaseous mixture of sulfur trioxide in nitrogen. As it can be seen, there are four main components : a reactor, a internal gas circulation loop, a external gas circulation loop and oleum storage containers. The process to product sulfur trioxide is as following:



**Figure 4.1: Schematic Diagram of Sulfonation System
(B. Erickson, 1993)**

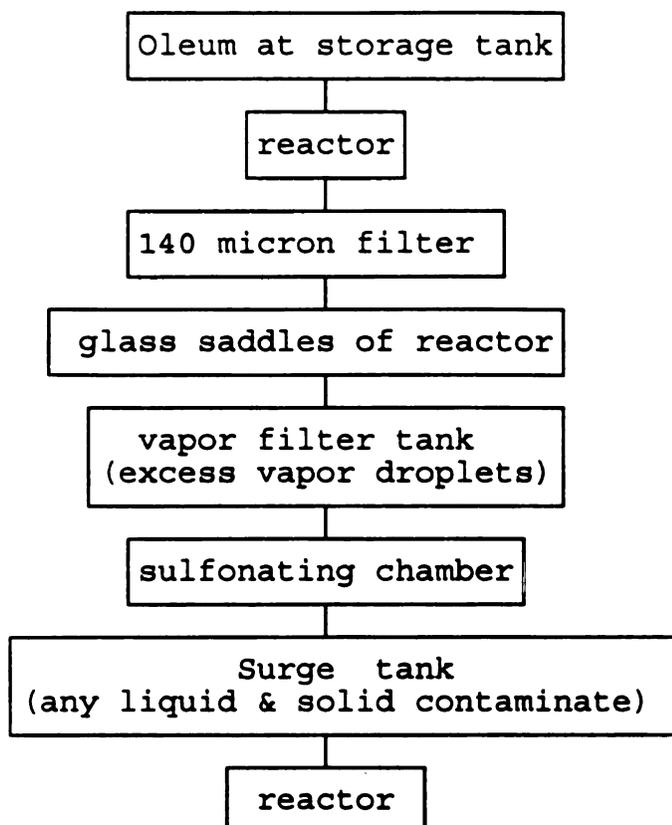


Figure 4.2 : Schematic of the process to generate sulfur trioxide

4.3 Experimental Procedure

The sulfonation process was performed at the Composite Materials and Structures Center (CMSC), MSU. All the polymers in the present work were sulfonated using the same experimental protocol which included cleaning, sulfonating and neutralizing steps. The independent variety used was time exposure. Temperature was kept constant at $23 \pm 1^\circ\text{C}$.

4.3.1 Cleaning Procedure

Prior to any surface treatment, the polymer surfaces were cleaned to remove any contaminants such as residual mold release agents, organic from material handling, and other contaminates.

All of the polymer samples measured 31.75 cm x 15.25 cm and cleaned with a 2% Micro™ solution, using Lint-Free disposable laboratory tissues. After this, they were washed by deionized water. The films were hanged to dry by air at room temperature.

4.3.2 Sulfonation Procedure

Clean, dry film samples were mounted on a metal rack and placed in the sulfonating chamber equipped with an inlet tube for gaseous SO_3 , an inlet tube for N_2 gas and an exhaust tube. The chamber was then closed using C-clamps to form a vacuum tight seal with the chamber.

Nitrogen gas was flowed at a rate of 32 l/min for 3 min into the sulfonating chamber to replace the air inside. Stopped purging nitrogen gas and vacuum the chamber for 10 min that inner pressure was reduced to about 300 $\mu\text{m Hg}$, followed by another 3 min purge nitrogen gas at the same flow rate in order to reach atmosphere pressure and replace dry N_2 gas. This process was intended to eliminate air, water vapor and any active gas that may react with SO_3 gas and interfere with the sulfonation reaction.

Sulfur trioxide gas was circulated through the sulfonating chamber to surface react with the films during the selected time intervals of 1, 2, 3 minutes. The sulfur trioxide gas was generated in the sulfonation unit and transferred to the sulfonating chamber via the external circulation lines. The temperature was adjusted at $32 \pm 1^\circ\text{C}$ to obtain the desired concentration about 1% (v/v) SO_3 . A gas sample was taken during each running from sulfonating chamber to determine the Ph in order to measure the concentration of the sulfur trioxide in the chamber. The SO_3 concentration was determined by the following expression (Erickson, 1993).

$$Y = 209.9436 * \{ \exp[-2.0649 (pH)] \} \quad (11)$$

Where : Y = SO_3 Percentage (v/v)

Ph = the value of the acid which was generated by SO_3 reacted with water.

After a period of sulfonating time, the SO_3 gas tube was closed and a purge of N_2 gas at a rate of 32 liter per minute was flown for 5 minutes to remove SO_3 gas before the chamber was opened. This was done to avoid releasing SO_3 gas into the working area.

4.3.3 Neutralization Procedure

After sulfonation, the polymer films were immediately removed from the sulfonating chamber and neutralized by

dipping in a bath containing 5 % aqueous ammonium hydroxide in water. The films were kept in the bath for 5 minutes. The films were then washed using deionized water and air dried at room temperature. This process yielded a ammonium cation neutralized sulfonated PP films.

4.3.4. Ion Exchanging Procedure

The NH_4^+ cation in the sulfonated PP films were replaced by Na^+ cation by immersing in 5% NaCl aqueous solutions for 3 hours. The films were then removed from the NaCl solutions and washed with deionized water to remove the excess of NaCl from the surface of the films. The films were dried by air for 24 hours. Before doing permeation studies, the films were put into vacuum chamber to remove most of the moisture from the films for 8 hours.

PERMEABILITY MEASUREMENT

The sulfonated film samples were evaluated in terms of the surface composition, oxygen permeability, carbon dioxide permeability, and water vapor transmission rate, then were compared to the non-treated films.

5.1 Electron Spectroscopy for Chemical Analysis (ESCA)

All the film samples were analyzed by X-ray Photoelectron Spectroscopy or Electron Spectroscopy for Chemical Analysis (ESCA). The analysis was performed by Dan Hook on a Perkin Elmer 5400 XPS at Composite Materials and Structures Center, MSU. This analysis determined the surface compositions of the films up to a depth of 50 angstrom. Each composition is reported as atomic percentage.

5.2 Oxygen Permeability Measurement

Oxygen permeability studies were performed using a MoCon Ox-Tran 100 Permeability Tester (Minneapolis, MN). (figure 5.1). In order to control the water activity of the carrier gas (N_2) and Oxygen gas, a device was built attach to mix the dry gas with 100% wet gas (see figure 5.2). It was connected between the gas tanks and MoCon Oxtran 100. This device allowed the two streams, O_2 and carrier gas (N_2), to

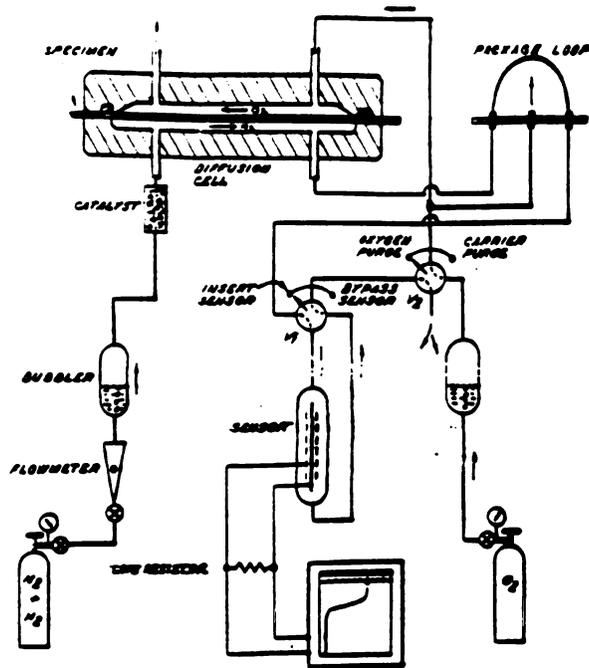


Figure 5.1: Schematic Diagram of Oxygen Permeability Test System (MoCon Inc.)

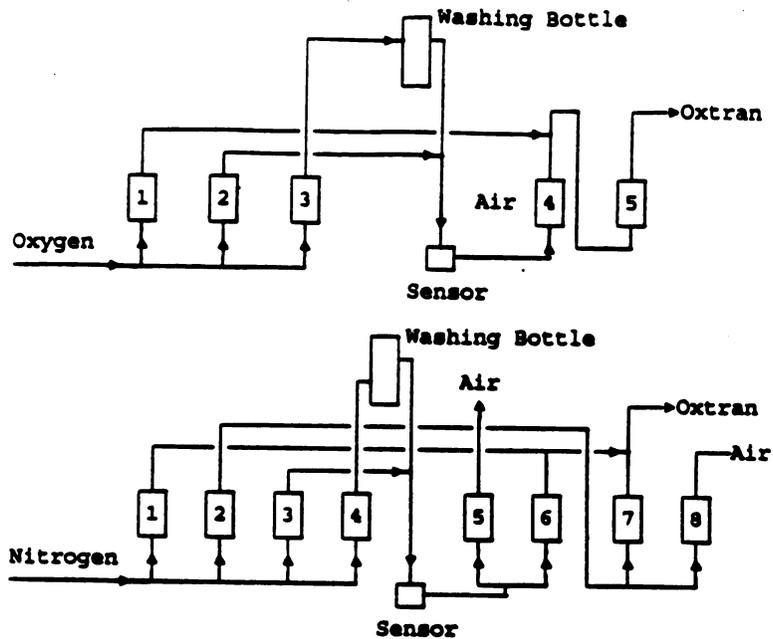


Figure 5.2: Schematic Diagram of Water Activity Control System

be adjusted to selected water vapor activity, by operating the flow of the wet and dry gas stream. Water vapor activities of each gas were measured using a hygrometer sensor from Hydrodynamics Inc. (Sliver Spring, MO) (No. 45-100-15). The relative humidity of each temperature was determined by using humidity calibration curve (see Appendix A) supplied by Hydrodynamics Inc.

The testing procedure for measuring oxygen transmission rates was based on the "Standard Method of Test for Oxygen Gas Transmission Rate through Plastic Film and Sheet Using Colometric Sensor", according to the ASTM D-3985. The O₂ permeability of two film replicates were determined at 3 different temperatures (13°C, 25°C, and 35°C) at 0% RH and 70% RH. The reported value was obtained by averaging the values obtained on each of the two replicates.

5.3 Carbon Dioxide Transmission Rate

CO₂ transmission rate was measured by using MoCon Permatran C-IV built by MoCon Inc. (Minneapolis, MN). The procedure recommended by the instrument manual was followed. The CO₂ transmission rates of film samples were determined at 23°C and 0% RH.

5.4 Water Vapor Transmission Rate

A Permatran W from MoCon Inc. (Minneapolis, MN) was employed to measure the WVTR of each samples at 3 different

temperatures (27°C, 33°C, 37.8°C). The test procedures for Conventional Flat Barrier Materials was followed

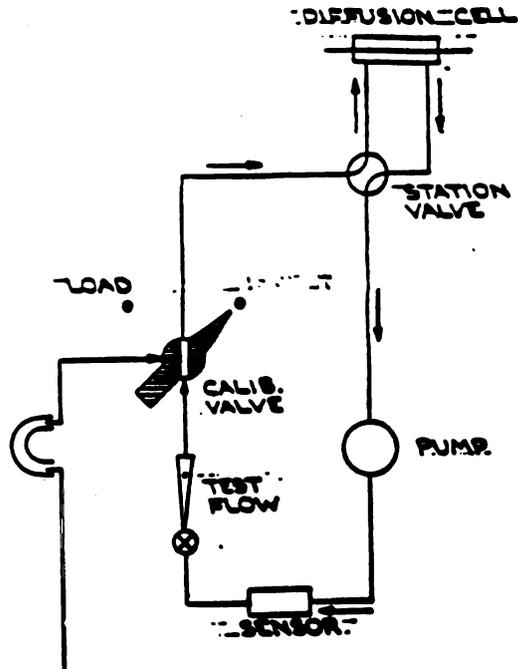


Figure 5.3: Schematic Diagram of Carbon Dioxide Permeability Test System (MoCon Inc.)

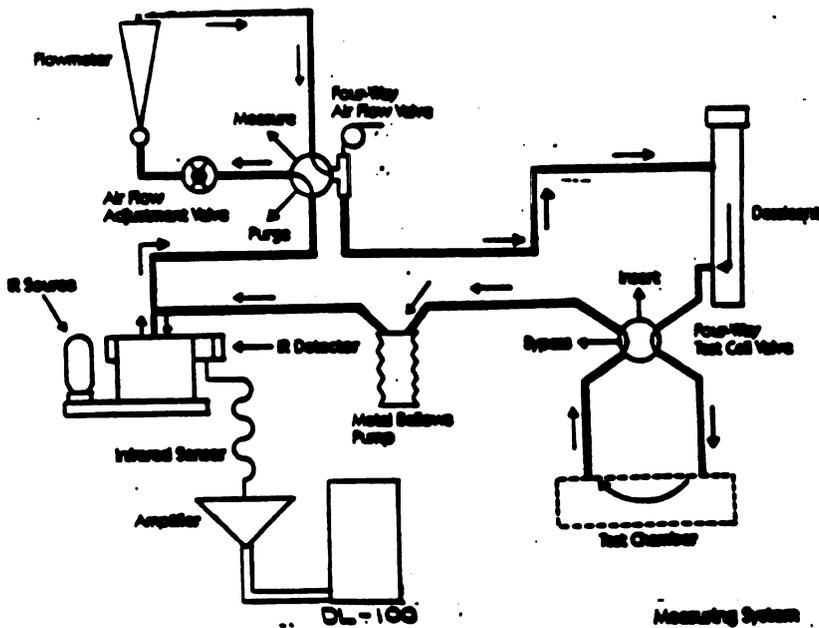


Figure 5.4: Schematic Diagram of Water Vapor Permeability Test System (MoCon Inc.)

RESULTS AND DISCUSSION

6.1 Sulfonation

6.1.1 Quantitative Chemical Analysis by ESCA

The surface composition of the untreated polypropylene film and the sulfonated polypropylene sample films were determined by Electron Spectroscopy for Chemical Analysis (ESCA). The results are presented in Table 6.1 and 6.2. These results are also presented graphically in Figure 6.1 and 6.2.

Table 6.1 : Percent atomic composition for polypropylene sulfonated from 0 to 3 minutes as obtained by ESCA on the surface.

Sulfonation Time (min)	Carbon (atom %)	Oxygen (atom %)	Nitrogen (atom %)	Sulfur (atom %)
0	93.1	6.9	0	0
1	63.60	24.05	3.07	4.14
2-a	61.76	25.09	3.40	5.20
2-b	58.0	28.90	6.60	6.50
3-a	61.28	24.79	4.04	4.20
3-b	62.13	26.07	5.06	6.74
3-c	65.42	22.88	4.91	6.79

Table 6.2 : Relative Atomic ratios of Sulfonated PP films on the surface

Sulfonation Time (min)	C/S (atom/atom)	N/S (atom/atom)	S/C (percent atom /atom)
0	—	—	—
1	15.36	0.74	6.51
2-a	11.88	0.65	8.42
2-b	11.20	1.01	8.93
3-a	14.59	0.96	6.85
3-b	9.22	0.75	10.85
3-c	9.63	0.72	10.68

Table 6.1 are the atomic concentrations for carbon, oxygen, nitrogen, and sulfur determined as a function of sulfonation time. This table indicates that, for example, for each 100 atoms, 63.6 are carbon atoms for a sulfonation time of 1 minute. The oxygen detected in the non-sulfonated film can be attributed to a small oxidation process by air, perhaps during corona treatment. The following comments can be made from the data in the tables.

1. The larger change in atomic compositions takes place at the first minute. This indicates that a rapid chemical reaction takes place when SO₃ contact the film.

2. The sulfur concentration increases as the treatment time increased. Asthana (1993) investigated the sulfonation of PP film at 4 minutes and 5 minutes and found that there was a maximum amount of sulfonation that could be carried out without extensively damaging the surface. According to his data, the maximum degree of sulfonation that can be achieved without damaging the surface of PP is one SO_3 group per three repeat monomer units of PP, in other words that the ratio of carbon and sulfur is around 9. The similar results can be seen in Table 6.2 and Figure 6.1 at 3 min sulfonated PP film. C/S is about 9. Compared the percentage of S atomic on the surface, it increased rapidly from 0 min to 2 min sulfonation and increased slowly from 2 min to 3 min sulfonation. It can be concluded that increasing the sulfonation time can increase the sulfonation level on the surface of the polymer before achieving a saturation value. The saturation sulfonation value on PP film surface in this study is reached at 3 minutes treatment.

3. Concentration of the sulfur on the surface in 3-a sample was very low compared with the other two samples which were at same treatment time. The result may be caused by following reason.

- a. Eventual surface contamination
- b. Variation of sulfur trioxide vapor concentration

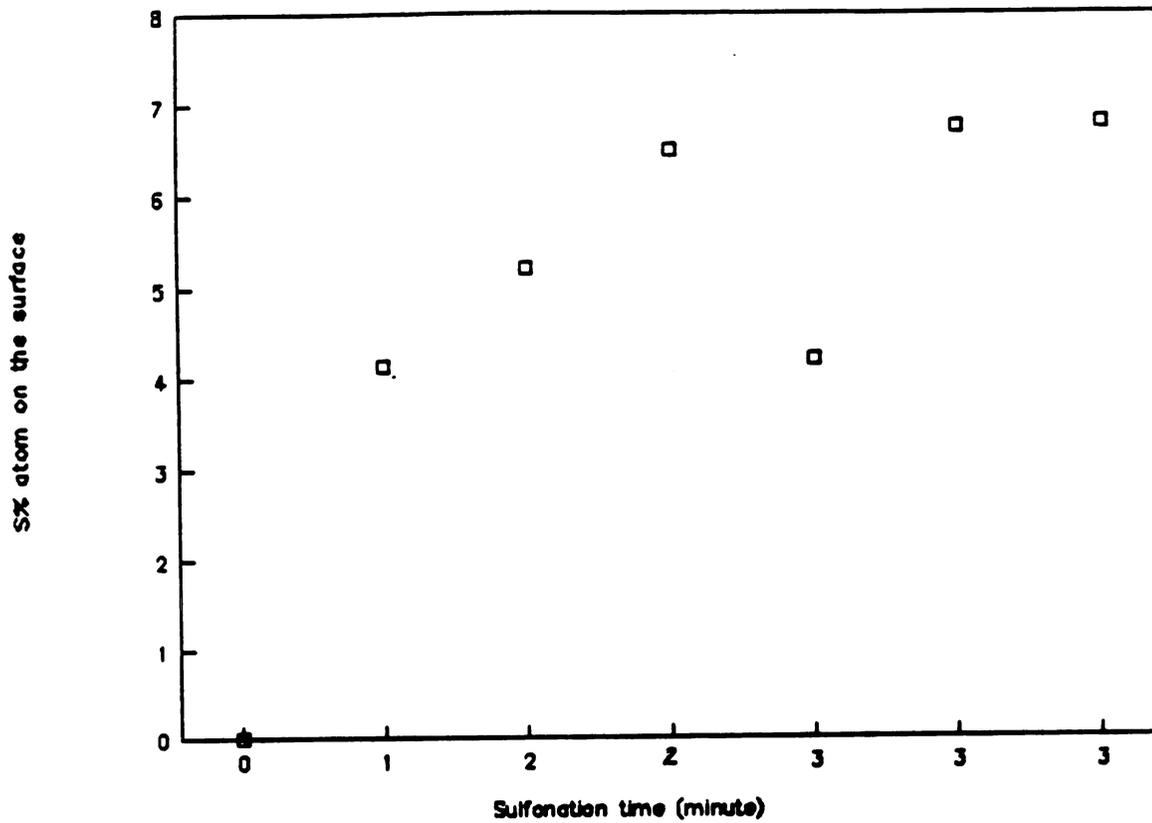
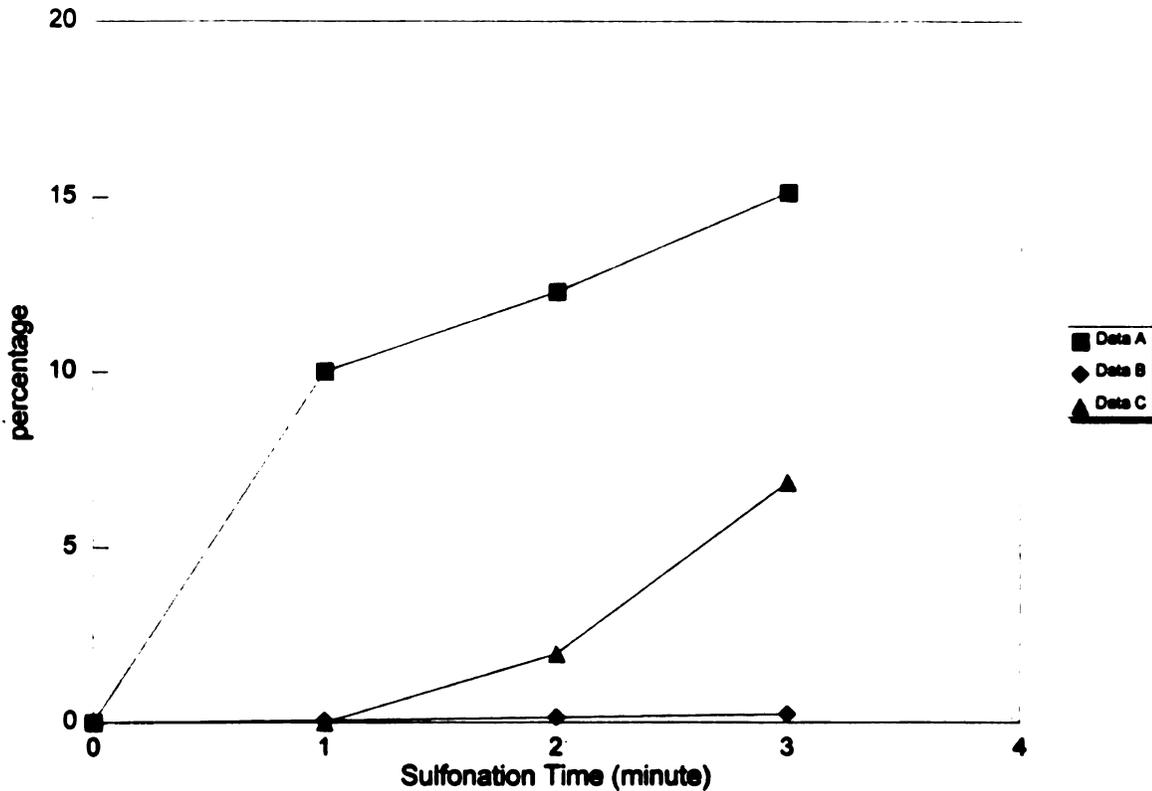


Figure 6.1: Sulfur concentration on the PP film surface as a function of sulfonation time





-- percentage wt. (g/g) of sulfur on the surface of the sulfonated PP (ESCA)
 -- Percentage weight of sulfur of the sulfonated PP (K. Wangmuatsilp, 1993)
 -- Percentage weight change of the sulfonated PP (J. Tardiff, 1993)
 Data attached at Appendix D.

Figure 6.2: Percentage weight of sulfur on the surface of the sulfonated PP, of the sulfonated PP, and percentage weight change of the sulfonated PP vs sulfonation time.

6.1.2 SO₃ Gas Reacting and Diffusion with Polypropylene

It was observed that starting as a transparent film, the sulfonated PP was dark brown after sulfonation. This observation was also made by J. Ihata when polyethylene samples were sulfonated. The presence of the conjugated bond in the polymer backbone for sulfonated polyethylene and polypropylene have also been supported by FT-IR experiments, as indicated in page 9. With longer reaction times, the color of PP film will be darker and a layer of the dark sulfonated film will eventually slough off after rinsed with water. This indicates that the strong degradation processed that the polymer film surface was sulfonated. The film surfaces became light pale green within one minute of the sulfonation changing to yellowish and later to dark brown as the sulfonation processed. Two degradation process may take place during sulfonation. One process involves oxygen from air to form ketone compounds, the other mechanism removes hydrogen atom to give conjugated polyenes. Figure 6.3 illustrates the formation of conjugated double bonds in the polymer chain as a result of sulfonation.

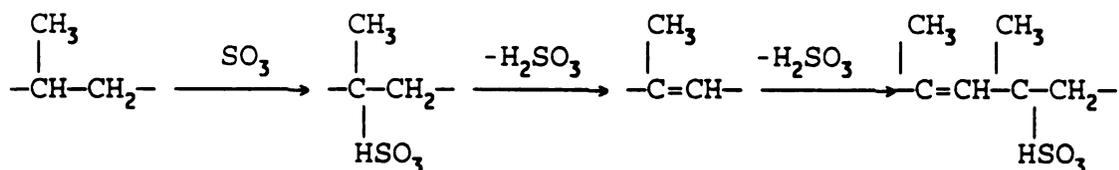


Figure 6.3 : Sulfonation reaction scheme of polypropylene

ESCA analysis indicates that the percent sulfur at the 3 min sulfonated PP film surface reached a maximum value. However, the total weight percent sulfur in the whole sample, determined by Wangwiwatsilp, 1993, increased linearly with sulfonation time. This indicates them that SO_3 gas diffused into the film and continued reacting with PP beyond the surface. This result is supported by the linear relationship of mass uptake in PP versus sulfonation time reported by J. Tardiff (1993). In Tardiff's study, polystyrene and polypropylene films were sulfonated while using a quartz spring balance to measure the weight gain as a functional time. In her experiment at 20°C sulfonation temperature, the percent mass uptake for polypropylene was 85% after 8 min (PS was 6.44%). Unlikely that such a high mass uptake is due strictly to the diffusion SO_3 and the reaction to form sulfonated polymer. It appears that sulfurous acid formed by the side reaction condenses on the film to produce the large weight gain. The reaction mechanism of sulfonation in polypropylene is much more complicated than originally

expected. On the other hand, the weight gain in polystyrene appears to have reached a steady state value. Therefore, the concentration of SO_3 at the interface can be determined by the following equation with great confidence (J. Tardiff, 1993).

$$D = \frac{dC}{dt} = D_0 \exp^{ac} \quad (12)$$

where:

D_0 = the diffusion coefficient in the limit of zero concentration

a = a variable determined empirically

C = Concentration of the SO_3 in the sulfonated polymer.

For Polypropylene, the relation between the sulfur weight gain within the polymer film as a function of sulfonation time is linear and did not reach steady state model at the end of the experimental run. Although the diffusion coefficient and depth of the reaction within the film bulk phase can not be calculated by exact number using Equation (12), it can be calculated as following under the assumption that the sulfonation layers are homogenous.

$$l_1 = \frac{B\%}{A\%} \times \frac{2 \times l_s}{1} \times l_s \quad (13)$$

where : $A\%$ = the sulfur concentration on the surface

$B\%$ = the sulfur concentration of the total film

l_s is the depth of the sulfur determined by ESCA

l = the thickness of the film

l_1 is the depth of the sulfonation of the film

The results of sulfonation depth are presented in Table 6.3.

Table 6.3: Depth of the sulfonation of the sulfonated PP films at different sulfonation time.

Sulfonation Time (min)	Percentage of the sulfur atom on the surface	Depth of the sulfonation (cm)
0	0	0
1	4.14	1.6×10^{-5}
2	5.20	3.1×10^{-5}
3	6.74	4.0×10^{-5}

It can be concluded as following:

1. In figure 6.2, as expected, the concentration of the sulfur on the surface of the film is the highest, followed by the weight changed of the film. The sulfur percentage of the total film is smallest. The sulfonation reaction happened at the surface of the films.
2. In Table 6.3, the depth of the sulfonation increased with increasing the treatment time.

6.2 Oxygen Permeation Study

6.2.1 Film neutralized with NH_4^+

The isostatic method was employed to determine oxygen permeability. Oxygen permeability studies were carried out with air at a flow rate of 25 cc/min, at different temperatures, and a water vapor activity of $a=0$ and at 26°C with $a=0.7$. Oxygen permeability was measured at 0% RH on film samples sulfonated for 1, 2, 3 minutes and blank samples. Results of these measurements at 13°C , 26°C , and 35°C are presented in Table 6.4 and Figure 6.4. Oxygen permeability as a function of sulfonation time is presented in Table 6.5 in which the activation energies included. Data from Table 6.5 is graphed in Figure 6.5. From these results, it can be seen that oxygen permeability at 0% RH was reduced as the sulfonation time increased. As expected, the oxygen permeability of sulfonated PP films decreased as the temperature decreased. The activation energy of the oxygen permeability for all samples of sulfonated PP was the same as for the untreated PP films. As indicated above, the sulfonation on the surface was not the same for all the samples. For example, S% atom on the surface of the three 3 min sulfonation PP films are 4.2 %, 6.74 %, and 6.79%, respectively. This difference in atomic sulfur was reflected in the oxygen permeability value. The lower the percent of atomic of sulfur on the surface, the higher oxygen

Table 6.4: O₂ permeability of sulfonated PP with 0% RH at 13°C, 26°C, and 35°C neutralized with NH₄⁺.

Temp.	Sulfonated Time (min)	%S on the surface of the PP	O ₂ Permeability (cc.mil/m ² .day.atm)		
			#1	#2	Average
13°C	untreated	0	1007	998	1002
	1	4.14	910	872	891
	2	5.2	726	717	722
	3-a	4.2	700	705	702
	3-b	6.74	436	436	436
	untreated	0	2315	2363	2339
26°C	1	4.14	2228	2228	2228
	2-a	5.2	1932	1937	1935
	2-b	6.5	1840	1840	1840
	3-a	4.2	1695	1700	1697
	3-b	6.74	920	954	937
	untreated	0	3666	3734	3700
35°C	1	4.14	3351	3414	3382
	2	5.2	2673	2721	2697
	3-a	4.2	2688	2707	2697
	3-b	6.74	1579	1550	1564
	untreated	0	3666	3734	3700

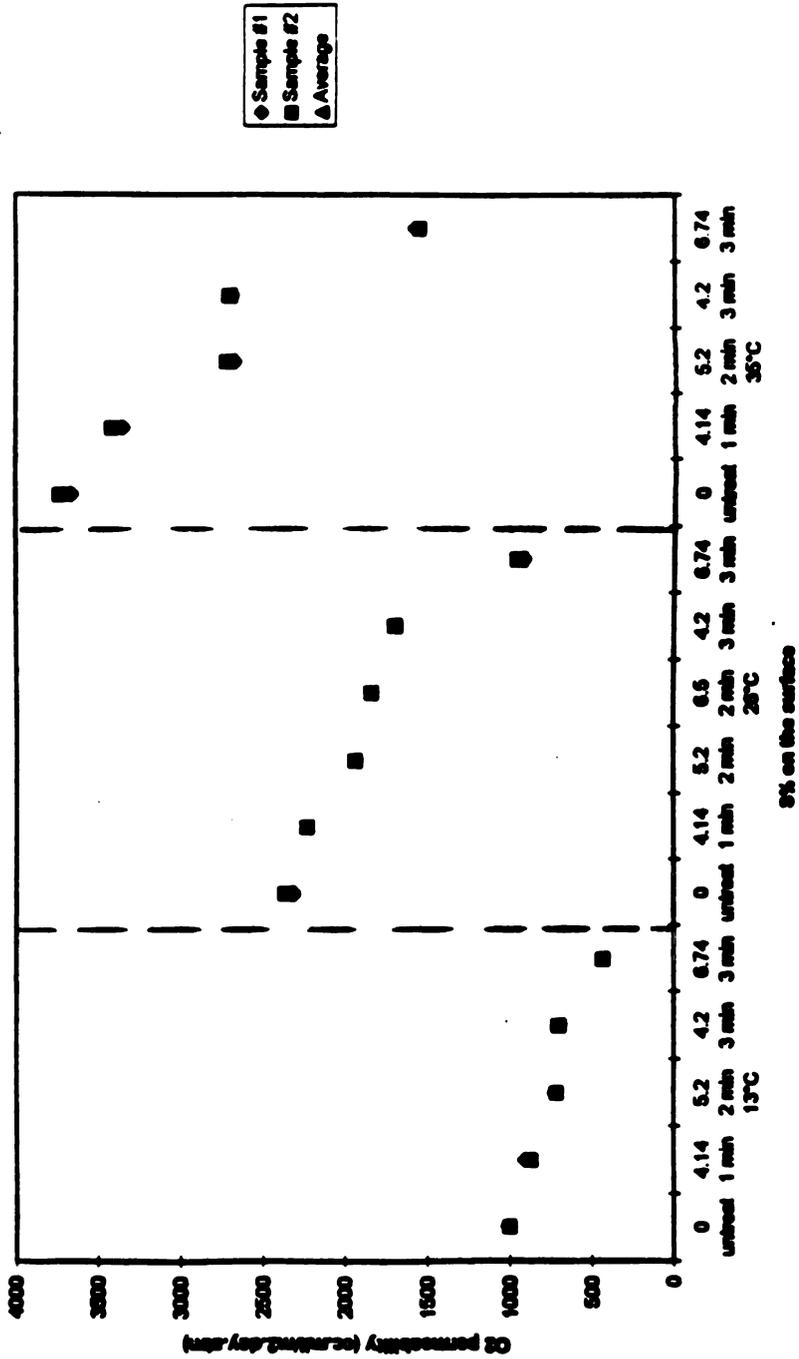


Figure 6.4: O₂ permeability of sulfonated PP at 13°C, 26°C and 35°C with 0%RH (NH₄⁺)

Table 6.5: Activation energy of the oxygen permeability as a function of sulfonation degree of PP.

Temp.		Log P			Slope	Activation Energy (KJ/mol)
		13°C	26°C	35°C		
1/T (K)		0.00350	0.00335	0.00325		
s% on the surface of the film	untreated	3.00104	3.36902	3.56816	2266	10354
	4.14	2.94989	3.34783	3.52924	2325	10628
	5.2	2.85826	3.26485	3.43092	2305	10535
	4.20	2.84644	3.22976	3.43092	2337	10680
	6.74	2.63931	3.00333	3.19427	2189	10141

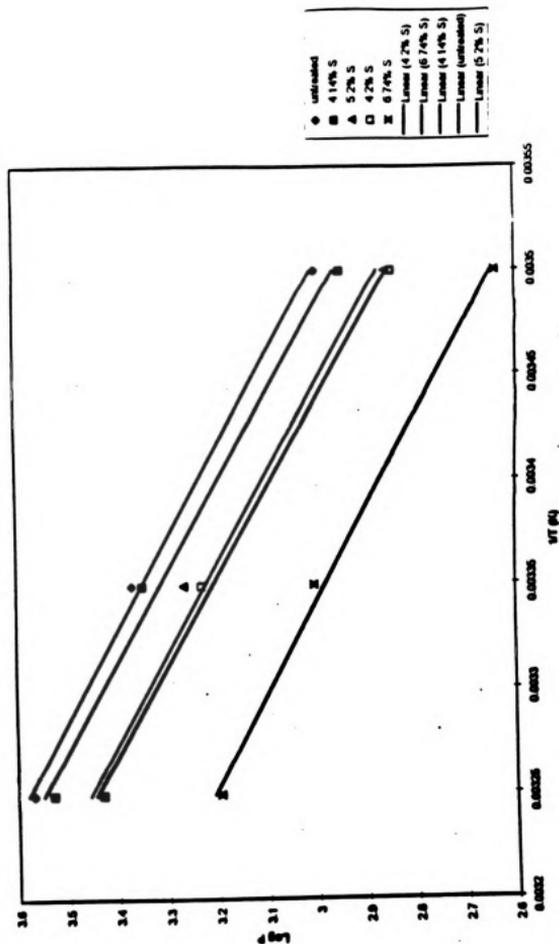


Figure 6.5: Activation energy of the oxygen permeability as a function of sulfonation degree of PP

permeability. But the oxygen permeability was not only affected by the surface concentration S, it also by the sulfonation time with the same S concentration value. For example, the permeability of the sample sulfonated for 3 minutes with 4.2% S at the surface was lower than the 1 min sulfonation sample with 4.14% S at the surface. The reasons will be discussed in the diffusion coefficient & solubility studies.

Calculation of Diffusion Coefficient

The diffusion coefficient (D) was calculated from the unsteady state fraction of the oxygen transmission rate data. The calculation procedure follows the procedure described by R.Hernandez (1986).

Equation (5) was rewritten as:

$$A = X^{1/2} \exp(-X) \quad (14)$$

where :

$$A = \frac{\sqrt{\pi}}{4} \frac{(\Delta M / \Delta t)_t}{(\Delta M / \Delta t)_\infty}$$

$$X = \frac{l^2}{4Dt} \quad (15)$$

The equation can be rewritten as :

$$G = X^{1/2} \exp(-X) - A \quad (16)$$

with G being equal to zero, to satisfy Equation (14). The iteration process is described by

$$X(k+1) = X(k) - \frac{G(k)}{\exp(-X(k)) \{1/2 [X(k)]^{1/2} - [X(k)]^{1/2}\}} \quad (17)$$

where (k) is one iteration step.

Here, a basic program (see Appendix B) was written based on equation (17) using for calculating the oxygen diffusion coefficient of PP films. The results of oxygen diffusion coefficient of sulfonated PP at 13°C, 26°C, and 35°C with 0% RH neutralized by NH_4^+ are summarized in Table 6.6 and presented graphically in Figure 6.6. As expected, the oxygen diffusion coefficient of sulfonated PP decreased with decreasing temperature. No change was found on the diffusion coefficient as a function of sulfur content.

An apparent oxygen solubility was calculated by Equation (4). The results of oxygen solubility at 13°C, 26°C and 35°C with 0% RH neutralized by NH_4^+ are listed in Table 6.7 and presented graphically in Figure 6.7. The solubility of PP is affected by concentration of the SO_3NH_4^+ on the sulfonation. The higher the S% atomic on the surface, the lower the

Table 6.6: Diffusion Coefficient of sulfonated PP at 13°C, 26°C and 35°C with 0% RH neutralized with NH_4^+

Temp	Sulfonated Time (min)	S% on the surface of the film	O_2 Diffusion Coefficient (cm ² /sec.)		
			#1	#2	Average
13°C	untreated	0	1.06	1.05	1.05
	1	4.14	1.05	1.00	1.02
	2	5.2	1.05	1.07	1.06
	3-a	4.2	1.00	1.08	1.04
	3-b	6.74	1.02	1.00	1.01
	untreated	0	1.24	1.25	1.24
26°C	1	4.14	1.16	1.35	1.26
	2-a	5.2	1.37	1.41	1.39
	2-b	6.5	1.41	1.43	1.42
	3-a	4.2	1.16	1.18	1.17
	3-b	6.74	1.17	1.25	1.21
	untreated	0	1.21	1.30	1.25
35°C	1	4.14	1.21	1.24	1.23
	2	5.2	1.49	1.42	1.46
	3-a	4.2	1.25	1.49	1.37
	3-b	6.74	1.46	1.45	1.46
	untreated	0	1.21	1.30	1.25

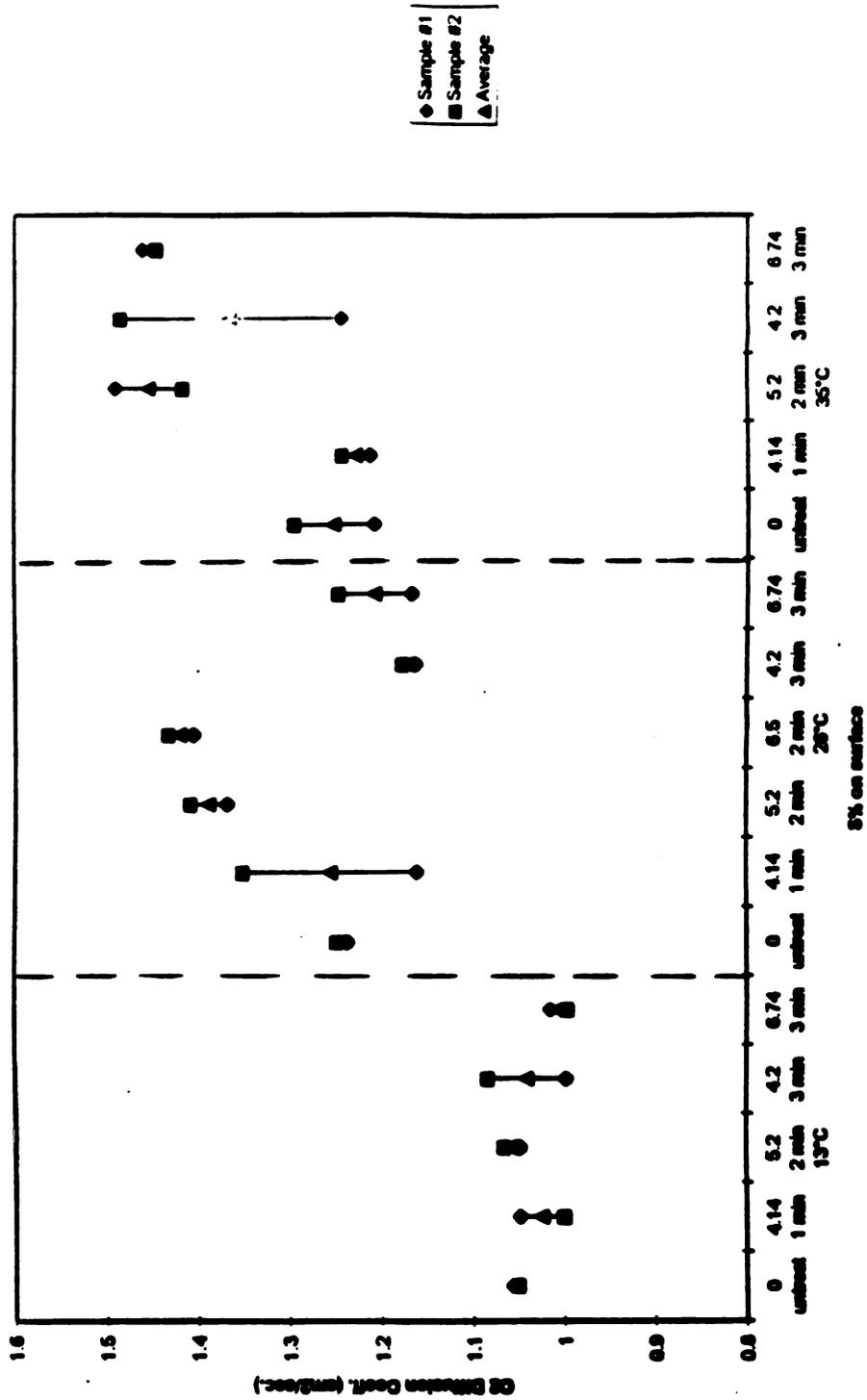


Figure 6.6: O₂ diffusion coefficient of sulfonated PP at 13°C, 26°C and 35°C with 0%RH (NH₄⁺)

Table 6.7: O₂ Solubility of Sulfonated PP at 13°C, 26°C, and 35°C with 0% RH neutralized with NH₄⁺

Temp	Sulfonated Time (min)	S% on the surface of the film	O ₂ Solubility (cc O ₂ / cc Polymer)		
			#1	#2	Average
13°C	untreated	0	0.28	0.28	0.28
	1	4.14	0.26	0.26	0.26
	2	5.2	0.20	0.20	0.20
	3-a	4.2	0.19	0.20	0.20
	3-b	6.74	0.13	0.13	0.13
	26°C	untreated	0	0.55	0.56
26°C	1	4.14	0.50	0.54	0.52
	2-a	5.2	0.42	0.41	0.41
	2-b	6.5	0.39	0.38	0.38
	3-a	4.2	0.42	0.43	0.43
	3-b	6.74	0.22	0.28	0.25
	35°C	untreated	0	0.83	0.92
35°C	1	4.14	0.79	0.83	0.81
	2	5.2	0.53	0.56	0.55
	3-a	4.2	0.63	0.54	0.59
	3-b	6.74	0.32	0.32	0.32

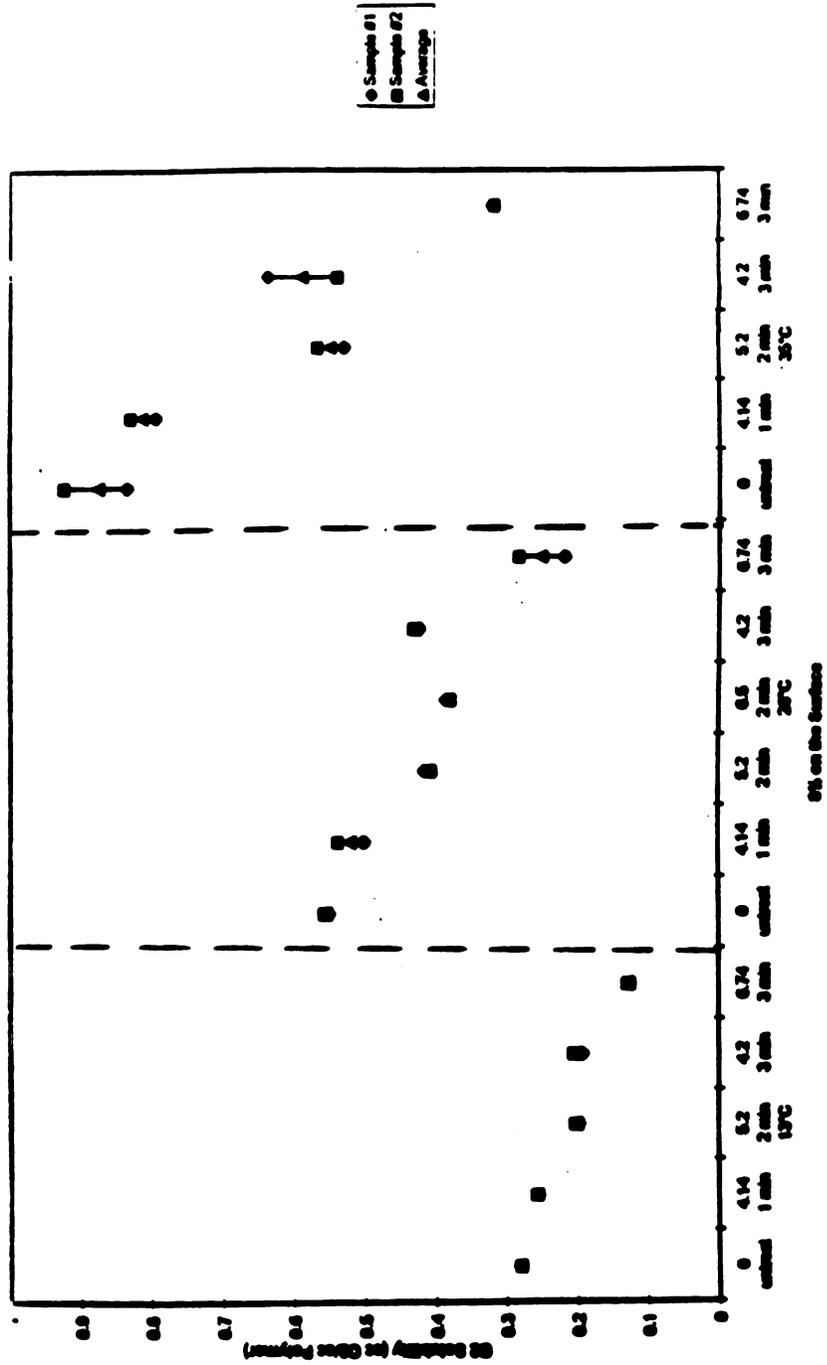


Figure 6.7: O₂ solubility of sulfonated PP at 13°C, 26°C and 35°C at 0%RH (MR₄)

apparent oxygen solubility. The longer the sulfonation time, the lower the apparent oxygen solubility, too. The same as oxygen permeability pointed at page 50 that even at same percent S on the film surface (3 min sulfonated PP film with 4.2% S and 1 min sulfonated PP film with 4.14% S), the oxygen solubility decreased as increasing sulfonation time. It appears that an increase surface energy and polarity of the surface created by the sulfonic groups reduces the oxygen solubility.

All the measurements and calculation above were based on the 2 mil PP films. Since the sulfonation only happened on the surface of the PP film. To determine the barrier properties of the sulfonation layer will help us full understand the sulfonation to contribution to the oxygen barrier properties. There are 3 layers in the sulfonated PP films: sulfonated PP surface/PP/sulfonated PP. The permeability of the sulfonated PP surface layer can be calculated as following:

$$\frac{l}{P} = 2x \frac{l_1}{P_1} + \frac{l_2}{P_2}$$

$$P_1 = \frac{2xl_1}{\frac{l}{P} - \frac{l_2}{P_2}} \quad (18)$$

Where : l_1 is the thickness of untreated PP layer

P_1 is the oxygen permeability of the untreated pp layer

P_2 is the oxygen permeability of the sulfonated PP surface.

Assume that oxygen solubility of the sulfonated PP surface is the same as that of total sulfonated PP film. The diffusion coefficient can be calculated as following:

$$D_1 = \frac{P_1}{S} \quad (19)$$

Where D_1 = diffusion coefficient of the sulfonated PP surface.

The oxygen permeability and diffusion coefficient of the sulfonated PP surface layer are presented in Table 6.8

Table 6.8: Oxygen permeability and diffusion coefficient of the sulfonation layer of the sulfonation PP films

sulfonation time (min)	percentage sulfur atom on the surface	Oxygen Permeability	Oxygen diffusion coefficient	Oxygen Solubility
0	0	2339	1.24	0.55
1	4.14	248	0.14	0.52
2	5.20	129	0.09	0.41
3	6.74	24	0.03	0.25

The oxygen permeability and diffusion coefficient of the sulfonated PP surface are dramatically decreased compared

with unsulfonated PP film under the assumption. while increased the sulfonation time, the oxygen permeability and diffusion coefficient decreased.

Values of the oxygen permeability, diffusion coefficient and solubility at 26°C and 70%RH neutralized with NH_4^+ are summarized in Tables 6.9, 6.10, and 6.11, respectively.

These values are also presented graphically in Figure 6.8, 6.9, and 6.10, respectively, together with values obtained at 0% RH. It is clearly shown that the oxygen permeability of sulfonated PP at 70% RH decreased a little compared with the significant changed at 0%RH as well as solubility. The diffusion coefficient with 2 min or less than 2 min sulfonated PP at 70% RH were almost same as those at 0%RH. The diffusion coefficient with 3 min sulfonated PP films increased at 70% RH. It indicates that sulfonated PP films are moisture sensitive and loss their barrier property when present in a moisture circumstance.

Sulfonation PP ion neutralized with Na^+

The oxygen permeation for this studies was carried out at 13°, 26°, and 35° with 0% RH. The results of oxygen permeability, diffusion coefficient & solubility are in Table 6.12, 6.13 and 6.14 and presented graphically in Figure 6.11, 6.12 and 6.13, which are provided for comparison with sulfonated PP neutralized by NH_4^+ . The oxygen permeability of the sulfonated PP with Na^+ decreased



Table 6.9: O₂ permeability of sulfonated PP at 26°C at 70%RH and neutralized with NH₄⁺.

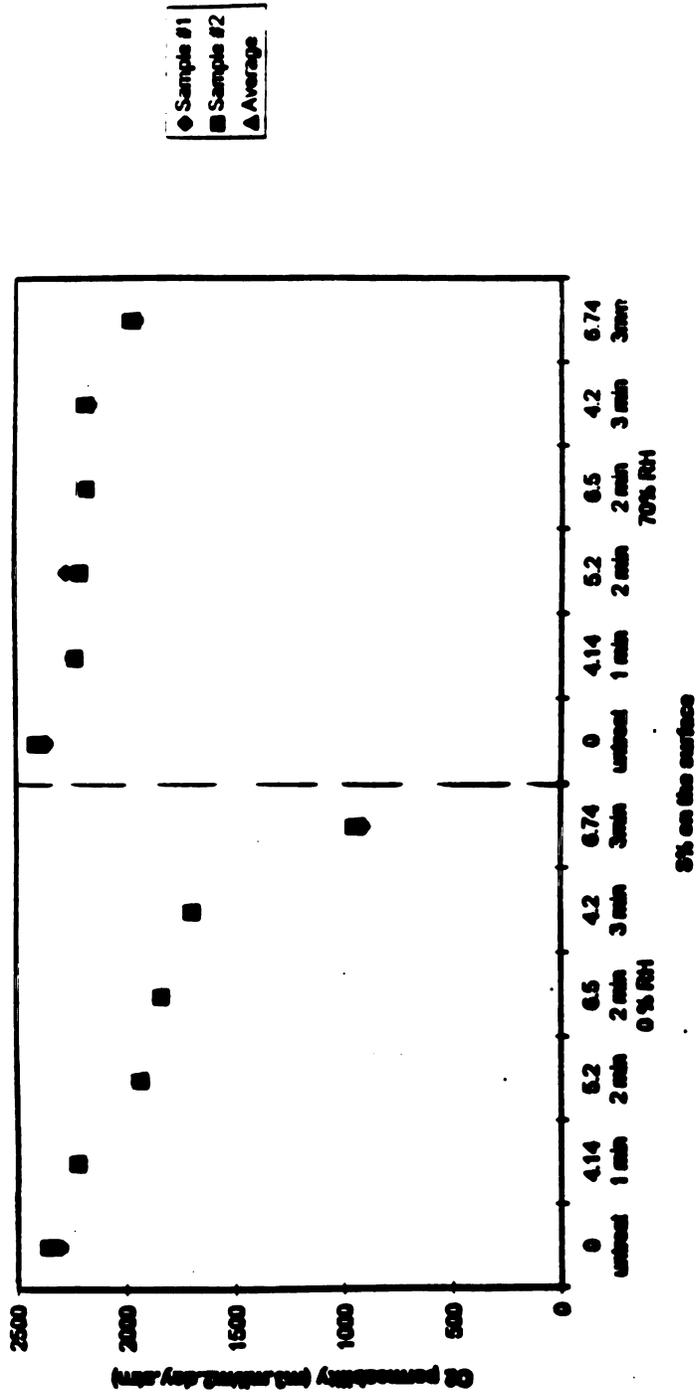
Sulfonated Time (min)	SX on the surface of the PP	O ₂ Permeability (cc.mil/m ² .day.atm)		
		#1	#2	Average
untreated	0	2370	2412	2391
1	4.14	2237	2228	2232
2-a	5.20	2266	2203	2235
2-b	6.50	2179	2174	2177
3-a	4.20	2169	2189	2179
3-b	6.74	1956	1981	1968

Table 6.10: O₂ Diffusion Coefficient of sulfonated PP at 70%RH neutralized by NH₄⁺.

Sulfonated Time (min)	SX on the surface of the film	O ₂ Diffusion Coefficient (cm ² /sec.)		
		#1	#2	Average
Untreated	0	1.25	1.26	1.26
1	4.14	1.26	1.27	1.27
2-a	5.2	1.29	1.41	1.35
2-b	6.5	1.37	1.30	1.34
3-a	4.2	1.39	1.38	1.38
3-b	6.74	1.34	1.27	1.31

Table 6.11: O₂ Solubility of Sulfonated PP at 26°C , 70 %RH
neutralized with NH₄⁺

Sulfonated Time (min)	SX on the surface of the film	O ₂ Solubility (cc O ₂ / cc Polymer)		
		#1	#2	Average
Untreated	0	0.56	0.56	0.56
1	4.14	0.52	0.52	0.52
2-a	5.2	0.52	0.46	0.49
2-b	6.5	0.47	0.49	0.48
3-a	4.20	0.46	0.46	0.46
3-b	6.74	0.43	0.46	0.44



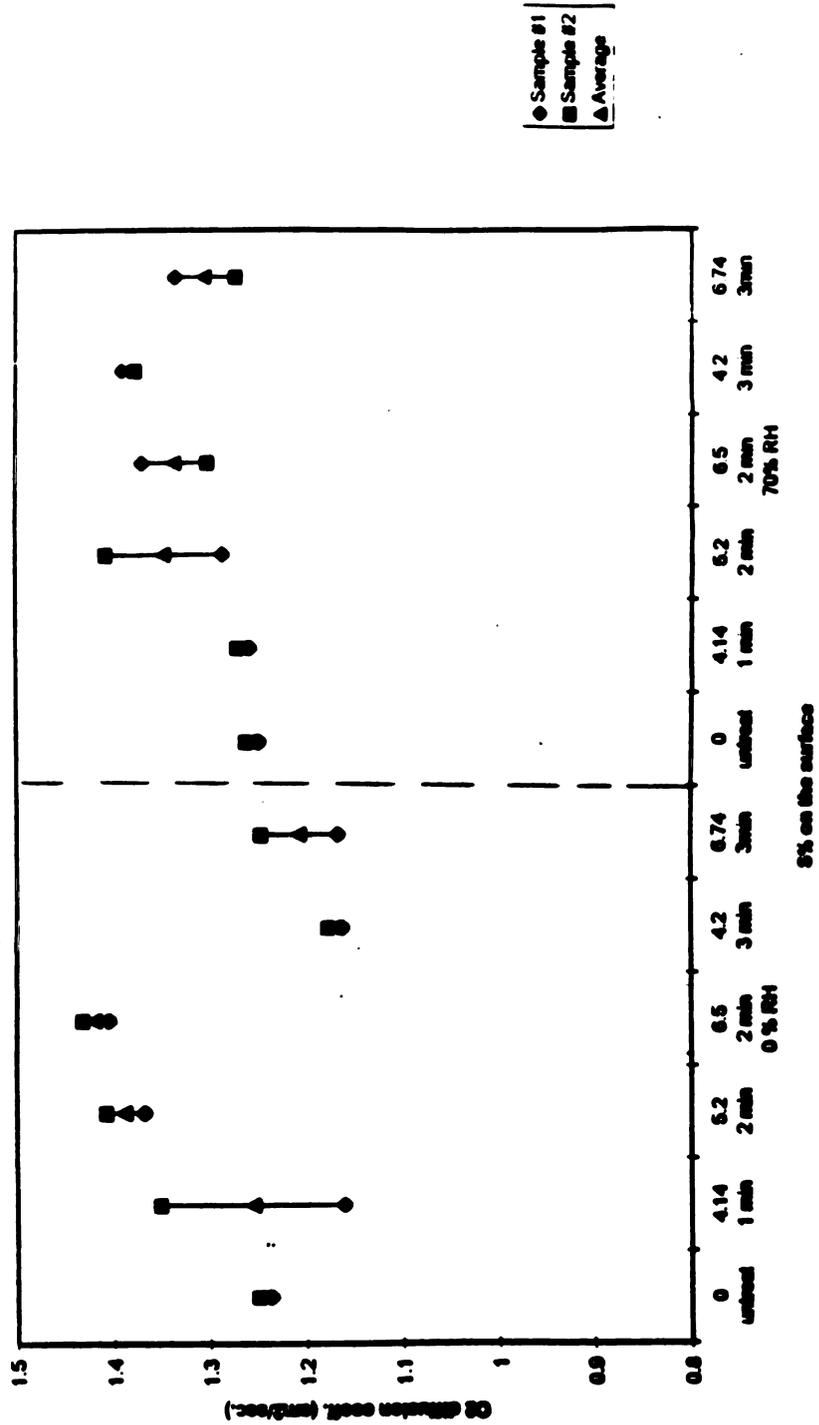


Figure 6.9: Comparison of O_2 diffusion coefficient of sulfonated PP at 26°C with 0%RH and 70%RH (NH_4^+)

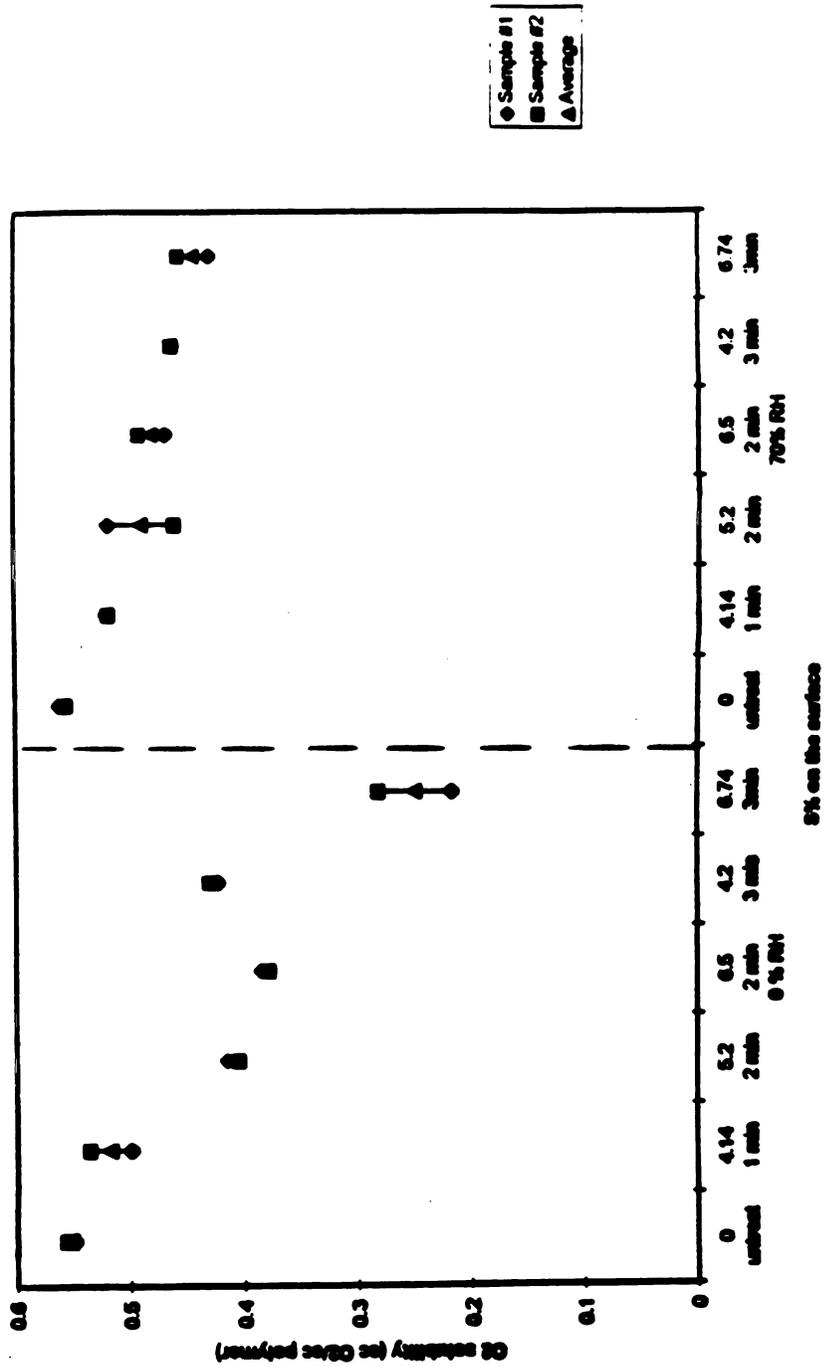


Figure 6.10: Comparison of O₂ solubility of the sulfonated PP at 26°C with 0%RH and 70%RH (RH₀)

as the sulfonation time increased. Compared with the sulfonated PP with NH_4^+ and Na^+ at same sulfonation time, the permeability of sulfonated PP with Na^+ is higher than that of sulfonated PP with NH_4^+ . At the same sulfonation time, the diffusion coefficient of sulfonated PP with Na^+ is much lower than that of sulfonated PP with NH_4^+ . The solubility of sulfonated PP with Na^+ is much higher than that of sulfonated PP with NH_4^+ . It is found that Na^+ ion which substituted NH_4^+ via an ion exchange reaction of a sulfonated PP film could decrease the diffusion coefficient, but increase the oxygen solubility. Compared the 2 min with 3 min sulfonation PP ion exchanged by Na^+ , oxygen permeability of 2 min sulfonated PP film is higher than that of 3 min sulfonated PP film with similar concentration of SO_3^- on the surface. It is confirmed that increasing sulfonation time, the chemical reaction take place under the surface of the film and contribute to film barrier characteristic.

6.4 CO₂ permeability studies.

CO₂ permeability studies were carried out in Permeatran C-IV apparatus at constant dry CO₂ gas flow rate of 80 cc/min and N₂ as carrier gas with a flow rate of 250 cc/min, at 25°. The results of CO₂ permeability studies of each film sample at 25°C are presented in Table 6.15. There values are

Table 6.12: O₂ Permeability of the sulfonated PP ion exchanged by Na⁺ at 13°C, 26°C and 35°C with 0 %RH

Temp.	Sulfonated Time (min)	%S on the surface of the PP	O ₂ Permeability (cc.mil/m ² .day.atm)		
			#1	#2	Average
13°C	untreated	0	1007	998	1002
	2	6.58	881	906	893
	3	6.97	625	630	627
26°C	untreated	0	2315	2363	2339
	2	6.58	2048	2082	2065
	3	6.97	1501	1453	1477
35°C	untreated	0	3666	3734	3700
	2	6.58	3588	3632	3610
	3	6.97	2475	2518	2496

Table 6.13: O₂ Diffusion Coefficient of sulfonated PP ion exchanged by Na⁺ at 13°C, 26°C and 35°C with 0 %RH

Temp.	Sulfonated Time (min)	%S on the surface of the film	O ₂ Diffusion Coefficient (cm ² /sec.)		
			#1	#2	Average
13°C	Untreated	0	1.06	1.05	1.05
	2	6.58	0.95	0.96	0.96
	3	6.97	0.72	0.75	0.73
26°C	Untreated	0	1.24	1.25	1.24
	2	6.58	1.15	1.13	1.14
	3	6.97	1.04	0.93	0.99
35°C	Untreated	0	1.21	1.30	1.25
	2	6.58	1.16	1.17	1.17
	3	6.97	1.05	1.10	1.08



**Table 6.14: O₂ Solubility of sulfonated PP ion exchanged by Na⁺
at 13°C, 26°C, and 35°C with 0%RH**

Temp.	Sulfonated Time (min)	S% on the surface of the film	O ₂ Solubility (cc O ₂ / cc Polymer)		
			#1	#2	Average
13°C	Untreated	0	0.28	0.28	0.28
	2	6.58	0.27	0.28	0.28
	3	6.97	0.26	0.25	0.25
	Untreated	0	0.55	0.56	0.55
	2	6.58	0.52	0.54	0.53
	3	6.97	0.42	0.46	0.44
	Untreated	0	0.83	0.92	0.87
	2	6.58	0.91	0.91	0.91
	3	6.97	0.69	0.63	0.66

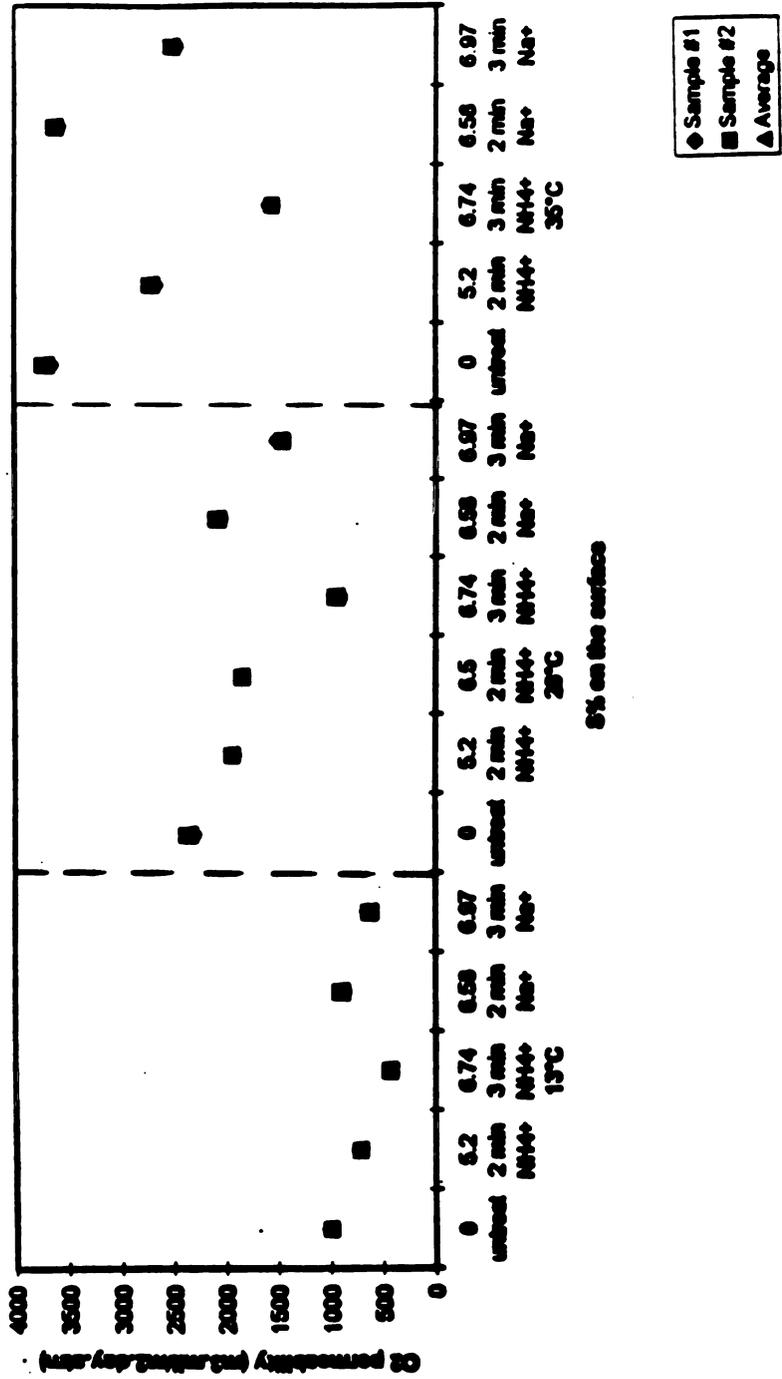


Figure 6.11: Comparison of O₂ permeability of the sulfonated PP ion exchanged by NH₄⁺ and Na⁺ at 13°C, 26°C and 35°C with 0%RH



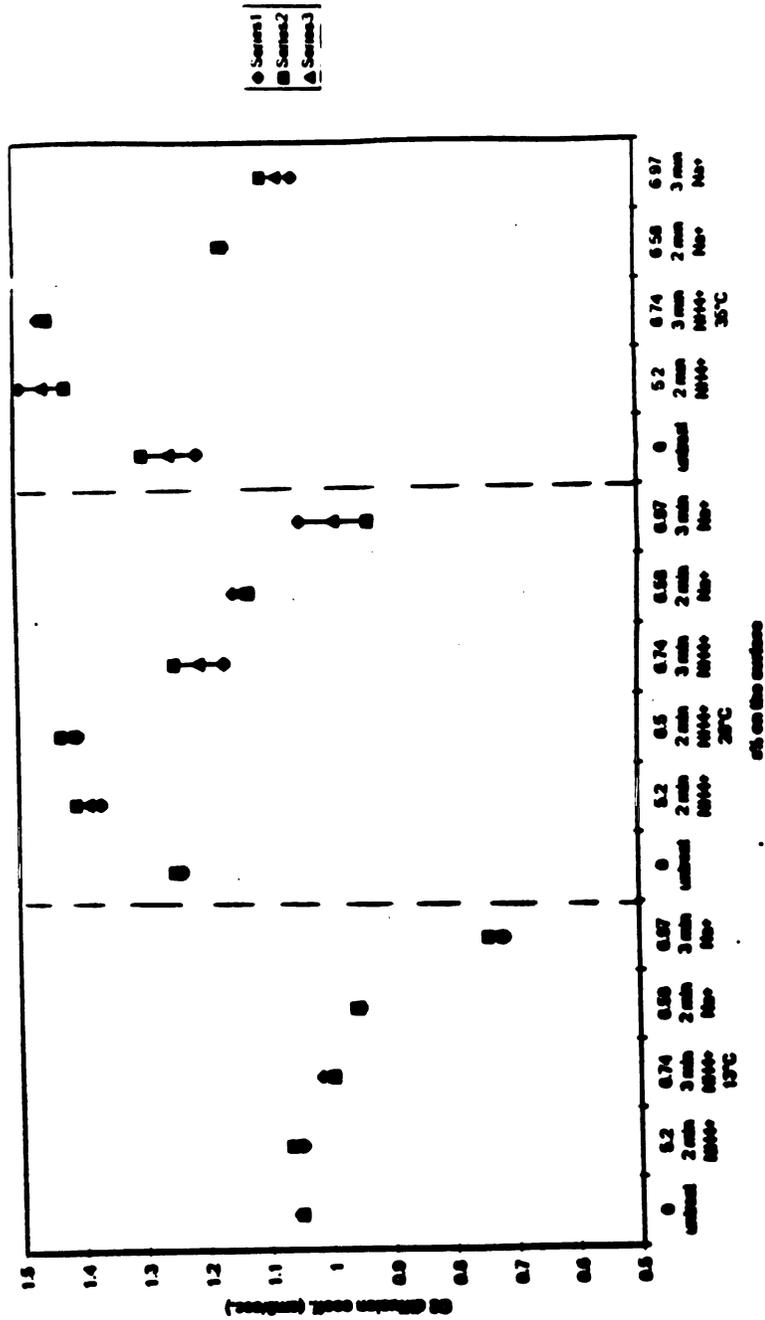


Figure 6.12: Comparison of O₂ diffusion coefficient of the sulfonated PP ion exchanged by Na⁺ and NH₄⁺ at 13°C, 26°C and 35°C with 0%RH

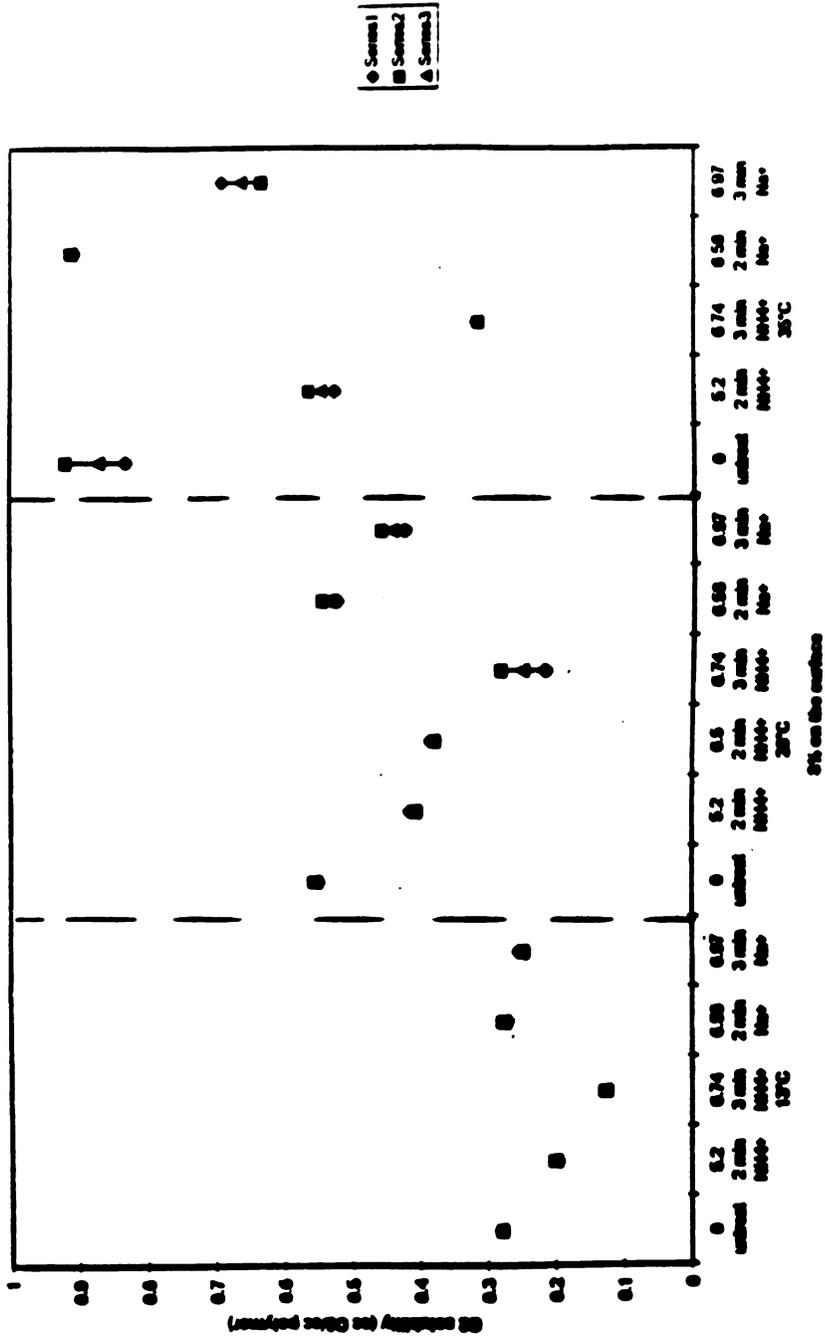


Figure 6.13: Comparison of O₂ solubility of the sulfonated PP ion exchanged by Na⁺ and NH₄⁺ at 13°C, 26°C and 35°C with 0%RH

plotted as a function of the percent of atomic sulfur on the surface in Figure 6.14. It was found that as the percent S atomic increased, the CO₂ permeability decreased. The CO₂ permeability of the film with 6.5% S on the surface is about 15% lower than that of the film with 5.2% S on the surface. These results confirm the same trend observed for oxygen permeation studies.

6.5 Water Vapor Permeation Studies

Water vapor permeability were carried out at 90% RH at a carrier gas flow rate of 65 cc/min, at 27°C, 33°C, and 37.8°C.

Results of the water vapor permeability studies at 27°C, 33°C and 37.8°C are summarized in Table 6.16. The higher the sulfonation degree, the higher the water vapor permeability. This confirms that sulfonation makes PP films moisture sensitive as previously observed with the oxygen permeability measurements at 0% RH and 70%RH.

Table 6.15: CO₂ Permeability of the sulfonated PP neutralized with NH₄⁺ at 25°C with 0% RH

Sulfonated Time (min)	S% on the surface of the film	CO ₂ Permeability (cc.mil/m ² .day.atm)		
		#1	#2	Average
untreated	0	6478	6834	6656
1	4.14	6201	6399	6300
2-a	5.20	6057	5958	6106
2-b	6.50	4616	4999	4807
3-a	4.20	5261	6027	5644
3-b	6.74	4059	4344	4201

Table 6.16: Water vapor permeability of the sulfonated PP at 27°C, 33°C and 37.8°C.

Temp.	S% on the surface of the film	Water Vapor Permeability (mg.mil/m ² .day.atm)		
		27°C	33°C	37.8°C
	0	0.68	0.79	1.20
	4.14	0.79	0.92	1.33
	5.20	1.13	1.45	2.12
	6.74	1.35	1.84	2.92

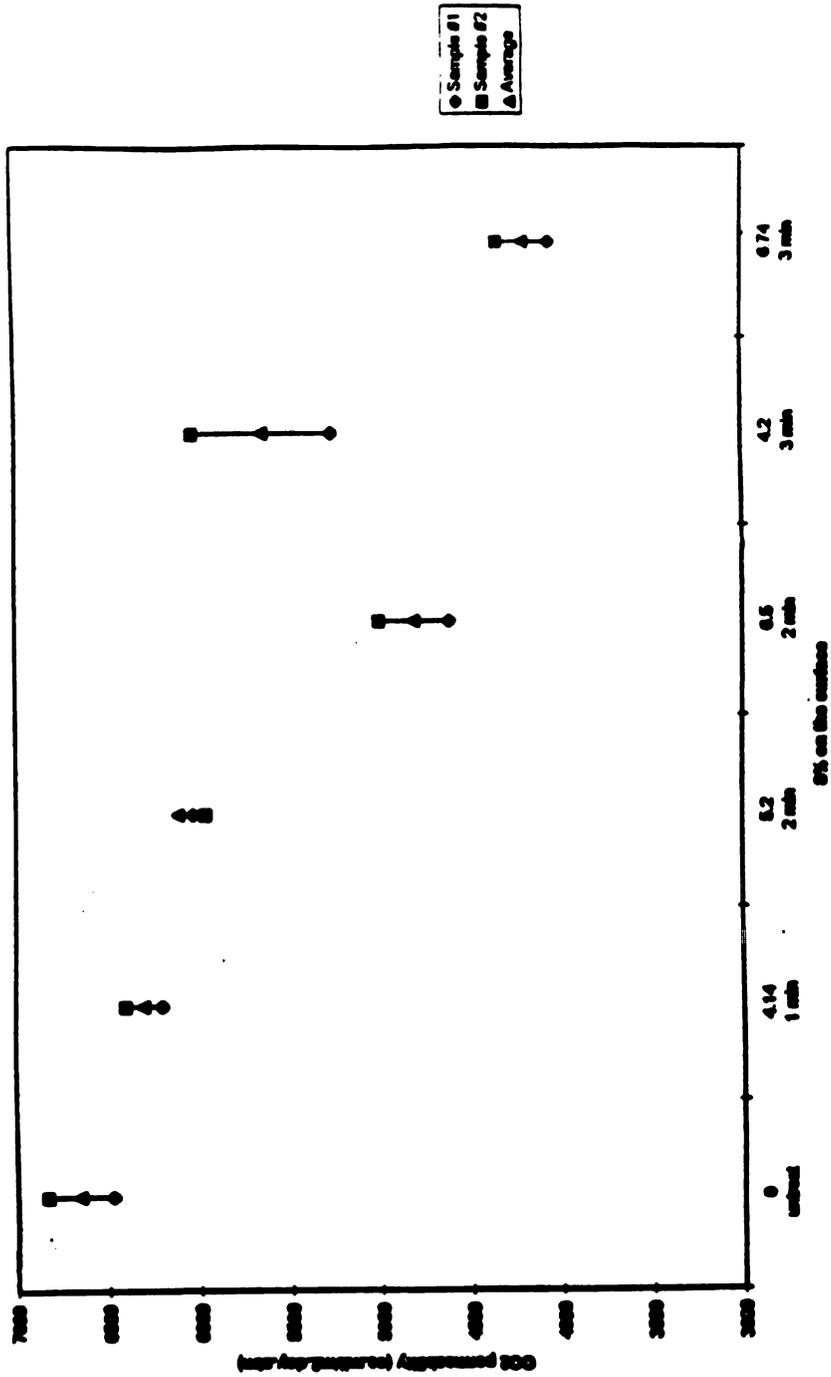


Figure 6.14: CO₂ permeability of the sulfonated PP at 25°C with 0%RH (NH₄⁺)

EXPERIMENT ERROR

Sulfonation

1. Film Contamination

Although the films were cleaned before sulfonating, some contamination can not be visually seen. It impacted to sulfonate films uniformly.

2. Stability of Oleum

This factor is very important. If the dissolved SO_3 level is reduced, it would result in a deviation in SO_3 vapor concentration generated. In the study, the oleum concentration used was found to be weaker after each run. It could not generate a consistent SO_3 concentration at each time. The reactor temperature was therefore raised to obtain the required SO_3 concentration or waiting 4 hours more until dissolved SO_3 level recover.

3. Batch Process

Since the sulfonation procedure used 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 which result in variation in permeation study.

4. Moisture

Moisture present in the system can react with SO_3 to form sulfuric acid and the SO_3 concentration will be reduced due to above reaction. Although a vacuum pump was used to withdraw the moisture from the sulfonation chamber, prior to the sulfonation reaction, the levels of moisture present in the system of each batch is not certain.

Permeation

1. Film Samples

The uniformity of sulfonation of the film was variety.

2. Instrument

The Mocon Ox-Tran 100 and MoCon Permatran CIV were calibrated with a standard material (PET), 1470 polyester film from the US department of commerce, National Institute of Standard and Technology. The Permatran W used to measure the water vapor permeability was calibrated with 5 mil standard material and 1 mil standard material (PET). The sensor Hydrodynamics from New Part Scientific Inc., was used to measure relative humidity during oxygen permeability tests. Each run with a sensitivity error is 2-4%

3. Temperature

The temperature was controlled within $\pm 1^\circ\text{C}$.

4. Gas Flow Regulator

The flow regulators used to generate an identical flow rate during the test. The fluctuation of gas flow is $\pm 5\%$

SUMMARY AND CONCLUSIONS

1. Mild surface sulfonation was found to be very effective in modifying the barrier properties on the PP films. Sulfonation was found to reduce the permeability of oxygen, CO₂ at 0% RH as compared to the untreated PP film.
2. Improvement of the barrier properties on the PP film was attributed to the presence of SO₃⁻ at the film surface. While the sulfonation time increased, the SO₃ diffused into the PP film and reacted with PP beneath of the surface of the PP films. The more the sulfonation time, the deepest the sulfonated PP layer. The permeability and diffusion coefficient of sulfonated layer of the PP films were dramatically decreased when increased the sulfonation time.
3. Sulfonated PP films are moisture sensitive. Barrier properties of sulfonated polymers are effected by water activity. At high relative humidity, the gas barrier is similar to the untreated PP films. The water vapor permeability was higher than untreated PP film.
4. Na⁺ neutralizing counterions exchanged with NH₄⁺ showed that the diffusion coefficient reduced but the permeability of oxygen increased.



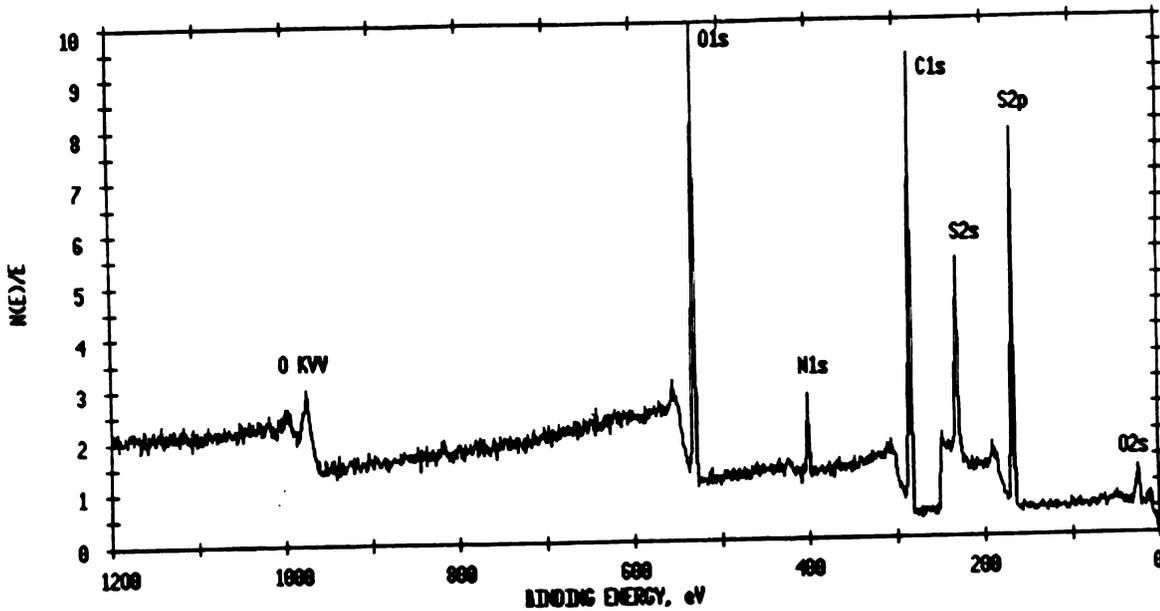
APPENDICES

APPENDICES

Appendix A

ESCA Analysis

ESCA 3/4/94 ANGLE= 65 deg ACQ TIME=4.89 min
 FILE: PP161 Sulf PP / NH4 - 4
 SCAN 1: SCALE FACTOR= 1.422 k c/s. OFFSET= 0.013 k c/s PASS ENERGY= 89.450 eV
 SCAN 2: SCALE FACTOR= 0.355 k c/s. OFFSET= 0.003 k c/s Al 600 M



Mode Height Baseline Linear New Element Name
 Regions C1 O1 N1

PP156 3 min Sulf PP / NH4+ Monochromated
 Large Area Omni-Focus

Element	Area (cts-eV/s)	Sensitivity Factor	Concentration (%)
C1s	30589	0.296	65.42
O1s	25698	0.711	22.88
N1s	3698	0.477	4.91
S2p	6109	0.570	6.79



Appendix B

O₂ Diffusion Coefficient Calculation Computer Model

```

5  REM THIS PROGRAM CALCULATES THE DIFFUSION COEFFICIENT FROM PERMEABILITY
6  REM CONTINUOUS FLOW EXPERIMENTS.
7  REM PROGRAM WRITTEN BY RUBEN J. HERNANDEZ. JAN/1988. MODIFIED BY JING YI ZHU
8  REM      ON 4-10-93
10 DIM V(50), F(50), T(50), X(50), DF(50)
30 REM THE UNITS OF TIME USED WILL DETERMINE THE UNITS IN THE DIFF. COEFF.
32 PRINT "ENTER RELATIVE HUMIDITY IN PERCENT"
33 INPUT HUM
35 PRINT "ENTER THE RUN IDENTIFICATION NUMBER"
36 REM
37 INPUT SUN
38 PRINT "ENTER THE TEMPERATURE AT STEADY STATE "
39 INPUT W
40 PRINT "ENTER THE NUMBER OF DATA POINTS"
50 INPUT D
60 PRINT "ENTER THE MILLIVOLUME V AND TIME T STARTING FROM ZERO"
70 FOR I=1 TO D
80 PRINT "ENTER V"
90 INPUT V(I)
100 PRINT "ENTER T"
110 INPUT T(I)
120 NEXT I
160 PRINT "ENTER YOUR GUESS FOR X"
170 INPUT GUESS
180 PRINT "ENTER INFINITE VALUE FOR V"
190 INPUT VI
191 PRINT "ENTER THE AREA RADIO"
192 INPUT AR
193 PRINT "ENTER THE PARTIAL PRESSURE IN ATM"
194 INPUT P
195 PRINT "ENTER THE THICKNESS OF THE FILM IN MIL"
196 INPUT L
198 F1=VI*10
200 FOR I=1 TO D
205 DF(I)=V(I)/VI
210 A=.44313*V(I)/VI
220 X=GUESS
230 FOR J=1 TO 7
240 B=SQR(X)
250 C=EXP(-X)
260 U=1/B
270 H=(.5*U-B)*C
280 E=(B*C)-A
290 X=X-(E/H)
300 NEXT J
310 X(I)=X
320 GUESS=X
330 NEXT I
380 REM LINEAR REGRESSION

```

```

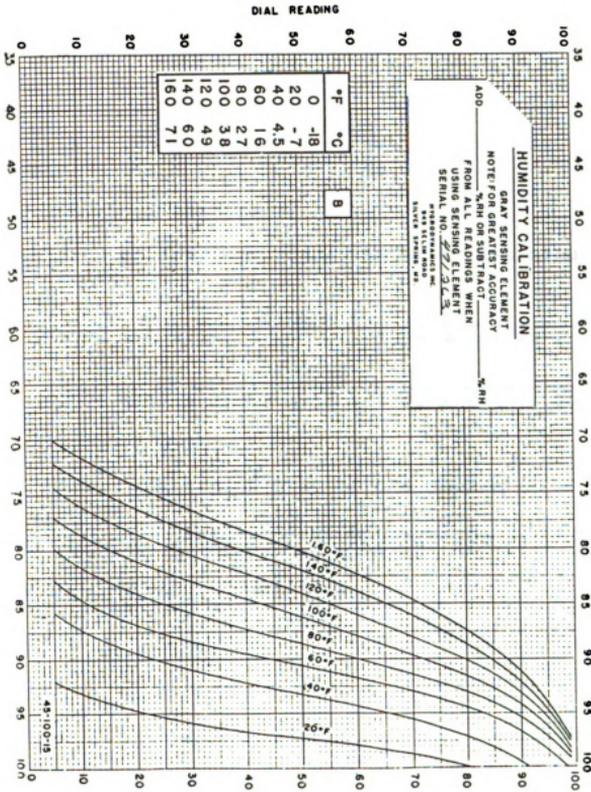
390 ST=0
400 SX=0
410 SXT=0
420 STSQ=0
430 SXSQ=0
440 FOR I=1 TO D
445 X(I)=11/X(I)
450 ST=ST+T(I)
460 SX=SX+X(I)
470 SXT=SXT+(X(I)*T(I))
480 SXSQ=SXSQ+(X(I)*X(I))
490 STSQ=STSQ+(T(I)*T(I))
500 NEXT I
510 SLOPE=(ST*SX-D*SXT)/(ST*ST-D*STSQ)
520 DUM1=(D*SXT)-(SX*ST)
530 DUM2=(D*STT)-(SX*ST)
530 DUM2=(D*STSQ)-(ST*ST)
540 DUM3=(D*SXSQ)-(SX*SX)
550 DUM4=SQR(DUM2*DUM3)
560 R=DUM1/DUM4
562 LPRINT "RUN NUMBER: " SUN
563 PRINT
564 LPRINT "TIME (MIN) ", " VOLT ", " X ", "FLOW PERCENT"
570 FOR I=1 TO D
600 LPRINT T(I),V(I),X(I),DF(I)
610 NEXT I
620 PRINT
630 PRINT
635 DIFF=L*L*.00254*.00254*SLOPE/4/60
636 LPRINT "DIFFUSION COEFF IN cm2/sec, =" DIFF
637 LPRINT
638 LPRINT "THE PERMEABILITY COEFF IN cm3.mil/m2.day.atm="F1*L*AR/P
639 LPRINT
640 LPRINT "THE SOLUBILITY IN cc O2/cc polymer = "2.94E-12*F1*L*AR/P/DIFF
642 LPRINT
645 LPRINT "THE CORRELATION COEFF. =" R
646 LPRINT
647 LPRINT "TEMPERATURE IN C =" W
648 LPRINT "WATER ACTIVITY aw =" HUM/100
650 END
OK

```



Appendix C

Humidity Calibration Curve of Sensor :45-100-15B





Appendix D

Data of sulfonation PP analysis from ESCA, K. Wangwiwatsilp (1993) and J. Tardiff (1993).

Sample	%S gram of sample surface (ESCA)	% S gram of sample (K. Wangwiwatsilp)	% total Weight gain gram of sample (J. Tardiff)
0 min	0		
1 min	10.0	.062	0.098
2 min*	12.3	0.15	1.965
3 min	15.1	0.24	6.845

* Calculation Examples:

%S gram of sample surface (ESCA) at 2-a minute sulfonation from Table 6.1

$$\begin{aligned}
 & \frac{5.20 \times S}{61.76 \times C + 25.09 \times O + 3.40 \times N + 5.20 \times S} \times 100 \% \\
 = & \frac{5.20 \times 32}{61.76 \times 12 + 25.09 \times 16 + 3.40 \times 14 + 5.20 \times 32} \times 100 \% \\
 = & 12.3 \% \text{ (g/g)}
 \end{aligned}$$

% total weight gain gram of the sample :

$$\begin{aligned}
 & \frac{\text{Weight Gain}}{\text{Weight of untreat PP} + \text{Weight Gain}} \times 100\% \\
 = & \frac{0.001}{0.0499 + 0.001} \times 100\% \\
 = & 1.96 \% \text{ (g/g)}
 \end{aligned}$$

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BIBLIOGRAPHY

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