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THE EFFECT OF NEUTRALIZING CATIONS ON THE BARRIER CHARACTERISTICS OF A SURFACE SULFONATED POLYSTYRENE FILM

By

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ABSTRACT

THE EFFECT OF NEUTRALIZING CATIONS ON THE BARRIER CHARACTERISTICS OF A SURFACE SULFONATED POLYSTYRENE FILM

By

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The effect of the following cations; NH_4^+, Li^+, Na^+, K^+, Mg^{++}, Ca^{++} and Ba^{++}, on the barrier properties of a surface sulfonated polystyrene film was investigated.

The polystyrene film (4 mil) was sulfonated to a level of approximately 0.8 μg S/cm², with a depth of sulfonation of approximately 50 Å. Based on ESCA, it was estimated that the film contained 1 SO_3^- group per 2¼ monomer repeat units.

Permeability of limonene vapor (a=0.6) through both a control and the ammonium stabilized sulfonated polystyrene film exhibited anomalous behavior, which was attributed to the solubility of limonene in the polymer.

The permeability of oxygen and water vapor through the respective cation stabilized sulfonated polystyrene films showed no correlation between the cation valance, atomic radii, or atomic number, and the diffusion coefficient and permeance. At the level of surface sulfonation of the test film, the barrier properties were found to be equivalent to an unmodified polystyrene film.

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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 is chemically modified and is inert to the attack of most organic compounds (Mehta and Bush, 1988). Polyethylene can also be readily sulfonated by treatment with gaseous SO_3, with fuming sulfuric acid, or with SO_3 in chlorinated hydrocarbons to provide useful industrial materials (Ihata, 1988a).

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 75-200 $\mu g\ SO_3/cm^2$ surface area. Further, the sulfonation process was readily adapted to both post-mold (Walles, 1973, 1971) and in-mold sulfonation (Walles, USP applied). Sulfonation thus offers a new approach to chemically induce specific barrier properties in polymers, independent of their chemical composition and molecular structure through surface modification.

Kinetic studies showed that sulfonation was 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. In SO_3 gas sulfonation, the SO_3 gas is able to penetrate below the surface resulting in up to two-thirds of the sulfonic acid groups, $C-SO_3H$, not being neutralizable by aqueous NaOH, while NH_3 gas can diffuse, react and neutralize all acid groups (Walles, 1989).

The oxygen barrier properties of sulfonated polyethylene (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 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 70 μg SO_3/cm^2 surface area, which for a 25 μm film equals about 1 % bulk sulfur.

Data on the permeation of water vapor, oxygen, and low molecular weight organic penetrants through a sulfonated polystyrene (PS) film have not been presented. This study, therefore, focuses specifically on determining the barrier properties of a sulfonated polystyrene, and the relationship of the films transport characteristics to the nature of the neutralizing cation.

The primary objectives of the proposed study include:

1) Characterization of the sulfonated polystyrene film to provide an understanding of the spatial and depth distribution of the sulfur groups.
2) Determination of the transmission rates of oxygen and water vapor through sulfonated polystyrene film as a function of the neutralizing cation, to include: NH_4^+, Li^+, Na^+, K^+, Ca^{++}, Mg^{++} and Ba^{++}, under similar conditions of test.
3) Determination of the effect of the nature of the neutralizing cation on the mechanical properties of the surface modified polystyrene.

LITERATURE REVIEW

Sulfonation Process

SO_3 CHEMISTRY :

The chemistry of sulfur trioxide (SO_3) is complicated, as it exists in both the monomeric and several polymeric forms. The SO_3 molecule is planar, triangular, and symmetrical, and is a resonance hybrid in which the oxygen atoms are equivalent. The exact distribution of electrons between sulfur and oxygen is uncertain. Figure 1 (Gilbert, 1965) represents possible canonical forms.

Figure 1. Possible Canonical Forms of Sulfur Trioxide (Gilbert, 1965)

When undergoing chemical reactions sulfur trioxide exhibits a marked tendency toward increasing the number of electrons in the outer shell from eight to ten, or even to twelve, indicating a strongly electron-deficient sulfur atom. At the same time, the oxygen atoms are electron-rich. The SO3 molecule may thus be described as a "Lewis acid on one side (i.e. the sulfur), and a Lewis base on the other (oxygen)", in other words; it is amphoteric (Gilbert, 1965). These characteristics account for the ease with which sulfur trioxide polymerizes, and its activity as a sulfonating agent, with the acidic sulfur atom attacking electron-rich (basic) systems, and the basic oxygen atoms accepting acidic protons.

Sulfur trioxide vapor is monomeric, as are solutions of SO_3 in SO_2, CCl_4, SO_2Cl_2, and other solvents. Whereas in more concentrated solutions, there is an increasing quantity of the trimeric form, as represented in Figure 2 (Gilbert, 1965).

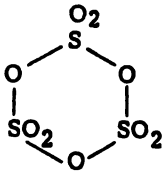


Figure 2. Trimeric Form of Sulfur Trioxide (Gilbert, 1965)

The freshly distilled liquid will revert to solid polymers of various possible chain lengths and degrees of cross-linking if exposed to moisture. The polymeric form of SO_3 may be represented as illustrated by Figure 3 (Gilbert, 1965).

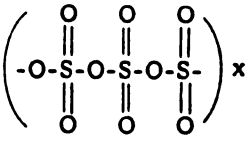


Figure 3. Polymeric Form of Sulfur Trioxide (Gilbert, 1965)

SULFONATING AGENTS :

8A comparison of sulfuric acid and sulfur trioxide as sulfonating agents is presented in Table 1.

Table 1. Sulfuric Acid and SO_3 as Sulfonating Agents (Gilbert, 1965).

FACTOR COMPARED	H_2SO_4	SO_3
reaction rate	slow	instantaneous
heat input	requires heat for completion	strongly exothermic throughout
extent of reaction	partial	complete
side reactions	minor	sometimes extensive
viscosity of reaction mixture	low	sometimes high
boiling point	290-317°C	44.5°C
solubility in halogenated solvents	very low	misable

The reported disadvantages of SO_3, namely it's high heat of reaction with consequent decomposition or side reactions, and high viscosity, can most often be overcome by choice of reaction conditions, or the use of a solvent.

REACTION MECHANISM OF SULFONATION :

The sulfonation of many aromatic compounds involves the following steps; (Morrison and Boyd, 1983)

$2H_2SO_4 \rightleftarrows H_3O^+ + HSO_4^- + SO_3$ (1)

$SO_3 + C_6H_6 \rightleftarrows \oplus C_6H_5\text{-}H\text{-}SO_3^-$ slow (2)

$\oplus C_6H_5\text{-}H\text{-}SO_3^- + HSO_4^- \rightleftarrows C_6H_5SO_3^- + H_2SO_4$ fast (3)

$C_6H_5SO_3^- + H_3O^+ \rightleftarrows C_6H_5SO_3H + H_2O$ equilibrium far to the left (4)

The sulfonation of polystyrene (PS) will follow the above pattern, as the repeating unit of PS contains a phenyl-group (mono-substituted benzene).

In step (2) the electrophilic reagent, SO_3, is attached to the benzene ring to form the intermediate carbocation. In step (3) a hydrogen ion is lost to form the resonance-stabilized substitution product, as represented in Figure 4. As shown, the anion of benzene sulfonic acid, being a strong acid, is highly dissociated (step 4).

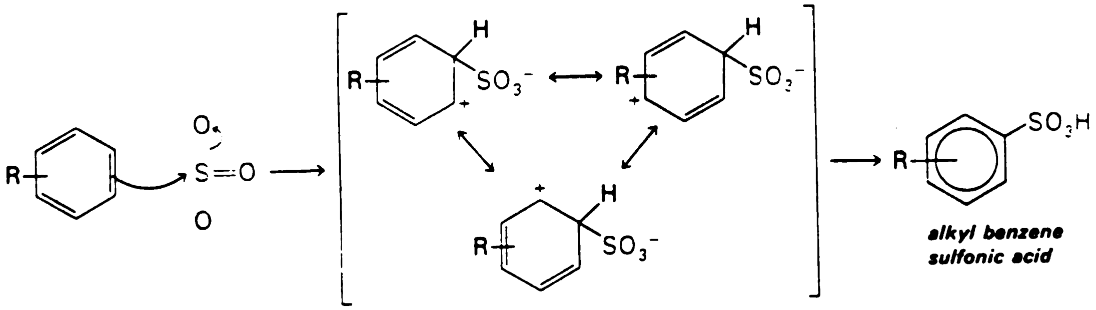


Figure 4. Resonance Configurations Resulting from Reaction of Benzene with Sulfur Trioxide (Moore and Barton, 1978)

Sulfur trioxide is thus a powerful electrophile, capable of reacting with the aromatic π electron system to form a neutral, but dipolar intermediate. Transfer of a proton from the ring to the SO_3^- group provides re-aromatization of the ring, and forms benzene sulfonic acid (Moore and Barton, 1978).

SULFONATION IN DILUTE SOLUTION :

Sulfonation is a method of preparing new polymers through chemical modification of existing ones. To establish the mechanism, kinetics, and steric aspects of the process, sulfonation of dilute solutions of polynorbornene (PN) in CCl_4 was carried out using SO_3-triethyl phosphate complexes of various stoichiometries dissolved in dichloroethane (DCE) or trifluoro-trichloroethane (TTE) (Planche et al., 1988). The use of unassociated SO_3 was shown to lead to extensive degradation. Therefore, SO_3-triethyl phosphate (TEP) was used to allow for easy control of the reagent strength by regulating the SO_3/TEP ratio. A SO_3/TEP ratio of 1/1 was utilized for the sulfonating solution. The reation was allowed to progress for 15 to 300 minutes, whereafter it was stopped by addition of methanol. The acid polymer was neutralized by adding a concentrated solution of NaOH in methanol. The reaction mechanism appeared to be one of electrophilic substitution on the double bond, yielding high sulfonation ratios (ca. 85 %). The unstrained cyclopentane ring in the PN structure remained untouched, acting as a screen between two successive double bonds which may be considered independent and of equal reactivity, whatever their environment. Kinetic studies revealed the initial reaction to be of first order in both reactants (SO_3 and PN). At room temperature the reaction quickly became diffusion-controlled due to precipitation of the partially sulfonated polymer. The initial rate was almost independent of the isomeric structure (cis or trans) of PN. Furthermore, the molecular weight and solution viscosities had no influence on reaction rate and final sulfonation ratio. The absence of an effect of molecular weight may be due to similar chain flexibility of the polymers, resulting in similar glass transition temperatures. Moreover, a large part of the reaction is carried out in heterogeneous medium, where the role of diffusion is predominant, mainly depending on the particle size and porosity. The final sulfonation ratio obtained was strongly dependent upon the concentration of SO_3 and seemed to be controlled by the conditions of diffusion inside the precipitated solid (Planche et al., 1988).

REACTION OF POLYETHYLENE FILMS WITH SO_3 :

Surface sulfonation of polyethylene (PE) with gaseous SO_3 was reported by Ihata (1988a) to lead to the formation of sulfonic acids with highly conjugated C=C unsaturated bonds. HDPE was sulfonated with gaseous SO_3 and with SO_3 in ethylene dichloride, whereafter it was neutralized with aqueous NaOH. The sulfonated PE films were characterized by spectrophotometric analyses including infrared, resonance Raman, and UV-VIS spectroscopy. The reaction of PE film with SO_3 was suggested to be initiated by the abstraction of a hydrogen atom by SO_3 to give a PE 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 spectrophotometric analyses indicated an increase in the latter reaction as the sulfonation reaction proceeded (Ihata, 1988a).

PHOTOREACTION OF POLYENESULFONIC ACIDS :

Ihata (1988b) reported conjugated polyenesulfonic acids to be sensitive to UV and visible light. The photoreaction induced desulfonation by cleavage of C-S bonds to eliminate sulfonic acid groups.

EFFECT OF SULFONATION UPON MECHANICAL PROPERTIES :

The exposure of linear PE to a sulfuric acid atmosphere was reported by Balta Calleja (1984) to substantially improve the mechanical properties of the thin sulfonated surface of the polymer. The surface microhardness of polyethylene increased with sulfonation time, yielding hardness values which were in the vicinity of some metals. Furthermore, Fonseca et al. (1985) reported an increase in suface conductivity, as well as the critical surface tension of linear PE exposed to fuming sulfuric acid at room temperature. This improvement of surface properties was attributed by the authors to the insertion of polar SO_3 groups at the polyethylene surface.

EFFECT OF SULFONATION UPON BARRIER PROPERTIES :

Walles (1989) has reported the treatment of the inside of HDPE automotive gas tanks with about 20 % SO_3 in air, followed by air purging and neutralization with NH_3 gas, to result in an excellent gasoline barrier, at a surface concentration of about 75-200 μg SO_3/cm^2. This barrier layer was found to have $-C-SO_3^-NH_4^+$ groups to a depth of 20-25 μm. The barrier characteristics obtained by applying the sulfonation process were, however, found to be strongly dependent upon the nature of the counterion. For example, the NH_4^+ ion may be replaced by various metal ions from water solution via ion exchange. Best barrier results were obtained with Li, Na, Cu, Mg, Sr, V, Mn, Co, and Ni. Na^+ was shown to be 6 times as effective to create a barrier to O_2 diffusion, as was NH_4^+. Li^+ was 12 times better than $NH4^+$, all at a surface concentration of about 70 μg SO_3/cm^2, of a 25 μm thick polyethylene gas tank.

Highly reflective metal layers with a metallic-type total barrier were also obtained when using copper and silver as counterions. This ultra thin, very regular, super barrier metallic layer was created applying two different methods. The first being combining sulfonation with reductive metallization. Here a barrier layer was created containing polymer molecules and free metal atoms. The second method was a very light sulfonation to which tin ions were bonded, followed by a spray of water-based silver-ammonia complex freshly mixed with a reducing agent. The tin catalysed deposition of silver resulting in a very dense metallic layer. For very demanding applications the sulfo-metallization may be repeated (Walles, 1989).

Polystyrene Characteristics

The polymer polystyrene (PS) is a high molecular weight thermoplastic with the repeating unit; $(-CH_2-CHC_6H_5-)x$. Polystyrene is crystal-clear, hard, rigid, and free of odor and taste. Moldings, extrusions, and films of very low unit cost, resulting from ease of fabrication, thermal stability, low specific gravity, and low cost, are obtainable. Furthermore PS materials are useful as low-cost insulating materials due to excellent thermal and electrical properties.

Commercial polystyrenes are normally rather pure polymers. PS containing a negligible amount of monomer and other solvents are useful in the packaging of food.

A wide variety of speciality polystyrenes are also available. While these polymers are essentially pure PS, their molecular structures and/or additives are so adjusted as to make them customized to special applications (Kirk-Othmer, 1969).

MECHANICAL BEHAVIOR OF POLYSTYRENE :

Tensile testing of polystyrene may be conducted in accordance with ASTM D882-83 (1987) "Test Methods for Tensile Properties of Thin Plastic Sheeting". The stress-strain data, namely being; tensile strength and elongation at yield and rupture, and modulus, are usually reported for room-temperature measurements.

The determined strength of a material is dependent upon the following variables :

(1) the rate of extension; With increasing rate of extension, the tensile strength and modulus increase, whereas the elongation at break tends to decrease.

(2) the temperature; Increased temperature lowers the strength of PS, whereas elongation and modulus are only slightly affected.

(3) polymer orientation; Tensile strengths as high as 18,000 psi have been reported for PS films and fibers. PS tensile strengths below 2,000 psi have been obtained in the direction perpendicular to the flow. Thus, the orientation of the polymer in a fabricated specimen can significantly alter the stress-strain data, as compared with the data obtained on an isotropic specimen (i.e. compression molded).

Impact strength may be determined using a notched impact test or various dart-drop tests. Polystyrene is a brittle polymer under normal-use conditions exhibiting very low impact strength (Kirk-Othmer, 1969).

Typical mechanical property values of polystyrene are summarized in Table 2.

Table 2. Mechanical-Property Guide for Polystyrene (Plastics Technol.)

PROPERTY	PS
specific gravity	1.05
tensile yield, psi	6,100
elongation, rupture, %	1.8
modulus, psi	460,000
impact strength, notched Izod, ft-lb/in	0.4
dart-drop impact strength	very low
relative ease of fabrication	excellent

SOLUBILITY OF POLYSTYRENE :

The solubility of a nonpolar polymer, such as polystyrene, is determined largely, but not entirely, by the absolute value of the difference between the solubility parameter of the polymer, and that of the solvent. It has been observed that with nonpolar solvents, the difference beween the solubility parameters must be less than 0.9. Whereas, with many polar solvents the solubility parameter difference may be larger, and still a certain degree of solubility is achieved. The swelling of slightly cross-linked polystyrene in a variety of solvents increases in general, as the difference in solubility parameter value decreases. As polystyrene is a high molecular weight glassy polymer, it does not dissolve easily in low-molecular-weight solvents (Ueberreiter, 1968). The gross solubility of polystyrene in solvents of differing solubility parameter is given in Table 3.

Table 3. Solubility of Polystyrene in Various Solvents
(Suh, 1967)

POLYMER	SOLUBILITY PARAMETER $(cal/cm^3)^{1/2}$	g POLYSTYRENE/ 100 g SOLVENT (GROSS SOLUBILITY)
polystyrene	9.1	
SOLVENT		
n-heptane	7.45	0.016
ethyl acetate	9.03	>90
benzene	9.15	>90
acetone	9.81	0.30
ethyl alcohol	12.80	0.00

CRAZING AND STRESS CRACKING IN POLYSTYRENE :

Internal crazes in polystyrene may start at flaws, or in regions where polymer chains are aligned normal to the applied stress, and ultimately stop instead of becoming catastrophic cracks as they encounter other regions with polymer chains aligned parallel to the stress (Maxwell, 1949). At a given strain level, the crazes will grow slowly with time. However, if the strain level is increased, new crazes will appear and start to grow.

The application of nonsolvents/solvents for polystyrene will markedly interfere with the crazing process. Nonsolvents can significantly lower the critical stress and the critical crack elongation needed to cause crazing (Raetz, 1970). Whereas good solvents can lead to immediate catastrophic failure when applied to a mildly stressed polystyrene. The critical stress value increases as the difference between the solubility parameters of the polymer and solvent is increased. Also influencing the critical stress value are surface tension, and molecular size and shape of the solvent. The rate of craze formation may be at least partially diffusion-controlled. Thus, the molecular size of the stress-cracking reagent can affect craze initiation and growth (Hopfenberg, a).

Permeation Theory

Permeability may be defined as the transmission of gases or vapors through a resisting material which has no macroscopic pores (Paine, 1983). The transport of a gas or vapor through polymeric films commonly utilized for packaging purposes typically involves the activated diffusion process. This process consists of three steps; (1) absorption of the permeating species, with gas or vapor dissolving into the polymer matrix at the high penetrant concentration surface; (2) diffusion through the polymer wall along a concentration gradient; and (3) desorption from the surface at the lower concentration (Stannett and Yasuda, 1965).

The diffusion flux (F) of a permeant in a polymer can be defined as the amount passing through a surface of unit area normal to the direction of flow during unit time, independent of the aggregation of polymer.

That is:

$$F = Q / At \tag{5}$$

Where Q is the total amount of permeant passing through area A during time t. Fick's first law of diffusion expresses the existing proportionality of the transfer of a diffusant through a unit area to the negative gradient of concentration at any point in the polymer (Crank and Park, 1968).

Given by:

$$F = - D (dC/dx) \tag{6}$$

Where D is the diffusion coefficient with units of $(\text{length})^2$ time^{-1}, x is the length in the direction of diffusion, and C is the concentration of the permeant in the polymer. As the diffusion proceeds, Fick's second law of diffusion describes the non-steady state (Crank, 1975).

$$dC/dt = d/dx (D * dC/dx) \tag{7}$$

Solutions of Equation (7) depend upon the initial and boundary conditions, as well as on whether or not D can be considered a function of penetrant concentration, and/or time.

Equation (5) can be integrated, assuming D is independent of permeant concentration, to give:

$$F = D (C_1 - C_2) / L \tag{8}$$

Where C_1 and C_2 are the steady state concentration at the two surfaces of the film, and L is the film thickness.

For experimental and predictive purposes, the concentration of the permeant at the polymer surface may conveniently be related to the concentration of permeant in the surrounding gas phase. For gases and vapors, the permeant concentration is proportional to the partial pressure of the permeant, through the ideal gas law equation (Henry's Law). The concentration of the permeant in the polymer, C, can thus be expressed in terms of the solubility (Sp) and the partial pressure, as:

$$C = (Sp)(\Delta p) \qquad (9)$$

Where the solubility is a function of temperature, and may be a function of the partial pressure or the concentration. Assuming Henry's Law is applicable, it follows:

$$C = S\ (\Delta p) \qquad (10)$$

Where S is the Henry's Law solubility coefficient, which is independent of Δp and C (Crank, 1975). Substitution in Equation (8) yields:

$$F = D{*}S\ (p_1 - p_2)\ /\ L \qquad (11)$$

Where p_1 and p_2 are the permeant pressures at the two surfaces of the film, and the product D*S defines the permeability coefficient (P) (Barrer, 1939), by the relationship;

$$D * S = P \tag{12}$$

When both D and S are independent of penetrant concentration, P is a constant at any given temperature. However, where considerable interaction between the polymer and the permeant occurs, P is no longer constant but will vary with C and Δp (Zobel, 1982; Hernandez et al., 1986 and references cited therein). For the specific case, where the diffusion coefficient is time-dependent, the transmission process will be anomalous, and is said to be non-Fickian (Fujita, 1961; Meares, 1965; Crank and Park, 1968).

Diffusion in Amorphous Polystyrene

Various regions of penetrant transport in high polymers exist, which may be illustrated by a temperature-penetrant concentration (or penetrant activity) diagram (Alfrey, 1965 and Hopfenberg, b). The diagram delineates the proposed regions of diffusional transport in terms of the two controllable variables; namely temperature and penetrant concentration, as represented by Figure 5.

The feature distinguishing the three proposed diffusion regions is the ratio of the characteristic time of diffusion and some characteristic time for the molecular rearrangement and relaxation process in the polymer-solvent system.

Zone I; here the combination of low solvent activity and a temperature below the glass transition temperature (Tg) results in a polymer matrix essentially unaffected by the presence of the penetrant during the entire diffusion process. The lack of interaction between the polymer and penetrant is due to the frozen state of the polymer under these conditions. Above Tg the penetrant molecules must migrate through a discontinuous network of microvoids which is constantly being altered by the random oscillations of chain segments. This Fickian-type migration is described by Equation (6). The diffusion process can however be assumed to be concentration-independent and can be related to the temperature only by an Arrhenius-type expression;

$$D = Do \exp(-E/RT) \qquad (13)$$

where for a given polymer, the pre-exponential factor, Do, and the activation energy for diffusion, E, are functions only of the molecular properties of the penetrant. Table 4 summarizes the diffusion of relatively small inert molecules in polystyrene in zone I.

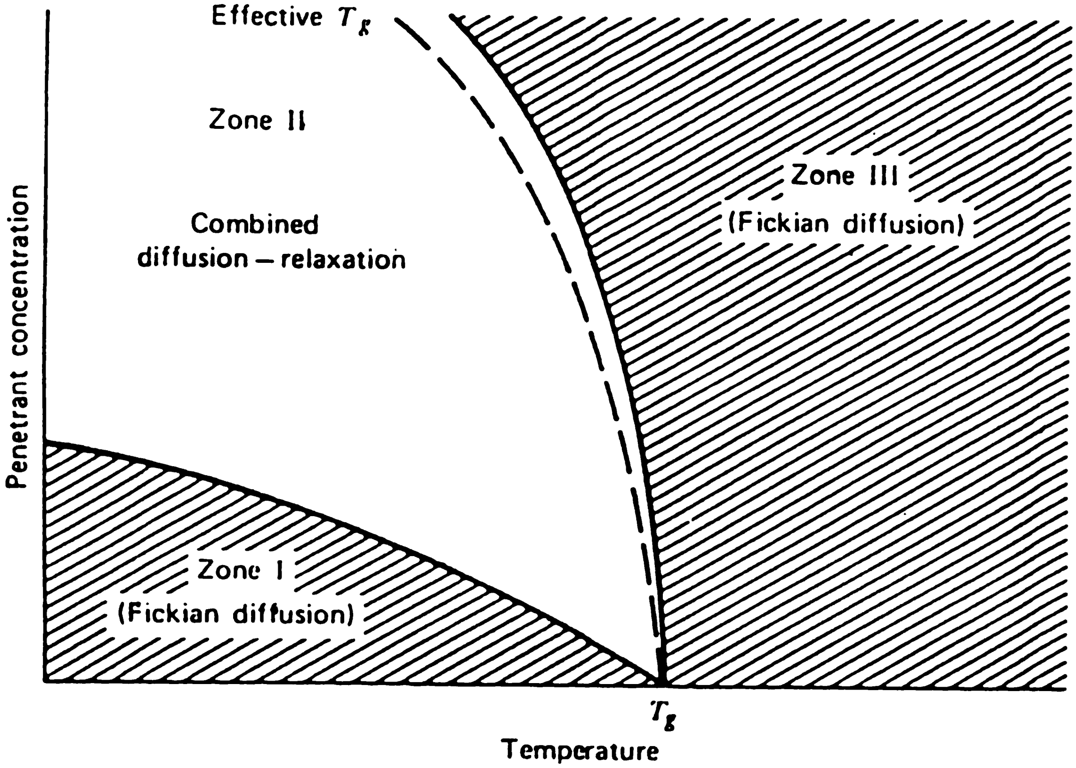


Figure 5. Temperature-Concentration Diagram for Penetrant-Polymer Diffusion (Alfrey, 1965)

Table 4. Diffusivity Data for Various Penetrants in Polystyrene ($T < Tg$)

Penetrant	Temp, Celsius	$D \times 10^6$, cm^2/sec	Do, cm^2/sec	E, kcal/g-m	Reference
water	25	0.035			Cutler, 1953
	25	0.21			Thomas, 1945
	35	0.022			Deeg, 1944
oxygen	25	0.11	0.125	8.3	Stannett,
carbon dioxide	25	0.058	0.128	8.7	1968
n-pentane	30	1.85×10^{-6}		5.6	Hopfenberg
	40	2.5×10^{-6}			
	45	2.9×10^{-6}			
	50	3.35×10^{-6}			

The inconsistencies between these diffusivity data may be due to difference in the structural characteristics of the polystyrene samples. Furthermore, contributing to the nonreproducibility of this type of measurement is the possibility of the presence of voids and/or cracks allowing for convective transport, thus complicating the transport process (Schulz, 1956). However, the data show that the diffusion rate decreases with increasing penetrant molecular size.

Another expression for mass transport through polymer films is in terms of permeability, which is the product of the diffusion coefficient and the penetrant solubility. Available permeability data for polystyrene in zone I are presented in Table 5.

Table 5. Permeabilities for Various Penetrants in Polystyrene in Zone I

PENETRANT	TEMPERATURE Celcius	PERMEABILITY x 10^9 cc*cm/ cm^2*s*cmHg	REFERANCE
oxygen	22	0.174	Davis, 1946
	23	0.174	Brown, 1959
	23	0.18	Dow
	25	0.21	Major, 1962
water	20	100	Muller, 1942
	25	83.5	Aiken, 1945
	32	84.0	
	38	83.0	
	25	97	Korvezee, 1947
	50	107	
	25	79.5	Thomas, 1945
	25	104	
	25	107	
	35	107	Cutler, 1953
	35	108	Simril, 1950
benzene	35	1060	Simril, 1950

The data presented are quite consistent considering that permeability measurements are relatively sensitive to imperfections in the film structure, such as cracks and pinholes, which may very likely occur in the thin films employed for permeation studies. The permeability observed for benzene is relatively large, possibly due to swelling of the polymer, and thus more indicative of steady-state transport in zone II (Simril, 1950).

Zone II; here the characteristic relaxation time of configurational change of polymer chains and the characteristic diffusion time are quite similar. Thus, the diffusion and the molecular relaxation processes are coupled phenomena, and cannot be regarded as individual and independent of each other. Under such conditions there is no certain relationship between penetrant concentration and the molecular spacing and orientation of polymer chains. Thus, the classical theory of diffusional transport is not applicable in zone II. Studies at moderate penetrant activities will yield anomalous sorption and permeation curves. The methylene chloride-polystyrene sorption curves of Park (1953) at 25°C exhibit a distinct sigmoid character and a pronounced thickness effect, both distinctive features of non-Fickian diffusion phenomena. Experiments at somewhat higher penetrant activities will yield case two transport, solvent crazing, and swelling fracture.

Zone III; a temperature above the glass-transition temperature of the polymer leads to high mobility of polymer segmental units and to a characteristic relaxation time, which is small compared to the characteristic diffusion time. The polymer molecules are assumed to instantaneously reach an equilibrium configuration consistent with the penetrant concentration at any point in the polymer, and the diffusion coefficient becomes purely concentration-dependent. The penetrants can thus interact with the polymer and change the state of same. The diffusion process can therefore be defined by Equation (7).

The amount of available diffusivity data is rather limited, as it is very difficult to perform sorption and permeation experiments at temperatures above the glass transition of polystyrene (Boyer, 1970).

MATERIALS AND METHODS

Film Samples

In this study, a surface sulfonated polystyrene film provided the base polymer structure. The film characteristics were varied by incorporating a series of neutralizing cations into the base structure.

Films :

A 4 mil polystyrene (PS) film, surface sulfonated to a level of 0.8 μg sulfur/cm^2 surface area which is represented as: $-C-SO_3^-$, provided the base structure. The film structures with the respective neutralizing cations incorporated are represented as follows:

a. $-C-SO_3^-NH_4^+$, Cation; ammonium

b. $-C-SO_3^-Li^+$, Cation; lithium

c. $-C-SO_3^-Na^+$, Cation; sodium

d. $-C-SO_3^-K^+$, Cation; potassium

e. $-C-SO_3^-Mg^{++}$, Cation; magnesium

f. $-C-SO_3^-Ca^{++}$, Cation; calcium

g. $-C-SO_3^-Ba^{++}$, Cation; barium

Sulfonation Process

The surface sulfonation process was performed on a solid phase sulfonator at Coalition Technologies, Ltd. (Birmingham, MI). The polystyrene film was exposed to 2 % SO_3 in air for less than 0.1 sec.

Surface Analysis

A surface analysis of the $-C-SO_3^-NH_4^+$ film structure by X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), was conducted on a Perkin-Elmer PHI 5400 system at the Composite Materials and Structures Center, M.S.U. The test specimen is irradiated with monoenergetic X-ray resulting in photoionization of atoms in the surface region, followed by emission of electrons. The photons can penetrate the solid sample to a depth of 1-10 μm, whereas the emitted electrons can escape only tens of Angstroms of solid. Therefore, the electrons detected originate within the tens of Angstroms of the top surface region and are thus representative of this region only.

An evaluation of the surface tension of both an unmodified and the various surface sulfonated polystyrene films was performed by Accu Dyne Test (Diversified Enterprises, East Wallingford, VT 05742). The wetability of the films was estimated utilizing water/glycerol solutions of differing surface tensions. The results are presented in Appendix D, Table D1.

Ion Exchange

MATERIALS:

1) Salts;

a. Lithium Chloride, GR, obtained from EM Science, (Cherry Hill, N.J.).

b. Sodium Chloride, Analytical Reagent, obtained from Mallinckrodt, Inc. (Paris, KY).

c. Potassium Chloride, A.C.S. Grade, obtained from Columbus Chemical Industries, Inc. (Columbus, WN).

d. Magnesium Chloride 6-Hydrate, Baker Analyzed Reagent, obtained from J.T. Baker Inc. (Phillipsburg, N.J.).

e. Calcium Chloride Dihydrate, Baker Analyzed Reagent, obtained from J.T. Baker Inc. (Phillipsburg, N.J.).

f. Barium Chloride Dihydrate, GR, obtained from EM Science, (Cherry Hill, N.J.).

2) Acid;

Hydrochloric Acid, 36.5-38.0 %, Baker Instra Analyzed Reagent for Trace Metal Analysis, obtained from J.T. Baker Inc. (Phillipsburg, N.J.).

3) Water;

Double-deionized water obtained from The Department of Food Science, (Michigan State University, East Lansing).

PROCEDURE:

The $C-SO_3^-NH_4^+$ structure film was immersed in 5 % solutions of the above mentioned salts for 1 hour to allow for cation exchange to take place. The films were then removed from the salt solutions and washed with double-deionized water to remove excessive salt solution from the surface of the film.

Confirmation of the cation exchange reaction was carried out as follows; 50 cm^2 samples of the above mentioned film structures were immersed in 100 ml of 5 % HCl for 1 hour, thus resulting in a proton exchange, leaving the former neutralizing cations in solution, and the film structure as $-C-SO_3^-H^+$. The solutions containing the respective neutralizing cations, and a sample of the 5 % HCl as reference were then submitted to The Animal Health Diagnostic Laboratory, Analytical Toxicology Section, Veterinary Clinical Center, (M.S.U.), for cation analysis. The cation analysis was performed on a Thermo Jarrell Ash Polyscan 61E, whose method of operation is based on Inductively Coupled Plasma Atomic Emission Spectroscopy.

Organic Vapor Permeability

MATERIALS:

1) Permeant

The permeant, limonene was used as the organic vapor. The selection is based on the ease of analysis and the known contribution of this compound to the aroma profile of food products.

(R)-(+)-limonene, 97%, was obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI).

2) Carrier Gas

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

PROCEDURE:

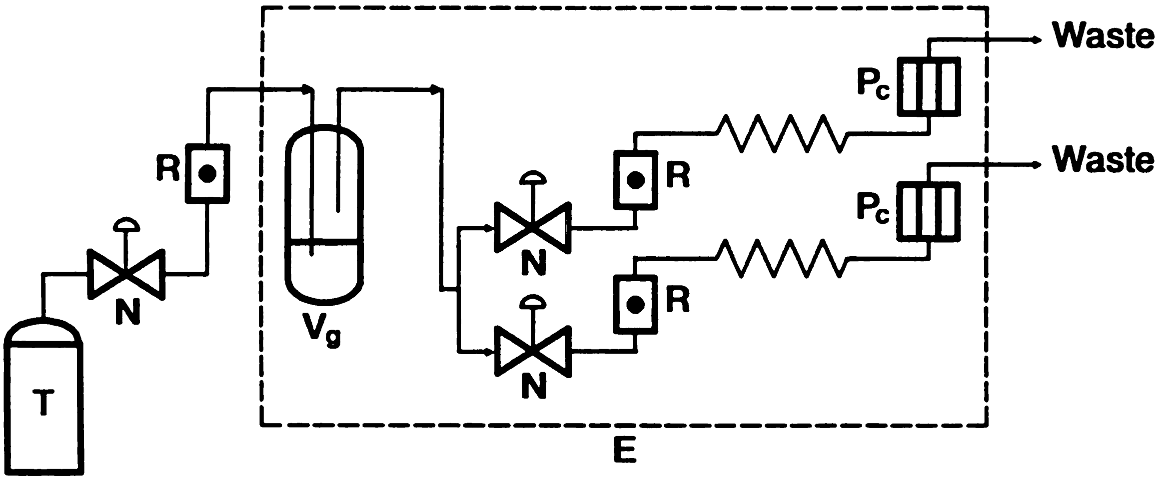
1) Permeability Measurements

The permeation test system, based on the quasi-isostatic method, was assembled and tested as part of this study. A schematic diagram of the permeation test apparatus is represented by Figure 6. It allows the collection of permeation data as a function of temperature and vapor concentration.

The permeability cell, constructed of aluminum, is composed of two cell chambers and a hollow center ring. The right and left cell chambers both have a volume of 50 cm^3, which is also the approximate volume of the center cavity. In operation, the test films, two to each permeation cell, are placed so as to effectively isolate the right and left cell chambers. Hermetic isolation of the chambers from each other, and from the atmosphere is achieved by the compression of overlapping Viton o-rings on the film specimens. Viton is a fluorocarbon elastomer resistant to attack and swelling by most organic vapors. The cell chambers and the center ring are equipped with an inlet and outlet valve and sampling port.

A constant concentration of permeant vapor is produced by bubbling nitrogen gas through the liquid permeant contained in a gas washing bottle. To obtain a lower vapor concentration, the permeant vapor stream is mixed with a stream of pure carrier gas (nitrogen). Flow meters were used to provide a continuous indication of the maintenance of a constant flow rate. Gas flows were regulated with NU PRO needle valves, Type B-25G.

When performing permeation runs, the films to be tested are mounted in the permeability cell and the cell assembled. A constant, low partial pressure of permeant vapor is then flowed through the center cell chamber at a flow rate of approximately 10 ml/min. This allows the permeability of two film specimens to be determined concurrently, under identical conditions, at a selected temperature and vapor concentration (Baner et al., 1986).



E = Environmental Oven

V_g = Organic Vapor

P_c = Permeability Cell

R = Rotameter

T = Nitrogen Tank

N = Needle Valve

Figure 6. Schematic of Permeation Test Apparatus

2) Operation

In the quasi-isostatic procedure, the increase in penetrant concentration in the lower concentration cell chambers is monitored by utilizing gas chromatography with flame ionization detection for analysis. At predetermined time intervals, a specific volume of headspace gas is removed from the right and left cell chambers with a gas-tight syringe and injected directly into the gas chromatograph. Throughout the run a constant pressure in the high concentration cell chamber is maintained by continually flowing the vapor stream through and discharging it at atmospheric pressure. In the low concentration cell chambers a constant, total pressure is maintained by replacing the volume of headspace gas removed for analysis with an equal volume of nitrogen.

The quantity of vapor permeated over time is then monitored until a steady-state rate of diffusion is reached.

The film specimens were stored at ambient conditions for a period of at least two weeks prior to being tested.

3) Gas Chromatographic Analysis

Analysis of permeant concentration was carried out by a gas chromatographic procedure. A Hewlett-Packard Model 5890 gas chromatograph equipped with flame ionization detection interfaced to a Hewlett-Packard Model 3392A integrator was employed for quantification. The gas chromatographic conditions were as follows;

Column:	60 meter; 0.25 mm I.D.; Fused silica capillary; Polar bonded stationary phase; Supelcowax 10 (Supelco Inc., Bellefonte, PA)
Carrier Gas:	Helium at 32.6 ml/min;
Temperature:	Injection temperature -- 80°C; Detector temperature -- 250°C; Oven temperature -- 150°C; Temperature program rate -- 4°C/min;

Retention time of limonene: 10.21 min;

A standard curve of detector response vs. absolute quantity injected was constructed from standard solutions of known concentration. Standard solutions were prepared by dissolution of known quantities of limonene in dichloromethane.

Solubility Experiments

MATERIALS:

Solvents;

a. (R)-(+)-limonene, 97%, obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI)

b. Ethyl acetate, 99.5+% A.C.S. Spectrophotometric Grade, obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI)

c. Acetone, ChromAR, HPLC, obtained from Mallinckrodt, Inc. (Paris, KY)

d. 1-Propanol (Normal), Certified, Obtained from Fisher Scientific (Fair Lawn, N.J.)

PROCEDURE:

1 in^2 samples of both the unmodified PS and the $-C-SO_3^-NH_4^+$ film structure were exposed to saturated vapor of the above mentioned solvents to enable observance of the degree of their solubility in the polymer. Saturated vapors were generated from the liquid solvents contained in glass jars stored at ambient conditions.The samples were weighed initially and then visually examined over a period of 4 days, and finally weighed again.

Oxygen Permeance

MATERIALS:

1) Permeant

Oxygen supplied in the form of compressed air (O_2 partial pressure equals 0.21 atm), obtained from AGA Gas, Inc. (Cleveland, OH)

2) Carrier Gas

Nitrogen dry grade gas containing 1% hydrogen, supplied by AGA Speciality & Medical Gases Division (Maumee, OH)

PROCEDURE:

1) Permeance Measurements

The permeance of oxygen through the film samples (exposing the unmodified polystyrene surface to air) was determined in accordance with ASTM STD D 3985-81 "Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using A Coulometric Sensor" (1981). The studies were carried out on an Ox-Tran 100 Permeability Tester (Modern Controls, Inc., Elk River, MN), whose operation is based on the isostatic method.

As the transmission rate of oxygen through PS is rather high, precautions were taken to protect the sensor. This was achieved by utilizing a masked sample, thus reducing the exposed area by a factor 10. Furthermore the permeant was supplied in the form of air, thus reducing the partial pressure of oxygen by a factor 4.8.

2) Operation

During a permeation run on the Ox-Tran 100 the test specimen is clamped into a cell having a 100 cm^2 diffusion area or when modified a 10 cm^2 diffusion area. A silicone lubricant was applied to the cell rim to assure a tight seal. Initially both cell sides are purged with oxygen free carrier gas (nitrogen containing 1% hydrogen). When a stable zero reading has been established on the recorder, oxygen is introduced into the upper half of the diffusion cell. The nitrogen is continually flowed through the lower cell. A flow diagram of the apparatus is illustrated by Figure 7. As oxygen diffuses through the barrier, it is entrained by the nitrogen and carried to the detector. The detector current rise is recorded on a strip chart. The recorder value levels off when the oxygen transmission rate is at a steady state transmission rate. The detector current measured is directly related to oxygen transmission rate.

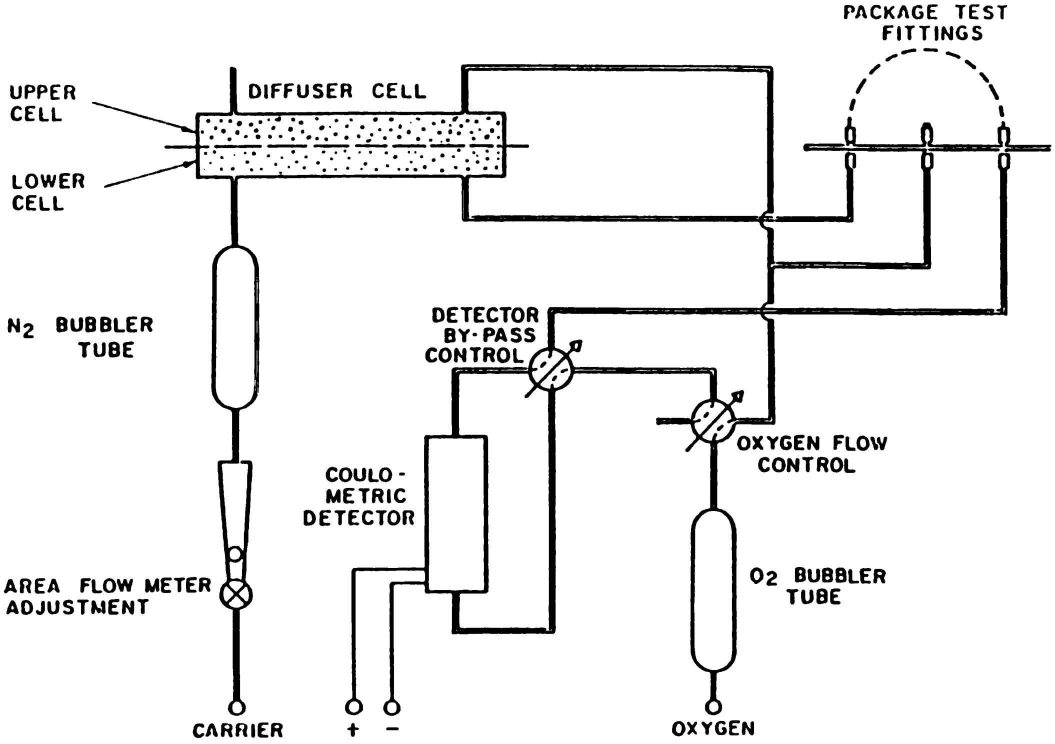


Figure 7. Ox-Tran 100 Oxygen Permeability Tester - Flow Diagram (Soroka and Castelletti, 1979)

3) Calibration

Standard Reference Material 1470 (polyester) obtained from The National Bureau of Standards (Washington, D.C.) was employed to calibrate the instrument. The Certificate (Barnes, 1982) lists the oxygen permeance for the standard material to be; 0.352 pmol/m^2*s or 69.1 cc/m^2*day. This standard permeance value divided by the detector current in mV, obtained when testing the standard PET, thus defines the convertion factor to be applied when converting from mV output to permeance for various test specimens.

Water Vapor Permeance

MATERIALS:

Desiccant; Drierite, Anhydrous $CaSO_4$ supplied by W.A.
Hammond Drierite Co., Xenia, OH.

PROCEDURE:

Determination of water vapor transmission rate through the test specimens (exposing the unmodified polystyrene surface to the water vapor) was carried out in accordance with ASTM STD E 96 "Water Vapor Transmission of Materials" (1980). Replicate samples of all film structures were sealed to the open mouth of a test dish with a diameter of 0.082 m, the exposed film surface area thus being 0.0053 m2. After recording the initial weights, the dishs were placed in an environmental chamber set at 37.8°C and 85% R.H. Periodic weighings on a Mettler H80 Balance (Mettler Instrument Corp., Hightstown, N.J.) then allowed the determination of the rate of water vapor transmission through the test specimens.

Tensile Properties

MATERIALS:

Test specimens; length;7 in, width;1 in, thickness;0.004 in
cross-sectional area;0.004 in^2

PROCEDURE:

Determination of the tensile properties of replicate samples of all film structures was carried out in accordance with ASTM STD D 882-83 "Tensile Properties of Thin Plastic Sheeting". The tensile testing was performed on an Instron 4201 (Canton, MA), whose operation is based on the static weighing method. A force (lbs) versus extension (in) recording was obtained for each sample.

Instron Operating Settings were as follows;

Gage length: 5 in
Crosshead speed: 0.5 in/min
Load range: 25% of full scale load = 50 lbs
Extension, full scale: 1 in

RESULTS AND DISCUSSION

Sulfonation Process

Based on information obtained from Coalition Technologies, Ltd. (Birmingham, MI 48009) the sulfonation process resulted in a polystyrene film modified to; 0.8 μg S/cm^2, with the depth of sulfonation being 50 Å. The above values for the extent of sulfonation and the depth of sulfonation are average values typical for the process employed for the sulfonation of the polystyrene film evaluated in the present study.

Surface Analysis

X-ray Photoelectron Spectroscopy (XPS or ESCA) analysis confirmed the presence of ammonium-stabilized sulfonate groups on the polymer surface (see Figure 8). The measured atomic concentrations of sulfur, oxygen, nitrogen and carbon (hydrogen is not detectable) are listed in Table 6

Table 6. Atomic Concentration Determined by the ESCA Technique

Element	Concentration (%)
O 1s	17.90
N 1s	5.63
C 1s	72.15
S 2p	4.32

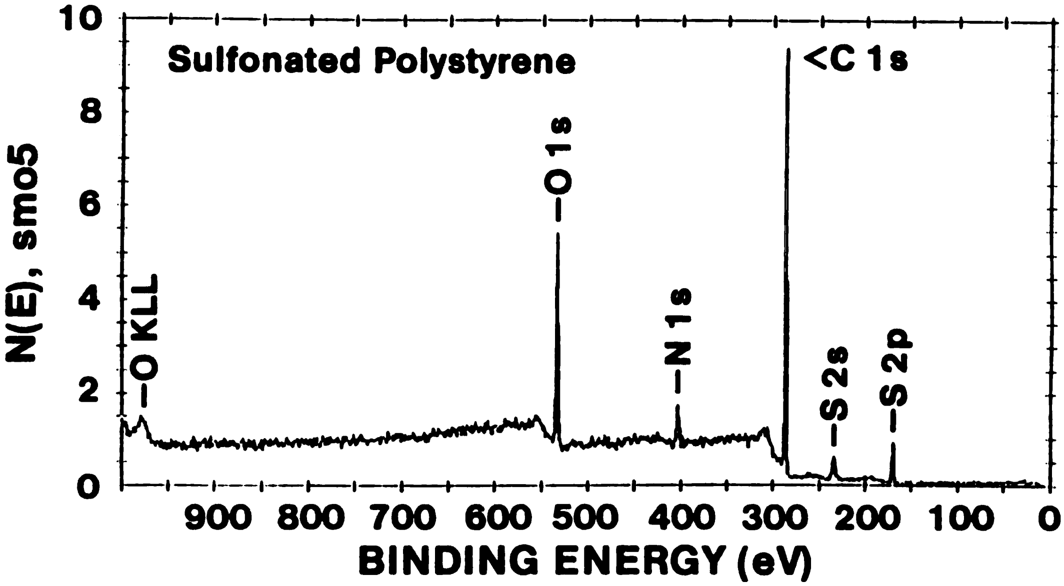


Figure 8. ESCA Spectra of $-C-SO_3^-NH_4^+$ Film Structure

Based on the proposed composition of the surface layer, the expected relationships between the elements are as follows: 1 S : 3 O, and 1 S : 1 N. Assuming the polymer surface is free of sulfur contamination (non-bonded sulfur), the true atomic concentration of sulfur equals the measured value of 4.32 %. The expected atomic concentration of nitrogen is thus exceeded by 30.3 %. A closer examination of the nitrogen peak (see Figure 9.) reveals the presence of two peaks, with one peak accommodating for 73.42 % of the total peak area. This percentage of the determined total nitrogen atomic concentration equals 4.13 %, suggesting a 96 % level of neutralization with ammonium. The expected oxygen atomic concentration is exceeded by 38.1 %. Assuming the excess nitrogen and oxygen derive from contamination on the surface, the actual atomic concentration of carbon is equal to 78.40 %. The relationship between carbon and sulfur is then as follows: 18 C : 1 S. Each repeating unit of polystyrene contains 8 carbons, thus based on a stoichiometric relationship, 1 sulfonate group is present for 2¼ repeating unit of PS. This is illustrated in Figure 10. The dimensions are derived from the length of a carbon-carbon single bond being equivalent to 1.54 Å (Jastrzebski, 1976). In addition to the stoichiometric relationship, the size relationship between the molecular volume of the repeat styrene unit and the sulfonate group could provide further insight into the spatial distribution of the sulfonate groups. Such an approach would allow consideration of steric hindrance to both substitution, and carbon bond rotation.

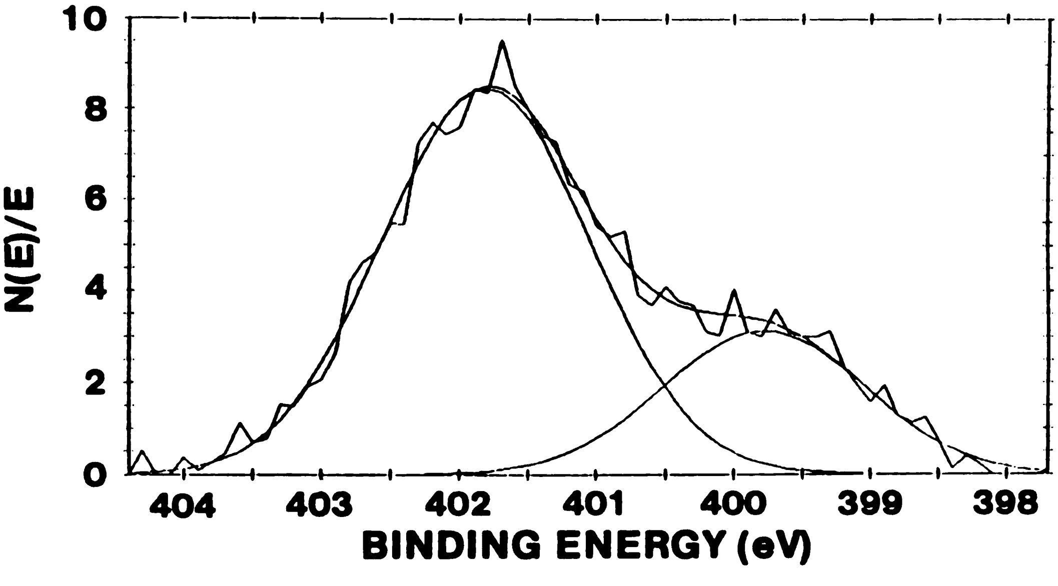


Figure 9. A Narrow Detailed Scan of the Nitrogen Peak Obtained from ESCA Survey

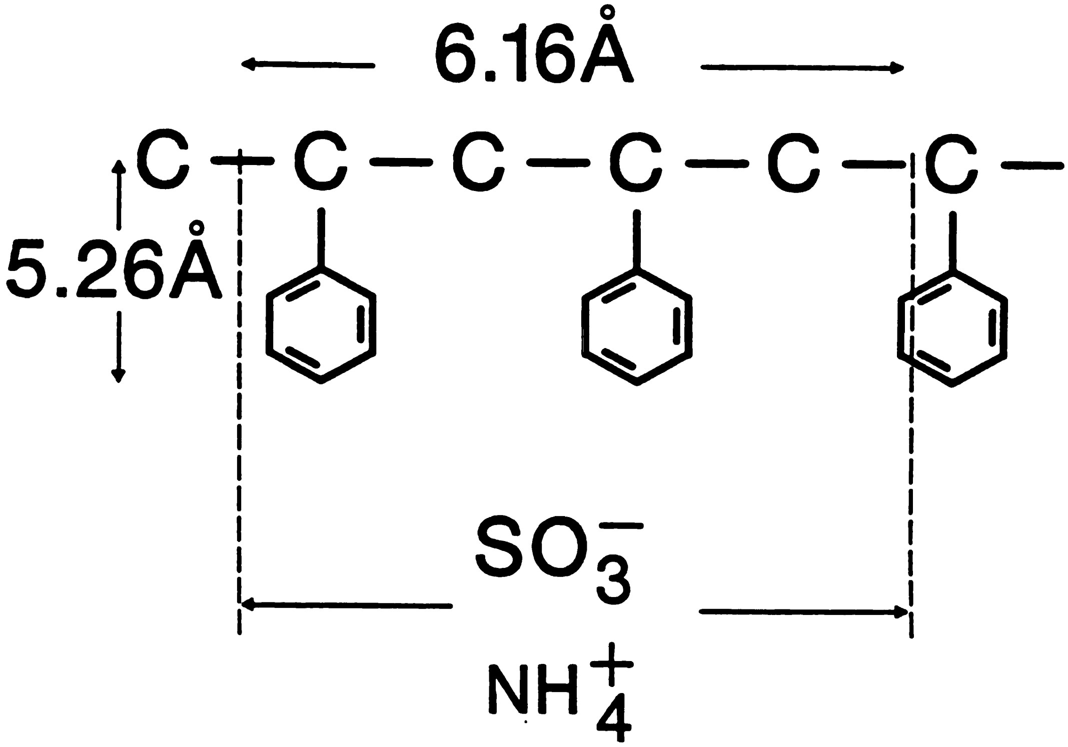


Figure 10. Schematic of Sulfonated Polystyrene Surface Structure Based on ESCA Survey.

Ion Exchange

The bonding between SO_3^- and NH_4^+ on the polystyrene film surface is ionic in nature. Ionic compounds dissociate completely in an aqueous solution (Thorup, 1986). When immersing the $-C-SO_3^-NH_4^+$ structure in 5 % salt solutions the NH_4^+ ions will therefore dissociate into solution, whereas the SO_3^- ions will remain on the polymer surface, covalently bonded to the carbon backbone. The positively charged cations in solution are electrostatically attracted to the negatively charged sulfonate groups, and since the concentration of the cation from the respective salt solution is in great excess, the probability of exchanging the ammonium ions is high.

In order to determine achieved levels of ion exchange, 100 ml solutions of the respective cations exchanged from 50 cm^2 film samples in 5 % HCl were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES). The results from the ICPAES analysis are presented in Table 7., where [c] denotes the concentration of the respective exchanged cations in solution, and $[c_b]$ denotes the concentration of the cations in question in the aqueous blank solution.

Table 7. Cation Concentrations as Determined by ICPAES

Cation	Concentration; [c] ppm (w/v)	Concentration in blank; [c_b] ppm (w/v)
lithium	.014	.013
sodium	.290	.106
potassium	.586	.210
magnesium	.0289	.006
calcium	.335	.057
barium	.398	.000

The cation concentration to be expected can be estimated based on an assumed sulfur surface concentration of 0.8 μg S/cm^2, as follows:

Monovalent cations:

1 mole S = 1 mole SO_3^- = 1 mole Li^+, Na^+ or K^+

S : Molecular weight = 32.0 g/mole

Moles Na^+ = $8x10^{-7}$ g S/cm^2 x 50 cm^2 / 32.0 g/mole

= $2.5x10^{-6}$ moles

Na^+ : Molecular Weight = 23.0 g/mole

g Na^+/100 ml = $2.5x10^{-6}$ moles x 23.0 g/mole

= $2.875x10^{-5}$ g/100 ml

= $2.875x10^{-7}$ g/ml

= 0.288 ppm Na^+

Divalent cations:

The calculation follows the same principle except;

1 mole S = 1 mole SO_3^- = 0.5 mole Mg^{++}, Ca^{++} or Ba^{++}

The estimated cation concentrations [c_e], the actual measured concentrations ([c]-[c_b]) and the derived percentage level of ion exchange are presented in Table 8.

Table 8. Level of Cation Exchange Achieved Expressed as a Percentage

Cation	Estimated Conc.; $[c_o]$ ppm (w/v)	Measured Conc.; $([c] - [c_b])$ ppm (w/v)	% Ion Exchange $\frac{([c] - [c_b])}{[c_o]}$
lithium	.173*	.001	0.6
sodium	.288	.184	64
potassium	.489	.376	77
magnesium	.152	.0229	15
calcium	.251	.278	111
barium	.858	.398	46

*sample size = 100 cm^2

The low values obtained for the estimated percent ion exchange for Li^+ and Mg^{++} are not fully understood. However, a diffusional resistance does not appear to be the cause, as high levels of exchange were observed for both monovalent and divalent cations of larger atomic radii. While not fully understood, the apparent low level of Li^+ and Mg^{++} exchange may be the result of experimental error in preparation of the aqueous solutions for analysis, or during the ICPAES analysis itself. Both of which could result in significantly lower values of ion concentration than theoretical. In future studies, an alternate analytical procedure such as ESCA is recommended to quantify the surface concentration of neutralizing cation, and thus confirm the percent ion exchange values obtained by the spectroscopic method. Alternatively, the apparent low levels of ion exchange effected by Li^+ and Mg^{++} may be the result of the lack of dissociation of the ammonium sulfonate groups at the pH of the aqueous LiCl and $MgCl_2$ solutions employed, or the relative electronegativity of the respective cations. However, since the ion exchange of Li^+ and Mg^{++} has been previously reported by Walles (1989) for surface sulfonated polymers, these effects seem unlikely to account for the low exchange values obtained in the present study.

Organic Vapor Permeability and Solubility Experiments

The repeatability of permeation results obtained when exposing both unmodified and surface sulfonated polystyrene film to limonene vapor was not acceptable, as illustrated by Figures A2 and A3 in Appendix A. Due to the anomalous results obtained for limonene vapor permeability, these studies were discontinued.

However, in order to provide an explanation of the abnormal diffusional behavior observed, solubility experiments were initiated:

The aggressiveness of limonene and ethyl acetate vapors toward unmodified polystyrene and surface sulfonated polystyrene was found to be significant. For example after less than 15 min. exposure to limonene and ethyl acetate vapor ($a=1$), swelling, stress cracking and initial stages of dissolution were observed. After 1 hour the samples were totally dissolved.

After 1 hour exposure to acetone vapor the unmodified PS sample weight is increased by 22 % and the surface sulfonated PS by 23 %, whereas propanol vapor has no evident influence on polystyrene. After 4 days exposure to propanol vapor the sample weight is increased by 2 % and 0.7 %, respectively.

The high solubility of organic vapors in polystyrene is furthermore confirmed when comparing the solubility parameters presented in Table 3. The difference in polystyrene and ethyl acetate solubility parameters is only 0.07, thus resulting in a significant solubility of polystyrene in ethyl acetate.

A similar relationship between polystyrene and limonene accounts for the non-Fickian diffusional behavior observed for the organic vapor permeability experiments. In this case the relatively high penetrant activity employed resulted in a type two transport phemonena (Boyer, 1970).

The polystyrene-limonene interaction furthermore resulted in solvent induced crazing, which was enhanced by increasing temperature. After exposure of the surface sulfonated PS to limonene vapor at a vapor activity of 0.6 at 25°C for 9 days, a certain degree of solvent induced crazing was evident by the formation of a regular pattern of white one directional lines in the material. After exposure at identical conditions for a period of 6 days, followed by exposure at 60°C and a corresponding higher vapor activity for 1 day, extensive solvent induced crazing was observed. A regular pattern of white perpendicular lines was etched into the surface of the material (see Figure 11.). The same formation of perpendicular lines without etching onto the surface was observed for unmodified polystyrene.

The data from both the permeation and solubility experiments indicates the poor barrier properties of unmodified and surface sulfonated polystyrene toward organic penetrants. Furthermore if clarity is a critical factor caution is suggestable when utilizing a surface sulfonated polystyrene at elevated temperatures for packaging of products containing aggressive organic compounds.

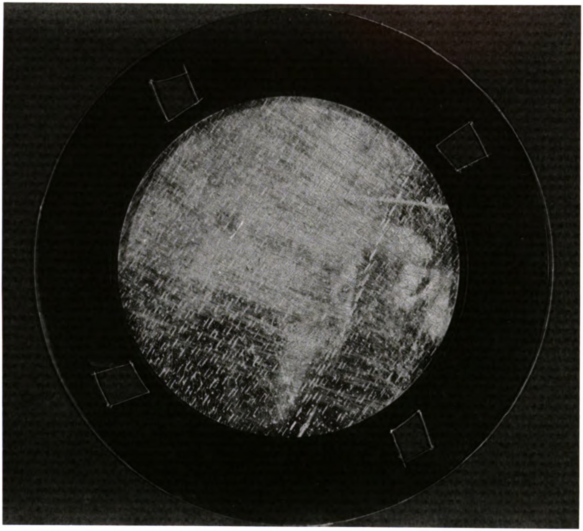


Figure 11. Photographic Illustration of Limonene-Surface Sulfonated Polystyrene Interaction

Oxygen Permeance

The oxygen diffusion coefficient, DO_2, and permeance, PO_2, for the various film structures were determined by utilizing a computer program for calculating these parameters, as presented in Appendix B. The data necessary for running the computer program is in the form of time (sec) versus voltage output (mV), which is obtained by performing permeation runs on the Ox-Tran 100 Permeability Tester.

Table 9. presents average values for DO_2 and PO_2, based on replicate determinations at 23°C and 50 % R.H., as a function of neutralizing cation. Table 9. also lists cation atomic radii, and the atomic number for the respective neutralizing cations.

Table 9. The Influence of the Neutralizing Cation on Oxygen Barrier Properties of a 4 mil Surface Sulfonated Polystyrene Structure

Cation	Ion Radii (pm)	Atomic Number	Diffusion Coef $(cm^2/sec)x10^8$	Permeance $(cc(STP)/m^2*day*atm$
ammonium		7	8.3 ± 1.0	1110 ± 10
lithium	76	3	7.4 ± 1.0	1260 ± 70
sodium	102	11	8.0 ± 0.4	1160 ± 30
potassium	138	19	8.1 ± 0.2	1190 ± 110
magnesium	72	12	7.756 ± 0.004	1200 ± 60
calcium	100	20	7.50 ± 0.06	1240 ± 110
barium	135	56	7.7 ± 0.2	1170 ± 10

Figures 12. and 13. plot oxygen diffusion coefficient and oxygen permeance, respectively, versus neutralizing cation atomic radii. Whereas Figures 14. and 15. plot the same parameters versus atomic number of the respective cations. As shown, there is no correlation between neutralizing cation radii or atomic number and oxygen diffusion coefficient and oxygen permeance. Thus, at the level of surface sulfonation, the neutralizing cation has little or no influence upon the oxygen barrier properties of the test films. Values from the literature for the oxygen diffusion

coefficient (DO_2) and oxygen permeability ($P\rho O_2$) through polystyrene obtained at 23°C and 25°C, respectively, are listed in Tables 4. and 5., and are summarized below;

$DO_2 = 11 \times 10^{-8}$ cm^2/sec

$P\rho O_2 = 4,650$ $cc(STP)*mil/m^2*day*atm$

Experimental values obtained for an unmodified 1.5 mil PS film under similar test conditions are stated below;

$DO_2 = 2.4 \pm 0.2 \times 10^{-8}$ cm^2/sec

$P\rho O_2 = 4,680 \pm 150$ $cc(STP)*mil/m^2*day*atm$

The range of values obtained for the various surface sulfonated 4 mil PS films are as follows;

$DO_2 = 6.4 - 9.3 \times 10^{-8}$ cm^2/sec

$P\rho O_2 = 4,400 - 5,400$ $cc(STP)*mil/m^2*day*atm$

STATISTICAL ANALYSIS :

A statistical analysis of the obtained data for oxygen barrier characteristics was carried out. The statistical test applied was; Analysis of Variance I or ANOVA (Steel and Torrie, 1980).

In order to determine whether a statistically significant difference exists between oxygen barrier property values for an unmodified and a surface modified PS, oxygen diffusion coefficient and permeability data for the unmodified polystyrene (1.5 mil) were compared with the various cation stabilized surface sulfonated polystyrene structures (4 mil). The ANOVA data are presented in Appendix B, Table B1. A statistically significant difference was found to exist for the oxygen diffusion coefficient data, with a confidence level of; 90 % for NH_4^+, 95 % for Li^+, 99 % for Na^+ and 99.5 % for K^+, Mg^{++}, Ca^{++} and Ba^{++}. The difference in oxygen diffusion coefficient values may however derive from a difference in thermo-mechanical history between the test and control films. No statistically significant difference was found to exist for the oxygen permeability data.

Furthermore, the same parameters for the surface sulfonated PS, neutralized with the various cations, were compared to the ammonium stabilized structure, as presented in Table B2. No statistically significant difference was found to exist for neither oxygen diffusion coefficient nor oxygen permeability values, except for the oxygen permeability value obtained for the barium stabilized structure.

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

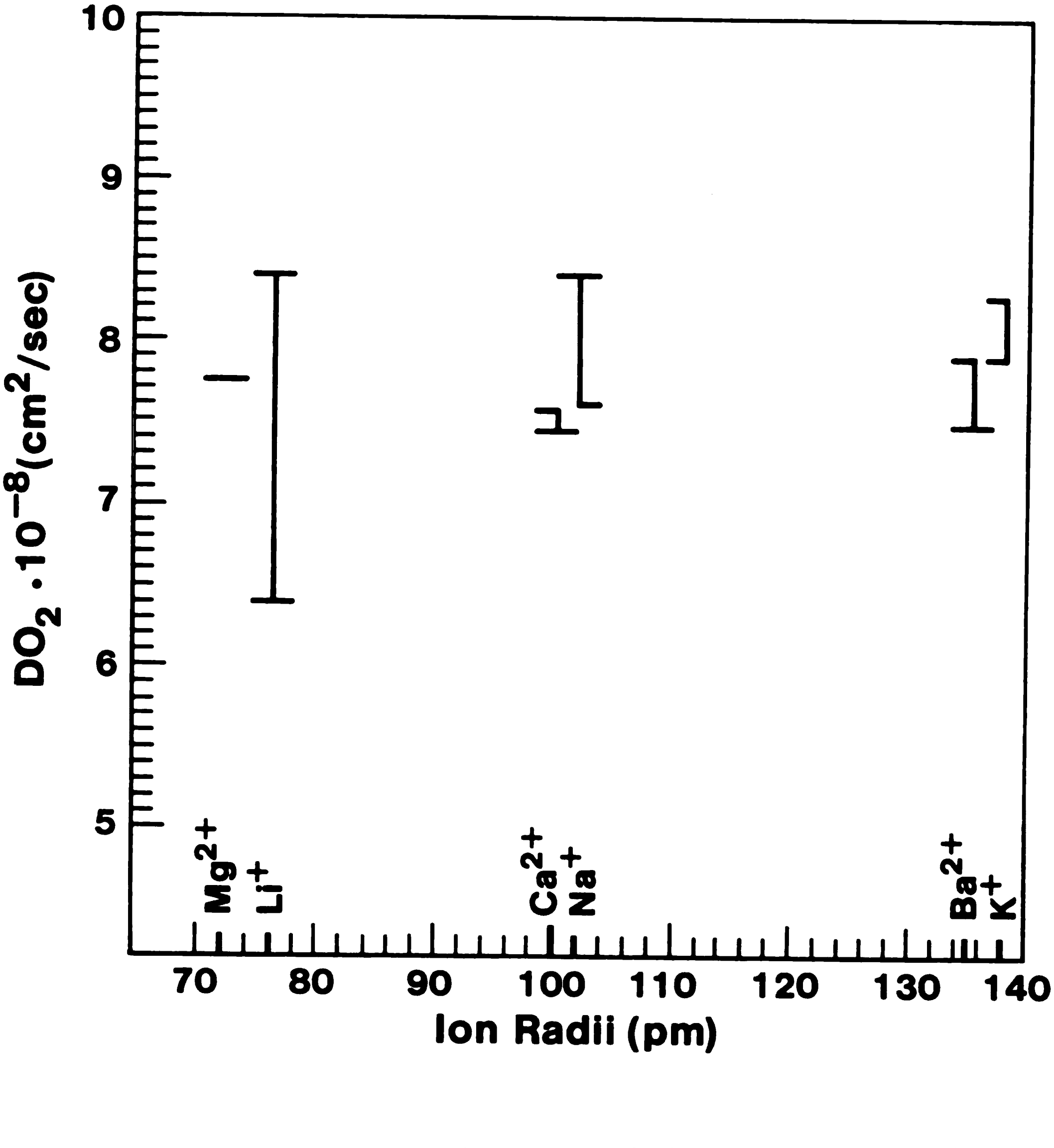


Figure 12. Oxygen Diffusion Coefficient as a Function of Neutralizing Cation Radii

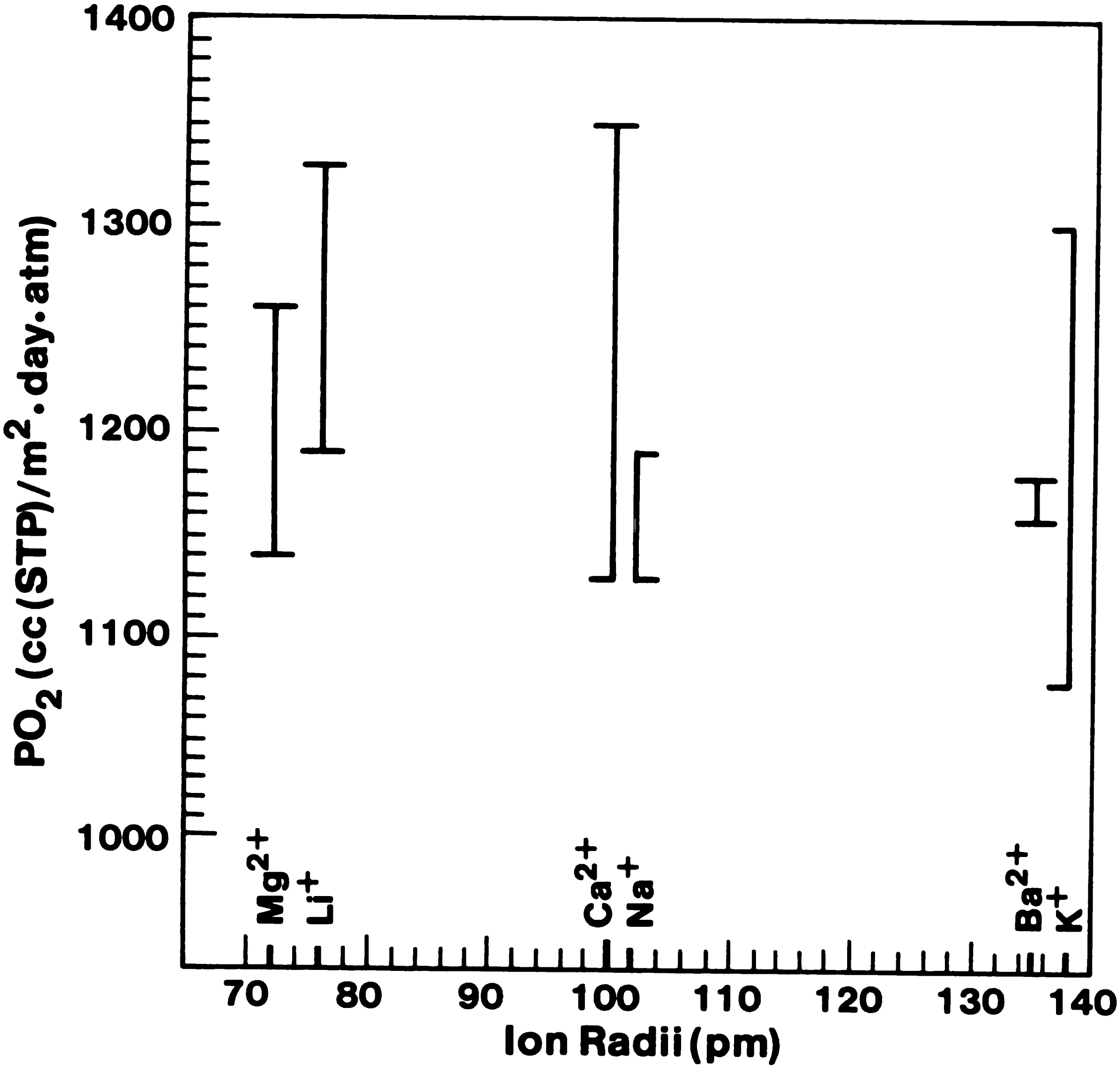


Figure 13. Oxygen Permeance as a Function of Neutralizing Cation Radii

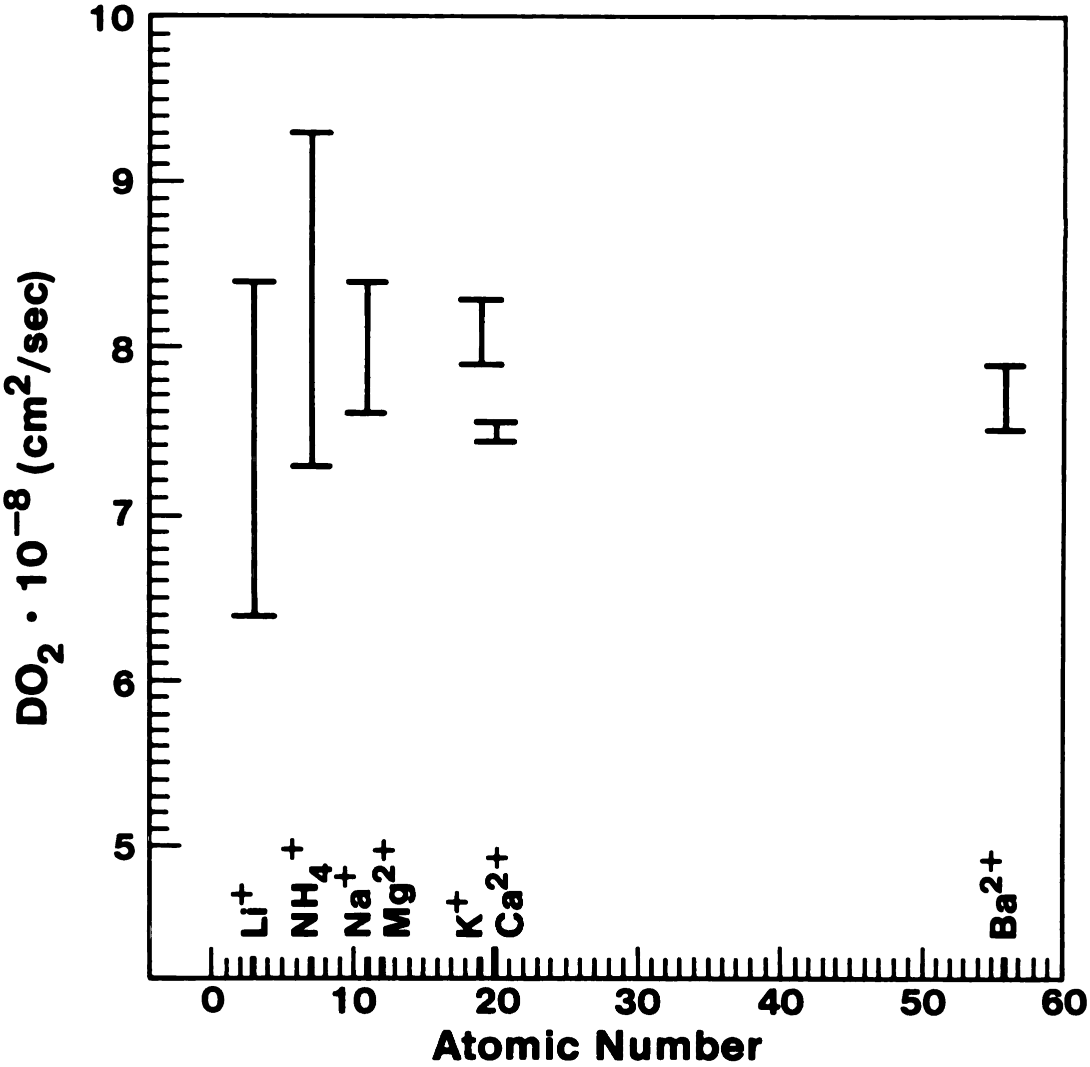


Figure 14. Oxygen Diffusion Coefficient as a Function of Atomic Number Corresponding to Neutralizing Cation

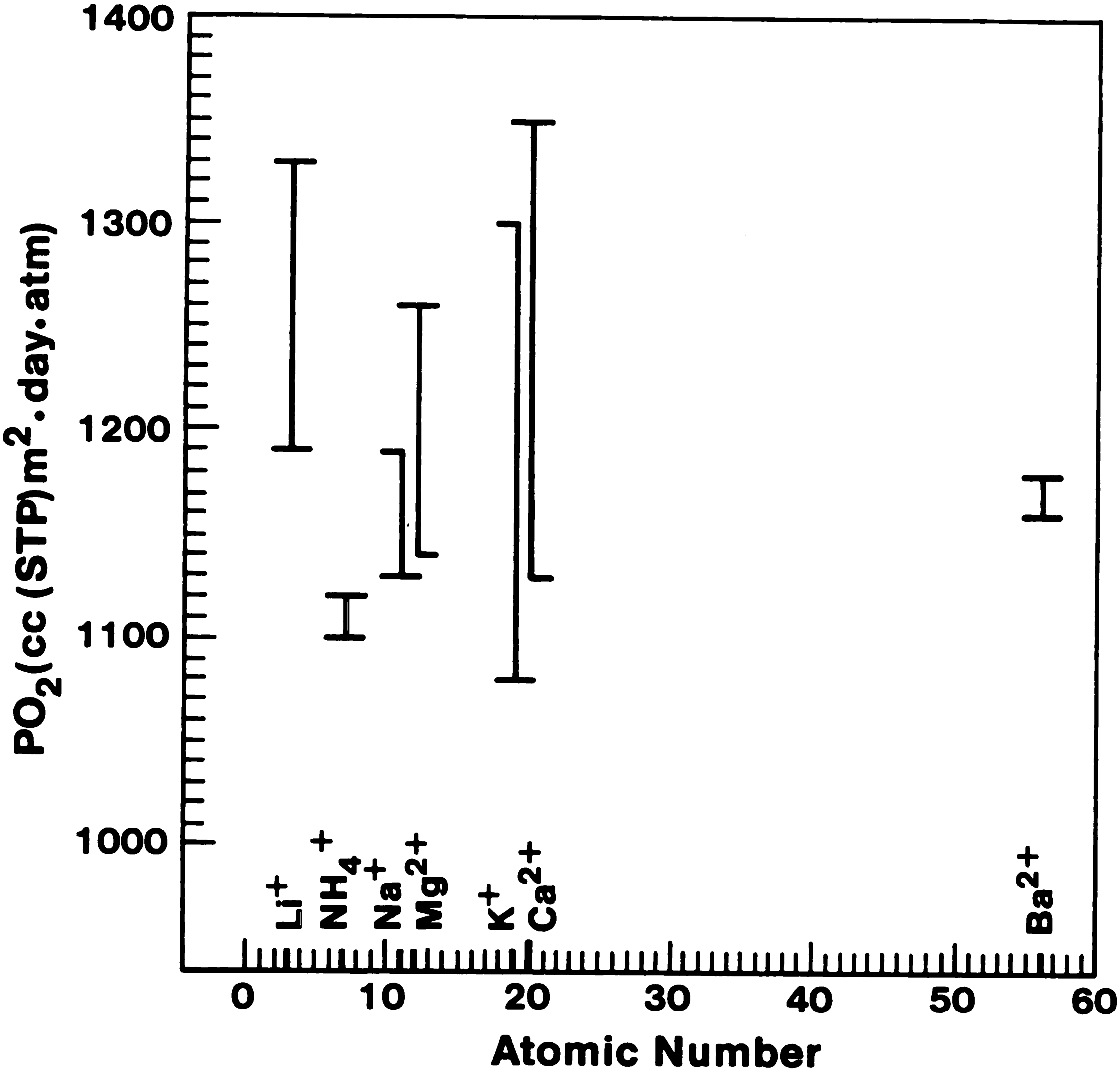


Figure 15. Oxygen Permeance as a Function of Atomic Number Corresponding to Neutralizing Cation

Water Vapor Permeance

The data in form of weight gain as a function of elapsed time, obtained for the various film structures, are presented in Appendix C, Table C1. As a typical example of the linear relationship exhibited by the respective film structures, Figure C2. presents a plot of weight gain (g H_2O) as a function of elapsed time (hrs) for the ammonium stabilized surface sulfonated polystyrene. The slope of the curve thus equaling the water vapor transmission rate. Water vapor transmission rate may be converted to permeance by taking into account the exposed surface area and water vapor pressure difference at the conditions of test. Average values of water vapor permeance through the various film structures, based on replicate determinations at 37.8°C and 85 % R.H., are presented in Table 10.

Table 10. The Influence of the Neutralizing Cation on Water Vapor Barrier Properties of a 4 mil Surface Sulfonated Polystyrene Structure

Cation	Ion Radii (pm)	Atomic Number	Permeance (g/m^2*day*atm)
ammonium		7	514 ± 6
lithium	76	3	517 ± 1
sodium	102	11	507 ± 4
potassium	138	19	531 ± 3
magnesium	72	12	513 ± 0
calcium	100	20	536 ± 4
barium	135	56	532 ± 1

Figures 16. and 17. plot water vapor permeance as a function of neutralizing cation atomic radii, and atomic number of the corresponding cation, respectively. At this level of sulfonation no influence of neutralizing cation atomic radii or atomic number upon water vapor barrier properties is evidenced.

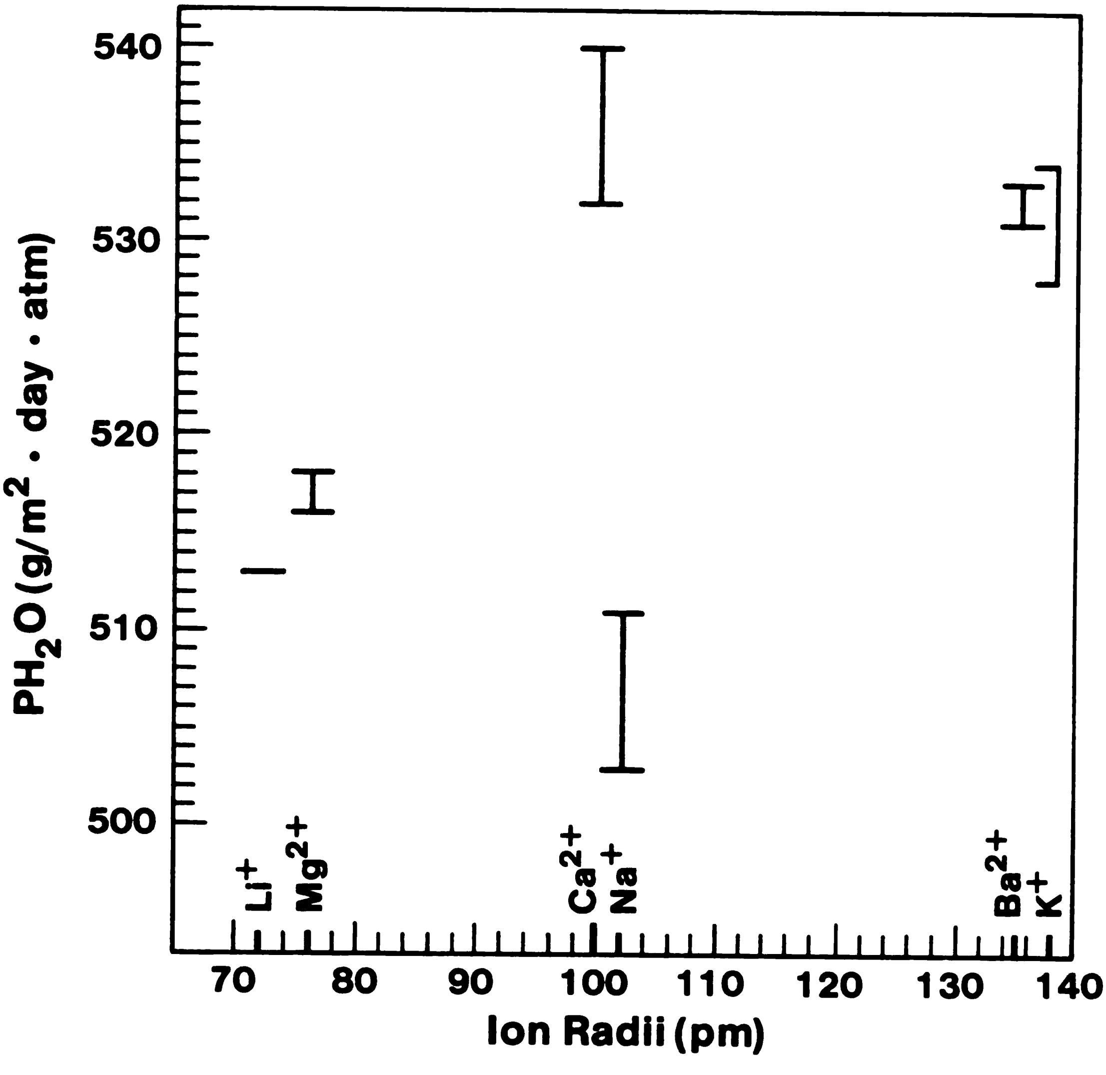


Figure 16. Water Vapor Permeance as a Function of Neutralizing Cation Radii

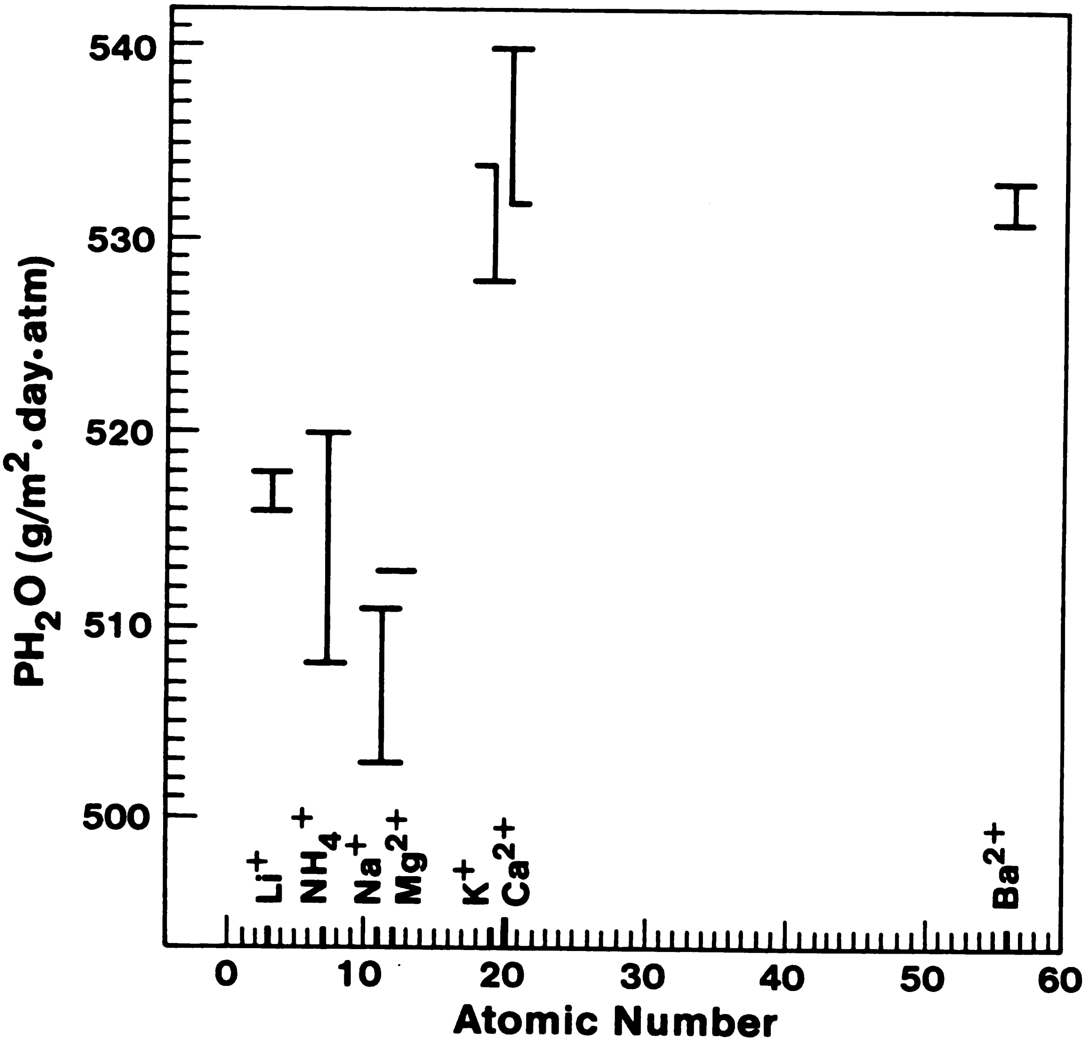


Figure 17. Water Vapor Permeance as a Function of Atomic Number Corresponding to Neutralizing Cation

Tensile Properties

Average values of tensile strength and modulus of elasticity for the various film structures, based on replicate determinations, are presented in Table 11.

Table 11. Effect of Neutralizing Cation upon Tensile Properties

Cation	Mean Tensile Strength (psi)	Standard Deviation (psi)	Mean Modulus of Elasticity x10^5 (psi)	Standard Deviation (psi)
NH_4^+	11,205	166	3.40	2,200
Li^+	9,938	742	3.23	0
Na^+	11,056	90	3.42	10,600
K^+	10,279	147	3.11	3,600
Mg^{++}	10,624	37	3.20	1,400
Ca^{++}	11,168	152	3.23	16,300
Ba^{++}	11,301	47	3.42	1,000

The tensile properties exhibit no evident correlation with the valance of the neutralizing cation, nor with the atomic ion radii, or atomic number of the cation.

SUMMARY AND CONCLUSIONS

The effect of a series of neutralizing cations on the barrier properties of a surface sulfonated polystyrene film was investigated. The cations evaluated included : NH_4^+, Li^+, Na^+, K^+, Mg^{++}, Ca^{++} and Ba^{++}. The respective structures were obtained by an ion exchange procedure from the ammonium stabilized sulfonated polystyrene film.

The estimated values for the extent of sulfonation, and the depth of sulfonation of the polystyrene film (4 mil) were as follows: 0.8 $\mu g\ S/cm^2$ and 50 Å, respectively. The presence of ammonium-stabilized sulfonate groups on the sample surface was confirmed by an ESCA survey. The determined atomic concentrations of sulfur, oxygen, nitrogen and carbon indicated a 96 % level of neutralization with ammonium, and a surface concentration of 1 sulfonate group per 2¼ monomer repeat unit on the polymer surface.

Permeability of limonene vapor, at a vapor activity of 0.6 and 25°C, through the ammonium-stabilized surface sulfonated polystyrene exhibited anomalous behavior, which was attributed to the solubility of limonene in the polymer. Similar results were obtained for a non-sulfonated polystyrene film serving as a control. The high level of solubility of limonene in polystyrene is supported by

numerical values of the solubility parameters of limonene and polystyrene. The polystyrene-limonene interaction furthermore resulted in solvent induced crazing, which was enhanced by increasing temperature. An etching of white perpendicular lines into the material was observed after exposure to limonene vapor (a=0.6) for a period of 6 days at 25°C, followed by exposure at 60°C for an additional day.
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 level of sulfonation present in the test structures. There was no correlation between the valance, atomic radii, or atomic number of the respective neutralizing cations and the oxygen diffusion coefficient, oxygen permeance, and water vapor permeance of the test film structures. Further, the barrier characteristics for oxygen and water vapor were found to be equivalent to an unmodified 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.

At the level of sulfonation the only significant difference as compared to an unmodified polystyrene is an increase in surface polarity, which can be attributed to insertion of polar sulfonate groups at the polystyrene surface, thus enhancing the wetability of the polymer.

APPENDICES

Appendix A

Standard Calibration

A calibration curve for limonene was generated based on the following concentrations of limonene in solvent; 8.4, 16.8, 42, 168 and 210 ppm (w/v). A 1.0 μl sample was injected directly into the gas chromatograph and the area response recorded. Limonene concentration was plotted versus area response. The slope equals the calibration factor in (ppm/A.U.) which may be converted into (g/A.U.) by considering the quantity of sample injected.
Table A1. and Figure A1. show the calibration data and the standard calibration curve for limonene, respectively.

Limonene standard calibration factor
$= 5.300 \times 10^{-13}$ (g/A.U.)

Table A1. Limonene Calibration Curve Data

ppm (w/v)	Area Unit First Trial	Area Unit Second Trial	Area Unit Average
8.4	15541	15232	15387
16.8	31761	29844	30803
42	82862	78201	80532
168	307270	313990	310630
210	398110	402070	400090

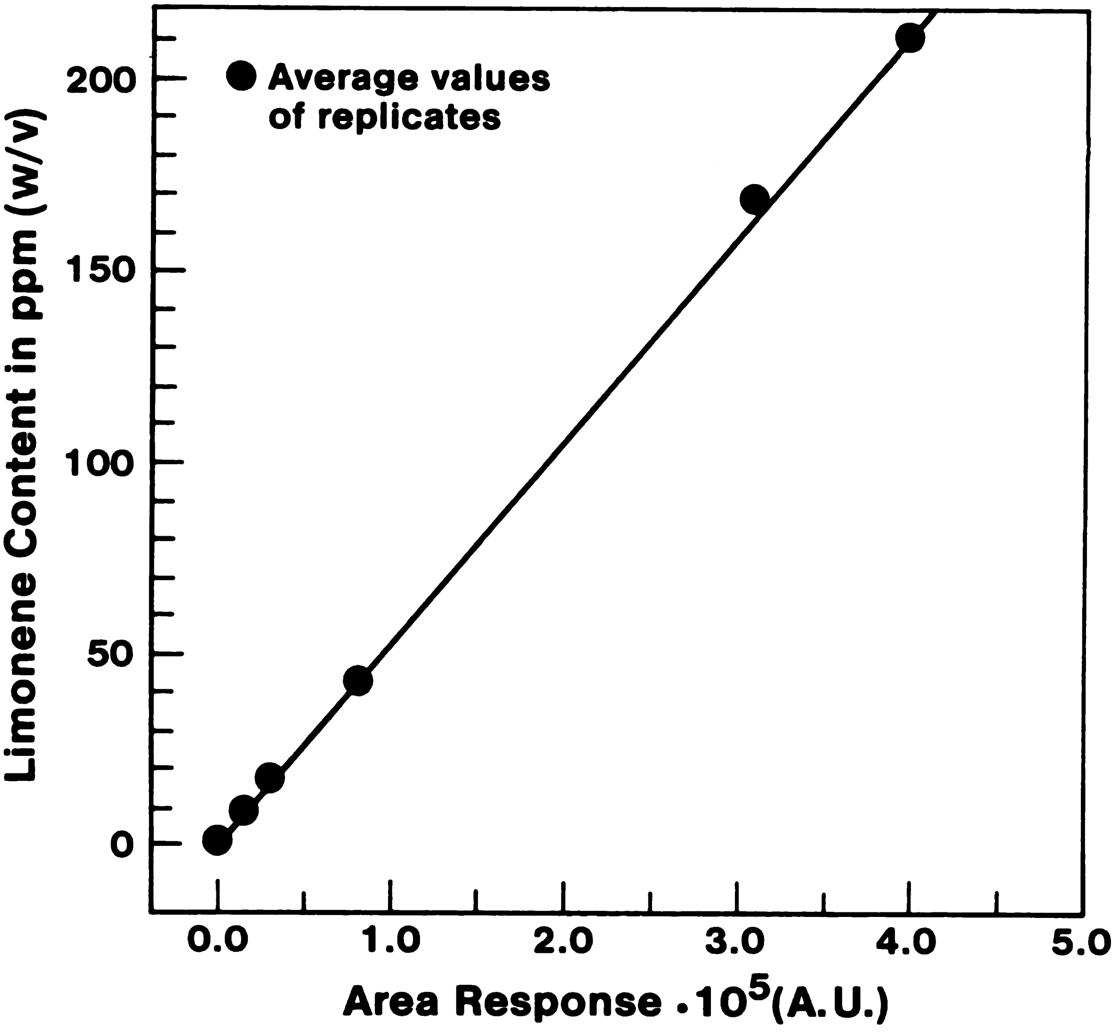


Figure A1. Limonene Standard Calibration Curve

Limonene Permeation

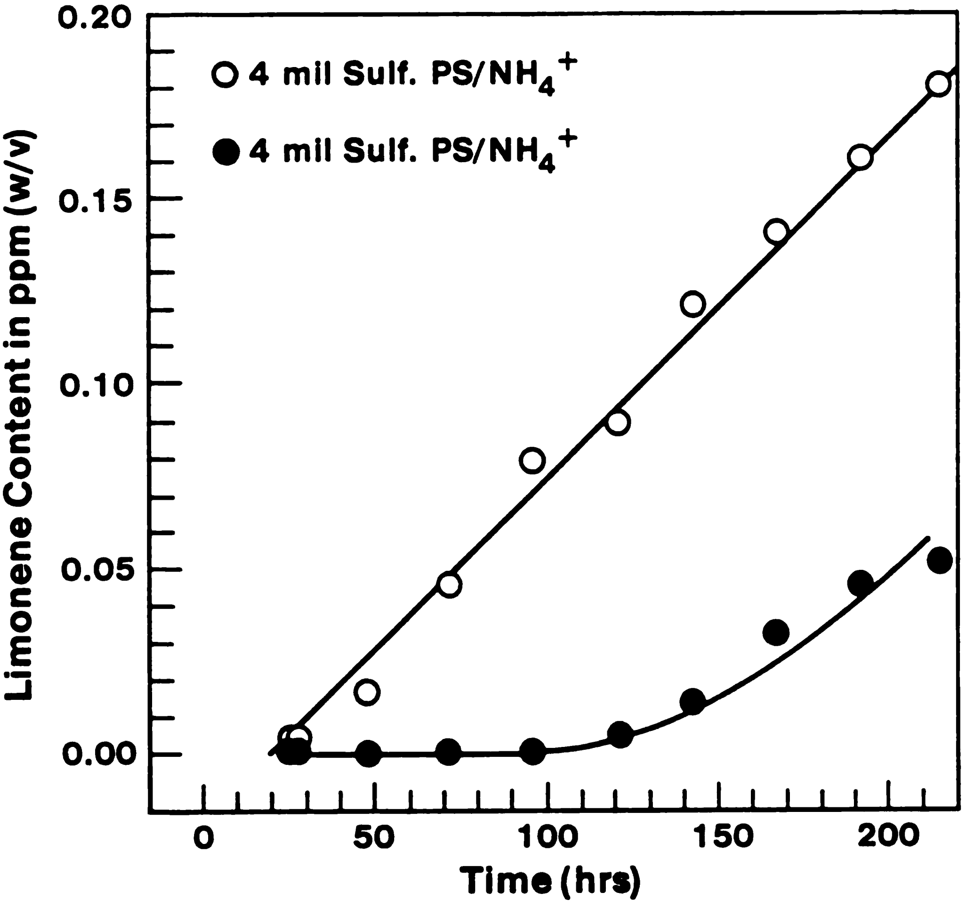


Figure A2. Replicate Determination of Limonene Permeation through Ammonium Stabilized Surface Sulfonated PS

(Performed at 25°C and a Vapor Activity of 0.6)

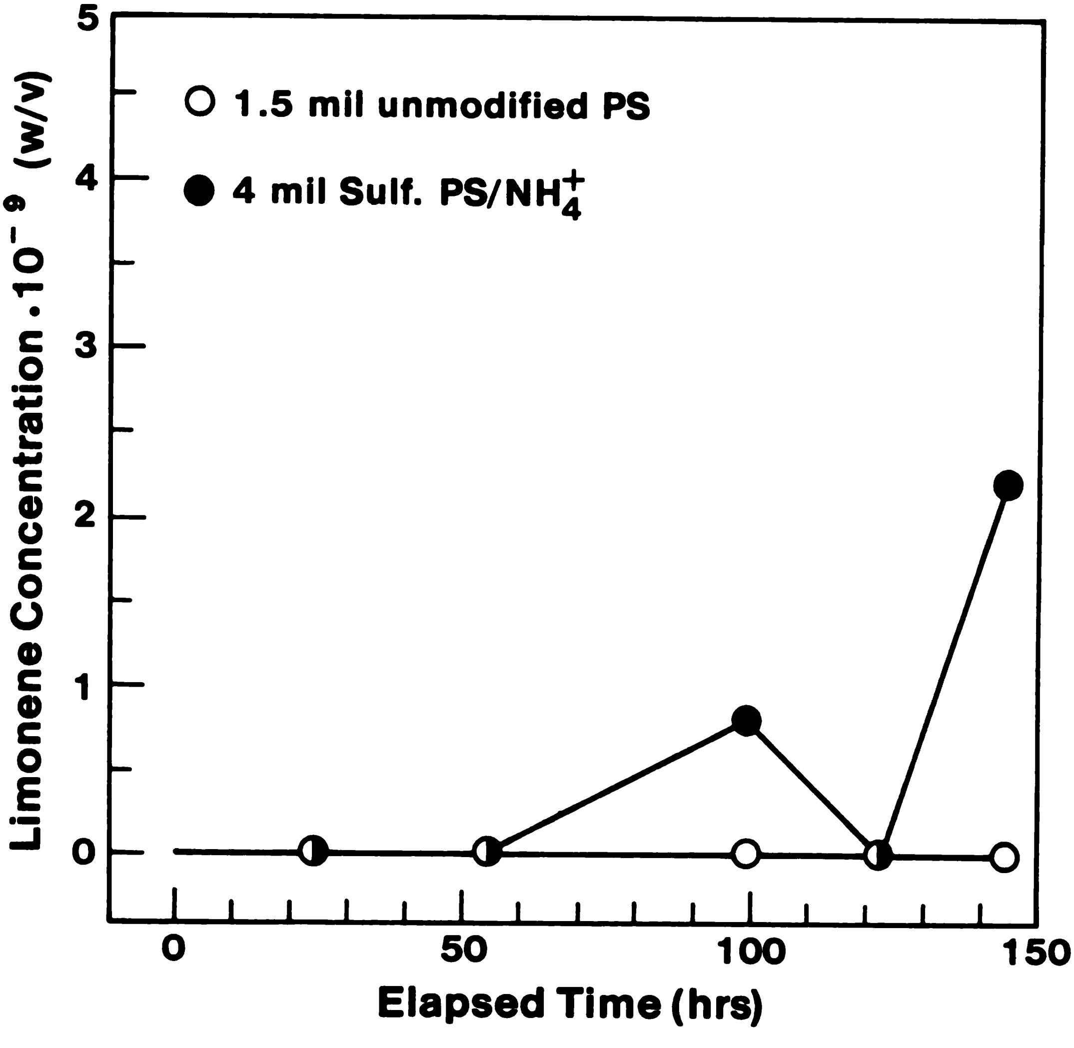


Figure A3. Replicate Determination of Limonene Permeation through 1.5 mil PS and 4 mil Sulfonated PS (Performed at 25°C and a Vapor Activity of 0.6)

Appendix B

Computer Program for Oxygen Diffusion Coefficient and Permeance

```
  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 L. ESBENSEN
  8  REM ON 12-9-91
 10  DIM F(50), T(50), X(50), DF(50)
 30  REM THE UNITS OF TIME USED WILL DETERMINE THE UNITS IN
     THE DIFF. COEFF.
 32  REM
 33  REM
 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 FLOW F AND TIME T STARTING FROM ZERO"
 70  FOR I=1 TO D
 80  PRINT "ENTER F"
 90  INPUT F(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 F"
190  INPUT FI
200  FOR I=1 TO D
205  DF(I)=F(I)/FI
210  A=.44313*F(I)/FI
220  X-GUESS
230  FOR J=1 TO 7
240  B=SQR(X)
250  C=EXP(-X)
260  L=1/B
270  H=(.5*L-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)=1!/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*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 (SEC) ", "FLOW", "X", "FLOW PERCENT"
570  FOR I=1 TO D
600  LPRINT T(I),F(I),X(I),DF(I)
610  NEXT I
620  PRINT
630  PRINT
635  DIFF= ((.01016^2)*SLOPE/4
636  LPRINT "DIFFUSION COEFF IN  cm2/sec. =" DIFF
637  LPRINT
638  LPRINT "PERMEANCE IN  cm3(STP)/m2.day.atm
     ="FI*69.1*10/(4.775*.21)
639  PRINT
640  LPRINT
642  REM
645  LPRINT "THE CORRELATION COEFF. =" R
646  LPRINT
647  LPRINT "TEMPERATURE IN C =" W
648  LPRINT
650  REM THE VALUE OF THE DIFFUSION COEFFICIENT IS FOR TIME
     IN SECONDS
655  REM THE THICKNESS IS L=1-/16E-03 cm (4.0 mil)
659  END
```

Statistical Analysis

Table B1. ANOVA for Oxygen Diffusion Coefficient and Permeability (1.5 mil PS vs. the Various Sulfonated 4 mil PS Structures)

Comparing:	Observed F		Required F			
	DO_2	$P\rho O_2$	10%	5%	1%	0.5%
PS/NH_4^+	9.46	8.29	8.53	18.51	98.50	198.5
PS/Li^+	23.81	1.55				
PS/Na^+	156.5	0.10				
PS/K^+	324.0	0.030				
PS/Mg^{++}	576.0	0.24				
PS/Ca^{++}	520.0	0.39				
PS/Ba^{++}	281.0	-0.056				

Table B2. ANOVA for Oxygen Diffusion Coefficient and Permeability (Ammonium Stabilized Sulfonated PS vs. the Various Neutralizing Cations)

Comparing:	Observed F		Required F			
	DO^2	$P\rho O^2$	10%	5%	1%	0.5%
NH_4^+/Li^+	0.13	4.52	8.52	18.51	98.50	198.5
NH_4^+/Na^+	0.012	2.56				
NH_4^+/K^+	-0.0099	0.53				
NH_4^+/Mg^{++}	0.098	2.19				
NH_4^+/Ca^{++}	1.02	1.39				
NH_4^+/Ba^{++}	0.065	19.33				

Appendix C

Water Vapor Transmission Rate Data

Table 1C. Water Vapor Transmission Rate Data Obtained for The Various Film Structures at 37.8°C and 85 % R.H. Based on Replicate Determinations

	NH_4^+	Li^+	Na^+	K^+	Mg^{++}	Ca^{++}	Ba^{++}
Time (hrs)	Wt. gain	of H_2O	(g)	-	-	-	-
19.0	.1192	.1197	.1183	.1247	.1188	.1256	.1249
24.0	.1482	.1491	.1470	.1548	.1478	.1559	.1551
46.0	.2863	.2889	.2832	.2980	.2863	.3004	.2986
67.0	.4199	.4232	.4153	.4359	.4197	.4390	.4360
72.0	.4484	.4511	.4430	.4657	.4486	.4693	.4663
91.0	.5664	.5699	.5600	.5886	.5675	.5933	.5889
115.3	.7181	.7220	.7085	.7443	.7179	.7501	.7448
145.3	.9052	.9108	.8926	.9377	.9044	.9447	.9395
163.0	1.017	1.023	1.003	1.053	1.015	1.061	1.053

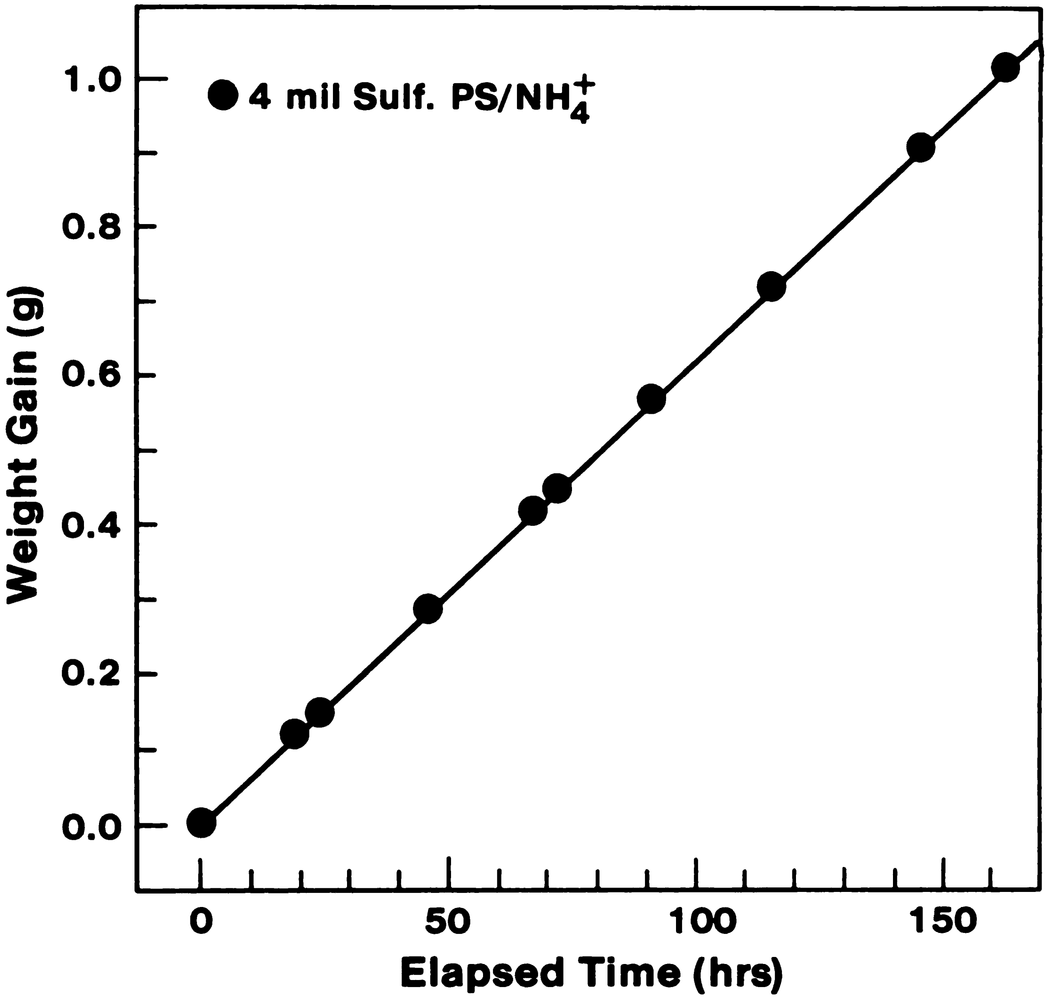


Figure C1. Weight Gain as a Function of Elapsed Time for Ammonium Stabilized Surface Sulfonated PS

Appendix D

Surface Analysis

Table D1. Surface Tension of an Unmodified PS and the Various Surface Sulfonated PS Films

Film Structure	Surface Tension (dynes/cm)	
polystyrene	32	(Skeist, 1977)
non-sulfonated PS	< 36	
ammonium-sulf. PS	56	
lithium-sulf. PS	56	
sodium-sulf. PS	56	
potassium-sulf. PS	56	
magnesium-sulf. PS	56	
calcium-sulf. PS	56	
barium-sulf. PS	56	

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