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Irradiation Grafted Polymeric Films. II. Gas Transport Properties of Hydrated Potassium Acrylate-Grafted Polyethylene Films

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Summary

The permeability constants of oxygen and carbon dioxide through hydrated potassium acrylate-grafted polyethylene films increase rapidly as the degree of hydration of the films increases above about 28 wt %. Below about 28 wt %, the carbon dioxide permeability constant increases with the degree of hydration. In the case of oxygen, the opposite is true.

The separation factor (CO_2/O_2) increases rapidly with film hydration up to about 28 wt %. Above this degree of hydration, the separation factor gradually approaches the value for pure water. An explanation for the results obtained is presented.

INTRODUCTION

The ability of membranes to either transmit or exclude gases or vapors is of great significance for many applications. In the packaging field, the resistance of films to moisure, oxygen, and carbon dioxide is essential for the preservation of many items. On the other hand, advantage has been taken of the ability of films to pass penetrants in widely varying applications. For example, the ability of films to transmit a small amount of oxygen into meat packages is necessary to maintain the red color. Membranes permeable to water are being used for desalination of seawater and the separation of other mixtures not readily separated by conventional means.

The gas permeability characteristics of a large number of membranes have been reported (*1–4*). Several review articles develop the theory of molecular transport through plastic membranes and describes various factors that control the permeation process (*5–7*). The majority of the permeability data have been obtained using dry membranes; however, for many applications, the membranes will be used in either a humid or wet environment. For these applications, the gas permeability constants for wet or moist films are of interest.

Simril and Hershberger (*1*) studied the effect of relative humidity on the permeability constants of various gases through three regenerated cellulose membranes with and without plasticizers. For the nonplasticized membranes, they found that the increase in permeability of a wet film over a dry film is related to the solubility of the permeating gas in water. Plasticization of the membrane facilitated hydration and further enhanced the permeability constants. Other investigators (*8, 9*) reported a pronounced effect of water vapor on the permeability constants of oxygen, nitrogen, and carbon dioxide through regenerated cellulose. The greatest effect occurred in the vicinity of 70 to 80% relative humidity where the mechanism of water sorption appears to change and simultaneous structural changes occur in the membrane.

Very high gas permeability constants have been obtained using polyelectrolyte hydrogels. Markley (*10*) obtained an oxygen permeability constants of 3.4×10^{-7} cc (STP), cm/cm^2, sec, atm through a polyelectrolyte hydrogel containing 80 wt % water and a CO_2/O_2 separation factor of 20 which is essentially the same selectivity for carbon dioxide over oxygen in water.

In this study, the effect of hydration on the oxygen and carbon dioxide permeability constants for a series of potassium acrylate-grafted polyethylenes was determined.

DESCRIPTION AND OPERATION OF THE APPARATUS

The permeability constant P for a polymer–gas system can be determined by measuring the mass flux of the gas under a known pressure difference across the film. The methods used to determine the mass flux are the pressure method and the volume method. The pressure method consists of the measurement of the pressure increase in the calibrated low-pressure side of the cell. Either superatmospheric (*8*) or high vacuum (*4*) methods can be used.

The volume method is based on measuring the volume of gas permeating into the low pressure side of the cell (*2*). The apparatus used in this study was designed to measure the volume of permeating

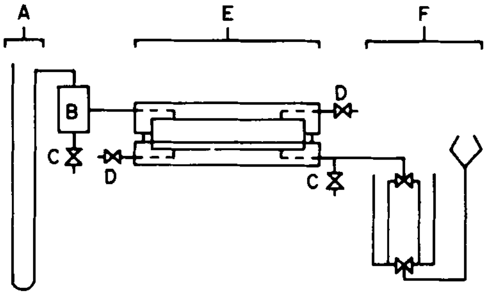

FIG. 1. Schematic diagram of the gas permeability cell. A, Manometer; B. 500 cc gas reservoir; C, gas inlet valve; D, gas exit valve; E, permeability cell; F, gas measuring unit.

gas at a constant pressure. This apparatus is depicted in Fig. 1. The permeability cell (E) is fabricated from aluminum and has a permeability area of 24.59 cm^2. A thin rubber gasket having the same inside diameter as the cell is used to seal the membrane between the two sections of the cell. To keep the volume of the low pressure side of the cell small, this section comprises a series of concentric rings cut $\frac{1}{16}$-in. deep and $\frac{1}{16}$-in. apart. The rings are connected by two two channels, $\frac{1}{16}$-in. deep and $\frac{1}{16}$-in. wide cut across the diameter of the cell chamber at right angles to each other. The inlet (C) and exit (D) valves to both the high and low pressure chamber are $\frac{1}{8}$-in. in diameter.

The high pressure side of the cell is connected with $\frac{1}{4}$-in. polyethylene tubing to a manometer (A) and a 500-cc gas reservoir (B) which is large enough to maintain constant pressure on the high pressure side of the membrane.

The low pressure side of the cell is connected to the gas measuring section (F) with $\frac{1}{8}$-in. stainless steel tubing. The gas measuring section consists of two calibrated tubes connected in parallel to the system through a 3-way stopcock. For slow permeability rates, one tube is calibrated in hundredths of a milliliter and measures a maximum of 1 cc. The second tube, which is used for fast permeability rates, is calibrated in tenths of a cubic centimeter and measures a maximum of 5 cc. Two tubes, identical to the calibrated tubes and open to the atmosphere, are located adjacent to the gas measuring tubes. A mercury leveling bulb is connected to the gas measuring section through a 3-way stopcock. All metal-to-metal connections are either silver soldered or connected with high-pressure tubing fittings.

The glass-to-metal connections are made using tubing fittings with O-ring seals.

The apparatus with the membrane in place is operated as follows. The inlet and exit valves on both sides of the cell are opened. The gas to be studied is bubbled through a column of water and then through both sides of the cell. This is continued for at least 0.75 hr to rid the system of contaminants and to equalize the water vapor pressure on both sides of the membrane. The exit valve on the high pressure side of the cell is closed, and the test gas is introduced to the desired pressure. The inlet and exit valves in the low pressure side of the cell are then closed. The mercury leveling bulb is used to level the mercury column in the calibrated gas measuring tube and the adjacent tube. The change in volume with time is then recorded maintaining an equal mercury level in the two tubes. The gas measuring tubes are vibrated during the run to prevent the mercury from sticking and to insure a uniform rate of travel.

The gas transmission measurements are conveniently recorded by plotting the change in volume with time. The volume flow rate V_r, in cubic centimeters of transmitted gas per second, is obtained from the steady-state portion of the curve.

The volume flow rate V_r is then corrected for the vapor pressure of water and converted to standard conditions by the following equation:

$$V_{\text{STP}} = V_r \times \frac{B - p}{76} \times \frac{273}{273 + T}$$

where V_r = cc of transmitted gas per second, B = barometric pressure in cm Hg, p = vapor pressure of water at temperature of test in cm Hg, and T = test temperature in °C. The gas permeability constant P is calculated from the following equation:

$$P = V_{\text{STP}} \times \frac{L}{A \Delta p}$$

where V_{STP} = cc of transmitted gas per second at standard conditions, L = film thickness in cm, A = surface area of the film in cm^2, and Δ_p = test gas pressure differential across the film in cm Hg.

All of the gas permeability data obtained in this investigation are reported in terms of the permeability constant, P, which is defined as the number of cubic centimeters of gas at standard conditions passing through 1 sq cm of film, 1-cm thick, per second, per cm of mercury pressure differential across the film.

EVALUATION OF THE TEST EQUIPMENT

To evaluate the previously described permeability cell, the oxygen and carbon dioxide permeability constants were determined for low-density polyethylene using the test cell. Dow-400 polyethylene film was used since this was the base film for preparation of the potassium acrylate grafted-polyethylene films utilized in this study. The oxygen was obtained from Linde and the carbon dioxide from Southwest Cryogenics, Inc. Their purities were 99.5 and 99.7%, respectively.

The permeability constants were also determined for the same polymer using a Dow Permeability Cell as manufactured by Custom Scientific Instruments, Inc. Table 1 lists the oxygen and carbon dioxide permeability constants obtained with both cells as well as the corresponding value reported by other investigators. It is apparent that the values obtained with both cells agree very well with those previously reported.

TABLE 1

Permeability Constants of Low-Density Polyethylene Films at 25°C

	$P \times 10^9 \left[\frac{\text{cc(STP), cm}}{\text{cm}^2\text{, sec, cm Hg}}\right]$		
Source	O_2	CO_2	Ref.
Brubaker and Kammermeyer	0.28–0.35	1.2–1.9	*3*
Lebovits[a]	0.11–0.59	0.43–2.8	*7*
Modern Plastics Encyclopedia	0.30	1.6	*11*
This work:			
Dow cell	0.36	1.4	
Test cell	0.37	1.4	

[a] These data are listed as ranging from high-density to low-density polyethylene.

EXPERIMENTAL PROCEDURE

The films used in this study were a series of hydrated potassium acrylate-grafted polyethylene films. The polyethylene films are grafted by irradiation in a benzene solution containing various amounts of acrylic acid monomer and carbon tetrachloride terminator. A detailed description on the preparation and properties of these modified polyethylene films will appear in a later publication. Table 2 lists

TABLE 2

Composition of Acrylic Acid-Grafted Polyethylenes

Film No.	Grafting solution composition, wt %: Acrylic acid	Carbon tetrachloride	Benzene	Polyacrylic acid in product: Wt %	meq/g copolymer
S-81	25	5	70	46.4	6.35
S-82	20	4	76	41.2	5.64
S-83	15	3	82	33.9	4.64
S-84	10	2	88	27.5	3.77

the composition of the grafting solutions and the average compositions of the acrylic acid-grafted polyethylene films used in this study.

To assure that all of the films were treated in an identical manner, the four grafted polyethylene films were placed in a beaker and boiled for 1 hr in 5 wt % aqueous potassium hydroxide. The caustic solution was decanted; the films were washed with deionized water until neutral to litmus. The films then remained in deionized water for 3 days during which time the water was changed twice a day. They were then air-dried.

The oxygen and carbon dioxide permeability constants were determined for these films at two degrees of hydration. In the first series, disks from each of the films were soaked in deionized water for 48 hr prior to determining the permeability constants. A disk of filter paper having the same diameter as the effective film area was soaked in deionized water, blotted dry, and placed over the concentric rings forming the low-pressure side of the cell. The film was removed from the deionized water, blotted dry, and placed over the filter paper. After sealing the cell, the seal was checked for leaks by closing the inlet and exit valves on both sides of the cell. Lowering the mercury leveling bulb will create a slight vacuum inside the cell. If the mercury level in the 1-cc calibrated tube does not change in 0.5 hr, the system is considered sealed. The techniques used to determine the gas flux and calculate the permeability constants were previously described.

At the completion of each run, the film was removed from the cell, and the film thickness was rapidly determined by averaging five thickness readings obtained with a Starrett thickness gauge. The film was then placed in a tared glass vial and weighed. To determine the weight per cent water in the membrane, the film was dried at 140°C for 18 hr and reweighed.

For the second degree of hydration, disks from each of the dried films were placed in a closed container. The test gas was bubbled through a column of water at ambient temperature and then passed over the film disk in the container for at least 3 hr before it was used. The procedures used to determine the permeability constants, film thickness, and weight per cent water in the film were previously described. For each degree of hydration, a minimum of three runs was made with each gas.

RESULTS AND DISCUSSION

The equilibrium water contents of the potassium acrylate-grafted polyethylene films are listed in Table 3. The water content of the films in both series of hydration increased with the degree of grafting. This was expected since an increase in the degree of grafting increases the hydrophilic characteristics of the film.

Figure 2 shows the pronounced effect of water content of the potassium acrylate-grafted polyethylene films upon the permeability constants of oxygen. It is apparent that at the low degrees of hydration, the oxygen permeability constants are less than that obtained with polyethylene. This can be due to a decrease in both the diffusion process and the solubility of oxygen in the films as a consequence of the change in polymer composition and the resulting change in water content

TABLE 3

Equilibrium Water Content of Potassium Acrylate-Grafted Polyethylene Films

Film No.	Degree of grafting[a]	Water content of films after permeability tests, wt %	
		Series 1[b]	Series 2[c]
S-81	0.87	57.3	27.6
S-82	0.70	57.1	26.7
S-83	0.52	48.0	23.2
S-84	0.38	37.8	17.8

[a] Weight of polyacrylic acid in the graft copolymer/weight of starting polyethylene.

[b] Films soaked in deionized waters for 48 hr before testing.

[c] Films exposed to water vapor for 3 hr before testing.

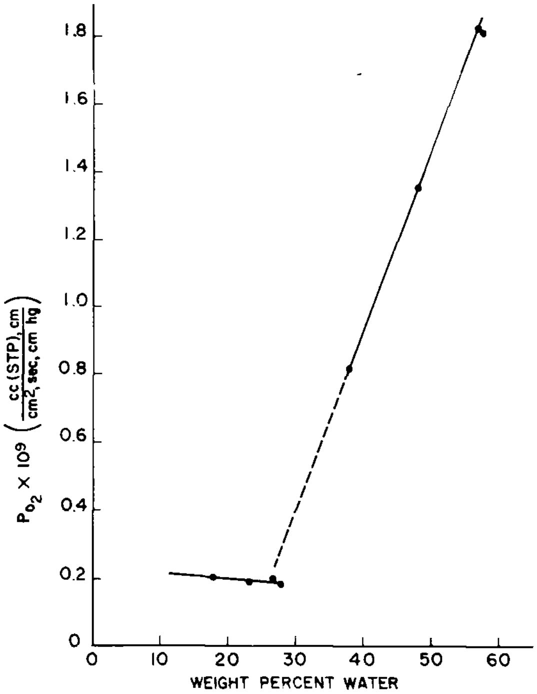

FIG. 2. Oxygen permeability constant as a function of the water content in potassium acrylate-grafted polyethylene films.

of the films. One factor that lowers the diffusion of oxygen through the film is when the acrylic acid is grafted onto the polyethylene, the resulting poly(acrylic acid) branches tend to fill the voids in the film. Huang and Kanitz (*12*) found that the gas permeability constants of polyethylene, irradiation grafted with styrene, decreased with an increase in grafting until the film contained between 20 to 30% styrene. Beyond this, the permeability constant increased with an increase in styrene content. They concluded that the decreased permeability was caused by the styrene filling the void volumes in the polyethylene film which decreased the diffusion rate of the gases. Beyond 30% grafting, disruption of the crystallites resulted in an increased gas permeation. Similar results were reported by Myers and associates (*13*) who studied the permeability of nitrogen through polyethylene grafted with styrene or acrylonitrile.

A second factor that will decrease the diffusion process through a film is to increase the polarity of the film. The introduction of poly (potassium acrylate) onto the polymer chain increases the polarity of the film which increases the tightness of the film network due to hydrogen bonding. We have observed similar results with other polymers having functional pendant groups.

It is of interest to note that at the low degrees of hydration, the oxygen permeability constants tend to decrease with increasing water content. When the water content of the film is in the range of 26 to 28 wt %, there is an abrupt change in the permeability constant. Beyond this range, the permeability constant rapidly increases with an increase in water content.

With respect to the change in the oxygen permeability with increasing water content below the inflection point at 26 to 28 wt %, one would assume that the oxygen permeability constant should increase with the water content. However, the increase in water content is a result of an increase in the amount of poly(potassium acrylate) in the film. Since the polymer is ionic, an increase in the poly(potassium acrylate) content in the film increases the ionic strength of the film and decreases the solubility of oxygen. Similar results were obtained by Ward and Robb (*14*). They incorporated basic salts in a water supported membrane which decreased the solubility of oxygen causing a decrease in the permeability constant. Thus, the decrease in solubility combined with the decrease in the diffusion process results in oxygen permeability constants that are lower than the base polyethylene and tend to decrease with increasing water content.

The abrupt change in the oxygen permeability constant which occurs when the potassium acrylate-grafted films contain approximately 26 to 28 wt % water indicates a significant change has occurred in the permeation process. One explanation may be that as the dry film is hydrated, the water is strongly associated with the ionic group in the film. When the water content reaches the range of 26 to 28 wt %, the ionic groups are completely hydrated and a change occurs in the film. This allows an equilibration of the bound water with the free water that may be contained in the voids of the film. This equilibration may in part consist of a uniform hydration throughout the hydrophilic portions of the membrane. In other portions, the cohesive forces of the water are greater than the interacting forces between the water and the hydrophobic base polyethylene film. In these areas, the water tends to form clusters. When these changes occur, the factors that influence the diffusion rate and solubility of oxygen in the film are no longer controlling. Beyond this range, the permeability constant appears to increase linearly with the water content of the film.

Figure 3 shows the change in the carbon dioxide permeability constant as a function of the amount of water in the potassium acrylate-grafted polyethylene films. At the low degrees of hydration, the permeability constants gradually increase with an increase in water content. Unlike the oxygen permeability constants in this range of hydration, the carbon dioxide permeability constants are larger than that obtained with the base polyethylene. Undoubtedly, the same factors that decrease the diffusion rate of oxygen in this region also exist here. However, the potassium acrylate-grafted film is basic, and this significantly increases the solubility of carbon dioxide in the membrane resulting in an over-all increase in the permeability constant. This increase continues linearly until the water content in the membrane is in the range of 26 to 28 wt %. Then, as with oxygen,

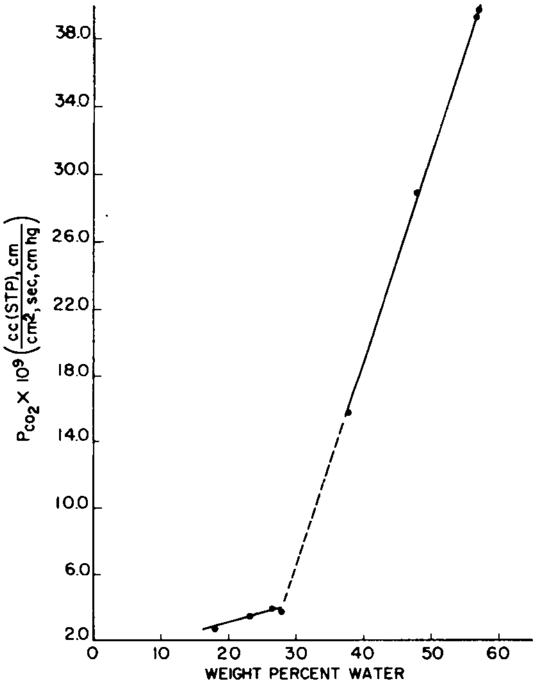

FIG. 3. Carbon dioxide permeability constant as a function of the water content in potassium acrylate-grafted polyethylene films.

there is an abrupt change in the permeability constant. The same concepts that account for the change in the oxygen permeability constants over this range are considered to apply here.

It is of interest to note that the change in the carbon dioxide permeability constant as a function of the water content in the potassium acrylate-grafted polyethylene films as shown in Fig. 3 is quite similar to that obtained by Pilar (*8*) who studied the permeability of carbon dioxide through hydrated regenerated cellulose films. He obtained a similar abrupt change in the permeability constant when the film contained between 13 and 16 wt % water. This agreed with the findings of Simril and Smith (*15*) who studied the water sorption properties of regenerated cellulose. They found that at 13 wt % water the regenerated cellulose underwent a structural change. The agreement between the findings of Simril and Smith and the results of Pilar explain the changes that can occur in a hydrophilic film like regenerated cellulose which causes a drastic change in the carbon dioxide permeability constant. This type of change can occur in the hydrophilic portion of the potassium acrylate-grafted polyethylene, but it is also concluded that the hydrophobic segments contributed by the base polyethylene will give rise to water clustering.

Figure 4 shows the separation factor (CO_2/O_2) as a function of the water content in the potassium acrylate-grafted polyethylene films. The separation factor increases linearly with the amount of water in

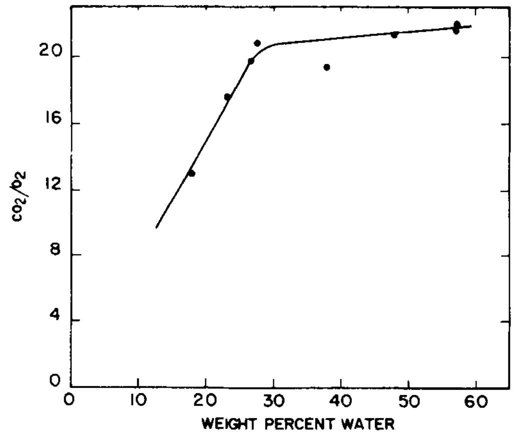

FIG. 4. Change in the separation factor as a function of the water content in potassium acrylate-grafted polyethylene films.

the film until the water content in the film is in the range of 26 to 28 wt %. Beyond this range the separation factor gradually approaches 22, which is that reported for the two gases through pure water.

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