JOURNAL OF APPLIED POLYMER SCIENCE VOL. 14, PP. 2739-2751 (1970)

The Permeation of Gases Through Modified Polymer Films. II. Gas Permeability and Separation Characteristics of Gamma Ray-Irradiated Polyethylene

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Synopsis

A study has been made of the diffusion, solubility, and separation of nitrogen and methane gases in a series of air- and vacuum-irradiated polyethylene films in the temperature range of 15° to 50°C. Samples were air irradiated to 90 Mrads and vacuum irradiated to 80 Mrads. The major structural differences between the modified films were the presence of oxygenated species in the air-irradiated samples. The oxidation of these samples reduced the amount of crosslinking normally found in vacuum-irradiated samples. Diffusion and permeability coefficients for both gases decreased with irradiation dose. The solubility coefficients for the air-irradiated samples increased with increasing irradiation dose while little change was observed for vacuum-irradiated film. The gas mixture permeabilities could be predicted from the pure component permeabilities, and the methane–nitrogen separation factor decreased with increasing irradiation dose.

INTRODUCTION

A number of studies have been made on the feasibility of utilizing selective permeation in commercial gas separation processes.[1] Recent gas mixture separations include C_2H_6–C_4H_6,[2] C_2H_6–C_3H_8,[2,3] and the separation of helium from natural gas.[4] Several methods have been proposed to improve the efficiency of the process including improved permeation cell design and various membrane materials.[4] Generally, membranes for gas separation processes have been limited to commercially available films, with little work reported on the modification of these films for the enhancement of permselective characteristics. In this laboratory, investigations have been made on the gas transport properties of a number of radiation-modified polymer films. In the previous papers of this series, results on radiation-induced styrene–polyethylene graft copolymers[5] and gamma-irradiated Teflon FEP copolymer films[6] have been reported. It is the purpose of the present work to investigate the gas permeation and separation characteristics of gamma ray-irradiated polyethylene films.

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The results of several investigations on the effects of radiation on the single gas permeation properties of polymers have been reviewed by Rogers.[7] For vacuum-irradiated polyethylene, it was found that crosslinking induced by irradiation decreased the permeability of the polymer to gases. For an air-irradiated sample exposed to 10^8 roentgens, it was reported that the permeability decreased but the solubility constant increased compared to unirradiated polyethylene. This was attributed to chemical composition changes induced by the irradiation.

In this investigation, polyethylene samples were irradiated by gamma rays in air and in vacuo. The gas transport properties of the modified films were then determined by using nitrogen–methane gas mixture as the permeating species.

EXPERIMENTAL

Materials

Dry nitrogen gas was obtained from the Linde Division of Union Carbide Canada Ltd. High-purity helium and methane were obtained from Matheson of Canada Ltd. Polyethylene films, of nominal thicknesses 2 and 10 mils, were supplied by Canadian Industries Limited. The films contained no plasticizer or antiblock agents.

Apparatus

The irradiation of samples in air and under vacuum was carried out in a Gammacell 220 cobalt 60 irradiation unit at the University of Waterloo. The intensity of the source during use was approximately 0.8 Mrad/hr.

The permeation apparatus used in determining single-component gas permeabilities was based on Barrer's high vacuum technique and has been

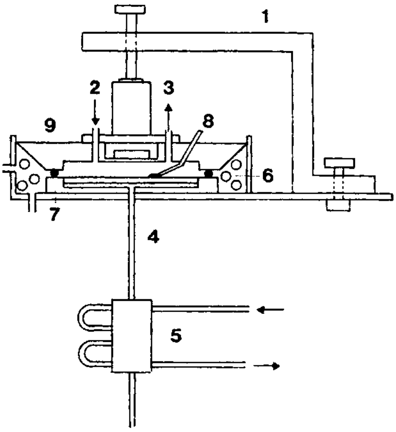

Fig. 1. Schematic diagram of film holder: (1) clamp; (2) gas inlet; (3) gas outlet; (4) gas measuring chamber; (5) gas sampling valve—to chromatograph; (6) heating coils in mercury-filled sealing chamber; (7) film support plate; (8) thermistor surface probe; (9) film holder cover.

described in the previous paper in this series.[5] To determine the composition of gas mixture, a Carle gas sampling valve was incorporated into the pressure measuring chamber, as shown in Figure 1. One sample loop was continuously a part of the measuring chamber. Whenever a sample was taken, the other loop automatically took its place. The gas analysis was performed by means of a Varian Aerograph 1520-C gas chromatograph. A clamping arrangement as shown in Figure 1 was used when the upstream pressure was close to or above atmospheric pressure. The film temperature was measured by a thermistor and controlled by water from an external circulating bath. The pressure increase in the measuring chamber was recorded either continuously by a Varian Millitorr ionization gauge or intermittently by a McLeod gauge.

Infrared spectra were determined using a Perkin Elmer Model 337 infrared spectrophotometer. A Perkin Elmer DSC 1B differential scanning calorimeter was used for the thermal measurements.

Procedure

Polyethylene samples were placed inside constricted Pyrex ampoules, evacuated to 10^{-6} mm Hg, and then the tubes were sealed off at the constriction. These samples were then subjected to various gamma ray irradiation doses. For irradiation in air, polyethylene samples were irradiated in stoppered ampoules. After removal from the irradiation source, density, infrared, and thermal measurements were made by standard procedures.

Nitrogen and methane gases were blended in a mixing tank. The composition of the resulting gas mixture was determined by operating the permeation apparatus without a film in the sample holder and analysing the gas stream by means of the gas chromatograph. For the permeability and separation runs, the composition of the test gas was varied from 0 to 100% methane over a temperature range of 15° to 50°C. Gas permeabilities were determined by the time-lag method to obtain the diffusion and solubility coefficients. The pressure differential between the upstream and downstream sides of the film was varied from 100 to 760 mm Hg. For the separation runs, the differential was 760 mm Hg.

DISCUSSION OF RESULTS

Effect of Gamma Irradiation on Polyethylene

The effects of irradiation on the density and crystallinity of the irradiated polyethylene samples are presented in Table I. As can be seen, the densities of both air- and vacuum-irradiated polymer films increased with irradiation dose. Polyethylene exhibits a greater tendency to crosslink than to degrade.[8] The principal changes in polyethylene subjected to ionizing radiation in a vacuum are unsaturation, crosslinking, and disruption of lattice spacings due to crosslinking. When polyethylene is irradiated in air,

TABLE I
Effect of Gamma Ray Irradiation on the Physical and Transport Properties of Polyethylene

Sample no.	Irradiation dose, Mrads	Irradiation atmosphere	Density (23°C), g/cm^3	Crystallinity,[a] wt-%	D_0, cm^2/sec		E_a, kcal/mole		Heat of solutions, kcal/mole	
					N_2	CH_4	N_2	CH_4	N_2	CH_4
1	0	air	0.9157	54	3.9	3.6	10.6	11.2	1.2	0.1
2	40	air	0.9164	55	4.3	4.5	10.7	11.4	1.1	0
3	78	air	0.9192	52	5.4	5.5	11.0	11.7	1.4	0.3
4	90	air	0.9209	52	9.9	4.7	11.4	11.7	1.5	0.2
5	30	vacuum	0.9161	54	3.8	3.8	10.6	11.3	0.9	0.1
6	44	vacuum	0.9169		6.0	5.1	10.9	11.5	1.0	0
7	64	vacuum	0.9181	53	11.3	5.6	11.4	11.7	1.1	−0.1
8	80	vacuum	0.9204	50	13.6	7.5	11.6	12.0	1.3	0.2

[a] Calorimetric method.[10]

oxidation of the polymer also occurs. In the range of irradiation doses used in this study, the degree of chain scission as determined by tensile measurements was very small compared to that of crosslinking and was therefore considered negligible.

Infrared and differential scanning calorimetry measurements were performed on air- and vacuum-irradiated polymer to follow the chemical and physical changes induced by gamma ray irradiation. The infrared spectra of air-irradiated polyethylene showed a peak at 5.8 microns which could be attributed to the presence of carbonyl groups. The peak increased with increasing irradiation dose but was not observed in the spectra of the vacuum-irradiated samples. When polyethylene is irradiated in air, the radicals produced react with oxygen to give various oxygenated species such as carbonyls, hydroxyls, and peroxides. The magnitude of the carbonyl peak as compared to that of the other species indicated that this was the predominant reaction. It has been reported that the formation of the oxygenated species leads to a reduction in crosslinking in air-irradiated polymer.[9]

The weight per cent crystallinity of the irradiated polyethylene was determined by the method of Dole.[10] The magnitude of the thermogram peak determined by differential scanning calorimetry depends on the amount of crystalline material in the polymer. In the present study, it was found that the areas of the thermograms for irradiated polyethylene remained fairly constant up to 90 Mrads although the melting point decreased for the highly irradiated polymers. The peaks for these samples also broadened, indicating a possible change in the size distribution of the crystallites. It was concluded that the irradiation doses used in this study had only a slight effect on the total weight of crystalline material present in the polyethylene.

Gas Transport in Irradiated Polyethylene

Pure-Component Gas Permeation

To determine the permeation properties of the air- and vacuum-irradiated films, samples were examined by the time-lag method and by gas mixture separation studies. Bixler et al.[11] have discussed the validity of using the time-lag method for diffusion in air-irradiated polyethylene. In this study it was assumed that the processes of crosslinking, oxidation, and unsaturation took place at random through the polymer. For an average run, the 95% confidence limits on the permeability and diffusion coefficients as measured by the time-lag method were ±8%. The solubility coefficients were subject to greater error since they were derived from the permeability and diffusion coefficients.

The results of the pure-component gas permeation through the air- and vacuum-irradiated films are shown in Figures 2 and 3. In each case, the permeabilities of the air-irradiated films were higher than those of vacuum-irradiated films. It can also be seen that the permeabilities of both air-and vacuum-irradiated films decreased with increasing irradiation dose. Significant differences in permeability did not occur until irradiation doses of 10–20 Mrads were reached. From the results in Table I, it can be seen that the densities of the highly vacuum-irradiated samples were slightly greater than those of the air-irradiated samples, although the crystallinity was not altered to any great extent by either treatment. This indicates that a tightening of the polyethylene structure due to crosslinking occurs to

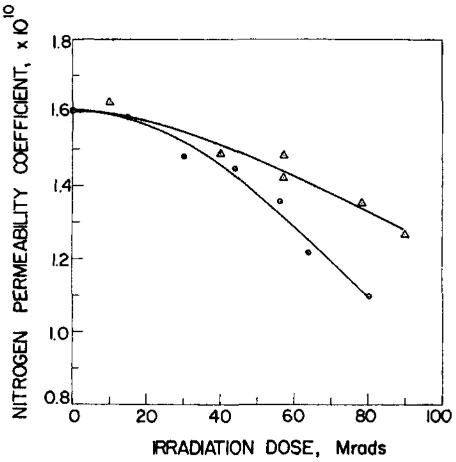

Fig. 2. Nitrogen permeability coefficients in gamma-irradiated polyethylene film at 30°C: (Δ) polyethylene film irradiated in air; (O) polyethylene film irradiated in vacuo. Film temperature 30°C; units of permeability coefficient, cc(STP) cm/cm Hg sec cm^2.

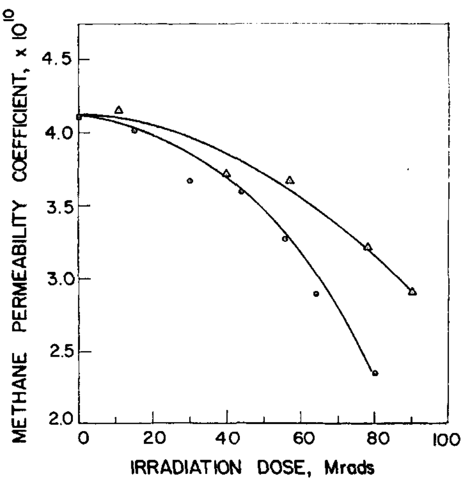

Fig. 3. Methane permeability coefficients in gamma-irradiated polyethylene film at 30°C: (Δ) polyethylene film irradiated in air; (O) polyethylene film irradiated in vacuo. Film temperature 30°C; units of permeability coefficient, cc(STP) cm/cm^2 cm Hg sec.

a greater extent in vacuum-irradiated samples than in air-irradiated film. To gain further insight into the difference between the two types of film, measurements of the diffusion and solubility properties of the irradiated films were carried out.

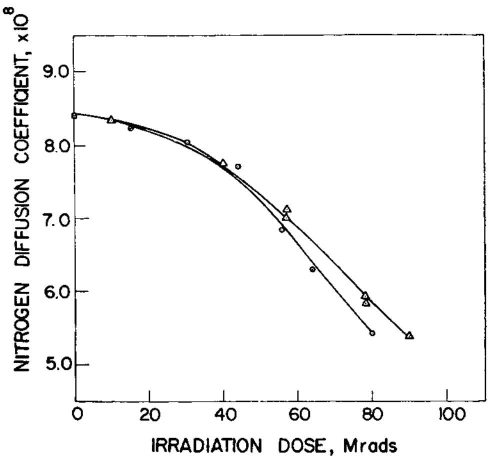

Fig. 4. Nitrogen diffusion coefficients in gamma-irradiated polyethylene films at 30°C: (Δ) nitrogen diffusion coefficient in air-irradiated film; (O) nitrogen diffusion coefficient in vacuum-irradiated film. Film temperature 30°C; units of diffusion coefficient, cm^2/sec.

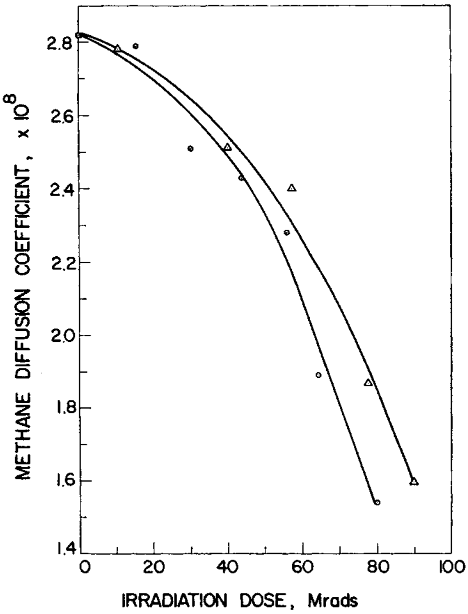

Fig. 5. Methane diffusion coefficients in gamma-irradiated polyethylene film at 30°C: (Δ) methane diffusion coefficient in air-irradiated film; (O) methane diffusion coefficient in vacuum-irradiated film. Film temperature 30°C; units of diffusion coefficient, cm^2/sec.

From Figures 4 and 5, it can be seen that the diffusion coefficients for nitrogen and methane for both types of films decreased with increasing irradiation dose. Above 40 Mrads, the vacuum-irradiated films have lower diffusion coefficients than those of air-irradiated films. Crosslinking would explain the reduction in both the permeability and diffusion coefficient. However, the formation of various oxygenated species occurs only in the air-irradiated samples. Oxidation can lead to a drop in the crosslinking efficiency for irradiations carried out in air from the following two effects: (1) the oxidative degradation of the crosslinked polymer, which corresponds to the opposite of crosslinking, and (2) the inhibition of the crosslinking process by oxygen (free-radical scavenger). Therefore, the vacuum-irradiated samples would have a higher crosslink concentration leading to a more pronounced decrease in the diffusion coefficient than for air-irradiated films.

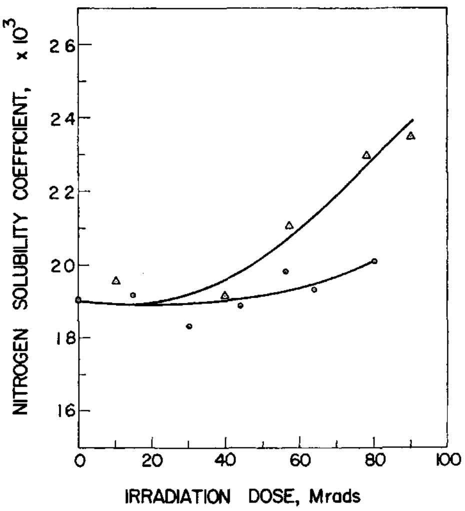

Fig. 6. Nitrogen solubility coefficients in gamma-irradiated polyethylene film at 30°C: (Δ) nitrogen solubility coefficient in air-irradiated polyethylene film; (O) nitrogen solubility coefficient in vacuum-irradiated polyethylene film. Film temperature 30°C; units of solubility coefficient, cc(STP)/cc cm Hg.

Salovey and Keller[12,13] have shown that in polyethylene the folds of the lamellae are the most susceptible to attack and that crosslinking takes place between the folds of molecules in adjacent lamellae as well as in various types of defects within the lamellae. Keller and co-workers[14] also found that chemical reactions were not restricted to the amorphous regions as was previously believed. The difference between the effects of crosslinking and oxidation would show up in the resulting changes produced in the polymer matrix. Crosslinking would decrease the lattice spacings between lamellae and reduce the mobility of the chain segments, resulting in a decrease in available free volume.

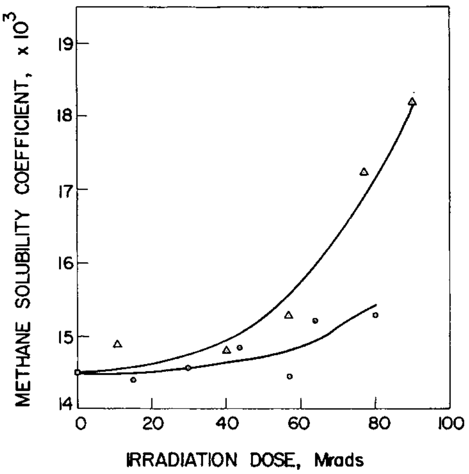

Fig. 7. Methane solubility coefficients in gamma-irradiated polyethylene film at 30°C: (△) methane solubility coefficients in air-irradiated polyethylene film; (O) methane solubility coefficient in vacuum-irradiated polyethylene film. Film temperature 30°C; units of solubility coefficient, cc(STP)/cc cm Hg.

The nitrogen and methane solubility coefficients in irradiated polyethylene are shown in Figures 6 and 7. The solubility of both gases in air-irradiated polyethylene increased significantly with increasing irradiation dose. Bixler[11] has attributed this increase to the chemical changes in the polymer induced by oxidation and found no evidence of crystallite disruption. Since oxidation decreases the amount of crosslinking in this type of film, any contribution in solubility from such crystallite disruption would be very slight. However, for vacuum-irradiated samples, there is a slight increase in solubility which is not significant until irradiation doses of 50–60 Mrads have been reached. Since crosslinking occurs in both types of films, it would appear that there may be a slight contribution to solubility resulting from crystallite disruption at high irradiation doses.

The Arrhenius plots of the nitrogen and methane diffusion coefficients gave linear relationships, as shown in Figure 8. Similar plots of the permeability and solubility coefficients also gave linear results. Activation energies of diffusion, heats of solution, and pre-exponential factors are given in Table I. It was found that the temperature dependence of the diffusion process could be described by

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

where D is the diffusion coefficient, D_0 is the pre-exponential factor, E_a is the apparent activation energy of diffusion, and R and T are the gas constant and temperature, respectively. Similar expressions were found to adequately describe the temperature dependence of the permeability and solubility coefficients in the temperature range investigated in this study.

For samples irradiated up to 40 Mrads, the activation energy of diffusion increased slightly (although the data still falls within the precision limits of the experimental work). Above this irradiation dose, the increase in the activation energy was more pronounced. The increase in activation energy can be attributed to the crosslinks which join chain segments and diminish the probability of hole formation for passage of the penetrant. As the degree of crosslinking is increased, the crosslinks further restrict the segmental mobility and affect the activation energies to a larger extent.

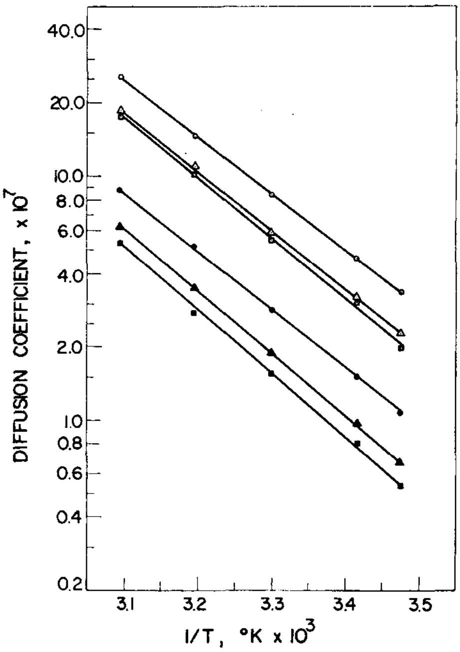

Fig. 8. Effect of temperature on the nitrogen and methane diffusion coefficients in gamma-irradiated polyethylene film: (O) nitrogen diffusion coefficient in polyethylene film; (●) methane diffusion coefficient in polyethylene film; (Δ) nitrogen diffusion coefficient in air-irradiated polyethylene film, 78 Mrads; (▲) methane diffusion coefficient in air-irradiated polyethylene film, 78 Mrads; (□) nitrogen diffusion coefficient in vacuum-irradiated polyethylene film, 80 Mrads; (■) methane diffusion coefficient in vacuum-irradiated polyethylene film, 80 Mrads. Units of diffusion coefficient, cm^2/sec.

The heats of solution were not greatly influenced by irradiation for either air- or vacuum-irradiated films.

By combining the diffusion and solubility results, it appears that the major difference in structure between the two types of film is the oxidation of the air-irradiated polymer. The presence of various oxygenated species decreases the number of crosslinks normally found in vacuum-irradiated samples. The net result is a difference between the diffusion and solubility properties of the two types of film resulting in corresponding differences in their permeation properties.

Gas Mixture Transport in Irradiated Polyethylene

The permeability and diffusion coefficients for gas mixtures were measured by the same method used for determining those of the pure components. The experimental results are given in Table II and are compared with theoretical values calculated from the following equations:

$$P_t = \frac{\sum P_i p_i}{\sum p_i} \tag{2}$$

TABLE II

Measured and Calculated Values for the Permeation of Methane–Nitrogen Gas Mixtures in Irradiated Polyethylene Films

Sample no.	CH_4/N_2 mole ratio	P calculated[a] $\times 10^{-10}$	P measured[a] $\times 10^{-10}$	D calculated $\times 10^{-8}$, cm²/sec	D measured $\times 10^{-8}$ cm²/sec	Separation factor P_{CH_4}/P_{N_2} calculated	Separation factor P_{CH_4}/P_{N_2} measured
1	1.0	2.85	2.98	3.47	3.36	2.57	2.88
2	1.4	2.78	2.95	2.95	2.99	2.50	2.65
3	1.2	2.38	2.30	2.28	2.11	2.37	2.54
4	1.2	2.17	2.24	1.98	1.71	2.29	2.37
5	1.0	2.57	2.62	3.13	3.41	2.54	2.59
6	1.0	2.52	2.43	3.02	3.19	2.48	2.57
7	1.4	2.20	2.32	2.36	2.44	2.38	2.37
8	1.4	1.83	2.10	1.80	2.11	2.15	2.03

Temperature to entire experiment 30°C.

[a] Units of permeability coefficient P: cc(STP) cm/cm² cm Hg sec.

where p_t is the steady-state permeability of the gas mixture, P_i is the steady state permeability of component i in the gas mixture, and p_i is the partial pressure of component i in the gas mixture, and

$$D_t = \frac{\sum D_i c_i'}{\Sigma c_i'} \tag{3}$$

where D_t is the diffusion coefficient of the gas mixture, D_i is the diffusion coefficient of component i in the gas mixture, and c_i' is the concentration of component i in the gas mixture.

As observed previously for the pure-component studies, the permeability and diffusion coefficients for the gas mixtures decreased with increasing irradiation dose. The coefficients of the vacuum-irradiated samples were also generally lower than those of the air-irradiated films. There was good agreement between the calculated and experimentally measured coefficients, which indicates that there was little interaction between the gases and polymer. The diffusion coefficients for the gas mixture varied more than the permeability coefficients. This was due to the larger error inherent in the time-lag determination of the diffusion coefficient.

By analysing the composition of the gas permeating through the irradiated polyethylene films by gas chromatography, it was possible to determine the extent of gas mixture separation. Experimental values obtained by this method agreed well with those derived from the permeability coefficients of the pure components. The experimental separation factors as given in Table II were obtained from the equation

$$\alpha_{CH_4/N_2} = \frac{Y_{CH_4}/(1 - Y_{CH_4})}{X_{CH_4}/(1 - X_{CH_4})} \tag{4}$$

where Y_{CH_4} is the mole fraction of methane on the low pressure side of the membrane and X_{CH_4} is the mole fraction of methane on the high pressure side of the membrane. From this definition, it can be seen that a separation factor greater than 1 would indicate a higher rate of permeation of methane than for nitrogen gas. Any decrease in this factor would signify a decreased rate of permeation of methane relative to that of nitrogen. It can be seen that the separation factors of vacuum-irradiated polyethylene film decreased more rapidly than those of the air-irradiated polymer. The effect of crosslinking and oxidation appears to have reduced the methane permeability more rapidly than that of nitrogen.

For vacuum-irradiated samples, the separation factors for 2-mil and 10-mil films were the same within experimental error. However, for air-irradiated film, the separation factor of the 2-mil film was higher than that for the 10-mil film. This can be explained in terms of the difference in the relative oxidation states of the two films. Since oxidation effects are limited to the rate of diffusion of oxygen in the polymer, it is apparent that the thicker the sample, the less the oxidation at the same irradiation dose. The oxidation would decrease the crosslinking in the 2-mil sample to a greater degree than that in the 10-mil sample.

CONCLUSIONS

The difference in gas permeability between the two types of irradiated polyethylene can be explained by a reduction in crosslinking caused by the oxidation of the air-irradiated polymer. The reduced crosslink density leads to a higher diffusion coefficient than that observed in vacuum-irradiated film. The formation of oxygenated species in the air-irradiated polymer leads to increased gas solubility by chemical changes in the film. A slight increase in solubility in highly vacuum-irradiated samples may be the result of minor crystallite disruption caused by crosslinking.

The irradiation of polyethylene in air and in vacuum decreased both the total permeability and separation factor of a methane–nitrogen gas mixture. The results of the present investigation have shown that in the absence of significant gas–polymer interactions, the separation factors for a particular film and gas mixture can be predicted from single-component permeation results. The predominant factor that influences the separation characteristics is the change in diffusion coefficients, since there is only a very small change in the solubility coefficients. Crosslinking by gamma ray irradiation can be used to improve the separation factor in noninteracting systems if there is a significant difference in molecular size and shape between the permeating molecules. The crosslinks would affect the diffusion of the larger molecules to a greater extent than that of the smaller molecules and therefore result in an increase in the separation factor. In order to increase the separation of a gas mixture using a particular polymer film, it is necessary to modify it in such a manner that the diffusion and/or the solubility of one of the components is changed substantially relative to the other permeating component.

The research for this paper was supported in part by the Defence Research Board of Canada, Grant Number 7550-06. P. J. F. Kanitz wishes to thank the National Research Council of Canada for the award of scholarships in 1967–68 and 1968–69.

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Received July 30, 1970