Enhancing the Permeation Characteristics of Polyethylene by Membrane Irradiation in the Fully Swollen State*

RICHARD D. SIEGEL, *Northern Research and Engineering Corporation, Cambridge, Massachusetts 02139*, and ROBERT W. COUGHLIN, *Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015*

Synopsis

Fully swollen, low-density polyethylene films were irradiated, vacuum dried, reswollen, and subsequently permeability tested using tritiated toluene and benzene as penetrants.   The treatment improved the permeability of polyethylene up to 88%, with the enhancement strongly dependent on the choice of the irradiation solvent.   These results suggest a potentially practical process for improving the performance of semipermeable membranes.

INTRODUCTION

It has been reported[1,2] that selective permeability for paraxylene from a mixture of ortho-, meta-, and paraxylene was conferred upon a polyolefin membrane by maintaining (annealing) the membrane in contact with pure paraxylene at a temperature somewhat below the dissolution temperature of the polyolefin in that solvent.   The success of this treatment results from recrystallization and other molecular rearrangement that occurs during high temperature annealing.   During the recrystallization, larger crystallites are believed to form at the expense of smaller ones, thereby leaving larger intercrystalline amorphous regions.   These changes presumably lead to a significant increase in the ability of the polymer to swell after annealing and therefore to an even greater increase in its permeability.

More recently, Michaels and co-workers[3] have extended this kind of membrane conditioning to other solvents and were able to increase permeability, with up to a 15-fold increase relative to untreated membranes, but with reduced selectivity toward the permeants.   However, these enhanced permeabilities are not permanent.[11]

The experiments outlined here[4-6] show that when solvent annealing of a polyethylene film is accompanied by irradiation with cobalt 60 gamma ray

* Presented at the Third Joint Meeting of the American Institute of Chemical Engineers and the Puerto Rican Institute of Chemical Engineers, San Juan, Puerto Rico, May 19, 1970.

photons, with the film still in contact with the annealing solvent, permeabilities are greatly increased. Annealing by itself produces an enhanced permeability that diminishes with time after the film is removed from contact with the annealing solvent. However, the results reported here demonstrate that combining irradiation with annealing not only enhances permeability beyond that caused by annealing alone, but also that the enhancement is a far more permanent property of the polyolefinic film.

Effect of Irradiation on Polymer Membranes

Depending upon the dose rate, irradiation of polymers has been shown to cause either crosslinking or scission of polymer chains.[7,8] Furthermore, in the presence of oxygen, irradiation can form peroxides which in turn may initiate postirradiation reactions including chain scission.

Three types of reactive species can be formed during polymer irradiation: ions, free radicals, and peroxides. As discussed by Chapiro,[7,8] the primary interaction of radiation with matter will lead to the formation of excited molecules and positive ions, that is:

$$AB \rightsquigarrow AB^+ + e \qquad (1)$$

and

$$AB \rightsquigarrow AB^* \qquad (2)$$

The electrons liberated by reaction (1) also carry kinetic energy and may in turn ionize or excite many more AB molecules. Ultimately, the electrons lose most of their kinetic energy and become thermalized—either attaching themselves to a neutral molecule

$$AB + e \rightarrow AB^- \qquad (3)$$

or

$$AB + e \rightarrow A^{\cdot} + B^- \qquad (4)$$

or recombining with a positive ion from reaction (1)

$$AB^+ + e \rightarrow AB^{**}. \qquad (5)$$

Finally, the excited molecular species formed in reactions (2) and (5) may themselves dissociate to form radicals

$$AB^* \rightarrow A^{\cdot} + B^{\cdot} \qquad (6)$$

which in turn may interact with other radicals in a polymer to bind chains together by crosslinking.

Tracer Technique

Many studies to determine the diffusion coefficient for transport through polymer films utilizing time lag techniques[9] have been undertaken in recent years. Virtually all of these studies have required a pressure difference

across the membrane, with permeability being calculated from the rise in pressure with time on the low pressure side of the polymer.   The radiation differential approach[4-6, 10] has a decided advantage over this and other measurement procedures in that it presents a rapid and accurate means of calculating membrane transport properties without the need for highly complex laboratory procedures.

Tritiated toluene and benzene, the labeled penetrants used in this work, can be detected with great sensitivity efficiency and discrimination using liquid scintillation spectrometry.   A given sample is counted for a preset time period.   This count rate, divided by the efficiency, is the sample activity, or the number of tritium molecules which have decayed in unit time.   By dividing this activity of a sample by its volume, one computers the radioactivity concentration of the sample.   Permeabilities, diffusivities, and solubilities can then be calculated from a plot versus sampling time of this radioactivity concentration as measured on the low concentration side of the membrane.[4]

EXPERIMENTAL

Polyethylene films were pretreated by soaking for about 48 hr in solvent, and then, while the films remained in the same solvent, they were irradiated in a gamma ray field from cobalt 60 at a dose rate of about 10^6 rad/hr for different lengths of time.   After irradiation, the films were usually dried before placing in the permeation medium if that medium was different from the irradiation medium; if the permeation medium was identical with the irradiation medium, no attempt was made to dry the film, except as noted below.

All permeation measurements and annealing of films were carried out at 30.0°C.   During irradiation, the temperature of the medium fluctuated between 33°C and 38°C; the higher temperatures were due to heating from the gamma ray field, but they were insufficiently large to account for the observed increases in permeability.

To measure permeability, polyethylene films was placed between two compartments containing the same liquid—the permeation medium. After the film had equilibrated with the permeation medium for about 48 hr, a small amount of tritium-labeled permeant was introduced on one side of the membrane, and its passage through the membrane was measured using the radioactivity counting techniques previously discussed.   Permeabilities were computed from the data, and the discussion below is in terms of these measured permeabilities.   This techique eliminated nonuniformity along the transport path within the films and yielded transport rates for films fully and uniformly equilibrated with the liquid permeation medium. Experimental procedure and apparatus have been described elsewhere.[4, 10]

It should be emphasized that the experimental technique used in this work does not precisely simulate the physical situation met in many practical permseparation processes.   In the present work, the membranes

were homogeneously solvated to eliminate nonuniformities in transport properties along the permeation path. Although this usually is not the situation in practical membrane processes, there is no reason to suspect that the effects reported in the present work should not also be observed, at least qualitatively, in practical situations where membrane solvation is not uniform. Moreover, membrane permeation is often considered for separation where concentration driving force is small, and it is clear that the solvation of the membrane would be more uniform the smaller the concentration difference across the membrane.

The polymer film used in the tests described here was a low-density (0.915–0.917 g/cc) general-purpose polyethylene film nominally 5 mils thick, supplied by the Extrudo Film Corporation. The film was pretreated by a corona discharge to accept ink or glue on one side. Swollen and dry film thicknesses were measured to ±0.1 mil on a Federated Capacitance Gauge. Increase in thickness due to swelling ranged from 0.1 to 0.3 mils for these films, with the amount of increase dependent on the choice of the swelling solvent.

RESULTS

The results given in Table I are identified by the label $X_1X_2(t)X_3$. Position X_1 identifies the permeant or tracer molecule, X_2 identifies the irradiation medium, and X_3 identifies the permeation medium. The number in parentheses (represented by t) gives the number of hours the film was irradiated while it was in solvent X_2. The following code is used: C = cyclohexane, T = toluene, B = benzene, A = air; 0 in position X_2 means that the film received no irradiation treatment. Example: TC(3)C refers to permeation of toluene through a film irradiated 3 hr while in cyclohexane, with cyclohexane also serving as permeation medium in subsequent permeation measurement.

From a regression analysis and an estimate of the experimental errors in sampling, film thickness, and volume measurement, the values of permeability in this research are estimated to have an accuracy of about ±7% at the 95% confidence level.

The data in Table I are also plotted in Figure 1, where the effects of irradiation in solvent on increasing permeability (P) are evident. The blank tests (runs 20, 25; no irradiation) also showed an improvement in permeability, reaching approximately to the level corresponding to a 1-hr dosage of gamma radiation. Interestingly enough, a film swollen in cyclohexane, irradiated in cyclohexane for 3 hr, and permeability tested in cyclohexane showed approximately the same percentage improvement in permeability (run 28, TC(3)C; 24.1% increase) as one swollen in toluene, irradiated in toluene for 3 hr, and permeability tested in toluene (run 29, TT(3)T; 20.0% increase). The two experiments with films irradiated in air (runs 30, 31; TA(3)T) showed virtually no change in permeability when compared with similar membranes prepared with no irradiation

TABLE I
Polyethylene Permeability Data at 30°C[a]

Run no.	Identifica- tion	$P \times 10^7$ cm²/ sec	Remarks
1	T0C	6.28	
2	T0C	6.12	
28	TC(3)C	7.73	not dried between irradiation and permeation
15	T0T	4.14	preswollen in toluene, not irradiated
20	T0T	4.87	preswollen in cyclohexane and dried before immersion in toluene for permeation studies
25	T0T	4.81	run 25 is rerun of film from run 20 after it was soaked in toluene for almost 450 hr
21	TC(1)T	4.79	
27	TC(1)T	5.31	rerun of film from 21 after solvent annealing 550 hr in toluene
22	TC(3)T	5.80	
26	TC(3)T	5.16	rerun of film from 22 after solvent annealing 500 hr in toluene
23	TC(8)T	7.00	
24	TC(24)T	7.91	
32	TC(24)T	7.61	rerun of film from 24 after solvent annealing 520 hr in toluene
15	T0T	4.14	
29	TT(3)T	4.96	not dried between irradiation and permeation
30	TA(3)T	4.37	solvent annealing in cyclohexane and dried before irradiation in air
31	TA(3)T	4.10	irradiation dry in air
T1	B0T	5.45	all of these films were dried for 6 hr between irradiation treatment and permeability measurement
T5	B0B	4.56	
T3	TB(3)T	6.42	
T2	BB(3)T	6.71	
T6	BB(3)B	5.40	
T7	BT(3)B	6.71	
T4	BT(3)T	8.08	

[a] Permeability data for low-density polyethylene films exposed to gamma radiation while fully swollen. Results are identified by the label $X_1X_2(t)X_3$ where position X_1 identifies the permeant or tracer molecule, X_2 identifies the irradiation medium, and X_3 identifies the permeation medium. The number in parentheses (represented by t) gives the number of hours the film was irradiated while it was in solvent X_2.

(run 15, TOT). That there was substantially no difference between these two air irradiation tests indicates that it is neither the preequilibration alone nor the irradiation step alone that is responsible for the improvement in the membrane's permeability; rather it is irradiation of the membranes while they are fully swollen in a given solvent that causes permeability enhancement. However, one cannot conclude, based solely on these two tests, that there is no effect on permeability due to annealing at the higher temperature in the gamma cell, nor would it be reasonable to extrapolate the results of these tests to those conducted in an oxygen-free state.
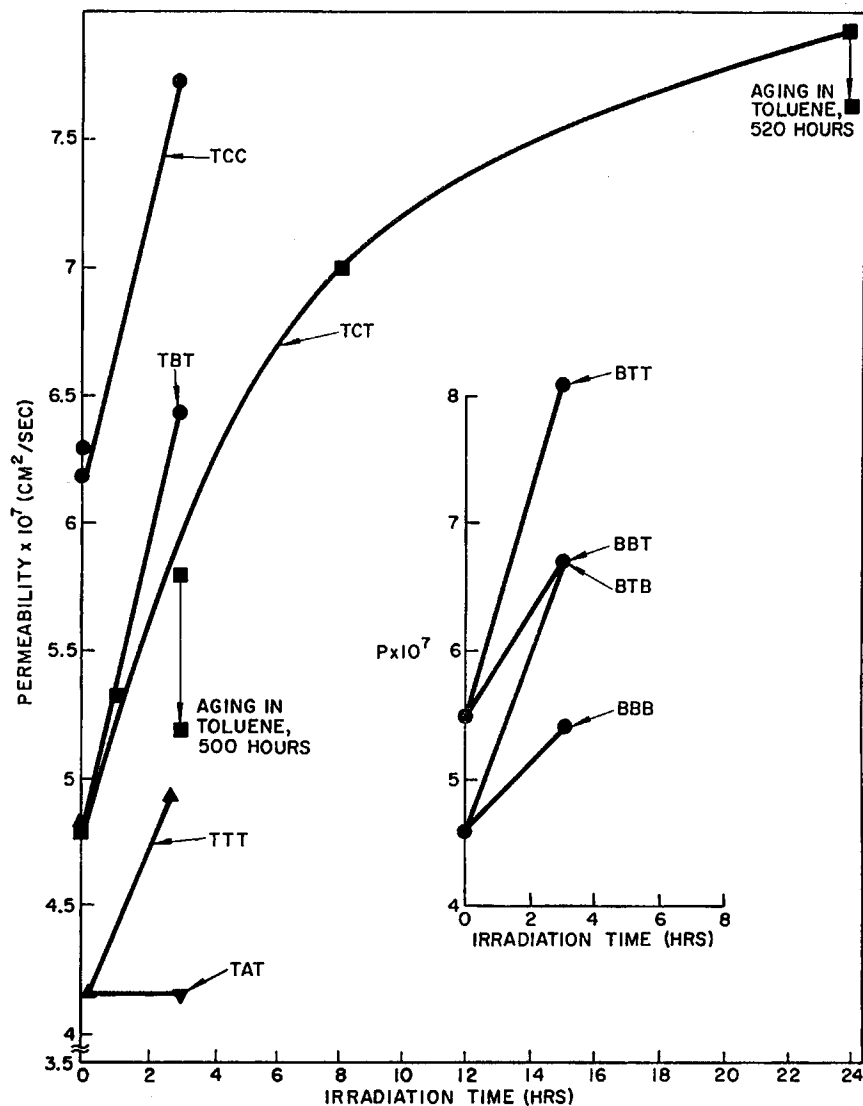
Fig. 1. Plot of the permeability data of Table I showing the effect of irradiation time on membrane permeability. Dose rate, 0.85×10^6 rad/hr; permeation temperature, 30°C.

From the data it is also possible to make an estimate of the increase in selectivity for separation of benzene from toluene which results when the film is irradiated in toluene. It is best to rewrite these results as shown in Table II. From these data it is clear that in the separation of small amounts of benzene from toluene, preirradiation of a toluene-swollen film for 3 hr increases the selectivity for benzene by about 24%. This suggests

TABLE II
Radiation Effect on Selectivity

System	$P \times 10^7$, cm²/sec	Selectivity = P_B/P_T
BOT	5.45 ⎤	1.31
TOT	4.14 ⎦	
BT(3)T	8.08 ⎤	1.63
TT(3)T	4.96 ⎦	

TABLE III
Permeability Benefaction Factors

Permeation medium	Factor	Permeation medium	Factor
BT(3)T/BOT	1.48	BT(3)BB(3)T	1.20
BT(3)B/BOB	1.47	BT(3)B/BB(3)B	1.24
BB(3)T/BOT	1.23	BB(3)T/BB(3)B	1.24
BB(3)B/BOB	1.29	BT(3)T/BT(3)B	1.21

that preirradiation of the film for longer irradiation periods might cause even larger increases in this selectivity.

Further, from data in Table I, it can be seen (Table III) that irradiation in toluene increases the membrane permeability for benzene by 47–48%, regardless of the permeation medium (BT(3)T/BOT; BT(3)B/BOB), while irradiation in benzene increases the permeability for benzene by 19–23%, also irrespective of the permeation medium (BB(3)T/BOT; BB(3)B/BOB). The degree of improvement in the permeability for benzene is thus better than 2/1 for films irradiated in toluene as compared with films irradiated in benzene. The ratios BB(3)T/BOT and BB(3)B/-BOB and the ratios BT(3)T/BB(3)T and BT(3)B/BB(3)B are further evidence that the benefaction of permeation of a given molecule (benzene) through the polyethylene is affected only by the choice of irradiation medium and is not affected by the choice of the permeation medium (benzene or toluene). That is, it appears that the final permeation solvent does not "wash out" or alter the improved performance of the membrane.

These results suggest that the permeability of a membrane will be greatly affected by the size and plasticizing effect of the solvent molecule in which the film is irradiated. Irradiation in the presence of a given solvent molecule, then, may result in crosslinking that locks in a polymeric structure with "holes" which depend in number and size not only on the size of the swelling molecule but also upon its ability to solvate the polymeric membrane.

With the exception of run T3, the data reported here indicate that membrane permeabilities are increased by the treatment solvent in the following order: cyclohexane > toluene > benzene. This is not only the order of molecular sizes but also the order of cohesive energy densities or solubility parameters of the solvents. Although it is tempting to rank the magnitudes of the phenomena reported here simply on the basis of

ability of the treatment solvent to solvate the polymer, as suggested by the order of solubility parameters, it should be remembered that Coughlin and Pollak[10] have reported the effects of eight different swelling solvents (with no irradiation) on the permeability of polyolefin membranes, and the order of these results could not be correlated with properties of the swelling solvents employed. Furthermore, although there was some suggestion of a correlation based on swelling–solvent boiling point in the previous work,[10] that idea is abrogated by the present results.

Films prepared as described here show no substantial loss of enhanced permeability after treatment by annealing plus irradiation, followed by removal from contact with the solvent; these membranes have been rechecked for permeability up to 500 hr after such treatment, and no material loss of the enhancement effect was observed. This time is about five times longer[11] than the persistence of the effect observed when no irradiation was employed.[1, 2]

When the results described here are considered together with a recent report,[3] it appears that greater enhancement of permeability may be expected than those reported here if simultaneous annealing and irradiation are carried out at higher temperatures. In the experiments described here, permeabilities were, in some cases, about doubled by annealing and irradiation at about room temperature. Michaels et al.[3] reported permeability enhancement (the nonpermanent kind) up to a factor of 14 by solvent annealing at higher temperatures. This suggests that even greater permeability enhancement (which should be permanently locked into the membrane structure) would be expected by combined solvent annealing and irradiation of polymeric membranes at elevated temperatures.

DISCUSSION

One plausible explanation of how solvent annealing may enhance permeability follows. A polyolefin film may be viewed as a system of spherulitic polymeric crystallites imbedded within an amorphous polymeric matrix. Diffusive transport within this system takes place predominantly within the amorphous part. When this system is annealed in a good solvent at an elevated temperature (but below the temperature of complete dissolution), the larger spherulitic crystallites may be expected to grow at the expense of the smaller crystallites, which simultaneously diminish. Thus the annealing process leads to larger crystals and causes the network of spherulitic polymer crystals within the amorphous polymeric matrix to become coarser. This produces a more open structure, and diffusive transport through this matrix of coarser, relatively impermeable spherulites is thereby enhanced.

Presumably, the effect of gamma irradiation upon the solvent-annealed polymer is to produce free radicals at sites both within crystallites and within the amorphous matrix. Interaction of these free radicals causes crosslinking which binds together the polymer chains within the enlarged crystallites into permanent structures that will not redissolve. Probably

this crosslinking within crystallites puckers the structure and destroys to some extent the crystalline regularity and perfection (crosslinking polymers by gamma irradiation is know to decrease crystallinity). Nevertheless, the net result would be to leave the former crystallites as dense, tightly bound-together entities. Moreover, interaction between free radicals produced within the amorphous phase and those produced at the surfaces of crystallites would be expected to bind polymer segments from the amorphous phase to the crystallites; this would produce additional holes within the permeable amorphous phase and thereby further enhance the permeability of the overall system.

It may be that the concept of crystallinity is out of place in discussions of fully solvated membranes. Rather, the process reported here may merely crosslink a fully solvated polymer, thereby providing an open network of polymeric molecules in which the chains are linked together in a way that restricts their thermal motion. Restricted thermal motion would interfere less with the passage of permeant molecules; and an expanded, solvated structure, preserved by crosslinking, would provide more abundant holes and wide passages for the movement of the transported species.

The procedure of irradiating swollen membranes appears to produce higher selectivity, i.e., a higher molecular discrimination capacity, as well as the high permeability normally associated with fully swollen polymers. The potential application of such membranes is evident in areas such as dialysis, ion exchange, reverse osmosis, and other separation processes. The authors have filed a patent application on this technique for improving the permeation characteristics of polymer membranes.

References

1. R. F. Baddour and A. S. Michaels, U.S. Pat. 3,299,157 (January 17, 1967).

2. A. S. Michaels, R. F. Baddour, H. J. Bixler and C. Y. Choo, *Ind. Eng. Chem., Prod. Res. Develop.*, **1**, (1), 14 (1962).

3. A. S. Michaels, W. Vieth, A. S. Hoffman and H. A. Alcaly, *J. Polymer Sci.*, **13**, 577 (1969).

4. R. D. Siegel, *Transport Through Fully Swollen Polymer Membranes*, Ph.D. Thesis, Lehigh University, Bethlehem, Pennsylvania, October 1969.

5. R. D. Siegel and R. W. Coughlin, *Nature*, **226**, 938 (1970).

6. R. D. Siegel, and R. W. Couglin, *J. Appl. Polym. Sci.*, in press.

7. R. F. Gould, Ed., *Irradiation of Polymers*, Advances in Chemistry Series No. 66, American Chemical Society, Washington, D.C. 1967.

8. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience, New York, 1962.

9. R. M. Barrer, *Diffusion in and Through Solids*, Cambridge University Press, Cambridge, England, 1951.

10. R. W. Coughlin and F. A. Pollak, *A.I.Ch.E.J.*, **15** (2), 208 (1969).

11. H. J. Bixler, private communication.

Revised June 19, 1970.