Effect of Ionizing Radiation on Styrene/Acrylonitrile Copolymer Hollow Fiber Membranes

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Synopsis

A thin layer of highly permeable, nonselective polymer is applied to the surface of an asymmetric membrane to reduce permeability through the membrane pores and defects and to render permeation through the matrix predominant. In environments which contain active moieties, the coating may be swollen and dissolved causing it to lose its effectiveness. The effects of irradiation to induce crosslinking between the hollow fiber membrane and the coating were studied. Fibers were irradiated both before and after coating with polydimethylsiloxane. Radiation dosages at 10, 25, and 50 Mrads were used. The increased stabilities of the cross-linked coating and substrate were reflected by the higher retention of H_2/CH_4 separation factor after exposure to a solvent (i.e., isopentane) which dissolves the coating. The results also suggest that ionizing radiation also alters the structure and morphology of the dense selective layer on the surface of the styrene/acrylonitrile copolymer hollow fiber.

INTRODUCTION

J. M. S. Henis and M. K. Tripodi developed membranes suitable for commercial gas separations by the application of a special coating procedure.[1] A thin layer of a highly permeable, nonselective polymer was applied to surface of an asymmetric membrane. This coating sufficiently reduces the permeability through the membrane pores and defects to render permeation through the matrix predominant. Consequently, performance close to that expected from intrinsic (dense film) properties of the matrix can be achieved.

As a result of this discovery, Monsanto commercialized PRISM® separators in which asymmetric polysulfone hollow fiber membranes are coated with polydimethylsiloxane.

A. Zampini demonstrated that condensation coatings which crosslink upon deposition not only improve environmental resistance of the coating but may be used to modify the permeation characteristics of the underlying membrane.[2]

The method discovered by Henis and Tripodi is general, and any matrix-coating combination with the appropriate permeability ratio can be used.[3] One such system, which was investigated in detail, was that of asymmetric hollow fiber membranes of styrene/acrylonitrile copolymer (SAN) coated with polydimethylsiloxane. Unlike polysulfone, SAN copolymer can be crosslinked by ionizing radiation[4] as predicted by the rule suggested by Miller et al.[5] Also, it is known that polydimethylsiloxanes crosslink upon irradiation.[6-10] Therefore, it seemed feasible that crosslinking induced by ionizing radiation in polydimethylsiloxane-coated SAN hollow fiber mem-

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branes should improve the chemical resistance of this system in gas streams containing reasonable concentrations of contaminants (e.g., H_2O, H_2S, hydrocarbons) accompanying the gas of interest. Yet, hopefully only small sacrifices in the permeation performance would occur.

In fact, earlier investigations suggested that radiation-induced crosslinking could be used to improve the environmental resistance of dense films and hollow fiber membranes. For example, E. V. Kirkland and J. F. Jennings noted that polyethylene films have improved permeation properties if irradiated prior to use.[11] S. Yamada and T. Takeo reported that permeation rates of benzene during pervaporation through irradiated polyethylene membranes were unchanged at dosage levels less 50 Mrads but decreased markedly at higher dosages.[12] These investigators also reported that irradiation crosslinking at dosages of 10 Mrads had little effect on either the permeation rates or separation factors of membranes made from poly(4-vinylpyridine) and polystyrene in spite of the changes in the degree of swelling and flexibility of these polymers.[13]

M. G. Katz and T. Wyderen Jr. used ionizing radiation to prepare crosslinked polyvinyl alcohol membranes in order to study their water and salt transport properties.[14] This technique also has been used to prepare ion-exchange membranes of polyacrylic acid and polyacrylate salts[15] as well as to improve the thermal stability and solvent resistance of ethylene/vinylacetate copolymer hollow fiber membranes.[16]

Therefore, it was believed that both the polydimethylsiloxane coating and the asymmetric styrene/acrylonitrile copolymer matrix could be crosslinked by ionizing radiation, both improving the environmental stability and increasing the adhesion between the coating and the substrate. These hollow fiber membranes were studied as to the changes of the gas transport properties and the susceptibility of coating removal by a solvent as a function of increasing radiation dosage.

EXPERIMENTAL

Sample Preparation

Asymmetric hollow fiber membranes were prepared and coated according to the teachings of Henis and Tripodi[3] using a copolymer of 47 wt % acrylonitrile and 53 wt % styrene. The wet fiber had a 490 μm outer diameter and a 239 μm inner diameter.

After drying, 3/8″ test cells were assembled from small bundles each made of ten 25 cm lengths of hollow fibers. One end of the bundle was encapsulated in an epoxy seal to allow the loop to be positioned in the gas testing device. The bores of the fibers at the opposite ends of the bundles were plugged with epoxy. Consequently, only gas which permeated across the fiber walls could exit from the open bores of the fibers encapsulated in the seal. Thirty-five identical test cells were made, and these were divided into seven sets of five each. One set would remain as the control, that is, it would be coated but not irradiated. Three sets would be coated and subsequently each set would be irradiated at different dose levels. The final three sets would be first irradiated at the same dosages and then coated.

Prior to coating or irradiating these test loops, it was necessary to select a range of irradiation dosages which imparted the maximum crosslinking into the fiber and coating but yet did not overly embrittle the fiber. Therefore, melt-pressed films of the styrene/acrylonitrile copolymer were irradiated at either 10, 25, 50, 100, or 200 Mrads using a 3 Mev Dynamitron to generate the electron beam. The SAN films, as later were the test loops, were treated at the facilities of Radiation Dynamics, Inc. of Westbury, New York. The samples were all placed in polyethylene bags which were purged with nitrogen to remove the air prior to heat sealing. The samples were positioned horizontally on a cart which was passed through the electron beam. During each pass the samples received a dosage of 2.5 Mrads. Each pass required 24 seconds, and the interval between each pass was sufficient to dissipate any heat generated in the fibers during exposure to the electron beam.

The irradiated films as well as an unirradiated control were weighed and placed in dimethylformamide (DMF) at room temperature for four days. Within the first day, the unirradiated control dissolved and the film irradiated at 10 Mrads became a highly swollen gel which was so weak that it was destroyed upon handling. The other extreme was encountered with films irradiated at 100 and 200 Mrads. After four days exposure to dimethylformamide, the 200 Mrad samples shattered into many small pieces. Numerous breaks and cracks were also observed in the 100 Mrad treated films, although the degree of breaking and cracking was not so pronounced as observed in the 200 Mrad films.

After the four-day DMF exposure, the films were removed from the solvent and placed in an oven for three days at 100°C to remove the solvent. The samples were then weighed, dried at 100°C for an additional day, and reweighed. The percent weight loss was calculated from the weights of the samples before and after dimethylformamide exposure. The results revealed a 40.6% weight loss for films treated with 20 Mrads, 16.5% loss for those treated with 50 Mrads, and 6.8% loss from those treated with 100 Mrads. These results are shown graphically in Figure 1. From these results it was decided to irradiate the SAN hollow fiber membrane test cells at 10, 25, and 50 Mrads using a procedure identical to that in which the films were treated.
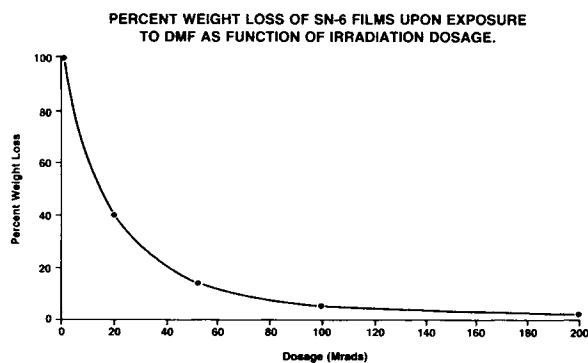

Fig. 1. Percent weight loss of SN-6 films upon exposure to DMF as function of irradiation dosage.

All of the test cells were coated from a 1% solution of polydimethylsiloxane in isopentane. The fibers were immersed in this solution for 10 min with a vacuum applied on the fiber bores at the seal end of the test cell. Then the fibers were removed from the coating solution and maintained under the vacuum for an additional 10 min to dry the coating.

As previously stated, sets of samples were coated either before or after the irradiation step.

Permeation Measurements

The pure gas permeation rates of hydrogen and methane through the hollow fiber were measured. After the samples were mounted in the gas testing device, the sample chambers were filled with either hydrogen or methane. The flux of hydrogen or methane gas through the membrane is obtained by measuring the gas emerging from the fiber bores with a mass flow meter. The measurements are made at 1000 psig at 25°C. The permeability may be calculated using Eq. (1).

$$P/l = \frac{Q \times \text{CF}}{n\pi Dl\,\Delta P}\frac{(14.7\ \text{psi/atm})}{(76\ \text{cmHg/atm})(60\ \text{s/min})} \tag{1}$$

where

P = the intrinsic permeability of the polymer,

l = effective thickness of the separating layer of the assymmetric membrane,

Q = the apparent gas flux reading from the mass flow reader $(\text{cm}^3(\text{STD})/\text{min})$,

CF = a conversion factor for the specific gas to change the apparent flux to the real flux,

n = number of fibers in a sample

D = outer diameter of fiber (cm), and

l = active length of the fibers (cm).

After the hydrogen and methane measurements were made on the samples, the samples were immersed in isopentane, a good solvent for the polydimethylsiloxane coating, for 24 h at room temperature. They were then dried overnight at ambient conditions and retested. The results are given in Table I.

The results for the unirradiated control samples are as expected. The samples which were not exposed to isopentane show moderate hydrogen permeability, low methane permeability, and high separation factor. Exposure to isopentane is sufficient to dissolve most of the polydimethylsiloxane from the surface hollow fiber (i.e., all of it on the fiber's smooth surface and most of it from the surface pores and defects). With the thin layer of highly permeable, nonselective coating removed, the permeability through the holes of the slow gas is sufficiently enhanced to dramatically alter the methane permeability .36 $\times$ 10^{-6} cm^3 (STD)/cm^2 – s – cmHg) to .88 $\times$ 10^{-6} cm^3(STD)/(cm^2 – s – cmHg). The fast gas permeability is only very minimally affected by removal of the coating. However, a drastic

TABLE I

Effect of Electron Beam Radiation on Coated SAN Hollow Fiber Membranes

Sample series[a]	Initial			After isopentane exposure			
	$(P/l)H_2 \times 10^{-6}$ cm³(STD) cm²-s-cmHg	$(P/l)CH_4 \times 10^{-6}$ cm³(STD) cm²-s-cmHG	α	$(P/l)H_2 \times 10^{-6}$ cm³(STD) cm²-s-cmHg	$(P/l)CH_4 \times 10^{-6}$ cm³(STD) cm²-s-cmHg	α	%Δ α
C	45.7 ± 2.8	.36 ± .05	129.0 ± 19.5	43.6 ± 2.3	.88 ± .29	53.9 ± 16.2	-59 ± 9
R10C	34.7 ± 4.9	.38 ± .17	105.6 ± 51.0	32.3 ± 8.2	2.0 ± .95	18.2 ± 10.3	-85 ± 2
R25C	35.9 ± 3.8	.35 ± .07	103.5 ± 10.1	34.3 ± 3.3	2.1 ± .2	16.7 ± .1	-84 ± 1
R50C	22.2 ± 4.9	.23 ± .06	101.6 ± 34.4	21.6 ± 6.8	1.7 ± .6	13.3 ± 2.6	-86 ± 4
CR10	44.8 ± 6.1	.40 ± .23	148.9 ± 86.7	39.5 ± .2	.40 ± .14	105.6 ± 37.3	-29 ± 16
CR25	42.1 ± 1.1	.47 ± .06	91.1 ± 11.5	33.2 ± 1.2	.37 ± .06	91.8 ± 12.3	-5 ± 4
CR50[b]	30.9	.4	78.5	29.1	.6	48.5	-38

[a] C = coated, no irradiation; R10C, R25C, R50C = irradiated by electron beam 10, 25, or 50 Mrads and then coated; CR10, CR25, CR50 = coated and then irradiated 10, 25, or 50 Mrads.
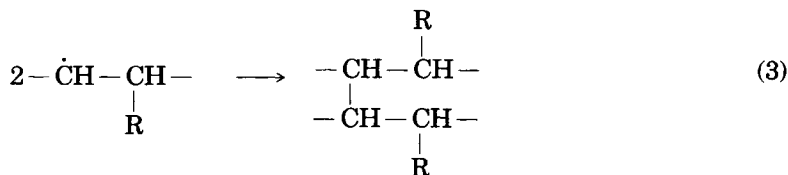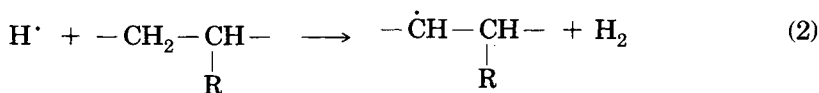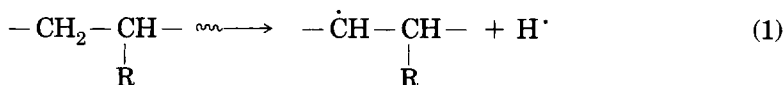[b] All samples but one exhibited leaks after irradiation.

decline in separation factor occurs. Similar results are also seen in the samples which were irradiated and subsequently coated (i.e., R10C, R25C, and R50C). All the samples revealed five- to sixfold increases in their methane permeability upon retesting after immersion in isopentane with concomitant declines in their separation factors.

However, the samples which were coated prior to irradiation exhibited negligible changes in methane permeability upon exposure to isopentane. Consequently, the fibers irradiated after coating possessed a superior retention of separation factor after exposure to active agents. Therefore, it appears that the chemical resistance of the composite is enhanced by ionizing radiation due to crosslinking of the coating and formation of chemical bonds between the coating and substrate. Unpublished results with condensation coatings on polysulfone hollow fibers suggest that both phenomena are occurring here. Condensation coatings, in which the coating polymer molecules are chemically crosslinked to each other but not to the fiber substrate, show increases in methane permeability upon exposure to isopentane. However, these increases are not so drastic as those seen with coatings that cannot be crosslinked. These increases are attributable to the swelling of polymer coating molecules in the surface pores of the fiber and their subsequent ejection (i.e., "popping out" from the pore). Upon subsequent drying of the chemically cross-linked composite hollow fiber membrane, the coating polymers do not re-enter the pore or defect as they did previously. Consequently, although the pore is still coated, the coating thickness in the pore or defect is reduced as is its effectiveness as a resistance to gas transport through the pores. Because no increases in methane permeability were observed in either the 10 Mrad or 25 Mrad samples irradiated after coating, it can be reasonably assumed that ionizing radiation not only crosslinks the polymer molecules in the coating with each other but crosslinks them with the molecules in the surface of the hollow fiber substrate.
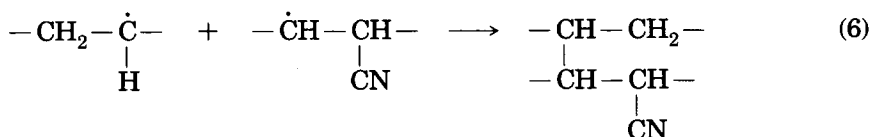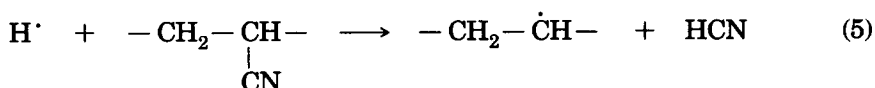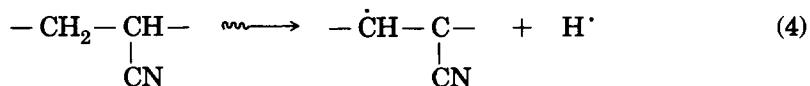
Not only does the irradiation crosslink the coating molecules to each other and to the SAN molecules in the substrate, but the SAN molecules in the substrate are also crosslinked which alters the structure and morphology throughout the hollow fiber.

The cross-linking process can be illustrated by the simplified mechanisms given in Eqs. (1)–(10). For example, the crosslinking of the acrylonitrile and styrene units may be represented by:

$$-CH_2-\underset{\underset{R}{|}}{CH}-\ \leadsto\longrightarrow\ -\underset{\underset{R}{|}}{\overset{\bullet}{C}H}-CH-\ +\ H^{\bullet} \tag{1}$$

$$H^{\bullet}\ +\ -CH_2-\underset{\underset{R}{|}}{CH}-\ \longrightarrow\ -\overset{\bullet}{C}H-\underset{\underset{R}{|}}{CH}-\ +\ H_2 \tag{2}$$

$$2-\overset{\bullet}{C}H-\underset{\underset{R}{|}}{CH}-\ \longrightarrow\ \begin{array}{c}\underset{\underset{R}{|}}{\overset{R}{|}}\\ -CH-CH-\\ \underset{\underset{R}{|}}{|}\\ -CH-CH-\end{array} \tag{3}$$
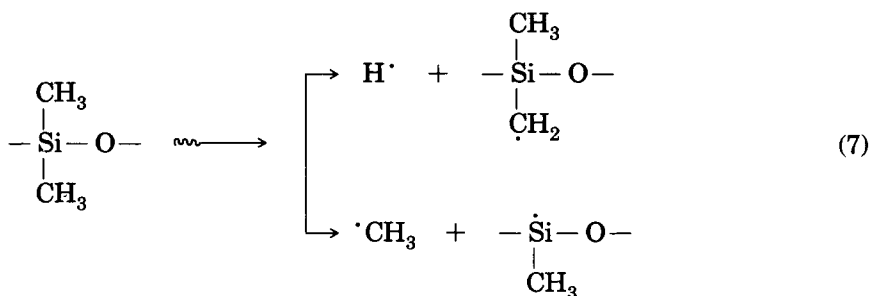
Because of the short life of the radicals, the activation results from one single absorption of energy.[17-20]
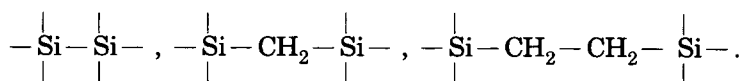
Irradiation of acrylonitrile in a nitrogen atmosphere also yields HCN.[21] Therefore, one could expect simultaneous processes of the type

$$-CH_2-\underset{\underset{CN}{|}}{CH}- \quad \leadsto \quad -\overset{\cdot}{CH}-\underset{\underset{CN}{|}}{C}- \quad + \quad H^{\cdot} \qquad (4)$$

$$H^{\cdot} \quad + \quad -CH_2-\underset{\underset{CN}{|}}{CH}- \quad \longrightarrow \quad -CH_2-\overset{\cdot}{CH}- \quad + \quad HCN \qquad (5)$$

$$-CH_2-\underset{\underset{H}{|}}{\overset{\cdot}{C}}- \quad + \quad -\overset{\cdot}{CH}-\underset{\underset{CN}{|}}{CH}- \quad \longrightarrow \quad \begin{matrix} -CH-CH_2- \\ | \\ -CH-CH- \\ | \\ CN \end{matrix} \qquad (6)$$

A similar mechanism occurs in the polydimethylsiloxane coating[7,8,22]

$$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{-Si}}-O- \quad \leadsto \quad \begin{cases} \rightarrow \quad H^{\cdot} \quad + \quad \underset{\underset{\overset{CH_2}{\cdot}}{|}}{\overset{\overset{CH_3}{|}}{-Si}}-O- \\ \\ \rightarrow \quad {}^{\cdot}CH_3 \quad + \quad \underset{\underset{CH_3}{|}}{-\overset{\cdot}{Si}}-O- \end{cases} \qquad (7)$$
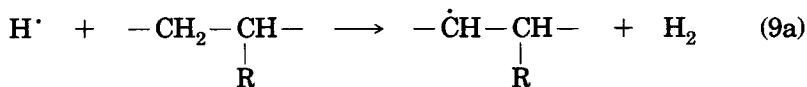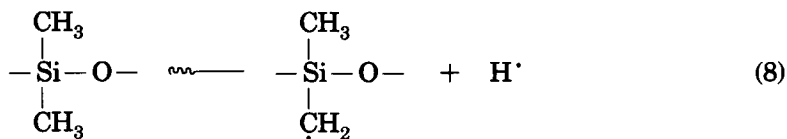
As a result of recombination of such radicals, there is a possibility of formation of various bridges between the polymer chains such as

$$-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{Si}}- \ , \quad -\overset{|}{\underset{|}{Si}}-CH_2-\overset{|}{\underset{|}{Si}}- \ , \quad -\overset{|}{\underset{|}{Si}}-CH_2-CH_2-\overset{|}{\underset{|}{Si}}- \ .$$
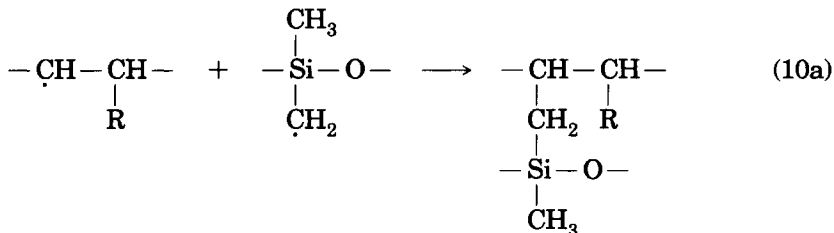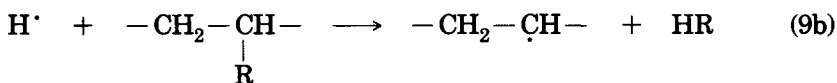
The methylene linkages occur twice as frequently as direct silicon–silicon links, and no evidence for ethylene linkages has been detected.[23]

At the coating–substrate interface, chains of both polydimethylsiloxane and polystyrene/acrylonitrile copolymer are in juxtaposition. Not only can free radicals generated in one polymer chain react to yield crosslinks with its polymeric congeners but can form crosslinks across the interface. There-
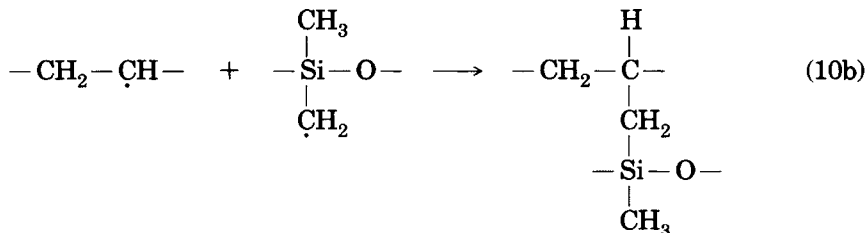
fore, one can envision interfacial cross-linking proceeding by the following processes:

$$
\begin{array}{ccc}
\underset{\displaystyle \underset{CH_3}{|}}{\overset{\displaystyle \overset{CH_3}{|}}{-Si-O-}} \quad \sim\sim\sim \quad \underset{\displaystyle \underset{\dot{C}H_2}{|}}{\overset{\displaystyle \overset{CH_3}{|}}{-Si-O-}} \; + \; H^{\displaystyle\cdot} & & (8)
\end{array}
$$

$$
H^{\displaystyle\cdot} \; + \; \underset{\displaystyle \underset{R}{|}}{-CH_2-CH-} \; \longrightarrow \; \underset{\displaystyle \underset{R}{|}}{-\dot{C}H-CH-} \; + \; H_2 \qquad (9a)
$$

or

$$
H^{\displaystyle\cdot} \; + \; \underset{\displaystyle \underset{R}{|}}{-CH_2-CH-} \; \longrightarrow \; -CH_2-\dot{C}H- \; + \; HR \qquad (9b)
$$

$$
\underset{\displaystyle \underset{R}{|}}{-\dot{C}H-CH-} \; + \; \underset{\displaystyle \underset{\dot{C}H_2}{|}}{\overset{\displaystyle \overset{CH_3}{|}}{-Si-O-}} \; \longrightarrow \; -CH-CH- \qquad (10a)
$$

with

$$
\begin{array}{c}
-CH-CH-\\
\underset{\displaystyle \underset{CH_3}{|}}{\underset{\displaystyle -Si-O-}{|}} \quad R\\
CH_2
\end{array}
$$

or

$$
-CH_2-\dot{C}H- \; + \; \underset{\displaystyle \underset{\dot{C}H_2}{|}}{\overset{\displaystyle \overset{CH_3}{|}}{-Si-O-}} \; \longrightarrow \; \underset{\displaystyle \underset{CH_3}{\underset{|}{\underset{-Si-O-}{\underset{|}{CH_2}}}}}{\overset{\displaystyle \overset{H}{|}}{-CH_2-C-}} \qquad (10b)
$$

By combining the various free radical reactions illustrated in Eqs. (1)–(10), numerous interfacial cross-linking processes may be derived.

Alterations of structure and morphology in the thin dense selective layer of the SAN hollow fiber should affect the transport properties of the membrane. Indeed, this does appear to be the case. The hydrogen permeability appears to decline with increasing dose levels as shown in the Table I. This decline is illustrated graphically in Figure 2 for fibers which had been irradiated before coating and in Figure 3 for those fibers which had been irradiated after coating. Therefore, the decline occurs regardless of the order of irradiation and coating, supporting the conclusion that the structure and morphology of the selective layer is altered. A reduction in either chain mobility or free volume in the selective layer could account for this decline in fast gas permeability.
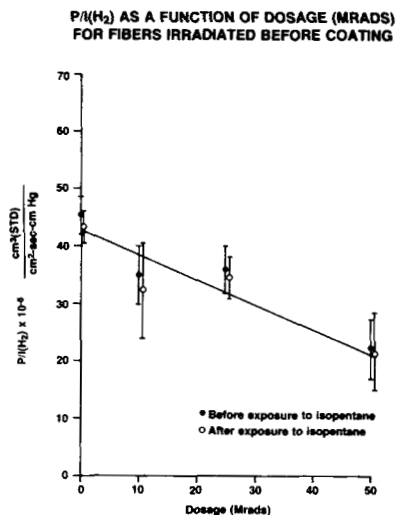
Fig. 2. Hydrogen permeability (P/l) as a function of dosage (Mrads) for fibers irradiated before coating.

Inspection of Table I also reveals that the slow gas (i.e., methane) permeability is much greater through the irradiated and subsequently coated samples after isopentane exposure than through the unirradiated control samples. In both cases, most of the polydimethylsiloxane coating would have been dissolved and subsequently removed from the selective layer at the hollow fiber membrane's surface. These differences imply that while irradiation crosslinking of the copolymer in the selective layer is decreasing fast gas transport by reducing free volume and chain mobility in the selective layer that it is simultaneously either increasing the number of defects or their average sizes to increase the slow gas transport.
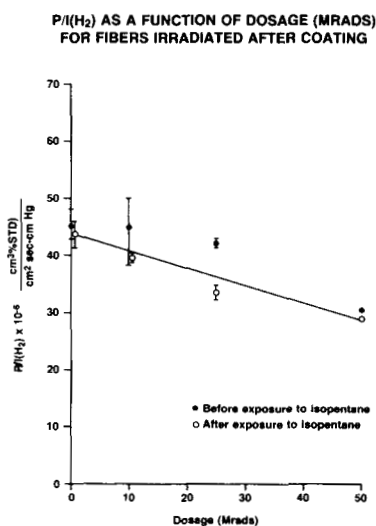

Fig. 3. Hydrogen permeability (P/l) as a function of dosage (Mrads) for fibers irradiated after coating.

CONCLUSIONS

Ionizing radiation induces crosslinking in polydimethylsiloxane-coated hollow fiber membranes of styrene/acrylonitrile copolymers. This treatment crosslinks polymer chains in both the coating and substrate and yields crosslinking between the coating and substrate. Samples which were irradiated after coating demonstrate increased stability of coating after exposure to a solvent for the coating (i.e., isopentane) as reflected by the retention of the separation factor.

The experiments demonstrated that ionizing radiation can be used to enhance coating stability and adhesion to substrates for membrane applications if both constituents are composed of polymers which undergo chain crosslinking rather than chain scission under radiation treatment.

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