Studies on Effect of Irradiation on Semipermeable Membranes

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Synopsis

The effect of γ irradiation on reverse osmosis (RO) semipermeable membranes has been studied in order to evaluate their performance under the radiation environment arising in the processing of various streams in nuclear industry by reverse osmosis process. Both cellulosic and noncellulosic membranes in dry as well as wet conditions were used. A Co^{60} source was used for γ doses from kilorads to megarads. The transport properties, namely, salt retention and water flux of membranes determined before and after irradiation, suggested deterioration in the membrane properties due to irradiation. The tensile strength and viscosity of membrane polymer also suggested membrane degradation. Differential scanning calorimetry was taken to look into any structural changes in the membrane polymer as a result of irradiation. IR spectra and X-ray of membrane polymer was also undertaken to understand the changes on the molecular level.

INTRODUCTION

Today, the membrane processes, particularly reverse osmosis, are considered for numerous applications included in nuclear industry involving separation, purification, and concentration of radionuclides from different streams. Because of the energetic radiations emitted by radionuclides, the membrane is exposed to radiation environment. In selecting a particular membrane material for any specific use in a radiation environment, a knowledge of its radiation stability is essential. The effect of energetic radiations on the physical and chemical properties of polymers has been extensively studied and reported.[1] The radiations deposit their energy at random in the parent molecule, producing ions or free radical centers. These cause further reactions, resulting in either breakdown of the molecule (degradation) or in the formation of new molecules by combining between themselves (crosslinking). Cellulose acetate polymer, which is mostly used for membrane making, is reported[2–4] to undergo degradation. However, detailed investigations on the mechanical and structural changes of these polymers, which in turn affect the transport properties, are not reported. A systematic study of radiation effects on various membrane polymer candidates, along with investigations on their transport properties under reverse osmosis conditions, has been reported in this paper. Studies were directed primarily towards the effect of γ irradiation on asymmetric cellulose acetate (CA), cellulose acetate urethane (CANCO), and polyamide (PA-300) membranes. Studies on the performance of these membranes for concentrating various radioactive solutions form part of another paper.

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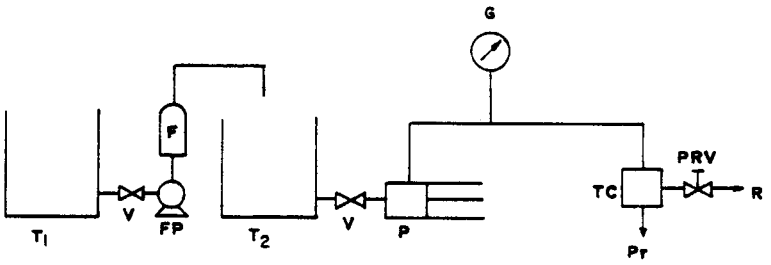

Fig. 1. RO circulation cell: (T_1,T_2) feed tanks; (FP,P) filter pump, main pump; (F,G) filter, pressure gauge; (TC) test cell; (Pr,R) permeate, reject; (V,PRV) valve, pressure regulator valve.

EXPERIMENTAL

CA membranes were prepared in the laboratory as per the Loeb–Sourirajan technique.[5] PA-300 membranes were obtained from M/s. UOP, San Diego, Calif. CANCO membranes were prepared from polymer samples procured from National Chemical Laboratory, Pune.

The radiation effects on membrane samples were studied in terms of the changes in the transport properties, tensile strength and η_{inh}. The samples were irradiated in wet condition in a Co^{60} source with a dose rate of 8 krads/min. The source was calibrated using a Fricke's dosimeter.

The transport properties were measured in terms of water removal rate ($L \cdot m^{-2} \cdot d^{-1}$) and percent salt retention using an RO circulation cell (Fig. 1) at an operating pressure of 40 kg/cm^2 with 200 ppm of sodium chloride as feed. The percent salt retention by the membranes was evaluated by measuring the conductance of feed and permeate solutions.

Relative viscosity values were determined by the falling liquid method using a Zeitfuch viscometer. These are subsequently reported as inherent viscosity. Glacial acetic acid was used as solvent for CA and CANCO membranes. Concentrated sulphuric acid was used as solvent for PA-300 membranes.

Tensile strength measurements were made using an Instron floor model tensile testing machine. The IR spectra of the membrane samples were recorded using a Perkin-Elmer model 577 spectrophotometer. DSC analysis was carried out using Perkin-Elmer DSC 1b apparatus with a heating rate of 16°K/min. X-ray diffractographs were taken using Perkin-Elmer X-ray diffractograph.

TABLE I
Transport Properties of Various Irradiated Membrane Systems

		CA		CANCO		PA-300	
No.	Dose (krads)	Water flux ($L \cdot m^{-2} \cdot d^{-1}$)	Salt retention (%)	Water flux ($L \cdot m^{-2} \cdot d^{-1}$)	Salt retention (%)	Water flux ($L \cdot m^{-2} \cdot d^{-1}$)	Salt retention (%)
1	0	254	83.1	803	92.6	324	98.3
2	200	322	85.7	—	—	—	—
3	500	244	82.4	—	—	—	—
4	1000	988	26.1	858	89.4	—	—
5	2500	692	30.1	1228	56.0	499	98.4
6	5000	—	—	—	—	875	79.5

RESULTS AND DISCUSSIONS

Transport Properties

The transport properties of various membrane systems exposed to different doses of radiations under wet conditions are given in Table I. In the case of CA membranes, the water flux is observed to suddenly increase with a corresponding decrease in salt retention around a 1000-krad dose, indicating membrane degradation. It is noticed that at a 2.5-mrad dose there is a slight reduction in the water flux with marginal increase in salt retention. The CANCO membranes are found to be relatively stable up to 1 mrad, whereas polyamide membranes show still higher radiation stability, ca. up to 2.5 mrad. Polyamide membranes also, however, show degradation in performance when irradiated to 5 mrads.

An energy of 40–100 kcal/mol is necessary[6] for breaking the various bonds in a typical polymer. For CA polymer with an average molecular weight of 40,000 a dose of 500 krads is equivalent to 50 kcal/mol. Hence performance failure beyond 500 krads in the case of CA membranes is suggestive of rapid polymer degradation, resulting in more open spaces for water and salt to pass through.

Inherent Viscosity

Determination of molecular weight or viscosity of the polymer solution helps in quantifying the extent of degradation or crosslinking. The inherent viscosity values obtained for the above membrane solutions are shown in Table II.

The inherent viscosity values are found to decrease gradually as the dose of irradiation increases for CA membranes, indicating the decrease in molecular weight of the polymer with increasing dose. For PA-300, the decrease in viscosity is noticeable beyond 1500 krad.

TABLE II
Inherent Viscosity η_{inh} of Irradiated Membrane Polymer Solutions

No.	Dose (krads)	CA	PA-300
1	0	1.27	1.87
2	200	1.28	—
3	500	1.18	—
4	1000	1.02	1.86
5	1500	—	1.75
6	2500	0.86	1.42

TABLE III
Inherent Viscosity of Dry and Wet Irradiated Polymers

No.	Dose (krads)	CA polymer		PA polymer	
		Dry	Wet	Dry	Wet
1	0	1.28	1.22	1.87	1.87
2	200	1.18	1.18	—	—
3	500	1.09	1.03	—	—
4	1000	0.92	0.75	1.86	1.86
5	1500	—	—	1.70	1.75
6	2500	0.87	0.68	1.76	1.42

Presence of Water

The effect of presence of water on the membranes during irradiation was investigated by irradiating CA and PA-300 polymers in dry as well as in wet conditions. The irradiated samples were tested for their inherent viscosity. The results are indicated in Table III.

In case of CA polymer, wet irradiation is seen to produce relatively greater damage particularly after a 1000–krad dose. In the case of PA polymer, it was found that wet irradiation produces appreciable radiation damage only beyond 2.5 mrads. These results indicate that presence of water seems to play a significant role in the degradation mechanism of CA and PA polymers. Depletion of dissolved oxygen and increasing acidity at higher doses were noticed in the irradiation medium, which is currently being investigated in greater detail to understand the chemical mechanism of degradation.

Dose Rate

The effect of dose rate on the degradation of CA membrane was investigated by using two different sources. The samples were irradiated to identical cumulative doses in the two cases, and the inherent viscosity of the irradiated polymer was evaluated. The results are shown in Table IV.

The results indicate that up to a total dose of 1000 krads the low-dose rate is associated with more detectable chain degradation under similar environments. This could perhaps be due to a higher probability of secondary events associated under low-dose-rate conditions.[1]

Tensile Strength

The tensile strength of the membrane polymer samples before and after irradiation are shown in Figure 2. The values are found to decrease with increasing dose, indicating degradation of the polymer. The figure indicates that the tensile strength starts decreasing right from the beginning of irradiation for CA as well as CANCO membranes. In the case of PA-300 membranes the tensile strength values are found to gradually decline with an increase in dose up to 5 mrads. These conform to the water flux and salt retention data obtained where a decline in performance was noted.

TABLE IV
Inherent Viscosity of Irradiated Cellulose Acetate Membranes under Different Dose Rates

No.	Dose (krads)	η_{inh} 8 krads/min	η_{inh} 3 krads/min
1	0	1.27	1.28
2	200	1.28	1.18
3	500	1.18	1.09
4	1000	1.02	0.92
5	2500	0.86	0.87

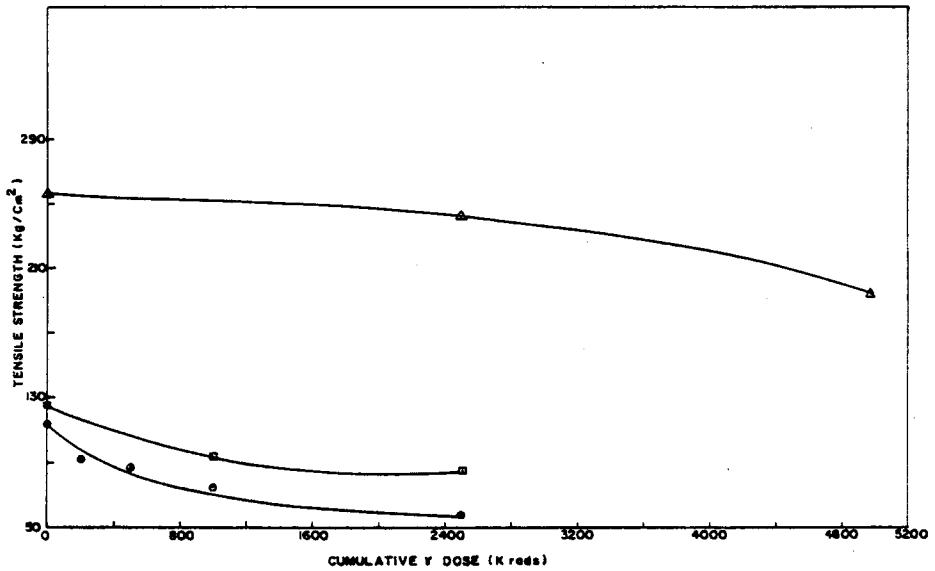

Fig. 2. Tensile strength characteristics of γ-irradiated membranes: (⊙) CA; (▲) PA-300; (⊡) CANCO.

Solubility Studies

From the transport, viscosity, and tensile strength measurements it was confirmed that CA membrane undergo degradation beyond 500 krads of dose. However, slight deviations in the observed trend in the case of water flux values, particularly at lower and higher doses, hinted at the possibility of some crosslinking. Solubility is an important criteria for determining the extent of crosslinking a polymer undergoes subsequent to irradiation. Decrease/increase in solubility of the polymer in a suitable solvent after irradiation indicates the extent of crosslinking/degradation. Solubility measurements for irradiated CA membranes in glacial acetic acid was attempted. No observable change in solubility was noticed up to 1-mrad dose. However, it was found that the solubility decreased drastically beyond 2.5-mrad dose.

DSC Studies

A DSC thermogram, obtained for CA membranes irradiated up to 1 mrad, is shown in Figure 3. All the samples show characteristic endothermic peaks around 510°K, corresponding to fusion. However, the peak melting temperatures are found to come down from 510° to 504°K with increasing dose. This decrease, along with a drastic increase in water flux data in the dose range, suggests the possibility of disordering in the cellulose acetate structure.[7] Quantitative interpretations of enthalpy changes from peak area measurements were not successful due to base line problems. Hence a decrease in crystallinity in the polymer sample after irradiation could not be ascertained.

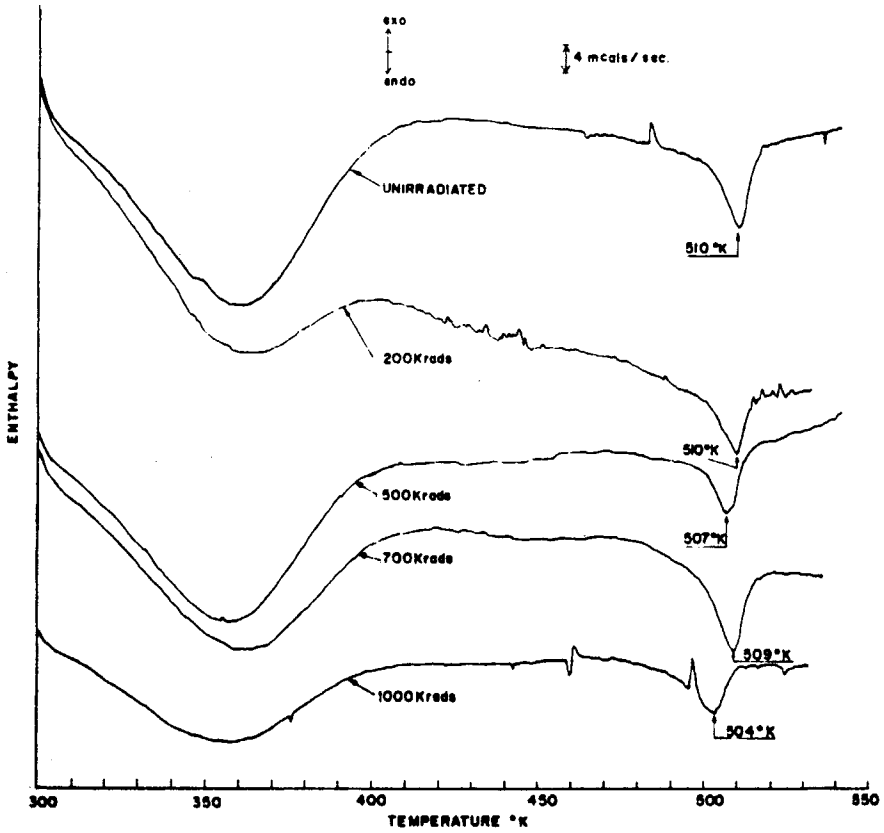

Fig. 3. DSC thermograms of irradiated CA Membranes.

X-Ray Studies

The X-ray diffractographs of CA polymer irradiated to 2.5 mrads are shown in Figure 4. The unirradiated CA polymer shows a general amorphous pattern with a characteristic peak[8] around 8°. Upon irradiation, multiple crystalline peaks were noticed between 8° and 15°. In the light of the above, the relative decline in water flux and improvement in % salt retention between 1-mrad and 2.5-mrad dose, observed in Table I, and also the drastic decline in solubility assume significance. Further investigations on this aspect is currently underway.

IR Studies

The infrared transmission spectra of the CA membrane samples were taken before and after irradiation, and the spectra obtained are shown in Figure 5. The spectra are generally found to be identical with each other, having characteristic bands at 3500 cm^{-1} (O—H group), 2940 and 2880 cm^{-1} (C—H group), 1750–1700 cm^{-1} (C=O group) and a broad band at 1400–1000 cm^{-1} (C—O group). The only difference noticeable in these spectra lies in their resolution and the depth of the absorption bands which was ascertained to the varying thickness of the samples.

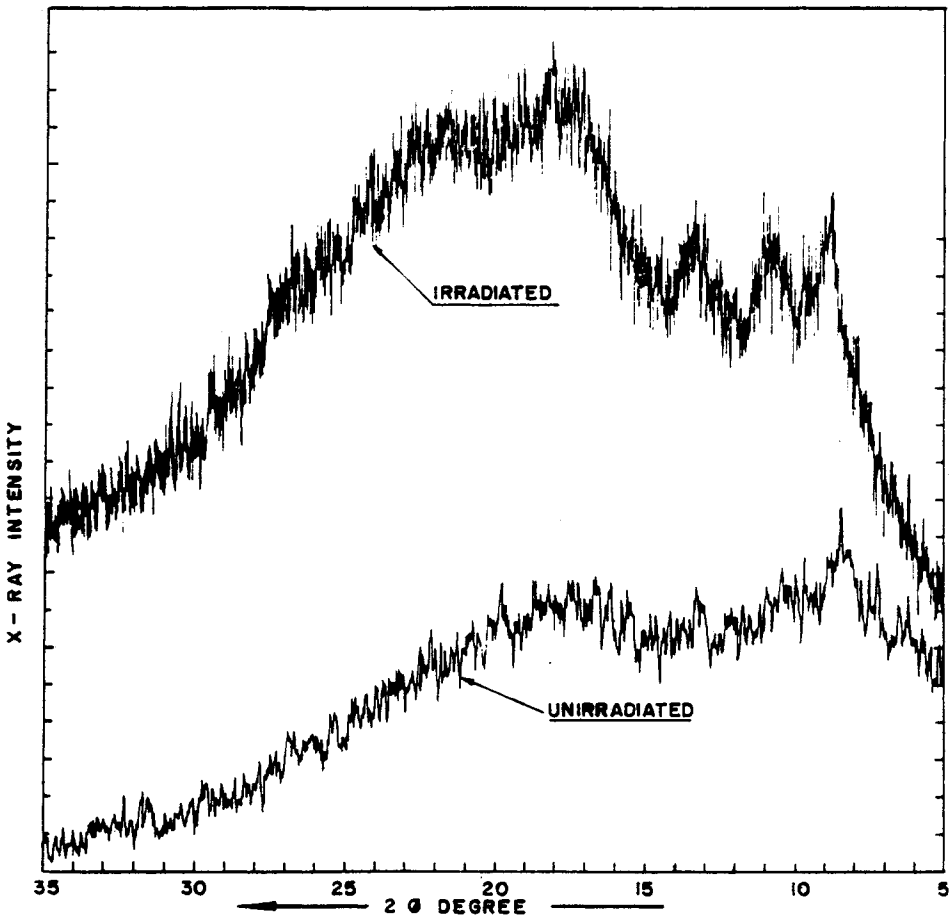

Fig. 4. X-ray diffractographs of CA polymer.

Effect of α Irradiation

The effect of α irradiation on membrane was studied. The irradiation was carried out by keeping the wet membranes in contact with an α source of 1 mCi strength for a certain duration (1 h). The water flux through the membranes before and after irradiation were evaluated and are presented in Table V.

It can be seen from the above results that the membranes do not seem to undergo any damage due to short duration irradiations. However, it is reported[9] that membranes lose their water flux characteristics when exposed to α radiation for considerably long durations (10^{-3} μci/mL solution for 24-month contact).

CONCLUSIONS

The preliminary studies on irradiation effect on semipermeable membranes carried out indicate that CA membranes undergo degradation beyond a dose of 500 krads. The degradation is marked by increased water flux and decreased salt retention. Viscosity and tensile strength measurements seem to confirm the above findings. Up to 1-mrad dose, the effect is observed to be mainly degradative in nature resulting in disordering of the structure. Beyond 1-mrad

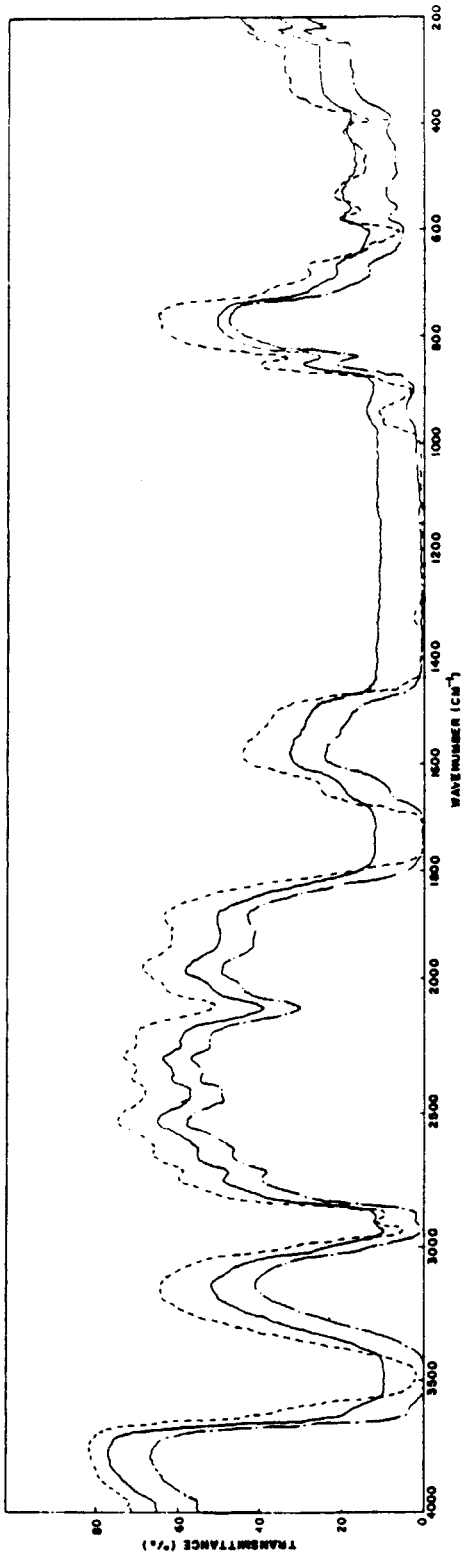

Fig. 5. IR spectra of irradiated annealed CA Membranes: (- - -) 500 krad; (—) 1000 krad; (- · -) unirradiated.

TABLE V
Effect of α Irradiation on Membranes

No.	Membrane	Water flux ($L \cdot m^{-2} \cdot d^{-1}$)	
		Before	After
1	CA (laboratory)	596	585
2	PA-300	158	153

dose, a decrease in water flux and solubility in the case of CA membranes suggests the possibility of some reordering in the structure. The DSC asnd x-ray data also support the changes reported above in different dose ranges. The IR spectra of irradiated and unirradiated CA membranes seem to be nearly similar. Presence of water during irradiation was found to adversely affect the membranes. The effect of dose rate on membrane damage was noticeable up to a certain dose limit.

The cellulose acetate urethane membranes are found to exhibit greater radiation stability compared to cellulose acetate membranes. Polyamide membranes were observed to undergo only slight degradation at higher doses.

Though cellulose and its derivatives are known to degrade in a random fashion, both in amorphous and crystalline regions, the exact mechanism of degradation is not well understood. Investigations on the identification of free radicals by ESR spectroscopy to understand the mechanism of radiation degradation and on the dose rate kinetics are presently being carried out.

The observed degradation effect of CA membranes beyond 500 krads suggests it to be the limiting dose for processing radioactive liquid streams. Polyamide membranes could be used in comparatively higher radiation environments.

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