

Studies on the Radiolytic Degradation of Cellulose Acetate Membranes

V. RAMACHANDHRAN and B. M. MISRA, *Desalination Division, Bhabha Atomic Research Centre, Bombay 400 085, India*

Synopsis

The effect of γ -irradiation on the performance of wet cellulose acetate membranes in the dose range of 2.5–10 Mrads was investigated using a ^{60}Co source. Changes in transport properties and inherent viscosity of the membranes suggested continued degradation as a result of irradiation. Solubility and specific gravity changes accompanying irradiation indicated some sort of structural aggregation occurring at higher doses. Consumption of dissolved oxygen during irradiation and the extent of deacetylation of the membrane polymer were determined to study the kinetics of the degradative process. Analysis of the end products of irradiation was attempted by UV spectroscopy. ESR spectra of membrane polymer after irradiation were analyzed to identify the free radicals generated. A tentative mechanism of radiolytic degradation causing the observed performance failure is proposed.

INTRODUCTION

Application of reverse osmosis technology for the removal of radioactive constituents in aqueous streams generated in nuclear industry has been extensively studied¹⁻¹³ and reviewed¹⁴ during the last few years. Detailed investigations were carried out¹⁵ in our laboratory on the selectivity aspects of trace radionuclides across cellulose acetate membranes of the Loeb-Sourirajan type. Since the synthetic polymeric membranes are expected to undergo physical and chemical changes under radiation environment possibly affecting its performance, studies on the radiation stability of various membrane polymer candidates were undertaken. Effect of γ -irradiation on the performance of a few membrane samples has been investigated in the dose range of 200 to 2.5 Mrads and reported.¹⁶ The performance data expressed as % solute separation and water flux ($\text{L m}^{-2} \text{d}^{-1}$) in an RO circulation loop indicated membrane failure beyond 500 krad dose. These were further confirmed by viscosity and tensile strength measurements of the irradiated membrane polymer samples. These properties, however, only suggested the general degradation of cellulose acetate polymer network. The DSC data reported¹⁶ earlier indicated changes in the crystallinity/amorphosity of the polymer due to irradiation. Beyond 1 Mrad dose, a slight decrease in membrane's water flux with subsequent improvement in solute separation and decrease in solubility in acetic acid of membrane polymer were noted, suggesting some sort of structural aggregation taking place. The x-ray diffractographs of the irradiated membrane samples beyond 1 Mrad dose supported the above inference.

Hence it is felt necessary to carry out further studies in the higher dose ranges to understand the precise changes taking place in the membrane during irradiation. Though cellulose acetate polymer is reported¹⁷⁻¹⁹ to

undergo random degradation at relatively higher doses in both amorphous and crystalline regions, the precise mechanism of degradation is not well documented. It is understood that both degradation and deacetylation of cellulose acetate polymer could lead to the observed performance failure of the membrane during irradiation. Also it is well known that degradation of the polymer chain and cleavage of the functional groups during irradiation are basically brought out by the free radical reactions. Since oxygen is known to take part in these reactions, oxygen measurements of aqueous solution contacting membranes were attempted. Detailed investigations are also undertaken using ESR and UV spectroscopy on the formation of free radicals and the accompanying chemical changes. The resulting changes in chemical environment of the aqueous solution was also followed by quantitative analysis.

EXPERIMENTAL

Cellulose acetate membranes were prepared in the laboratory as per Loeb-Sourirajan technique.²⁰ The samples were irradiated in a ⁶⁰Co source giving a dose rate of 3 krad/min. The radiation effects on the membranes were studied in terms of changes in inherent viscosity, solubility in 50% glacial acetic acid, and specific gravity. The relative viscosity was evaluated by falling liquid method using a Zeitfuch viscometer. These values were subsequently reported as η_{inh} . Solubility and specific gravity of the membrane samples were evaluated by standard techniques.

Consumption of dissolved oxygen from the aqueous solution contacting the polymer was followed by oxygen measurements using Winkler's method. The UV spectra of the aqueous samples was recorded using Varian Super-scan 3 UV-vis spectrometer in the region 100–500 nm. The extent of deacetylation of the membrane polymer was followed by measuring the yield of acetic acid for various doses of irradiation. The ESR spectra of the membrane samples irradiated under dry conditions were taken with Varian E-line ESR spectrometer employing 100 kHz field modulation. The membrane samples were irradiated in a quartz tube at 300 K and the ESR signals were recorded at 77 K with the help of a liquid nitrogen insert dewar.

RESULTS AND DISCUSSION

It was earlier reported¹⁶ that cellulose acetate membranes undergo performance failure beyond 500 krad dose resulting in increased water flux and poor solute separation in an RO circulation loop. Similar declining trend was observed to continue at higher doses also. However, at doses beyond 6.9 Mrads it was found that the membranes became brittle.

Inherent Viscosity

The inherent viscosity values of cellulose acetate membranes irradiated to different doses in wet conditions are shown in Table I.

The results in Table I indicate that the inherent viscosity values of the membrane samples decline steadily in the early stages and drastically at higher doses suggesting degradation of the polymer network. The percent

TABLE I
Inherent Viscosity Data for Irradiated Cellulose Acetate Membranes

Sample no.	Dose (Mrads)	η_{inh} (dL/g)	% Decline in η_{inh}
1	0	1.214	—
2	1	0.983	19.03
3	2.89	0.883	27.27
4	4.41	0.596	50.91
5	6.93	0.474	60.96

decline in inherent viscosity with dose of irradiation indicates that the rate of degradation of the polymer is slow below 1000 krad. Beyond 1000 krad dose there is a drastic decline in inherent viscosity suggesting increased chain scission occurring beyond that dose. It is reported²¹ that the scission of the polymer chain length in the case of cellulosic derivatives follows from the specific bond ruptures at glucosidic linkages. Though bond breakage at other C—O joints inside the glucosidic ring is not entirely ruled out, such a rupture does not lead to chain degradation.

Solubility and Specific Gravity

The solubility and specific gravity values for cellulose acetate membranes irradiated to different doses in wet conditions are shown in Table II.

The general decline in specific gravity values and increase in solubility values support the rapid degradation of the polymer at higher doses. The changes in specific gravity values and solubility values for cellulose acetate membranes for various doses of irradiation are shown in Figure 1. A slight increase in specific gravity values around 4 Mrads dose are also noted. In the light of this, the relative decline in water flux and slight improvement in the solute separation noted and reported¹⁶ at higher doses assumes significance. The reported¹⁶ x-ray diffractographs of cellulose acetate membranes irradiated to higher doses also revealed multiple peaks between 8° and 15°. These lead to the possibility of some sort of structural aggregation at a particular dose level by the formation of bonds between adjacent polymer chains. This event is overtaken by the rapid degradation reactions at further higher doses.

Dissolved Oxygen Studies

The dissolved oxygen concentration of water in contact with the membranes during irradiation was subsequently measured, and the results are

TABLE II
Solubility and Specific Gravity Data for Irradiated Cellulose Acetate Membranes

Sample no.	Dose (Mrads)	Solubility (g/100 mL 50% HAc)	Specific gravity
1	0	—	1.063
2	2.89	1.335	1.055
3	4.41	2.121	1.235
4	6.93	1.868	0.829
5	9.99	3.068	0.539

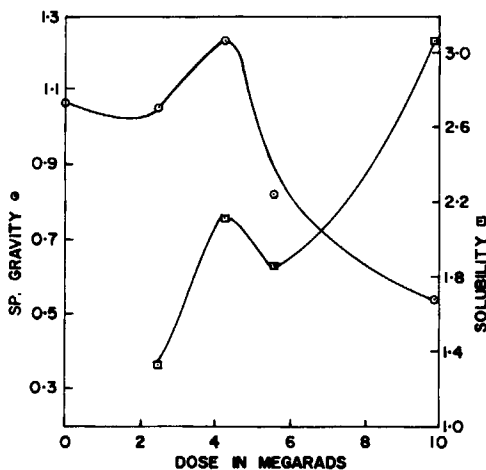


Fig. 1. Solubility and specific gravity data with dose of irradiation.

shown in Table III. The dissolved oxygen concentration in the irradiated water storing the membrane is found to fall exponentially with the dose of irradiation and beyond a dose of 1000 K rads the oxygen level falls below 0.1 ppm.

The depletion of dissolved oxygen for varying polymer concentrations under identical doses of irradiation is shown in Figure 2. It is seen that the increase in polymer concentration linearly reduces the dissolved oxygen concentration in water.

Deacetylation Studies

The UV spectra of the water in contact with the membranes during irradiation was scanned in the region of 100–500 nm and the spectra is shown in Figure 3. The spectra shows a single sharp peak around 194 nm, indicating the presence of acetic acid in the sample suggesting deacetylation of the membrane polymer.

The yield of acetic acid and percent deacetylation of the membrane for various doses of irradiation is shown in Table IV.

It is found that the amount of free acetic acid generated in the solution and percent deacetylation becomes significant above 1000 krad only. It is

TABLE III
Depletion of Dissolved Oxygen during Irradiation of Cellulose Acetate Membranes^a

Sample no.	Dose (krads)	Dissolved oxygen (ppm)
1	100	3.4
2	200	1.8
3	500	1.0
4	750	0.6
5	1000	0.2
6	2500	0.1

^a 1 g CA polymer in 125 mL distilled water.

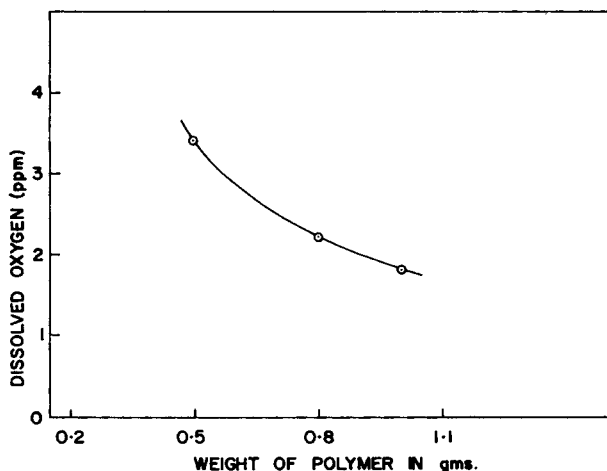


Fig. 2. Depletion of dissolved oxygen for increasing membrane/water ratio.

reported²² that the decline in transport properties of cellulose acetate membranes due to reduction of 2–3% of acetyl content is around 10–20% only. Though the degradation of acetyl radicals leading to the formation of CH_3 and $\text{CO}\cdot$ at lower doses is also possible, it appears that the observed performance failure of cellulose acetate membranes is not primarily due to deacetylation of the polymer but largely due to the polymer chain breakdown.

ESR Studies

The ESR spectra recorded at 77 K for cellulose acetate membranes after irradiation under dry conditions at ambient temperature to a cumulative dose of 3.47 Mrads is shown in Figure 4. The shape of the spectra obtained was found to be similar to those previously reported for cellulose acetate polymers.^{21,23,24} Although no attempt is made to evaluate the radical con-

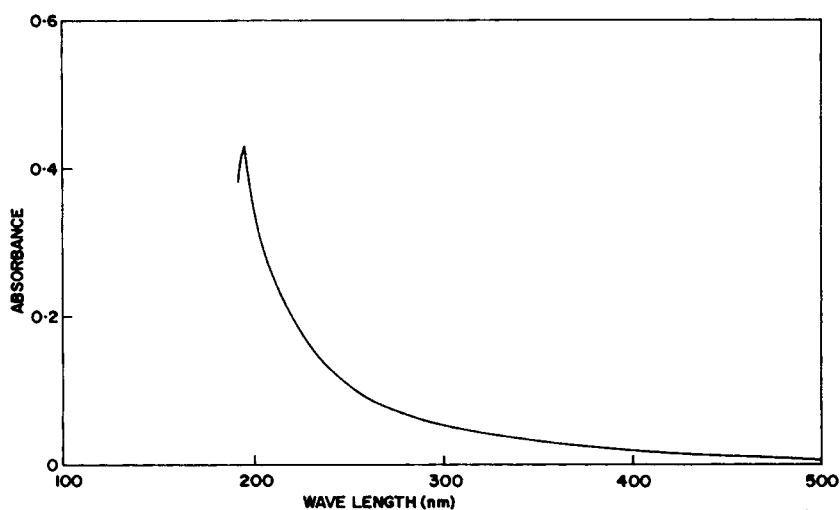


Fig. 3. UV spectra of water in contact with γ -irradiated CA polymer.

TABLE IV
Yield of Acetic Acid and Percent Deacetylation during Irradiation of
Cellulose Acetate Membranes^a

Sample no.	Dose (Mrads)	Concn of HAC (m)	% Deacetylation
1	2.5	1.45×10^{-7}	0.143×10^{-3}
2	4	2.29×10^{-4}	0.226
3	6	5.75×10^{-4}	0.568
4	8	1.45×10^{-3}	1.43

^a 1 g CA polymer in 125 mL distilled water.

centrations, identification of the free radicals, giving rise to the spectra were tried by comparing the reported ESR signals. The spectra appears to be consisting of a triplet and a quartet superimposed on a doublet signal. The doublet signal is ascribed²¹ to the formation of the radicals of the type $R-\overset{\cdot}{C}HO-\overset{\overset{O}{\parallel}}{C}-CH_3$ arising out of dehydrogenation at C₆ carbon atom of

glucosidic ring. The triplet signal could be due to the formation of a radical formed from the dehydrogenation of one of the acetyl methyl groups as follows:

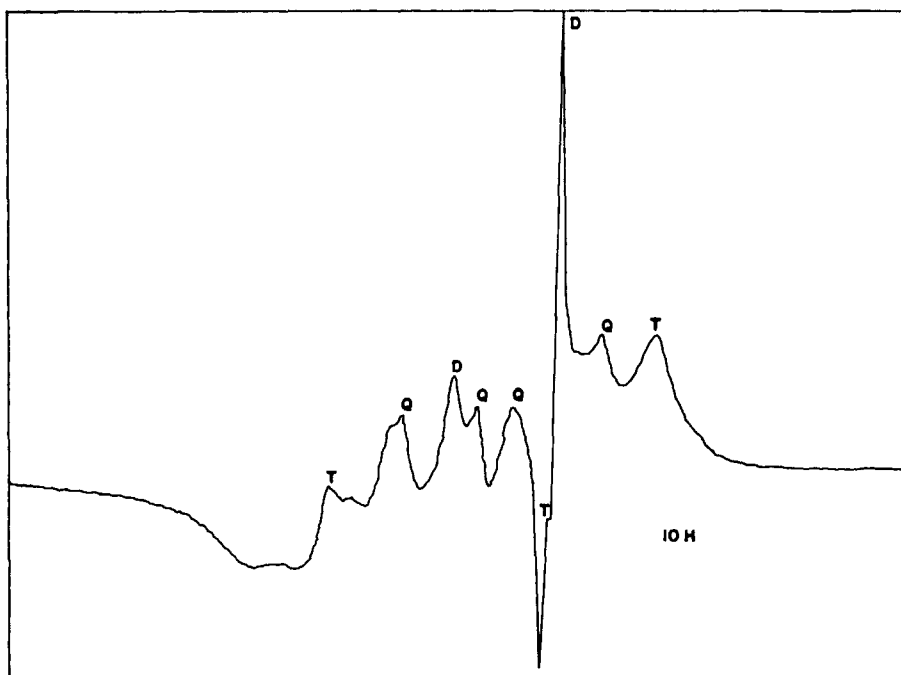
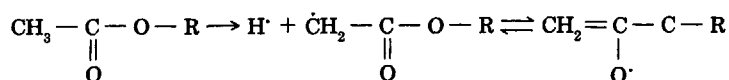


Fig. 4. ESR spectra of γ -irradiated CA polymer.

The quartet signal²⁵ could arise from either $\text{CH}_3\text{CO}\cdot$ or $\text{CH}_3\text{COO}\cdot$ radicals due to cleavage of functional group from the cellulose backbone. Though formation of both $\text{CH}_3\text{CO}\cdot$ and $\text{CH}_3\text{COO}\cdot$ radicals are equally probable, formation of $\text{CH}_3\text{COO}\cdot$ is reportedly ruled out.²¹

Tentative Degradation Mechanism

The decline of inherent viscosity, tensile strength solubility, and specific gravity values of cellulose acetate membrane polymer starting from the onset of irradiation suggest the breakage of polymer chain at the glucosidic linkages as the primary reaction in the early stages, as follows:



The observed performance failure beyond 500 krads could be primarily due to this event as the random breakage of the polymer chain creates large holes in the structure for more water and solute to pass through. The distinct difference in the rate of degradation above and below 1000 krads dose suggested by the viscosity values indicate the role of molecular oxygen in controlling the rate of degradation.

Oxygen as such is reported²⁶ to be an efficient free radical scavenger since it rapidly reacts with the free radical intermediates leading to the formation of peroxidic radicals of the following type:



The above peroxidic radicals are likely to decompose into smaller fragments (oxidative degradation), and thus oxygen would be expected in principle to enhance the yield of degradation. A comparison of Table III and Figure 1 clearly indicates that the rate of degradation of the polymer is rapid above 1000 krads dose where the oxygen level drops to very low level.

At higher doses deacetylation of the cellulose backbone and dehydrogenation at C_6 carbon atom and at acetyl methyl groups are suggested to occur along with rapid chain scission. Though deacetylation could occur at any of the C_2 , C_3 , and C_6 carbon atoms in the glucosidic ring, the possibility of deacetylation at C_6 carbon atoms is more due to the reduced reactivity of the primary links compared to the other two secondary hydroxy links:



The acetyl free radicals might be combining with the hydroxy radicals generated by the radiolysis of water releasing acetic acid in the solution:



The deacetylation of the polymer does not appear to be primarily responsible for the observed performance failure.

The structural aggregation at intermediate dose ranges suggested by the sudden reversal of transport properties and solubility and specific gravity

values could be due to some sort of structural readjustments between adjacent polymer chains by forming new bonds between dehydrogenated centers:



This effect could have been offset by the rapid chain scission at still higher doses.

CONCLUSIONS

Cellulose acetate membranes are found to exhibit performance failure under irradiation beyond 500 krads dose due to chain degradation. The degradation is observed to continue at higher doses as well up to 6.93 Mrads, after which it becomes brittle. Inherent viscosity, tensile strength, solubility, and specific gravity values of irradiated membrane polymer support this. The presence of dissolved oxygen significantly affect the rate of degradation. The rapid increase in the yield of acetic acid at higher doses suggest chain cleavage to be the primary event causing performance failure. A slight structural aggregation appears to take place briefly in the intermediate dose ranges, which is rapidly overtaken by the chain scission at still higher doses. The ESR spectra obtained for membranes irradiated at ambient temperatures indicate the presence of acetyl radicals. However, ESR signals of low temperature irradiated fibrous cellulose acetate polymers reported in the literature suggest dehydrogenation and deacetylation to take place. The studies indicate cellulose acetate membranes do not perform well at high radiation environment. This limits its possible use in separating radio-nuclides from effluents having very high levels of radioactivity.

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