

Effects of Ionizing Radiation on Perfluorosulfonic Acid Ion-Exchange Polymer

E. N. BALKO and J. T. CHAKLOS, *Direct Energy Conversion Programs, General Electric Company, Wilmington, Massachusetts 01887*

Synopsis

The effects of β and γ radiation on the Nafion perfluorinated ion-exchange polymer have been examined and the radiolysis products have been identified. The polymer degrades by simple chain scission, and the rate of degradation is not affected by the state of polymer hydration or the nature of the ion which occupies an exchange site.

INTRODUCTION

The relative fragility of fluorocarbon polymers with respect to degradation by ionizing radiation is well known. Numerous studies have described the behavior of a number of fluoropolymers when subjected to β and γ irradiation.¹⁻⁴

In recent years, a perfluorinated ion-exchange polymer, du Pont Nafion*, has become available (Fig. 1). Because of the great chemical stability inherent in the perfluorinated backbone of Nafion, it has found wide use of a cell separator in fuel cells, electrolysis cells, batteries, and other electrochemical devices.^{6,8}

There are a number of electrolysis applications, such as in the processing of tritiated water, which of necessity require exposure of the ion-exchange polymer to ionizing radiation. Similar exposure can occur where the polymer is used as a simple ion exchanger, such as in nuclear fuel processing.

While it might be inferred that much of the radiation chemistry of Nafion is similar to other perfluorinated materials, there are some substantial differences in the polymer phase.

Much greater variation in composition is possible with Nafion than ordinarily exists with other fluoropolymers. Nafion, being an ion-exchange material, will readily change its water content in response to external conditions. The different equivalent weights in which the polymer is available introduce additional variability in both the water content and the sulfonic acid functional group concentration. And, of course, the exchange sites within the polymer may be occupied by a variety of cationic species.

The relatively large quantity of water which Nafion will absorb at room temperature (28% for the 1200-EW material) suggests that the radiation chemistry of water might contribute to the overall radiation behavior of the polymer.

Hydrogen peroxide, formed electrochemically at the oxygen electrode, has been found to be capable of attacking a Nafion fuel cell separator in studies conducted in this laboratory. Irradiation of hydrated Nafion might lead to peroxide formation deep within the polymer phase. Iron (III), common in many potential applications, is a known promoter of peroxide attack and could potentially aggravate peroxide-induced deterioration of the material.

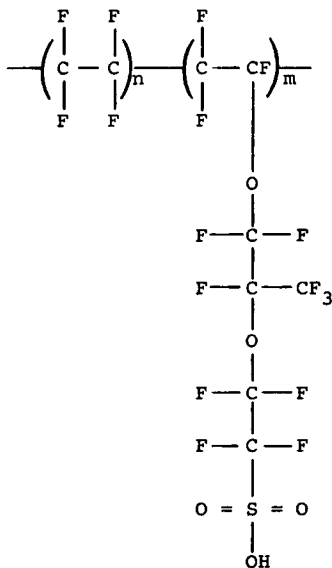


Fig. 1. Nafion ion-exchange polymer (Ref. 5).

Little, if any, information is available in the literature concerning the effects of ionizing radiation on the Nafion polymer. This study was undertaken to quantify the influence of radiation on Nafion with the polymer in different hydration states, ionic forms, and equivalent weights. The question of the contribution of peroxide attack to the overall radiation chemistry of the polymer was addressed by including among the samples irradiated in the study both a group containing a peroxide inhibitor, disperse platinum metal, and a group in the Fe (III) ionic form.

The 1200-EW material was examined in the proton, sodium, and thorium forms. The 1100-EW material was examined in the acid form only. Beta radiation was of the greater interest, and thus most of the work was done with radiation of this type. The effects of γ radiation were examined briefly with the acid form of the 1200-EW polymer.

EXPERIMENTAL

Sample Preparation

All samples were in the form of 0.25-mm-thick film and were initially brought to the acid form by immersion in 1.2M HCl, and then washed and boiled for 60 min in distilled water to achieve a standard initial condition.

The hydrated acid form samples were given no further treatment. The dry acid form samples were dried for 16 hr at 110°C in air prior to being sealed in polyethylene bags. The different ionic forms were prepared by immersion of the samples in 1M solutions of NaOH, FeCl₃ (at pH 1), and Th(NO₃)₄, respectively. The samples were then rinsed and boiled for 30 min in distilled water. The peroxide-inhibitor membranes were prepared by a proprietary General Electric process which resulted in a dispersion of finely divided platinum being distributed throughout the membrane at a density of 0.6 mg/g of dry resin.

Irradiation

Irradiation by β particles was accomplished with an electron beam process system (High Voltage Engineering Co., Burlington, MA). Samples were sealed in air, in 0.05-mm polyethylene bags during irradiation. Dosimetry was performed with a Far West Technology plastic film dosimeter; an accuracy of $\pm 5\%$ is estimated. A 20 mA beam of 500-kV electrons was used; dosages in excess of 5 Mrad were accumulated by multiple exposures over a 15-min period in order to prevent a temperature increase of greater than 20°C . For total dosages in excess of 5 Mrad, the instantaneous dose rate was approximately 150 Mrad/hr. Gamma irradiation was performed by Neutron Products Corp., Dickerson, MD, using a ^{60}Co source. The γ dose rate was 1 Mrad/hr. Dosimetry and sample containment were the same as those used for β irradiation.

Characterization Methods

Ion-Exchange Capacity and Water Content

The ion-exchange capacity was determined by the following method. Samples were equilibrated in 6M HCl, boiled in distilled water to remove imbedded acid, and reequilibrated with K_2SO_4 . The displaced protons were titrated to a phenothalein endpoint with NaOH. The water content, based on the dry weight of the polymer was taken as the weight difference before and after drying the titrated samples at 110°C .

Fluoride Yield

Samples of the irradiated polymer were placed in distilled water and brought to pH 12 by the addition of sodium hydroxide using a glass electrode. The quantity of fluoride ions released into solution was then determined by the method of Bellack and Schaubert.⁹

Tensile Properties

Samples were equilibrated with 6M HCl, washed, and then boiled for 30 min in distilled water. Specimens for measurement were die cut into test bars 0.187 in. wide. Measurements were made at an elongation rate of 2 in./min using an Instron model TM instrument. Measurements were made at room temperature with a visible quantity of water on the surface of the polymer film. Multiple measurements were made on all samples. The data reported herein are the means of at least ten measurements, except for the 100-Mrad samples, where data from no less than three measurements are reported.

Infrared Spectra

Samples which were not in the acid form during irradiation were equilibrated with 6M HCl. All samples were then washed with distilled water and equilibrated with 1M CsOH for a minimum of 10 hr. Adherent droplets of solution were wiped from the surface of the polymer films and they were dried at 110°C in air. Spectra of the 0.25-mm films were then recorded using a Perkin-Elmer model 21 spectrophotometer.

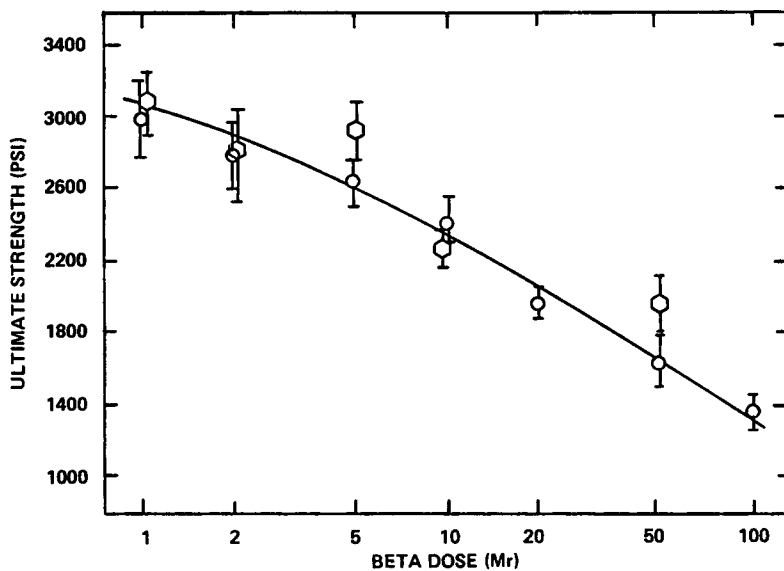


Fig. 2. Tensile strength of β -irradiated 1200-EW Nafion. ○, Nafion 120, H^+ ion form hydrated; ○, Nafion 120, H^+ ion form dry; \pm , denotes mean $\pm \sigma$.

Membrane Conductivity

The membranes were converted to the potassium ion form in the manner described for the IEC measurements, substituting KCl for the sulfate salt. The polymer films were placed in a small dialysis cell of 10.7 cm² active area, and

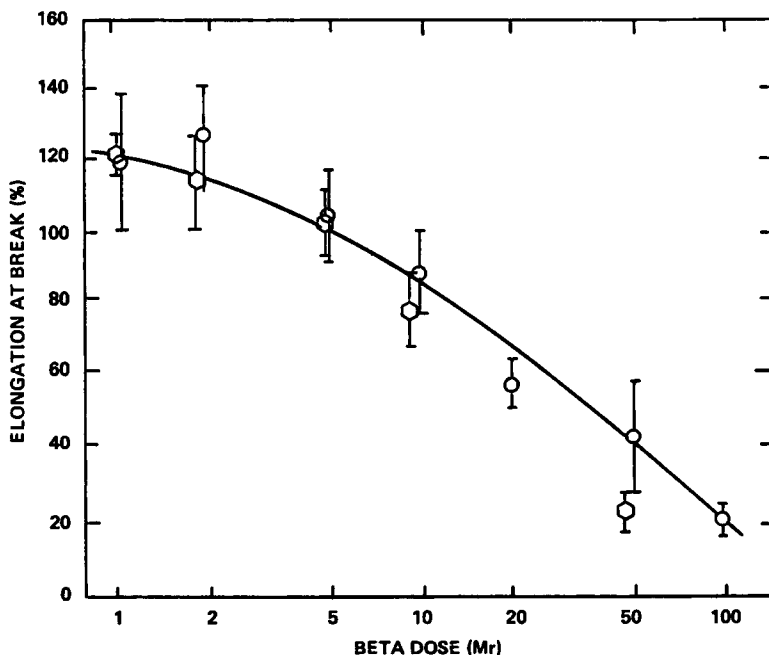


Fig. 3. Elongation of β -irradiated 1200-EW Nafion. ○, Nafion 120, H^+ ion form hydrated; ○, Nafion 120, H^+ ion form, dry; \pm , denotes mean $\pm \sigma$.

mercury was added to each side of the cell to form the test electrodes. Measurements were made at 1000 Hz and room temperature.

RESULTS

Beta Irradiation

Polymer Mechanical Properties

Figures 2 and 3 present the results of tensile strength measurements of the 1200-EW polymer irradiated in the fully hydrated and dry states. Figures 4 and 5 show similar results for the fully hydrated 1100-EW material. The data for the 1200-EW polymer in the sodium, iron, and thorium forms, as well as those for the samples containing the disperse platinum, are superimposable on Figures 2 and 3.

With increasing β dose, the Nafion polymer becomes an increasingly weak and brittle material. Despite Nafion being a branched fluoropolymer, there is no evidence in these curves (or any other parameter measured in this work) for crosslinking. In this regard, Nafion resembles linear poly(tetrafluoroethylene) rather than branched FEP (tetrafluoroethylene-hexafluoropropene copolymer). The onset of statistically significant change in Nafion occurs at about a 20-Mrad dose, a level somewhat greater than that necessary to detect a significant decrease in the mechanical strength of PTFE.

The congruence of the tensile strength versus dose curves for all forms of the polymer exposed to β radiation would imply that the mechanism of polymer degradation involves only the fluorocarbon chain, and that it is independent of the other material present in the swollen polymer phase.

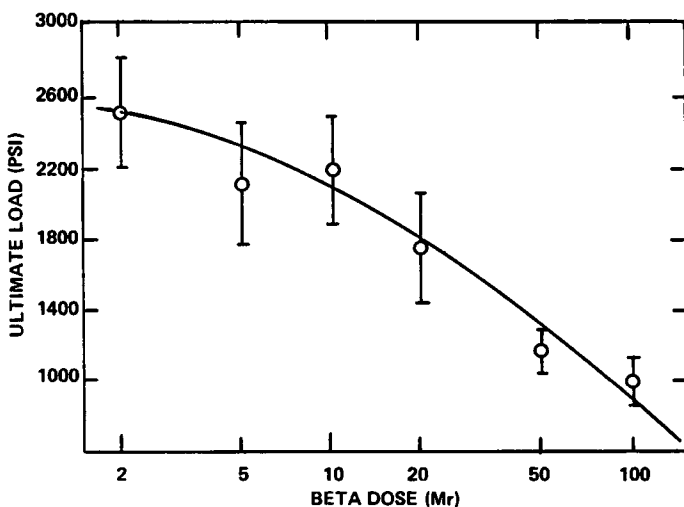


Fig. 4. Tensile strength of β -irradiated 1100-EW Nafion. \pm , denotes mean $\pm \sigma$.

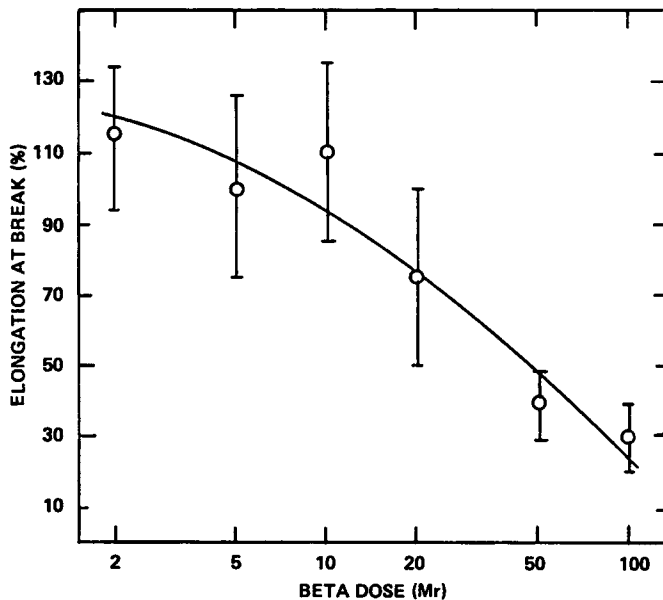


Fig. 5. Elongation of β -irradiated 1100-EW Nafion. \bar{x} , denotes mean $\pm \sigma$.

Radiolysis Products

The volatile products present after β irradiation were identified by analyzing the contents of the gas space in the sample bags using a mass spectrophotometer/gas chromatograph, immediately following exposure. The products were CF_4 , SO_2 , COF_2 , and $\text{CF}_2=\text{CF}-\text{CF}_3$, for the fully hydrated acid form of the polymer (both with and without the platinum dispersion), the dry acid form, and the sodium salt of the polymer. In addition, there were several nonvolatile products.

A considerable quantity of HF was liberated during the irradiation. Figure 6 presents the ionic fluoride yield as a function of the β dose. The slope is similar for both the 1100-EW and 1200-EW materials, having a value of 8.8×10^{-7} moles fluoride/Mrad g dry resin. The fluoride yield of the Nafion is at least an order of magnitude greater than that which has been reported for the PTFE polymer.¹

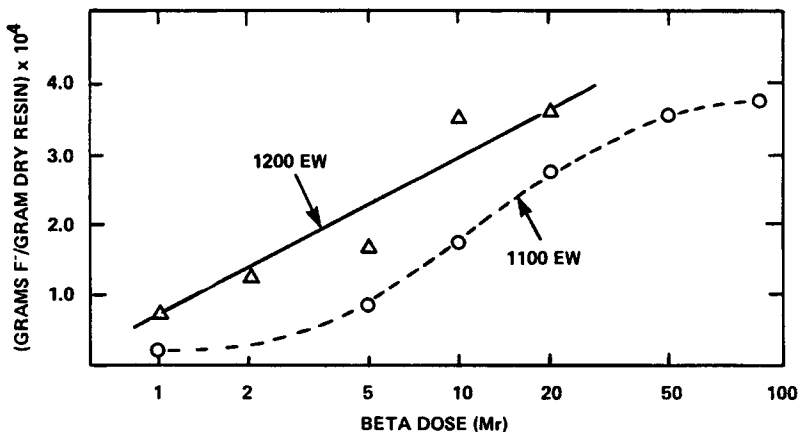


Fig. 6. Fluoride yield of β -irradiated Nafion.

The other nonvolatile product was a fluorocarbon grease, presumably a mixture of low-molecular-weight chain fragments. This colorless grease could be separated from the polymer film by Soxhlet extraction with chloroform after the membrane had been air dried at 110°C to remove sorbed water. The infrared spectrum of the grease is shown in Figure 7.

Infrared spectra of the cesium form of the irradiated polymer film exhibited evidence of oxygen attachment to the fluorocarbon backbone of the polymer. In the hydrated samples, a strong infrared absorption appeared at 1690 cm^{-1} , the intensity of the band being proportional to the dose received. Figure 8 presents the spectrum of the cesium form of a sample which had received a dose of 10 Mrad while in the fully hydrated acid form. By comparison with literature data¹⁰ and with the spectrum of the sodium salt of perfluoro-*n*-octanoic acid (Fig. 9), this absorption was assigned to the formation of carboxylic acid functional groups in the polymer.

Several attempts were made to determine the pK value(s) of the carboxylic acid groups by titration of the membrane in the acid form with NaOH using a glass indicator electrode. In all cases, the titration curves were those characteristic of a strong acid. Literature values¹¹ for the dissociation constants of fluorinated organic acids indicate that strong acid behavior (pK greater than 0.1) occurs where the acid group is attached to a perfluorinated chain. This suggests that the acid groups formed in the Nafion are new chain ends.

The carboxylic acid groups were reactive and esters could readily be formed. Figure 10 is the IR spectrum of the methyl ester produced by refluxing a sample of an as-irradiated, acid-form sample in methanol. There was sufficient HF in the polymer after the 50-Mrad dose it experienced to catalyze the esterification without the need for additional acid.

In addition to the formation of carboxylic acid groups, a carbon-hydrogen

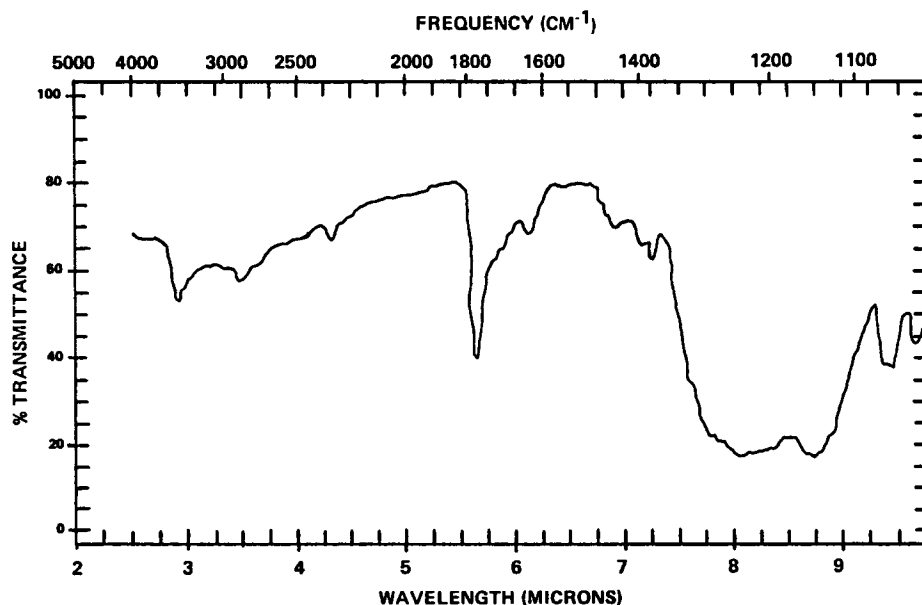


Fig. 7. Infrared spectrum of fluorocarbon grease extracted from irradiated Nafion. Sample was a smear on NaCl window.

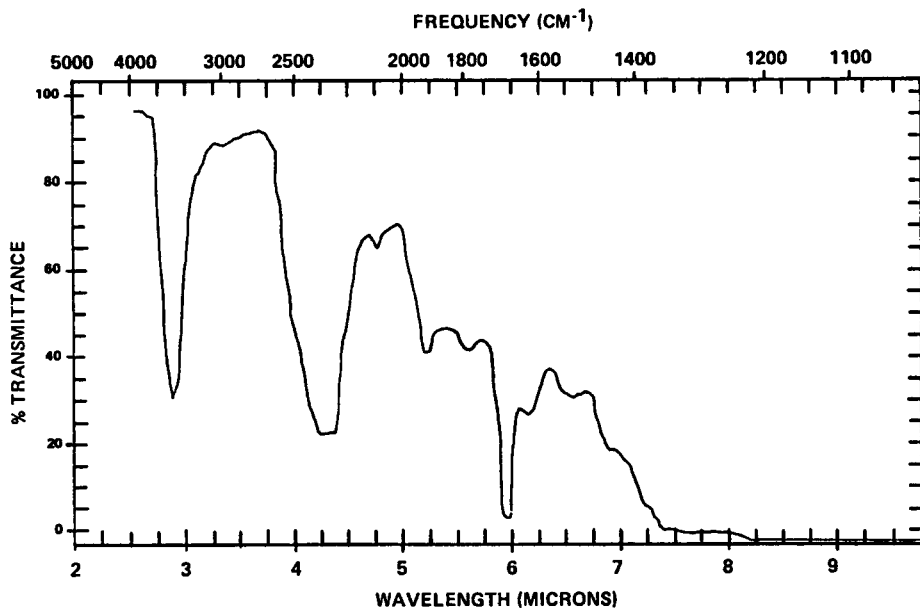


Fig. 8. Infrared spectrum of 1200-EW Nafion irradiated in fully hydrated acid form (cesium salt).

stretching vibration appeared in the spectrum at 2950 cm^{-1} (Fig. 8). No such absorption appears in the spectrum of the non-irradiated polymer. The fluorocarbon grease extracted from the membranes also had both of these new absorptions.

The samples of Nafion irradiated in the dry acid form had a third carbonyl absorption at 1775 cm^{-1} (Fig. 11). By comparison with literature data, this intense band was assigned to a perfluorinated ketone carbonyl group.

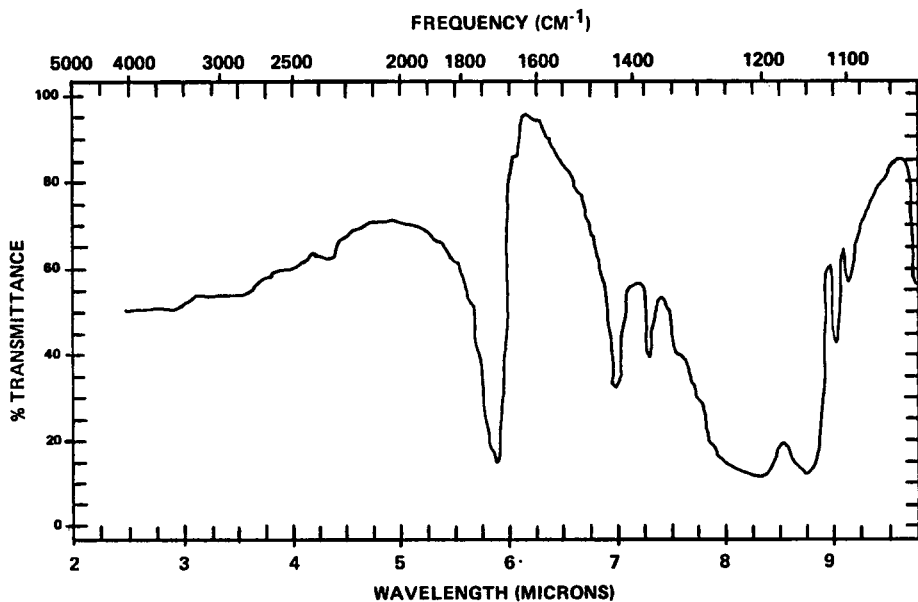


Fig. 9. Infrared spectrum of sodium salt of perfluoro-*n*-octanoic acid, KBr pellet.

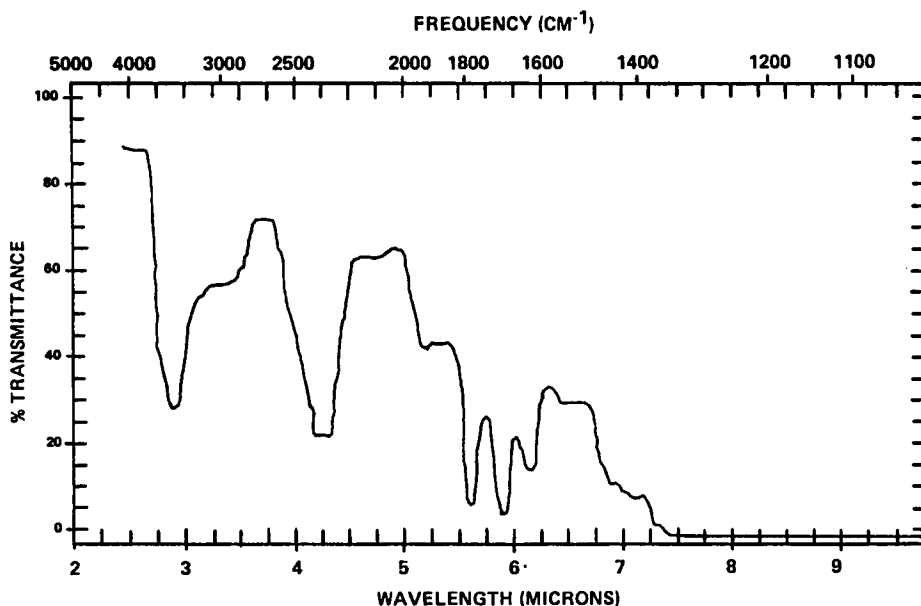


Fig. 10. Infrared spectrum of methyl ester formed by refluxing 50-Mrad Nafion 1200-EW sample in methanol (sodium salt).

Ion-Exchange Properties

The water contents of the samples irradiated in the fully hydrated acid form are plotted in Figure 12 as a function of the β dose. The quantity of water sorbed increased by approximately 15% at a 50-Mrad dose.

The ion-exchange capacity of the same samples is plotted in Figure 13. The 50-Mrad dose resulted in a 5% decrease in the ion-exchange capacity of the ma-

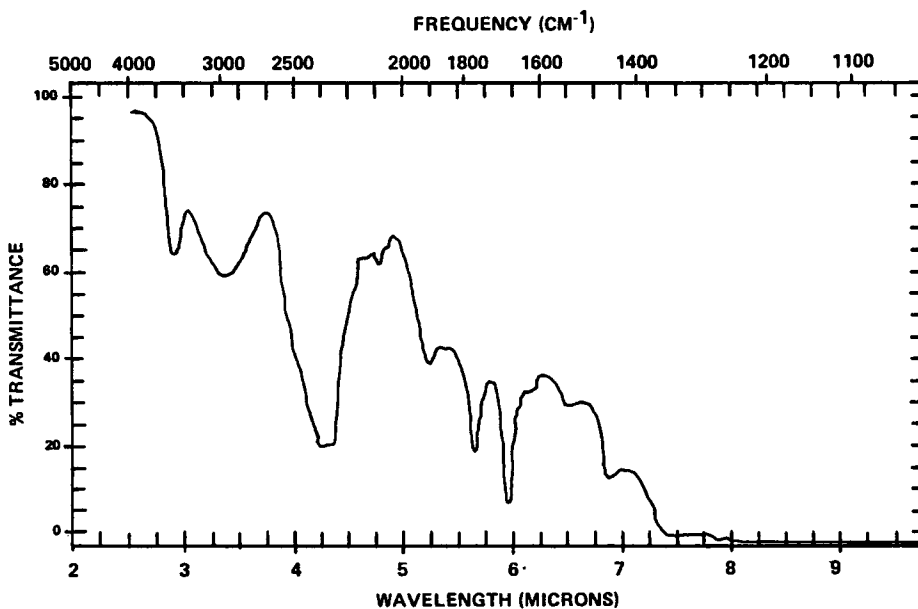


Fig. 11. Infrared spectrum of Nafion polymer irradiated in dry, acid form (cesium salt).

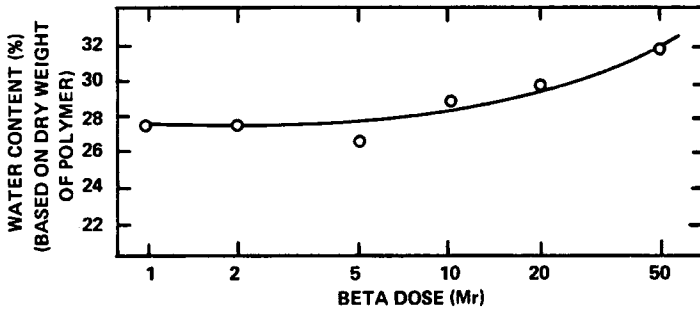


Fig. 12. Water sorption of β -irradiated 1200-EW Nafion.

terial. The analytical method did not discriminate between types of exchange sites, and the capacities shown in Figure 13 represent the sum of the capacity owing to the remaining sulfonic acid sites and the new capacity introduced by the formation of the strong carboxylic acid groups.

The samples irradiated in the dry proton form and the fully hydrated sodium form were identical in variation of ion-exchange capacity and water content with the β dose.

The membrane conductivity was not altered in any systematic fashion by the irradiation. Measured resistance values were $4.8 \pm 0.3 \Omega/\text{cm}^2$ for the 0.25-mm films, irrespective of the state of the polymer during irradiation.

Gamma Irradiation

The tensile strength and elongation of the fully hydrated, acid-form platinized and unplatinized polymers are shown in Figures 14 and 15. The decrease in physical strength at doses greater than 10 Mrad is far more severe when the source was a γ emitter.

Embrittlement of the polymer was so severe that it was not possible to make conductivity measurements of samples which had received a γ dose in excess of 10 Mrad. Attempts to mount specimens in the measurement cell resulted in cracking of the film. Measured resistance values for the 2, 5, and 10 Mrad samples were $4.7 \pm 0.2 \Omega/\text{cm}^2$.

The infrared spectra of the γ -irradiated samples were similar to those in Figure 8.

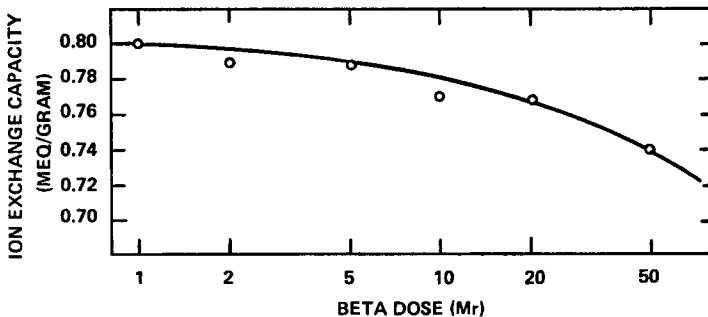


Fig. 13. Ion-exchange capacity of β -irradiated 1200-EW Nafion.

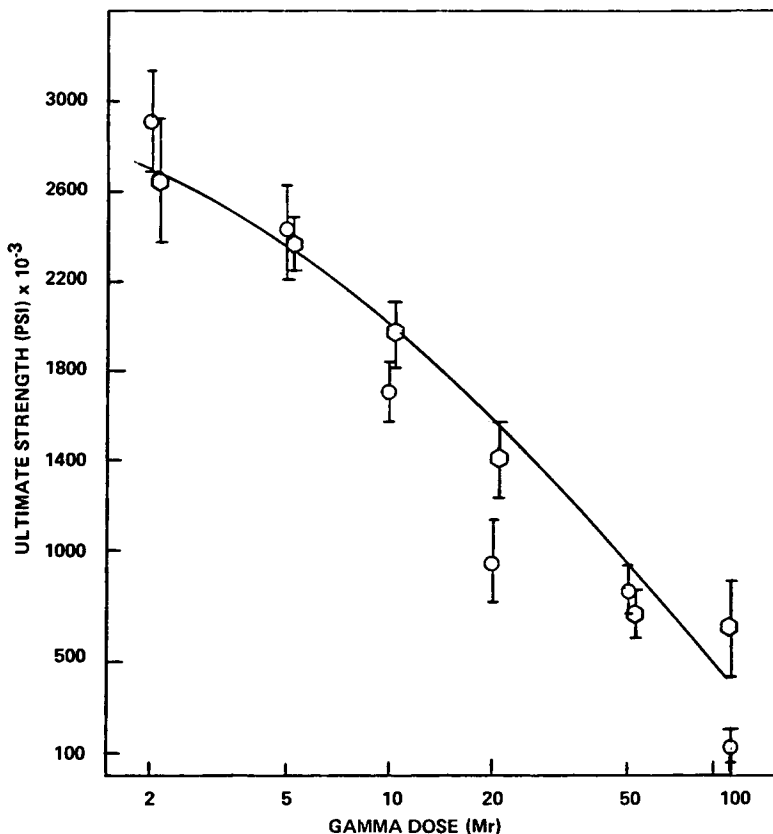


Fig. 14. Tensile strength of γ -irradiated 1200-EW Nafion. \circ , H⁺ form, fully hydrated; \odot , H⁺ form, fully hydrated, platinized.

DISCUSSION

It would appear that the radiation-induced formation of peroxide is unimportant in the radiolysis of the Nafion polymer. This conclusion is supported by the identity of the measured physical properties of the polymer samples when irradiated in the absence of significant water, when they are fully hydrated and when peroxide promoters or inhibitors are present. The limited amount of data available for the γ -irradiated materials further supports the conclusion.

The data measured in this article are consistent with a simple chain cleavage model as the dominant mechanism in the interaction of ionizing radiation with this fluoropolymer. Short-chain fragments (such as the volatile monomers) and larger fragments (the fluorocarbon grease) can be collected and identified. The observed water sorption behavior is also consistent with a decrease in chain length. In a linear ion-exchange polymer, shorter chain length permits greater hydration of the exchange sites.¹² In the irradiated Nafion, the decreased molecular weight permitted the smaller total number of exchange sites to increase their water of hydration sufficiently to produce a net increase in sorbed water. Greater water content also tends to increase conductivity. Apparently the effects of the greater sorbed water and reduced concentration of exchange sites were compensative, leaving the bulk conductivity unchanged.

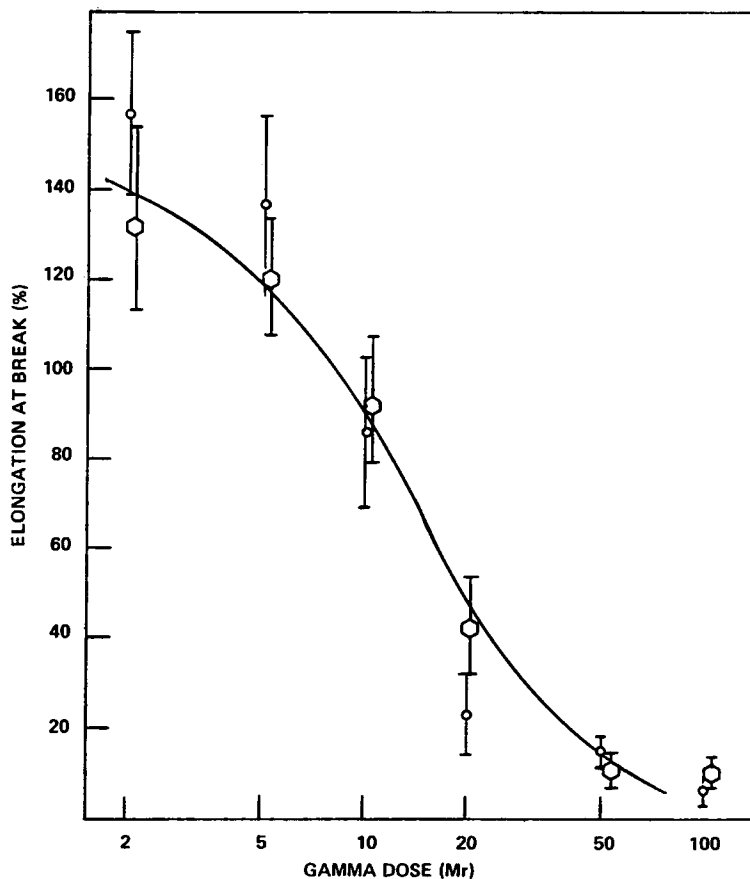


Fig. 15. Elongation of γ -irradiated 1200-EW Nafion. \circ , H^+ form, fully hydrated; \square , H^+ form, fully hydrated, platinized.

The large difference in the extent of polymer degradation measured for the β - and β -irradiated materials suggests that further study would be useful. The difference may be a result of dose rate; the β - and γ -dose rates employed in this study were considerably different.

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