

Irradiation of Poly(vinyl Alcohol) Fibers in the Presence of Chloroform and Carbon Tetrachloride

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Synopsis

Radiolysis of poly(vinyl alcohol) fibers (PVA) in the presence of chloroform and carbon tetrachloride was investigated. Decrease in intrinsic viscosity was observed at lower dosages (up to 2.3 megarads); and above this, an increase was noted. The blank samples irradiated under similar conditions showed a continuous decrease in intrinsic viscosity. A discoloration in the samples irradiated in the presence of CCl_4 and CHCl_3 was also observed. It is attributed to double bond formation in the backbone. A marginal decrease in the tensile strength of the irradiated fibers was observed. However, the surface characteristics of the fibers did not change on irradiation. The thermogravimetric analysis revealed a better heat resistance in irradiated fibers.

INTRODUCTION

Radiation-induced graft copolymerization of vinyl monomers on poly(vinyl alcohol) fibers has been reported in the literature.¹⁻¹¹ We were interested in the grafting of methyl methacrylate and related monomers on PVA fibers in the presence of solvents using γ -radiation. A large number of solvents were investigated, and development of a brown color in PVA fibers was observed when chlorinated hydrocarbon solvents such as carbon tetrachloride, chloroform, 1,2-dichloroethane, and methylene chloride were used. A systematic study of the radiolysis of PVA fibers in chloroform and carbon-tetrachloride was, therefore, carried out to investigate the accompanying changes in the properties of the fibers.

EXPERIMENTAL

Poly(vinyl alcohol) fibers were Soxhlet extracted with petroleum ether (40°-60°C) for 24 hr to remove the finishing agents and then dried. The washed fibers were then conditioned for 24 hr at a temperature of 27°C.

Chloroform (B.D.H.), carbon tetrachloride (B.D.H.), methylene chloride (B.D.H.), and 1,2-dichloroethane (B.D.H.) were purified by distillation.

About 0.5 g of the fiber was taken in a test tube and 5 ml of the purified solvent was added. It was then irradiated with γ -radiation at a dose of 252 krad/hr in the presence of air. The fibers were irradiated for six different dosages: 0.5,

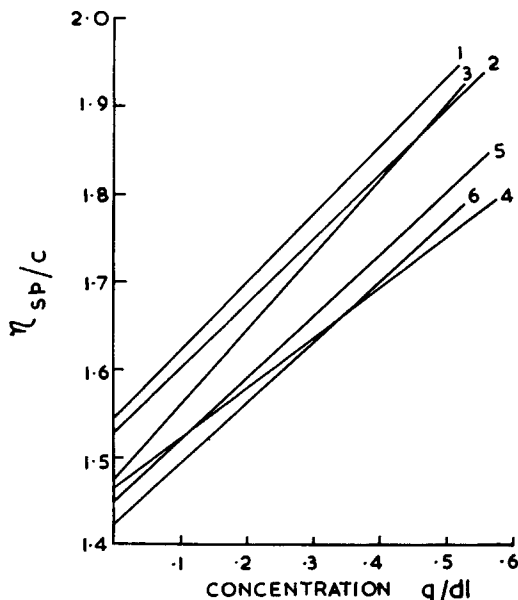


Fig. 1. Intrinsic viscosity evaluation of PVA fibers (PVA-I) (solvent formic acid) irradiated at 0.5 (1), 1.0 (2), 1.5 (3), 2.0 (4), 2.5 (5), and 3.0 (6) megarads.

1.0, 1.5, 2.0, 2.5, and 3.0 megarads. A sample without solvent was also irradiated under these dosages to serve as the blank. After irradiation, the solvent was removed; fibers were washed and then dried in the vacuum oven at 40°C.

Viscosity was measured with an Ubbelohde suspension level viscometer at 41°C using formic acid (B.D.H. analytical grade) as the solvent.

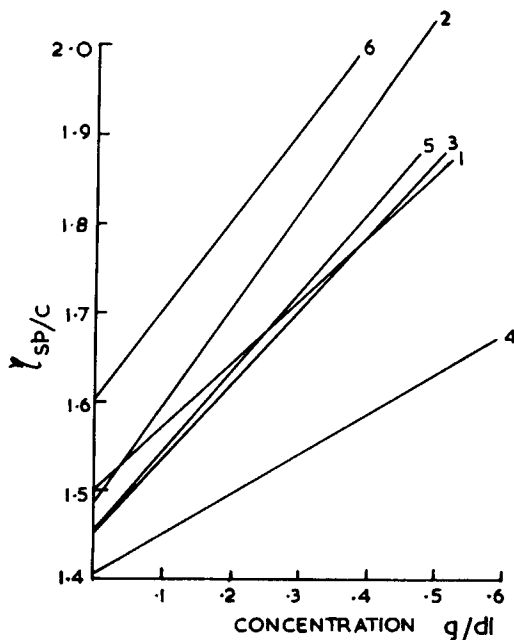


Fig. 2. Intrinsic viscosity evaluation of PVA fibers (PVA-II) (solvent formic acid) irradiated in the presence of chloroform at 0.5 (1), 1.0 (2), 1.5 (3), 2.0 (4), 2.5 (5), and 3.0 (6) megarads.

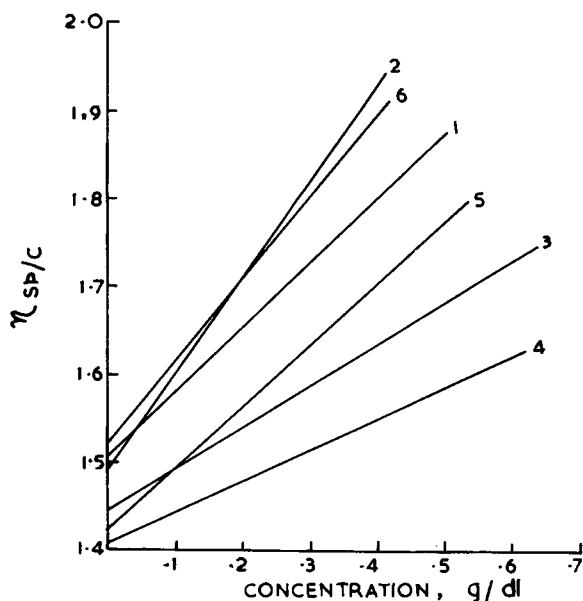


Fig. 3. Intrinsic viscosity evaluation of PVA fibers (PVA-III) (solvent formic acid) irradiated in the presence of carbon tetrachloride at 0.5 (1), 1.0 (2), 1.5 (3), 2.0 (4), 2.5 (5), and 3.0 (6) megarads.

A Stanton HT-D thermogravimetric balance in air was used for thermogravimetric analysis. Fibers were cut into approximately 2–3 mm length, and 20 ± 7 mg of the sample was taken for each analysis. The analysis was carried out in air from room temperature to 500° – 600° C. The primary thermograms were obtained by plotting percent residual weight against temperature.

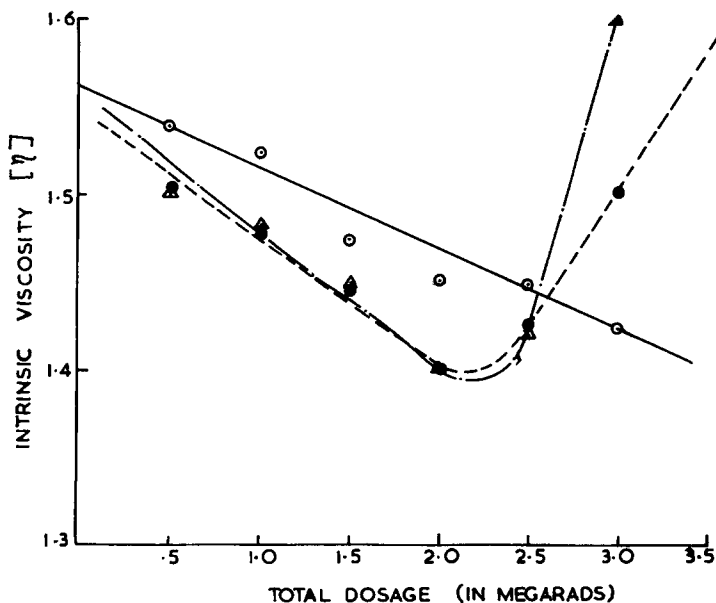


Fig. 4. Plot showing the effect of dosage on the intrinsic viscosity of PVA fibers irradiated as such (○) or in the presence of CHCl_3 (Δ) or CCl_4 (●).

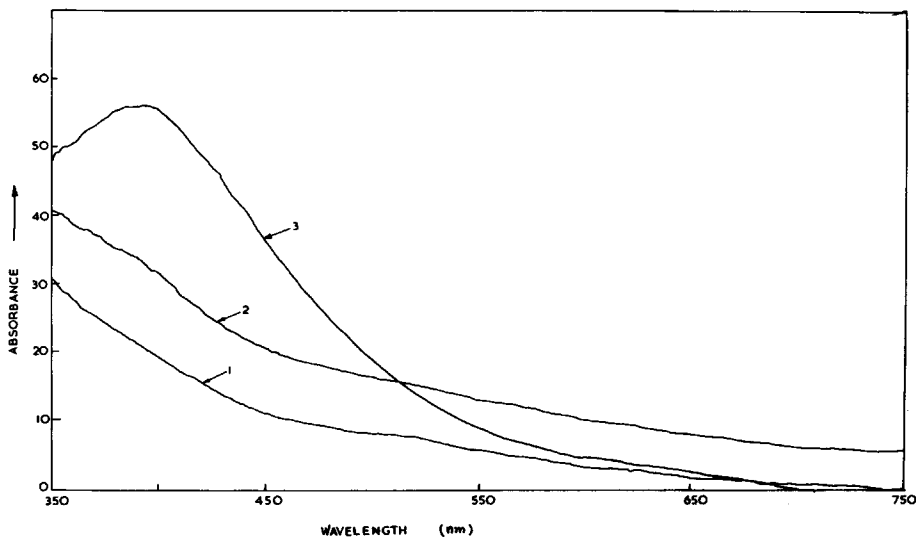


Fig. 5. Visible range spectra (in formic acid) of PVA fibers irradiated in chloroform at 1.0 (1), 2.0 (2), and 3.0 (3) megarads.

The infrared spectra of the fibers in KBr pellets were recorded using a Hilger-Watt spectrophotometer in the range of $4000\text{--}700\text{ cm}^{-1}$.

The visible range spectrum of the fibers in formic acid was recorded using a Beckmann-DK-2A spectrophotometer in the range of 350–750 nm.

The x-ray diffraction photographs were recorded with a Philips Norelco x-ray diffraction unit utilizing the flat film technique. A bundle of parallel fibers was fixed near the collimator. A specimen to film distance of 4 cm was maintained for the entire study. The x-ray equipment was adjusted so as to completely be fixed near the collimator. A specimen to film distance of 4 cm was maintained for the entire study. The x-ray equipment was adjusted so as to completely bathe the bundle of the fibers. The undiffracted beam was so aligned as to fall at the center of the photographic plate. The generator was operated at 30 kV and 22 mA for 3.5 hr. The Joyce-Loebel microdensitometer Mark II with linear and polar tables was used for scanning the x-ray films.

A S4-10 scanning electron microscope (Cambridge Instruments Ltd.) was used to study the surface characteristics at 5 kV.

The breaking load of the fibers was determined using an Instron. The following specifications were used: Gauge length, 5 cm; chart speed, 10 cm/min; jaw speed, 1 cm/min; full scale load, 100 g; number of specimens, 36.

RESULTS AND DISCUSSION

Contradictory results are reported in the literature about the irradiation behavior of PVA. Some authors have indicated that crosslinking takes place on irradiation,¹²⁻¹⁴ while others claim a decrease in molecular weight.¹⁵⁻¹⁸ The presence of water in the PVA causes a crosslinking reaction¹⁹ on irradiation.

Figures 1–3 give the viscosity evaluation at different dosages for PVA fibers irradiated in air from 0.5 to 3.0 megarads at a dose rate of 252 krad/hr in the presence of chloroform, carbon tetrachloride, and without solvent.

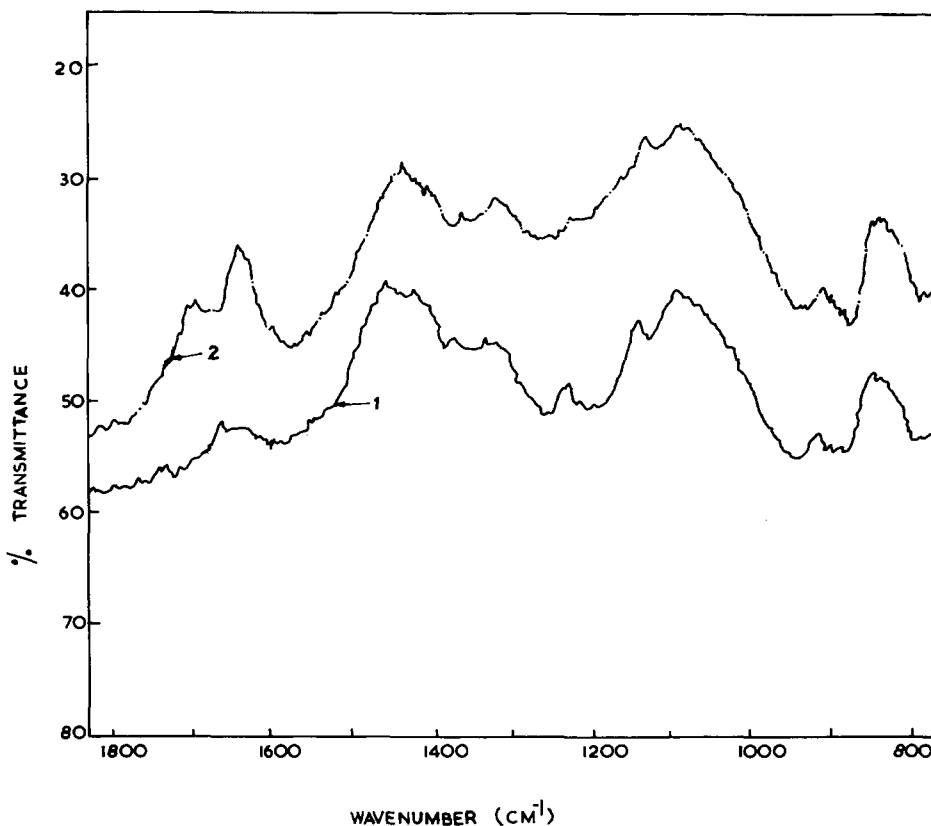


Fig. 6. IR spectra of PVA fibers (in KBr pellets); (1) unirradiated fibers; (2) fibers irradiated at 3.0 megarads in the presence of CCl_4 .

Our results indicate a regular decrease in the $[\eta]$ of PVA. In chlorinated solvents, however, an increase is observed at later stages (Fig. 4).

The decrease in $[\eta]$ indicates a chain scission reaction. However, when the dosage was high, an insoluble gel was left and also an increase in viscosity was observed. Thus, crosslinking may become significant at higher dosages.

However, the development of color in the fibers (brownish) indicates some dehydration reaction leading to olefinic bonds in the backbone which may impart color. The visible-range spectra of the various samples were recorded. Poly(vinyl alcohol) fibers dissolved in formic acid did not show any maxima in the region of 350–750 nm. The maxima at 388 nm were obtained with fibers irradiated in the presence of chloroform (PVA-II) at 3.0 megarads (Fig. 5). For the samples (PVA-II) irradiated for 1.0 and 2.0 megarads, the intensity was less. It was found that the intensity of the color increases with dosage.

The presence of double bonds in the polymer was also indicated by the IR spectra of samples irradiated in carbon tetrachloride (Fig. 6). The spectra of the PVA-III at 3.0 megarads show a sharp and intense peak at 1645 cm^{-1} .

One would obviously conclude that the appearance of the peak at 1645 cm^{-1} in the IR spectrum is due to extended conjugation which imparted a brown color to the fiber.

Thus, the PVA fibers irradiated in CHCl_3 and CCl_4 undergo not only cross-

TABLE I
Integral Procedural Decomposition Temperature for PVA Fibers

Symbol	Fiber	IPDT, °C
PVA	nonirradiated	378
PVA-I	irradiated without solvent (3.0 megarads)	387
PVA-II	irradiated in the presence of CHCl_3 (3.0 megarads)	400
PVA-III	irradiated in the presence of CCl_4 (3.0 megarads)	413

TABLE II
Average Breaking Load and Percentage Elongation of PVA Fibers^a

Fiber	Breaking load, g	% Elongation
PVA	44.5 (21.8)	13.35 (13.4)
PVA-I	43.5 (22.6)	12.20 (13.7)
PVA-III	40.8 (26.3)	12.20 (14.1)

^a C. V. percent is given in parentheses.

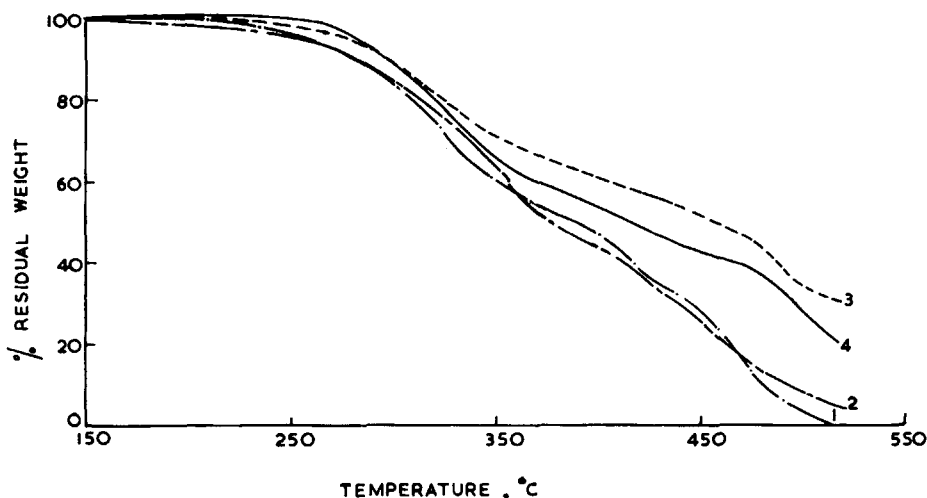


Fig. 7. Primary thermograms of the PVA fibers: (— — — —) unirradiated fibers; (— — — —) irradiated at 3.0 megarads; (—) irradiated in CHCl_3 at 3.0 megarads; (- - - -) irradiated in CCl_4 at 3.00 megarads.

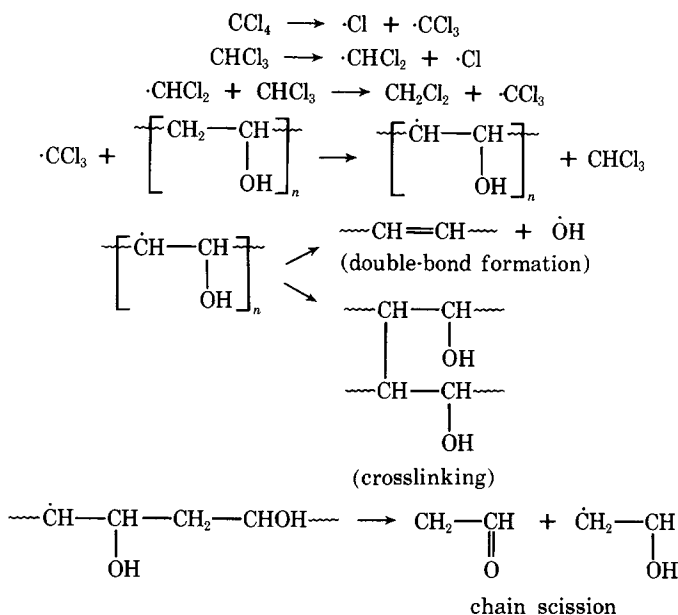
linking at higher dosage but also elimination reactions leading to conjugated double bond formation in the backbone. Such structures may influence the thermal behavior and tensile properties of the fibers.

The thermal stability of PVA, PVA-I, PVA-II, and PVA-III was examined by primary thermograms (Fig. 7). The integral procedural decomposition temperature (IPDT) values²⁰ for PVA-II and PVA-III were found to be higher than those of PVA and PVA-I (Table I). Since the IPDT values may be considered to be semiquantitative measures of polymer stability, one can conclude that irradiation of PVA in CHCl_3 and CCl_4 imparts higher stability to PVA fibers.

The average breaking load and percentage elongation of PVA fibers irradiated with or without solvent is less than that of the nonirradiated fiber (Table II). Decrease in average breaking load was about 9% for PVA fibers irradiated for 3.0 megarads in the presence of carbon tetrachloride.

The scanning electron micrograph of the fibers, however, did not show any change in the surface characteristics. Similarly, no change in x-ray diffraction pattern was observed.

Based on these observations, one can conclude that solvents such as carbon tetrachloride and chloroform which can readily yield free radicals²¹⁻²⁴ help in the discoloration of PVA fibers at high dosages, and also crosslinking is significant. One can write the following mechanism for these reactions:



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