

# Effect of $\gamma$ -Irradiation and Temperature on the Structure of Metal-Chloride-Treated Poly(vinyl Alcohol)

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## Synopsis

The infrared and ultraviolet spectra of poly(vinyl alcohol) (PVA) treated with ferric chloride and zinc chloride were recorded. Careful examination of the infrared spectra revealed that these treatments cause significant changes in the crystallinity of PVA, particularly in the case of the treatment with  $\text{ZnCl}_2$ . The results showed that exposure of untreated and  $\text{FeCl}_3$ -treated PVA to 12 or 28 Mrads results in no observable changes in their ultraviolet and infrared spectral features, whereas exposure of  $\text{ZnCl}_2$ -treated PVA at the same dosages, results in the appearance of an absorption band at  $1595\text{ cm}^{-1}$  corresponding to  $\beta$ -diketone groups. It was also found that  $\gamma$ -irradiation of  $\text{ZnCl}_2$ -treated PVA produces a remarkable change in its crystallinity. Moreover, the effect of heat on the spectral features of the  $\text{ZnCl}_2$ -treated PVA was discussed. It was found that the treatment of PVA with  $\text{ZnCl}_2$  helps in oxidative degradation of PVA.

## INTRODUCTION

Metal-polymer complexes have been the subject of interest in the recent years.<sup>1-5</sup> Many attempts have been made to improve the natural flame resistance of polymers. Metal polymer complexes, e.g., with Fe(III), Cu II, Ti(III), and Zn(II) have been considered as flame retardants. For example, Kurose et al.<sup>2</sup> concluded that nonflammability properties were imparted to PVA by complexing with Fe(III) ion at low contents. Also many metal complexes have been used in dehydrogenation catalysis.<sup>5</sup> These complexes may act as catalysts for dehydrogenation of the hydrocarbon chains during pyrolysis and graphitic structure may be formed.

The present study is carried out to investigate the effects of  $\gamma$ -irradiation and temperature on the structure of metal-chloride-treated poly(vinyl alcohol) (PVA) by using infrared (IR) and ultraviolet (UV) spectroscopic techniques.

## EXPERIMENTAL

The experiments were carried out on commercial poly(vinyl alcohol) (PVA). Mixtures of PVA (10 wt %) aqueous solution and ferric chloride (10 and 20 wt %) or zinc chloride (5, 10, 20, and 30%) in water were stirred overnight at room temperature. The mixtures were then treated with potassium hydroxide

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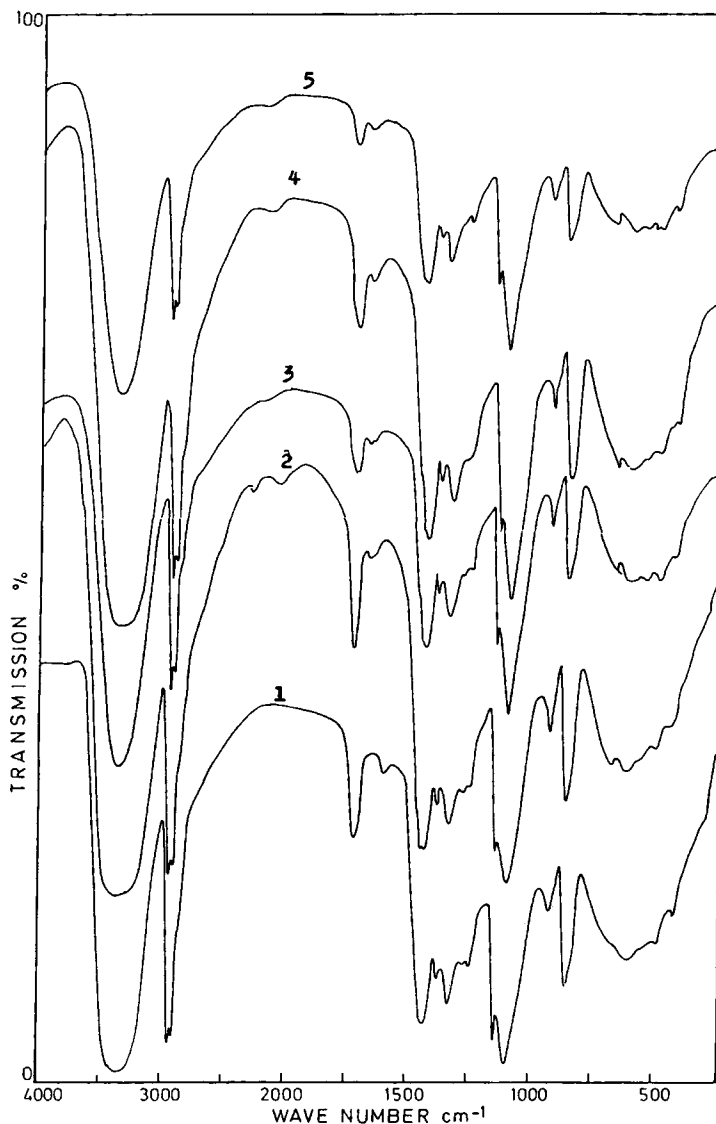


Fig. 1. Infrared spectra of  $\text{FeCl}_3$ -treated PVA: (1) untreated PVA; (2) treated with 10%  $\text{FeCl}_3$   $\text{KOH}/\text{FeCl}_3 = 1$ ; (3) treated with 10%  $\text{FeCl}_3$  and  $\text{KOH}/\text{FeCl}_3 = 2$ ; (4) treated with 20%  $\text{FeCl}_3$  and  $\text{KOH}/\text{FeCl}_3 = 1$ ; (5) treated with 20%  $\text{FeCl}_3$  and  $\text{KOH}/\text{FeCl}_3 = 2$ .

(1 and 2 eq  $\text{FeCl}_3$  or  $\text{ZnCl}_2$ ) and stirred overnight at room temperature. The treated samples were then cast onto polyethylene sheets and air-dried overnight at ambient temperature resulting in somewhat wet films. The films were further dried at  $70^\circ\text{C}$  for 6 h in an oven.

The samples were irradiated by  $\text{Co}^{60}$  source, Noratom control A.S. gamma 3500 unit at a rate of 23 rad/s. The IR spectra were recorded on a Beckman spectrophotometer 4250 and the UV spectra were recorded on Beckman spectrophotometer, UV 5260. The obtained absorbances of the infrared absorption

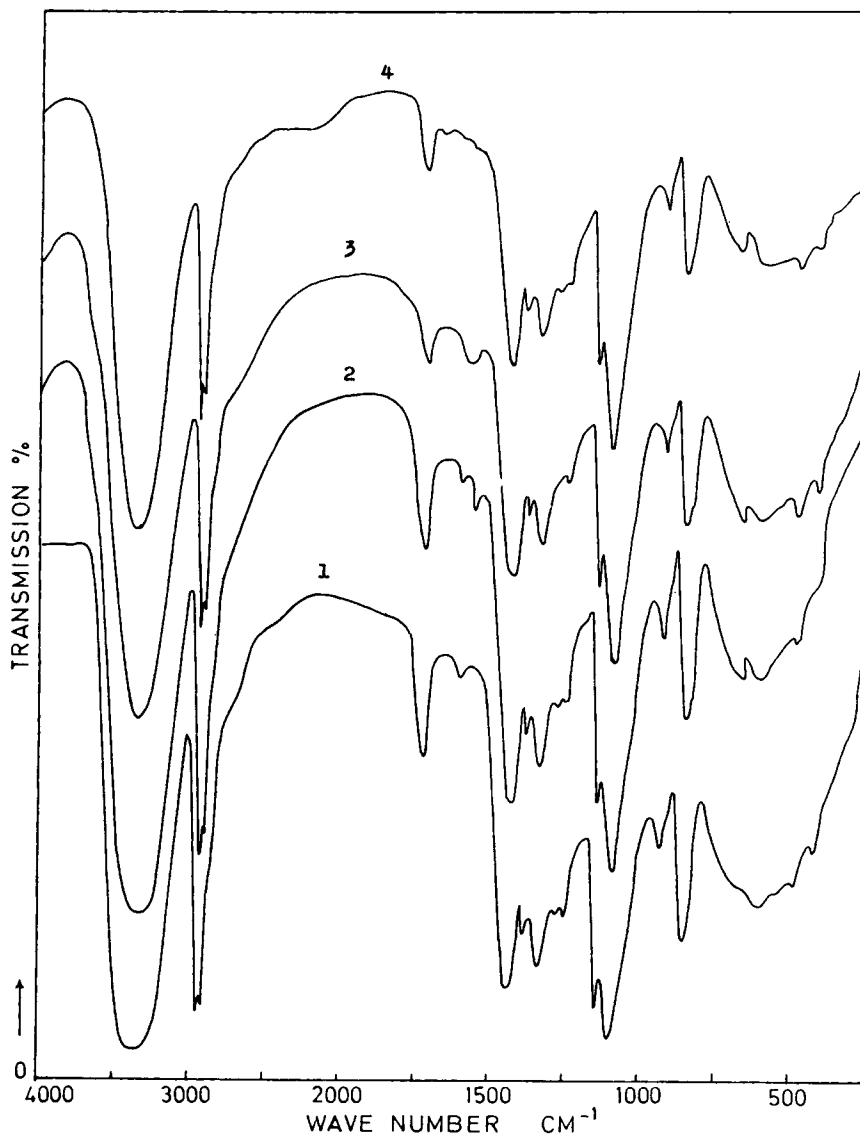


Fig. 2. Infrared spectra of  $\text{ZnCl}_2$ -treated PVA: (1) untreated PVA; (2) treated with 5%  $\text{ZnCl}_2$  and  $\text{KOH}/\text{ZnCl}_2 = 2$ ; (3) treated with 10%  $\text{ZnCl}_2$  and  $\text{KOH}/\text{ZnCl}_2 = 2$ ; (4) treated with 20%  $\text{ZnCl}_2$  and  $\text{KOH}/\text{ZnCl}_2 = 2$ .

bands are the averages of four replicate runs. The accuracy of the measured values was found to be 4%.

## RESULTS AND DISCUSSION

Figures 1 and 2 represent the infrared spectra of untreated and metal-chloride-treated PVA. All spectra exhibit the characteristic absorption bands of PVA in addition to the  $\text{C}=\text{O}$  band of some residual acetate groups at  $1710\text{ cm}^{-1}$  as reported in the literature.<sup>6,7</sup> It can be noticed that these treatments do

TABLE I  
Percent Crystallinity and Changes in Hydroxyl Level of FeCl<sub>3</sub>-Treated PVA

	% Crystallinity			$A_{3300\text{ cm}^{-1}}/A_{2950\text{ cm}^{-1}}$		
	Unexposed	12 Mrad	28 Mrad	Unexposed	12 Mrad	28 Mrad
PVA	20.20	17.00	19.72	1.35	1.38	1.39
PVA + 10 wt % FeCl <sub>3</sub> + KOH/FeCl <sub>3</sub> = 1	20.61	16.04	18.90	1.32	1.27	1.21
PVA + 10 wt % FeCl <sub>3</sub> + KOH/FeCl <sub>3</sub> = 2	18.97	17.44	19.72	1.44	1.32	1.28
PVA + 20 wt % FeCl <sub>3</sub> + KOH/FeCl <sub>3</sub> = 1	11.05	9.92	12.36	1.38	1.42	1.29
PVA + 20 wt % FeCl <sub>3</sub> + KOH/FeCl <sub>3</sub> = 2	20.95	17.88	20.64	1.49	1.44	1.39

not cause observable changes in the spectral features of the samples apart from slight changes in the intensities of some absorption bands.

To establish the results on a quantitative basis and because the CH group is unaffected by the chemical modification, the absorbances ratio of the OH absorption at 3350 cm<sup>-1</sup> to that of the CH absorption at 2950 cm<sup>-1</sup> was determined for each sample by using the baseline method. A baseline was drawn across the two bands from 2200 to 3800 cm<sup>-1</sup>. The determined values are listed in Tables I and II.

It is apparent from Tables I and II that the absorbances ratio  $A_{3350\text{ cm}^{-1}}/A_{2950\text{ cm}^{-1}}$  for all samples assumes more or less equal values. The slight differences between the absorbances ratios can be considered in the range of the experimental errors. This result provides strong evidence that no formation of oxygen to metal bonds (M—O) occurs as a result of these chemical treatments.

The percent crystallinity of the samples was determined by using the relation<sup>8</sup>

TABLE II  
Percent Crystallinity and Hydroxyl Level of ZnCl<sub>2</sub>-Treated PVA

	% Crystallinity			$A_{3300\text{ cm}^{-1}}/A_{2950\text{ cm}^{-1}}$		
	Unexposed	12 Mrad	28 Mrad	Unexposed	12 Mrad	28 Mrad
PVA	20.20	17.00	19.72	1.35	1.38	1.39
PVA + 5 wt % ZnCl <sub>2</sub> + KOH/ZnCl <sub>2</sub> = 1	21.45	28.42	38.86	1.35	1.33	1.29
PVA + 5 wt % ZnCl <sub>2</sub> + KOH/ZnCl <sub>2</sub> = 2	20.05	26.71	37.93	1.36	1.52	1.32
PVA + 10 wt % ZnCl <sub>2</sub> + KOH/ZnCl <sub>2</sub> = 1	23.45	37.20	43.82	1.32	1.34	1.30
PVA + 10 wt % ZnCl <sub>2</sub> + KOH/ZnCl <sub>2</sub> = 2	32.15	40.42	46.40	1.43	1.35	1.43
PVA + 20 wt % ZnCl <sub>2</sub> + KOH/ZnCl <sub>2</sub> = 1	31.20	39.04	52.24	1.36	1.28	1.29
PVA + 20 wt % ZnCl <sub>2</sub> + KOH/ZnCl <sub>2</sub> = 2	30.42	41.80	59.28	1.36	1.25	1.29

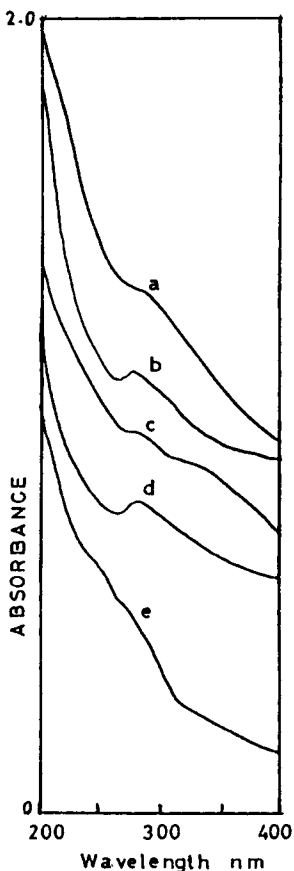


Fig. 3. Ultraviolet spectra of  $\text{ZnCl}_2$ -treated PVA: (a) untreated PVA; (b) treated with 5 wt % and  $\text{KOH}/\text{ZnCl}_2 = 1$ ; (c) treated with 5 wt % and  $\text{KOH}/\text{ZnCl}_2 = 2$ ; (d) treated with 10 wt % and  $\text{KOH}/\text{ZnCl}_2 = 1$ ; (e) treated with 10 wt % and  $\text{KOH}/\text{ZnCl}_2 = 2$ .

$$\text{percent crystallinity} = 92(d/c) - 18$$

where  $d$  is the absorbance of the  $1141 \text{ cm}^{-1}$  peak and  $c$  is absorbance of the  $1425 \text{ cm}^{-1}$  peak. The absorbances were measured by using the baseline method. A baseline was drawn across each band.

Tables I and II indicate the following:

1. When PVA is treated with 10 wt %  $\text{FeCl}_3$  and hydrolyzed by  $\text{KOH}$  (1 or 2 eq  $\text{FeCl}_3$ ) its crystallinity does not change.
2. The crystallinity of the samples treated with 20 wt % depends on the ratio  $\text{KOH}/\text{FeCl}_3$ . It undergoes considerable decrease when the ratio equals 1 and remains constant when the ratio equals 2.
3. The treatment of PVA with 5 wt %  $\text{ZnCl}_2$  ( $\text{KOH}/\text{ZnCl}_2 = 1$  or 2) and with 10 wt %  $\text{ZnCl}_2$  ( $\text{KOH}/\text{ZnCl}_2 = 1$ ) results in no significant changes in its crystallinity.
4. The treatment of PVA with 10 wt %  $\text{ZnCl}_2$  ( $\text{KOH}/\text{ZnCl}_2 = 2$ ) and with

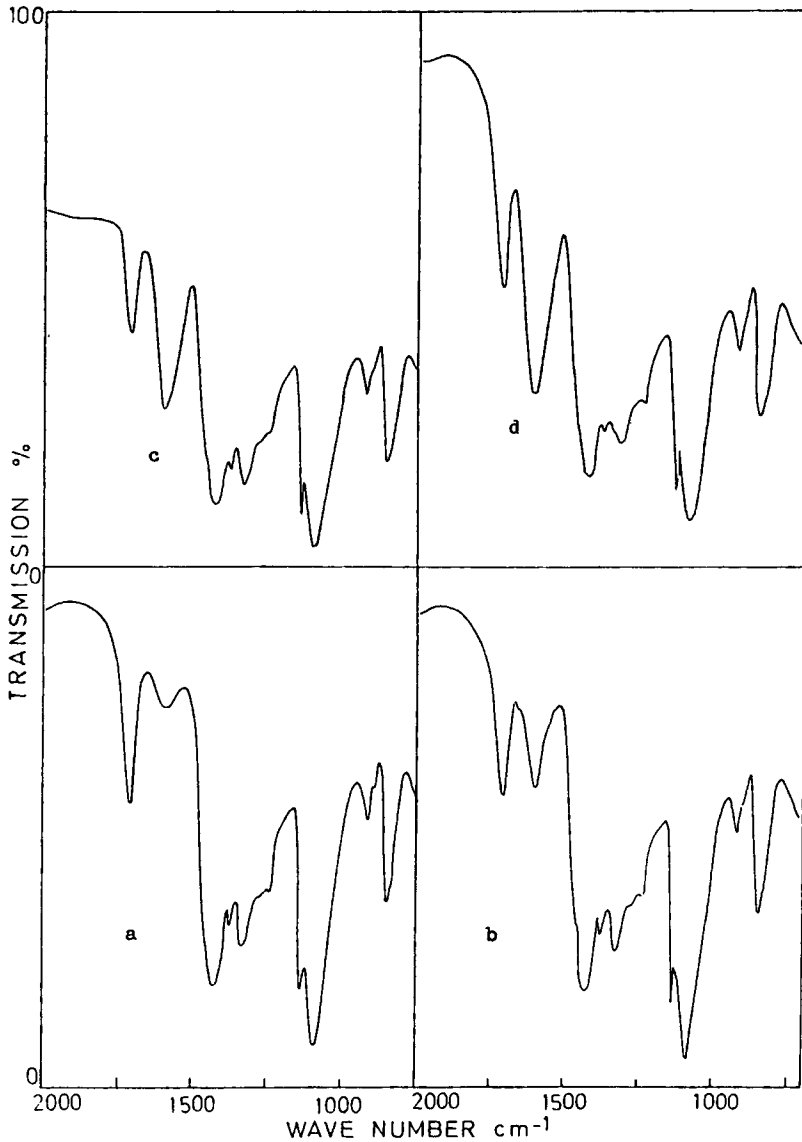


Fig. 4. Partial infrared spectra of  $\gamma$ -irradiated  $\text{ZnCl}_2$ -treated PVA ( $\text{KOH}/\text{ZnCl}_2 = 1$ ): (a) treated with 5 wt %; (b) treated with 10 wt %; (c) treated with 20 wt %; (d) treated with 30 wt %.

20 wt %  $\text{ZnCl}_2$  ( $\text{KOH}/\text{ZnCl}_2 = 1$  and 2) increases its crystallinity by approximately the same value (about 55%).

The UV spectra of the samples under investigation were recorded. The spectra of untreated and  $\text{ZnCl}_2$ -treated samples are shown in Figure 3.

Examination of the recorded spectra revealed that the spectrum of untreated PVA exhibits, in addition to the strong bands appearing at 197 nm, a very weak band at about 280 nm. This band at 280 nm is assigned to the carbonyl groups

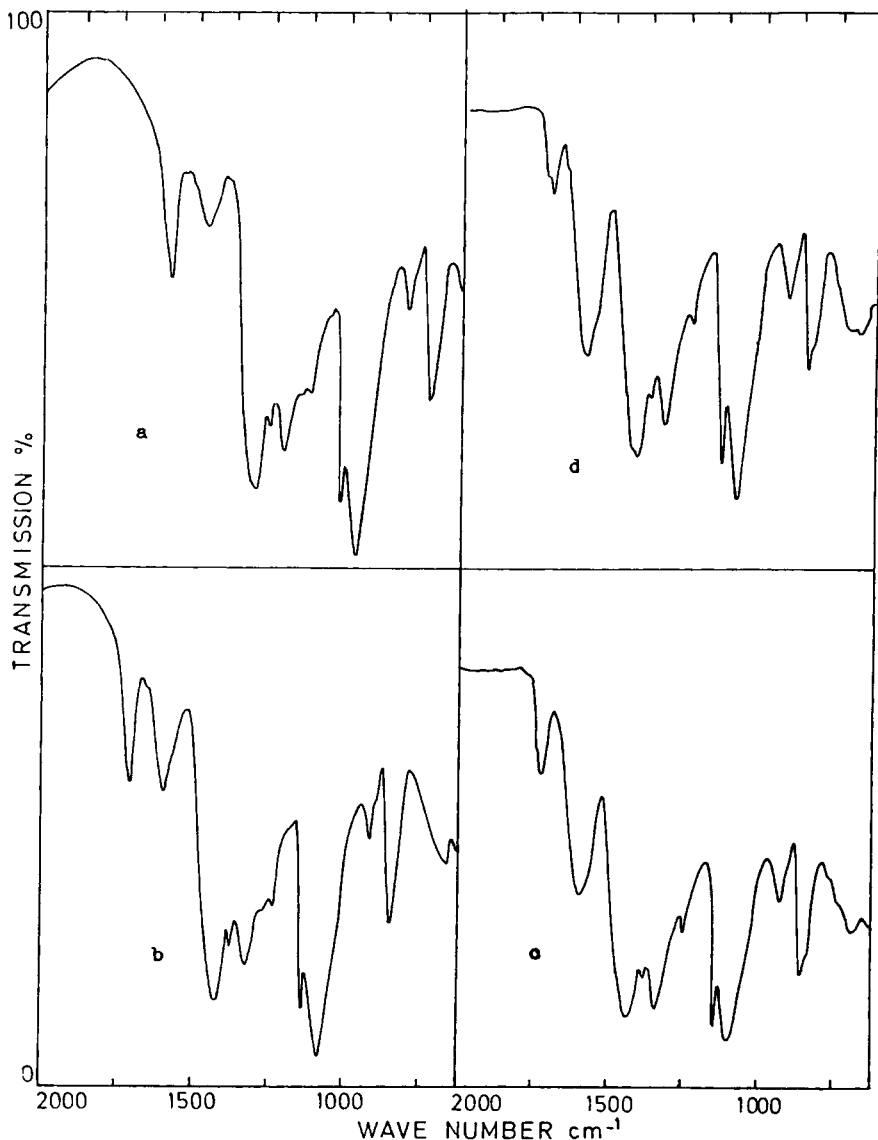


Fig. 5. Partial infrared spectra of  $\gamma$ -irradiated  $\text{ZnCl}_2$ -treated PVA ( $\text{KOH}/\text{ZnCl}_2 = 2$ ): (a) treated with 5 wt %; (b) treated with 10 wt %; (c) treated with 20 wt %; (d) treated with 30 wt %.

associated with ethylenic unsaturation of the type  $-\text{CO}-(\text{C}=\text{C})_2-$ .<sup>6</sup> The 280 nm band could also be due to simple ketone structure.

The treatment of PVA with  $\text{FeCl}_3$  has no influence on the intensities of these two bands. However, it appears from Figure 3 that treatment of PVA with 10 or 20 wt % ( $\text{KOH}/\text{ZnCl}_2 = 1$ ) results in slight increase in the intensity of the 280 nm band and increasing the  $\text{KOH}/\text{ZnCl}_2$  ratio to 2 causes the reverse, i.e., reduces the intensity of this band.

The untreated and treated samples were then exposed to 12 and 28 Mrad of  $\gamma$ -radiation in an atmosphere of air at room temperature. The analysis of the

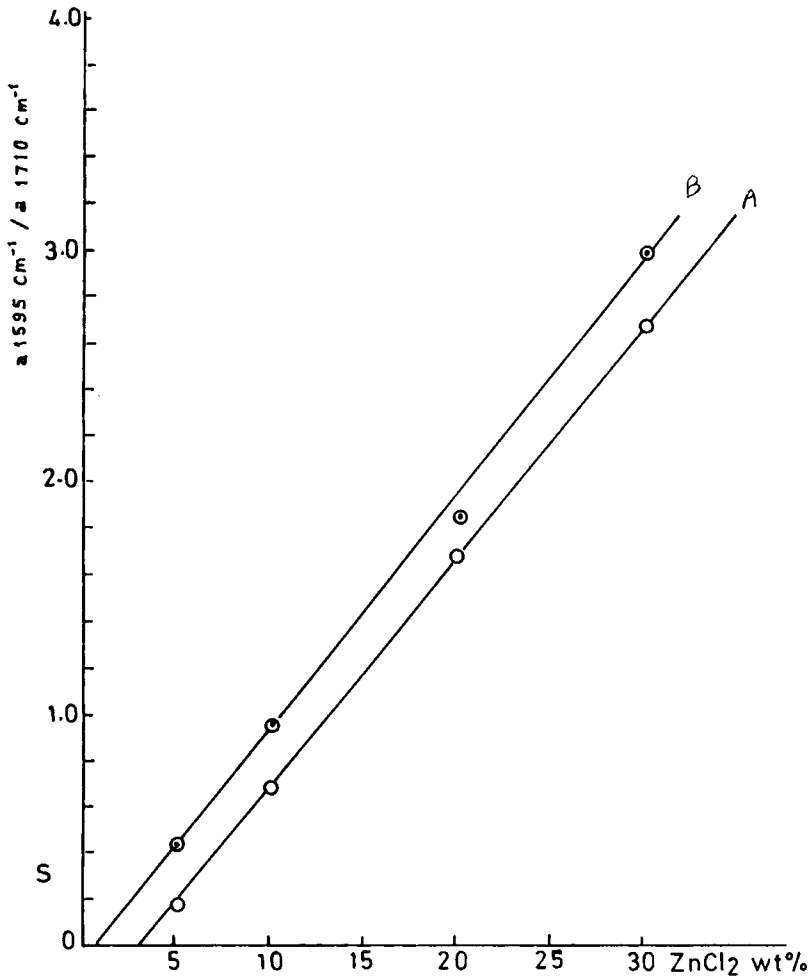


Fig. 6. Relationship between the concentration and  $A_{1595 \text{ cm}^{-1}}/A_{1710 \text{ cm}^{-1}}$ : (a)  $\text{KOH}/\text{ZnCl}_2 = 1$ ; (b)  $\text{KOH}/\text{ZnCl}_2 = 2$ .

infrared spectra of the  $\gamma$ -irradiated samples showed that irradiation of untreated and  $\text{FeCl}_3$ -treated samples produces no noticeable changes in their spectral features, whereas the irradiation of the samples treated with  $\text{ZnCl}_2$  results in the appearance of an absorption band at about  $1595 \text{ cm}^{-1}$ . This band may be assigned to  $\beta$ -diketone groups. The intensity of the  $1595 \text{ cm}^{-1}$  band depends on the applied dosage, concentration of  $\text{ZnCl}_2$ , and the  $\text{KOH}/\text{ZnCl}_2$  ratio. It appears very weak in the spectra of the samples exposed to the lower dosage and becomes more intense in the spectra of the samples exposed to the higher dosage. Figures 4 and 5 show the partial infrared spectra of  $\text{ZnCl}_2$ -treated samples irradiated with 28 Mrad. The absorbance ratio  $A_{1595 \text{ cm}^{-1}}/A_{1710 \text{ cm}^{-1}}$  was measured for the  $\text{ZnCl}_2$ -treated samples exposed to 28 Mrad. A baseline was drawn across the two bands from  $1525$  to  $1800 \text{ cm}^{-1}$ . The relation between the concentration of  $\text{ZnCl}_2$  and the absorbances ratio  $A_{1595 \text{ cm}^{-1}}/A_{1710 \text{ cm}^{-1}}$  is rep-



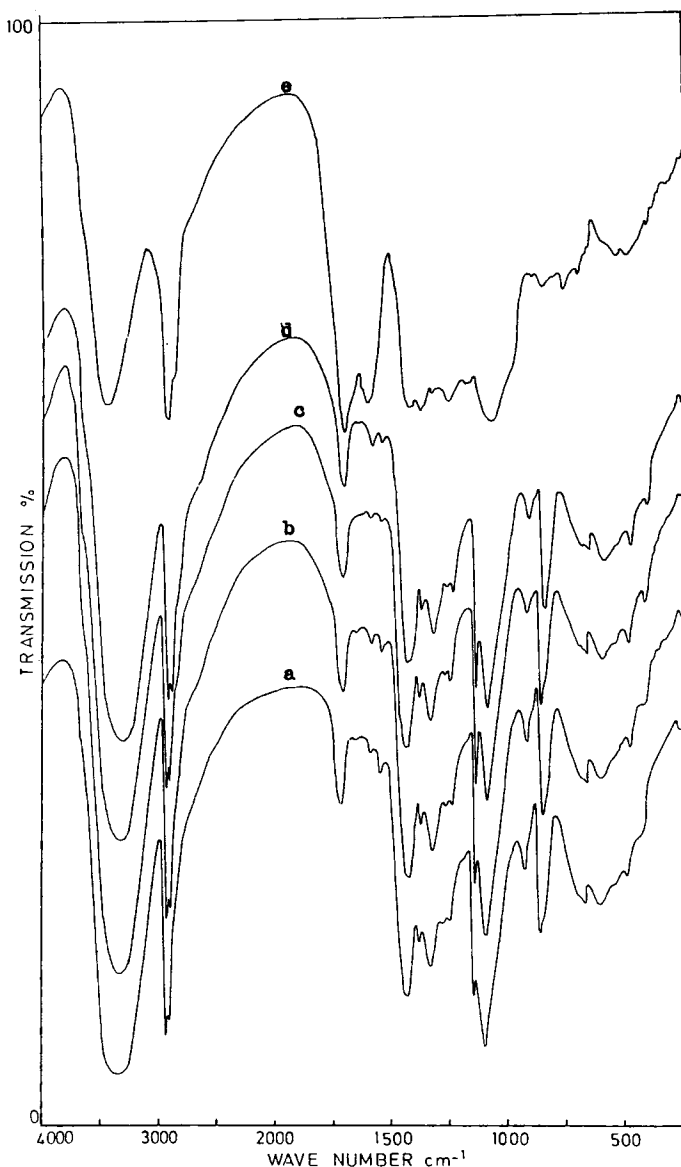


Fig. 7. Infrared spectra of treated samples 5 wt % and  $\text{KOH}/\text{ZnCl}_2 = 2$  heated in air at: (a) room temperature; (b) 60°C; (c) 90°C; (d) 120°C; (e) 150°C.

resented graphically in Figure 6 for the two ratios of  $\text{KOH}/\text{ZnCl}_2$  1 and 2. It is clear from Figure 6 that the absorbances ratio  $A_{1595 \text{ cm}^{-1}}/A_{1710 \text{ cm}^{-1}}$  increases linearly with the increases of  $\text{ZnCl}_2$  concentration and for any given concentration of  $\text{ZnCl}_2$  the value of the  $A_{1595 \text{ cm}^{-1}}/A_{1710 \text{ cm}^{-1}}$  for samples treated with  $\text{KOH}/\text{ZnCl}_2 = 2$  is always higher than that for the samples treated with  $\text{KOH}/\text{ZnCl}_2 = 1$ .

The absorbances ratio  $A_{3350 \text{ cm}^{-1}}/A_{2950 \text{ cm}^{-1}}$  for all  $\gamma$ -irradiated samples were determined and are given in Tables I and II. It can be easily seen from these

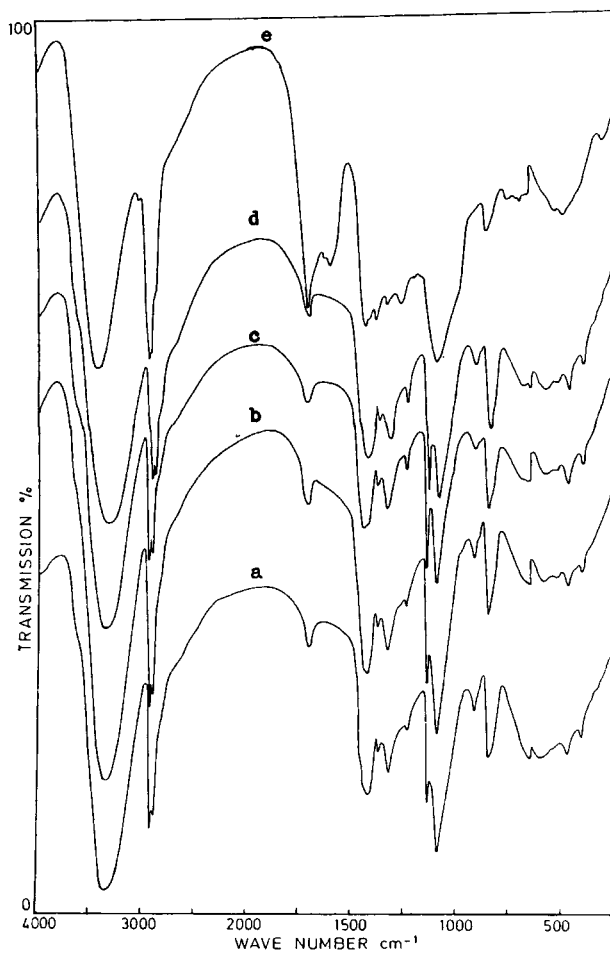


Fig. 8. Infrared spectra of ZnCl<sub>2</sub>-treated sample 10 wt % and KOH/ZnCl<sub>2</sub> = 2 heated in air at: (a) room temperature; (b) 60°C; (c) 90°C; (d) 120°C; (e) 150°C.

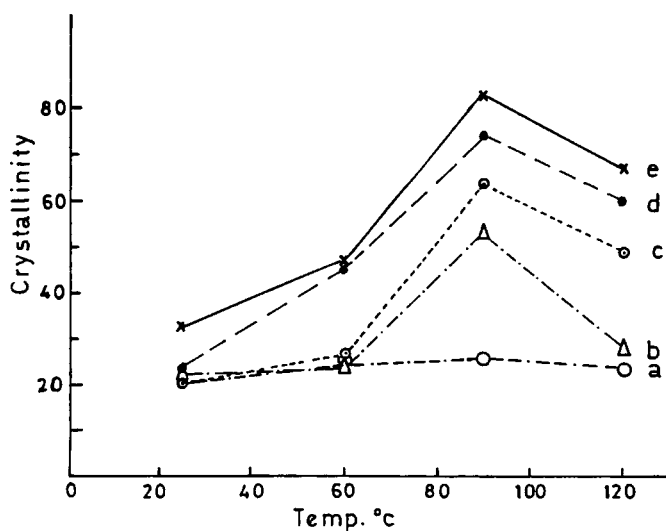


Fig. 9. Relationship between temperature and crystallinity of the samples heated with ZnCl<sub>2</sub>: (a) untreated with 5 wt % KOH/ZnCl<sub>2</sub> = 1; (b) treated with 5 wt % KOH/ZnCl<sub>2</sub> = 2; (c) treated with 10 wt % KOH/ZnCl<sub>2</sub> = 1; (d) treated with 10 wt % KOH/ZnCl<sub>2</sub> = 2.

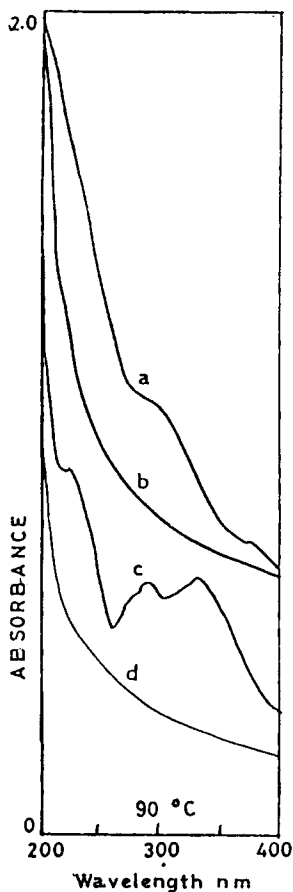


Fig. 10. The ultraviolet spectra of the heat-treated samples at 90°C: (a) treated with 20 wt % KOH/ZnCl<sub>2</sub> = 1; (b) treated with 20 wt % KOH/ZnCl<sub>2</sub> = 2; (c) treated with 30 wt % KOH/ZnCl<sub>2</sub> = 1; (d) treated with 30 wt % KOH/ZnCl<sub>2</sub> = 2.

tables that exposure of FeCl<sub>3</sub>- or ZnCl<sub>2</sub>-treated PVA to 12 or 28 Mrad causes no significant changes in the value of this ratio.

The percent crystallinity of all exposed samples are given in Tables I and II. These tables indicate the following:

1. While  $\gamma$ -irradiation of untreated and FeCl<sub>3</sub>-treated samples of PVA with 12 Mrad causes a slight decrease in their crystallinity  $\gamma$ -irradiation with 28 Mrad produces no changes in their crystallinity.
2.  $\gamma$ -irradiation of ZnCl<sub>2</sub>-treated PVA with either 12 or 28 Mrad results in a sharp increase in their crystallinity. For any given sample the increase in the crystallinity of the samples irradiated with 28 Mrad is always higher than that for the samples irradiated with 12 Mrad. Also, the crystallinity of the irradiated samples increases as the ratio KOH/ZnCl<sub>2</sub> increases.

The analysis of the UV spectra of  $\gamma$ -irradiated ZnCl<sub>2</sub>-treated PVA revealed that exposure of untreated and chemically treated PVA with 12 and 28 Mrad

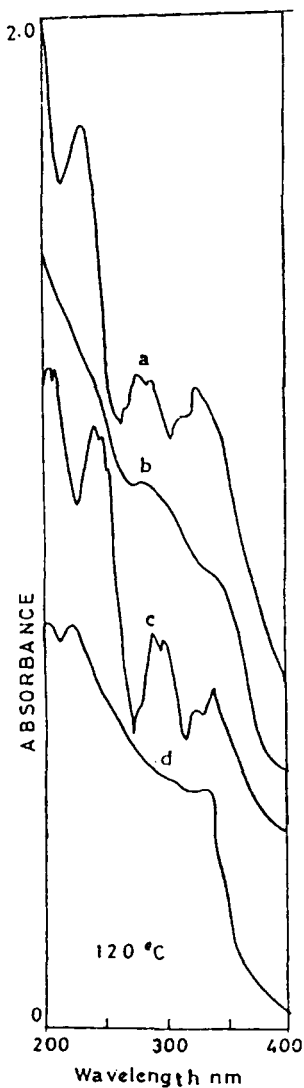


Fig. 11. The ultraviolet spectra of samples heated at 120°C: (a) treated with 20 wt % KOH/ZnCl<sub>2</sub> = 1; (b) treated with 20 wt % KOH/ZnCl<sub>2</sub> = 2; (c) treated with 30 wt % KOH/ZnCl<sub>2</sub> = 1; (d) treated with 30 wt % KOH/ZnCl<sub>2</sub> = 2.

has no influence on their UV spectral features. Bravar et al.<sup>6</sup> mentioned that even prolonged exposure of PVA to UV irradiation did not provoke an increase of the existing bands nor the appearance of a new band. This means, practically, that under mild conditions of irradiation the oxidation of PVA is not possible.

Varma et al.<sup>9</sup> pointed out that the infrared spectrum of PVA irradiated in the presence of CCl<sub>4</sub> at 3 Mrad shows a sharp and intense peak at 1645 cm<sup>-1</sup>. They concluded that the appearance of this peak is due to extended conjugation which imparted brown color to the fiber. Rabiel and Daghestani<sup>10</sup> concluded that exposure of PVA to  $\gamma$ -irradiation at the range from 0.5 to 5 Mrad does not result in the appearance of new infrared absorption bands, but the exposure

at 10 and 15 Mrad causes a remarkable increase in the intensity of the carbonyl band at  $1710\text{ cm}^{-1}$ . Bravar et al.<sup>6</sup> observed that the photooxidation of PVA increases with increasing exposure of dichromated films to UV irradiation. The rise of the content of carbonyl groups is more evident at major dichromate/PVA ratio. They assigned the bands at  $1710$  and  $1590\text{ cm}^{-1}$  to the carbonyl groups and  $\beta$ -diketone groups, respectively.

Based on the above exposure of  $\text{ZnCl}_2$ -treated PVA to  $\gamma$ -irradiation results in the formation of  $\beta$ -diketone groups, which is indicated by the appearance of the absorption band at  $1595\text{ cm}^{-1}$ .

The  $\text{ZnCl}_2$ -treated samples were also heated in air at 60, 90, 120, and  $150^\circ\text{C}$ . The infrared spectra of the samples treated with 5 and 10 wt % ( $\text{KOH}/\text{ZnCl}_2 = 2$ ) are shown in Figures 7 and 8. The analysis of the infrared spectra of the heat-treated PVA revealed that heat treatment of PVA at 60, 90, 120, and  $150^\circ\text{C}$  causes no observable changes in their infrared spectral features.

It is apparent that the spectrum of PVA shows two bands at about  $1425$  and  $1435\text{ cm}^{-1}$  and the peak maximum of the former is higher than that of the latter. It was observed that heat treatment of the samples chemically treated with 5 wt %  $\text{ZnCl}_2$  ( $\text{KOH}/\text{ZnCl}_2 = 2$ ) and with 10 wt % ( $\text{KOH}/\text{ZnCl}_2 = 1$  and 2) at 90 and  $120^\circ\text{C}$  causes the reverse. The heat treatment of all chemically treated samples at  $150^\circ\text{C}$  produces very striking changes in their spectral features. First, a strong sharp band appears at  $1600\text{ cm}^{-1}$  whereas the band at  $1710\text{ cm}^{-1}$  becomes very strong. Second, the crystalline band at  $1141\text{ cm}^{-1}$  disappears. Third, the O—H stretching band at  $3350\text{ cm}^{-1}$  shifts to  $3450\text{ cm}^{-1}$ .

The crystallinity of the heat-treated samples are drawn against the temperature in Figure 9. As can be seen from this figure, heat treatment of  $\text{ZnCl}_2$  samples increases its crystallinity. The maximum value of crystallinity is obtained when the samples are heated at  $90^\circ\text{C}$ . Continued increase of temperature to  $120^\circ\text{C}$  results in a remarkable decrease in the crystallinity. Figure 9 indicates that the crystallinity of the heat-treated PVA samples depends on both the  $\text{ZnCl}_2$  concentration and the  $\text{KOH}/\text{ZnCl}_2$  ratio. The increase in crystallinity may be attributed to annealing.

The UV spectra of the heat-treated samples provide strong evidence that the most striking changes in their spectra occur only when the samples treated with 20 and 30 wt % are heated at 90 and  $120^\circ\text{C}$  (Figs. 10 and 11). The spectra of the sample chemically treated with 20 and 30 wt % ( $\text{KOH}/\text{ZnCl}_2 = 1$ ) exhibit strong absorption at 197 nm, a doublet at 280 nm and 290 nm, a weak band at 310 nm, and a strong band at 330 nm. The intensities of these bands decrease with increasing the  $\text{KOH}/\text{ZnCl}_2$  ratio to 2. The band at 280 nm is assigned to the carbonyl groups associated with the ethelen unsaturation of the type  $-\text{CO}-(\text{C}=\text{C})-$ , while the band at 330 nm is assigned to  $-\text{CO}-(\text{C}=\text{C})_3-$  groups.

The degradation reactions of PVA which appear possible under the experimental conditions are unsaturation, chain scission, crosslinking, increased crystallinity, and oxidation to ketone and carboxylate groups.<sup>11</sup> The significant change in the infrared spectra of the membrane during heating is the development of absorption in the carbonyl ( $1700\text{ cm}^{-1}$ ) and alkene ( $1600\text{ cm}^{-1}$ ) region.<sup>11</sup> Bravar et al.<sup>6</sup> assigned a band at  $1590\text{ cm}^{-1}$  to  $\beta$ -diketone groups. The results of the present study are in good agreement with the above-mentioned findings.

### CONCLUSION

The infrared spectra of FeCl<sub>3</sub>- or ZnCl<sub>2</sub>-treated PVA provide no evidence for the formation of oxygen to metal (M—O) band. The treatment results in considerable changes in its crystallinity, particularly for the samples treated with ZnCl<sub>2</sub>. The exposure of untreated and FeCl<sub>3</sub>-treated samples to 12 and 28 Mrad of  $\gamma$ -radiation results in no observable changes in their UV and IR spectral features, whereas the exposure of ZnCl<sub>2</sub>-treated samples to these dosages results in the appearance of an infrared absorption band at 1595 cm<sup>-1</sup> corresponding to the  $\beta$ -diketone groups.

$\gamma$ -Irradiation of the ZnCl<sub>2</sub>-treated samples also causes remarkable changes in their crystallinity. Moreover, the obtained data revealed that heat treatment of PVA up to 150°C causes only slight changes in its crystallinity, while degradation reactions such as changes in crystallinity and oxidation appear in the ZnCl<sub>2</sub>-treated PVA. This means that treatment of PVA with ZnCl<sub>2</sub> under the experimental condition carried out in this study helps in oxidative degradation of PVA.

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