Optical Studies of Pure and Gelatin-Doped Poly(vinyl alcohol) Films Irradiated with Fast Neutrons

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ABSTRACT: The ultraviolet (UV) and infrared (IR) spectra of pure poly(vinyl alcohol) (PVA) and gelatin-doped PVA films with concentrations (2, 5, 7, 10, and 15 wt %) were studied before and after irradiation with neutron fluences in the range of 10^5-10^8 n/cm². The obtained data revealed that the addition of gelatin and neutron irradiation causes structural variation in the PVA network. The analysis of the UV spectra showed that the increase of dopant concentration above 5 wt % gelatin makes the sample less resistant to a degradation effect caused by neutron irradiation. It was also found that the intensity of the band at 210 nm increases by increasing dopant concentration. Careful examination of the infrared spectra indicated that the induced percent crystallinity of the sample containing 5 wt % gelatin has more stability than the other doped samples. Neutron irradiation also results in the appearance of new absorption bands and irregular change in the absorbance of some IR bands. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1395–1406, 1999

Key words: fast neutron; gelatin-doped PVA; degradation; crystallinity; absorbance

INTRODUCTION

Physical, as well as chemical, studies on modified films of pure and doped polymers are traditionally interesting because of their importance in developing well-characterized materials for various engineering and technological purposes.¹⁻⁴ Exposure of polymers to fast neutron irradiation causes changes in structure and, hence, in chemical and physical properties.⁵⁻⁹

Poly(vinyl alcohol) (PVA) is a nontoxic watersoluble synthetic polymer that is widely used in biochemical and biomedical applications.^{10–11} Doping PVA with a potentially useful natural biopolymer such as gelatin seems to be an interesting way of preparing a polymeric composite.¹² Such a composite reported improved absorbability when used as an implant^{12,13} and as matrices for silver halide photographic emulsions.¹⁴ In particular, the ultraviolet (UV) and infrared (IR) spectroscopy methods are very sensitive, accurate, and rapid. Therefore, these methods are capable of following small and rapid changes in crystalline structure arising from both doping concentration and ionizing irradiation.^{15–18}

The present work is carried out to investigate the effect of both doping with gelatin and neutron irradiation on the structure of gelatintreated PVA by using UV and IR spectroscopic techniques.

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EXPERIMENTAL

Commercial samples of PVA and gelatin were obtained from El-Nasr Company, Egypt. PVA material was dissolved in a mixture consisting of distilled water and ethanol in a ratio of 4:1. Gelatin was dissolved in distilled water and added to a PVA solution in different percentages of gelatin (2, 5, 7, 10, and 15 wt %). The films of pure and doped PVA were cast on glass plates of distilled water and ethanol solutions and slowly dried in an air oven at 25°C for 72 h to minimize gelation effects. Thin films of approximately 0.2 mm were cut into square pieces. Samples were irradiated at room temperature with fast neutrons from a 252 CF source over the range of 10^5 – 10^8 n/cm². The source emits neutrons with a yield of 2.5×10^6 n/s during the time of measurements.

The UV-visible absorption spectra of unirradiated and irradiated samples were carried out using a Berkin–Elmer 4-B spectrophotometer in the wavelength range of 200–900 nm. The IR spectral analysis of the previous samples were performed using PYE Unican spectrophotometer over the range of 400–4000 cm⁻¹. All measurements were done 24 h after irradiation.

RESULTS AND DISCUSSION

UV Absorption Spectra

Optical absorption measurements are carried out in particular to check the presence of gelatin in the PVA polymer matrix. Figure 1 shows the UV absorption spectra of pure PVA, pure gelatin, and gelatin-doped PVA with concentrations of 2, 5, 7, 10, and 15 wt %. The spectrum of pure PVA shows a weak band at about 282 nm and moderate broadband centered at about 360 nm. The first band at 282 nm is attributed to the absorption of carbonyl groups.^{6,17,19} The second band at 360 nm is not reported in previous studies, thus it may be due to the difference in molecular weight of PVA, purity, and the method of preparation.

The absorption spectrum of pure gelatin films shows a band at 210 nm that is sharp and intense. This band has a shoulder at the longer wavelength side at about 240 nm.

The absorption spectra of gelatin-doped PVA samples show only two bands centered at 210 and 350 nm. The band at 282 nm and the shoulder at 240 nm in pure PVA and gelatin, respectively, disappeared. The disappearance of the absorption band at 282 nm indicates that the ligand PVA becomes opaque in the UV region.²⁰ The position of the bands at 210 and 350 nm is nearly kept unchanged with increasing gelatin concentration. On the other hand, the absorption intensity of the band at 210 nm increased linearly with increasing gelatin concentration (see the inset of Fig. 1). However, the absorption intensity of the 350-nm band changed irregularly with increasing gelatin concentration.

Figure 2 shows the absorption spectra of pure PVA samples before and after irradiation with fast neutron fluences in the range of 10^5-10^6 n/cm². The PVA sample irradiated with 10^5 n/cm² neutron fluence shows approximately the same behavior as the unirradiated one except that the position of the band at 360 nm is shifted to a longer wavelength at 370 nm. Further increase of the radiation dose up to 10^7 n/cm² entails the disappearance of the two absorption bands at 282 and 360 nm. At 10^8 n/cm² neutron fluence, the absorption band at 282 nm reappeared with a shift in position to a shorter wavelength at 370 nm disappeared.

The disappearance of the absorption bands at 282 and 360 nm at most neutron fluence for PVA sample can be interpreted in terms of induced defects (color centers) according to a crosslinking or degradation process caused by neutron fluence.

The absorption spectra of the irradiated doped PVA samples containing 2, 5, and 7 wt % gelatin show the same behavior, therefore, the 2 wt % sample is taken as a representation (see Fig. 3). In the range of neutron fluence used, only one band appeared for gelatin content, whereas the other band for ligand PVA disappeared. It is clear from Figure 3 that the position of the gelatin absorption band shows irregular remarkable variation with increasing radiation dose. However, the inset of Figure 3 indicates that the absorption intensity of the gelatin band increases with increasing neutron fluence up to 10^7 n/cm² followed by a decrease up to 10⁸ n/cm². It must be mentioned that in the sample containing 7 wt % (figure is not shown), the intensity of the gelatin band increases with increasing neutron fluence up to 10^6 n/cm², followed by a decrease up to 10^8 n/cm^2 .

At higher concentrations of 10 and 15 wt % gelatin, there is also one band of gelatin content for irradiated samples up to 10^6 n/cm^2 (for sake of brevity, only 10 wt % spectra are shown in Fig. 4). At neutron fluences of 10^7 and 10^8 n/cm^2 , a shoul-



 $\label{eq:Figure 1} \begin{tabular}{l} Figure 1 & Absorption spectra for unirradiated gelatin-PVA samples of different concentrations. \end{tabular}$

der appeared in the gelatin band at 220 and 225 nm, respectively, for samples containing 10 wt % gelatin and at 215 and 219 nm, respectively, for samples containing 15 wt % gelatin (figure is not shown). The inset of Figure 4 shows an increase in the absorption intensity of the gelatin band

with increasing neutron fluence up to 10^6 n/cm^2 , followed by a decrease up to 10^8 n/cm^2 . Therefore, the increase of dopant concentration above 5 wt % gelatin appears to make the sample less resistant to degradation effects usually caused by neutron irradiation.



Figure 2 Absorption spectra for pure PVA samples irradiated with different neutron fluences.

IR Spectra

The IR spectrum and assignment of the most evident absorption bands for pure PVA thin film is illustrated in Figure 5. It appears from Figure 5 that there is no appreciable difference in the absorption bands of PVA when compared with that previously reported,^{1,17,21,22} except for the appearance of absorbed H₂O band at 1660 cm⁻¹.

Water is probably present since vacuum drying is not used. The broad OH absorption (stretching) at 3340 cm^{-1} results from the superposition of multiple polymeric H bonds associated with the crystalline phase and dimeric H bonds associated with the amorphous phase.

The IR spectrum and assignment of the most evident absorption bands for pure gelatin thin



Figure 3 Absorption spectra for 2 wt % gelatin–PVA samples irradiated with different neutron fluences.

film is illustrated in Figure 6. Careful examination of the spectrum showed that the regions of 3000-3600 and 1100-1700 cm⁻¹ contain the most potentially useful information bearing on the structure of gelatin. The bands identified as N—H stretching vibrations are considered to be hydrogen bonded.²³ The existence of two or more frequencies for the same band might be interpreted as indicating two different types of hydrogen bond. The stretching frequency N—H band showed at 3360 cm⁻¹ that it is characteristic of the collagen fold.²⁴ Figure 7 shows the IR spectra of doped PVA samples with concentrations of 2, 5, 7, 10, and 15 wt % gelatin. A slight variation was observed in the position and the intensity of the absorption band in an irregular way as a result of increasing the dopant gelatin concentrations. In addition, the distinctive C—H stretching doublet appearing at 2914 and 2945 cm⁻¹ in pure PVA becomes a single band at $\sim 2930 \text{ cm}^{-1}$ at 2, 5, and 7 wt % gelatin-doped concentrations. On the other hand, no variation has been observed in the absorption bands of gelatin-doped PVA when compared with that shown for pure PVA thin film (see Fig. 5). This may be attributed either to the lower percentage of gelatin added to PVA, or to the occurrence of the most active infrared groups in the structure of PVA, or to both factors.

The infrared spectra of pure PVA, 5, 7, and 15 wt % gelatin-doped PVA samples before and after



Figure 4 Absorption spectra for 10 wt % gelatin–PVA samples irradiated with different neutron fluences.

exposure to various neutron fluences in the range of 10⁵-10⁸ n/cm² are shown in Figure 8. In general, it appears from Figure 8 that there is no appreciable difference between the spectra of irradiated and unirradiated samples apart from the change in intensity and position of the absorption bands, appearance of new bands, and overlapping at certain doses in some investigated samples. In the case of pure and 2 wt % gelatin-doped PVA [see Fig. 8(i)] (for sake of brevity, 2 wt % gelatin spectra are not shown), a new band at \sim 2855 $\rm cm^{-1}$ appeared at neutron fluences 10^5 and 10^6 n/cm^2 , whereas the band at 1418 cm⁻¹ overlapped with the next band at 1444 cm^{-1} at neutron fluences 10^7 and 10^8 n/cm² in both samples. For samples containing 5 and 7 wt % gelatin [Figs. 8(ii) and 8(iii)], a new band at 2860 cm⁻¹ appeared at 10^7 n/cm^2 for 5 wt % gelatin and at doses of 10^5 and 10^8 n/cm^2 for 7 wt % gelatin samples. At higher concentrations of 10 and 15 wt % gelatin [Fig. 8(iv)] (for sake of brevity, 10 wt % gelatin spectra are not shown), the neutron fluences exhibit a new band in the range of $2360-2860 \text{ cm}^{-1}$, except that the doublet C—H stretching becomes a single band at 10^6 n/cm^2 for 15 wt % gelatin sample. In addition, the band at 1418 cm⁻¹ is overlapped with the next band at 1444 cm⁻¹ in both concentrations for all neutron fluences except at 10^8 n/cm^2 . It is worth mentioning that new bands appeared in the region of $500-1000 \text{ cm}^{-1}$ for the irradiated samples of different concentrations.

The absorbance values of the bands at 1140, 1444, and 1715 $\rm cm^{-1}$ were determined for pure PVA and gelatin-doped PVA samples before and



Figure 5 Infrared spectrum of pure PVA thin film.

after irradiation using the baseline method and are given in Table I. The variations of the absorbances of the IR bands at 1140, 1444, and 1715 cm^{-1} of pure PVA and gelatin-doped PVA with neutron fluences are represented graphically in Figure 9. It can be easily noted that the charac-



Figure 6 Infrared spectrum of pure gelatin thin film.



Figure 7 Infrared spectra of gelatin-doped PVA samples: (a) 2 wt % gelatin–PVA, (b) 5 wt % gelatin–PVA, (c) 7 wt % gelatin–PVA, (d) 10 wt % gelatin–PVA, and (e) 15 wt % gelatin–PVA.

teristic features of this relation for each band in different samples are not similar. The absorbance of the band at 1140 cm^{-1} increases with increasing doses to 10^6 n/cm^2 , and then was followed by a decrease until 10^8 n/cm² for pure PVA of 7, 10, and 15 wt % gelatin-doped PVA. However, for samples containing 2 and 5 wt % gelatin, the absorbances of the band at 1140 cm^{-1} increases at an exposure dose $10^5~n/cm^2;$ then a decrease until doses 10^6 and $10^7~n/cm^2,$ respectively; and then by an increase until a dose of 10^8 n/cm^2 for both samples. The absorbance of the band at 1444 cm^{-1} increases with increasing doses to 10^{6} and 10^7 n/cm² and then is followed by a decrease until 10^8 n/cm² for 7 and 15 wt % gelatin and 2, 5, and 10 wt % gelatin, respectively. However, for pure PVA samples, the absorbance of the band at 1444

 $\rm cm^{-1}$ increases as the dose is raised to 10⁵ n/cm², followed by a decrease at 10⁶ n/cm², and then it increases with increasing the dose to 10⁸ n/cm².

The absorbance of the band at 1715 cm^{-1} increases as the dose is raised to 10^5 n/cm^2 , followed by a decrease at 10^6 and 10^7 n/cm^2 , and then it increases until 10^8 n/cm^2 for 7 wt % gelatin and pure PVA and 10 wt % gelatin, respectively. However, samples containing 5 and 15 wt % gelatin have a similar characteristic feature, that is, an initial increase at 10^5 n/cm^2 , followed by a decrease at 10^6 n/cm^2 , followed by a decrease at 10^6 n/cm^2 , followed by an increase at 10^7 n/cm^2 . For samples containing 2 wt % gelatin, the absorbance of the band at 1715 cm^{-1} increases with increasing neutron fluence up to 10^6 n/cm^2 , then a minimum value is obtained at 10^7 n/cm^2 , and



Figure 8 IR spectra for (i) pure PVA, (ii) 5 wt %, (iii) 7 wt %, and (iv) 15 wt % gelatin-doped PVA samples at different neutron fluences; (a) unirradiated, (b) 10^5 n/cm², (c) 10^6 n/cm², (d) 10^7 n/cm², and (e) 10^8 n/cm².

Sample	$\begin{array}{c} Frequency \\ (cm^{-1}) \end{array}$	Neutron Fluences (n/cm ²)					
		Unirradiated	10^{5}	10 ⁶	107	10 ⁸	
Pure PVA	1140	0.05	0.14	0.20	0.17	0.16	
	1444	0.10	0.14	0.06	0.11	0.24	
	1715	0.11	0.18	0.11	0.09	0.13	
$2 ext{ wt } \%$	1140	0.09	0.22	0.15	0.18	0.19	
Gelatin-PVA	1444	0.06	0.14	0.17	0.25	0.24	
	1715	0.06	0.16	0.20	0.08	0.13	
5 wt %	1140	0.05	0.21	0.10	0.04	0.12	
Gelatin-PVA	1444	0.04	0.11	0.15	0.19	0.17	
	1715	0.06	0.12	0.09	0.13	0.09	
7 wt %	1140	0.04	0.18	0.28	0.19	0.05	
Gelatin–PVA	1444	0.05	0.18	0.31	0.24	0.11	
	1715	0.04	0.14	0.02	0.05	0.06	
10 wt %	1140	0.11	0.12	0.34	0.22	0.07	
Gelatin-PVA	1444	0.08	0.09	0.30	0.45	0.18	
	1715	0.04	0.07	0.06	0.05	0.08	
15 wt %	1140	0.04	0.06	0.31	0.12	0.11	
Gelatin-PVA	1444	0.05	0.09	0.41	0.24	0.18	
	1715	0.05	0.14	0.08	0.12	0.06	

Table I Values of the Absorbance at IR Bands 1140, 1444, and 1715 cm^{-1} of Pure PVA and Gelatin-Doped PVA with Neutron Fluences

finally, an it increases until 10^8 n/cm^2 . The induced formation of the carbonyl group band at 1715 cm⁻¹ can be interpreted on the basis of the peroxide-mediated oxidative degradation mechanism. Neutron irradiation of the polymers results in bond cleavage giving free radicals that in the presence of oxygen react by a chain mechanism to form oxidation products that include hydroperoxides. The radical steps set in motion during the course of the reactions include pathways that lead to polymer chain scission and crosslinking.

In view of the above-mentioned data, it can be concluded that the exposure of pure PVA and gelatin-doped PVA in the range of 10^5-10^8 n/cm² doses result in the appearance of new absorption bands and remarkable irregular change in absorbance and position of the IR bands.

The percent crystallinity of pure and gelatindoped PVA samples are calculated using the relation 25

Percent crystallinity =
$$92(d/c) - 18$$
 (1)

where d is the vertical distance between the 1140 cm⁻¹ peak and the intercept point of a straight line drawn across the portion of the spectrum be-

tween 1125 and 1150 cm⁻¹, and c is the vertical distance between the 1444 cm⁻¹ peak and baseline.

The percentage crystallinity of the investigated samples of different neutron fluences are listed in Table II. The data in Table II reveal that the percent of crystallinity for unirradiated samples increased with increasing gelatin concentrations up to 5 wt %, followed by a decrease until 15 wt %. For the irradiated pure PVA, 2 and 5 wt % gelatin-doped PVA samples of the values of percent crystallinity are increased with neutron fluence up to 10^6 n/cm², and then are decreased until 10^8 n/cm^2 . However, for higher concentrations of 7, 10, and 15 wt % of gelatin-doped PVA samples, the values of percent crystallinity are increased at a neutron fluence of 10^5 n/cm², followed by a decrease until 10⁸ n/cm². Therefore, it must be mentioned that the sample containing 5 wt % gelatin has more radiation resistance than the other doped samples. The decrease in the percent crystallinity by neutron irradiations may be attributed to the superficial degradation that starts mainly in the amorphous regions, followed by the crosslinking process.⁶ This behavior of the dopant polymer is due to the molecular motions allowed in their amorphous phases. These results agree well



Figure 9 Variation of the absorbance of IR bands 1140, 1444, and 1715 cm^{-1} of pure and gelatin-doped PVA with neutron fluence.

with many studies carried out to explore the location of crosslinking that occurs both in crystalline and amorphous regions, but predominantly in the latter region and in the interface between them.^{26,27}

CONCLUSION

The results of this investigation indicate the role of both the dopant concentrations and the fast neutrons on polymer structure forming crosslinking and/or degradation. This is clearly shown by the change of the absorbance in the UV and IR spectra and is confirmed by the percent of crystallinity data for pure and gelatin-doped PVA samples. In the UV spectra, the increase of dopant concentration above 5 wt % gelatin appears to make the sample less resistant to degradation effects usually caused by neutron irradiation. Moreover, the percent of crystallinity data calculated from IR spectra reveal that the 5 wt % gelatin concentration specimen has more radiation stability than the other pure and doped samples. Thus, one may conclude that there is a limiting

	Neutron Fluence (n/cm ²) (Percentage Crystallinity)						
Sample	Unirradiated	10^{5}	10 ⁶	107	10 ⁸		
Pure PVA	12.30	37.80	57.00	55.00	12.00		
2 wt % Gelatin–PVA	27.20	31.80	34.80	32.20	7.50		
5 wt % Gelatin–PVA	45.30	49.90	53.16	41.00	38.00		
7 wt % Gelatin–PVA	33.75	47.40	35.40	7.00	6.10		
10 wt % Gelatin–PVA	30.70	43.70	36.70	10.00	7.60		
15 wt % Gelatin–PVA	14.66	43.70	41.00	14.30	10.80		

concentration beyond which more energy is transferred to the polymer yielding a rupture of the bonds in polymer matrix. Therefore, it is recommended to take into consideration the role of additive concentration of chemical compounds in obtaining polymeric materials with specific characterization.

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