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Optical studies of fast neutron irradiated poly(vinyl alcohol)/ hydroxypropyl cellulose blends

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ABSTRACT

Thin transparent films of poly(vinyl alcohol)/hydroxypropyl cellulose (PVA/ HPC) (0/100, 92/8, 88/12, and 0/100 wt/wt%) were prepared by using solution-cast technique. The effects of HPC concentration on the optical characterizations by analyzing the transmittance spectra in the spectral region 200–900 nm as well as the variations in the group coordination by using FTIR technique in the region (4000-1000 cm^{-1}) of the prepared PVC/ HPC blends have been done before and after irradiation with two fast neutrons fluencies (1 x 10^5 and 1 x 10^7 n/cm^2). The study has been extended to include the changes in the optical parameters including the band tail width and band gap energies for the samples. The results noticed that the optical band gap was derived from Tauc's extrapolation and increases with the HPC contents. Also, the results obtained by the FTIR indicate that the increase in the concentration of HPC with PVA changed the chemical bonds and hence changed the molecular configuration of PVA. Moreover, the results obtained by the effect of different weight percent of HPC were compared with that detected by the effect of fast neutrons.

KEYWORDS

Poly(vinyl alcohol);
Hydroxypropyl cellulose;
Fast neutrons irradiation;
Absorption coefficient;
Optical parameters;
FTIR analysis.

INTRODUCTION

Blending is an especially important process for developing industrial applications of polymeric materials[1]. Blending, natural polymer with synthetic polymer seems to be an interesting way of polymeric composites. The selection and use of polymers can potentially form hydrogen bonds when two polymers mixed, as well as the study of blends properties, are of importance to find further applications of the resulting blend materials for biomedical and pharmaceutical devices[2]. Cellulose was blended with poly(N-vinyl-2-pyrrolidone)[3], poly(methyl methacrylate)[4] and poly(2-hydroxy ethyl methacrylate)[5]. Poly(vinyl alcohol) can be blended with poly(N-vinyl-2-pyrrolidone)[6], hydroxypropyl cellulose and hydroxypropyl methyl cellulose[7]. Here, hydrogen bonding interaction is an important aspect of miscibility since intermolecular interactions regulate the compatibility among the component polymer molecules[8].

Poly(vinyl alcohol) is used in surgical devices, sutures, hybrid islet transplantation, implantation, blend membrane[9], in synthetic cartilage in reconstructive joint surgery[10], as a new type of soft contact lens[11], as sheets to make bags for premeasured soap, for washing machines, or to make longer bags used in hospitals[12]. PVA was selected in the present study, as the hydrogel component based on its favorable water-soluble, desirable physicochemical properties and its biocompatibility[13].

Hydroxypropyl cellulose (HPC) belongs to the group of cellulose ethers which has been used already for a year by paper of conservators as glue and sizing material. The material is soluble in water as well as in polar organic solvents (makes it possible to combine aqueous and non-aqueous conservation methods)[14]. Hydroxypropyl cellulose can be used for production of time controlled delivery systems and is also used as a topical ophthalmic protectant and lubricant[15]. In pharmaceuticals HPC used as a disintegrants and a binder for the wet granulation method of making tablets[16-19].

The objective of the present study is to prepare and characterize the PVA and HPC blend. UV/VIS analysis gives an evidence for understanding energy band diagram and optical parameters which is relatively affected by processing conditions. Fourier transform infrared (FTIR) technique was employed to characterize and reveal the miscibility map and the structure properties of such blending system. Therefore, in the present work, the effects of HPC concentrations on the optical properties of PVA/HPC blends by performing UV/VIS and FTIR analyses before and after irradiation with two different fast neutrons of fluencies, were reported.

EXPERIMENTAL

Materials and sample preparation

Poly(vinyl alcohol) (PVA) granules with molecular weight of 125 kg/mole was supplied from El-Nasr Company, Cairo, Egypt. Hydroxypropyl cellulose (HPC; Pharmacoat 606) with molecular weight of 95 kg/mole was supplied by Shin Etsu Chemical Co., Tokyo, Japan.

Thin transparent films of poly(vinyl alcohol)/ hydroxypropyl cellulose (PVA/HPC) blend (0/100, 92/8, 88/12, and 0/100 wt/wt%) were prepared by using solution-cast technique[19-23]. This method depends on the dissolution, separately, the weighted amounts of the poly(vinyl alcohol) (PVA) granules and hydroxypropyl cellulose (HPC) powder in double distilled water. Complete dissolution was obtained using a magnetic stirrer in a 50 °C water bath. To prepare thin films of the homopolymers (PVA and HPC) and the blend of their samples (PVA/HPC) with different weight percentages 100/0, 92/8, 88/12, and 0/100 wt/wt%, the solutions were mixed together at 50 °C with a magnetic stirrer. Thin films of appropriate thickness (about 0.01 cm) were cast onto stainless steel Petri dishes (10 cm diameter). The prepared films were kept at room temperature (ca. 25 °C) for 7 days until the solvent completely evaporated and then kept in desiccators containing fused calcium chloride to avoid moisture. The samples were measured at room temperature (about 25 °C) as solid films (slabs) of dimensions 1 x 4 cm.

The prepare thin films of the blend of PVA/HPC were irradiated with fission neutrons with mean energy of approximately 4.2 MeV from Americium-Beryllium (^{241}Am-Be) neutron source of activity 5 Ci (185 GBq) and with emission rate 0.87 x 10^7 n/s at the Physics Department, Faculty of Science, Al-Azhar University, Cairo, Egypt. During irradiation the prepared samples were fixed in positions that neutrons were incident approximately normal. The irradiation temperature was adjusted to be about 25 °C. The films were exposed to two different fast neutron fluencies 1 x 10^5 and 1 x 10^7 n/cm^2. The fast neutron fluence was measured using a calibrated TLD-700 Thermoluminescence detector at the location of the sample.

Optical measurements

The optical transmittance for the prepared PVA/ HPC blended samples were carried out in the range from 200-900 nm using a Shimadzu UV/VIS/NIR Double Beam Spectrophotometer with standard illuminant C (1174.83) and has a serial number B44360512, Model V-530 and band width 2.0 nm covers the range 200-2500 nm with accuracy ±0.05%.

The color parameters: tristimulus transmittance value (y_t), the brightness (L), the color constants (A) and (B), the whiteness index (W) and the yellowness index (Ye)] are estimated using the CIE system[21,23-25]. The recorded color parameters for each sample were an average of five measurements taken from five randomly selected locations on the films.

Fourier transform infrared (FTIR) spectroscopy

The Fourier transform infrared transmission (FTIR) spectra of the samples under investigations were performed over the range 4000-400 cm^{-1} using a Bruker Vector 22 FTIR Spectrophotometer (Germany) with accuracy better than ±1%.

RESULTS AND DISCUSSIONS

Optical transmittance and color parameters calculations

The optical transmission spectra for PVA/HPC blended samples in the ultraviolet/visible (UV/VIS) region from 200 to 900 nm before and after fast neutron irradiation with two fluencies 1×10^5 and 1×10^7 n/cm^2 are shown in Figures 1a, 1b and 1c, respectively. From Figure 1a, it is found that, the spectrum of pure PVA shows one transmission band at about 281 nm which may be attributed to the absorption of carbonyl groups[26,27]. Moreover, there is an observable decrease in the transmittance value for the whole spectrum with increasing the concentration of HPC which may be due to the fact that increasing HPC concentration decreases the transparency of the sample which means that there is a change in the molecular configuration[28]. It is clear from Figures 1b and 1c that, the transmittance band for pure PVA sample (100/0 wt/wt%) at about 281 nm disappeared with increasing neutron fluencies. This disappearance of the transmittance band for the irradiated samples may indicate that the ligand PVA matrix becomes opaque in the ultraviolet region[28]. Moreover, this may be interpreted in terms of induced defects (color centers) according to cross-linking and/or degradation processes caused by neutron fluence[29]. Furthermore, the obtained variations in the blend samples may be due to some sort of interaction between the color centers created by the interaction of radiation with both PVA and HPC matrices.

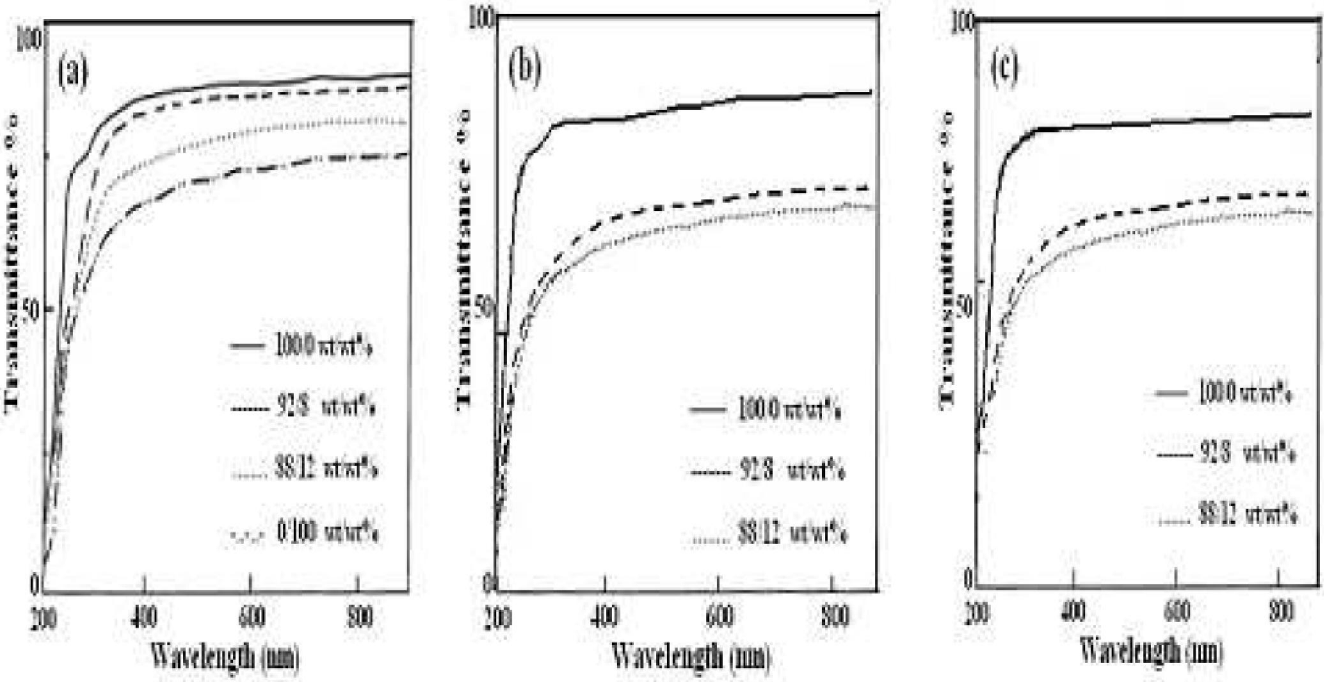

Figure 1 : The transmission spectra of PVA/HPC blended samples before (a) and after irradiation with fast neutron fluencies 1×10^5 n/cm^2 (b) and 1×10^7 n/cm^2 (c).

The tristimulus transmittance values (y_t) calculated from the transmittance data of wavelengths in the range 400-700 nm for PVA/HPC blend samples before and after irradiation with fast neutrons are represented in Figure 2a. It is clear that the behaviours of y_t for the samples are similar and nearly have the same peak position at about 555 nm as that of the most polymers. It is noticed from the figure that, y_t values decrease by about 9.2 and 11.6% with 92/8 and 88/12 wt/wt% PVA/HPC samples, respectively, in comparison with the pure

PVA value (100/0 wt/wt%).

Figures 2b and 2c illustrate the tristimulus transmittance values (y_t) as function of wavelength for the fast neutrons irradiated PVA/HPC blended samples with fluencies 1 x 10^5 and 1 x 10^7 n/cm^2, respectively. It is clear from the figures that for the pure PVA sample, the tristimulus transmittance values (y_t) increase with neutron fluencies in comparison with the unirradiated one. The change observed may be attributed to the process of photodegradation; formed during neutron interaction (scission); and/or due to the cross-linking occurred during photodegradation; results from the oxidation of free radicals in the polymer material. Due to this process, change in the color of the polymeric material is occurred[30]. Also, from the figures, it is noticed that the tristimulus transmittance values (y_t) and the broadening of the bands are changed with neutron fluencies without changing in their positions. The observed behaviours of the blended samples are opposite to that obtained for pure PVA but agree well and confirm the obtained results of the infrared analyses (observed later). This may be attributed to that there is a change in the molecular configuration which indicates to the formation of new color centers. TABLE 1 presents the variation of the tristimulus transmittance values (y_t) and their percentage changes due to irradiation with two fast neutron fluencies for PVA/HPC blended samples at band position (about 555 nm).

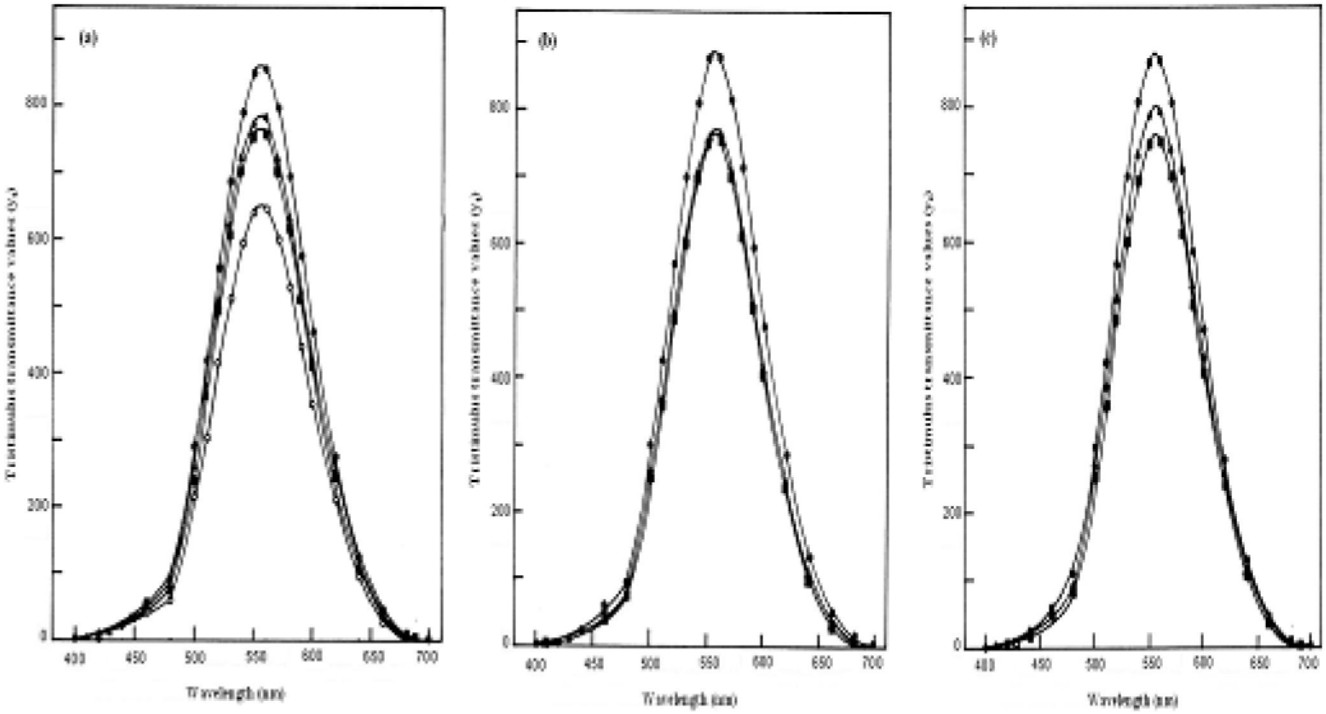

Figure 2 : The tristimulus transmittance values (y_t) of PVA/HPC blended samples before (a) and after irradiation with fast neutron fluencies of 1 x 10^5 n/cm^2 (b) and 1 x 10^7 n/cm^2 (c). (●) 100/0, (▲) 92/8, (■) 88/12 and (0)0/100 (wt/wt%).

TABLE 1 : The variations of the tristimulus transmittance values (y_t) and their percentage changes due to fast neutron irradiation for PVA/HPC blended samples at 555 nm.

Blended Sample	PVA/HPC (wt/wt%)					
Neutron fluence (n/cm^2)	100/0	92/8		88/12		0/100
	y_t	y_t	Δy_t%	y_t	Δy_t%	y_t
Unirradiated	865.0	785	9.2	765	11.6	655
1 x 10^5	887.5	775	12.7	765	13.8	-
1 x 10^7	885.0	805	9.0	760	14.1	-

The variation of color parameters [brightness (L), color constants (A) and (B), whiteness index (W) and yellowness index (Ye)] calculated from the transmittance values (Figure 1) and their percentage changes for PVA/HPC blended samples are given in TABLE 2. It is clear from the table that, the brightness (L) increases by increasing the HPC concentrations which means that the samples become brighter in color. The color constants (A) decreases while (B) increases with increasing the concentration of HPC which indicates that there is an increase in the green component instead of red one and yellow component instead of blue one, respectively. The decrease in the whiteness index (W) and increase in yellowness index (Ye) indicate that variation in color difference between the samples are occurred by the presence of HPC with PVA. The color parameters for PVA/HPC blended samples as functions of fast neutron fluencies (1 x 10^5 and 1 x 10^7 n/cm^2) calculated from the transmittance values are presented in TABLE 3. It is clear from the table for unirradiated and irradiated pure PVA samples that, nearly there are no detectable variations in the color parameters due to irradiation with fast neutrons. For 92/8 and 88/12 wt/wt% PVA/HPC blended samples, it is noticed that the values of the color parameters show opposite behaviour to that obtained for the pure PVA samples. Moreover, the results of the color scales ΔE, ΔC and ΔH indicate that changes in color difference between the samples before and after irradiation were existed.

TABLE 2 : The results of the color parameters and their percentage changes for PVA/HPC blended samples before irradiation with fast neutrons.

Color parameters	PVA/HPC (wt/wt%)			
	100/0	92/8	88/12	0/100
L	6.253	8.297	8.213	7.585
ΔL%	-	32.7	31.3	-
A	-1.894	-2.556	-2.482	-2.261
ΔA%	-	-35.0	-31.0	-
B	1.609	2.161	2.153	2.143
ΔB%	-	34.3	33.8	-
W	-3.703	-6.532	-6.407	-5.532
ΔW%	-	-76.4	-73.0	-
Ye	24.327	12.481	12.479	12.477
ΔYe%	-	-51.3	-48.7	-

TABLE 3 : The variations of the color parameters and their percentage changes for PVAHPC blended samples due to fast neutrons irradiation.

PVA/HPC blended samples	Color parameters							
	L	A	B	W	Ye	ΔE	ΔC	ΔH
100/0 wt/wt%								
Unirradiated	6.253	-1.894	1.609	-3.703	24.327	-	-	-
1 x 10^5 n/cm^2	6.253	-1.894	1.600	-3.700	24.057	0.009	-0.006	0.007
1 x 10^7 n/cm^2	6.253	-1.894	1.609	-3.703	24.327	0.000	0.000	0.000
92/8 wt/wt%								
Unirradiated	8.297	-2.556	2.161	-6.532	12.481	-	-	-
1 x 10^5 n/cm^2	8.263	-2.411	2.182	-6.492	12.479	0.015	-0.010	0.0182
1 x 10^7 n/cm^2	8.400	-2.538	2.185	-6.694	12.480	0.011	0.000	0.0149
88/12 wt/wt%								
Unirradiated	8.213	-2.482	2.153	-6.407	12.479	-	-	-
1 x 10^5 n/cm^2	8.250	-2.479	2.148	-6.457	12.480	0.004	-0.006	0.0053
1 x 10^7 n/cm^2	8.171	-2.465	2.148	-6.344	12.480	0.005	-0.017	0.006

From the data obtained, it is observed that the transmittance values and the induced changes in the color parameters indicate that irradiation with fast neutrons may lead rupture in the bonds and formation of free radicals and finally cross-linking. Furthermore, the results of PVA/HPC blended samples indicate that the variation induced coloration is both concentration and fast neutron fluence dependent. It may be presumed that the effect of fast neutron radiation on the macromolecules of the blended samples is the destruction of the chemical bonds and linkages as well as creation of highly energetic electrons and ions[31]. These highly energetic species migrate in the plastic network causing further damages to the adjacent macromolecules through tracks. The highly active groups may recombine again at random leading to cross-links. The presence of oxygen enhances such recombination through its interaction with these active macromolecules. Therefore, the highly energetic ions and electrons thus formed during irradiation may be trapped somewhere in the plastic network forming color centers whose intensities will increase with the increase of the fast neutron fluence.

It can be concluded that the changes occurred in the color parameters due to fast neutron irradiation may reflect the actual changes in the macromolecular structure of the polymer network. In addition, the obtained results are of great important for the improvement of the optical properties of PVA. Moreover, color parameters and color differences increase and decrease with increasing fast neutron fluencies according to the principle phenomena; cross-linking and degradation[32]. Their degrees depend mainly on the total quantity of radiation received by the material.

Optical absorption measurements

The absorption coefficient (α) was calculated from the optical transmission spectra by using the relation[22,23,30,33,34]:

$$\alpha = (1/d)\,[\ell n\,(1-R)^2/T] \qquad (1)$$

where d is the thickness of the sample in cm, T is the transmittance and R is the reflectance (neglected in the present calculations). Figure 3a shows the relation between the absorption coefficient (α) as a function of photon energy (hυ) for PVA/HPC blended samples before irradiation with fast neutrons. It is clear from the figure that the absorption coefficient (α) increases gradually with increasing HPC content and photon energy which may be attributed to the changes of the molecular configuration which indicates to the formation of new color centers[22,23,35].

For many amorphous materials, in the low absorption region the absorption coefficient (α) shows an exponential dependence on photon energy (hν) and obeys the Urbach relation[22,23,30,33]:

$$\alpha = \alpha_o \exp(h\upsilon/E_b) \qquad (2)$$

where α_o is a constant, υ is the frequency of radiation and E_b is the energy interpreted the width of the tail localized states in the normally forbidden band gap which are associated with the amorphous nature of the polymeric materials. Figure 3b shows the relation between (ℓn α) and (hυ) for PVA/HPC blended samples. The obtained straight lines suggest that the absorption follows the quadratic relation for inter-band transitions given by Mott and Davis[36]. The values of E_b can be deduced from the slopes of the straight lines and listed in TABLE 4. It is noticed that E_b increases with increasing HPC concentration. This increase in the band tail may be due to the variation in the internal fields associated with structure disorder in the system[21,23,35].

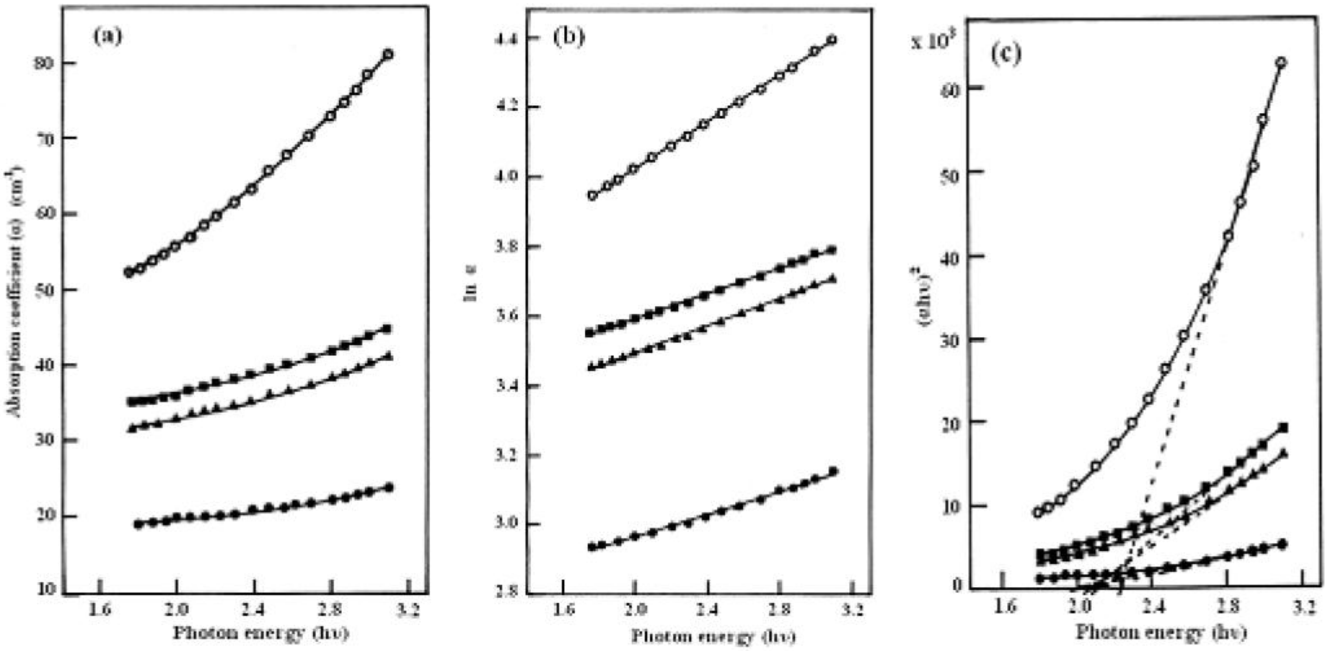

Figure 3 : The absorption coefficient, α (a), Urbach law plots (b) and the variation of $(\alpha h\upsilon)^2$ (c), for unirradiated PVA/HPC blended samples as functions of photon energy (hυ) in the visible range. (●) 100/0, (▲) 92/8, (■) 88/12 and (0) 0/100 (wt/wt%).

TABLE 4 : The values of absorption coefficient (α) at 555 nm, band tail energy (E_b), and direct energy gap (E_d), and their percentage changes for PVA/HPC blended samples before irradiation with fast neutrons.

PVA/HPC (wt/wt%)	α at 555 Nm(cm^{-1})	Δα%	E_b (eV)	ΔE_b%	E_d (eV)	ΔE_d%
100/0	20.08	-	0.1598	-	2.0251	-
92/8	34.75	73.1	0.1762	10.3	2.0438	0.92
88/12	38.25	90.5	0.1901	18.9	2.0856	2.99
0/100	62.25	-	0.3315	-	2.2404	-

According to the generally accepted model proposed by Tauc for higher values of absorption coefficient where the absorption is associated with inter-band transitions, it yields the power part which obeys the Tauc[37] and Mott & Davis[36] relations as:

$$\alpha h\upsilon = B(h\upsilon - E_g)^n \qquad (3)$$

Where B is the slope of the Tauc edge called the band tail parameter and n is the type of electronic transition responsible for absorption, being 0.5 for direct transition and 2 for indirect one. Figure 3c shows the variation of $(\alpha h\upsilon)^2$ as a functions of (hυ) for PVA/HPC blended samples. From the figures, the allowed direct energy gap (E_d) is determined from extrapolating of the linear parts of the curves at zero absorption and the values are represented in TABLE 4. It is clear that, E_d increases with increasing the HPC concentration which indicates that the obtained results of E_d show the dependence on the composition of the sample. It may be presumed that the variation may be due to the difference in the number of HPC ions per unit length available for conduction and, in addition, the change in molecular configuration induced by HPC concentration[21,23,35].

It is noticed that the variations in the values of E_b and E_d with increasing the concentration of HPC may be due to HPC-induced structural changes in the system. On other hand, these changes may arise from the random fluctuations of the internal fields associated with the structure disorder in the amorphous region of polymer material. Furthermore, it was recognized that dopant plays a dominant role in morphological and microstructure changes occurring in the polymer matrix[22,23,35].

The relations between the absorption coefficient (α) as a function of photon energy (hυ) for irradiated PVA/HPC blended samples with fast neutron fluencies 1 x 10^5 and 1 x 10^7 n/cm^2 are illustrated in Figure 4a. It is noticed that, α of the irradiated pure PVA decreases with neutron fluencies. The variation in the values of the absorption coefficient with fast neutrons may be attributed to change of the molecular configuration which leads to the formation of new color centers and also due to the formation of highly active free radicals which recombine to form molecular species[20,21,23,35,38].

The relation between (–!n α) and (hυ) for PVA/HPC blended samples at the two different neutron fluencies are plotted in Figure 4b. The values of the band tail energy (E_b) calculated from the slopes of the straight lines are presented in TABLE 5. It is obvious that the values of E_b for 100/0 and 92/8 wt/wt% PVA/HPC blended samples decrease with neutron fluencies. The behavior is in opposite to that obtained for the 88/12 wt/wt% PVA/HPC blended sample (TABLE 5). The obtained change may arise from the random fluctuations of the internal fields associated with structure disorder in the amorphous region of the polymer material. Moreover, it is recognized that both HPC concentrations and fast neutrons irradiation play a dominant role in morphological and microstructure change occurring in the polymer matrix[38,39].

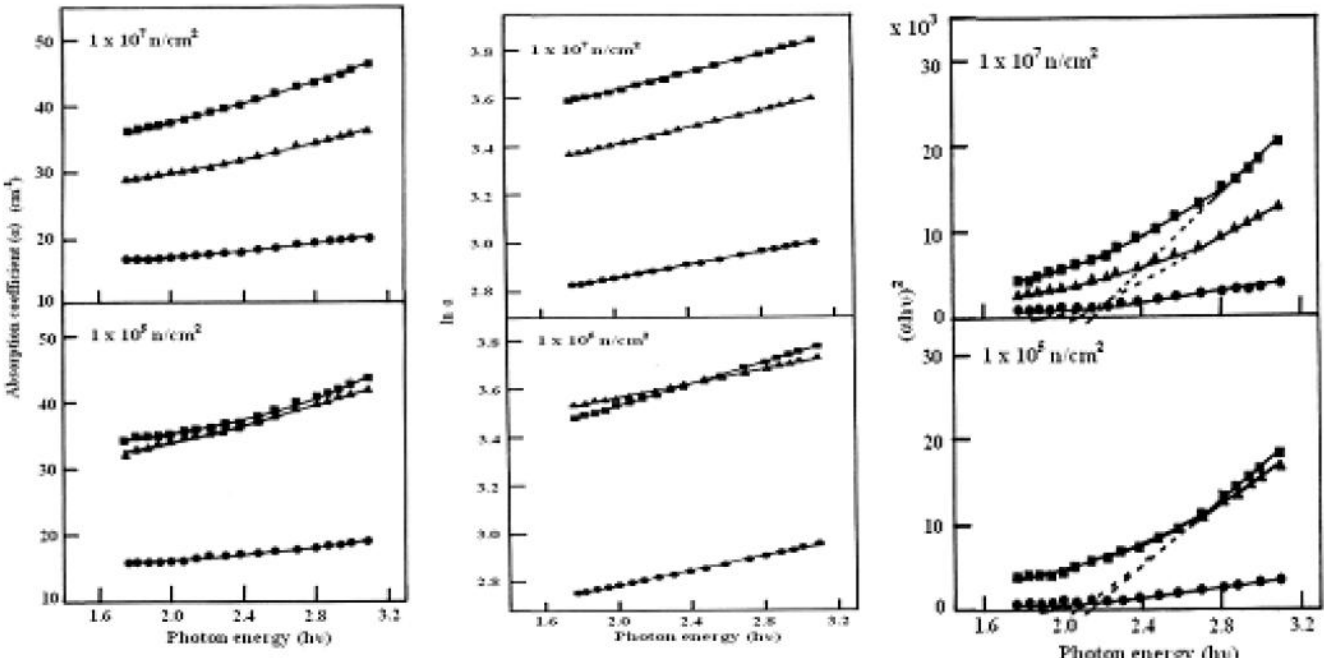

Figure 4 : The absorption coefficient, α (a), Urbach law plots (b) and the variation of $(\alpha h\upsilon)^2$ (c), for PVA/HPC blended samples after irradiation with fast neutron fluencies. (●) 100/0, (▲) 92/8 and (■) 88/12 (wt/wt%).

Figure 4c shows the relation between $(\alpha h\upsilon)^2$ and (hυ) for PVA/HPC blended samples before and after irradiation with fast neutron fluencies. The allowed direct transition energies were determined by extrapolating the linear portion of the curves to zero absorption. It is noticed that for irradiated pure PVA in comparison with 8 and 12 wt% HPC contents samples, the values of E_d have opposite trends. These irregular trends may be attributed to which is predominant cross-linking or degradation process. The values and their percentage changes in α, E_e and E_d with fast neutron fluencies for PVA/HPC blended samples are tabulated in TABLE 5. The observed variation means that the polymeric network of the sample is changed which indicate the role of fast neutrons on polymer structure forming cross-linking and/or degradation processes[38,39].

TABLE 5 : Values of absorption coefficient (α) at 555 nm, band tail energy (E_b) and direct energy gap (E_d) as well as their percentage changes for PVA/HPC blended samples before and after irradiation with fast neutrons.

PVA/HPC blended samples	α at 555 Nm(cm^{-1})	Δα%	E_b (eV)	ΔE_b%	E_d (eV)	ΔE_d%
100/0 wt/wt%						
Unirradiated	20.08	-	0.1598	-	2.0251	-
1 x 10^5 n/cm^2	17.25	-14.1	0.1445	-9.6	1.9637	-3.03
1 x 10^7 n/cm^2	17.25	-14.1	0.1313	-17.8	1.9001	-6.17
92/8 wt/wt%						
Unirradiated	34.75	-	0.1901	-	2.0438	-
1 x 10^5 n/cm^2	36.75	5.8	0.1632	-14.2	2.0643	1.00
1 x 10^7 n/cm^2	31.75	-8.6	0.1486	-21.8	2.0862	2.07
88/12 wt/wt%						
Unirradiated	38.25	-	0.1762	-	2.0856	-
1 x 10^5 n/cm^2	36.75	-3.9	0.2183	23.9	2.1274	2.00
1 x 10^7 n/cm^2	39.75	3.9	0.2001	13.6	2.1678	3.94

Fourier transform infrared spectral analyses

The FTIR transmittance spectra for PVA/HPC blended samples as functions of wavenumber in the range 4000-600 cm^{-1} are shown in Figure 5. The spectra of PVA and HPC seem to be consistent with that previously reported in the literatures[20,21,23,38,40,41]. The chemical assignments for PVA, HPC and their blended samples were considered and are also illustrated in TABLE 6.

It is clear from Figure 5a and TABLE 6 for pure PVA spectrum that, a relatively broad and intense υ(OH) absorption stretching band is observed between 3515-3154 cm^{-1} indicating the presence of a polymeric association of the free hydroxyl group and bonded OH stretching vibration. This broad and intense band usually occurs along with sharp less intense "monomeric" and "dimeric" OH absorption[23,42]. Also, two distinct absorption bands occurring at 2936 and 2918 cm^{-1} result from antisymmetric $\upsilon_{as}(CH_2)$ and symmetric $\upsilon_s(CH_2)$ stretching vibrations, respectively. The bands at 1712 and 1567 cm^{-1} of the carbonyl group are due to absorption of the residual acetate group. The band at 1712 cm^{-1} was assigned to 'free' unassociated and to associated hydrogen-bonded carbonyl group in the sample. The band at 1660 cm^{-1} was attributed to the absorption of H_2O. The symmetric bending mode $\upsilon_s(CH_2)$ is found at 1430 cm^{-1}. In addition, the bands at 1376 and 1240 cm^{-1} result from rocking methyl groups (CH_3) or wagging vibrations of CH_2 and CH, respectively. The band at about 1331 cm^{-1} is assigned to mixed υ_s(CH and OH) bending modes and is attributed to the associated alcohols. The stretching band at 1140 cm^{-1} is known to be the crystallization-sensitive band of PVA and is taken as a measure of the degree of crystallinity. It is believed that this band arises from the symmetric υ(C-C) stretching mode related to the regular repetition of the trans-configuration of the zigzag chain in a crystalline region. In addition, it is inferred that the 1140 cm^{-1} band might be due to a kind of absorption mechanism related to the presence of the oxygen atom. The band at about 1096 cm^{-1} is assigned to υ(C-O) stretching vibration of ether group. The band at 919 cm^{-1} is related to syndiotactic structure and is assigned to the $\upsilon_r(CH_2)$ rocking vibration. The band at 851 cm^{-1} is assigned to -CH_2 rocking vibration and at 607 cm^{-1} due to O-H twisting[20,23]. The data obtained also indicate that both PVA and HPC are approximately showed similar macrostructure. Moreover, from Figure 5a and TABLE 6, it is noticed that:

- The absorbance band observed at 3515-3154 cm^{-1} which is due to the presence of hydrogen bonded O-H group in pure PVA sample becomes narrower by adding HPC.
- The strong band at 2936 cm^{-1} associated with C-H stretching vibration of pure PVA shows little shifts in its position and decrease in its intensity by adding HPC.
- The band at 1712 cm^{-1} associated with carbonyl group (C=O) of pure PVA shows unremarkable shifts in its position and intensity by adding HPC.
- The band at 1660 cm^{-1} associated with water absorption and C=O stretching shows shift in its position and its intensity decreases with increasing HPC concentration.
- The band at 1567 cm^{-1} associated with carbonyl group C=O shows unremarkable shift in its position.
- The band at 1430 cm^{-1} associated with O-H bending and CH, CH_2 deformation shows shift in its

position and decrease in its intensity by adding HPC.

- The bands at 1376 and 1331 cm^{-1} associated with CH_2 wagging and C-H or O-H bending show unremarkable shift in their positions and intensities by adding HPC.
- The bands at 1140, 1096 and 851 cm^{-1} associated with C-O stretching vibration, skeletal and CH_2 rocking, respectively show nearly unremarkable shift in their positions.
- The band at 607 cm^{-1} associated with O-H twisting shows shift in its position and decrease in its intensity by adding HPC.

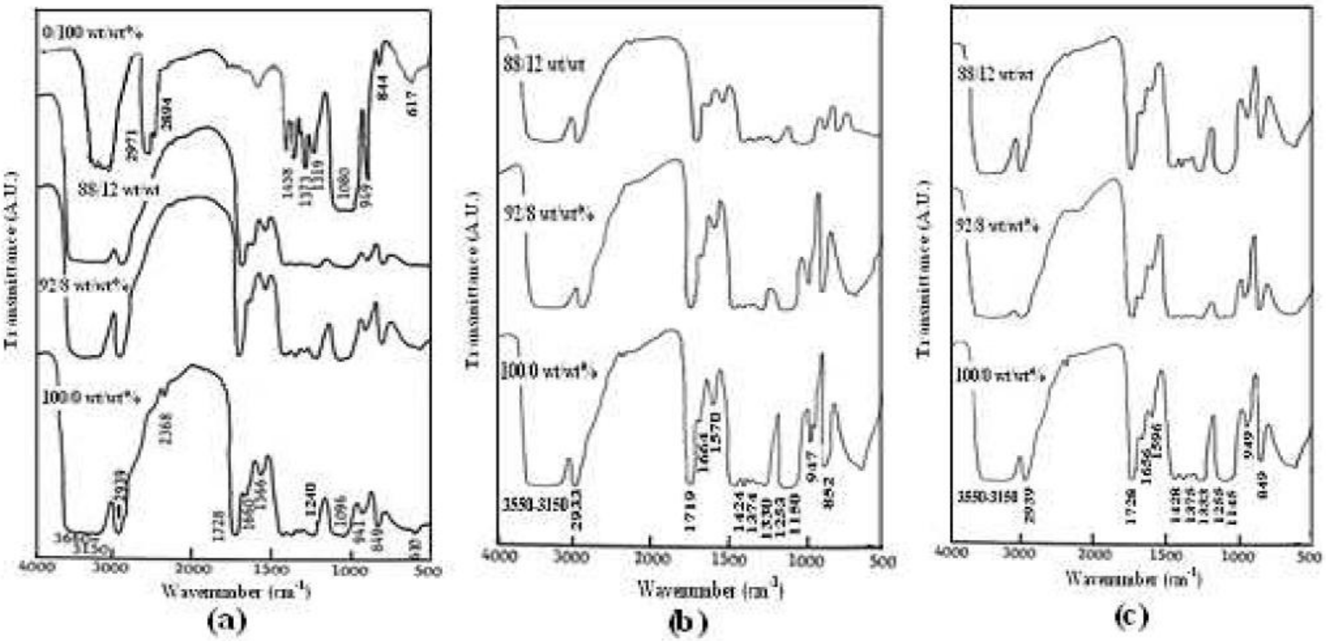

Figure 5 : Variations in FTIR spectra of PVA/HPC blended samples before (a) and after irradiation with fast neutron fluencies of 1 x 10^5 n/cm^2 (b) and 1 x 10^7 n/cm^2 (c).

TABLE 6 : Positions and assignments of the most absorption bands of PVA/HPC blended samples before irradiation with fast neutrons.

Wavenumber (cm^{-1})				Assignments
PVA/HPC blended samples (wt/wt%)				
100/0	92/8	88/12	0/100	
3515-3154	3500–3217	3503–3208	3516-3348	Hydrogen bonded and hydroxyl O-H group
2936	2934	2932	2971	CH_2 or CH_3 stretching vibration
2918	2911	2914	2911	C- H stretching vibration
-	-	2880 shoulder	2894	C-H stretching vibration
1712	1711	1712	1716	Carbonyl group C=O stretching
1660	1654	1651	1646	Water absorption and C=O stretching
1567	1566	1566	-	Carbonyl group C=O stretching
1430	1435	1444	1456	O-H, C-H bending and -CH_2 deformation
-	-	-	1413	Bending vibration mode of CH_2
1376	1376	1375	1374	-CH_2 wagging
1331	1330	1327	1327	C-H and O-H bending
1240	1258	1258	1272	O-H bending and C-H wagging
1140	1139	1136	1134	C-C stretching vibration
1096	1093	1091	1090	C-O stretching vibration
-	-	-	1040	C-O stretching vibration
919	920	926	949	C-O deformation and -CH_2 rocking
851	850	849	844	Skeletal and -CH_2 rocking
607	610	617	617	O-H Twisting

High energy radiation, such as fast neutron fluencies are expected to make large chemical and physical changes in the polymers either by direct damage or by reaction with any oxygen present[43]. The infrared spectra of 100/0, 92/8 and 88/12 wt/wt% PVA/HPC blended samples after irradiation with fast neutron fluencies 1 x 10^5 n/cm^2 (Figure 5b) and 1 x 10^7 n/cm^2 (Figure 5c), are presented. TABLE 7 shows the variations in the spectral positions and assignments of both unirradiated and irradiated PVA/HPC blended samples. It is clear that, in comparison between the unirradiated and irradiated spectra beside the decrease in the transmittance of the spectra with neutron fluencies, the band at 1567 cm^{-1} which is assigned as carbonyl group (C=O stretching) shows shift in its position and its intensity decreases as well as becomes broad. A sharp drop in intensities of the bands at 1735 and 849 cm^{-1} which are assigned as carbonyl group (C=O stretching) and $-CH_2$ rocking, respectively are observed by fast neutron fluencies. The strong band at 1712 cm^{-1} which is due to the presence of carbonyl group (C=O) is affected by irradiation and its intensity increases by increasing the neutron fluence. The induced formation of the carbonyl groups at 1735 and 1566 cm^{-1} can be interpreted on the basis of the peroxide mediated oxidative degradation mechanism.

TABLE 7 : The positions and assignments of the most absorption bands of unirradiated and irradiated PVA/HPC blended samples.

PVA/HPC blended samples (wt/wt%)									Assignments
100/0			**92/8**			**88/12**			
Neutron fluencies (n/cm^2) and wavenumbers (cm^{-1})									
0	**10^5**	**10^7**	**0**	**10^5**	**10^7**	**0**	**10^5**	**10^7**	
35153154	35503150	35503150	35003217	35403162	35653108	35033208	35003200	34783195	Hydrogen bonded and hydroxyl O-H group
2936	2933	2939	2934	2935	2947	2932	2939	2939	CH_2 or CH_3 stretching vibration
1712	1719	1728	1711	1732	1732	1712	1735	1728	Carbonyl group C=O stretching
1660	1664	1656	1654	1662	1662	1651	1660	1658	Water absorption and C=O stretching
1567	1570	1596	1566	1574	1574	1566	1566	1569	Carbonyl group C=O stretching
1430	1424	1428	1435	1431	1431	1444	1430	1427	O-H, C-H bending $-CH_2$ deformation
1376	1374	1375	1374	1369	1369	1375	1370	1373	$-CH_2$ wagging
1331	1330	1333	1330	1327	1326	1330	1320	1326	C-H and O-H bending
1240	1253	1255	1258	1250	1234	1258	1257	1257	O-H bending and C-H wagging
1140	1150	1145	1139	1148	1141	1136	1135	1130	C-C stretching vibration
919	947	949	920	945	948	926	948	948	C-O deformation $-CH_2$ rocking
851	852	849	850	848	848	849	848	848	Skeletal and $-CH_2$ rocking

Briefly, the decrease in the intensities of some bands can be attributed to the radiation induced changes in the intermolecular bonds of PVA chains caused by fast neutron fluencies which indicate that cross-linking of the chains may occur[38,44]. Fast neutron irradiation of polymers results in bond cleavage giving free radicals, which in the presence of oxygen react by a chain mechanism to form oxidation products that include by hydroperoxides. The radicals steps set in motion during the course of the reactions include pathways which lead to polymer chain scission and cross-linking[38,45]. The rate of the two reactions is the limiting factor so that one of them is found to be the predominant. Furthermore, the changes in the intensities and positions of some bands by fast neutron fluences may be attributed to change occurred in the concentrated of some infrared active groups or bands, so that the structural modification of irradiated samples can be detected from their infrared spectra[46].

CONCLUSION

Dopant concentration and neutron irradiation plays a dominant role in both morphological and microstructure change occurring in polymer matrix. Samples under investigation exhibit a radiation sensitization characteristic for each doping concentration. Both degradation and cross-linking processes induced neutron irradiation occur simultaneously, one or the other generally being dominant. They are non-equilibrium radiation – chemical process that change the structure, and hence the physical properties, of the polymer. This is clearly shown by the change of optical parameters obtained and infrared spectra.

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