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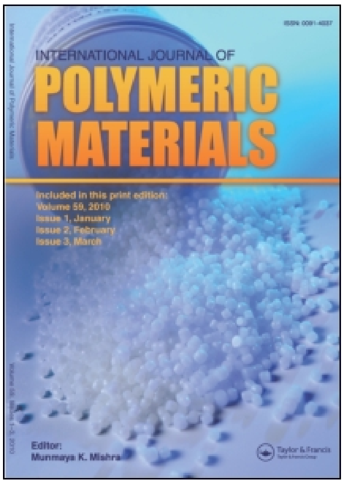

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Radiation Effect on the Molecular Structure of Dyed Poly(vinyl alcohol)

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To cite this Article El-Ahdal, M. A.(2000) 'Radiation Effect on the Molecular Structure of Dyed Poly(vinyl alcohol)', International Journal of Polymeric Materials, 48: 1, 17 — 28
To link to this Article: DOI: 10.1080/00914030008048376
URL: http://dx.doi.org/10.1080/00914030008048376

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Intern. J. Polymeric Mater., 2000, Vol. 48, pp. 17-28
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Radiation Effect on the Molecular Structure of Dyed Poly(vinyl alcohol)

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(Received 12 October 1999; In final form 18 October 1999)

Cast films of poly(vinyl alcohol) doped with anilidine with different concentrations were prepared. The molecular absorption spectra in the range 200-700 nm for ultraviolet and 400-4000 cm^{-1} for infrared were carried out before and after gamma irradiation with doses up to 40 kGy. The state of the composite, whether crosslinked or degraded, *via* the crystallinity percentages of the composites was controlled by means of the gamma irradiation doses and the different concentrations of dye.

Keywords: Poly(vinyl alcohol); γ-Radiation; Degradation; Crosslinking; IR-; UV-Spectra

INTRODUCTION

Studies of polymer composites have been continued vigorously in recent years due to their wide range of applications. Poly(vinyl alcohol) is one of the polymers most capable of polymer-ion complexation. PVA forms ion-complexes with various ions, such as borate, cupric, and vanadate [1-4]. Other modifications has been developed to alter its characteristics and increase its use [5, 6].

Gamma irradiation of polymers have mainly produced noticeable changes in physical and mechanical properties accompanying very small changes in their chemical structure [7, 8].

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The infra red and ultra violet absorption spectra are used to study the effect of gamma radiation on the molecular structure of PVA films doped with different concentrations of dye.

EXPERIMENTAL PROCEDURE

Equimolar mixture of 4-amino 2′,3-diethyl azobenzole and *p*-nitro acetophenone in absolute ethanol (50 ml) was refluxed for one hour, cooled and then filtered. The solid thus obtained was recrystallized from methanol to give anilidine. Dye was dissolved in ethyl alcohol and different concentrations of it were mixed with the poly(vinyl alcohol) solution. Films of appropriate thickness were prepared by casting the solution onto glass plate and dried in air oven at 40°C for 48 hours. The molecular structure of the prepared dye is $2\text{-}NO_2\,C_6H_4\text{—}C(CH_3)\text{=}N\text{—}C_6H_4\text{—}2CH_3\text{—}N\text{=}N\,C_6H_4\text{—}2\text{—}CH_3$.

The samples were irradiated with Co^{60} Indian gamma cell Ge 400A. Optical absorption spectra of the samples were measured with Uvikon 860 spectrophotometer in the region 200–900 nm. Mattson 1000 FTIR spectrophotometer was used for the range 400–4000 cm^{-1}.

RESULTS AND DISCUSSION

Poly(vinyl alcohol) PVA industrially prepared from the hydrolysis of poly(vinyl acetate). The monomer vinyl alcohol evidently does not exist in the free state. During polymerization chain–transfer interactions with monomer, solvents, and active impurities occurs more frequently than initiation and termination reactions. Therefore, end groups such as carboxyl and carbonyl are more frequent than end groups derived from the initiator [9]. The optical absorption of PVA in the range 200–400 nm is due to the presence of acetaldehyde and oxygen, which are often present during polymerization, and are responsible for the presence of carbonyl group [10].

The structure of PVA is a poly(1,3-glycol). The hydrolysis of poly(vinyl acetate) leads to 1,2-glycol structure rather than 1,3-glycol. The degree of crystallinity and chemical properties of PVA is dependent on the number of 1,2-glycol units [11]. The crystallization

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percentages were calculated according to Mallapragada [12]. Figure 1 illustrates the crystallinity percentages, estimated from the infra red spectrum response, of undoped PVA for different gamma doses. The crystallinity of PVA showed a decrease with gamma doses declearing the degradation behaviour of PVA till almost 20 kGy. Further increase of doses showed a stability against the radiation doses. From the previous relation, the role of gamma radiation doses is clear, where gamma radiation controls the presence of 1,2-glycol structure inside the PVA.

Most commercial PVA absorb strongly in the 200–400 nm region of the ultraviolet spectrum. The ultraviolet spectrum of undoped PVA is illustrated as in Figure 2. The appearance of a band at 263 nm is due to the presence of aldehyde and was assigned to the $\pi \rightarrow \pi^*$ transition in the molecule. The optical energy gap represents an important parameter for studying the gamma ray interaction with polymers. The optical energy gap of the unirradiated and irradiated PVA samples were estimated from the PVA spectrum in the region 200–700 nm according to Urbach [13]. Figure 3 shows the variation of the optical energy gap of undoped PVA with the different gamma ray doses. This interaction depicts a decrease of the optical energy

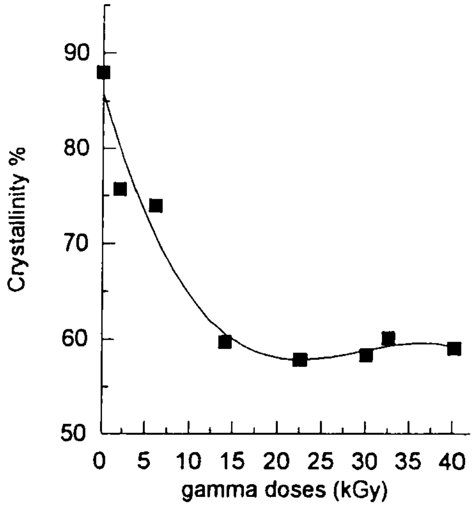

FIGURE 1 Crystallinity dependence of undoped PVA on the gamma radiation doses.

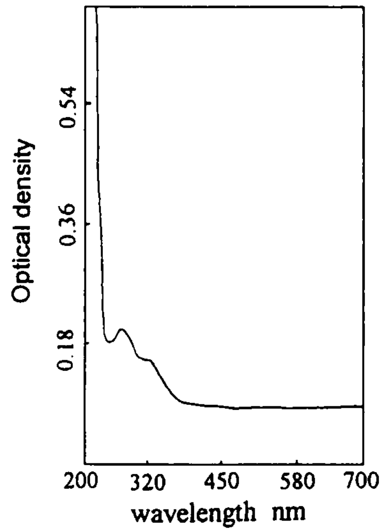

FIGURE 2 Optical spectrum of PVA doped 1.33% concentration of anilidine.

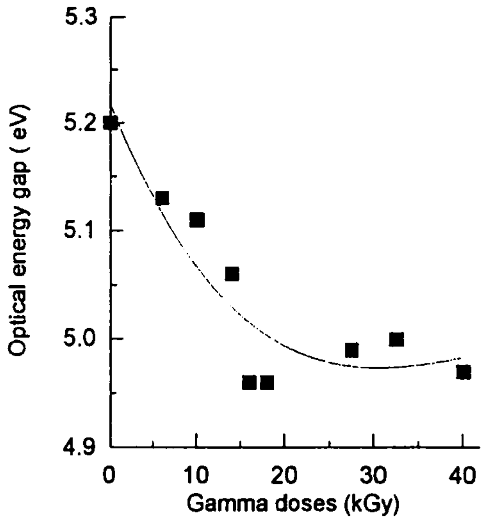

FIGURE 3 Optical energy gap dependence of undoped PVA on gamma radiation doses.

gap with doses till almost reaches 20 kGy. After 20 kGy optical energy gap showed a stability against the gamma doses which is in consistence with the degradation region of gamma doses shown by Miller

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[14]. The behaviour of the optical energy against the gamma radiation doses reinforced the crystallinity behaviour in Figure 1.

Poly(vinyl alcohol) doped with the anilidine dye with concentration 1.33% shows two bands at 263 nm and 395 nm which are assigned to $\pi \rightarrow \pi^*$ transition of the dye overlaped with that of PVA and $n \rightarrow \pi^*$ transition of the dye as in Figure 4. Crystallinity change of dyed PVA with this concentration shows gamma radiation doses dependence as in Figure 5. The occurrence of crosslinking is clearly apparent (compared with the undoped polymer) as the sharp increase of crystallinity with increasing the gamma radiation doses. This means the creation of free radicals that take part in the construction of three dimensional polymer. The doping of PVA with that concentration of dye increases the optical energy gap of the unirradiated composite and this is an ordinary behaviour which corresponds to the existence of the new band of the composite at 395 nm. The effect of gamma irradiation doses on the optical energy gap of the composite appeared as a decrease in their values upon the increase of gamma radiation doses as in Figure 6. Reaching to the end of degradation the composite starts to crosslink with increasing gamma ray doses.

The optical energy gap under the gamma radiation effect indicates the chain scission of the polymer and the production of

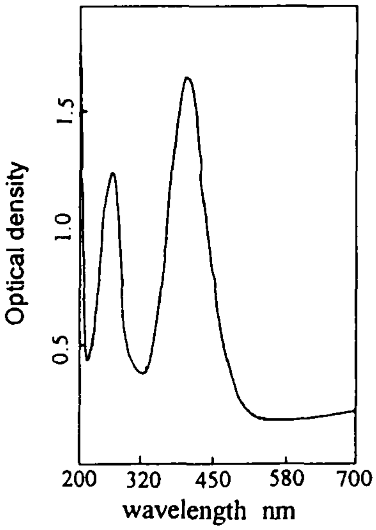

FIGURE 4 Optical spectrum of PVA.

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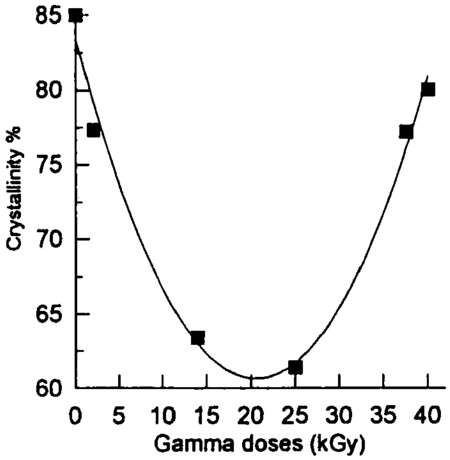

FIGURE 5 Crystallinity dependence of PVA doped with 1.33% anilidine on gamma radiation doses.

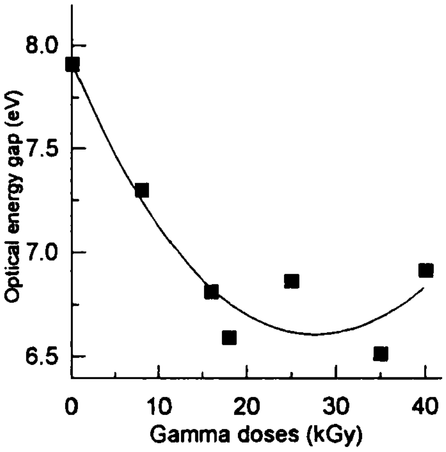

FIGURE 6 Optical energy gap dependence of PVA doped with 1.33% anilidine on gamma radiation doses.

chromophores through degradation and consequently increasing the population of the excited states by gamma radiation doses. The crosslinking of polymer is a three dimensions network which increases the crystallinity and decrease the numbers of chromophores in the

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higher energy state. Figure 7 confirms the degradation and crosslinking trend of the dependence of the composite optical energy gap with gamma radiation doses through the change of the absorbance ratio of the bands at 263 nm and 395 nm. The crosslinking of the polymer is a process at which side chains move to bind the main chains and construct three dimensional network and increases the molecular weight of the composite and decreases the distance at which the molecule is free to move. In other words, under the effect of gamma irradiation doses, the mean free path ratio between the bands at 395 nm and 263 nm increases (degradation) while decreases in the second range of doses (crosslinking) as plotted in Figure 8.

Gamma irradiation effect on the composite predicted by means of spectroscopic studies mainly appears as a change in the area under curve lies in a certain range of wavelengths or wavenumbers. This change can be detected through the change of the peak intensity in addition to the half band width. The latter parameter manifests the occurence of crosslinking and degradation on gamma irradiation. The decrease of the band width means the deficient of the number of groups (positioned around the peak) produced with radiation. This means the consumption of gamma ray intensity which concentrates to produce more chromophores responsible for the existence

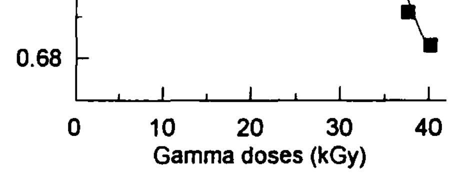

FIGURE 7 The variation of absorbance ratio of bands at 263 nm and 395 nm of PVA doped with 1.33% anilidine with gamma radiation doses.

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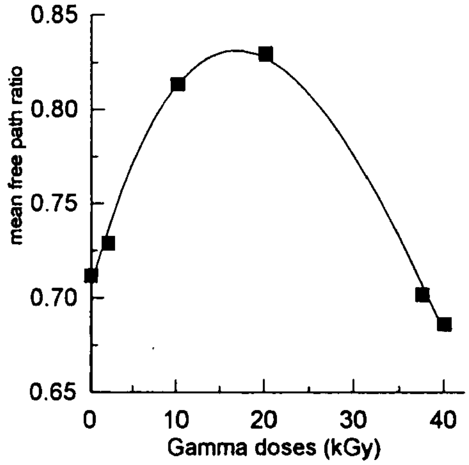

FIGURE 8 The variation of mean free path ratio of bands at 395 nm and 263 nm of PVA doped with 1.33% anilidine with gamma radiation doses.

of the peak intensity at a certain wavelength. This behaviour is a proof of chain siccision. Crosslinking appeared as the broadening of the band around peak *i.e.*, more groups are produced which bind the main chains into high molecular weight composites. The half band width variation of the two bands of the composite upon irradiation with gamma ray doses were illustrated as in Figures 9a, b. From figure it was noted that the bands assigned to the $\pi-\pi^*$ and $n-\pi^*$ transitions were not sensitive to the change of the gamma radiation doses up to nearly 20 kGy. Further increase of doses, the two bands showed an increase in their half band widths. At the second stage of gamma rays irradiation the two bands at 263 nm and 395 nm are responsible for the crosslinking of the composite through bridging the polymer chains.

The increase of the dye concentration doped into the polymer firstly increases the optical energy gap and then starts to decrease for both unirradiated and irradiated samples with different gamma doses as in Figure 10. According to the change of the optical energy gap the absorbance ratio of the two bands, the mean free path ratio, the crystallinity and the half band width of the two bands are changed with and without gamma irradiation doses depending on the increase of dye concentration percentages as should be explained later.

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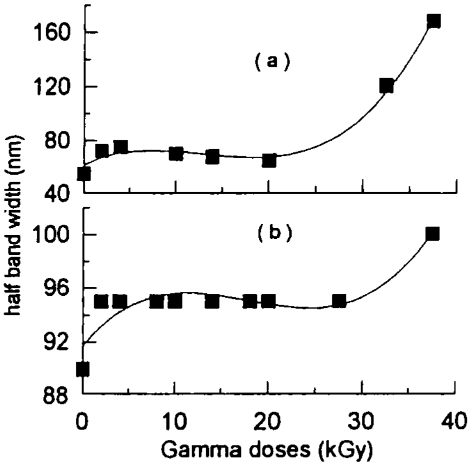

FIGURE 9 The half band width change of PVA doped with 1.33% anilidine with gamma radiation doses. (a) 263 nm and (b) 395 nm.

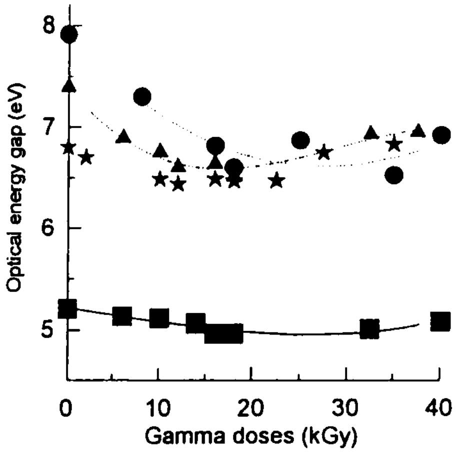

FIGURE 10 The change of the optical energy gap with gamma radiation doses for different concentrations of anilidine.

The doping of PVA with an increasing amount of dye affects the unirradiated polymer behaviour as in Figures 11a, b. The change of the optical energy gap with the dye concentration was early discussed. This change translated into a similar behaviour of the crystallinity percentages and the mean free path ratio as in Figures 11a, b.

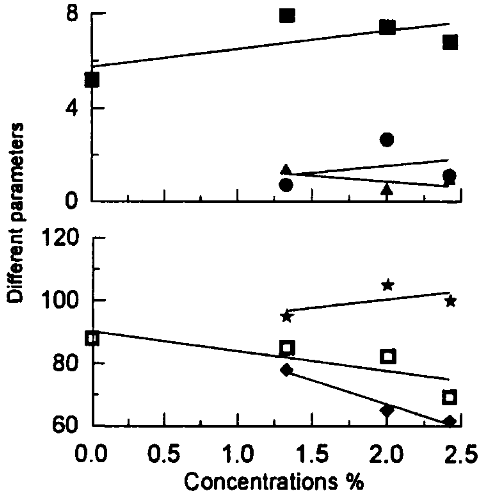

FIGURE 11 The change of different parameters on the different anilidine concentrations of unirradiated composite. ■ optical energy gap (eV), ● absorbance ratio at 263 nm and 395 nm, ▲ mean free path ratio at 263 nm and 395 nm, ◆ half band width at 395 nm, □ crystallinity, ★ half band width at 263 nm.

The interaction of gamma radiation doses with the polymer doped with different concentrations of dye reflects the occurrence of two mechanisms, crosslinking and degradation. One of these mechanisms predominates while the other still nonreactive. The transition from one mechanism to the other takes place through a certain region. The intersection of these two regions defined a critical dose. This critical dose may be used as an indication for the explanation of the gamma radiation interaction with the composite. The critical dose at a certain parameter and consequently the corresponding value dependence on the dye concentrations for the all studied parameters reveals the effect of the gamma rays interaction with these composites. Figure 12 plotted the critical doses, deduced from the optical energy dependence on gamma radiation doses, and the corresponding optical energy gap changes with the dye concentrations. The critical dose and the optical energy gap linearly increase with the dye concentrations. For crystallinity study, the solution of the two equations expressing the previous straight relations

$$y = x - 76.84$$
$$x = x_1 + 9.68x_2$$

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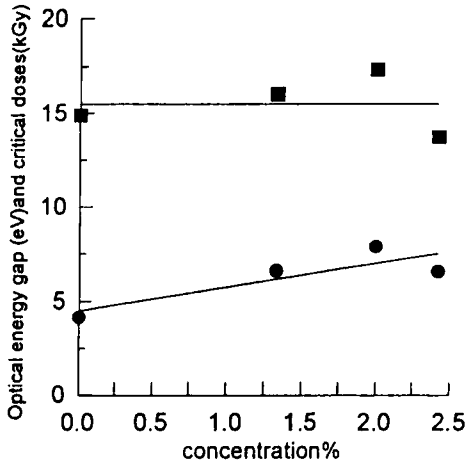

FIGURE 12 The change of optical energy gap and critical doses with the anilidine concentrations. ● optical energy gap, ■ critical dose.

where

y critical dose from the crystallinity study.
x_1 crystallinity percentage.
x_2 dye concentration.

From this equation knowing the dye concentration and the crystallinity percentage, the critical dose at which the degradation of composite finishes and its crosslinking starts, can be predicted when it is important. The reverse behaviour response of the half band widths at 263 nm and 395 nm also was accomplished as the change of the sign of the slope of the critical dose and the corresponding half band width values.

CONCLUSION

Poly(vinyl alcohol) doped with different concentrations of dye was exposed to different doses of gamma radiation. The effect of gamma irradiation on the doped polymer can be controlled through a critical dose by which the state of the composite whether hard or flexible (crosslinked or degraded) can be predicted. An example is the prediction of a composite absorbing or transmitted a certain range of light. This can be accomplished by following the behaviour of the optical energy gap of the doped composite exposed to different gamma radiation doses.

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