

Effect of additive concentration and X-ray irradiation on the thermal and color properties of Polyvinyl alcohol

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Abstract: Thermogravimetric analysis TGA was carried out to obtain the activation energy of thermal decomposition for Polyvinyl alcohol PVA stabilized by Polyethylene glycol PEG. The effect of addition of PEG, with different concentrations, to PVA was studied. The results indicated that the addition of PEG with 0.015 g/1 g PVA led to a more compact structure of pure PVA which resulted in an improvement in its thermal stability with an increase in the isotropic character of the polymer samples. Samples from the 0.015 g PEG/1 g PVA were irradiated with X-rays in the dose range 10-100 Gy. The variation of onset temperature of decomposition, activation energy of thermal decomposition and refractive index has been investigated. In addition, the transmission of these samples in the wavelength range 370–780 nm, as well as any color changes, was studied. The color intensity ΔE was increased with increasing the X-ray dose indicating that the color difference is largely dependent on the proportions of the red and yellow color components.

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1. Introduction

The structural properties of Polyvinyl alcohol PVA continues to be a subject of active research. PVA has fascinating properties and a wide variety of applications. Also, it has high dielectric strength, good charge storage capacity, high elasticity and good film forming by solution casting [1]. PVA has a carbon chain backbone with hydroxyl groups which can act as a source of hydrogen bonding [2, 3]. It has also gained increasing attention as a biomedical material [4]. Mixing PVA with polyethylene glycol (PEG) is a candidate method for broadening the clinical and pharmaceutical applications of PVA. This is because the intrinsic molecular properties of PEG include the good water solubility, resistance to protein adsorption, low immunogenicity, the absence of toxicity, and do not cause damage when it come in contact with the skin or lips [5]. Consequently, the field of polymer additives has attracted strong interest in today's materials research, as it is possible to achieve impressive enhancements of material properties as compared with the pure polymers. On the other hand, irradiation of polymers has established itself as one of the most acceptable approach to alter polymer properties significantly [6]. Irradiation of polymers destroys the initial structure by introduce defects inside the material that are responsible for the change in the properties of the polymer. El Sayed *et al.*, [7] studied the dielectric and optical properties of PVA/PEG polymer blend via e-beam irradiation. They concluded that the e-beam irradiation can be used to control the dielectric and optical properties of PVA/PEG blend. Therefore this blend is a candidate for several industrial and electronic

devices with improved dielectric strength. Also, this blend could be useful in the field of radiation dosimetry. Kaiser *et al.*, [8] studied the feasibility of modifying the optical properties of PVA and PEG with different concentrations of (NiNO_3). They investigated that the absorption coefficient is increasing with increasing of the filler wt% content. of NiNO_3 additive. Various modifications in PVA have been observed due to additive or irradiation [9-13]. In our previous work [14], we studied the effect of electron beam irradiation on the structural, thermal and optical properties of poly(vinyl alcohol) thin film. We concluded that the electron beam irradiation in the dose range 95–210 kGy enhances the scope of this polymer in high temperatures. In the present, PEG is used as additive stabilizer to PVA. The aim is to investigate the feasibility of modifying its thermal and optical properties to study the possibility of further enhancement of these properties using X-ray irradiation.

2. Experimental

2.1 Samples

Pure PVA films and those doped with PEG, with different concentration, were prepared using the casting technique. PVA and PEG used in the present work were supplied by Sigma-Aldrich GMBH. The components, free from impurities, were prepared by swelling the PVA in twice-distilled water for 24 h at room temperature. The solution was then warmed to 80°C and stirred thoroughly for about 1h until the PVA was completely dissolved. PEG solution was prepared by dissolving the salt with in twice-distilled water.

Appropriate amounts of PVA and PEG solution were mixed, poured onto a level glass plate, and left to dry at room temperature for about 120h [6]. A thin film of nearly 0.05 mm thickness was formed. The thickness was measured by a thickness gauge Model 11/2704 Ast MD 370 standard which calibrated by Arab British Dynamics.

2.2 Irradiation facilities

The X-ray irradiation was carried out using an Oxford Instrument XF5011 50 kV X-ray tube with a molybdenum target, which produced a maximum 1 mA current. The same instrument was used in previous work [15, 16].

2.3 Analysis of the samples

Thermogravimetric analysis (TGA) was performed on irradiated and non-irradiated Bayfol samples using the TGA apparatus model Shimadzu-50 with platinum cells. Thermal experiments were carried out on all samples at a heating rate of 10°C/min with nitrogen as a carrier gas at a flow rate of 30 ml/min.

The transmission measurements were carried out using a Shimadzu UV-Vis-Nir scanning spectrophotometer, type 3101 PC. This unit measures in the wavelength range from 200 to 3000 nm. The Commission International de E'Claire (CIE units x , y and z) methodology was used in this work for the description of colored samples [17].

The refractive index measurements were carried out using an Abbe refractometer (Type Reichert; mark II, Model-10480, New York). The wavelength of the light used is 5893 Å. The accuracy of measuring the values of refractive indices and surface temperature of the prism were ± 0.0001 and 28 °C, respectively. Several values were measured on the same sample and the average value was considered.

3. Results and Discussion

3.1 The effect of concentration of PEG on the thermal properties of PVA

3.1.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis TGA was performed for the PVA polymer stabilized by different concentrations of PEG and the pure PVA sample at a heating rate of 10 °C/min. The obtained TGA thermograms are shown in Figure 1. It is seen that the PVA decomposes in one main weight loss stage. Using the TGA curves, values of the onset temperature of decomposition T_o , the temperature at which the decomposition starts, were calculated. Figure 2a shows the variation of T_o with the PEG concentration. The figure shows that T_o increases reaching a maximum value around the 0.015 g PEG/1 g PVA sample, then decrease with increasing concentration up to 0.02 g PEG/1 g PVA. This indicates that the suitable concentration of the stabilizer required for maximum thermal stability is 0.015 g PEG/1 g PVA.

Evaluation of the activation energy of thermal decomposition is useful for studying the thermal stability of the materials. Various thermogravimetric methods based on either the rate of conversion or the heating rates have been reported to determine the thermal kinetic parameters. The method proposed by Horowitz and Metzger [18] has been used in the present study for measurement of the activation energy of thermal decomposition. Using the TGA data, values of activation energy of thermal decomposition E_a were calculated for all the PVA-PEG and the pure PVA samples. Figure 2b shows the variation of E_a with the PEG concentration. From the figure it is seen that E_a exhibited a similar trend to that of T_o , where it increases in magnitude up to a maximum value around the 0.015 g PEG/1 g PVA and then decreases on increasing the PEG concentration. These results can be explained that addition of PEG molecules to the PVA polymer with concentrations up to 0.015/1 g PVA causes the consumption of the PEG stabilizer into the PVA chains, displacing some of the structural defects for the 0.015 g PEG sample. Thus, the thermal stability increases. Excess concentrations, above 0.015 and up to 0.02 g PEG/1 g PVA may lead to a detachment of the stabilizer that is previously incorporated into the polymeric chains due to steric hindrance.

3.1.2 Refractive index

The refractive indices of solid sheets of the PVA polymer stabilized by different concentrations of PEG and the pure PVA sample were measured. Figure 3 shows the variation of the refractive index with the dose. The refractive index showed an increase in magnitude up to a maximum value at 0.015 g PEG/1 g PVA, followed by a decrease with increasing the concentration up to 0.02/1 g PVA. The increase of refractive index can be due to the formation of bonds between the PEG stabilizer and the PVA molecules, since PVA has a carbon chain backbone with hydroxyl groups which can act as a source of hydrogen bonding to enhance the formation of polymer complexes [19]. Also, the structure of PEG contains oxygen in its carbon backbone [20]. On the other hand, increasing the PEG concentration up to 0.02 g/1 g PVA leads to the repulsion between the excess PEG stabilizer molecules and the monomer moieties in the PVA backbone causing the break of some bonds and causing the decrease in refractive index.

In conclusion the study of the effect of concentration of added PEG to PVC shows that the sample with 0.015 g PEG/1 g PVA concentration is more thermally stable. This sample was chosen to be a subject for the further study to investigate the effect of X-ray irradiation, in the dose range 10-100 Gy, on its properties.

3.2 The effect of X-ray irradiation on the thermal and color properties of the 0.015 g PEG/1 g PVA sample

3.2.1 Thermogravimetric Analysis (TGA)

TGA was performed on the PVA/PEG samples in the temperature range from room temperature up to 600°C, at a heating rate of 10°C min⁻¹. Figure 4 shows the TGA thermograms for the non-irradiated and irradiated 0.015 g PEG/1 g PVA samples. Figure 5a shows the variation of T_o with the X-ray dose. The figure shows that T_o decreases until a minimum value around the 20 Gy irradiated sample due to degradation (i.e. preferentially chain scission) followed by an increase with increase in the dose up to 100 Gy, due to the cross-linking process.

Using the TGA curves, values of E_a were calculated for the non irradiated and irradiated PVA/PEG samples and are shown in Figure 5b. The figure shows that E_a almost exhibited the same trend as T_o . The interpretation of these results may be that, at the dose range up to 20Gy, initial scission occurs. This is reflected in a decrease in E_a of the co-polymer samples. At the dose range 20-100 Gy, the free radicals formed due to scission are chemically active and can share in some chemical reactions that lead to the cross-linking mechanism.

3.2.2 Refractive index

The refractive indices of solid sheets of the non-irradiated and irradiated 0.015 g PEG/1 g PVA samples were measured. Figure 6 shows the variation of the refractive index with the X-ray dose. The refractive index showed a decrease in magnitude until a minimum value at 20 Gy followed by an increase up to 100 Gy. This behavior can be explained in terms of degradation and cross-linking induced by X-ray irradiation. Such behavior facilitates the formation of free radicals that are chemically active. This allows the formation of covalent bonds between different chains (crosslinking), and in turn minimizes the anisotropic character of the polymer samples, leading to the increase in refractive index. These results are in good agreement with those obtained by Shams-Eldin *et al.* [21], where, they illustrated that the incident radiations activate the main polymer chain implying a main chain scission which result in a decrease of the refractive index. The same effect was also investigated by Ranby and Rebek, [22].

3.2.3 Color difference measurements

The transmission spectra of the non irradiated and irradiated PVA/PEG samples, in the wavelength range 370-780 nm, have been measured (Figure 7). Using these transmission data, values of the color intercepts (L^* , a^* and b^*) were calculated. The variation of L^* , b^* and a^* with the dose is shown in figure 8. The accuracy in measuring L^* is ± 0.05 and ± 0.01 for a^* and b^* . It is seen that the color parameters a^* , b^* and L^* were significantly changed after exposure to X-rays. The

green color component ($-a^*$) of the non irradiated sample was changed to red ($+a^*$) after exposure to X-ray dose up to 100Gy (see Figure 8a). At the same time, the blue color component ($-b^*$) of the non irradiated film was changed to yellow ($+b^*$) (Figure 8b). This is accompanied by a net increase in the darkness of the samples ($-L^*$) (Figure 8c).

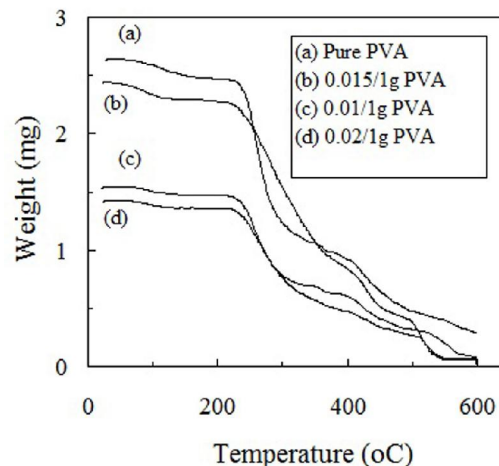


Figure 1. TGA thermograms, measured in the temperature range from room temperature up to 600°C, at a heating rate of 10°C min⁻¹ of the pure PVA sample and that with different PEG concentrations.

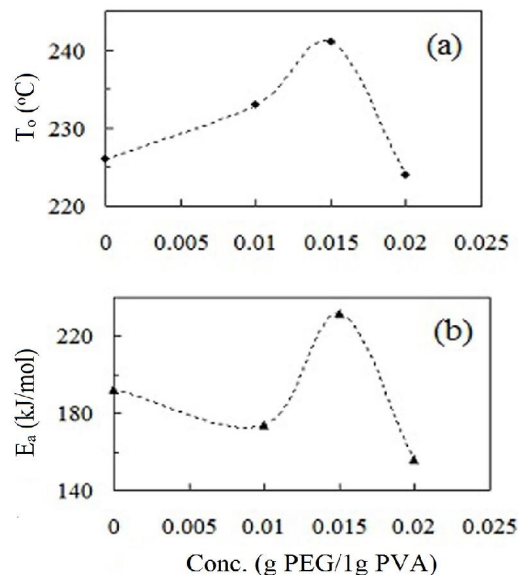


Figure 2. Variation of (a) onset temperature of decomposition T_o and (b) activation energy of thermal decomposition E_a with the PEG concentration.

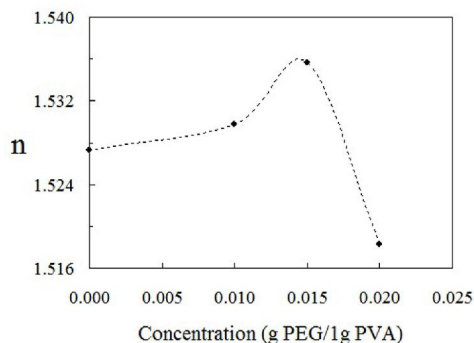


Figure 3. Variation of the refractive index with the PEG concentration.

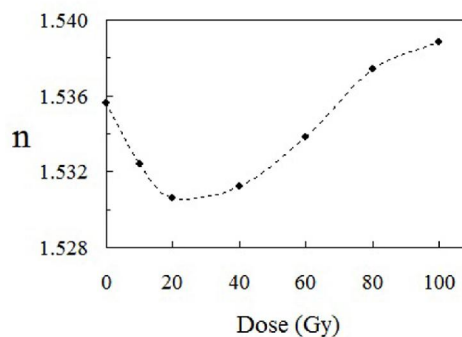


Figure 6. Variation of the refractive index with the X-ray dose.

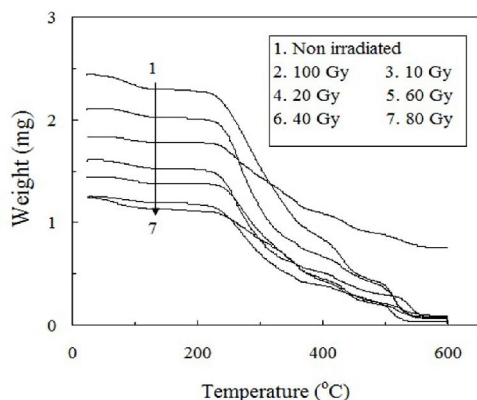


Figure 4. TGA thermograms, measured in the temperature range from room temperature up to 600°C, at a heating rate of 10°C min⁻¹ of the non-irradiated and X-ray irradiated 0.015 g PEG/1 g PVA samples

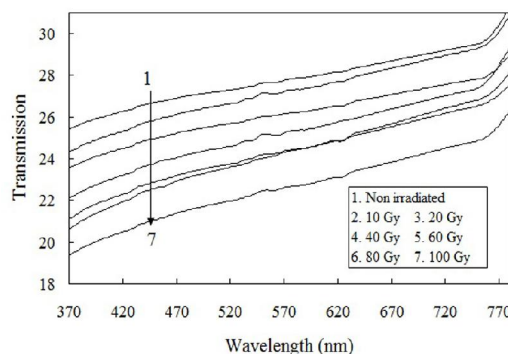


Figure 7. The transmission data of the non irradiated and irradiated 0.015 g PEG/1 g PVA samples measured in the wavelength range 370-780nm.

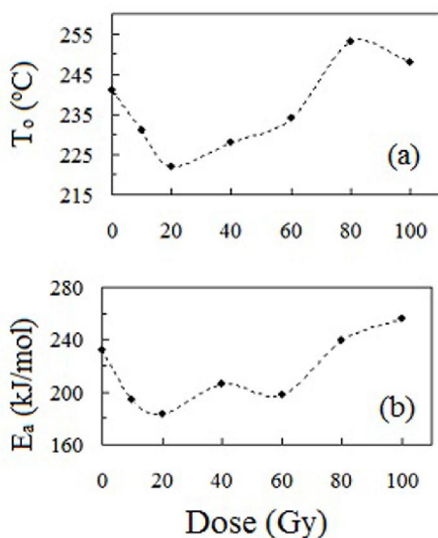


Figure 5. Variation of (a) onset temperature of decomposition T_o and (b) activation energy of thermal decomposition E_a with the X-ray dose.

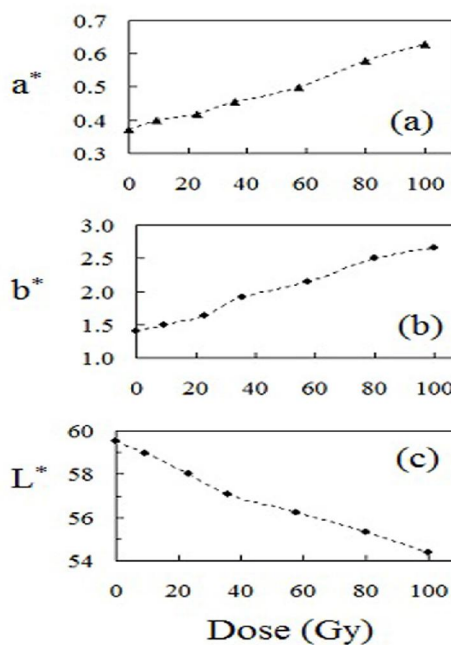


Figure 8. Variation of color intercepts (a) a*, (b) b* and (c) L* with the X-ray dose.

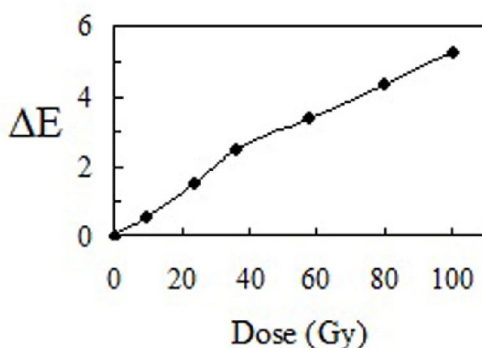


Figure 9. Variation of the color intensity ΔE with the X-ray dose.

The color intensity ΔE , color difference between the non irradiated sample and those irradiated with different X-ray doses, was calculated and is plotted in Figure 9 as a function of dose. From the figure it is seen that ΔE increases with increasing the dose up to 100 Gy. This indicates that the PVA/PEG copolymer has a response to color change by X-ray irradiation. These changes in color can be attributed to the trapping of the excited free radicals that are formed by indirect ionization. Also, the trapped free radicals resulting from radiation-induced rupture of co-polymer molecules have electrons with unpaired spin. Such species may also give optical coloration [23].

4. Conclusion

From the above study one can draw the conclusion that the addition of PEG to PVA with concentration of 0.015 g PEG/1 g PVA led to a more compact structure of PVA polymer, which resulted in an improvement in its thermal stability with a decrease in the anisotropic character of the PVA polymer.

The TGA thermogram indicates a degradation of the matrix of the 0.015 g PEG/1 g PVA copolymer under X-ray irradiation at doses up to 20 Gy causing the polymer to decompose earlier than the non irradiated sample. In this case the crosslinking by X-ray irradiation at higher doses (20-100 Gy) seems to be the dominant process. The dominance of the crosslinking effect has led to an increase in activation energy of thermal decomposition of the polymer.

The refractive index measurement indicated that the X-ray irradiation induce degradation and crosslinking, thus facilitates the formation of free radicals and allows the formation of covalent bonds between different chains leading to the decrease in the anisotropic character of the 0.015 g PEG/1 g PVA copolymer.

The non irradiated 0.015 g PEG/1 g PVA copolymer is nearly colorless; however, it showed significant color sensitivity after X-ray irradiation. The

sensitivity in color change appeared clearly in the change in the blue and green color components to yellow and red, respectively. This was accompanied by an increase in the darkness of the polymer samples.

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