Thermal, Structural, and Optical Properties of γ-Irradiated Poly(vinyl alcohol)/Poly(ethylene glycol) Thin Film

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ABSTRACT: Poly(vinyl alcohol)/poly(ethylene glycol) (PVA/PEG) copolymer was prepared using casting technique. The obtained PVA/PEG thin films have been irradiated with gamma rays with doses ranging from 1.5 to 20 Gy. The resultant effect of gamma irradiation on the thermal properties of PVA/PEG has been investigated using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The onset temperature of decomposition T_o and activation energy of thermal decomposition E_a were calculated, results indicating that the PVA/PEG thin film decomposes in one main weight loss stage. Also, the gamma irradiation in dose range 4–12 Gy led to a more compact structure of PVA/PEG copolymer, which resulted in an improvement in its thermal stability with an increase in the activation energy of thermal decomposition. The vari-

ation of transition temperatures with gamma dose has been determined using DTA. The PVA/PEG thermograms were characterized by the appearance of an endothermic peak due to melting of crystalline phase. In addition, structural property studies using X-ray diffraction and infrared spectroscopy were performed on both nonirradiated and irradiated samples. Furthermore, the transmission of the PVA/PEG samples and any color changes were studied. The color intensity (*E* was greatly increased with increasing the gamma dose and was accompanied by a significant increase in the blue and green color components. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 654–660, 2012

Key words: γ-irradiation; polymers; thermal; X-ray; FTIR; optical properties

INTRODUCTION

Polyvinyl alcohol (PVA) is the world's largest volume, synthetic, water-soluble polymer. PVA is nonhazardous and is used in many adhesives, films, and elastomers. It has high tensile strength and flexibility as well as high oxygen and aroma barrier properties, which are dependent on humidity. PVA is fully degradable and is a quick dissolver. It is an atactic material but exhibits crystallinity as the hydroxyl groups are small enough to fit into the lattice without disrupting it. On the other hand, poly (ethylene glycol) (PEG) refers to polymer of ethylene oxide, it is liquid or low-melting solid, depending on his molecular weight. PEG with different molecular weighs has different physical properties due to chain length effects.

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 when compared with the pure polymers. Examples of such material property enhancements

are the decreased permeability to gases and liquids, a better resistance to solvents, an increased thermal stability, and improved mechanical properties. PVA has many desirable characteristics that allowed it to achieve its present status as one of the important commercial polymers. It is a water-soluble polymer extensively used in paper coating, textile sizing, and flexible water-soluble packaging films.[1] In spite of its enormous technical and economic importance, PVA is still in need to enhance its thermal stability due to the structure defects that may be formed during the polymerization process.[2] Therefore, the stabilization of PVA polymer using variety of additives is required.[3] Organic materials as additives are of advantage, as being metal-free and environmentally acceptable.[4–6]

Additionally, irradiation of polymers has established itself as one of the most acceptable approach to alter polymer properties significantly.[7] Irradiation of polymers destroys the initial structure by way of crosslinking, free radical formation, irreversible bond cleavages that results in the fragmentation of molecules and formation of saturated and unsaturated groups.[8–14] All these processes introduce defects inside the material that are responsible for the change in optical and structural properties of the polymer. Also, the study of color changes in irradiated polymers is an important technique that has

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been used to assess physical changes in polymers. In our previous work,[6] we studied the effect of both nickel chloride concentrations and gamma irradiation on the thermal properties of PVA. The results indicated that the addition of nickel chloride with concentrations above 8% and up to 20% enhances the thermal stability of pure PVA. Also, the thermal activation energies of decomposition were found to be dependent on the gamma dose. The present work deals with the modifications induced in structural, thermal, and optical properties of PVA/PEG thin film using gamma irradiation.

EXPERIMENTAL

Samples

Pure PVA films and those doped with PEG, with concentration of 0.13 g PEG/1 g PVA, 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 1 h 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 120 h.[15] 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.

Irradiation facilities

The PVA/PEG samples were exposed to a gamma ray from ^{137}Cs source in the National Institute for Standards (NIS) of Egypt. The dose rate was 50 Gy/h.

Analysis of the irradiated samples

Thermal properties

Thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) were performed on irradiated and nonirradiated PVA/PEG samples using the TGA and DTA apparatus model Shimadzu-50 with platinum cells. α-Al$_2$O$_3$ was used as a reference material for DTA measurements. 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 20 mL/min.

X-ray

The X-ray diffraction measurements were carried out with a Philips powder diffractometer type PW 1373 goniometer. The diffractometer was equipped with a graphite monochromator crystal. The wavelength of the X-rays was 1.5405 Å, and the diffraction patterns were recorded in the 2θ range (10°–60°) with scanning speed of 1°/minute.

FTIR

Fourier transform infrared spectroscopy was carried out using a spectrophotometer Type Shimadzu, Model 8201 PC. This instrument measures in the wavenumber range 400–4000 cm^{-1}, with an accuracy better than ±4 cm^{-1}.

Color difference measurements

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. The tristimulus values and the CIELAB color difference were calculated using the methodology described earlier.[9,14]

RESULTS AND DISCUSSION

Thermal analysis techniques

TGA

Thermogravimetric analysis (TGA) was performed on PVA/PEG samples in the temperature range from room temperature up to 600°C, at a heating rate of 10°C min^{-1}. Figure 1 shows the TGA thermograms for the nonirradiated and irradiated samples. It is clear from the figure that the PVA/PEG thin film decomposes in one main breakdown stage. Using the TGA thermograms, the values of onset temperature of decomposition T_o, the temperature at which the decomposition starts, were calculated. Figure 2(a) shows the variation of T_o with the gamma dose. The figure shows that T_o decreases until a minimum value around the 4 Gy-irradiated sample due to degradation (i.e., preferentially chain scission) followed by an increase with increase in the gamma dose up to 12 Gy, due to the crosslinking process. Above 12 and up to 20 Gy, it decreases again.

Activation energy of thermal decomposition (E$_a$)

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
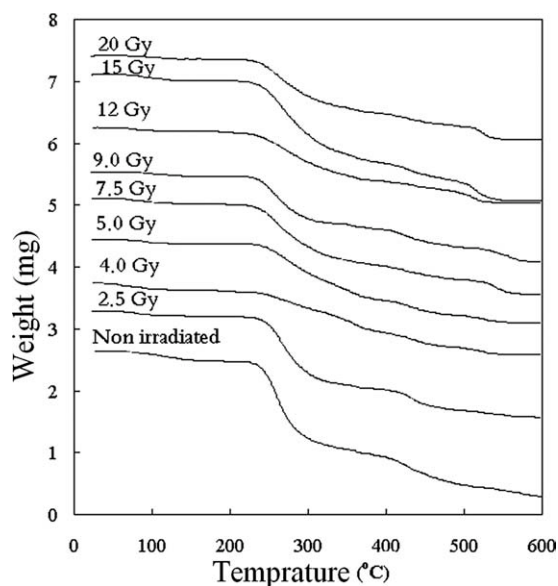
Figure 1 TGA thermograms, measured in the temperature range from room temperature up to 600°C, at a heating rate of 10°C min^{-1} for the nonirradiated and irradiated PEG/PVA samples.

proposed by Horowitz and Metzger[16] has been used in the present study for measurement of the activation energy of thermal decomposition. Using the TGA curves, values of E_a were calculated for the nonirradiated and irradiated PVA/PEG samples and are shown in Figure 2(b). The figure shows that E_a exhibited the same trend as T_o. The interpretation of these results may be that, at the dose range 1.5–4 Gy, initial scission occurs. This is reflected in a decrease in E_a of the copolymer samples. At the dose range 4–12 Gy, the free radicals formed due to scission are chemically active and can be used in some chemical reactions that lead to the crosslinking mechanism. Increasing the dose at the range 12–20 Gy leads to a random breaking of bonds, thus degradation predominates. This means that the two main effects modifying the polymer are sequentially first scission and then crosslinking.

DTA

Differential thermal analysis (DTA) was performed in the temperature range from room temperature up to 300°C at a heating rate of 10°C min^{-1}. The obtained thermograms are shown in Figure 3. The PVA/PEG samples are characterized by the appearance of an endothermic peak at the melting temperature T_m. The values of these melting temperatures could be calculated, and the variation of T_m with the gamma dose is shown in Figure 2(c). The figure shows that T_m increases up to a maximum value around 4 Gy and then decreases with increase in gamma doses up to 12 Gy. Above 12 and up to 20
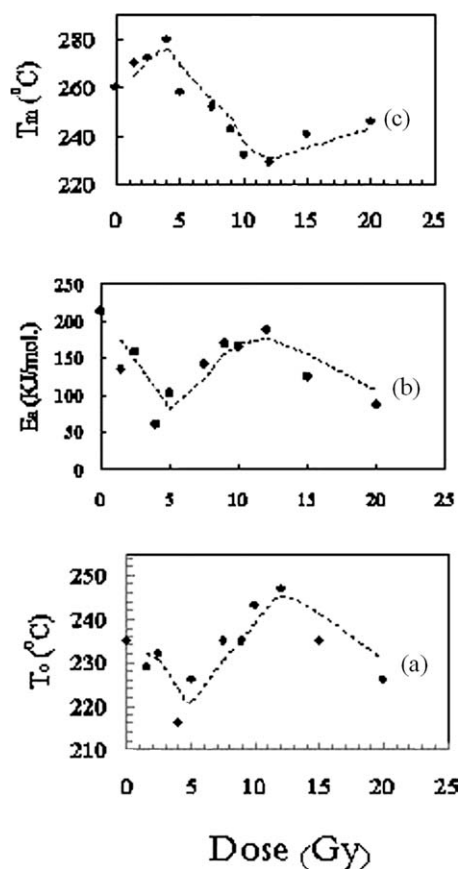

Figure 2 The variation of (a) onset temperature of decomposition T_o, (b) activation energy of thermal decomposition E_a, and melting temperature T_m with the gamma dose.
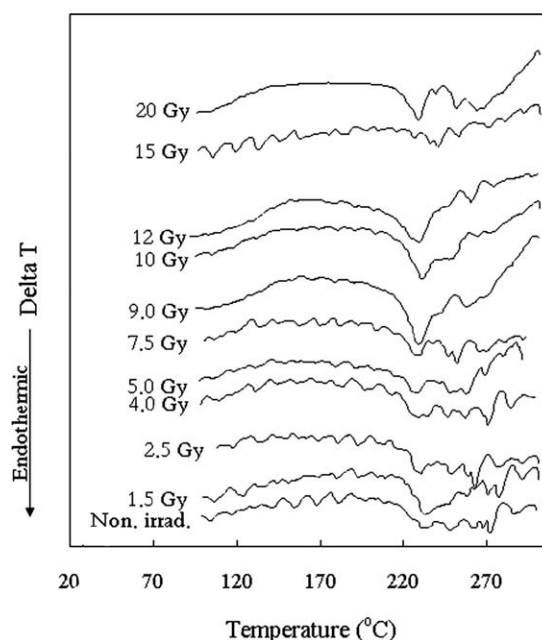

Figure 3 DTA thermograms measured in the temperature range from room temperature up to 300°C at a heating rate of 10°C min^{-1}.
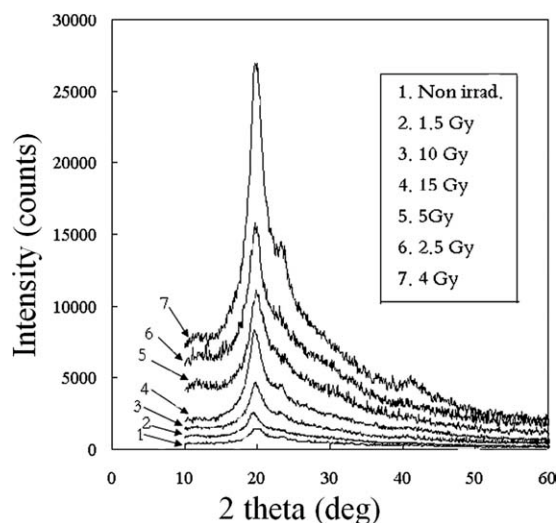
Figure 4 X-ray diffraction patterns of the nonirradiated and irradiated PVA/PEG samples.

Gy, it increases. Usually, the increase in melting temperature of polymer is attributed to the cross-linking and vice versa. The apparent discrepancy between the dependence of T_o and T_m on dose results from the fact that T_m is sensing the crystalline domains of the polymer. It is possible to speculate that at low doses, the thickness of crystalline structures (lamellae) is increased. At higher doses, defects generation splits the crystals depressing the melting temperature. For such doses, the decrease of the co-polymer length contributes also to the shift of T_m toward lower temperatures. Similar results were obtained by Nasef et al.[17] when studying the electron beam irradiation effects on partially fluorinated polymer films, where they investigated that the corss-linking inhibits the crystallization, and this is coupled with gradual decease in T_m with the irradiation dose. Also, Nouh and Hegazy studied the effect of neutron irradiation on the thermal properties of cellulose nitrate.[18] They obtained similar results.

X-ray diffraction

To study the effect of gamma irradiation on the degree of ordering of the PVA/PEG copolymer, X-ray diffraction measurements were carried out on 50-µm thick samples. Figure 4 shows the X-ray diffraction patterns of the nonirradiated and irradiated PVA/PEG samples. From the figure, we see that the X-ray diffraction patterns of the samples are characterized by halos extending in the 2θ range 10°–30°. The profile of the halos shows that the PVA/PEG copolymer is partly crystalline with a dominant amorphous phase. The spectra of all samples were fitted with a Lorentz function. Thereby, the integral intensities I (area) of the main diffraction peak were extracted and are represented in Figure 5 as a function of the gamma doses. The integral intensity

shows an increase up to a maximum value around the 4 Gy-irradiated sample, followed by a decrease on increasing the gamma dose up to 12 Gy. Above 12 and up to 20 Gy, it increased again.

Becasue the halo's width at the half of maximal intensity ΔW is inversely proportional to the crystallite size, values of ΔW were calculated using the Scherrer equation:

$$L = (0.89\ \lambda)/(\Delta W \cos\ \theta)$$

where ΔW is the peak's width at the half of maximal intensity and λ is the wavelength of the X-rays. The obtained values are plotted in Figure 5 as a function of the gamma dose. The peak's half width exhibited an opposite trend to that of the integral intensity.

The increase in integral intensity indicates an increase in the ordering character of the PVA/PEG samples, which can be attributed to degradation induced by gamma. This degradation reduces the number of entanglements per molecule, thus increasing chain mobility. The increase in mobility permits some molecules to re-crystallize, because crystalline state is a thermodynamic stable state. On the other hand, the decrease in integral intensity denotes a decrease in the amount of ordered phase in the samples, indicating that the crystalline structure has been destroyed due to crosslinking.

Fourier transform infrared spectroscopy

The effect of gamma irradiation on the infrared absorption of PVA/PEG thin film was investigated.
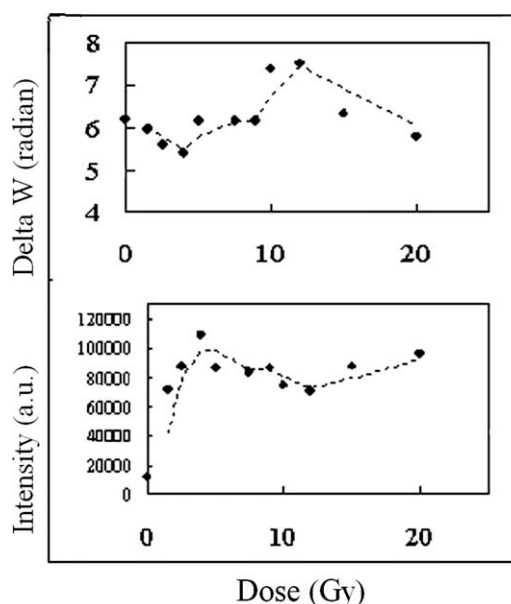

Figure 5 Variation of the integral intensity I and the peak's width at the half of maximal intensity ΔW with the gamma dose.
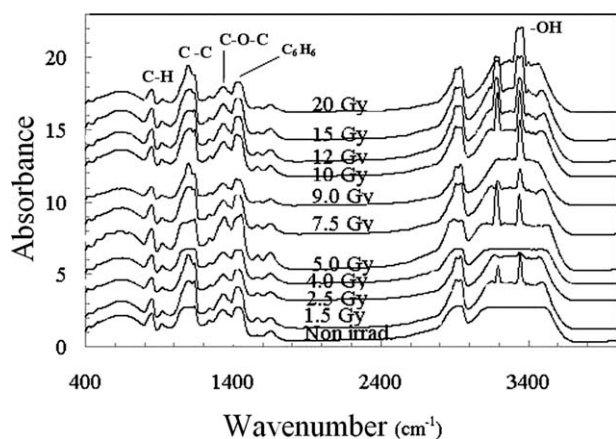
Figure 6 The infrared absorption spectra of the nonirradiated and irradiated PVA/PEG samples.

The infrared absorption spectra of the nonirradiated and irradiated samples are shown in Figure 6. The characteristic absorption peaks of PVA/PEG are observed at 1330 cm^{-1}, 1421 cm^{-1}, 1100 cm^{-1}, 3300 cm^{-1}, and 851 cm^{-1} corresponding to the C—O—C, C$_6$H$_6$, C—C, —OH, and C—H bonds, respectively.[19–21] Figure 7 shows the variation of the absorbance measured at these characteristic wavenumbers with the gamma doses. From the figure, it is clear that the intensity of ether bond C—O—C increased up to dose 4 Gy, followed by decrease on increasing dose up to 12 Gy. Above 12 and up to 20 Gy, it increased again. The intensity of the peak corresponding to hydroxyl group OH almost increased with increasing the gamma dose up to 20 Gy.

The absorbance corresponding to benzene ring C$_6$H$_6$ increased with increasing dose from 4 to 20 Gy. The absorbance of alkane bond C—C shows an increase up to a maximum value around the 12 Gy-irradiated sample, followed by a decrease on increasing dose up to 20 Gy. The absorbance of carbon-hydrogen bond C—H decreased up to a minimum value around the 2.5 Gy-irradiated sample
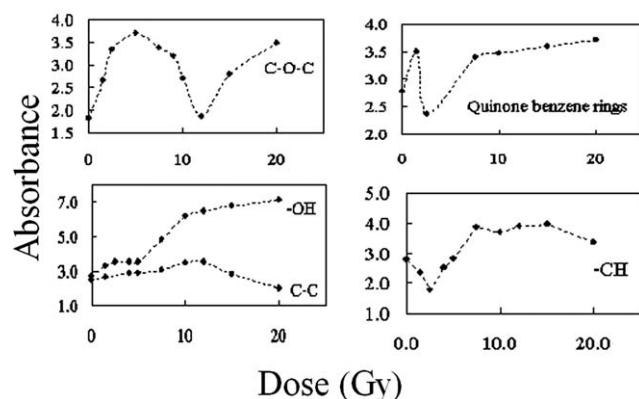

Figure 7 Variation of the absorbance measured at the characteristic wavenumbers with the gamma dose.
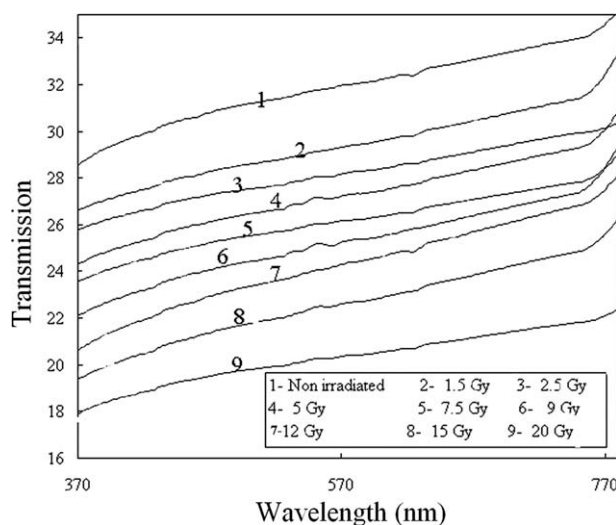
Figure 8 The transmission data of the nonirradiated and irradiated PVA/PEG, measured in the wavelength range 370–780 nm.

then increased up to a maximum value around 12 Gy. Above 12 and up to 20, it decreased again.

Color changes

The transmission spectra of the nonirradiated and irradiated PVA/PEG samples, in the wavelength range 370–780 nm, have been measured (Fig. 8). Using these transmission values, both the tristimulus values and chromaticity coordinates were calculated. Figure 9 shows the variation of tristimulus values (X, Y, Z) with the gamma does. From the figure, it is clear that X, Y, and Z exhibited the same trend, where they decreased on increasing the gamma dose up to 20 Gy.

Figure 10 shows the variation of chromaticity coordinates (x, y, z) with the gamma dose. From the figure, it is clear that x and y exhibited the same trend, where they increased with increasing the gamma dose up to 12 Gy. Above 12 and up to 20 Gy, it decreased. The chromaticity coordinate z exhibited an opposite trend with the gamma dose.
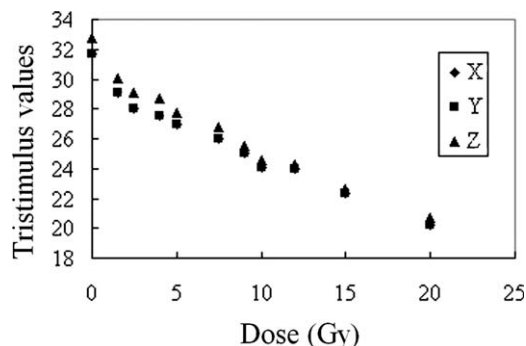

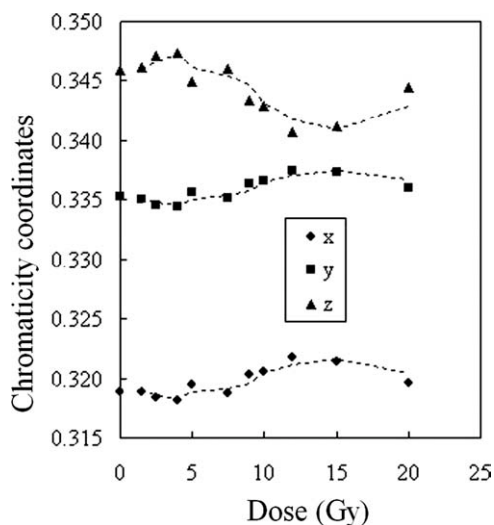**Figure 9** Variation of tristimulus values (X, Y, Z) with the gamma dose.

Figure 10 Variation of chromaticity coordinates (x, y, z) with the gamma dose.

The variation of color intercepts (L^*, a^*, and b^*) with the gamma dose is shown in Figure 11. The accuracy in measuring L^* is ±0.05 and ±0.01 for a^* and b^*. It can be seen that the color parameters
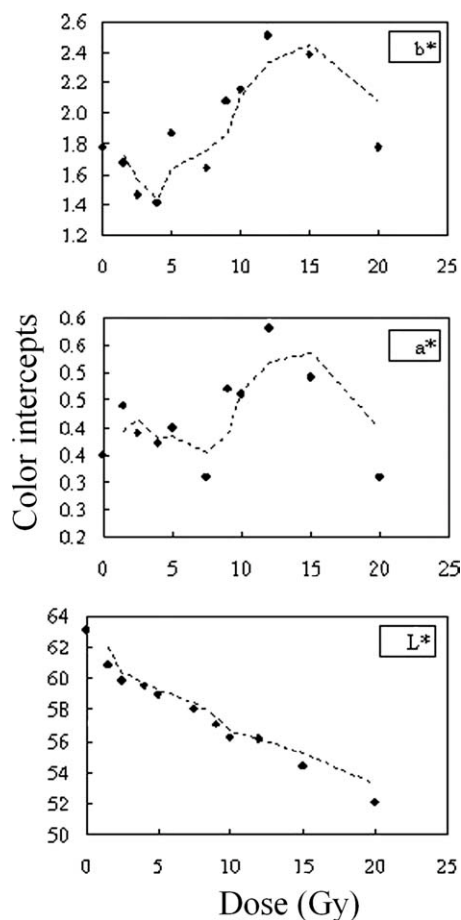

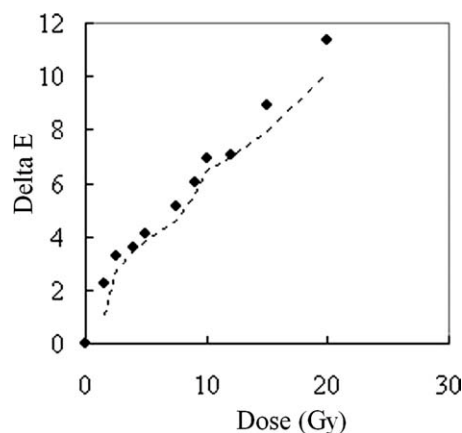**Figure 11** Variation of color intercepts (L^*, a^*, and b^*) with the gamma dose.

Figure 12 Variation of the color intensity ΔE with the gamma dose.

a^*, b^*, and L^* were significantly changed after exposure to gamma irradiation. The yellow ($+b^*$) color component of the nonirradiated film was changed to blue ($-b^*$) after exposure to gamma dose up to 20 Gy. This is accompanied by a net increase in the darkness of the samples ($-L^*$). At the same time, the red ($+a^*$) color of the nonirradiated sample was also changed to green ($-a^*$) by the gamma dose.

The color intensity ΔE (color difference between the nonirradiated sample and those irradiated with different gamma doses) was calculated and is plotted in Figure 12 as a function of gamma dose. From the figure, it is seen that ΔE increases with increasing the dose up to 20 Gy. This indicates that the PVA/PEG co-polymer has a response to color change by gamma 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 copolymer molecules have electrons with unpaired spin. Such species may also give optical coloration.[14]

CONCLUSIONS

The gamma irradiation in the dose range 4–12 Gy leads to a more compact structure of PVA/PEG copolymer, which results in an increase in the onset temperature of decomposition and activation energy of thermal decomposition. This enhances the scope of this copolymer in high-temperature applications.

The gamma irradiation of PVA/PEG copolymers leads to chain scission followed by crosslinking, and, as a result, there are changes in its structural, thermal, and optical properties.

The irradiation of PVA/PEG samples at the dose range 4–12 Gy were characterized by dominate amorphous regions that give a copolymer toughness. Thus, the PVA/PEG copolymer may be a suitable

candidate for industrial applications requiring its bending without breaking.

Fourier transform infrared measurements show that the alkane bond C—C degrades under gamma irradiation in the dose range 12–20 Gy, indicating that the carbonyl group is the most sensitive group to gamma irradiation. Also, the irradiation of PVA/PEG copolymer in the dose range 4–12Gy leads to the enhancement of crosslinking mechanism, reflected in an increase in the average molecular mass.

The nonirradiated PVA/PEG sample is nearly colorless; however, it showed significant color sensitivity toward gamma irradiation. This appeared clearly in the change in the yellow and red color components of the nonirradiated PVA/PEG thin film to blue and green, respectively. This was accompanied by a net increase in the darkness of the samples.

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