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X-ray irradiation-induced changes in (PVA–PEG–Ag) polymer nanocomposites films

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ABSTRACT

The effects of X-ray irradiation on the structural, thermal and optical properties of polyvinyl alcohol–polyethylene glycol–silver (PVA–PEG–Ag) nanocomposites have been investigated. The samples of nanocomposites were prepared by adding Ag nanoparticles with 5 wt% to the (PVA–PEG) blend. The films of 0.05 mm thickness were prepared by the casting method. These films were irradiated with X-ray doses ranging from 20 to 200 kGy. The resultant effect of X-ray irradiation on the structural properties of PVA–PEG–Ag has been investigated using X-ray diffraction and Fourier transform infrared spectroscopy. Also, thermal property studies were carried out using thermogravimetric analysis. Further, the transmission of the PVA–PEG–Ag samples and any color changes were studied. Fourier transform infrared spectroscopy measurements showed that the crosslinking is the dominant mechanism at the dose range 50–200 kGy. This led to a more compact structure of PVA–PEG–Ag samples, which resulted in an improvement in its thermal stability with an increase in the activation energy of thermal decomposition. Moreover, the color intensity ΔE was greatly increased with an increase in the dose, and was accompanied by a significant increase in the yellow color component.

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irradiation; nanocomposites; XRD; FTIR; TGA; color

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1. Introduction

The field of nanotechnology is one of the most popular areas for recent research that obviously includes polymer science and technology (*1*). The incorporation of metal nanoparticles in the polymer matrix will certainly enhance its physical properties so that the obtained nanocomposite will be a suitable candidate for several applications such as biotechnology, packaging, microelectronics, energy storage, optical devices and food-stabilizing systems (*2*–*6*). Polymers as base materials have natural properties providing a good host matrix for the embedding of metal nanoparticles. They are also characterized by chemical stability after chemical and physical doping (*7*–*13*). Nanocomposites fabricated from polymers with silver often exhibit remarkable improvement in its optical, electrical, thermal and

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mechanical propertie (*14*–*18*). This can be due to the attractive physical and chemical properties of silver nanoparticles (*2*). On the other hand, irradiation-induced modification of polymers is a promising technique for the production of new polymeric materials, which can be engineered with specific physical and optical properties. It may lead to specific changes in the polymer properties due to induced chain scissions and crosslinking (*19*). It destroys the initial structure by way of crosslinking, free radical formation and irreversible bond cleavages that result in the fragmentation of molecules and formation of saturated and unsaturated groups. All these processes introduce the so-called defects inside the material that are responsible for change in the structural properties of the material (*20*, *21*). The particular bonds that are broken may be identified by the Fourier transform infrared spectroscopy (FTIR) analysis (*22*). In addition, the study of color changes in irradiated polymers is an important technique that has been used to assess physical changes in polymers. Several investigations have been introduced to study the effects of Ag concentration on the physical and optical properties of polyvinyl alcohol–polyethylene glycol–silver (PVA–PEG–Ag) nanoparticle composites (*1*–*6*). The present work investigates the effect of X-ray irradiation on the structural, thermal and optical properties of PVA–PEG–Ag nanoparticle composites. This study aimed not only to give evidence about the physical and chemical changes in the investigated polymer but also to study the feasibility of enhancing its properties to make it more applicable.

2. Experimental

2.1. Samples preparation

2.1.1. Preparation of PVA–PEG–Ag nanocomposite films

Polymers nanocomposites films have been prepared by mixing (85%) of PVA with (15%) of PEG, supplied by Sigma-Aldrich GMBH, in 25 ml of distilled water, by using a magnetic stirrer for the mixing process for an hour to obtain a more homogeneous solution with a temperature of 80°C. Then weight percentages of nano particle 5% of Ag were added and allowed for 10 min to make the mixture more homogeneous, later the mixture was put in an ultrasonic bath for 5 min in order to spread the nano particles and mix fully with polymers blend, then they were poured onto the template (Petri dish), and left to dry at room temperature for about 120 h. Finally, a thin film of nearly 0.05 mm thickness is formed. The thickness was measured by a gauge Model 11/2704 Ast MD 370 standred which was calibrated by Arab British Dynamcs (*23*).

2.1.2. Preparation of Ag-nanoparticles

Ag-nanoparticles were prepared by vinylpyrrolidone reduction of Ag NO_3 in ethanol solution. Five milligram of of $AgNO_3$ was dissolved in 100 ml of ethanol (EtOH), poured in a reflux condenser and heated while stirring for 15 min. Then 1.2 g of poly(vinylpyrrolidone) is added, with stirring, and kept in a reflux condenser for about 10 min. After that NaOH (1 wt%, 0.5 ml) was added and kept for boiling while stirring for 30 min. The mixture was then kept stirred until it cooled to room temperature. In the preparation of the Ag aggregate, ethanol solution of $AgNO_3$ (25 mg) in 25 ml of EtOH was mixed with 25 ml of colloid at boiling temperature while stirring. Then, 4 ml of NaOH (1 wt%) was added to the mixture which was stirred at boiling temperature for 30 min and then it was cooled to room temperature (*24*).

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2.2. Irradiation facilities

In the present work, the samples were irradiated with different X-ray doses ranging from 20 to 200 kGy. 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 of 1 mA current. The same instrument was used in our previous work (*25*).

2.3. Analysis of the irradiated samples

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 A° and the diffraction patterns were recorded in the 2θ range (4–60°) with a scanning speed of one degrees per minute.

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 $\pm 4\ cm^{-1}$.

Thermogravimetric analysis (TGA) was performed 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. The tristimulus values and the CIELAB color difference were calculated using the methodology described before (*26*, *27*).

3. Results and discussion

3.1. X-ray diffraction

In order to study the effect of X-ray irradiation on the degree of ordering of the PVA–PEG–Ag nanocomposites, X-ray diffraction measurements were carried out on 0.05 mm thin films. Figure 1 shows the X-ray diffraction patterns of the non-irradiated and irradiated PVA–PEG–Ag nanoparticle 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–Ag sample is partly crystalline. 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 2 as a function of the dose. The integral intensity shows an increase up to a maximum value around the 50 kGy irradiated sample, followed by a decrease on increasing the dose up to 200 kGy.

The Halo's width at the half of maximal intensity ΔW is inversely proportional to the crystallite size *L*, according to the Scherrer equation:

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

where λ is the wavelength of the X-rays and the values of ΔW were calculated. Figure 2 shows the variation of ΔW with the dose. The figure shows that ΔW and thus the thickness of the lamella was not affected by the X-ray irradiation doses. The increase in integral intensity indicates an increase in the ordering character of the PVA–PEG–Ag samples which

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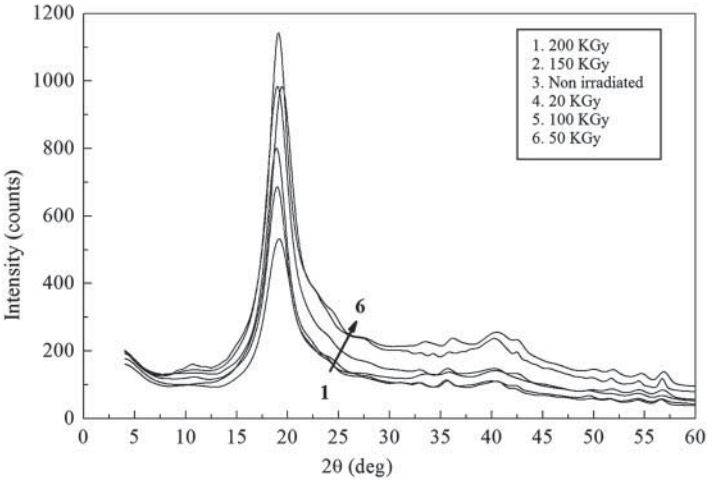


Figure 1. X-ray diffraction patterns of the non-irradiated and irradiated PVA–PEG–Ag nanocomposite samples, measured in the 2θ range 4–60°.

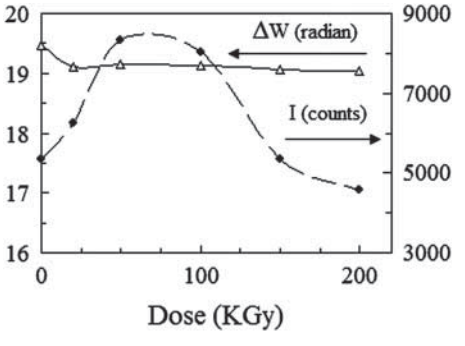


Figure 2. Variation of integral intensity *I* and the Halo's width at the half of maximal intensity ΔW with the dose.

can be attributed to degradation induced by X-ray irradiation. 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. Also, this increase in ordering character can be due to the strong intermolecular interaction of PVA chains and intermolecular hydrogen banding (*7*). In addition, adding Ag to PVA–PEG may cause repulsion between the additive molecules, resulting in an increase in ordering character of the chains. On the other hand, the decrease in integral intensity indicates a decrease in particle size (*1*). This means that the crystalline structure has been destroyed due to crosslinking.

3.2. Fourier transform infrared spectroscopy

The effect of X-ray irradiation on the infrared absorption of PVA–PEG–Ag nanocomposites has been investigated. The infrared absorption spectra of the non-irradiated and

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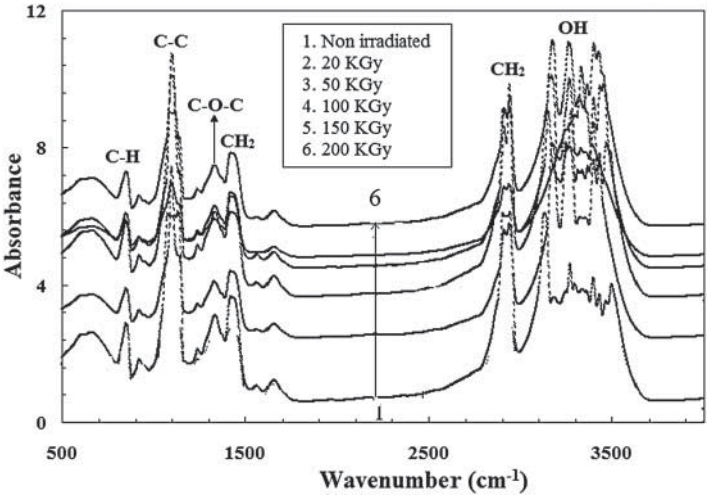


Figure 3. FTIR absorbance spectra of the non-irradiated and irradiated PVA–PEG–Ag nanocomposite samples.

irradiated samples are shown in Figure 3. The characteristic absorption peaks of PVA–PEG are observed at 1330, 1100, 3180–3527, 851, 2944 and 1425–1475 cm^{-1} corresponding to the C–O–C (acetal ring), C–C, –OH (non-bonded hydroxyl stretching band), C–H (broad alkyl stretching band) and the duplet CH_2 bonds (a duplet absorption with peaks attributed to the alkyl chain), respectively (*28*–*30*). Figure 4 shows the variation of the absorbance measured at these characteristic wavenumbers with the dose. The variation of both C–H broad alkyl stretching band and C–O–C acetal ring with the dose is shown in Figure 4(a). It can be observed that the two bands exhibited an opposite trend with the dose, where the decrease in CH band was accompanied by an increase in C–O–C band. The decrease in intensity of CH band suggests the formation of chemical conjugation of Ag nanoparticles with PVA molecules (*1*). Also, the C–H stretching is related to aldehydes (*14*), while the acetal ring (C–O–C) bands are formed by the crosslinking reaction of PVA with Ag (*17*, *18*). This indicates that crosslinking is dominant, the result that could be confirmed by the decrease of the O–H stretching vibration peak at the dose range 50–200 kGy (Figure 4(b)) suggesting that the hydrogen bonding between Ag with the adjacent OH group becomes weaker in crosslinked PVA than in pure PVA because of the reduction in the number of OH groups and the formation of both acetal ring and C–C bands (Figure 4(b)) (*14*). Further, the irradiation with X-rays enhances the number of inter-chain interactions, resulting in the change in molecular weight distribution that led to crosslinking. Figure 4(c) illustrates the variation of the duplet CH_2 bands with the dose. It is clear that both CH_2 decreased with increasing dose up to 200 kGy. This duplet absorption is attributed to the alkyl chain (*14*).

3.3. Thermogravimetric analysis

TGA were performed on PVA–PEG–Ag nanocomposite samples to obtain a better understanding of the changes in its thermal stability due to X-ray irradiation. The TGA was performed in the temperature range from room temperature up to 350°C, at a heating rate

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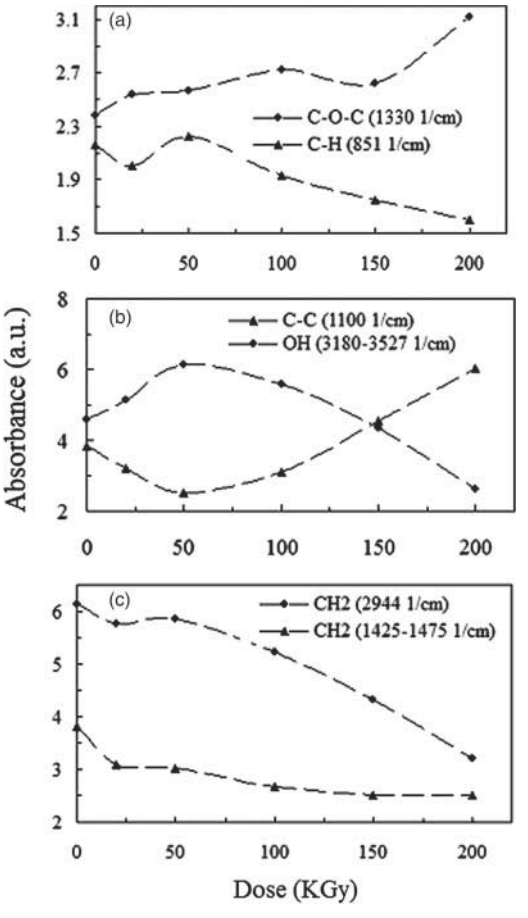


Figure 4. Variation of the absorbance, measured at the characteristic wave numbers with the dose.

of 10°C/min. Figure 5 shows the TGA thermograms for the non-irradiated and irradiated samples. It is clear from the figure that the PVA–PEG–Ag nanocomposites decompose in one main breakdown stage. Using the TGA thermograms, the values of onset temperature of decomposition T_0, the temperature at which the decomposition starts, were calculated. Figure 6 shows the variation of T_o with the dose. From the figure it is seen that T_0 shows a decrease until a minimum value around the 50 kGy irradiated sample, due to preferential chain scission, followed by an increase with an increase in the dose up to 200 kGy, due to the crosslinking.

TGA not only measures the temperature at which thermal decomposition starts T_0, but also measures the activation energy of thermal decomposition E_a, which is useful for studying the thermal stability of the materials. Various thermogravimetric methods based on either the rate of conversion or the heating rate have been reported to determine the thermal kinetic parameters. The method proposed by Horowitz and Metzger (*31*) has been used in the present study for measurement of the activation energies of thermal decomposition. Using the TGA curves, values of E_a were calculated for the non-irradiated and irradiated samples. Figure 6 shows the variation of E_a with the dose. E_a exhibited a similar trend to that

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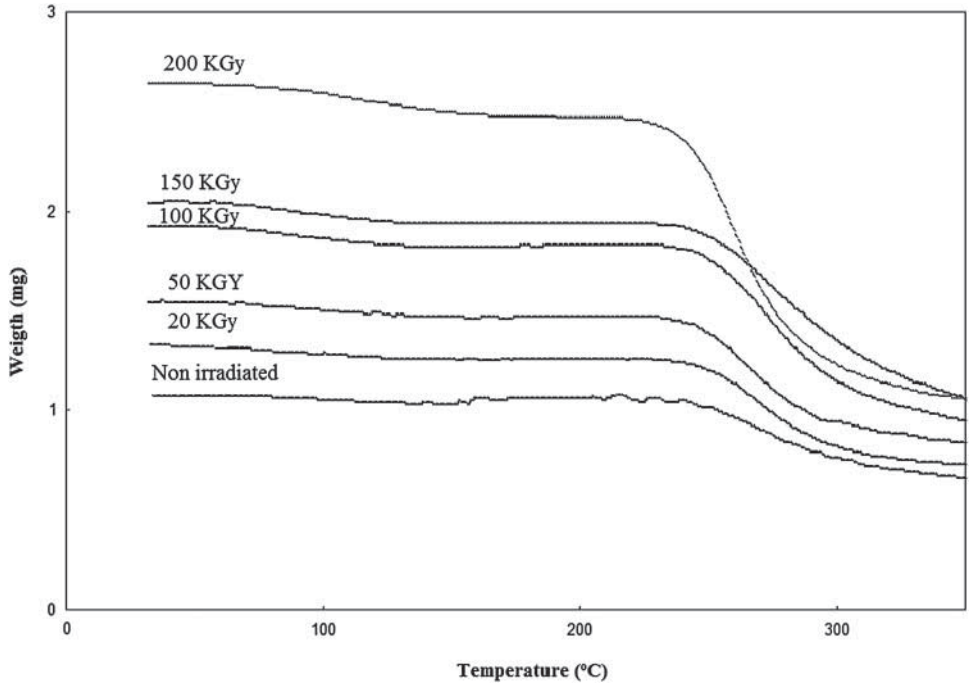


Figure 5. TGA thermogram, measured in the temperature range of room temperature to 350°C, for the non-irradiated and irradiated PVA–PEG–Ag nanocomposite samples.

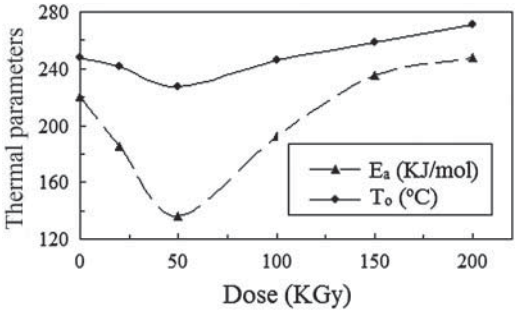


Figure 6. Variation of onset temperature of decomposition T_0, and activation energy of thermal decomposition E_a with the dose.

of T_0. These results may be interpreted on the basis that the X-ray irradiation up to 50 kGy causes initial scission. This is reflected in a decrease in E_a. At the dose range 50–200 kGy, crosslinking is achieved.

3.4. Color changes

The transmission spectra of the non-irradiated and irradiated PVA–PEG–Ag samples, in the wavelength range 370–780 nm, have been investigated (Figure 7). Using the transmission data, both the tristimulus values and chromaticity coordinates were calculated. Figure 8

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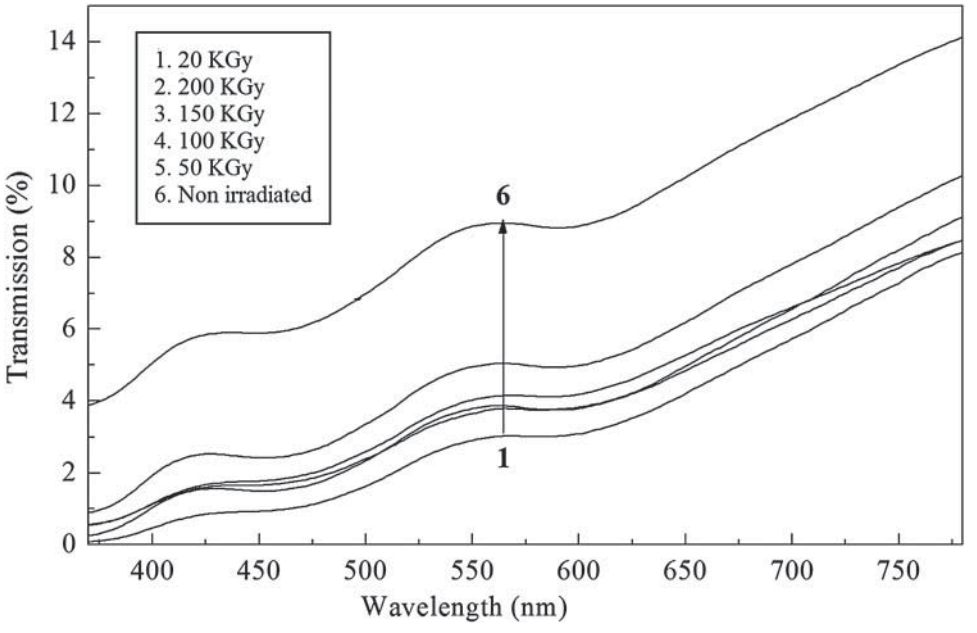


Figure 7. Transmission spectra of the non-irradiated and irradiated PVA–PEG–Ag nanocomposite samples, measured in the wavelength 370–780 nm.

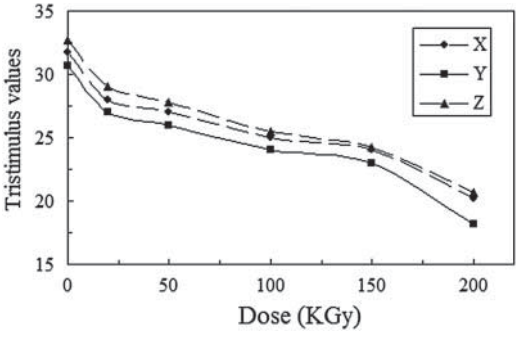


Figure 8. Variation of tristimulus values (*X*, *Y*, *Z*) with the dose.

shows the variation of tristimulus values (*X*, *Y*, *Z*) with the dose. From the figure it is clear that *X*, *Y* and *Z* exhibited the same trend, where they decreased on increasing the dose up to 200 kGy. Figure 9 shows the variation of chromaticity coordinates (*x*, *y*, *z*) with the dose. It is clear that *x* and *y* exhibited the same trend, where they increased with an increase in the dose up to 200 kGy. The chromaticity coordinate *z* exhibited an opposite trend with the dose. The variation of color intercepts (*L** and *b**) with the X-ray dose is shown in Figure 10. It could be noted that the *L** intercepts of zero and 100 integers represent the standard dark and white colors, respectively. The positive values of *a** and *b** represent the red and yellow components, whereas the negative values represent the green and blue color components, respectively (*26*, *27*). The accuracy in measuring *L** is ±0.05 and is ±0.01 for *a** and

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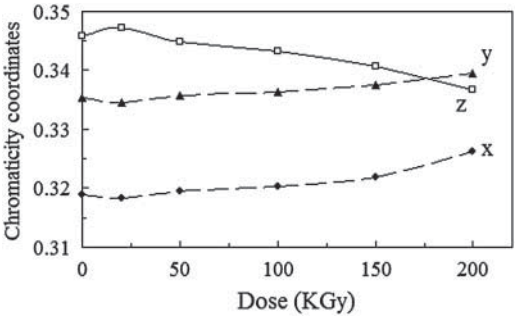


Figure 9. Variation of chromaticity coordinates (*x*, *y*, *z*) with the dose.

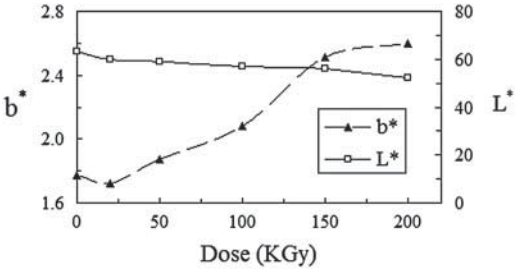


Figure 10. Variation of color intercepts (*L** and *b**) with the dose.

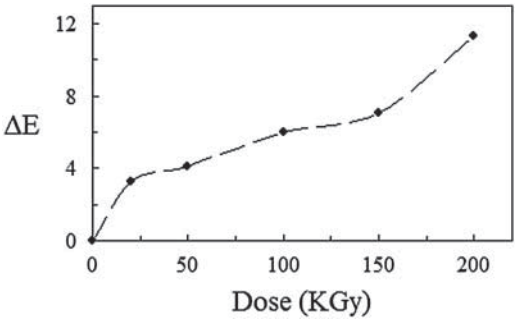


Figure 11. Variation of the color intensity ΔE with the dose.

*b**. It can be seen that the color parameters *b** and *L** were significantly changed after exposure to X-ray. The proportions of blue ($-b^*$) color component of the non-exposed film was converted into yellow ($+b^*$) after exposure to X-rays up to 200 kGy. Moreover, the *L** values were decreased with increasing fluence, indicating the deepness in color strength. The red green color component *a** of the non-irradiated sample was not affected by the irradiation up to 200 kGy. The color difference ΔE was significantly increased with the dose (Figure 11), indicating that the color difference is largely dependent on the proportions of the yellow color component. These changes in color can be attributed to the trapping of the excited free radicals that are formed. Also, the trapped free radicals resulting from X-rays induced

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rupture of polymer molecules having electrons with unpaired spin. Such species may give optical coloration (*26*).

4. Conclusion

The X-ray irradiations of PVA–PEG–Ag nanocomposites lead to chain scission followed by crosslinking and as a result there are changes in its structural, thermal and optical properties. The X-ray diffraction measurements show that the irradiation at the dose range 50–200 kGy enhances the number of inter-chain interactions, resulting in the change of molecular weight distribution which led to crosslinking that reduces ordering character and increases the amorphous regions enhancing the samples resilience.

FTIR analysis indicated the formation of chemical bonding/conjugation between the Ag nanoparticles and PVA chains. Such induced structural changes explain the observed changes in the properties of PVA–PEG–Ag nanocomposites after X-ray irradiation.

The TGA indicates a degradation of the nanocomposite polymer matrix under X-ray irradiation at doses up to 50 kGy causing the polymer to decompose earlier than the non-irradiated sample. In this case, the crosslinking by X-ray irradiation at higher doses seems to be the dominant process. The dominance of the crosslinking effect has led to a more compact structure of the nanocomposite polymer, which resulted in an improvement in its thermal stability with an increase in the activation energy of thermal decomposition.

The non-irradiated PVA–PEG–Ag nanocomposite polymer is nearly colorless; however, it showed significant color sensitivity toward X-ray irradiation. This sensitivity appeared clearly in the change in the blue color component to yellow, accompanied by an increase in the darkness of the polymer samples.

Disclosure statement

No potential conflict of interest was reported by the authors.

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