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Optical Characterization of Gamma Irradiated Bayfol DPF 5023 Nuclear Track Detector

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ABSTRACT

One of the distinctive nuclear track detectors (SSNTDs) is the Bayfol (DPF) which is distinct by its high strength and stability. The author used UV spectroscopic methodology to obtain information concerning the influence of γ doses (8-50 kGy) on the optical character of DPF films. The alternations of Urbach energy (E_u), optical band gap (E_g) and refractive index (n) with the γ dose were interpreted. An increase in both E_u (0.26-0.61 eV) and n (1.5663-1.5764) associated with a reduction of E_g (6.71- 6.58 eV) was noticed when increasing the dose up to 50 kGy. These trends were assigned to the dominance of chain crosslinks. The γ radiation encourages the transesterification interaction between PC and Ps leading to a more compact structure of the Bayfol copolymer. Additionally, the CIE technique was used to calculate the color differences among the uncolored pristine and the irradiated films. The induced crosslinking formed color centres that led to the increase of the color difference (ΔE) values to be more than 5, thus Bayfol could be used in dosimetry applications.

1. INTRODUCTION

Among the thermoplastic polymers that are widely used in several applications are Polycarbonate (PC) and polyester (Ps). PC is an engineered amorphous polymer having an excellent transparency that allowed it to be used in instruments that store optical data, such as DVDs or CDs. Moreover, it is used in extra engineering sectors, such as transportation, building and automotive. On the other hand, Ps is semicrystalline polymer that is used in several industries requesting such films and fibers. Lately, the interest in industry was the PC-Ps blends [1].

One of the most interesting fields that aids in improving industry is the polymer blends [2]. This field yields new high performance polymers. As an example, the combination of polycarbonates (PC) and Polyester (Ps) yields a class of nuclear track detectors (NTDs) known as Bayfol. Blend of PC and Ps is an essential field of commercial blends. The product blend is chemically stable with excellent physical and chemical characteristics relative to the blended polymers [3]. The transesterification reaction was postulated to be the greatest significant one that arises among PC and Ps, resulting in a novel construction of copolymers with

novel IR function groups [4,5]. These copolymers possess the brilliant effect durability, great thermal and mechanical characters, and the excellent dimensional stability of both PC and Ps [6].

Additionally, γ irradiation breaks down the polymer chains producing biochemically active free radicals that act to form newly covalent bonds causing chains crosslinks, consequently the polymer properties are changed [7]. Besides, the γ irradiation induces lattice defects, altering the polymer character [6]. The characterization of optical properties of irradiated polymers is extensively used in optoelectronic apparatuses [8]. Refractive indices of polymeric materials give knowledge about their vital properties [9]. Moreover, the changes in color owing to irradiation assess the optical characteristics of the matter. It is one of the most important methodologies that have been applied to assess physical changes in irradiated polymers. This is a significant evidence for their application in commercial requests and dosimetry [10]. Some investigations were carried out to highlight the significance of color alternation of the irradiated polymers in the field of dosimetry [11-13]. They

explored that the color change technique pledges the fundamentals which should be considered in the creation of radiation sensors. They assigned the alternation in color in irradiated DPF to the created free radicals that lead to the growth of conjugated bonds [14]. Furthermore, they attributed the variation of color in exposed PC to radical species, relieved benzophenones, and extremely conjugated bonding or rearranged isopropylidene radicals. The current work aims to study the feasibility of modifying the optical properties of Bayfol so as to enhance its presentation in numerous applications. Moreover, the study of color changes introduces the basis that can be used in constructing simple sensor for γ irradiation.

2. EXPERIMENTAL

2.1 Materials

Bayfol DPF 5023 is a PC/Ps blend film of chemical configuration, average thickness and density are $C_{16}H_{14}O_3$, $380\mu m$ and $1.23 g/cm^3$, respectively. It is fabricated by Farbenfabriken Bayer A.G., Leverkusen (Germany).

2.2 Irradiation tool

The DPF films were irradiated using a ^{60}Co source (Canada A.E.A Ltd.) of a dose rate of 1 kGy/h. The irradiation was carried out at Atomic Energy Authority, Egypt.

2.3 Methodology

The refractive index of the DPF films were measured applying an Abbe refractometer (Model 10480, Type Reichert, mark II, New York).

A Tomos spectrophotometer, Model No. 1800 was used to measure the UV-vis absorbance spectrum.

The Commission International de E'Claire (CIE) approach was used to evaluate the color changes in the films under study. Full data about the calculation of color changes were illustrated in a previous study [8]. The values of X, Y and Z substitute the definite red, green and blue lights known as the tristimulus values [15]. The CIE explains a standardization technique to calculate x, y and z chromaticity coordinates that identify the color saturation.

We used the 1976 CIE intercepts a^* , b^* and L^* indicating the green-red, blue-yellow and dark-white axes, respectively. The accuracy in calculating L^* is ± 0.05 and is ± 0.01 for both a^* and b^* , correspondingly.

The color difference (color intensity), ΔE could be calculated from the following equation :

$$\Delta E = [(L_1^* - L_2^*)^2 + (b_1^* - b_2^*)^2 + (a_1^* - a_2^*)^2]^{1/2} \quad (1)$$

The subscripts 1 and 2 indicate to the irradiated and pristine films.

3. RESULTS AND DISCUSSION

3.1 Absorption analysis

An absorbance study was carried out to obtain knowledge about the optical micro-electronic transitions. This helps to investigate the structure of the optical bandgap (E_g) and study its dependence on the γ dose. Figure (1) shows the variation of the absorbance with the wavelength for the pristine and irradiated DPF samples. It was assigned that the reduction of the absorbance increasing the wavelength to the reduced number of phenyl group ($\pi-\pi^*$) transitions and ($n-\pi^*$) carbonyl group [16].

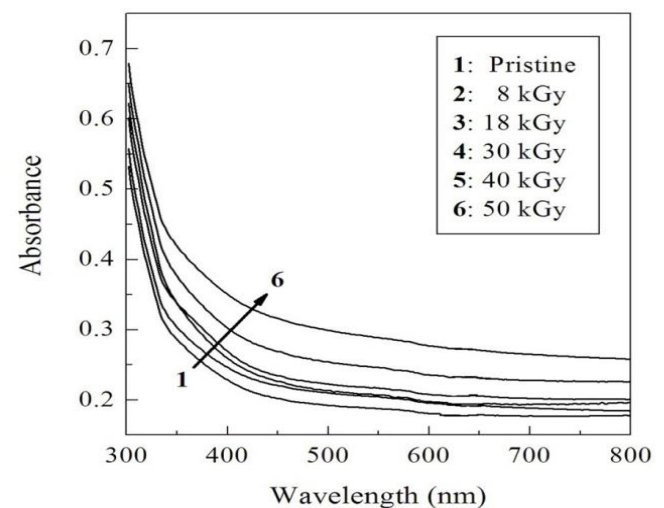


Fig. (1): The UV-Vis absorbance spectra of the Bayfol films

Additionally, the absorbance of the DPF films increased with raising the dose up to 50 kGy due to the progress of bonding through crosslinks. The energy transferred by the incident γ photons creates a novel chemical configuration that enhances the absorbance [17].

3.2 Urbach energy analysis

One of the important parameters that gives information about the fractional dispersal of the incident radiation when scattered and absorbed by the penetrated medium is the extinction coefficient (k). The values of k were calculated by means of:

$$k = (\lambda\alpha/4\pi) \quad (2)$$

In which, λ denotes the wavelength and α means the absorption coefficient that can be computed from:

$$\alpha = \text{Absorbance} \times 2.303/\text{thickness of the sample} \quad (3)$$

In Figure (1), an exponential rise was observed in the absorbance adjacent to the edge that matches the movement from the localized states in the valence band tail. In the disordered polymers, there are tail states seem in the gap area to be lower than the main absorption edge [18]; that can be estimated through applying the absorption coefficient (α) in the Urbach rule [19];

$$\alpha = \alpha_0 \exp\left(\frac{hv}{E_u}\right) \quad (4)$$

In which, the constant α_0 identifies the matter and E_u is the Urbach energy that indicates the width of the tail of localized states in the forbidden bandgap [20] and hv is the photon energy. The values of E_u were obtained from the slope of exponential dependence of absorption coefficient edge vs. hv . The variation of E_u with the γ dose is shown in Figure (2). The values of E_u increased from 0.26 to 0.61 eV with raising the dose up to 50 kGy. This was assigned to the increase of the disordered phase due to the action of γ radiation [21].

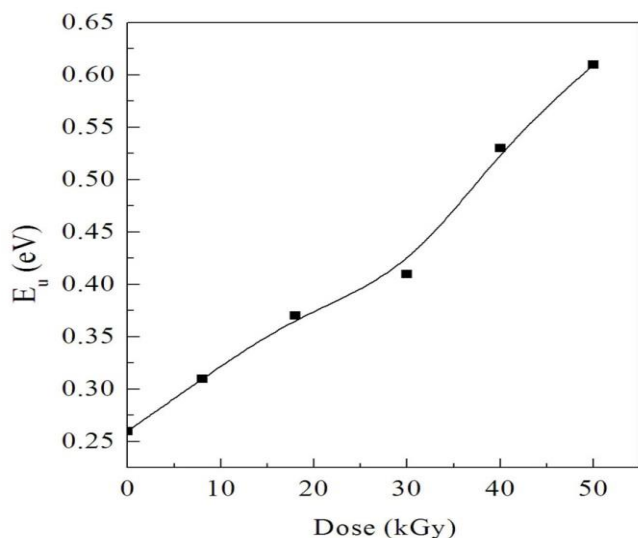


Fig. (2): Variation of the Urbach energy with the γ dose

3.3 Refractive index analysis

The measured values of the refractive index (n) of the solid DPF films were plotted in Figure (3) as a function of γ dose. The accuracy of assessing the

values of n , the temperature of the prism surface and the wavelength of the used light were ± 0.0001 , $19-22^\circ\text{C}$ and 5893\AA , correspondingly. Figure (3) displays the change of n with the γ dose. An increase of the n values was observed with increasing the dose up to 50 kGy. The increase of n with dose was attributed to the prevalence of crosslinking. The γ radiation breaks down the carbonate group, isopropyl and aromatic groups, thus produces chemically active free radicals [22]. These free radicals initiate reactions; hence, forming covalent bonding through crosslinking. Extra factor that boost crosslinking is the role of blended P_s that permits the creation of extra bonding between it and PC via the transesterification reaction [10]. This interpretation agrees well with that obtained previously.[23]

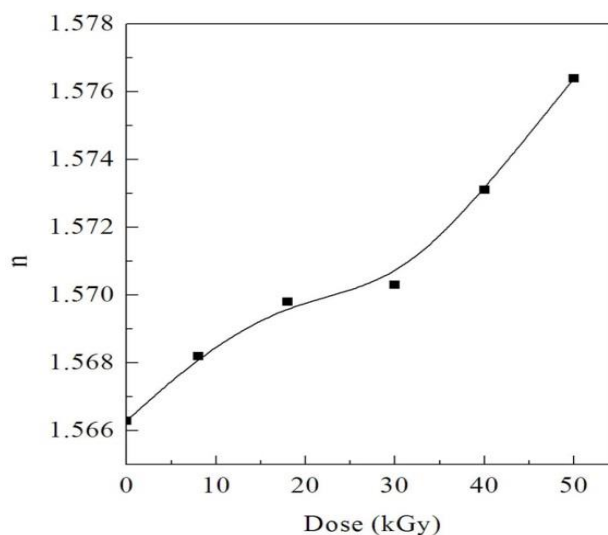


Fig. (3): Variation of the refractive index with the γ dose

3.4 Bandgap analysis

The bandgap (E_g) was calculated using the refractive index values by means of the formula [24]:

$$\left(\frac{n^2-1}{n^2+1}\right) = 1 - \sqrt{\frac{E_g}{20}} \quad (5)$$

The resultant values are displayed in Figure (4) against the γ dose. The E_g values reduced with increasing the dose up to 50 kGy. This drop in E_g was attributed to crosslinkins that increase the amorphous part of the DPF films. This forms structural deficiencies, permitting the creation of localized states in the E_g construction producing micro-electronic transitions. Then, the major act of the γ radiation on the DPF films was the development of free radicals that improve the conjugated bonds and thus decreasing the E_g [17].

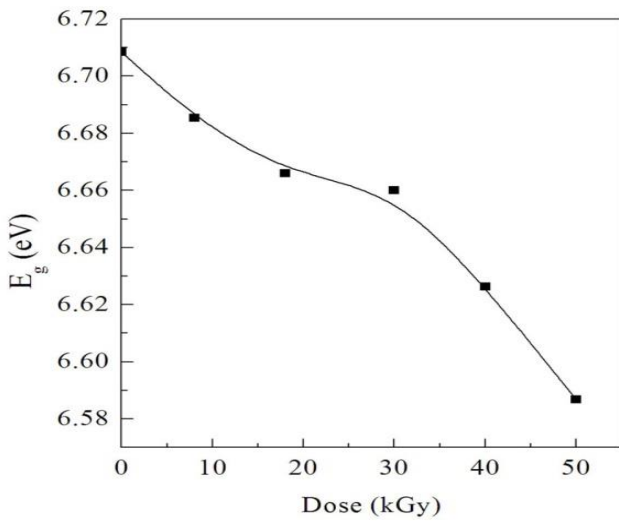


Fig. (4): Variation of the optical band gap with the γ dose

3.5 Color changes analysis

A distinct application of solid state nuclear track detectors (SSNTDs) is the valuation of color differences with changing the γ dose. The author computed the color factors using the transmission records in the wavelength range from 370 to 780 nm (Figure 5). The tristimulus values were measured and presented in Figure (6) versus γ dose. Their values decreased on raising the γ dose up to 50 kGy. Additionally, the chromaticity coordinates were calculated and plotted in Figure (8) versus γ dose. There is an observed increase of x and y coordinates with raising the dose up to 50 kGy, while, the coordinate z decreased.

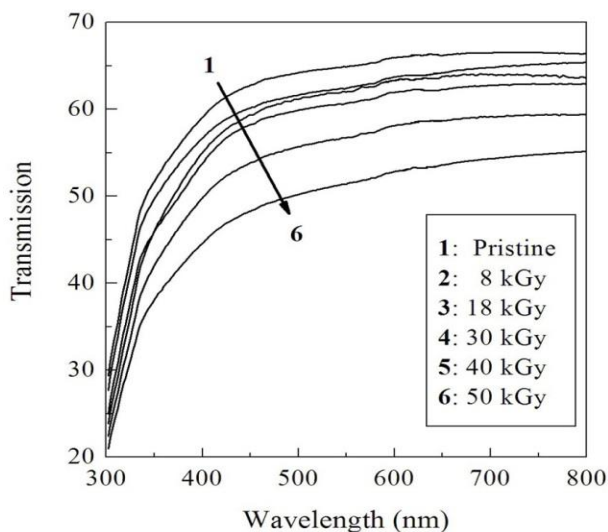


Fig. (5): The UV-Vis transmission spectra of the Bayfol films

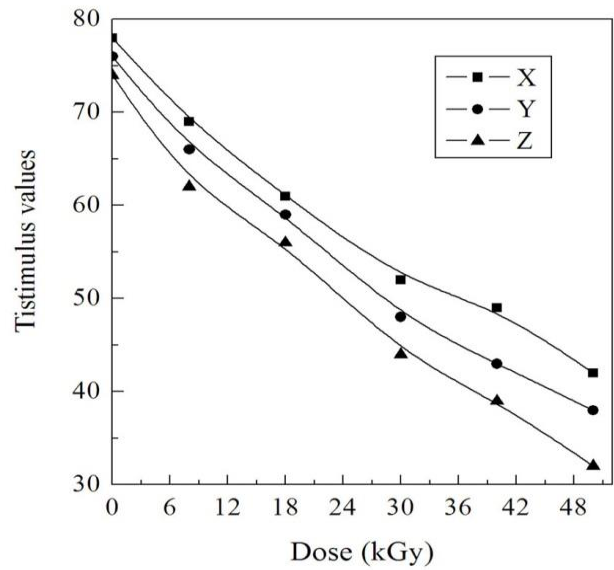


Fig. (6): Variation of the tristimulus values with the γ dose

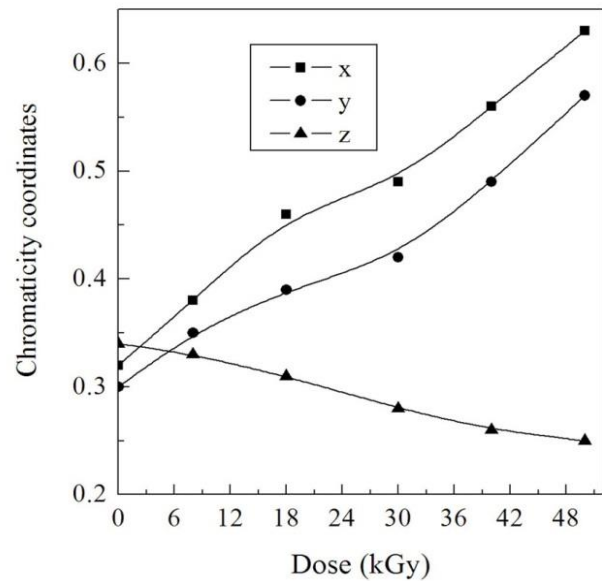


Fig. (7) Variation of the chromaticity coordinates with the γ dose

The change of color intercepts a^* and b^* with the γ dose is displayed in Figure (8). The b^* intercept exhibited negative values that increased with raising the dose up to 50 kGy. This identifies the change of the blue color component into yellow. The a^* color intercept did not change with increasing dose up to 50 kGy, indicating that the green-red color components was not affected by the used γ doses. This was accompanied by the increase of darkness ($-L^*$) as shown in Figure (9).

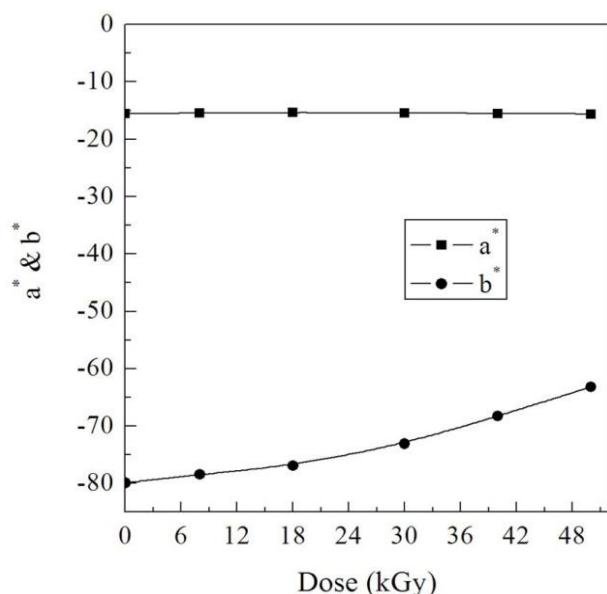


Fig. (8): Variation of a^* and b^* color intercepts with the γ dose

The color intensity (ΔE) was calculated using equation 1 and is plotted in Figure (9) against dose. The ΔE values augmented with raising the dose up to 50 kGy. ΔE achieved values greater than 5. This indicates a significant color change [25,26]. The change in the color of the DPF films is attributed to the created chemically active free radicals that allow the creation of high conjugated bonds though out crosslinking [14]. The chemically active free radicals form chemical reactions caused crosslinking. This creates color centers. Moreover, these active free radicals of unpaired spin electrons produce color changes [17].

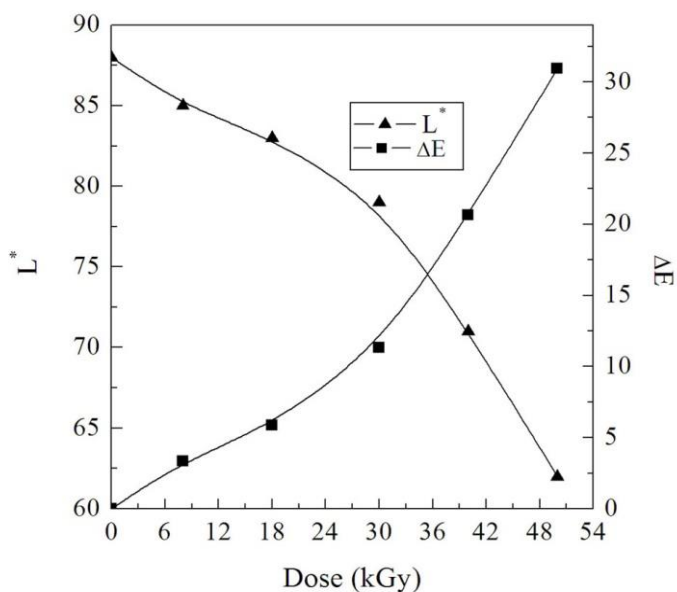


Fig. (9): Variation of L^* and ΔE with the γ dose

4. CONCLUSION

Both the refractive index and Urbach energy were increased with increasing the γ dose up to 50 kGy due to crosslinking. This was linked with a reduction in the optical bandgap. The achieved optical changes may optimize the Bayfol films for the use in optoelectronic. Moreover, the non-irradiated Bayfol film is nearly colorless, it showed a significant color sensitivity toward γ irradiation. The sensitivity in the color change toward γ radiation appeared obviously in the change in the blue color component into yellow, accompanied by an increase in the darkness of the Bayfol films.

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