1. Introduction
Interest in the area of proton irradiation treatment of polymers has increased in recent years. This may be due to the fact that the proton irradiation may lead to many processes, such as the production of primary and secondary radicals, formation of double bonds and transformation of C–C bonds. These reactions depend on the dose as well as on the environmental conditions during and after irradiations (1). These are accompanied by changes in chemical, structural, geometrical, optical and electrical properties of the polymer (2-4). The obtained chemical system is characterized by new functional groups, a different backbone with different electronic structure and different physical properties (5).

Proton irradiation can also modify the track registration properties of polycarbonates (6) and thus its properties. On the other hand, Polycarbonates have found widespread applications in many domains of techniques in industrial applications as well as in nuclear technologies. Also, Polymer blends have always been considered to be interesting combinations for obtaining new high-performance polymeric materials (7). Bayfol is a class of polymeric nuclear track detectors (NTDs). It is a Makrolon polycarbonate/polyester blend. Blends of polycarbonate and polyester are an important class of commercial blends with numerous applications providing good chemical resistance, impact resistance even at low temperatures, and improved flow characteristics as compared with the neat polymers (8). It is found that the postulated transterification to be the most important exchange reaction occurring between polycarbonates and polyester, resulting in a new chemical structure of copolymers with new IR bands (9). The effects of proton irradiation on polymers have been reported (10-16). The results revealed that the proton irradiation causes intermolecular crosslinking and allows the formation of covalent bonds between different chains, leading to an improvement in the structural, optical, and thermal properties of polycarbonates. Several authors studied the application of the proton irradiation effects in materials science and biomedical fields (17-19). In a previous study, we studied the induced changes in Bayfol DPF 5023 due to the 28 GeV $^{36}$Fe ion irradiation (8). The results indicated that the Fe ion irradiation in the fluence range $10^{15}$–$10^{16}$ ion/cm$^2$ led to a more compact structure of Bayfol polymer, which resulted in an improvement in its thermal stability with an increase in activation energy of thermal decomposition and crosslinking. This crosslinking enhanced the intrinsic viscosity of Bayfol indicating an enhancement in the average molecular mass. The aim of the present work is to investigate the modifications induced by protons on the structural and optical behavior of Bayfol DPF 5023 and to analyze these effects as a function of proton fluence.

2. Experimental
2.1 Samples
Bayfol DPF 5023 is a polycarbonate based film with a gloss first surface and a micromatte second surface. It has advantages over standard polycarbonate films in terms of dynamic strength, chemical resistance, dimensional stability, and cold formability. It is manufactured by Farbenfabriken Bayer A.G., Leverkusen (Germany), with an average thickness of 300 µm and density 1.23 g/cm$^3$.

UVVis spectroscopy measurements were conducted by UV/Vis Spectrophotometer (Model Tomos UV-1800) in the wavelength range from 1100 nm to 190 nm, in transmission mode, using thin solid film of synthesized quantum composites. The Commission International de E’Claire (CIE units x, y and z) methodology was applied in this work for the description of colored samples. The tristimulus values and the CIELAB color difference were calculated using the methodology described before (12).

3. Results and discussion
3.1 X-ray diffraction
In order to study the effect of proton irradiation on the mass fraction of the amorphous or crystalline phase, XRD is performed. Figure 1 shows the X-ray diffraction patterns of the non irradiated and irradiated Bayfol DPF 5023 samples, measured in the 2 range 10-35. From the figure we see that the X-ray diffraction patterns of the samples are characterized by halos extending in the 2 range from 1100 nm to 190 nm, in transmission mode, using thin solid film of synthesized quantum composites.

The Bayfol DPF 5023 samples were exposed to a 1 MeV proton beam at the Ion Beam Center, University of Surrey, UK. The current density of the proton beam was 0.05 µA/cm$^2$ and the beam diameter was 1.8 mm. The irradiation was carried out at fluences in the range 1x10$^{15}$-5x10$^{17}$ p/cm$^2$, with the sample held at a vacuum of 10$^{-4}$Torr.

A Shimadzu 6000 X-ray diffractometer identified with Cu-k$_\alpha$ radiation of wavelength $\lambda=1.5406$ Å was used to perform X-ray diffraction (XRD) patterns.
The increase in integral intensity indicates an increase in the crystallinity (ordering character) of the samples which can be attributed to degradation induced by proton irradiation. This degradation increases the chain mobility and thus permits some molecules to reorder (20). The free radicals created due to degradation are chemically active, can take part in chemical reactions that cause crosslinking. This is reflected on the trend of the integral intensity at the fluence range 1×1012-1×1014 p/cm² indicating that the crystalline structure has been destroyed due to crosslinking.

\[ L = \frac{0.89}{\Delta W \cos} \]  
(1)

where \( \Delta W \) is the peak’s width at the half of maximal intensity and is the wavelength of the X-rays. The variation of \( \Delta W \) with the proton fluence is shown in Figure 2. It is found that \( \Delta W \) decreases with increasing fluence up to 1×1014 p/cm² indicating an increase in the width of the lamella.

### 3.2 FTIR Spectroscopy

The effect of proton irradiation on the optical absorption of Bayfol detector was investigated. The infrared absorption spectra were obtained in the wave number range 400–4000 cm⁻¹, for non-irradiated and irradiated samples (Figure 3). The changes have been estimated from the relative increase or decrease in the intensity of the peak associated to the functional groups present in the polymer. The vibration modes of chemical bonds are characterized by the absorption bands in the FTIR spectra (21). Figure 4 shows the variation of the absorbance measured at the characteristic function groups of Bayfol with the proton fluence. From the figure it is clear that the absorbance measured at the wavenumbers 1783 cm⁻¹ decreases with increasing the proton fluence up to to 1×1012 p/cm² indicating the breaking of the C=O bond. This indicates that scission takes place at the carbonate site (Figure 4a). The intensity of the peak corresponding to hydroxyl group OH (3530 cm⁻¹) decreases with the proton fluence up to 1×1012 p/cm² and then increases with increasing the fluence up to 1×1014 p/cm² (Figure 4b). The increase in the hydroxyl groups means an increase in the end groups of macromolecules indicating that degradation process prevails in this fluence range. The synthesis of this polymer requires transesterification of diphenyl carbonate with bisphenol A with the elimination of phenol as side product. Therefore it is expected that the initial concentration of hydroxyl group will monotonously decrease with the increase in the chain length of the polymer (22). The presence of the two benzene rings of Bayfol polycarbonate can be confirmed from the absorption band due to C-H stretching which falls near 2923 cm⁻¹ (C-H, aliphatic). The absorbance measured at these wavenumbers shows an increase with increasing the proton fluence up to 1×1014 ion/cm² (Figure 4c). An opposite trend could be obtained for the absorbance measured at the wavenumbers 1253 cm⁻¹ (C-O) and 769 cm⁻¹ (C-H) where they decreased with increasing the proton fluence up to 1×1014 p/cm². These results indicate that both degradation and crosslinking occurs simultaneously, but degradation of them prevails.

### 3.3 Optical analysis

Bayfol DPF 5023 have been characterized through spectral absorption measurements. The UV–Vis absorption spectra of the irradiated and non-irradiated Bayfol samples are shown in Figure 5. As seen, the absorbance changes with changing fluence up to 11012 p/cm². This means that the levels at the energy band were affected by the proton fluences.

In amorphous, disordered and defected materials, there are tail states appear in gap region below the fundamental absorption edge which can be determined using the absorption coefficient (α). This absorption coefficient (α) obeys the Urbach rule (23):

\[ \alpha = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right) \]  
(2)

where \( \alpha_0 \) is a constant that characterizes the materials and \( E_u \) is the Urbach energy that refers to the width of the tail states. Plotting the relation between \( \ln \alpha \) and \( h\nu \) for the irradiated and non-irradiated Bayfol samples, the \( E_u \) could be obtained from the reciprocal of the slope of the straight line. The values of \( E_u \) were found to increase with increasing the proton fluence (Figure 6a), this means that the proton irradiation creates defects in the Bayfol samples (24). The energy band gap \( (E_g) \) is determined using the UV/Vis absorption spectra using Tauc’s relation (25):

\[ a\hbar\nu = B\left(\hbar\nu - E_g\right)^n \]  
(3)

where \( a \) is the absorption coefficient, \( \hbar\nu \) is the incident photon energy that can be approximated to \( \hbar\nu = 1240\alpha \), \( B \) is a constant and \( n \) assumes to be \( n = 2 \) for direct allowed and forbidden transitions, respectively, \( n = 3 \) and 3/2 for indirect allowed and forbidden transitions, respectively. The variation of optical band gap with the proton fluence is shown in Figure 6b. It is clear that the energy gap decreases with increasing the fluence. This indicates that the proton irradiation affect the samples to crosslink. This crosslinking is caused by the formation of new covalent bonds and therefore new different chains were obtained, in turn hindered the motion of molecules and reduce their activity and consequently decrease the optical band gap (26).

The refractive index of materials is very important for many electronic and optoelectronic applications. The refractive index of the Bayfol samples is calculated using the following equation (4) and is plotted in Figure 7 versus proton fluence.

\[ n = \frac{1 + R}{1 - R} - \frac{\sqrt{R}}{(1 - R^2)^{1/2}} \]  
(4)

where \( n \) is the real part of the complex refractive index. \( R \) is the reflection, which has been calculated from the absorbance spectra \( R = 1 - T^2/T \) (T is the transmittance) and \( k \) is the extinction coefficient calculated from the equation:

\[ k = (\alpha / 4) \]  
(5)

where \( \alpha \) is the absorption coefficient which can expressed by

\[ \text{Absorbance} = \frac{\alpha}{\text{Sample thickness}} \]

It is clear from figure 7 that the refractive index shows a decrease until a minimum value around the 51012 p/cm² irradiated sample followed by an increase on increasing the fluence up to 1×1013 p/cm². Above 1×1013 p/cm² and up to 1×1014 p/cm², it decreases. This behavior can be explained in terms of degradation and crosslinking induced by proton 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 Bayfol polymer, leading to the increase in refractive index. These results are in good agreement with those obtained by Shams-Eldin et al. (27), 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 (28).

### 3.4 Color difference measurements

The vision scientists created a special set of mathematical lights, X, Y and Z, to replace actual red, green and blue lights. Every color can be matched using the appropriate amount of X, Y and Z light. The amounts of X, Y and Z light needed to match a color are called the color’s tristimulus values (29). Figure 8 shows the transmission spectra of the non-irradiated and irradiated Bayfol samples, measured in the wavelength range of 370-780 nm. Using these transmission data, both the tristimulus values and chromaticity...
coordinates were analyzed. Figure 9 shows the variation of trismus values (X, Y, Z) with the proton fluence. From the figure, it is seen that X, Y and Z exhibited the same trend, where they decreased with increasing the fluence up to $10^8$ p/cm². Figure 10 shows the variation of chromaticity coordinates (x, y and z) with the proton fluence. It is seen that x and y exhibited the same trend, where they showed an increase with increasing the fluence up to $10^8$ p/cm². The chromaticity coordinate z exhibited an opposite trend. The variation of the color intercepts ($a^*$, $b^*$ and $L^*$) with the proton fluence is shown in Figure 11. 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 (30). The accuracy in measuring $L^*$ is ±0.05, and is ±0.01 for $a^*$ and $b^*$. It can be seen that the green color component ($a^*$) is changed into red ($+a^*$) (Figure 11a). At the same time, the blue ($b^*$) color component of the blank film is changed into yellow ($+b^*$) (Figure 11b) after exposure to proton fluence up to $10^8$ p/cm². This was accompanied by a slight increase in the darkness of the samples ($L^*$) (Figure 11c).

The color intensity $E$, which is the color difference between the non-irradiated and irradiated Bayfol samples could be calculated using the CIELAB color difference equation (31) and plotted in Figure 12 as a function of fluence. The color intensity $E$ shows a decrease with increasing the proton fluence. The changes in color could be attributed to the trapping of the excited free radicals that are formed by ionization. In addition, the trapped free radicals resulting from radiation-induced break of polymer molecules have electrons with unpaired spin, which may give optical coloration (31).

4. Conclusion

The proton irradiations of Bayfol DPF 5023 lead to chain scission followed by crosslinking and as a result there are changes in its structural and optical properties.

Bayfol DPF 5023 samples irradiated at the fluence range $1 \times 10^{-14} - 1 \times 10^{-12}$ p/cm² were characterized by dominate amorphous regions that give a polymer resilience. Thus, the Bayfol polymer may be a suitable candidate for industrial applications requiring its bending without breaking. Also, the results of optical properties reveal that the proton irradiation reduces the optical energy gap that could be attributed to the increase in structural disorder of the irradiated Bayfol samples. This allows the formation of color centers with an increase in the red and yellow color components that establish color differences between the non-irradiated sample and those irradiated with different fluences.

![Figure 1 X-ray diffraction patterns of the non-irradiated and proton irradiated Bayfol DPF 5023 samples.](image1)

![Figure 2 Variation of integral intensity I for Bayfol DPF 5023 samples, with the proton fluence.](image2)

![Figure 3 FTIR absorbance spectra of the non-irradiated and irradiated Bayfol DPF 5023 samples.](image3)

![Figure 4 Variation of absorbance, measured at the characteristic wavenumbers with the proton fluence.](image4)

![Figure 5 The UV–Vis absorption spectra of the non-irradiated and irradiated Bayfol DPF 5023 samples.](image5)
Figure 6 Variation of Urbach’s energy and the energy band gap with the proton fluence.

Figure 7 Variation of refractive index with the proton fluence.

Figure 8 The UV–Vis transmission spectra of the non-irradiated and irradiated Bayfol DPF 5023 samples.

Figure 9 Variation of tristimulus values (X, Y, Z) with the proton fluence.

Figure 10 Variation of chromaticity coordinates (x, y, z) with the proton fluence.

Figure 11 Variation of the color intercepts (a*, b* and L*) with the proton fluence.

Figure 12 Variation of the color intensity E with the proton fluence.

References


