

Thermal and structural modifications induced by X-Ray irradiation in polycarbonate

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Samples from sheets of the polymeric material Bayfol have been irradiated with X-rays, from a 50 kV X-ray tube, with different doses in the range 10-300 Gy. The resultant effect of X-ray irradiation on the thermal properties of Bayfol has been investigated using thermo-gravimetric analysis (TGA). The onset temperature of decomposition T_o and activation energy of thermal decomposition E_a were calculated, results indicating that the Bayfol decomposes in one weight loss stage. The variation of transition temperatures with X-ray dose has been determined using differential thermal analysis (DTA). The results of the thermograms was characterized by the appearance of an endothermic peak due to melting. Melting temperature was found to be dependent on the X-ray dose. In addition, structural property studies using X-ray diffraction, infrared spectroscopy and intrinsic viscosity were performed on both non irradiated and all irradiated Bayfol samples. The results indicate that the degree of ordering, the absorbance, and the intrinsic viscosity of the Bayfol polymer are dependent on the X-ray doses.

1. Introduction:

Polymers are a familiar part of everyday life that has found widespread applications in many domains of techniques especially in micro-electronics fabrication, space and nuclear technologies. When polymeric materials are exposed to radiation, their properties are changed to a certain extent as a consequence of the irreversible deterioration in their structure. Some of these changes have been attributed to the scissioning of the polymer chains due to the action of the radiation, breaking of covalent bonds, promotion of cross-linkages, formation of carbon clusters, liberation of volatile species and, in some cases, even formation of new chemical bonds [1,2]. As a consequence of this, the physico-chemical properties like optical, electrical, mechanical and chemical properties of the polymer are modified [3-5].

Radiation effects induced by ionizing radiations like X-rays and gamma rays have been largely used to modify the chemical and physical properties of the polymers [6-9]. Among these polymers, there are aromatic polycarbonates which are high performance engineering plastics with exceptionally high impact strength, clarity, heat resistance and dimensional stability.

The effect of radiation on the properties of polycarbonates was studied extensively using different types of radiation with different energy and fluence [10-13]. The primal effect of radiations on polycarbonate is chain scission. However, at higher doses, active sites or branching points created by scission may lead to intermolecular crosslinks.

The present work is devoted to the investigation whether the X-ray radiation will induce significant modification of the thermal and structural properties of Bayfol. For this purpose, the thermal and structural modifications in the X-ray irradiated Bayfol samples have been studied as a function of doses using different characterization techniques among which Fourier transform infrared (FTIR) spectroscopy to examine the methyl, phenyl ring, carbonyl, ether and hydroxyl functions and to analyze these effects as a function of X-ray doses.

2. Experimental:

The Bayfol is a bisphenol-A aromatic polycarbonate ($C_{16}H_{14}O_3$ blended with polyester). Its functional groups include methyl, phenyl ring, carbonyl, ether and hydroxyl. It is manufactured by Farbenfabriken Bayer A.G., Leverkusen (Germany), with an average thickness of $250\mu\text{m}$ and density 1.23 g/cm^3 . The irradiation process was performed in air using an Oxford instrument XF5011 50 kV X-ray tube with a molybdenum target.

2.3. Analysis of irradiated samples:

The thermal behavior was investigated using differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) with a differential scanning calorimeter (DSC) Setaram Labsys TG-DSC16 instrument. $\alpha\text{-Al}_2\text{O}_3$ powder was used as a reference for the DTA measurements. Thermal experiments were carried out on all samples at a heating rate of $10\text{ }^\circ\text{C/min}$ with Ar as carrier gas at a flow rate of $30\text{ cm}^3/\text{min}$.

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 \AA and the diffraction patterns were recorded in the 2θ range ($4^\circ\text{-}40^\circ$) with scanning speed of $2\text{ degrees per minute}$.

Fourier Transform Infrared spectra of non-irradiated and the irradiated Bayfol samples was recorded using model Shimadzu 8201 PC. All the measurements were done in the range of 4000 to 400 cm^{-1} . The spectra were obtained for the absorbance of the polymer as a function of wave-number with resolution 1 cm^{-1} and accuracy better than $\pm 4 \text{ cm}^{-1}$.

Solutions of different concentrations (0.2%, 0.4%, 0.6% and 0.8%) were prepared from the irradiated and non irradiated samples using pure chloroform as a solvent. The viscosity measurements were carried out in Oswald viscometer of the type pinkevitch Size 0 No. 2106, manufactured by Poulten, self, and LEE, LTD, England. This viscometer was calibrated in accordance with the standard method of test for kinematic viscosity specified in ASTM D 445-IP 71. The viscosity measurements were carried out at 35, 40, 45 and 50 $^{\circ}\text{C}$ using a bridge controlled thermostat bath E-270 Series III, Pownson, Oxford.

3. Results and discussion:

3.1. Thermal Properties:

3.1.1. Thermogravimetric Analysis (TGA):

Thermogravimetric analyses TGA was performed on Bayfol 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 600 $^{\circ}\text{C}$, at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. Fig. (1) shows the TGA thermograms for non-irradiated and irradiated samples. It is clear from the figure that the Bayfol detector decomposes in one main breakdown stage.

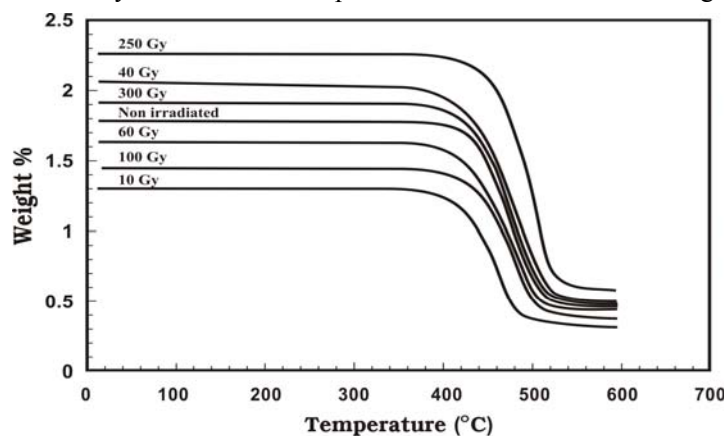


Fig.(1): TGA thermograms of the non-irradiated and irradiated Bayfol samples, measured in the temperature range from room temperature up to 600 $^{\circ}\text{C}$, at a heating rate of 10 $^{\circ}\text{C}/\text{min}$.

Using these TGA thermograms, the values of onset temperature of decomposition T_o were calculated. Fig. (2) shows the variation of T_o with the X-ray dose. From the figure it is clear that T_o decreases until a minimum value around the 20 Gy followed by an increase on increasing the dose up to 150 Gy. However, above 150 and up to 300 Gy, it decreases again.

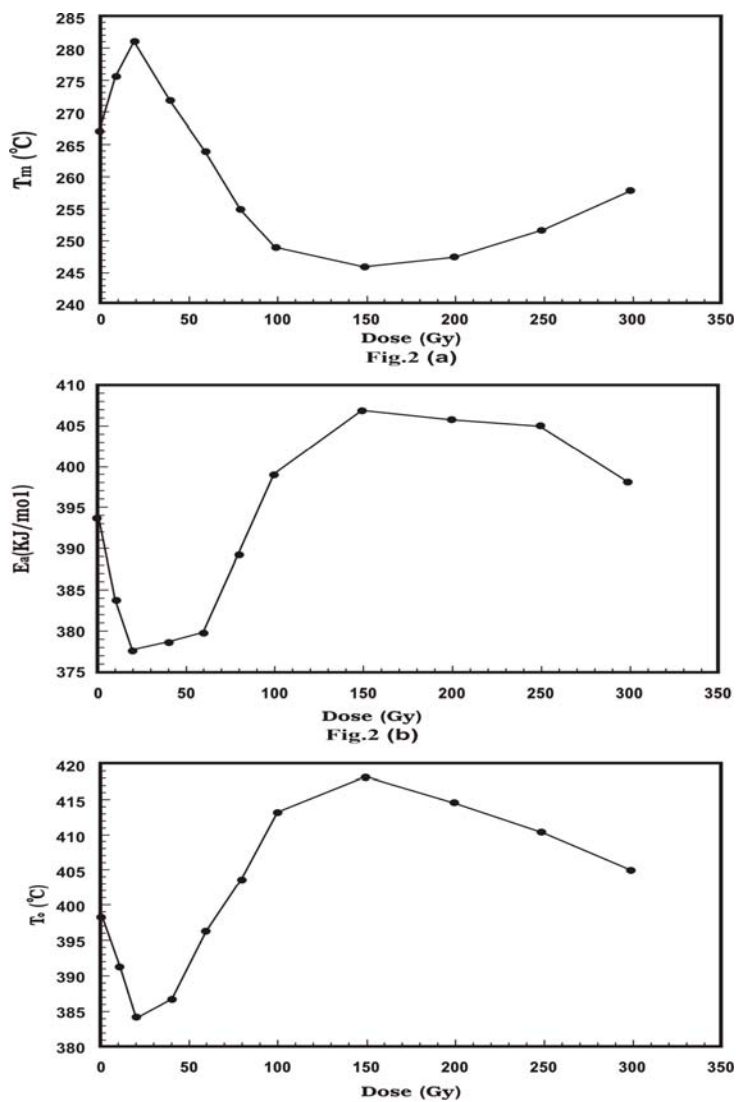


Fig.(2): Variation of the onset temperature of decomposition T_o , activation energy of thermal decomposition E_a and melting temperature T_m with the X-ray dose. (The line that connects the experimental points is solely a guide to the eye)

In the dose range 0-20 Gy, initial scission occurs. This led to the formation of low molecular weight products, which decrease the strength of the polymer, thereby decreasing its ability to withstand high temperatures. At the dose range 20-150 Gy, the free radicals produced from scission are chemically active and take part in some chemical reactions causing crosslinking. Thus the samples re-gain their thermal stabilities. On increasing the dose up to 300 Gy, more energy is pumped into the molecules then decomposition becomes more randomized, and thus breakdown increases.

3.1.2. Activation energy of thermal decomposition (E_a):

Evaluation of the thermal activation energy of decomposition is useful for studying the thermal stability of the materials. Various thermo-gravimetric 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 [14] has been used in the present study for measurement of the thermal activation energies. In this method TGA curves obtained at a heating rate of 10 °C/min are required where the following equation is valid:

$$\ln \{ \ln [(W_o - W_f) / (W - W_f)] \} = E_a \theta / R T_s^2$$

where R is the general gas constant, W_o and W_f are the initial and final weights of the stage, W is the remaining weight at a given temperature T, E_a is the activation energy of decomposition and θ is the temperature difference between T and T_s (for the latter see below).

According to the above equation, a plot of $\ln \{ \ln [(W_o - W_f) / (W - W_f)] \}$ against θ leads to a straight-line relationship in the range where the decomposed ratios are equal. Hence E_a can be evaluated from the slope of the line. T_s is the temperature which satisfies the equation:

$$[(W - W_f) / (W_o - W_f)] = (1/e) = 0.3679$$

Using the TGA curves, values of E_a were calculated for the non irradiated and irradiated Bayfol samples and are plotted in Fig. (2) as a function of dose. The figure shows that E_a exhibited a similar trend to that of T_o . The decrease in activation energy can be attributed to the initial bond scission in the polymer molecules.

3.1.3. Differential thermal analysis (DTA)

DTA was performed in the temperature range from room temperature up to 500 °C at a heating rate of 10 °C/min. The DTA thermograms showed that the Bayfol samples are characterized by the appearance of an endothermic peak

at the melting temperature T_m . Also, on heating, the samples pass through a range of poorly specified softening temperatures. This can be attributed to the fact that any polymeric chain has more degree of freedom than non-polymeric matter, and there is variability in the chain length. Fig. (2) shows the variation of T_m with X-ray dose. The figure shows that T_m exhibited an opposite trend to that of T_o and E_a , where it increases up to a maximum value around 20 Gy and then decreases with increase in dose up to 150 Gy. Above 150 and up to 300 Gy, it increases again. 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 the dose range 0-20 Gy, the thickness of crystalline structures (lamellae) is increased. At higher doses 20-150 Gy, defects generation splits the crystals depressing the melting temperature. For such doses, the decrease of the polymer length contributes also to the shift of T_m towards lower temperatures. Above 150 and up to 300 Gy the break down increases and thus the length of the chains is shorten, hence they have the ability to arrange themselves in an ordering manner.

3.2. X-ray diffraction:

In actual fact, a crystalline polymer has two components, the crystalline portion and the amorphous portion. The existence of amorphous portion leads to the appearance of characteristic amorphous halos in the diffraction pattern.

In order to study the effect of X-ray irradiation on the degree of ordering of Bayfol nuclear track detector, X-ray diffraction measurements were carried out on solid state samples. The X-ray diffraction patterns of the samples are characterized by halos extending in the 2θ range 12° - 34° Fig. (3). The profile of the halos shows that the Bayfol polymer is a partly crystalline polymer with a dominant amorphous phase. The area under these halos is proportional to the integral scattering intensity of the X-rays. The area under the halos was calculated and approximate indicative values are plotted in Fig. (4) as a function of X-ray dose. The figure shows that the integral intensity increases up to a maximum value around 20 Gy indicating some degree of ordering due to degradation, followed by a decrease on increasing the dose up to 150 Gy indicating disordering character due to cross-linking that destroys crystallinity. Above 150 and up to 300 Gy it increases again.

Since the halo's width at the half of maximal intensity ΔW is inversely proportional to the crystallite size, approximate indicative values of ΔW were calculated and are plotted in Figure 4 as a function of X-ray dose. From the figure it is seen that the half width exhibited an opposite trend to that of the integral intensity.

The increase in integral intensity indicates an increase in the crystallinity (ordering character) of the polymer samples which can be attributed to degradation (chain scission) induced by X-ray irradiation. This scission can reduce the number of entanglements per molecule. Chain scission can also act to relieve intermolecular stress in the amorphous region, thus increasing chain mobility. The increase in mobility permits some molecules to re-crystallize because crystalline state is thermodynamic stable state [15].

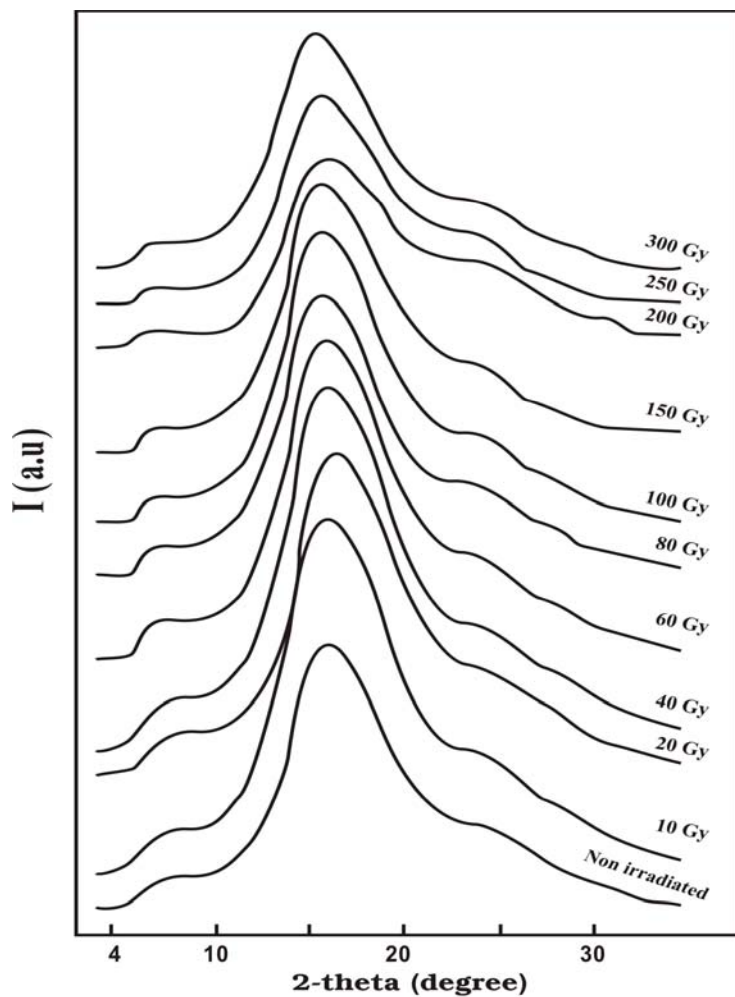


Fig. (3): X-ray diffraction patterns of the non-irradiated and irradiated Bayfol samples.

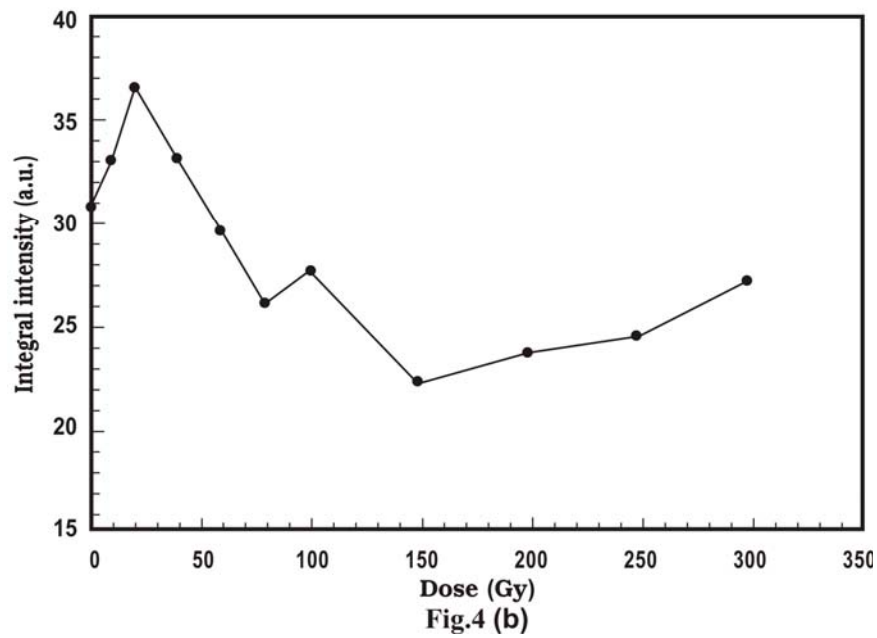
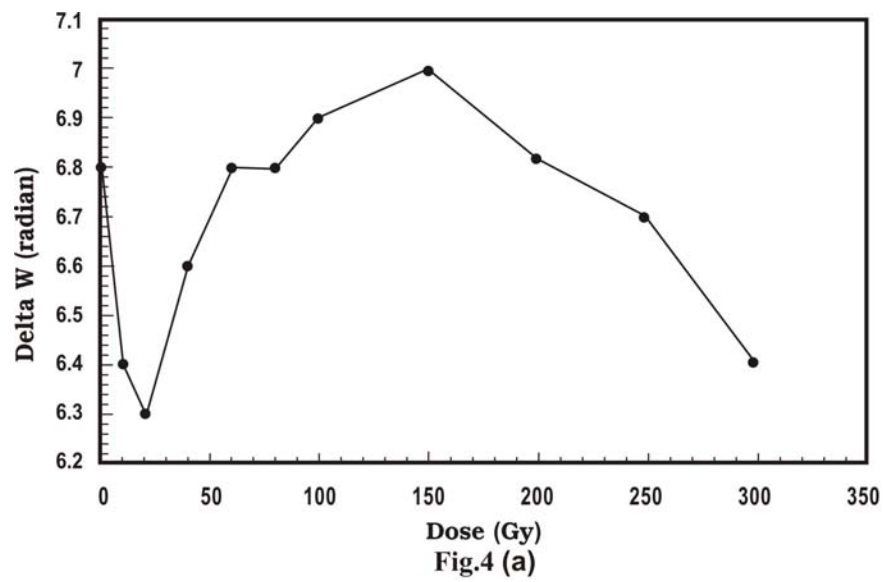


Fig. (4): Variation of integral intensity I , the halo width at half of maximal intensity ΔW for Bayfol samples as a function of X-ray dose. (The line that connects the experimental points is solely a guide to the eye)

On the other hand, the decrease in integral intensity at the dose range 20-150 Gy denotes a decrease in the amount of crystalline phase in the samples, indicating that the crystalline structure (lamella) has been destroyed. This could be attributed to the crosslinking which change the previously regularly arranged portions into non-arranged ones by forming new bonds between chains. On increasing the dose up to 300 Gy, the decomposition becomes more randomized, thus breakdown increases.

3.3. Infrared spectroscopy:

The FTIR spectral analysis has been performed to investigate the structural changes induced in the Bayfol polymer due to X-ray irradiation. 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 polymers. The infrared absorption spectrum, in the wavenumber range 400-4000 cm^{-1} , for the non-irradiated and irradiated samples has been obtained. The material used in this study is aromatic polycarbonate. Its functional groups include methyl, phenyl ring, carbonyl, ether and hydroxyl. The absorbance of different bands coming from the same function group exhibits the same trend with the X-ray dose. So, each characteristic group of polycarbonate is represented by only one wavenumber.

Figures (5a and 5b) show the variation of the absorbance with the dose. From the figure it is clear that the absorbance measured at the wavenumbers 1778 cm^{-1} and 889 cm^{-1} , decrease with increasing the dose up to 300 Gy, indicating the breaking of the C=O and C-O-C bonds.

The absorbance measured at the wavenumbers 2877 cm^{-1} and 3047 show a decrease in the intensity of C-H bond until a minimum value around the 20 Gy irradiated sample, followed by an increase on increasing the dose up to 150 Gy. Above 150 and up to 300 Gy, it decreases again.

The intensity of the peak corresponding to OH group (3533 cm^{-1}) exhibited an opposite trend to that of C-H bond. These results indicate that scission takes place at the carbonate site with elimination of carbon dioxide and formation of hydroxyl group. The abstraction of -H may be from isopropyl or aromatic group. The increase in the hydroxyl groups in the dose ranges 0-20 Gy and 150-300 Gy which mean an increase in the end groups of macromolecules indicates that degradation process prevails at these dose ranges. At the dose range 20-150 Gy, an opposite trend has been observed due to the formation of bonds through crosslinking mechanism.

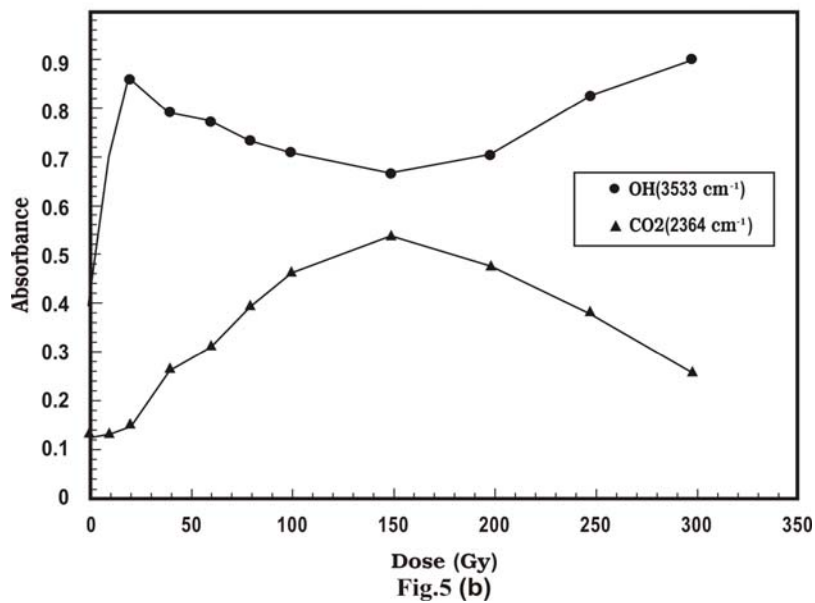
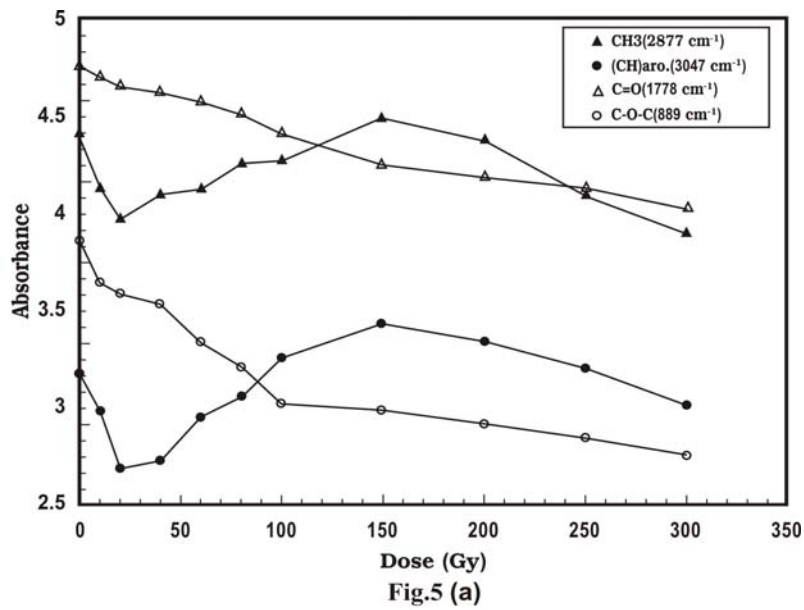


Fig. (5): Variation of absorbance, measured at some characteristic wavenumbers as a function of X-ray dose. (The line that connects the experimental points is solely a guide to the eye)

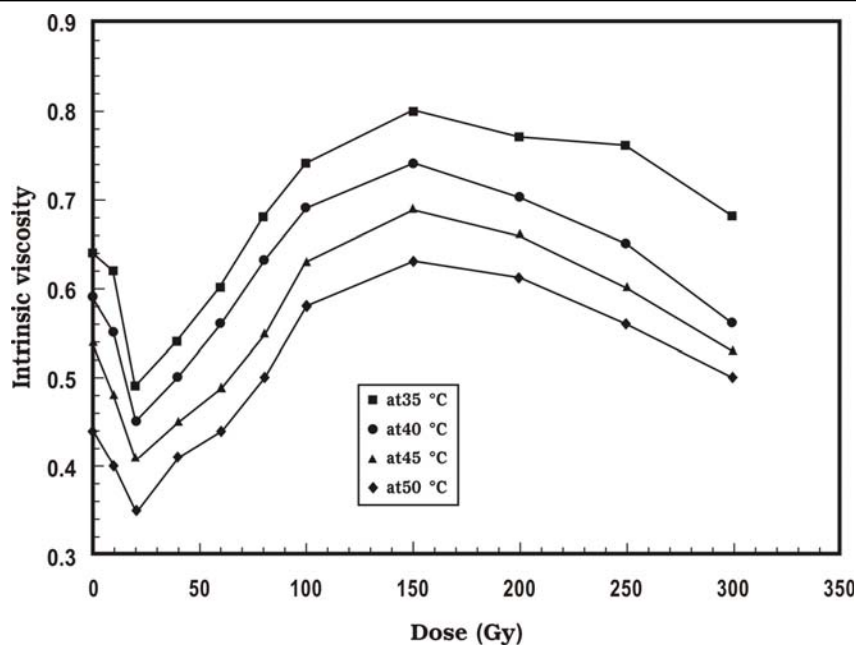


Fig.6

Fig. (6): Variation of intrinsic viscosity, measured at different temperatures, for the Bayfol liquid samples, with the X-ray dose.

3.4. Intrinsic viscosity:

Solutions of different loadings (0.2, 0.4, 0.6 and 0.8 %) were prepared from the non irradiated and irradiated Bayfol sheets using pure chloroform as a solvent. These diluted solutions were chosen to avoid any attractive secondary interactions between the polymer and solvent molecules which can be reflected in an increase of the viscosity in ways that accurate measurements can't be made. The kinematic viscosity of the liquid samples can be calculated by the product of the observed time of flow and the capillary constant of the viscometer. The result is always expressed as relative viscosity (η_{rel}), calculated as the ratio of the viscosities of polymer solution and the pure solvent. Additional values may be calculated such as specific viscosity ($\eta_{spc} = \eta_{rel} - 1$), a reduced viscosity ($\eta_{red} = \eta_{spc} / \text{concentration}$) and intrinsic viscosity, the limiting viscosity number ($\eta_{in} = \lim \eta_{red}$ when the concentration tends to zero) that is related to the mean molecular mass of the dissolved polymer and can give a qualitative idea of whether molecular weight is high or low.

The intrinsic viscosity of the Bayfol solutions was measured at different temperatures (35, 40, 45 and 50 °C). Figure 6 shows the dependence of intrinsic viscosity of Bayfol samples on the dose.

From the figure it is clear that the intrinsic viscosity decreases until a minimum value around the 20 Gy irradiated sample and then increases on increasing the dose up to 150 Gy. Above 150 Gy and up to 300 Gy, it decreases again. The dose range in which the intrinsic viscosity decreases can be explained by the formation of shorter molecules as a result of degradation which causes both a random breaking of bonds and the formation of stable molecules with a lower molecular weight. While the increase in intrinsic viscosity in the dose range 20-150 Gy, indicates an increase in the molecular mass of the polymer due to crosslinking process.

Conclusions:

The X-ray irradiation of Bayfol detector at the dose range of 20-150 Gy led to a more compact structure of Bayfol polymer that resulted in an increase in the activation energy of thermal decomposition. The irradiation of Bayfol detector in the dose range of 20-150 Gy causes crosslinking which reduces crystallinity and increases the amorphous regions that enhance polymer resilience. The X-ray irradiation effects on the intrinsic viscosity of Bayfol polymer may be considered as a simple way to optimize its quality since the processing and application properties of that polymer depend very largely on its molecular structure.

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