Thermal, Mechanical, and Structural Investigation of the Effect of Electron Beam-Irradiation in Bayfol Nuclear Track Detector

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ABSTRACT: Samples from sheets of the polymeric material Bayfol have been exposed to electron beam in the dose range 10–100 kGy. The resultant effect of electron beam irradiation on the thermal properties of Bayfol has been investigated using thermogravimetric analysis. The onset temperature of decomposition T_0 and activation energy of thermal decomposition E_a were calculated, results indicating that the Bayfol polymer decomposes in one main weight loss stage. Also, the electron irradiation in the dose range 40–100 kGy 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. The variation of transition temperatures with electron dose has been determined using differential thermal analysis. The results indicate that the electron irradiation in the dose range 40–100 kGy causes crosslinking that destroys the crystalline structure depressing the melting temperature and this is most suitable for applications requiring the molding of this polymer at lower temperatures. In addition, the mechanical and structural properties of Bayfol samples were measured and the results revealed that the tensile strength, elongation at break, yield strength, and intrinsic viscosity were affected by the electron doses. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3983–3987, 2007

Key words: electron beam irradiation; Bayfol; thermal properties; mechanical properties; intrinsic viscosity; IR spectroscopy

INTRODUCTION

Ionizing radiations are unique and powerful means for modifying the physical properties of polymers. In particular, electron beam irradiation of polymeric materials leads mainly to crosslinking and main chain scissions. For many polymers, both processes coexist and either one may predominate depending not only upon the chemical structure of the polymer, but also upon the conditions of irradiation.[1] The crosslinking and main chain scission that take place during irradiation may lead to sharp changes in the physical properties of the polymer.

Among the physical factors capable of initiating chemical reactions in polymers, the action of heat as it underlies one of the important characteristics of polymers to check their thermal stability and thus their suitability for service.[2] Also, the study of the radiation induced changes in the mechanical properties of polymers is of great interest, since it gives information concerning the structure of the materials.

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Radiation-induced modifications in polycarbonate have been studied extensively.[3–11] The effect of radiations on polycarbonate is primarily chain scission. However, at increased doses, active sites or branching points created by scission may lead to intermolecular crosslinking.[12] The present study deals with the investigation of the effect of electron beam irradiation on the thermal and mechanical properties of Bayfol polymer not only to obtain information concerning the interaction of electrons with Bayfol, but also to study the feasibility of modifying its properties, improving its performance in different applications.

EXPERIMENTAL

Samples

Bayfol is a bisphenol-A polycarbonate with a chemical composition of $C_{16}H_{14}O_3$ blended with polyester. It is manufactured by Farbenfabriken Bayer A.G., Leverkusen (Germany), with an average thickness of 250 μm and density 1.23 g/cm^3. The functional groups of Bayfol aromatic polycarbonate include methyl, phenyl ring, carbonyl, ether, and hydroxyl.

Irradiation facilities

The irradiation process was performed in air, at room temperature 25°C, using 1.5 MeV electron beam accelerator of the ICT-type which is available in NCRRT center, AEA, Cairo, Egypt. It operates with insulating core transformer, with a beam current of 25 mA. The conveyer was attached with a cooling system to avoid heating of the samples. The method of irradiating polymer films comprises multiple irradiations at 10 kGy/pass. The dose was adjusted frequently using FWT'60-00 dosimeter that was calibrated by irradiation in gamma facility against Ceric/Cerous dosimeter supplied by Nordion, Canada. It is recognized that transfer of the calibration from gamma to 1.5 MeV electron beam irradiation involves an added uncertainty. We estimate this uncertainty to be less than 5%.

Experimental apparatus

Thermal analysis

The thermal behavior was investigated using differential thermal analysis (DTA) and thermogravimetric analysis (TGA) with a type Setaram labsys TG–DTA16 instrument. α–Al_2O_3 powder was used as a reference for DTA measurements. Thermal experiments were carried out on all samples at a heating rate of 10°C/min with Ar as a carrier gas at a flow rate of 30 cm^3/min.

Mechanical properties

Mechanical measurements were carried out using Testometric M350–5Ax with 5 kN load cell, at room temperature. Dumbbell-shaped samples of standard dimensions (50 mm long with a neck of 27 mm and width of 3 mm) were placed between the jaws and the load was applied at a rate of 50 mm/min until failure occurred. Three pieces of the same sample were used and the results were averaged for each data point.

Viscosity measurements

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°C using a bridge controlled thermostat bath E-270 Series III, Pownson, Oxford.

Infrared spectroscopy

The infrared spectroscopic measurements were carried out using a Unicam SP1000 infrared spectrophotometer, which is a double beam, optical null, precision recording instrument. This instrument measures in the wavenumber range 400–4000 cm^{-1}, with wavenumber accuracy better than ± 3 cm^{-1} over 400–2000 cm^{-1} and better than ± 9 cm^{-1} over 2000–4000 cm^{-1}.

RESULTS AND DISCUSSION

Thermal properties

Thermogravimetric analysis

TGA was performed for irradiated and non irradiated Bayfol samples, in the temperature range from room temperature up to 600°C, and at a heating rate of 10°C/min. The results indicated that the Bayfol samples decompose in one main weight loss stage. Using the TGA thermograms, the values of onset temperature of decomposition T_0 were calculated. Figure 1 shows the variation of T_0 with the electron dose. The figure shows that T_0 decreases until a minimum value around 40 kGy indicating a decrease in thermal stability because of chain scission. This can be attributed to degradation in the isopropylidene and carbonate groups in the aromatic structures of the polycarbonate in the dose range 10–40 kGy, is likely to occur at the isopropylidene and carbonate group.[13,14] Above 40 and up to 100 kGy, the free radicals formed from scission are chemically active, can take part in some chemical reactions such as crosslinking, leading to an increase in T_0.

Activation energy of thermal decomposition (E_a)

Not only does TGA give the ability to find out the temperature at which the thermal decomposition

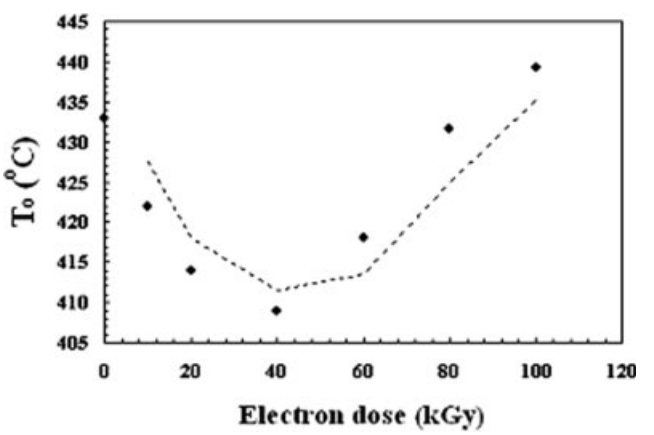

Figure 1 Variation of the onset temperature of decomposition T_0 with the electron dose.

starts (T_0) but it allows the measurement of 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[15] has been used in the present study for the measurements of the activation energies of thermal decomposition. In this method TG curves obtained at a heating rate of 10°C/min are required where the following equation is valid:

$$\ln\{\ln[(W_0 - W_f)/(W - W_f)]\} = E_a\theta/RT_s^2$$

where R is the Ideal Gas Constant, W_0 and W_f are the initial and final weights of the stage, W is the remaining weight at a given temperature T, θ is the temperature difference between T and T_s. T_s is the temperature which satisfies the equation:

$$[(W - W_f)/(W_0 - W_f)] = (1/e) = 0.3679$$

According to the above equation, a plot of $\ln\{\ln[(W_0 - W_f)/(W - W_f)]\}$ against θ leads to a straight-line relationship in the range where the decomposed ratios are equal. Hence, the activation energy of thermal decomposition E_a can be evaluated from the slope of the line.

Using the TGA curves, values of the activation energy of thermal decomposition E_a were calculated for the non irradiated and irradiated Bayfol samples. Figure 2 shows the variation of E_a with the electron dose. From the figure it is clear that E_a shows a decrease until a minimum value around the 40 kGy irradiated sample are likely to be because of chain scission. This decrease is attributed to the cleavage of the carbonate linkage and to the —H abstraction from the backbone of the polymer, associated with the formation of CO_2 and —OH with varied intensities.[13,14] Above 40 and up to 100 kGy, E_a increases on increasing dose up to 100 kGy because of cross-linking process.

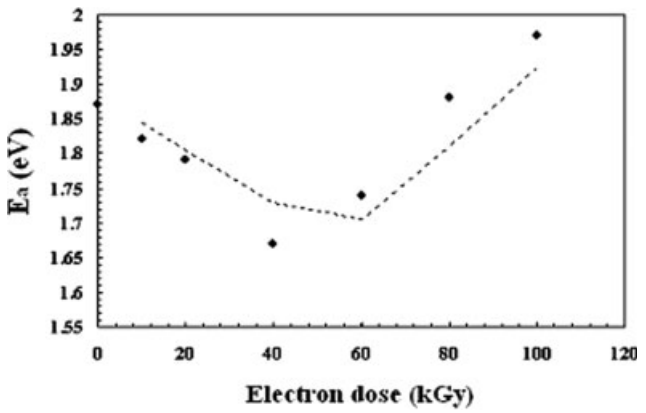

Figure 2 Variation of the activation energy of thermal decomposition E_a with the electron dose.

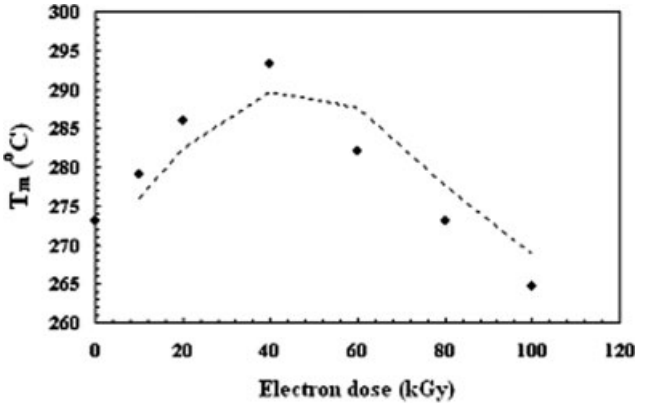

Figure 3 Variation of melting temperature T_m with the electron dose.

Differential thermal analysis

DTA was performed in the temperature range from room temperature up to 500°C, at a heating rate 10°C/min, on irradiated and non irradiated Bayfol samples. The obtained thermograms were characterized by the appearance of an endothermic peak because of the melting temperature T_m. Also, on heating, the samples pass through a range of badly specified softening temperatures. This can be attributed to the fact that any polymeric chain has more degree of freedom than nonpolymeric matter, and there is variability in the chain length. Figure 3 shows the variation of these melting temperatures with the electron dose. As can be seen from the figure, T_m increases up to a maximum value around the 40 kGy irradiated sample followed by a decrease with increasing the dose up to 100 kGy. The interpretation of these results can be that the scission reactions are dominant during the irradiation of Bayfol polymers at the dose range 10–40 kGy. Accordingly, the apparent discrepancy between the dependence of T_0 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 polymer length contributes also to the shift of T_m towards lower temperatures.[16]

Mechanical properties

A set of stress–strain curves for irradiated and non-irradiated Bayfol samples were measured. Those

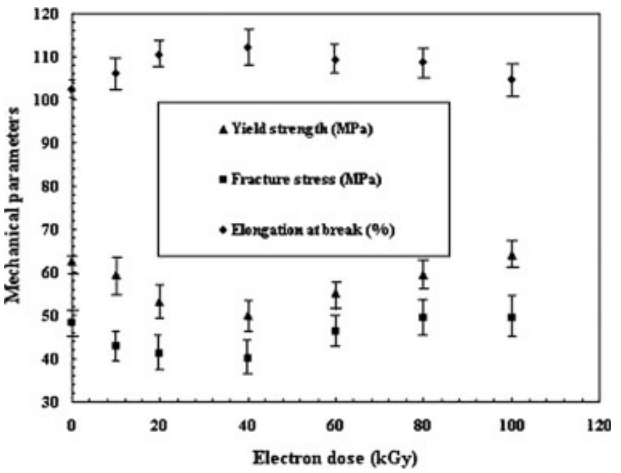

Figure 4 Variation of yield strength σ_y, tensile strength σ_f, and elongation at break ε_f for Bayfol samples with the electron dose.

curves were obtained by continuously measuring the force developed as the sample is elongated at a constant rate of extension. Generally, the strain increases on increasing the stress because of the increase in the flexibility of the chain in the macromolecules. The stress–strain curves serve to define several useful quantities including yield strength σ_y (the stress corresponding to a peak on the stress–strain curve), fracture strength σ_f (the stress corresponding to the fracture point) and fracture strain ε_f (elongation at the break).

Figure 4 shows the variation of σ_y, σ_f, and ε_f with the electron dose. It is clear from the figure that σ_y and σ_f exhibited the same trend with the dose, as they decreased gradually when increasing the electron dose up to 40 kGy, then increased with increasing the dose up to 100 kGy. The opposite trend could be observed by ε_f. The increase in yield stress may be attributed to the fact that high stresses enhance the flow mechanism by increasing the mobility of the macromolecular chains to yield higher flexibility. Also, in the dose range (10–40 kGy) in which σ_f decreases (while ε_f increases) the changes can be attributed to a degradation mechanism in which the standard chains and a great number of chain ends weaken and the material may become softer. On increasing the dose above 40 and up to 100 kGy crosslinking takes place.

Intrinsic viscosity

Solutions of different loadings (0.2, 0.4, 0.6, and 0.8%) were prepared from the Bayfol polymer 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 cannot 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 ($\eta_{red} = \eta_{spc}$/concentration) and intrinsic viscosity, the limiting viscosity number ($\eta_{in} = \lim \eta_{red}$ when the concentration tends to zero) that is related to the average molecular mass of the dissolved polymer. The intrinsic viscosity of the Bayfol liquid samples could be measured at 35°C. Figure 5 shows the variation of intrinsic viscosity of Bayfol samples with the electron dose. From the figure it is clear that the intrinsic viscosity decreases until a minimum value around the 40 kGy irradiated sample and then increases on increasing the electron dose up to 100 kGy. 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 increases in intrinsic viscosity in the dose range 40–100 kGy, indicates an increase in the molecular mass of the polymer because of crosslinking process.

Infrared spectroscopy

Infrared spectral analysis has been performed to investigate the structural changes induced in the Bayfol polymer because of electron 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 polymer. The material used in this study is Bayfol 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

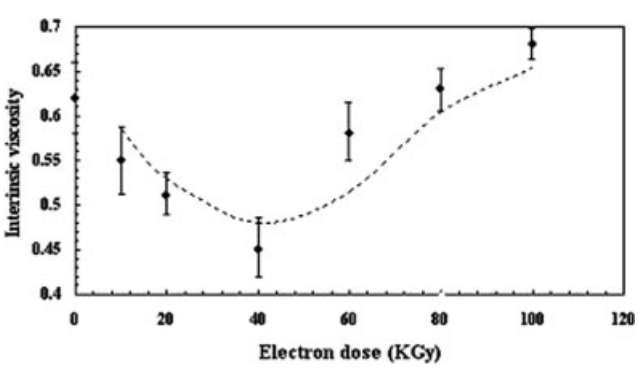

Figure 5 Variation of intrinsic viscosity of Bayfol samples, measured at 35°C, with the electron dose.

TABLE I
Values of the Absorbance of Characteristic Bands of Bayfol as a Function of Electron Dose

Electron dose (kGy)	CH_3 2877 cm^{-1}	$(CH)_{aro.}$ 3047 cm^{-1}	C=O 1778 cm^{-1}	C—O—C 889 cm^{-1}	OH 3533 cm^{-1}
0	1.82	1.80	1.98	1.96	0.54
10	1.84	1.81	1.89	1.91	0.43
20	1.88	1.87	1.82	1.83	0.39
40	1.88	1.86	1.74	1.71	0.33
60	1.92	1.91	1.73	1.82	0.49
80	1.93	1.94	1.69	1.88	0.53
100	1.96	1.94	1.63	1.91	0.58

the electron dose. So, each characteristic group of Bayfol polycarbonate is represented by only one wavenumber. Values of the absorbance of these absorption bands are given in Table I as a function of the electron dose. The absorbance of the band corresponding to C=O (1778 cm^{-1}) decreases with increasing the electron dose up to 100 kGy, indicating degradation in the carbonyl group.

The absorption bands corresponding to aromatic ether C—O—C (889 cm^{-1}) and to —OH (3533 cm^{-1}) decrease with increasing dose up to 40 kGy and then increase with increasing dose up to 100 kGy.

The absorbance measured at the wavenumber 2877 cm^{-1} and 3047 show an increase in the intensity of C—H group on increasing the dose up to 100 kGy. These results support the formation of C—H groups, associated with a decrease in O—H group, indicating a decrease in the end groups of the macromolecules caused by crosslinking process. The increase in the absorbance of the C—O—C group in the dose range from 40–100 kGy, is caused by the formation of new CO groups.[17] The increase of OH group in the same dose range along with increase of molecular weight of the samples indicate that a process of ''end-linking'' is happened, in which OH groups are linked to the main chain of polymer to give a branched molecule of a higher molecular weight.[18]

CONCLUSION

The changes in thermal properties of irradiated Bayfol polymer may be considered as a simple way to optimize the quality of the polymer since the processing and application properties of the polymer depend very largely on its thermal stability.

The TGA indicated that the electron irradiation in the dose range 40–100 kGy further enhances the thermal stability of Bayfol polymer and thus prolongs the service life time of articles made from this polymer.

The results of DTA indicate that the electron irradiation in the dose range 40–100 kGy leads to a decrease in its melting temperature and this is most suitable for applications requiring the molding of this polymer at lower temperatures.

The results of mechanical measurements indicated that irradiation with electrons at doses between 10 and 40 kGy increase the flexibility of the Bayfol polymer.

The intrinsic viscosity and thus the average molecular mass of the Bayfol polymer were found to be dependent on the electron dose because of the chain scission and crosslinking mechanisms.

Infrared spectroscopy show that the carbonyl group (—C=O) degrade under electron irradiation in dose range studied, which shows that the carbonyl groups are the most sensitive groups to radiation.

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