Study the Influence of Ion Beam Bombardment on the Thermal Properties of PVC Medical Device

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Abstract

Polyvinyl Chloride (PVC) is one of the most important polymeric materials available today and is used to manufacture many items. Ion beams have been found to be widely applicable in improving the structure and physical properties of polymers. In this paper, the effect of ion bombardment on the thermal properties of polyvinylchloride (PVC) was studied. Polymer samples were bombarded with 6 keV Ar ions have fluences 3×10^{17} and 6×10^{17} ions.cm^{-2}. The pristine and ion beam bombarded samples were investigated using TGA and DTG.

Key words: Activation energy, Ion beam, Polyvinyl Chloride (PVC), Thermal stability, TGA and DTG.

1.INTRODUCTION

Plasticized poly (Vinyl chloride) (PVC) is widely used in the production of a number of array of medical devices. PVC covers more than 25% of all plastic materials used in medical applications. Major medical uses of PVC include intravenous fluid bags and tubing, blood and plasma bags, internal feeding and dialysis equipment, catheters, and gloves. PVC possesses the largest share of the medical market, constituting 40% of all dedicated polymeric materials [1,2]. It is the first choice for medical applications due to its inertness, high transparency, facility of sterilization and strength. However, the inherent rigidity of PVC attested by its high glass transition temperature (80°C) limits its applicability. To extend its versatility PVC is commonly compounded with different amounts of plasticizers and is commercially available with different grades of flexibility according to the end-user applications. The advantage of PVC over other polymers for the later application is based in its low cost of production, processing, excellent mechanical properties, high compatibility with additives and their possibility to be recycled [3].

Modification of polymers using irradiation is a common method in many researches to enhance the physical and chemical properties of polymers. Ionizing radiation induces changes in the chemical structure and physical properties of polymers. Such changes may arise from crosslinking, main chain scission, or evolution of hydrogen, depending upon the chemical and physical nature of the polymer and the type of radiation [4].

The use of irradiation technologies nowadays are basically referred to the sterilization of medical and food products, as well as to the cross linking of polymers used in the production of electrical cables[5-6].

High energy irradiation category includes γ-radiation, β-irradiation (electron beam), and ion radiation. The latter is widely used to achieve either ion implantation at the top surface layer or to deposit coatings. For this purpose, several ions like hydrogen, noble gases, gold, *etc.* are employed. High energy photons can deliver surface radicals which act as initiating sites for subsequent functionalization. For the treatment of polymers, additional simultaneous chemical effects are also probable, e.g., free radical recombination and crosslinking, as well as chain scission [7-10]

This work is based on the comparison between two dose rates and inert conditions for the determination of the kinetics of degradation and calculation of Arrhenius activation energy (E_a) of such formulations. The E_a is commonly obtained by mathematical treatment of the series of TGA curves obtained under different temperature ramped conditions.

2.EXPERIMENTAL DETAILS

2.1. Sample prepared

Polyvinyl chloride (PVC) films of thickness 0.3 mm were exposed to, 6 KeV Argon ion energy for different time exposure using cold cathode broad beam ion source in Radiation Physics Department, National Center for Radiation Research and Technology, Egyptian Atomic Energy Authority. In this experiment different conditions can be used, the output characteristics, ion beam current, $I_b = 250 \ \Box A$, discharge current $I_d = 1mA$, extraction voltage, $V_{ex} = -500$ volt. Discharge and output characteristics were studied in the previous [11] in Radiation Physics Department, National Center for Radiation Research and Technology, Egyptian Atomic Energy Authority.

Thermogravimetric and derivative thermogravimetric analysis were made by using simultaneous DTA/TGA thermal analyzer apparatus (Shimadzu DTG 60H) the weight of samples is ranging from 4 to about 6 mg. using a platinum pan. Measurements were carried out from ambient to 580°C in dynamic nitrogen atmosphere with the flow rate 30 ml min^{-1} and heating rate of 10°C min$^{-1.}$

3.RESULTS AND DISCUSSION

3.1. Thermal decomposition

TGA is widely used to illustrate the thermal stability of polymers and used to determine the kinetic parameters of the thermal decomposition behavior. These parameters give a better understanding of the thermal stability of polymers. TGA provides quantitative information on the weight change process while differential thermal gravimetric (DTG) provides the rate of weight loss (dw/dT). TGA was performed for irradiated and non-irradiated *Polyvinyl chloride* samples in the temperature range from room temperature up to 580 °C, at a heating rate of 10 °C/ min.
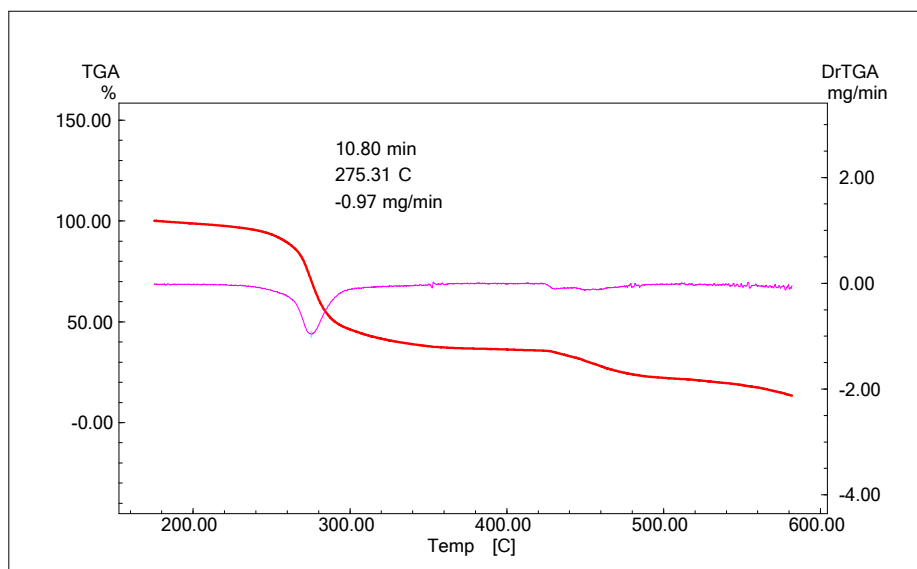
Using these TGA and DTG thermograms, the values of onset temperature of decomposition T_0 and melting temperature T_m were calculated for non-irradiated and irradiated samples and are given in Table 2
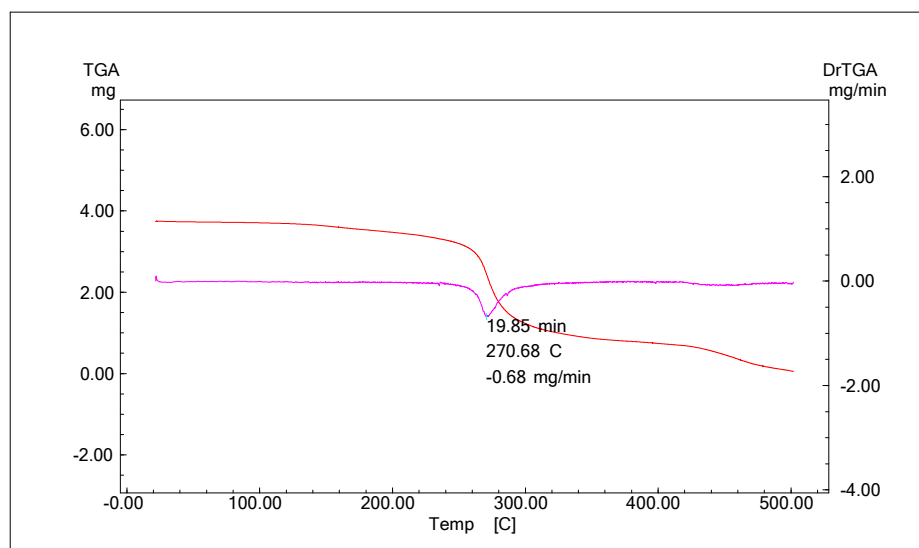
Fig(1) Shows TGA and Dr TGA for pristine PVC
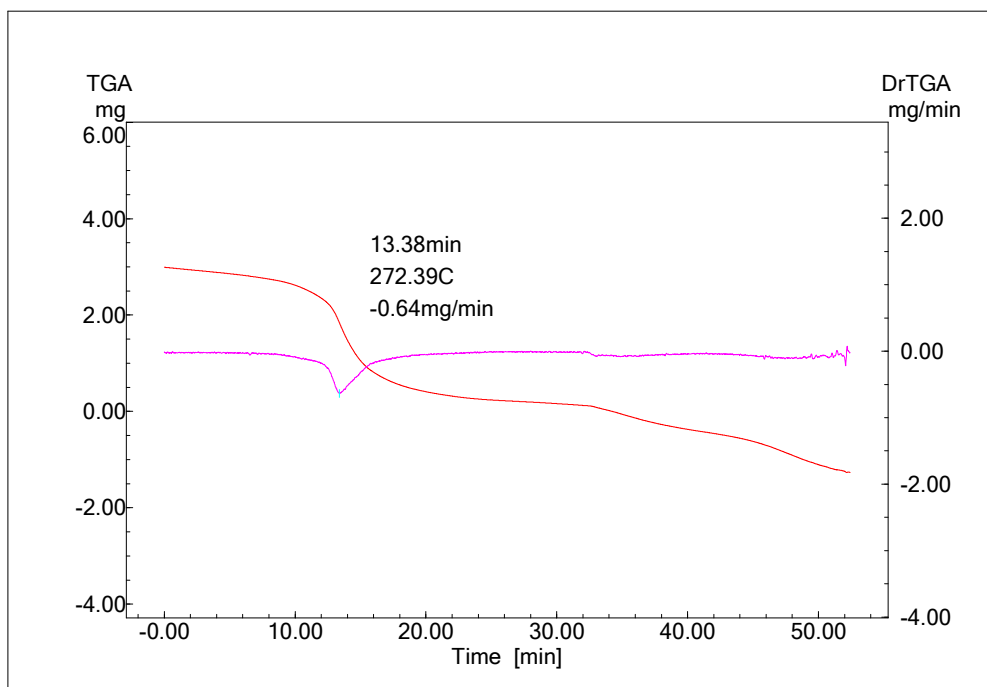
Fig(2) shows TGA for irradiated PVC with ion fluence 3 x 10 ^{17} cm^{-2}

Fig(3) shows TGA for irradiated PVC with ion fluence 6 x 10 ^{17} cm^{-2}

From figure (1-3) it was found that the pristine sample thermogram shows a small change in weight loss at 140°C this weight loss was due to water vaporization and was not significant. At 307°C the film suffers from a significant loss in weight by about 80% of the sample. After 307°C, there is a small decrease in weight loss due to emission of volatile gases. The thermal decomposition temperature for pristine Polyvinyl chloride was found to be 270.68°C.

Irradiated Polyvinyl chloride with argon ion beam at ion beam fluence 3 x 10 [17] cm^{-2} was thermally stable up to 177 °C and then there was a great loss in weight of the sample up to 307°C. In this region almost 70% of the sample was decomposed in to volatiles and corresponding thermal decomposition temperature was found to be 272.39°C.

Irradiated Polyvinyl chloride with argon ion beam at fluence 6 x 10 [17] cm^{-2} was thermally stable up to 210 °C and a great loss in weight of the sample up to 307°C and 58 % of the sample was decomposed in to volatiles. The Thermal decomposition temperature of irradiated Polyvinyl chloride with ion beam fluence 6 x 10 [17] cm^{-2} was found to be 275.31°C.

Table(1) Values of the onset temperature of decomposition T_0 and activation energy of decomposition E_a for pristine PVC and irradiated PVC with different ion fluences.

	T_0 (°C)	E_a(kj)	
		Coat	**Horowitz**
Pristine	270.68	83	0.19
3 x 10^{17}	272.39	76	0.17
6 x 10^{17}	275.31	37	0.15

3.2 Activation Energy

3.2.1 Horowitz and Metzger Method:

Horowitz and Metzger derived an approximate integral method to extract pyrolysis parameter using TGA [12].

$$ln \left\{ ln \left[\frac{W_0 - W_f}{W_0 - W_t} \right] \right\} = \frac{E_a \theta}{R T_S^2}$$

Where

W_0 = initial weight of the sample, W_t = the weight of the sample at temperature t., W_f = final weight of the sample, **R** = gas constant, θ = the temperature difference between T and T_s and T_s is the temperature which satisfies the equation:

$$\left[\frac{W_t - W_f}{W_0 - W_f} \right] = 1/e$$

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

The values of activation energies so determined for pristine as well as irradiated samples have been enlisted in Table 1.

3.2.2. Coats and Redfern Method:

Coats and Redfern derived an equation for the determination of activation in which the order of reaction is an important parameter [13].

The equation is given below.

$\log [1- (1-\alpha)^{1-n} / T^2 (1-n)] = [\log (AR/\alpha E_a) \{ 1- (2RT/E_a)\}] - (E_a / 2.303 RT)$

For first order reaction when n = 1 the equation is Log $[-\log (1-\alpha) / T^2]$ against 1000/T will result in a straight line having a slop $(E_a/2.303R)$ to calculate activation energy.

There is a clear cut increase in the values of activation energy with the increasing ion fluence. Such an increase may be attributed to the initialization of chain scissioning, possible evaporation of volatile side groups resulting in significant reduction of packing density, re- organization of molecular arrangements etc. in the polymeric sample which signifies the decrease in thermal stability of the polymer.

From table (1) T_0 increases with irradiated sample for 3x 10^{17} ion/cm^2 due to crosslinking process followed by an increase with irradiated sample for 6 x 10^{17}ion/cm^2 indicating a increase in thermal stability of the polymer samples due to degradation (i.e. preferentially chain scission),

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

The values of activation energies so determined for pristine as well as γ-irradiated samples have been enlisted in Table 2. There is a clear cut increase in the values of activation energy with the increasing ion fluence, this increase may be attributed to the initialization of chain scissioning, possible evaporation of volatile side groups resulting in significant reduction of packing density, re- organization of molecular arrangements etc. in the polymeric sample which signifies the decrease in thermal stability of the polymer [14].
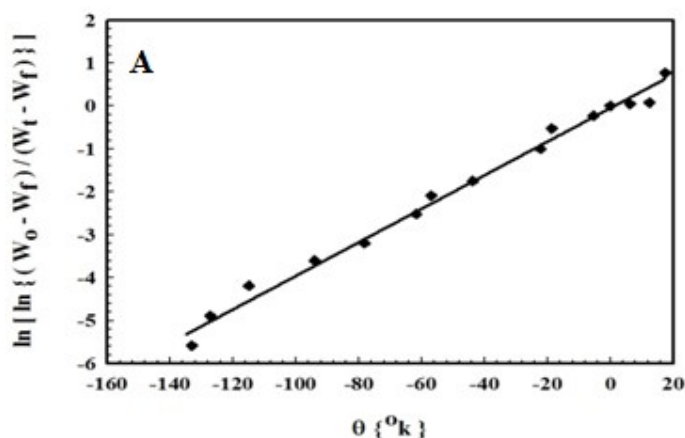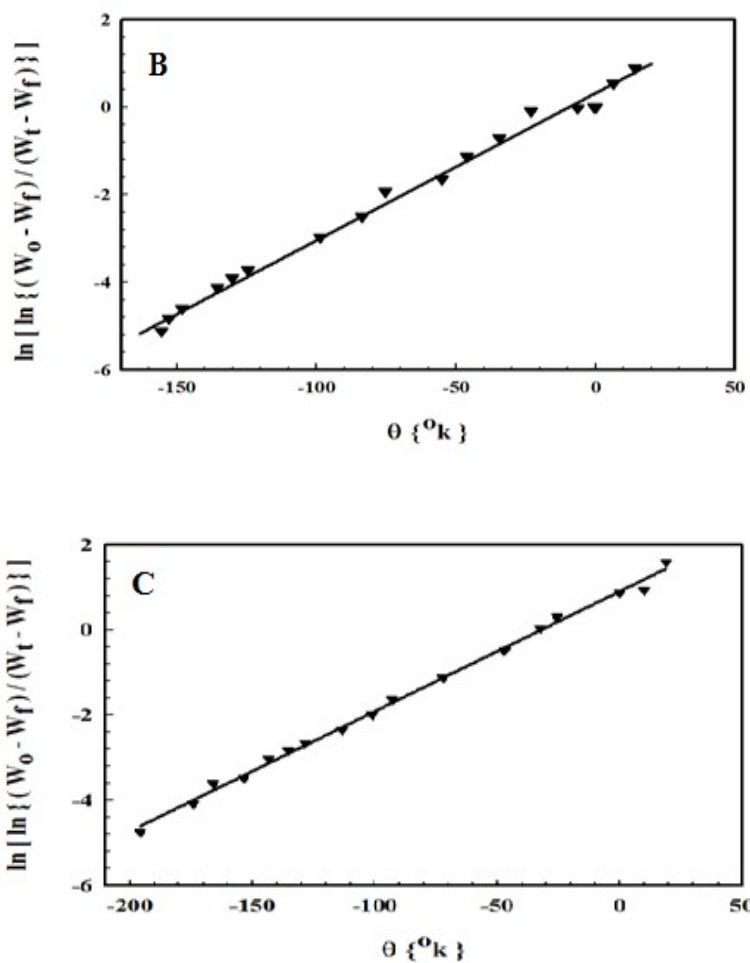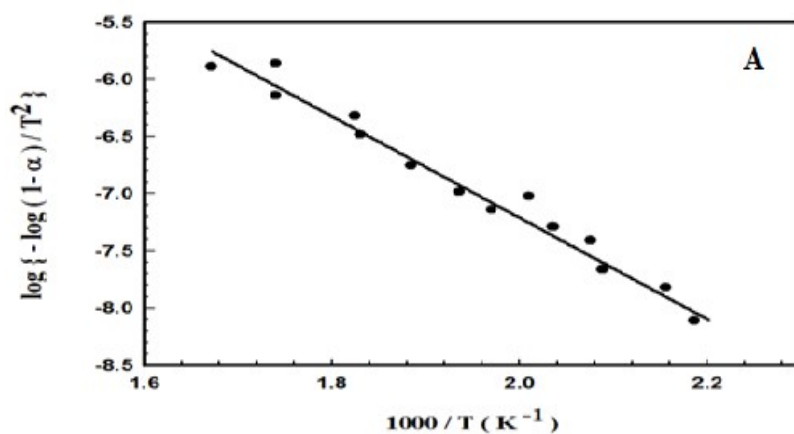
Fig (10) Calculation of activation energy by Horowitz and Metzger method for (A) pristine, (B) irradiated PVC with ion fluence 3 x 10 ^{17} cm^{-2} and (C) irradiated PVC with ion fluence 6 x 10 ^{17} cm^{-2}
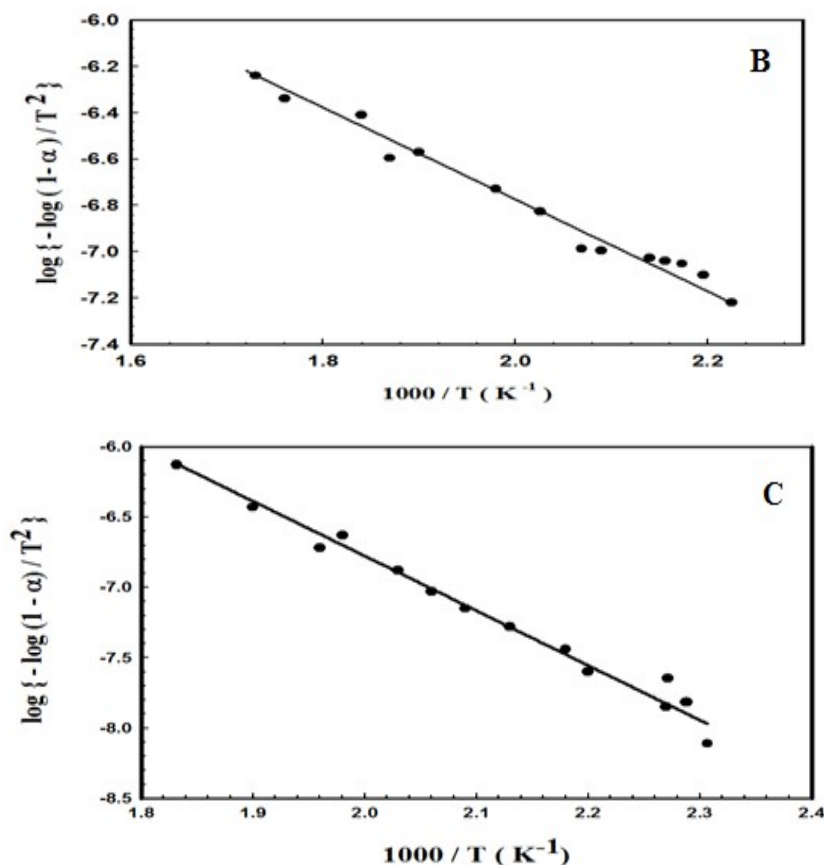
Fig (8) Calculation of activation energy by Coats and Redfern method for (A) pristine, (B) irradiated sample with ion fluence 3 x 10 ^{17} cm^{-2} and (C) irradiated sample with ion fluence 6 x 10 ^{17} cm^{-2}

Table (1) T_0 increases with irradiated sample by 3 x 10 ^{17} ion/cm^2 due to cross-linking process followed by an decrease with irradiated sample by 6 x 10 ^{17} ion/cm^2 indicating a decrease in thermal stability of the polymer samples due to degradation (i.e. preferentially chain scission).

4. CONCLUSION

The thermal stability for PVC increase with ion fluence increase and the thermal activation energy decrease from 1.89 eV to 1.44 eV . T_0 increases with irradiated sample for 3 x 10 ^{17} ion/cm^2 due to cross-linking process followed by an decrease with irradiated sample for 6 x 10 ^{17} ion/cm^{-2} indicating a decrease in thermal stability of the polymer samples due to degradation.

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