Effect of Ion beam irradiation on the Physical and Chemical Properties of plasticized poly ethylene terephthalate (PET) polymer used in Medical Device

Mahmmoud S. Abd-Elmonem*, Waheed M. Salem** and Manal A. Elshall**

Abstract— 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 physical and chemical properties of plasticized poly ethylene terephthalate (PET) was studied. Polymer samples were bombarded with 3 keV Ar ions to fluencies ranging from 2.8125×10^{17} to 5.625×10^{17} ions cm^{-2}. The pristine and ion beam bombarded samples were investigated using TGA thermal Analyzer and FTIR spectroscopy, PET were evidently changed after irradiation. Ionizing radiations always have a large effect on the physical properties of polymers. The thermal stability of PET at various ion fluencies was illustrated increase from 439.65 to 442.88°**C** the pristine sample and those samples bombarded with Ar ion at the highest fluence.

The kinetic parameters for the thermal stability of PET were evaluated applying isothermal thermogravimetric analysis (TGA). In such an analysis the apparent activation energy observed were within the range of **68** to **128** kJ/mol. There is a good agreement between the data obtained in this study with the values reported in the literature. Fourier transform infrared spectroscopy (FT-IR) shows the creation of polar groups on the surface which are responsible for surface wettability improvement.

Index Terms ion-beam irradiation; thermal stability; PET; medical device

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1 INTRODUCTION

The United States (U.S.) medical device manufacturing sector is a highly diversified industry that produces a range of products designed to diagnose and treat patients in healthcare systems worldwide. Medical devices differ from drugs in that they do not achieve their intended use through chemical reaction and are not metabolized in the body. Medical devices range in nature and complexity from simple tongue depressors and bandages to complex programmable pacemakers and sophisticated imaging systems.

There are several studies on the effect of radiation such as fast electron, gamma ray, and low-energy ions on poly(ethylene terephthalate) (PET);[1] studied the effects of gamma irradiation on PET by positron annihilation lifetime spectroscopy at doses up to 1.1MGy and dose rate of 1.08 kGy/h. Recently high energy ion irradiation of polymers has

knowledge, papers on the study of radiochemical yield degradation in the Ion beam irradiation of PET at deferent Ion fluence.

Radiation-modified PET can be applied in many fields, including biomedicine as well as to improve adherence for metalized polymers.[4]

Polyethylene terephthalate (PET) is an industrially mportant thermoplastic resin, which is extensively applied in the production of fibers, containers, and films. Many attempts are currently directed toward recycling of waste PET because of the interests in environmental protection and economic benefits [5].

The use of polyethylene terephthalate (PET), which is common in textiles and production of plastic beverages bottles are being enhanced worldwide. PET is not biodegradable and should be recycled. Recently pyrolysis or gasification of post-consumer plastics as thermal treatments have become of interest. With pyrolysis process, the waste plastics are thermally decomposed into smaller intermediate products, applicable as fuel or raw materials for the petrochemical industry [6].

The FDA considered the safety of polyethylene terephthalate when approving the following medical devices that include this material:

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- *Mahmmoud S. Abd-Elmonem is currently pursuing Analytical Chemistry, National Organization For Drug Control And Research (NODCAR), P.O. Box. 29, Giza, Egypt , PH-01150444241. E-mail:mahmmoud_sayed@yahoo.com*
- *Waheed M. Salem[1] and Manal A. Elshal- Analytical Chemistry, National Organization For Drug Control And Research (NODCAR), P.O. Box. 29, Giza, Egypt.*

☐ Surgical sutures (i.e., PremiCron® Nonabsorbable PET Surgical Suture,
    TRUBOND® Nonabsorbable Surgical Suture, U.S.P.[7,8]),
☐ Esophageal dilators (i.e., Bard® ELIMINATOR® PET Balloon Dialator.[9], and
☐ Surgical mesh (i.e., Peri-Strips® Staple Line Reinforcement.[10]

The use of polyethylene terephthalate to make surgical sutures was approved by the FDA as a Class II (special controls) medical device that requires premarket notification and adherence to standards (21CFR878.5000). Required testing includes acute and long-term (>30 day) biocompatibility testing for cytotoxicity, irritation or intracutaneous reactivity, sensitization, systemic toxicity, implantation effects, and hemocompatibility.[11]
The sutures may be provided uncoated, coated, undyed, or dyed with appropriate approved colors. The FDA found the data on the safety of PET to be adequate and determined that medical devices containing PETs are safe and effective when used for soft tissue approximation and/or ligation, including cardiovascular, ophthalmic, and neurological tissue. [12]
Esophageal and gastrointestinal dialators are Class II medical devices (21CFR876.5365) that must adhere to the same standards listed above for the surgical sutures. An esophageal dilator, used to dilate a stricture of the esophagus, may consist of a hollow cylindrical instrument (bougie), a weighted bougie with a mercury or metal olive-shaped weight that slides on a guide, such as a string or wire, or may consist of a bougie with a deflated ballon attached to a guidewire. The balloon is made of polyethylene terephthalate. Patches, pledgets, and intracardiac devices (surgical mesh) are made of polypropylene, polyethylene terephthalate, or polytetrafluoroethylene. They are fabric devices placed in the heart to repair septal defects, for patch grafting, to repair tissue, and to buttress sutures (21CFR870.3470). These devices are also Class II devices and adhere to the same standards listed above for the surgical sutures.

Polymers with improved mechanical, optical or electrical properties have been widely used in a variety of medical and industrial applications. However, their use is sometimes limited by unde- sired properties of the surface, contrary to very useful character- istics of the bulk, such as low wettability and surface free energy (SFE), chemical inertness and high impact resistance. Therefore it is of interest to modify the surface in a controlled manner to enhance wettability, printability and adhesion with other materials or with biological components. Many studies were performed to improve wettability and SFE of polymers to overcome the problems induced by their hydrophobic nature. SFE and wettability depend mainly on the amount of hydrophilic groups such as ether, ester and carboxyl groups and also on the development of surface roughness by forming micro-pores on the surface.[13-15]

In the present paper, we focus on the studying the effect of radiation with Ion Beam on physical, mechanical and thermal properties of the polymer polyethylene terephthalate with different dose. And show the clear differences between the Pristine and samples exposed to different doses of radiation

2 EXPERIMENTAL DETAILS
2.1 Chemicals
PET was a commercial polymer sheet with size 1 x1 cm^2 films were irradiated with various Oxygen ion fluence by cold

cathode ion source at the National Centre for Radiation Research and Technology (NCRRT), Atomic Energy Authority (AEA), Cairo, Egypt.
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}.
the activation energies of the PET polymer for the decomposition were obtained from TGA curves by using Coats-Redfren method and Horowitz-Metzgar method [16, 17]

3 Result and Discussion
3.1 Thermal analysis behavior:

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 *Polyethylene terphethalat* samples in the temperature range from ambient temperature up to 580 °C, at a heating rate of 10 °C/min.
The TGA and DTG curves of PET are shown in Figures 1,2 and 3. The DTG curves shows one stage of decomposition. 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
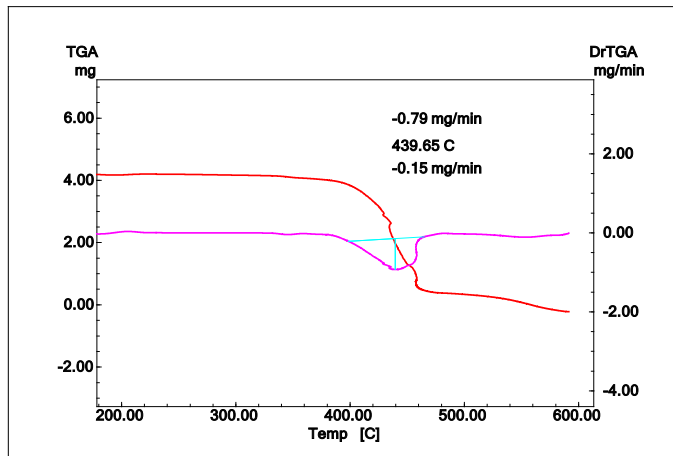
Fig(1) TGA thermogram and Derivative TGA measured in the temperature range from room temperature up to 600 °C for pristine PET
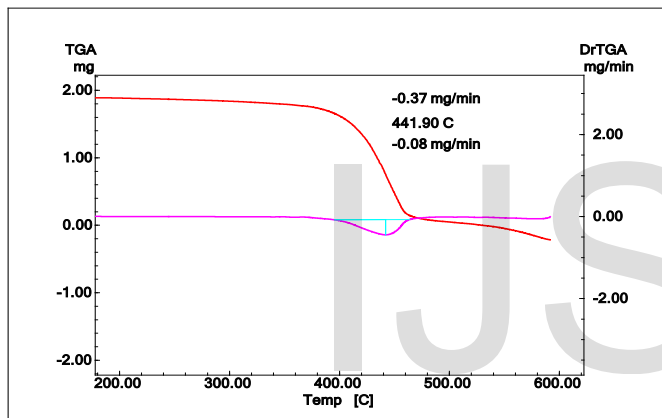
Fig(2): TGA thermogram and Derivative TGA measured in the temperature range from room temperature up to 500 °C for irradiated PET with ion fluence 2.8125 x 10 ^{17} cm^{-2}
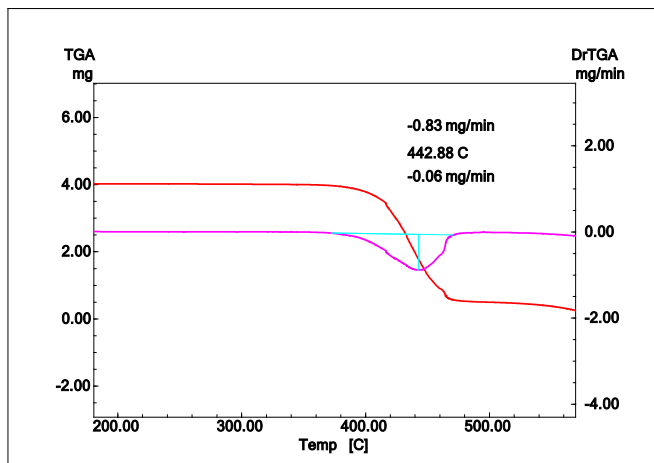

Fig(3) shows TGA thermogram and Derivative TGA measured for irradiated PET with ion fluence 5.625 x 10 ^{17} cm^{-2}

Table (1) . A comparison of TGA data

	Weight loss %		
	Pristine	2.8125 x 10^{17}	5.625 x 10^{17}
50 -380°C	9.25%	4.23%	3.04%
381-550 °C	97.62%	92.2%	87.9%

This results suggest increasing thermal stability in the same order. Kinetic studies were conducted to investigate these results through calculation and comparison of the activation energies obtained from the stage of decomposition of these polymer as show in Figures (4,5).
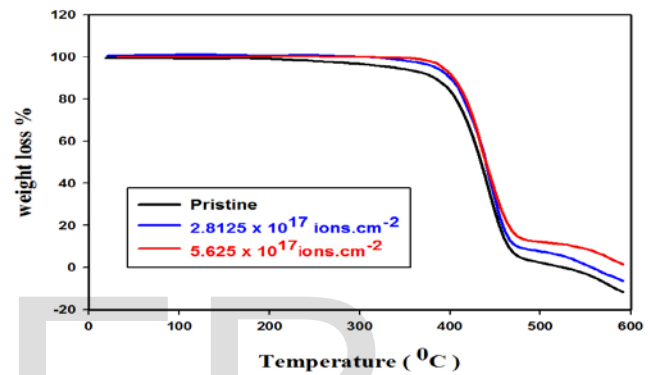
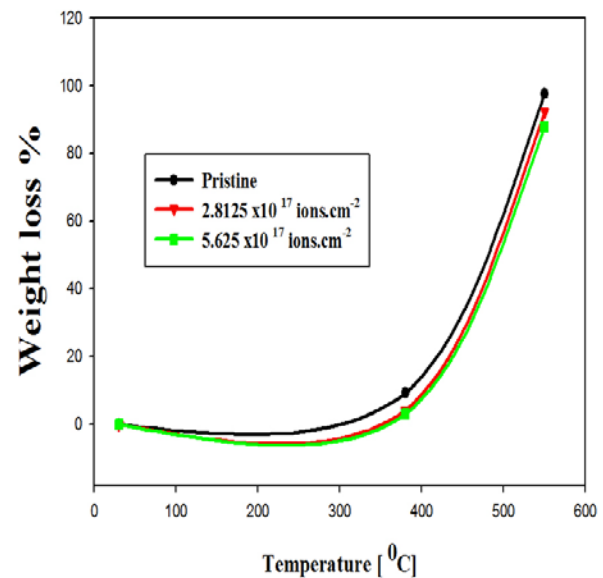Fig(4) shows TGA for Pristine and irradiated PET

Fig (5) show that the relationship between weight loss % and temperature for pristine and irradiated PET

3.1.1. Determination of Activation Energy:

For the first order kinetic process. The activation energy (E^*) values for the stage of decomposition of these PET polymer were determined by using Coats-Redfren method and Horowitz-Metzgar method. The results are shown in Figures 6:8. The activation energy (E^*) values of PET polymer were listed in table (2). These results are clear that the obtained values of activation energies of the used polymer are in reasonably good agreement. The activation energies obtained for the stage of decomposition of these polymer sample and its irradiated show different values. Suggesting the following sequence of thermal stability:

Pristine < irradiated PET with ion fluence 2.8125 x 10^{17} cm^{-2} < irradiated PET with ion fluence 5.625 x 10^{17} cm^{-2}

Horowitz and Metzger Method:

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

$$\text{Ln} \left\{ \ln \left[W_0 - W_f / W_0 - W_t \right] \right\} = E_{a\theta}/RT_s^2$$

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

T_s is the temperature which satisfies the equation:

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

According to the above equation, a plot of $\text{Ln} \left\{ \ln \left[W_0 - W_f / W_0 - W_t \right] \right\}$ against θ leads to a straight-line relationship in the range where the decomposed ratios are equal. Hence, the activation energy of decomposition Ea 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 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.

The equation is given below.

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

For first order reaction when n = 1 the equation is

Log $\left[-\log (1-\alpha) / T^2 \right]$ against 1000/T will result in a straight line having a slop (Ea/2.303R) to calculate activation energy.[18]

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 [19**]**

	T_0 (°C)	E_a(KJ/mol)		T_g (°C)
		Coats & Redfern	Horowitz & Metzger	
Pristine	**439.65**	**68**	**79**	**170**
2.8125 x 10^{17}	**441.90**	**127**	**93**	**192**
5.625 x 10^{17}	**442.88**	**128**	**108**	**202**

Table (2) Values of the onset temperature of decomposition T_0, activation energy of decomposition E_a, Glass Transition and Temperature for pristine PET and irradiated PET with different ion fluence .
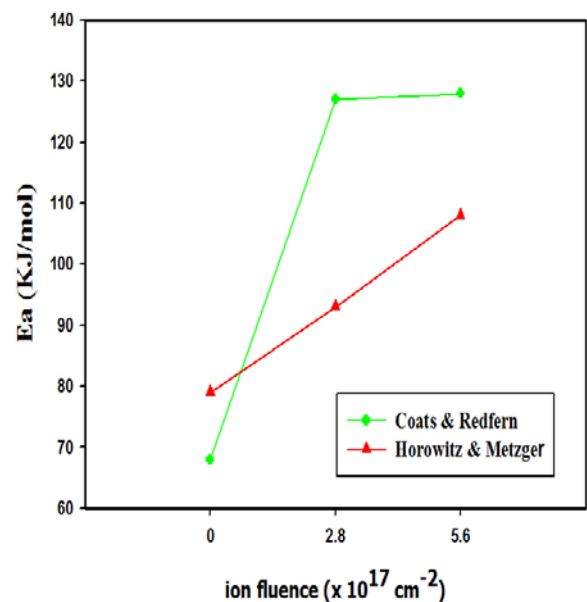

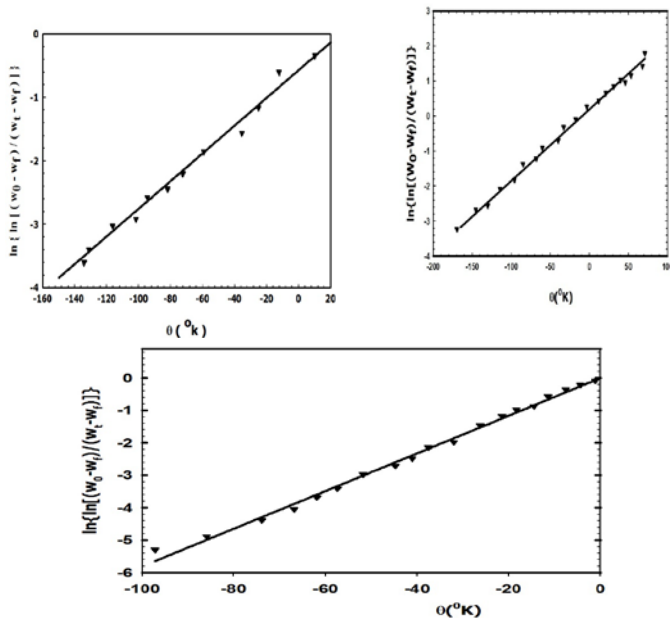Fig (6) relation between activation energy by Coats & Redfern method and horowitz & Metzger and ion fluence

Fig (7)

Calculation of activation energy by Horowitz and Metzger method for (A) pristine, (B) irradiated PET with ion fluence 2.8125×10^{17} cm^{-2} and (C) irradiated PET with ion fluence 5.625×10^{17} cm^{-2}

From table 1. T_0 increases with irradiated sample for 2.8125×10^{18} cm^{-2} due to crosslinking process. followed by an increase with irradiated sample for 5.625×10^{17} cm^{-2} indicating a increase in thermal stability of the polymer samples due to degradation (i.e. preferentially chain scission),
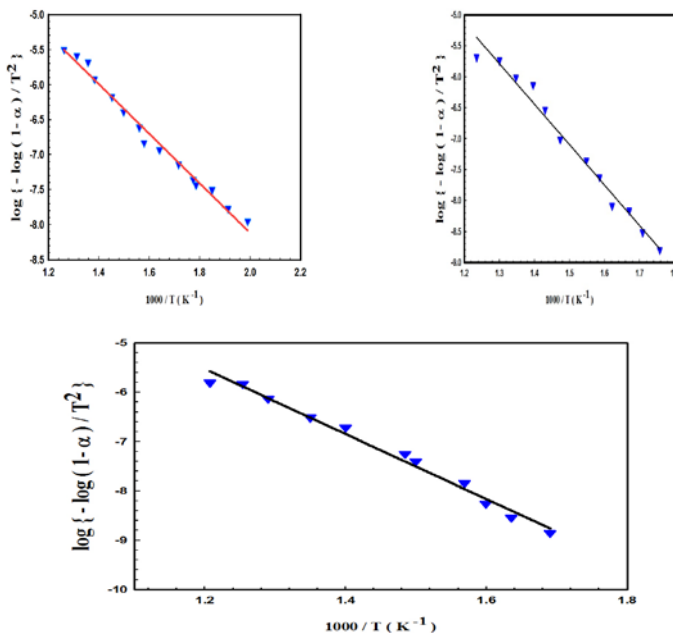

Fig (8)

Calculation of activation energy by Coats and Redfern method for (A) pristine, (B) irradiated PET with ion fluence 2.8125×10^{17} cm^{-2} and (C) irradiated PET with ion fluence 5.625×10^{17} cm^{-2}

3.2 FT-IR surface analysis:

FT-IR spectroscopy provides information regarding intermolecular interaction via analysis of FT-IR spectra were made by using (**FTIR 8400S Fourier and Transform SHIMADZO** apparatus) corresponding to stretching or bending vibrations of particular bonds. The position at which these peaks appear depends on the bond type.[20] As could be seen in Fig. 9, the monomer of PET film consists of four functional groups. These groups are as follows :two ester groups, one aromatic ring and one ethyl group. The two ester groups with the aromatic ring constitute the terephthalate group which in turn connects to the ethyl group to form the PET monomer. These functional groups consist of many bonds which are as follows: C–C, C–H, C–O, C=O and aromatic ring.
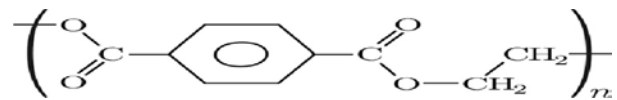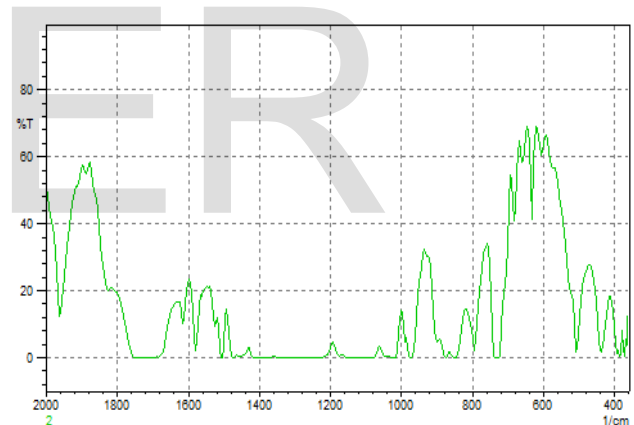

Fig 9: Molecular structure of PET film monomer.

Fig 10: FT-IR spectra of PET film before Ion beam treatment.

These bonds are clearly shown in Fig. 10 which shows the FT-IR spectra for the PET film before Ion beam treatment. The region to the right-hand side of Fig. 10 (from about1500 cm^{-1} to 500cm^{-1}) usually contains a very complicated series of absorptions and is known as the finger print region.[21] The C–O bond of ester group also has an absorption in the finger print region. Two bands exist for C–O stretching bond at 1110cm^{-1} and 1238cm^{-1}. The strong band found at 1725cm^{-1} is due to the stretching vibration of the C=O bond of the ester group. Absorption bands associated with C=O bond stretching are usually very strong because a large change in the dipole takes place in that mode. For

the ethyl group there exists two kinds of vibrations for the C–H bond :i) the medium C–H stretching bond which is found at $2970 cm^{-1}$ and ii) the strong C–H bending bond which is found at $731 cm^{-1}$. The C–H stretching band of the aromatic ring exists at $3055 cm^{-1}$. Also the band at $1578 cm^{-1}$ is assigned to the C–H bond stretching vibration of the phenyl ring. The C–C phenyl ring stretching band exists at $1408 cm^{-1}$.[22, 23]

Upon Ion beam treatment of PET samples with different fluences, free radicals, ions and neutral atoms are generated. As a result, many changes on the surface take place; the main change of interest in the present work is the change of surface polarity. It may be a result of the creation of OH and COOH groups in the oxidation processes by atmospheric air.[24] The oxygen from air reacts with the radiation-induced radicals to form C=O.[25] Consequently, C=O concentration of PET film increases with increase of the electrons fluence which in turn leads to the decrease of the transmitted IR intensity with electrons fluence increase (Fig. 11a). C–H transmission band intensities decrease as shown in Fig. 11b which may be attributed to hydrogen abstraction and free carbon atoms which may combine to increase the concentration of C–H bonds. Hence the electron beam treatment of PET films changes surface chemistry and increases its polarity and wettability by increasing the number of polar groups on the surface.

Fig (11): FT-IR transmittance spectrum of (A) pristine, (B) irradiated PET with ion fluence $2.8125 \times 10^{17} cm^{-2}$ and (C) irradiated PET with ion fluence $5.625 \times 10^{17} cm^{-2}$

It is clear from the above results that the transmittance of most of the FTIR peaks decreased, some peaks disappeared and some shifted towards the higher and lower wave number regions. The decrease in intensity is attributed to the cleavage of the carbonate linkage and to the C–H abstraction from the backbone of the polymer, associated with the formation of CO_2 and –OH with varied intensities. [26]

4. Conclusion:

After Ion beam irradiation of PET polymer, A rapid computer analysis of thermogravimetric weight-loss data and differential kinetic models has provided kinetic parameters of non-isothermal decomposition of polyethylene terephthalate films in inert atmosphere. Kinetic results demonstrated differences in thermal stability between the three samples and suggested the following sequence of stability:

Pristine < irradiated PET with ion fluence $2.8125 \times 10^{17} cm^{-2}$ < irradiated PET with ion fluence $5.625 \times 10^{17} cm^{-2}$

The molecular weight of PET samples decreases with dose up to ion fluence $2.8125 \times 10^{17} cm^{-2}$, because the chain scission is the predominant effect. After this dose an increase with dose was observed until with ion fluence $5.625 \times 10^{17} cm^{-2}$. In the range of ion fluence $2.8125 \times 10^{17} : 5.625 \times 10^{17} cm^{-2}$ several processes could occur, including chain scission, oxidative degradation, radiolysis, and crosslinking. Further studies must be done to understand the reactions, which take place after ion fluence. Crystallinity decreases with increase in dose because of the formation of a branching polymer and some crosslinking reactions. On the other hand that the transmittance of most of the FTIR peaks decreased, some peaks disappeared and some shifted towards the higher and lower wave number regions. The decrease in intensity is attributed to the cleavage of the carbonate linkage and to the C–H abstraction from the backbone of the polymer, associated with the formation of CO_2 and –OH with varied intensities

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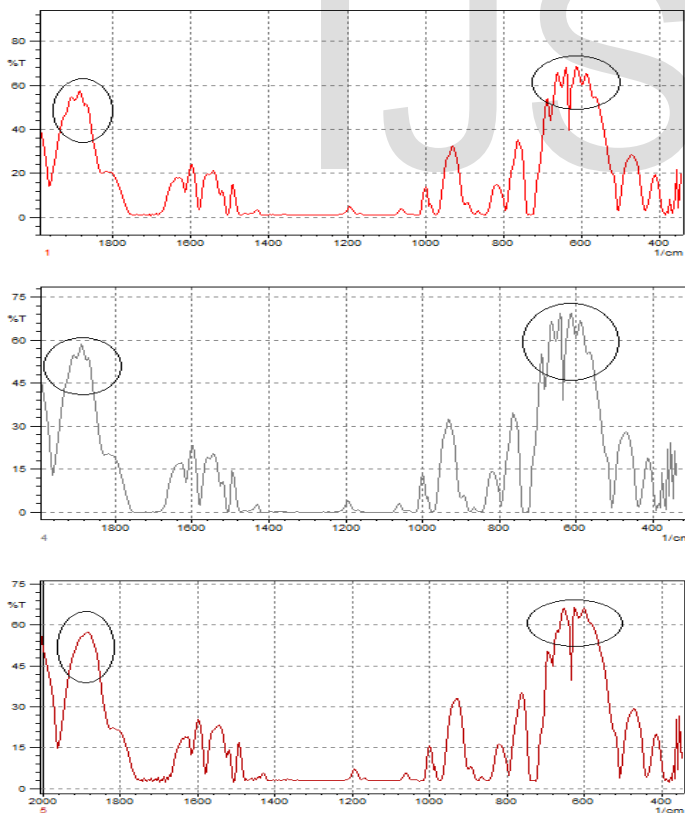[2] Wong, W., Yeung, K.W., Law, K.S., 2001. Mater. Res. Innov. 4, 344–349.

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