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Optical study of poly(ethyleneterephthalate) modified by different ionizing radiation dose

P Aggarwal[a,b], S Dhiman[a], G Kumar[a], U W Scherer[c], M L Singla[b] & A Srivastava[a,c]*

[a]Department of Chemistry & Centre for Advanced Studies in Chemistry, Panjab University, Chandigarh 160 014, India

[b]Agrionics, Central Scientific Instruments Organization, CSIR, Chandigarh 160 030, India

[c]Aachen University of Applied Sciences, Ginsterweg 1, Juelich 52428, Germany

*E-mail: alok@pu.ac.in

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Thin films of poly(ethyleneterephthalate) [PET]were exposed to radiation dose ranging from 10 to 30 kGy by using gamma rays in the range 12.8-177.8 MGy using swift light ions of hydrogen. There was no effect of the radiation dose on the optical behaviour of PET as a result of exposure to radiation dose up to 30 kGy brought about by gamma rays but a significant decrease in the optical band gap values was observed when PET was exposed to swift light ions of hydrogen. The data obtained are discussed in terms of optical studies carried out on PET using swift heavy ions.

Keywords: Optical study, Radiation dose, PET, Thin films

1 Introduction

It is now a well established fact that the exposure of polymers to ionizing radiation leads to a wide range of physico-chemical changes[1-6]. The origin of these changes can be traced to the rearrangement taking place in the chemical structure of the polymer as a result of energy deposition brought out by the ionizing radiation. The increasing application of polymers in hard radiation environments like those encountered in space missions and nuclear installations besides food and medical irradiators has given impetus to such studies. Poly (ethylenetererphthalate), generally, known as PET is widely used in numerous commercial applications because of its superior mechanical strength, good heat and chemical resistance, dimensional stability, flex-crack resistance properties besides optical clarity.

The changes brought out in its physico-chemical properties as a result of exposure to light as well as heavy ions has been a subject of investigation for many years. Mishra *et al*[7]. studied the changes in its optical and electrical properties by exposing it to swift light ions of protons. Bridwell *et al*[8]., Ueno *et al*[9]., Singh *et al*[10]., Ciesla *et al*[11]. and Fink *et al.*[12], Singh *et al*[13]. studied its modified physico-chemical properties by exposing it to swift heavy ions as varied as helium, lithium, boron, carbon, nitrogen, silicon, argon, lead and dysprosium. More recently, Liu *et al*[14,15]. and Zhu *et al*[16,17]. have extended its study by exposing it to heavy ions of argon, krypton, xenon and uranium having energy in the range 1.4-2.7 GeV.

Singh *et al*[18,19]. have too reported their findings on physico-chemical modifications in PET brought out with 120 MeV silicon ions. In the present work, the optical changes brought out in PET by exposing it to different radiation dose using gamma rays and swift light ions of hydrogen have been reported by carrying out UV-Vis studies. The data obtained has been discussed in the light of data earlier reported by Srivastava *et al*[20]. on optical characteristics of PET exposed to swift heavy ions of carbon, silicon and nickel.

2 Experimental Details

Thin films (12 and 100 micron) of poly(ethylenetererphthalate) sold commercially as HOSTAPHAN obtained from Hoechst A.G, Germany were exposed to different fluence of swift light hydrogen ions of 3 MeV energy ranging from 1×10^{12} to 1×10^{15} ions at the Cyclotron Facility of Physics Department, Panjab University, Chandigarh, India so as to deliver total radiation dose in the range 12.8-177.8 MGy. The sample thickness was selected in such a way that the physico-chemical changes brought out if any were entirely due to radiation induced modification and not due to radiation induced doping. The range of 3 MeV proton ions in PET as calculated from the SRIM code[21] is 129.83 μm. The irradiations were carried out at room temperature and under vacuum (10^{-6} Torr) in a way that an area of 1.3×1.3 cm^2 was uniformly irradiated. The beam current was kept low to suppress thermal decomposition and monitored intermittently with a Faraday cup. The gamma exposure was carried out using the gamma irradiator facility of the Radiation Protection Division, Research Centre, Juelich, Germany so as to deliver total dose in the range 10-30 kGy.

The foils in which visible changes could be observed after irradiation were separated and their UV-VIS measurements were carried out using a Perkin-Elmer LAMBDA 2 spectrophotometer which scanned the spectrum from 200 to 1100 nm in about a minute. The measurements were carried out nearly a week after exposure of foils to gamma rays and swift light ions of hydrogen, hence the reported results represent the stationary state of the irradiated foils where the metastable defects (if any) would have got annealed the radiation enhanced oxidation (if any), are expected to have got completed.

3 Results and Discussion

The optical characteristics of the PET exposed to different dose of ionizing radiation have been studied in terms of changes in the absorption characteristics (λ), optical band gap energy (E_g) and number of carbon atoms per cluster (N) formed. Table 1 presents the details of total dose to which the PET films were exposed by gamma rays as well as light and swift heavy ions along with the magnitude of optical band gap and carbon cluster size. The optical absorption edge can be correlated to E_g using Tauc's equation[22]. The E_g has been calculated using Plank's equation[23].

Tauc's equation, $\omega^2 \varepsilon_2(\lambda) = (h\omega - E_g)^2$ … (1)

Plank's equation, $E_g = hc/\lambda$ … (2)

where $\varepsilon_2(\lambda)$ imaginary part of complex refractive index i.e. optical absorbance, λ wavelength, h Planck's constant and c is speed of light. Table 1 gives the details of ion beam as well as the total dose to which the PET films were exposed besides the magnitude of optical band gap (E_g) and carbon cluster size (N).

The radiation dose can be calculated in terms of Grays using prescription given by Steckenreiter[24] as:

$$D = 1.6\times10^{-10}\cdot\Phi.\rho^{-1}.\ \Delta E/\Delta x \quad \dots (3)$$

where D is the radiation dose in Gray, Φ the ion fluence, ρ the density of material and $\Delta E/\Delta x$ is the rate of energy loss. The number of carbon cluster (N) is given by:

$$\sqrt{N} = 34.3/E_g \quad \dots (4)$$

A representative plot of absorption as a function of wavelength in the range 300-500 nm for foils exposed to different radiation dose is shown in Fig. 1 for PET film exposed to swift light ions of hydrogen.

It is clear from the plot of absorption as a function of wavelength that there is a general shift of the absorption edge towards the red end of the spectrum with the increase in the radiation dose which is perhaps indicative of the increase in the conjugation

Table 1—Optical parameters as a function of radiation dose

Radiation Source	Ion energy (MeV)	Dose (Grays)	Optical band gap (E_g)	Change in E_g (eV)	Cluster Size (N)	Change in cluster size
Without irradiation	-	0	3.82	-	81	0
Gamma rays		10 k	3.82	0	81	0
		20 k	3.82	0	81	0
		30 k	3.82	0	81	0
Hydrogen ion	3	12.8 M	3.70	0.18	86	5
		177.8 M	3.55	0.27	93	13
	62[a]	80 k	3.9	0	-	-
Carbon ion[b]	90	1.75 M	3.65	0.18	88	8
		3.50 M	3.49	0.34	96	16
		17.51 M	3.08	0.75	124	64
Silicon ion[b]	120	0.28 M	3.75	0.08	83	3
		1.91 M	3.60	0.23	90	10
		9.93 M	2.56	1.27	179	99
Nickel ion[b]	100	1.10 M	3.70	0.13	86	6
		3.45 M	3.64	0.19	89	9
		34.45 M	1.54	2.29	496	416

Data from literature: [a]Misra *et al*[7]., [b]Srivastava *et al*[20].

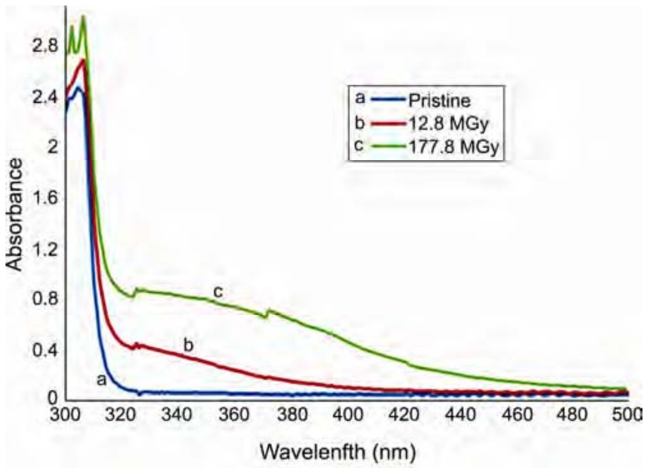

Fig. 1—Plot of absorbance as a function of wavelength of PET films exposed to 3 MeV hydrogen ions at different dose. (a) Pristine (b) irradiated with 12.8 MGy dose (c) irradiated with 177.8 MGy dose

length as result of bond breaking and reconstruction induced by the swift heavy ion beam. A physical examination of the PET films too corroborates the above mentioned observation. It is seen that the colour of the PET foil changes from transparent in the case of the pristine film to yellow. No such change was observed in the case of PET films exposed to gamma rays thereby, showing its radiation stability up to a gamma dose of 30 kGy. A similar study carried out by Mishra *et al*[7]. by exposing PET to 62 MeV protons too showed that PET was stable up to a dose as high as 80 kGy.

It is observed from Table 1 that the optical band gap values decrease with the increase in the radiation dose whereas the cluster size increases with the increase in radiation dose. The decrease in the optical band gap value in the case PET exposed to swift light ions of hydrogen up to a radiation dose of 122.8 MGy is 0.27 eV whereas the increase in the carbon clusters is 13 units. The same general trend is observed in case of PET exposed to different radiation dose using swift heavy ions of carbon, silicon and nickel[20].

A comparison of the data obtained in the present work with that reported in literature brings out a very interesting aspect about the role of the size of the bombarding ions used to bring about the optical modifications. It is observed that inspite of radiation dose brought out in the polymeric medium of interest by the swift light hydrogen ions being much higher than that brought out by swift heavy ions of carbon, silicon and nickel, the change in optical band gap values and the number of carbon atom clusters is found to be much lower in comparison. It would be interesting to carry out similar study with same radiation dose but different types of ionizing radiation.

4 Conclusions

It can, therefore, be stated that in the present work the optical modifications brought out by ionizing radiation have been investigated using UV-Vis technique. There was no effect on the optical characteristics of PET exposed to gamma radiation as high as 30 kGy. The study carried out showed that the total energy deposited in a given polymeric medium seems to play a significant role in determining the final nature of the physico-chemical characteristics of the polymeric material. The extent of change perhaps may not have one to one relationship with radiation dose and perhaps the size of the ions has to be taken into consideration.

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