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Optical and Structural Studies of Kapton Polymer Irradiated by 1.2 MeV Gamma Radiations

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Abstract: ***The virgin and Gamma irradiated kapton polymer samples were analysed by UV-Visible spectroscopy (JASCO, V-530) in the wavelength range of 190-900 nm to observe the energy gap variation with increasing dose. The structural aspect of the Kapton was also analysed by using X-ray diffraction technique. The XRD measurements were made on PW-1830 machine by using monochromatic CuK$_\alpha$(8.04 keV and λ = 0.154 nm) radiation. From the optical studies it was observed that the absorption edge is shifting in an unsymmetric manner after irradiation. The decrease in direct and indirect energy band gaps has been observed after irradiation may be due to the creation of electronic disorders. The value of direct energy band gap is found to be higher than the indirect band gap. The XRD patterns of gamma irradiated Kapton polymer samples at different doses shows that the overall peak intensity of the samples at 500 kGy dose is less as compared to the sample irradiated at 1500 kGy dose. However, at dose level 2000 kGy the peak intensity again increases and peak width decreases .However, a decrease in the overall peak intensity and a shift in the angular position towards the higher angle side can be explained in terms of a decrease in the lattice spacing.***

Keywords: Gamma irradiation; kapton; UV-Visible spectroscopy; XRD

1. Introduction

Kapton is known to be a high performance aromatic polymer and primarily used for insulation all over the world now with very high heat-durability and heat-stability. Kapton is a polyimide film that can remain stable in a wide range of temperature from -273ºC to +400ºC. It has some very good properties such as mechanical performance, electric insulation, radiation resistance, corrosion resistance (other than alkali), etc. Kapton polymer has been commercially used from many years and is now commonly applied in the electronics industry as an insulating barrier, gas separation membrane applications, etc. [1-3].Particularly the radiation resistance, and fire resistance, have made this polymer a favourite choice for applications like wire insulation, electrical components seal assemblies, in nuclear power plants, military aircraft and space shuttles [4,5]. It is worthy to have the knowledge about the properties of the material that change when it is exposed continuously for a long time by the radiations like gamma rays, etc. Hence, the qualitative as well as quantitative studies of the radiation damage of "radiation resistant" polymers like Kapton at such a high level dose, is gaining more and more importance in engineering and technology [6,7].

Kapton is also used as a control coating for exterior spacecraft surfaces due to its good thermal stability and chemical resistance [8]. This material layered on the outer surface of a spacecraft because of its resistance to harsh environmental conditions and fluctuated temperature [9]. Due to the importance of Kapton in aerospace applications, many experiments have been conducted over the last few decades to investigate the effect of exposure of this polymer after irradiation.

In this regard, out of a wide range of low as well as high energy radiations that can be used to modify/improve the properties of polymers. Gamma irradiation is one among them which induces several physico-chemical changes in the polymers such as cross linking, scissioning, formation of free radicals, radiochemical alterations, unsaturation or formation of double bonds, evolution of gases, formation of carbonaceous clusters, change in intrinsic free volume, creation of defects (free radicals or impurities), amorphization, phase transitions, etc. Kapton is known to be particularly resistant to ionizing irradiation, induced degradation when irradiated with heavier atom possessing kinetic energy in MeV.

In Kapton polymer, the gamma radiations interactions lead to a decrease in optical band gap and increase in absorbance in the UV–Visible region can be attributed to carbonization (formation of dehydrogenated amorphous graphite clusters whose size increases with the fluence) and conjugation (double bonds). The colour of Kapton polymer turns from amber to black with metallic lustre with the increase in gamma irradiation dose [10-12].

The XRD studies show that the crystalline peaks superimposed upon the broad amorphous peaks, confirming the partial crystalline structure of Kapton polymer. However, in this polymer the approximate percentage of the crystalline phase and amorphous phase has been 25% and 75%, respectively .The increase in glass transition temperature T_g from 392C$^\circ$ to 418C$^\circ$ in radiation induced Kapton polyimide as reported earlier has been attributed to be due to cross-linking[13].

2. Experimental Details and Analytical Techniques

The semi-crystalline pure research grade Kapton sheets of thickness 250 µm were obtained from M/S Good Fellow U.K. and used without any further treatment.

The polymer samples of size (2 x1) cm^2 were cut from the commercially available sheet. One sample was kept virgin and the other four samples were subjected to irradiation in

the dose range of 500-2000 kGy. The samples were irradiated using 1.25 MeV Gamma radiation source of Co^{60} in the radiation chamber (which is in the form of a cylindrical chamber of 14 cm length and 10 cm diameter) with dose rate 4 kGy/h and source strength 2 K Curie at UGC– DAE Consortium for Scientific Research, Kolkata Centre, Kolkata.

The irradiated samples were characterized by using five analytical techniques like UV-VIS spectroscopy, XRD.

2.1 UV-Visible Spectroscopy

The optical changes were analysed by UV-Visible spectroscopy (JASCO, V-530) in the wavelength range of 190-900 nm to observe the energy gap variation with increasing dose. All the spectra were recorded by mounting the samples in the integrating sphere assembly attached to the spectrophotometer, keeping air as the reference.

2.2 X-Ray Diffraction

The study of the structural aspect of the Kapton was analyzed using X-ray diffraction technique. The XRD measurements were made on PW-1830 machine by using monochromatic CuK_{α}(8.04 keV and λ = 0.154 nm) radiation. The scanning was set between 5^{o} to 90^{o}at a scanning rate of 1 step/s. The operating conditions were 25 kV and 30 mA, employing a 0.15-mm slit in front of the detector. The polymer samples were mounted one by one on a sample holder plate without using tape, the fitted profiles of the spectra were obtained from the software.

3. Results and Discussion

In the present study the results obtained from the different techniques/measurements of the virgin and gamma irradiated samples of Kapton polymer have been discussed separately as under:

3.1 Optical Studies

The absorption of light energy by polymeric materials in the ultraviolet and visible regions involves the promotion of electrons in σ, π and norbitals from the ground state to higher energy states. Ultraviolet-visible (UV/VIS) spectrophotometer has become an important tool for investigating these electronic transitions.

The optical absorption spectra of virgin and γ-irradiated Kapton samples are shown in Fig. 3.1 in the wavelength range 500nm-875nm. It is clear from the figure that the absorption edge is shifting in an unsymmetric manner after irradiation. This shift may be correlated with the formation of conjugated bonds showing the possibility of formation of carbon clusters [14]. This type of transition occurs in non bonding electron containing compounds and also in aromatic compounds due to bond cleavage and reconstruction [15-17].

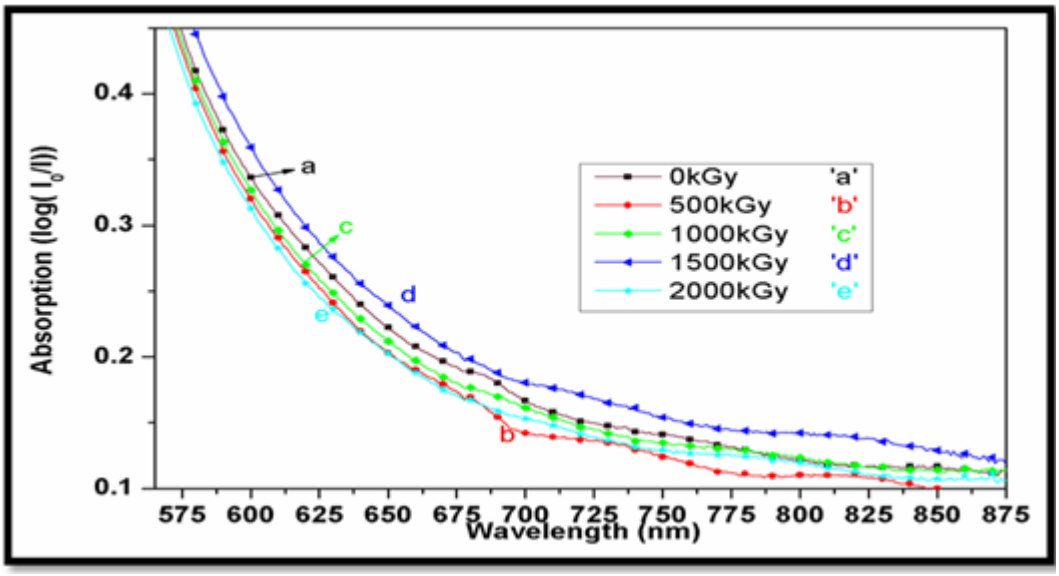

Figure 3.1: UV/VIS spectra of virgin and gamma-irradiated Kapton samples

Many of the optical transitions which result due to the presence of impurities have energies in the visible part of the spectrum, consequently the defects are referred to as colour centres [18, 17].

From a comparative study of the virgin and gamma irradiated spectra of Kapton polymer are shown in Fig. 3.2.It is observed that absorption of virgin sample is higher at allwavelengths than the absorption of irradiated samples at 500, 1000 and 2000 kGy, whereas lower than at 1500 kGy, respectively. It is further observed that absorption at 1000 kGy is higher as compared to the 2000 kGy and the absorption at 500 kGy is laying in between1000 kGy and 2000 kGy at lower frequency side and show a decreasing behaviour beyond 680 nm. Thus the absorption spectra of virgin and irradiated samples of Kapton are unsymetric in nature. The overall results reveal that intensity has been changed withthe increases of gamma dose, which may be attributed as the recrystallization occurs in Kapton polymer[14]. The optical absorption method can be used to investigate the optically induced transitions which in turn

can provide information about the bond structure and energy gap in crystalline and non crystalline materials.

Determination of band gap

The optical energy band gap for virgin as well as irradiated samples was calculated from the respective values of λ_g using the Formula

$$E_g = hc/\lambda_g \quad \text{..... (3.1)}$$

where h is the Planck's constant, c the velocity of light and λ the wavelength.

The present polymer obeys the rule of direct transition as well as indirect transition.

The relationship between optical absorption coefficient α(hν) and incident photon energy is given by Davis and Mott [149].

$$\alpha(h\nu) = \frac{B(h\nu - E_g)^q}{h\nu} \quad \text{... ... ... (3.2)}$$

where h is the Planck's constant, vthe frequency of the radiation, B a constant, E_g the value of the optical energy band gap between the valance band and the conduction band, q the power which characterizes the electronic transition, whether it is direct or indirect transition during the absorption process in the k-space. Especially q is an index which can assume values 0.5 for direct allowed and 1.5 for direct forbidden, 2 for indirect allowed and 3 for indirect forbidden transitions, respectively. The factor B depends on the transition probability and can be assumed to be constant within the optical frequency range.

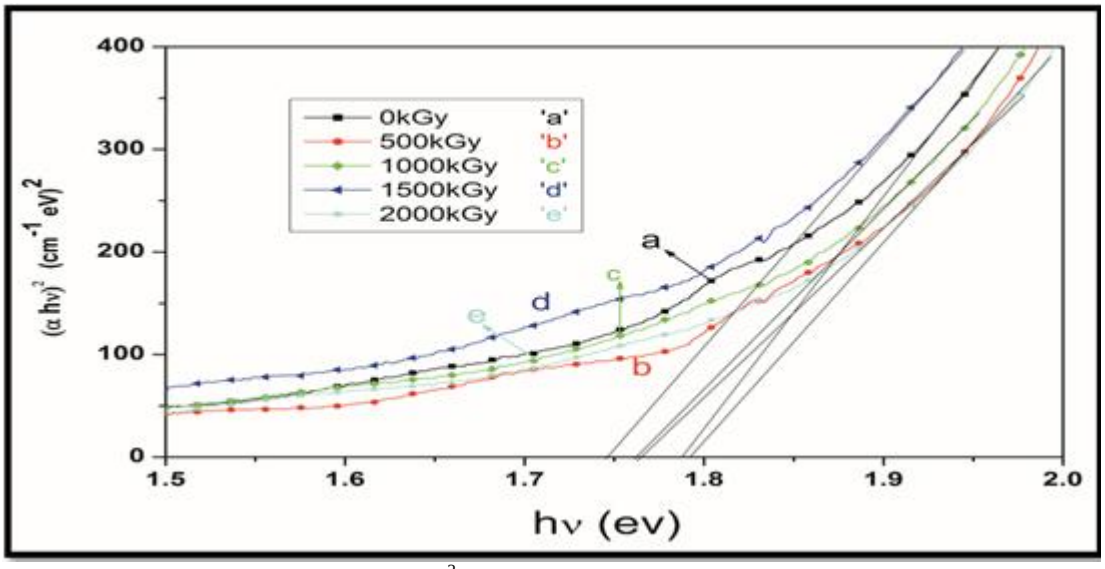

Figure 3.2: The dependence of $(\alpha h\nu)^2$ on $h\nu$) for virgin and irradiated Kaptonpolymer samples

For the determination of direct and indirect band gaps, $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ of theKapton polymer samples were plotted as a function of photon energy (hν). The values of the energy band gap were determined by taking the intercept on hν-axis. Figs. 6.3and 6.4 show the variation of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ with (hν) for the virgin and irradiated Kapton polymer samples.

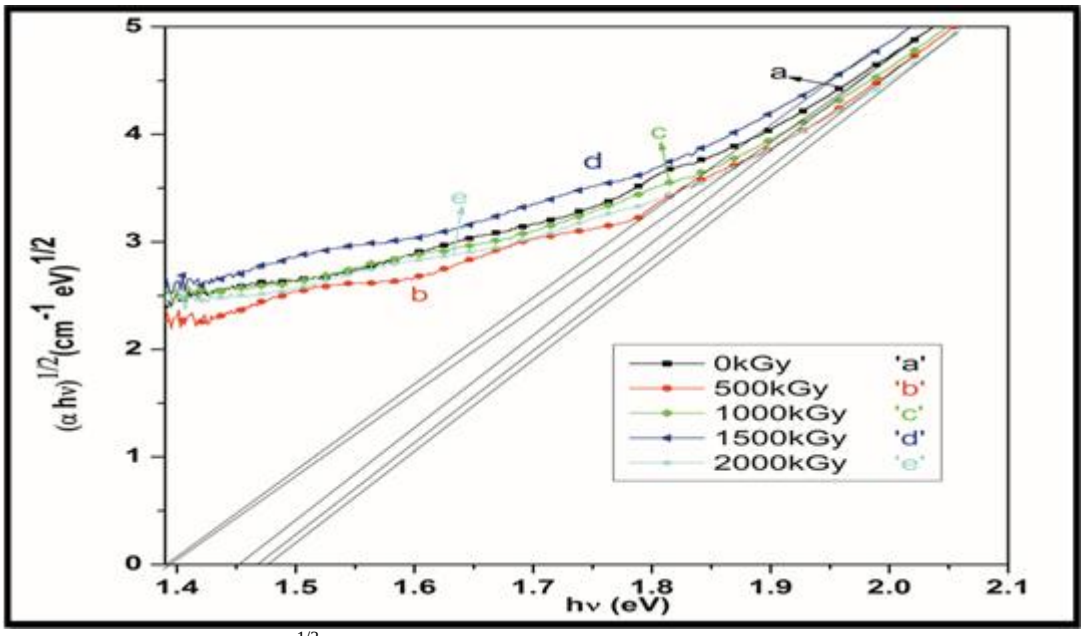

Figure 3.3: The dependence of $(\alpha h\nu)^{1/2}$ on photon energy ($h\nu$) for virgin and gamm air radiated Kapton polymer samples

From the intercept of the best fit lines on hν axis, direct and indirect energy band gaps were calculated for the virgin and gamma irradiated Kapton polymer samples and the results are presented in Table 6.1. It is clear from the tabulated values of the optical direct band gap that energy decreases from 1.79 eV to1.74 eV in the dose range of 500 kGy to 1500 kGy but increases from 1.74 eV to 1.76 eV at the highest dose 2000 kGy. Moreover, it is also observed from the data that the values of indirect band gap decreases in the dose range of 500 kGy to1000 kGy and remain constant at higher doses. The value of direct energy band gap is found to be higher than the indirect band gap in the whole range of exposure as presented in Table3.1. However, the decrease in direct and indirect energy band gaps may be due to the creation of electronic disorders.

Table 3.1: The variation of band gap and number of carbon atoms for virgin and irradiated Kapton

γ-radiation dose (kGy)	Band Gap Energy (eV)		(N)	
	Direct	Indirect	Direct	Indirect
0	1.78	1.48	~10	~12
500	1.79	1.47	~10	~12
1000	1.76	1.45	~10	~13
1500	1.74	1.39	~11	~13
2000	1.76	1.39	~10	~13

The number of carbon atoms (*N)* in a cluster is correlated with the optical energy band gap (E_g) determined with the modified Tauc's equation [189]

$$N = 2\beta\pi / E_g \quad \text{.....(3.3)}$$

where 2β (β∼2.9 eV) is the energy band structure of a pair of adjacent π sites as it is associated with π→π* optical transitions in -C=C- structure. The results presented in Table 3.1 suggests that Kapton polymer samples get crystallized after irradiation.

3.2 Structural Studies

Fig.3.4(a-e) shows the diffraction pattern of virgin and γ-irradiated Kapton polymer samples. The diffraction pattern of virgin sample shown in Fig.3.4(a) indicates that the virgin Kapton is partially crystalline in nature and the most intense peak occurs at 2θ= 30°, which as per the literature is an amorphous hump [19,20]. This semi-crystalline nature of polymer arises due to the systematic alignment of polymer chain folding. However, in case of irradiated samples, no significant changes are observed in the diffraction pattern.

Fig.3.4 (b-e) shows the XRD patterns of gamma irradiated Kapton polymer samples at different doses. The XRD spectra shows that the overall peak intensity of the sample irradiated at 500 kGy is less as compared to the sample irradiated at 1000 kGy and FWHM decreases. This indicates that crystallinity increases with increasing dose. Further, it is observed that the overall peak intensity decreases, whereas FWHM increases at higher doses which reflect that crystallinity decreases at higher dose. However, at dose level 2000 kGy the peak intensity again increases and peak width decreases. The reversal is attributed as a result of recrystallization taking place in Kapton polymer due to gamma irradiation. It is evident that the diffraction patterns of the gamma irradiated Kapton polymer samples are broader (diffused) as compared to the virgin sample[14]. The concept of crystallinity in case of polymers is quite different than that of solids [20].However, a decrease in the overall peak intensity and a shift in the angular position towards the higher angle side can be explained in terms of a decrease in the lattice spacing [21].

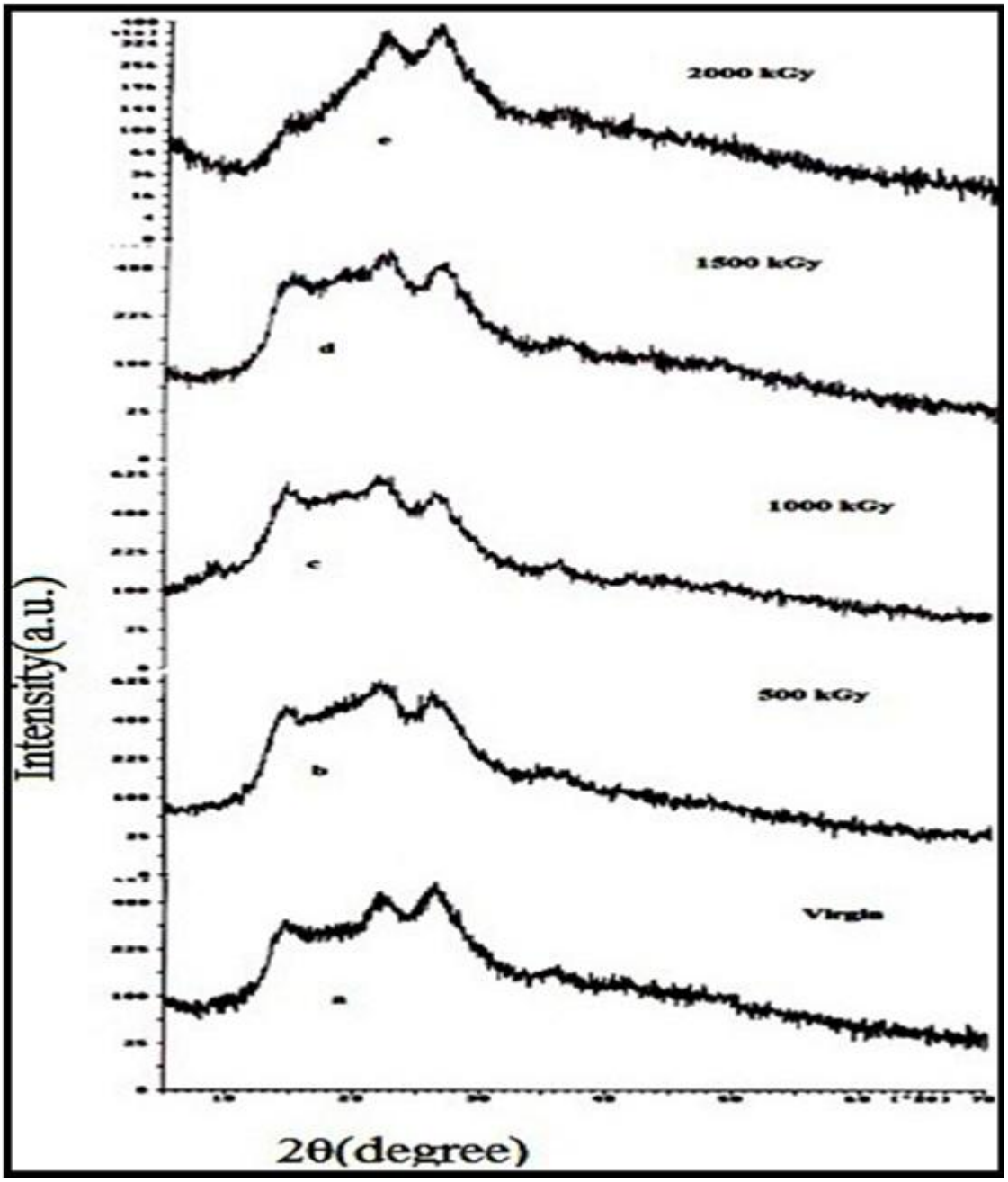

Figure 3.4: XRD pattern of virgin and irradiated Kapton polymer samples

4. Conclusions

The Optical, Structural, Chemical, Electrical and SEM studies of aromatic polymer like Kapton irradiated with gamma radiation source of Co^{60} was carried out by using UV-VIS spectroscopy, XRD, FTIR spectroscopy, High frequency impedance analyzer and Scanning electronic microscope (SEM) techniques. The following conclusions have been drawn:

The values of indirect band gap are found to be lower than the corresponding values of direct band gap in virgin and gamma irradiated kapton Polymer samples. The overall energy band gap (E_g) is found to decrease with increasing γ-irradiation dose. The XRD studies show that the overall peak intensity decreases and FWHM increases with increasing radiation dose.

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