

Optical and Chemical Response of 50 MeV Lithium Ion Irradiated Poly(Vinylidene Fluoride)Polymer

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ABSTRACT

The optical and chemical response of poly vinylidene fluoride (PVDF) polymer has been studied after one year of irradiation to avoid the short-lived activity and reactivity of the irradiated polymer with oxidation and reduction mechanism. The polymer samples were irradiated with 50 MeV lithium ion beam in the fluence range of 1.27×10^{11} – 2.15×10^{13} ions/cm². The post irradiation effect has been analysed using UV-visible and FTIR spectroscopic techniques. The results of UV-visible spectroscopic study show a decrease in the optical absorption and a shift in absorption edge towards higher wavelength with increasing fluence indicating a decrease in band gap. The FTIR analysis shows a dramatic increase in absorbance in the wavelength regions from 3600-2800 cm⁻¹ which may be ascribed to the oxidative degradation of the polymer and the increase in the absorption in the range of 2000-1500 cm⁻¹ indicating about the possibility of double bond formation.

KEY WORDS: Polymer film PVDF, lithium ion irradiation, UV-Visible and FTIR spectroscopy.

INTRODUCTION

The non-equilibrium processes associated with ion-solid interactions offer a great potential to modify polymer materials. Recent progress in ion beam synthesis and processing has allowed the development of advanced materials with properties designed and tailored specifically for their applications.

In the past, radiation effects have been the subject of intense investigation in radiation chemistry, mainly to understand the radiolysis and polymerization mechanisms induced by

ionizing radiation such as e-beam and γ -rays¹. However the work in past two decades showed that materials' response to high energy ion-beams was quite different from those induced by e-beam and γ -rays. In that work, it was established that cross-linking or scission efficiency depends not only upon polymer structure but also upon the characteristics of the radiation source, namely ion energy and species.

In the present work we have chosen an important polymer, poly vinylidene fluoride (PVDF), which is a semi-crystalline plastics

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with a melting point of about 160°C. It has good mechanical properties and resists distortion and creep at both high and low temperatures. It has very good weatherability and chemical and solvent resistance. The PVDF polymer can be used as coating, gasketing and wire - and cable-jacketing material, and in piping, molded and lined tanks, pumps and valves in the chemical and nuclear power industries. Therefore the study of optical and chemical behaviour after irradiation is important in view of academic interest and practical applications.

The optical spectra arise when molecules undergo transitions between quantum states corresponding to two different internal energies. The infra-red frequency in the wave-length range 1-50µm is associated with molecular vibration and vibration-rotation spectra². The Raman effect results when the frequency of visible light is altered in the scattering process by the absorption or emission of energy produced by changes in molecular vibration and vibration-rotation quantum state. The use of polymers in most diverse fields like industry, agriculture³, sensorics^{4,5}, microelectronics⁶ and even in nanotechnology^{6,7} is increasing at a fast pace.

Ion beam treatment of polymers has been found to produce, under appropriate conditions, useful improvements in their physical properties. Increase in hardness, strength, wear resistance⁸⁻¹¹, electrical conductivity¹²⁻¹⁴ and improvements in the optical transmission properties of polymers have been reported¹⁵; such improved polymers may be used as substitutes for metals, alloys and glasses, while retaining the inherent advantages of polymers such as light weight, moldability, and corrosion resistance. Concerning the high energy ion irradiation of polymers, the energy transferred onto the electrons related to the so-called electronic energy loss of the incident particle is released into: (i) radiative decay, (ii) production of new reactive species (radicals, gases) and defects (unsaturations, scissions, crosslinks), and (iii) heat¹⁶.

The radial expansion of the energy by the ejected electrons around the ion path is responsible for chemical modification of polymers. In the low dose regime, the radiation chemistry of the PVDF [CH₂-CF₂]_n has been extensively studied under electron and gamma rays irradiation¹⁷⁻²² and more recently under high energy ion irradiation²³⁻²⁷.

EXPERIMENTAL

The semi-crystalline PVDF polymer specimens in the form of flat, polished sheet of thickness 250µm and density of 1.79 g.cm⁻³, having upper working temperature of 135-150°C, were imported from UK (M/S Goodfellow). When heated above 400°C, PVDF can decompose to give highly toxic fumes of HF and F₂. The samples for irradiation were prepared in the size of 1 cm × 1 cm. They were used in as-received conditions without any further treatment. Three identical samples were mounted on a vertical vacuum-shielded sliding ladder and irradiated in general purpose scattering chamber using 50 MeV ⁷Li⁺³ ion beam available from the 15 UD Pelletron at the Nuclear Science Centre (NSC), New Delhi. The ion beam fluence was varied in the range of 1.27 × 10¹¹ to 2.15 × 10¹³ ions cm⁻². In order to expose the whole target area, beam was scanned in the x-y plane. The ion beam energy and the thickness of the target were chosen so that only the modification due to the electronic energy loss affected the exposed sample. The nature of optical and chemical modifications has been analyzed after one year of irradiation using UV-visible spectrophotometer (UV-1601 PC-Shimadzu) in the range of 200-600 nm and Fourier transform infrared spectroscopy (FTIR-8300 Shimadzu). All the measurements have been carried out at the ambient temperature between 22-25°C.

RESULTS AND DISCUSSION

The range of 50 MeV ⁷Li⁺³ ion beams in the poly (vinylidene fluoride) was calculated to be 351.26µm using the SRIM-97 code²⁸, which is 1.4 times the thickness of PVDF samples. The electronic energy loss is dominant for ions with high energy and involves the energy transfer to atoms in the target due to inelastic electron-electron interaction. Collision processes produce lattice vibration and the displacement of the target atoms. Displacement damage is usually considered to be the most important cause of material modification in sol-

ids. The SRIM-97 code indicates that 99.95% of energy lost by 50 MeV $^7\text{Li}^{+3}$ ion in 250 μm thick PVDF is electronic in nature. The electronic stopping power of the beam, $(dE/dx)_e$, is 8.387 eV/ \AA and the energy deposited in the medium comes out to be 40.8 MeV.

Ultraviolet-visible (UV-vis) spectroscopy, which gives us an idea about the value of band-gap (E_g), is thus an important tool for investigation. Fig. 1(a-d) shows the optical absorption behavior of the virgin and irradiated PVDF polymer samples at the fluence of 1.27×10^{11} , 1.45×10^{12} and 2.15×10^{13} ions/ cm^2 respectively. It is clear from the observation that the absorption decreases with increasing fluence which may be attributed to scission of the polymer chain. A shift in the absorption edge (λ_g) towards higher wavelength by 15.8 nm indicates the decrease in bandgap energy of the polymer samples. The quantitative value of the irradiation doses deposited in PVDF at three different fluences and energy bandgap

for the virgin and irradiated samples are given in Table 1.

TABLE 1. Quantitative Values of Absorbed Dose and Decrease in Bandgap Energy

Irradiation fluence (ions/ cm^2)	Irradiation deposited dose (Joules)	Absorption edge (λ_g) (nm)	Bandgap energy (eV)
0	0	228.9	5.42
1.27×10^{11}	0.82	231.6	5.36
1.45×10^{12}	9.40	236.8	5.34
2.15×10^{13}	140.25	244.7	5.07

Fig. 2 shows the variation of absorbance with fluence on a log-scale at two different characteristic wavelengths, 361nm and 301nm, respectively. It is clear from the plots that absorption is maximum at 361 nm. The decrease in absorption with increasing fluence may be correlated to the scission (degradation) of the polymer chains.

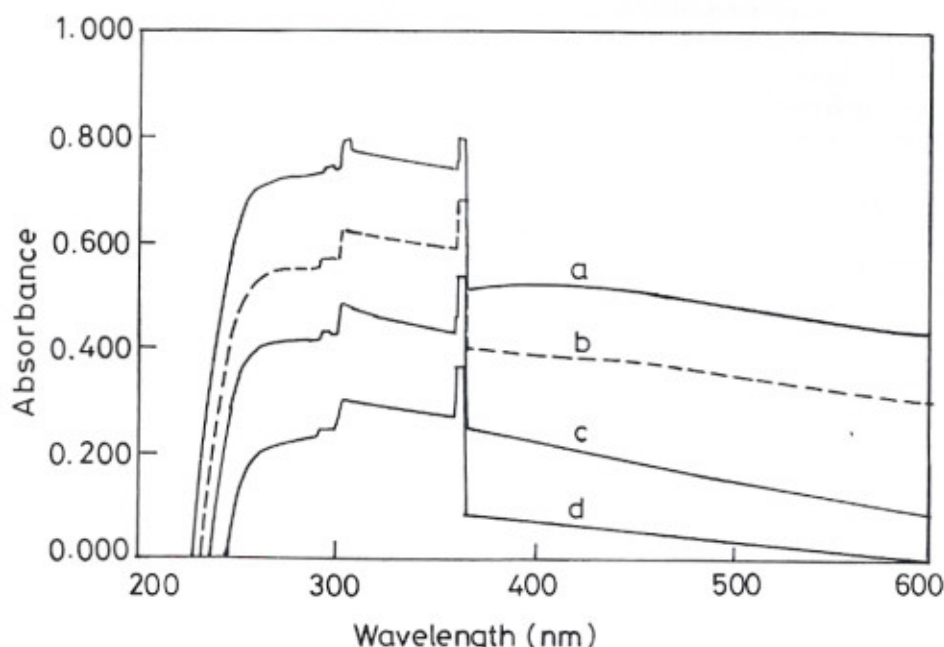


Fig. 1. Optical absorption spectra of (a) PVDF virgin sample, and (b-d) of the PVDF samples irradiated with a 50 MeV $^7\text{Li}^{+3}$ ion beam at the fluences of 1.27×10^{11} , 1.45×10^{12} and 2.15×10^{13} ions cm^{-2} , respectively.

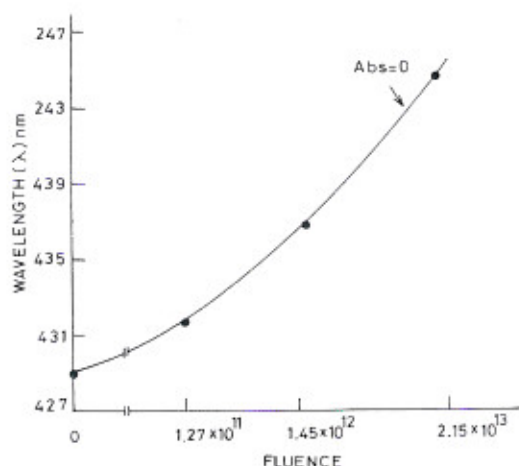


Fig. 2. Variation in absorbance with irradiation fluence at two characteristic wave-lengths (a) 361nm and (b) 301nm.

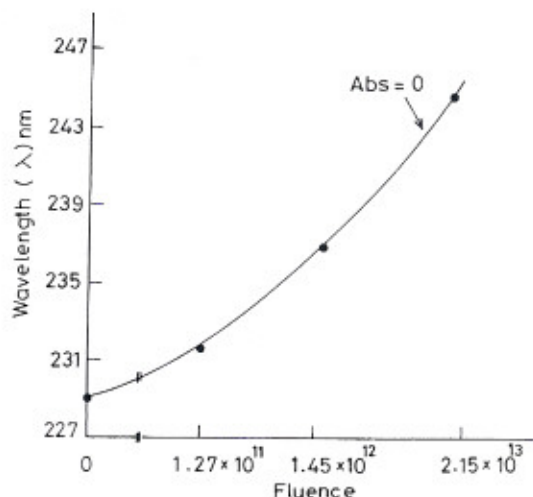


Fig. 3. Shift variation of absorption edge wavelength (λ_g) with irradiation fluence.

Fig. 3 reports the shift of absorption-edge with fluence on a log-scale, indicating that the absorption-edge approaches towards the higher wavelength with increasing fluence which is responsible for the decrease in the bandgap energy of the irradiated PVDF polymer samples. At the fluence of 2.15×10^{13} ions/cm² a light yellowish colour formation has been observed in the polymer due to irradiation. Fig. 4(a, b) shows the FTIR spectra in the range 400-500 cm⁻¹ of the virgin and one of the irradiated PVDF polymer samples at the fluence of 2.15×10^{13} ions/cm². The chemical bonds of the polymers can be studied through the characterization of the vibration modes by infrared spectroscopy. In the case of unirradiated sample the asymmetric and symmetric stretching vibrations of the CH₂ group in the PVDF sample are located, respectively, at 3025 cm⁻¹ and 2985 cm⁻¹; the 2000-1500 cm⁻¹ range is the double-bond stretching vibration zone. Fig. 4b shows the modification of the 3400-3000 cm⁻¹ zone due to irradiation. The increase in the absorption in the range of 2000-1500 cm⁻¹ indicates the possibility of double bond formation. A dramatic increase in the absorbance in the wavelength region from 3600 cm⁻¹ to 2800 cm⁻¹ due to irradiation indicates the oxidative

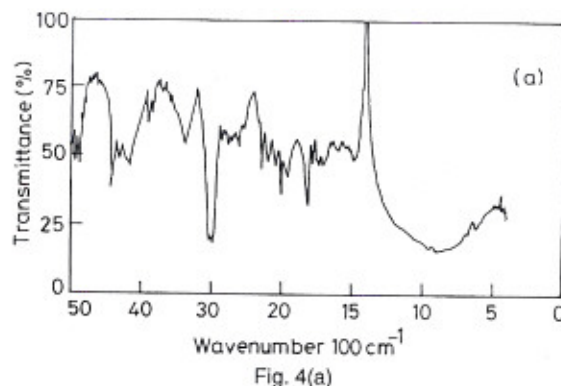


Fig. 4(a)

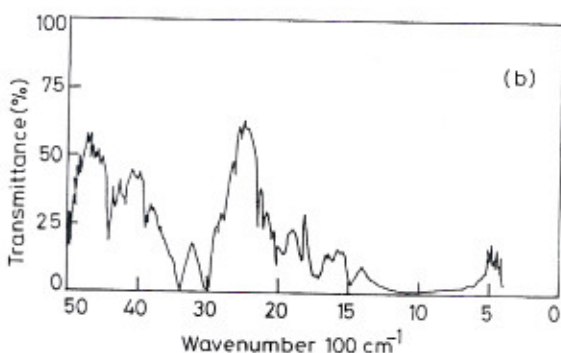


Fig. 4(b)

Fig. 4. FTIR spectra of (a) PVDF virgin sample and (b) the irradiated sample using a 50 MeV ⁷Li³⁺ ion beam at fluence of 2.15×10^{13} ions cm⁻².

degradation of PVDF polymer where C-H and O-H stretching vibrations of different types of H-bonds occur.

CONCLUSION

Due to irradiation, the decrease in the optical absorption along all the wavelengths can be correlated to the scission of polymeric chain. As the dose increases, the absorption edge shifts towards the higher wavelength, resulting in decrease of the bandgap in the irradiated samples. The FTIR analysis indicates the possibility of formation of double bonds and oxidative degradation of the polymer. Light yellow colour formation is due to trapped free radicals or charge species in the polymer medium.

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