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STUDY OF RADIATION INDUCED CHANGES IN PVDF POLYMER

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ABSTARCT

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/cm^2. The post irradiation effect has been analysed using UV- visible and FTIR spectroscopic techniques. The results of UV- visible spectroscopic study shows a decrease in the optical absorption and a shift in absorption edge towards higher wavelength with increasing fluence indication 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 WORD: Polymer film PVDF,Lithium ion irradiation,UV- Visible , FTIF spectroscopy

Polymers have proven their potential in all fields of life and specially in the fields of medical science, electronics and space research. PVDF is a widely studied semicrystalline polymer due to its piezoelectric, pyroelectric and ferroelectric properties. PVDF $[-CH_2-CF_2-]_n$ occurs in at least four different polymorphs nonpolar α- phase and polar β,γ and δ-phases.α-phase is more homogeneous. This enables it to be stable in nature and is nonpolarized because of mixed positive and negative charges. PVDF can form a different crystal depending on the condition of the crystallization. When PVDF is cooled from the melt, the crystalline phase formed is the non-polar α- phase with TGTG conformation. The β- phase crystal has all trans (TTTT) conformation that results in the most polar phase among other crystals. The γ- phase has the similar structure to β- phase crystal, however slightly different (TTGTTG) conformation. These crystals structures play a vital role tric field produces the polarization in the PVDF film due to alignment of hydrogen and fluorine ions according to their respective electrical polarities. The formation of these aligned dipoles can be accounted quite well for the observed piezoelectric and pyroelectric behaviour of the polymer (Arya et al .,2009) .

Irradiation causes the photons to penetrate the material, breaking the polymer chains and creating free redicals. These free redicals can also recombined to create crosslinks between adjacent molecule. Crosslinked material improved the long term performance. Different studies of effect of ion irradiation on polymer, reveal a variety of modification of structural and chemicals compositions including processes such as main chain scission, intermolecular crosslinking, creation of unsaturated bonds, formation of volatile fragments and creation of carbonaceous clusters. The PVDF films as well as there intrinsic physical properties, have been the subject of numerous publication . It has been commonly observed that the intrinsic physical and chemical properties of un-irradiated polymer films, slowly change with a time due to natural aging and finite permeability of polymer to various atmospheric gases(Dyer ,1994; Mott and Davis, 1979 and Spohr,1990).

For ion beam irradiation the following aspects are well established: (1) energy loss (dE/dx) by charge particle in the material medium is differential in nature and hence energy deposited is non-homogeneous in nature. (2) It is confined to the beam diameter only. However, the gamma irradiation have been found to have the ability to expose the whole area of the sample and hence expected to create homogeneous modification in it. These aspects attracted our attention to carry out a detail investigation of the effect (optical and chemical) of 50 MeV lithium ion irradiation on PVDF polymer.

EXPERIMENTAL

The semi-crystalline PVDF polymer specimens in the form of flat, polished sheet of thickness 250μm and

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density of 1.79 g.cm^{-3}, having upper working temperature of 135-150^{0}C, were imported from UK (M/S Goodfellow). When heated above 400^{0}C, PVDF can decompose to give highly toxic fumes of HF & F. The samples for irradiation were prepared in the size of 1cm×1cm. They were used in as- received condition without and 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 1.27×10^{11} to 2.15×10^{13} ions cm^{-2}. In order to expose the whole target area, beam was scanned in th 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 modification has been analyzed after one year of irradiation by using UV-visible spectrophotometer (UV-1601 PC-Shimadzu) in the range of 200-600nm and fourier transform infrared spectroscopy (FTIR- 8300 Shimadzu). All the measurements have been carried out at the ambient temperature between 22-25^{0}C.

RESULTS AND DISCUSSION

The range of 50 MeV $^7Li^{+3}$ ion beams in the PVDF was calculated to be 351.26μm using the SRIM-97 code, which is 1.4 times the thickness of PVDF samples (Ziegler, 1997). 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 solids. The SRIM-97 code indicates that 99.95% of energy lost by 50 MeV $^7Li^{+3}$ ion in 250 μm thick PVDF is electronic in nature.The electronic stopping power of the beam,$(dE/dx)_e$, is 8.387 eV/Å and the energy deposited in the medium comes out to be 40.8 MeV.

Ultraviolet-visible (UV-vis) spectroscopy, which gives us and idea about the value of band-gap (E_g), is thus an important tool for investigation. Figure1 shows the optical absorption behaviour 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 scissioning of the polymer chain. A shift in the absorption edge (λ_g) towards higher wave length by 15.8 nm, indicates the decrease in band gap energy of the polymer samples. The quantitative value of the irradiation doses deposited in PVDF at three different fluences and energy band gap for the virgin and irradiated samples are given in the table-1.

Figure 2 shows the variation of obsorbance with fluence on a log-scale at two different characteristics wave-length, 361 nm and 301 nm, respectively. It is clear from the plots that absorption is maximum at 361 nm. The decrease in absorption with increasing fluence may be correlated two the scissioning (degradation) of the polymer change.

Figure 3 reports the shift of absorption-edge with fluence on a log-scale, indicating that the absorption-edge is shifting towards the higher wave-length with increasing fluence which is responsible for the decrease in the band gap energy of the irradiated PVDF polymer samples. At the fluence 2.15×10^{13} ions/cm^2 a light yellowish colour formation has been observed in the polymer due to irradiation. Figure 4(a,b) shows the FTIR spectra in the range of 4000-500 cm^{-1} of the virgin and one of the irradiated PVDF polymer sample at the fluence of 2.15×10^{13} ions/cm$^{2.}$. The chemical bond 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 CH_2 group in the PVDF sample are located, respectively at 3025 cm^{-1} and 2985 cm^{-1}; the 2000-1500 cm^{-1} range iss the double-bond stretching vibration zone. Figure 4(b) shows the modification of the 3400-3000 cm^{-1} zone due to irradiation. The increase in the absorption in the range of 2000-15000 cm^{-1} is indicating about 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 about the oxidative 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 scissioning of polymeric chain.As the dose increase, the absorption edge shifts to wards the higher wave length, resulting in decrease of band gap in the irradiated samples. The FTIR analysis indicates about the possibility of formation of double bond and oxidative degradation of the polymer. Light yellow colour formation is duo to trapped free radicals or charge species in the polymer medium.

Table 1: Quantitative values of absorbed does and decrease in band gap energy

Irradiation fluence (ions/cm^{-2})	Irradiation deposited dos (Joules)	Absorption edge (λ_g) (nm)	Band –gap 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

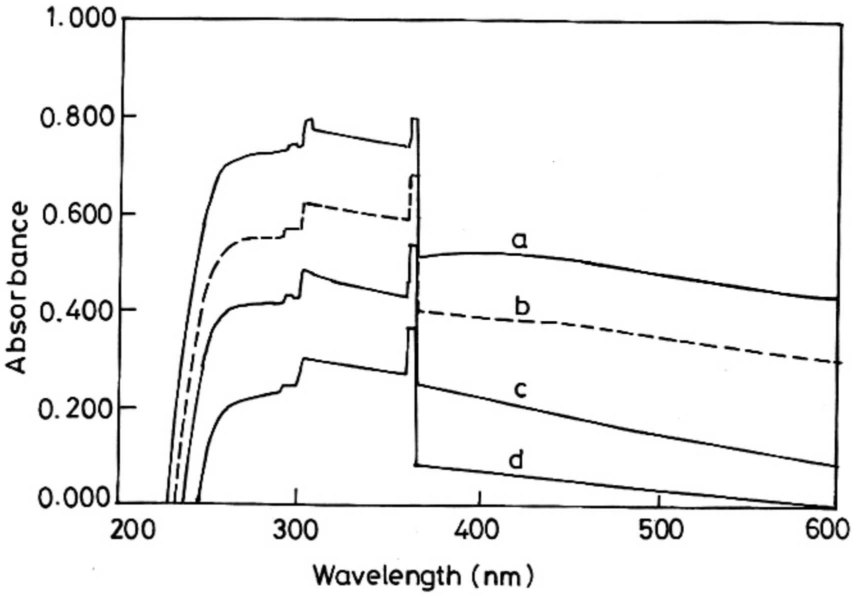

Figure 1: With a 50 MeV $^7Li^+$. Optical absorption spectra of (a) PVDF virgin sample, and (b-d) of the PVDF samples irradiated ^{3} ion at the fluencies of 1.27 ×10^{11}1.45×10^{12} and 2.15×10^{13} ions cm^{-2}

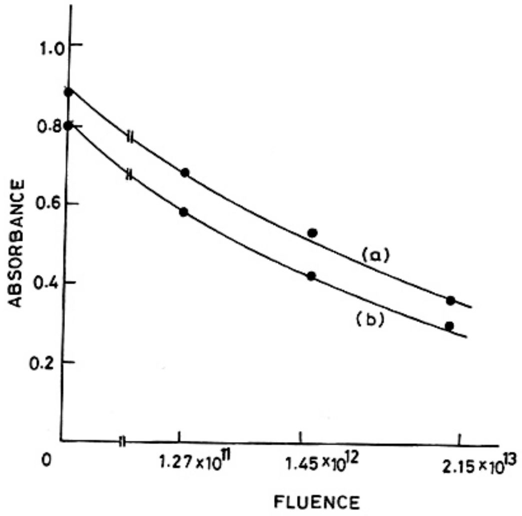

Figure 2: Variation in absorbance with irradiation fluence at two characteristics wave-lengths(a)361nm and (b) 301nm

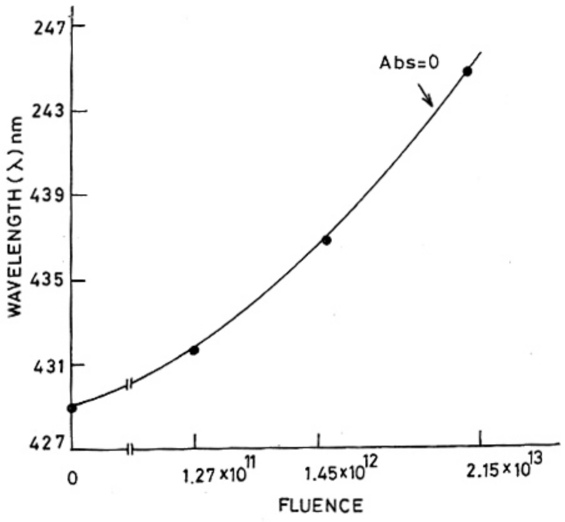

Figure 3: Shift Variation of absorption edge wavelength (λ_g) with irradiation fluence

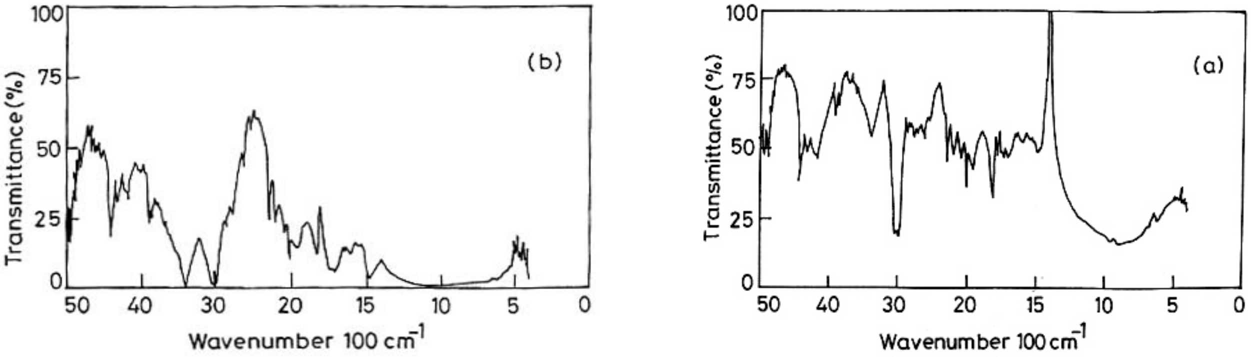

Figure 4: FTIR spectra of (a) PVDF virgin sample and (b) the irradiated sample using a 50 MeV $^7Li^{+3}$ ion beam at fluence of 2.15×10^{13} ions cm^{-2}

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