

1.25mev Gamma Irradiated Induced Physical and Chemical Changes in Poly Vinylidene Fluoride (PVDF) Polymer

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Abstract-Physical and chemical changes induced in poly vinylidene fluoride (PVDF) polymer by 1.25 MeV gamma radiations have been investigated. These changes were studied for the optical and chemical response using UV-VIS and FTIR techniques respectively. In this paper, we have studied the optical and chemical properties of virgin and gamma irradiated PVDF polymer samples in the dose range from 500 to 2000 kGy. The optical study of polymer samples shows a gradual increase in the absorption edge from 280 to 400 nm with increasing gamma dose. Further, the direct energy band gap (E_g) found to be decreased at higher dose. The recorded UV-visible spectra clearly show two characteristic peaks at 320 and 360 nm in the pristine sample. However, in irradiated samples the position of the peaks is shifted slightly, their intensity decreases and finally disappears at 2000 kGy of higher dose. The direct energy band gap has been observed in PVDF polymer samples. In the FTIR spectra, an appreciable change in peak intensity and broadening of peaks has been observed due to irradiation. The development of a new peak at 1700 cm^{-1} indicates the evolution of the HF group during irradiation.

Keywords-Gamma Radiation; PVDF (Polymer); Optical Properties; FTIR Analysis

I. INTRODUCTION

Poly vinylidene fluoride is a semi crystalline polymer, which has drawn both scientific and technological attention because of their useful pyroelectric, piezoelectric and ferroelectric properties. PVDF $[-\text{CH}_2-\text{CF}_2-]_n$ is an acid resistant and chemically inert polymer because of these properties it is widely used for fine separation processes, such as micro-filtration and ultra-filtration [1, 2]. As a result of its good biocompatibility, PVDF membranes also find potential applications in biomedical area [3, 4].

PVDF has also acquired immense importance in scientific and technological research because of its excellent mechanical, pyroelectric, ferroelectric, and piezoelectric properties. PVDF is a semi crystalline polymer in which each monomer unit (CH_2-CF_2) has a spacing of 2.6 \AA with two dipole moments, one due to CF_2 and the other due to CH_2 . It exhibits a variety of molecular conformations and crystalline phases such as α , β , γ , σ and ϵ [5]. The α -phase comprises helical structure whereas β -phase possesses all-trans planar zigzag conformation with dipole moments perpendicular to the chain axis, and the γ -phase with a structure intermediate to the helical α - and zigzag β -phases [4].

The β -phase and sometimes the γ -phase can undergo reversible changes in polarization to create high piezoelectric and pyroelectric activity, which make PVDF as a very useful material in electronic activity, such as electromechanical, electro-acoustic transducers, and actuators [6-9]. The light weight and chemical resistance of PVDF polymers promote their use for the development of micro sensors and actuators for space applications. Sensors are widely used in space research and structural health-monitoring systems [10]. The interaction of these radiations can change the physical, chemical, optical, structural, and morphological properties of polymeric material.

From both scientific and technological points of view, it is highly desirable to have PVDF-based ferroelectric polymer films with feature size down to micro- or nanometre scale. This would not only allow us to probe ferroelectricity and ferroelectric phase transition in one and even zero dimensions but also enable to micro and nanoscale ferroelectric arrays for various application [11]. The improved polymers may be used as substitutes for metals, alloys and glasses, while retaining the inherent advantages such as light weight, moldability, and corrosion resistance [12].

Gamma irradiation causes the photons to penetrate in to the material, breaks the polymer chains and creates free radicals. These radicals are responsible for the chemical transformations observed in the most of polymers. These free radicals can also recombine to create cross links between adjacent molecules. The study of the effects of gamma radiation on polymers reveals about the structural and chemical modifications through processes such as chain scission, intermolecular cross linking, creation of unsaturated bonds, formation of volatile fragments and creation of carbonaceous clusters [13-15].

In this article we report on the investigations of physical and chemical responses of 1.25 MeV gamma irradiated (PVDF) polymer samples. We carried out these investigations using UV-visible and FTIR spectroscopy techniques.

II. EXPERIMENTAL DETAILS

The semi-crystalline pure research grade Poly vinylidene fluoride (PVDF) sheet of thickness 80 μm was imported from MS Good fellow (UK). The polymer samples of size 1 x 1 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 in vacuum at the atmospheric pressure of 10^{-3} torr and the ambient temperature, using 1.25 MeV Gamma radiation source of Co^{60} in the radiation chamber (which is in a form of cylindrical chamber of 14 cm length and 10 cm diameter) with dose rate of 4 kGy/h and source strength 2K Curie at UGC-DAE Consortium for Scientific Research, Kolkata Centre, Kolkata.

The irradiated samples were characterized by using analytical techniques like UV-VIS and FTIR spectroscopy, to observe the possible modifications that could take place in the PVDF polymer by irradiation. The UV-Visible absorption spectra of virgin and high dose γ -irradiated PVDF polymer samples were studied by using UV-Visible spectrophotometer (JASCO, V-530) in the wavelength range of 190-900 nm. All the spectra were recorded by mounting the samples in the integrating sphere assembly attached to the spectrometer, keeping air as the reference.

Chemical changes of the PVDF polymer were evaluated using Perkin Elmer, Fourier transform infrared (FTIR) spectrophotometer, Model 1720 with 0.5 wave number resolution in the range (4300 – 500 cm^{-1}).

III. RESULT AND DISCUSSION

A. Optical Properties

The UV-visible absorption spectroscopy technique is used for the investigation of optical properties of the PVDF polymer samples in the wavelength range 190–800 nm. The UV-visible spectra of pristine sample and gamma irradiated polymer samples are shown in Fig.1 (a-e). The absorption of light energy by polymeric materials in the ultra violet and visible region involves the promotion of electrons in σ , π and n-orbitals from the ground state to higher energy state [16]. The optical absorption spectrum of the virgin sample in Fig. 1(a) shows that the absorption decreases sharply from 190 nm to 220 nm and then decreases gradually up to 320 nm. In between 320 nm and 360 nm, two distinct characteristics peaks are observed which may be correlated with electronic transition occurring in fluorocarbon (CF). After 360 nm the optical absorption decreases linearly at higher wavelength.

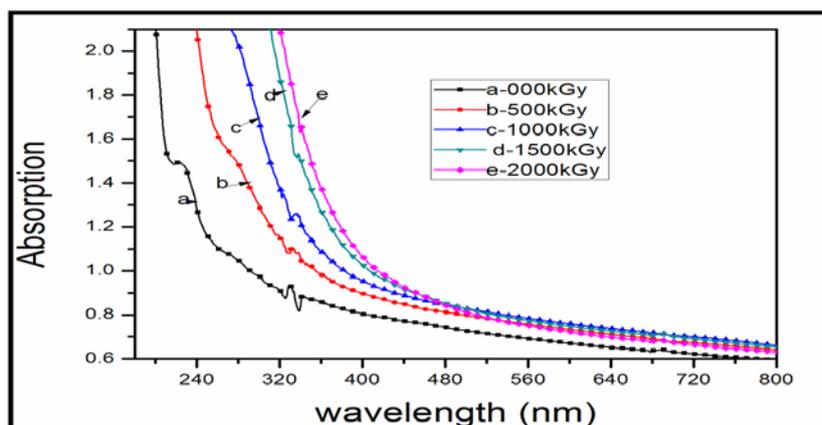


Fig. 1 UV/VIS spectra of virgin and gamma irradiated PVDF polymer samples

The relationship between optical absorption coefficient $\alpha(h\nu)$ and incident photon energy is given by Davis and Mott.

$$\alpha(h\nu) = \frac{B(h\nu - E_g)^n}{h\nu} \quad (1)$$

where h is the Planck's constant, ν the frequency of the radiation used, B a constant, E_g the value of the optical energy band gap between the valance band and the conduction band, n the power which characterizes the electronic transition, whether it is a direct or an indirect transition during the absorption process in the k -space.

It is well known that many molecules contain electrons that are not directly involved in bonding, e.g. the compounds containing fluorine, chlorine, nitrogen and oxygen etc. are capable of showing these types of characteristic absorptions due to the transition of non bonding electrons [11]. However, the deformation of polymer structure by gamma radiation leads to the formation of multiple bonds (C=C) due to the breaking of lateral bonds (C-F and C-H) and desparation of volatile spices such as H_2 , HF and F_2 in the PVDF polymer. It may also be due to the multiple phases (α , β , γ) found in un-irradiated (α -phase) and irradiated (β and γ -phases) [17]. Fig. 1 (b-e) shows the optical absorption spectra of gamma irradiated samples at dose level 500, 1000, 1500 and 2000 kGy, respectively. It has been observed that due to irradiation up to the dose level of 2000 kGy, there is a systematic increase in the optical absorption at lower range of wavelength. The size of the distinct characteristic peaks is found to be decreases with increasing gamma dose and finally the peaks disappear at higher dose. A gradual increase in the

optical absorption with increasing dose has been observed in UV-Visible region(190–800 nm). This change is observed due to transition from $n \rightarrow \sigma^*$ orbitals, occurring as a result of single bond between carbon and fluorine present in the PVDF polymer [17].

B. Determination of Band Gap

From the UV-Visible spectra, we determined the direct optical energy band gap of virgin and gamma irradiated PVDF polymer samples. To the best of our knowledge the direct energy band gap in PVDF polymer has been observed for the first time as no such report was found in literature survey. However, the indirect energy band gap has been found to be reported in Literature [17].

For the determination of direct energy band gap $(\alpha h\nu)^2$ was plotted as a function of photon energy $(h\nu)$ (Tauc Plot). The value of the energy band gap was determined by taking the intercept on $h\nu$ -axis. Fig. 2 (a-e) shows the variation of $(\alpha h\nu)^2$ with $(h\nu)$ for virgin and gamma irradiated PVDF polymer samples. From the intercept of the best fit lines on $h\nu$ axis, direct energy band gap was calculated for virgin and gamma irradiated PVDF polymer samples and the results are presented in Table 1. It is observed that the value of optical direct band gap decreases from 2.06 eV to 1.87 eV with increasing gamma radiation dose in PVDF polymer samples. The results indicate that the radiation produces faults in PVDF polymer structure (band, rupture free radical, etc.) which in turn increase the electronic disorder. The variation of the direct energy band gaps with the irradiation dose is also shown in Fig. 3

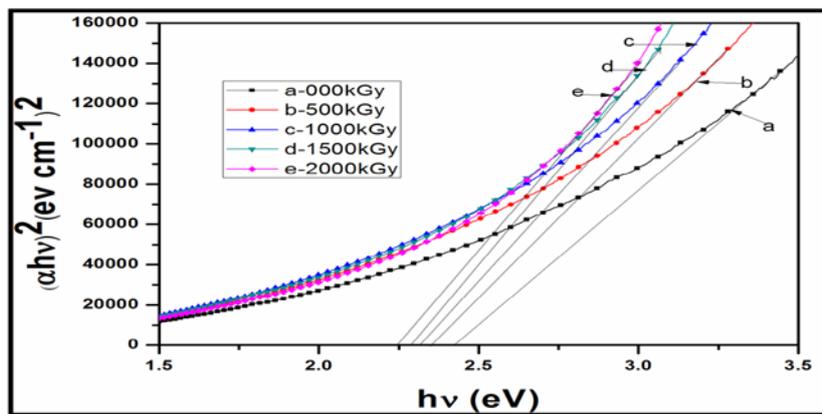


Fig. 2 The dependence of $(\alpha h\nu)^2$ on photon energy $(h\nu)$ for virgin and gamma irradiated PVDF polymer samples

TABLE THE VARIATION OF THE DIRECT ENERGY BAND GAP IN PVDF AND THE NUMBER OF CARBON ATOMS (N) IN A CLUSTER WITH DOSE

γ -radiation dose (kGy)	Direct Band Gap Energy (eV)	No. of carbon atom (N) in cluster
Virgin	2.06	8.79
500	2.01	9.01
1000	1.92	9.43
1500	1.91	9.48
2000	1.87	9.68

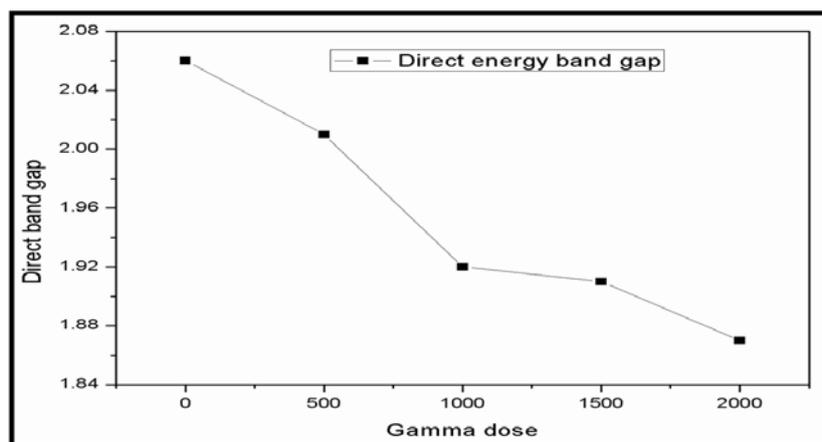


Fig. 3 Plot for direct band gap and gamma dose used for irradiation

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.

$$N = 2\beta\pi / E_g \tag{2}$$

where 2β is the band structure energy of a pair of adjacent π sites and the value of β is taken to be ≈ 2.9 eV as it is associated with $\pi \rightarrow \pi^*$ optical transitions in $-\text{C}=\text{C}-$ structure. The results are presented Table 1. These shows an increase in the value of (N) for PVDF polymer, which consequently implies that the crystallinity increases with the increasing dose.

The optical photographs of virgin and irradiated PVDF polymer samples are shown in Fig. 4. It indicates that this polymer became brittle after irradiation and this property increases with increasing dose. The brittleness is a significant property considered in product design and development of materials. Upon irradiation, the transparent PVDF polymer became yellow and the degree of yellowness was found to be increasing with increasing gamma irradiation dose. The samples are arranged in increasing order of doses (0,500, 1000, 1500 and 2000 kGy) from left to right.

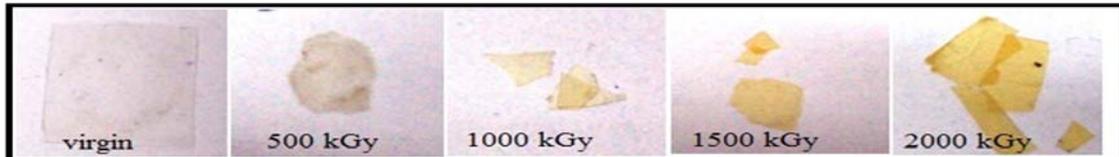


Fig. 4 Optical photograph of PVDF polymer samples

C. Fourier Transforms Infrared (FTIR) Studies

The FTIR spectra of virgin and irradiated PVDF polymer samples are shown in Fig. 5 (a-e). A strong absorption band is observed corresponding to the symmetric stretching vibration and asymmetric stretching vibration of the CH_2 groups located at 2990 cm^{-1} and 3020 cm^{-1} in the PVDF virgin sample [10, 16].

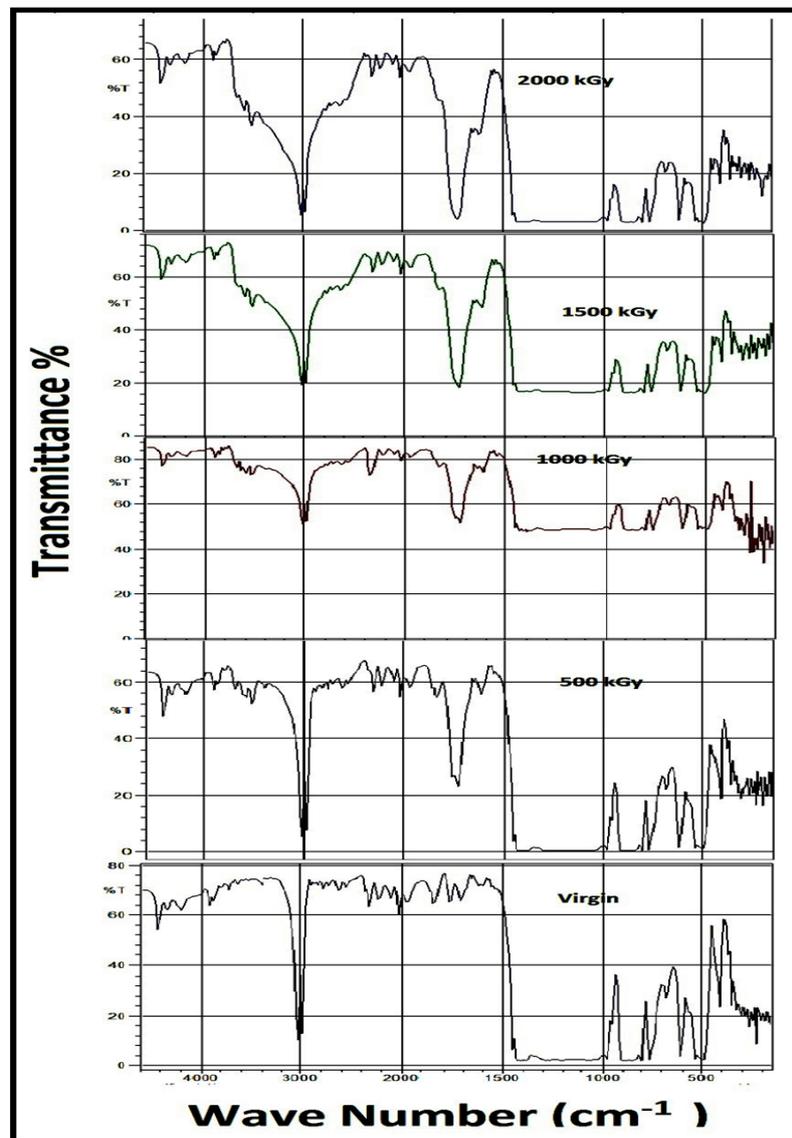


Fig. 5 FTIR spectra of virgin and gamma irradiated PVDF polymer samples

The FTIR spectra of gamma irradiated PVDF samples are shown in Fig. 5 (b-e). They correspond to the dose level of 500, 1000, 1500 and 2000 kGy, respectively. From these spectra of the irradiated PVDF polymer, we observe no appreciable change at dose 500 kGy. However, a new band appears at 1700 cm^{-1} due to the C=C stretching vibration [18]. The increase in absorption and broadening of new band indicates the possibility of evolution of HF bond. Conjugated double bonds are responsible for its broadening at higher dose towards the lower frequency side. The increase in overall absorption and the broadening of new band are enhanced with the increase of irradiation dose [14]. The constant absorption region in the FTIR spectra of PVDF from 1440 cm^{-1} to 1000 cm^{-1} corresponds to fluorocarbon absorption. The constant absorption band in the range 1440 cm^{-1} to 1000 cm^{-1} is important because it shows the changes produced by the irradiation corresponding to transformation from α -phase to β and γ -phases. Further, by increasing the gamma radiation dose, the transmittance bands are found to shift upwards indicating that intensity of bands increases with increasing irradiation dose.

IV. CONCLUSION

Modifications induced in PVDF polymer samples under 1.25 MeV gamma radiations (0-2000kGy) source of Co^{60} have been studied by using two techniques, UV-Visible and FTIR spectroscopy and following conclusions have been drawn.

The optical absorption increases with increasing gamma dose. Two distinct characteristics peaks were observed between 320–360 nm in the virgin sample. The size of the peaks was found to decrease and finally disappear with increasing gamma irradiation dose.

The direct energy band gap has been reported for the first time in the PVDF polymer to the best of our knowledge. In FTIR spectra we observe the development of new band at 1700 cm^{-1} . It confirms the evolution of the HF group during irradiation. The FTIR observation reveals that the destruction of CH_2 groups occurs due to the irradiation and there is possibility of formation of conjugate double bonds. These conjugated double bonds are responsible for the broadening of the new band at higher dose. The optical photograph shows the increases in the degree of brittleness and yellowness after irradiation.

REFERENCES

- [1] C.Gull, R.H. Davis, Membrane fouling during microfiltration of protein mixtures. *J. Membr. Sci.* 119 (1996) 269–284.
- [2] A. Bottino, G. Capannelli, O. Monticelli, P. Piaggio, Poly (vinylidene fluoride) with improved functionalization for membrane production. *J. Membr. Sci.* 166 (2000) 23–29.
- [3] V. Guenard, R.F. Valentini, P. Aebischer, Influence of surface texture of polymeric sheets on peripheral nerve regeneration in a two-compartment guidance system. *Biomaterials* 12(1991) 259–263.
- [4] H.F. Lu Lu, W.S. Lim, J. Wang, Z.Q. Tang, P.C. Zhang, K.W. Leong, S.M. Chia, H. Yu, H.Q. Mao, Galactosylated PVDF membrane promotes hepatocyte attachment (2003).
- [5] G. T. Davis, piezoelectric polymer transducers. Institute for Materials Science and Engineering, National Bureau of Standards, Gaithersburg, (1987) 45-49.
- [6] H. J.Kawai, *J. Appl. Phys.* 8 (1969) 975–976.
- [7] Q. Gao, J.I. Scheinbeim, dipolar Intermolecular Interactions, Structural Development, and Electromechanical Properties in Ferroelectric Polymer Blends of Nylon-11 and Poly(vinylidene fluoride). *Macromolecules* 33(2000) 7564–7572.
- [8] M. Benz, W.B. Euler, Determination of the Crystalline Phases of Poly (vinylidene fluoride) Under Different Preparation Conditions Using Differential Scanning Calorimetry and Infrared Spectroscopy, *J. Appl. Polym. Sci.* 89(2003) 1093–1100.
- [9] A. Nandi, L. Mandelkern, the Influence of Chain Structure on the Equilibrium Melting Temperature of (PVDF). *J. Polym.* 29 (2006) 287–1297.
- [10] B. Lin, and V. Giurgiutiu, Modeling and testing of PZT and PVDF piezoelectric wafer active sensors. *Smart Mater. Struct.* 15 (2006) 1085–1093. Melting Temperature of Poly (vinylidene fluoride). *J. Polym.* 29 (2006) 287–1297.
- [11] M.A. Doverspike, M.S. Conradi, Deuterium Magnetic Resonance Study of orientation and Poling in Polyvinylidene Fluoride and Poly (vinylidene-fluoride-co-tetrafluoroethylene), *J. Appl. Phys.* 65(1989) 541–547.
- [12] L. Calcagno, P. Musumeci, R. Percolla, G. Foti, Changes in the Physical and Chemical Properties of PVDF Irradiated by 4 MeV Protons, *Nucl. Instr. And Meth. B* 91(1994) 461–464.
- [13] Lei Zhang, Stephen, Ducharme, Li. Jiangyu, Microimprinting and ferroelectric properties of poly(vinylidene fluoride -trifluoroethylene copolymer films applied physics letters 91(2007) 172906 -172909.
- [14] A.K. Srivastava, H.S. Virk, 50MeV lithium ion beam irradiation effects in poly vinylidene fluoride (PVDF) polymer. *Bull. Mater. Sci.*, 23(2000) 533– 538.
- [15] D.R. Fink, L.T. Klett, J. Chadderton, R. Cardosa, M.H. Montiel, A. Vazquez, Karanovich, Carbonaceous clusters in irradiated polymers as revealed by small angle X-ray scattering and ESR *Nucl. Instr. Meth. B* 111(1966) 303-314.
- [16] J.R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Prentice Hall Inc., NJ, USA (1994).
- [17] Aarya, Suveda, Siddhartha, A.K. Srivastava, A.Saha, M.A. Wahab, Effect of 1.25 MeV gamma irradiation in α -phased PVDF. *Nucl. Instr. and Meth. B* 267(2009) 3545–3548.
- [18] D. Fink, W.H. Chung, R. Klett, A. Schmoldt, J. Cardoso, R. Montiel, M.H. Vazquez, L. Wang, F. Hosoi, H. Omichi, P. Goppelt-Langer, Carbonaceous clusters in irradiated polymers as revealed by UV-Vis spectrometry. *Radiat. Eff. Def. Solids* 1339(1995) 193-208.
- [19] A.M. Guzman, J.D. Carlson, J.E. Bares, P.P. Pronko, Chemical and physical changes induced in polyvinylidene fluoride by irradiation with high energy ions *NIMB* 7-8(1985) 468-472.