

Physico-chemical modifications induced by 70 MeV carbon ions in alpha phased polyvinylidene fluoride (α -PVDF) polymer

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In the present paper, the physico-chemical changes induced by 70 MeV carbon ions ($^{12}\text{C}^{+5}$) have been investigated in PVDF using UV-Visible, FTIR, XRD and HFIA techniques. The induced changes have been studied with respect to their optical, chemical, structural and electrical response. The polymer samples have been irradiated in the ion fluence ranging from 1×10^{11} to 3×10^{12} ions cm^{-2} . The UV-visible spectra show that the optical absorption increases with increasing ion fluence. Two new dips at 482 nm and 654 nm were appeared in the irradiated sample which may be due to the fluorinated defects created due to irradiation. In the FTIR spectra, it was found that transmittance intensity decreases with increasing ion fluence in the range $1500\text{-}4000 \text{ cm}^{-1}$. The diffraction pattern of PVDF indicates that crystallinity decreases with increasing ion fluence but the crystallite size is found to increase due to carbon ion irradiation. The variation of dielectric constant and dielectric loss for virgin and irradiated films have been studied in the frequency range 10 mHz-10 MHz at ambient temperature. There is an exponential increase in ac conductivity with increasing frequency and the effect of irradiation is significant at higher fluence. The dielectric constant and dielectric loss changed significantly due to ion beam irradiation, meanwhile the frequency exponents decreased with increasing ion fluence. It was found that dielectric response in both virgin as well as irradiated samples obey the Jonscher's power law.

Keywords: $^{12}\text{C}^{+5}$ ions, UV-Vis spectra, XRD, FTIR, HFIA, Dielectric loss, Conductivity

1 Introduction

Polyvinylidene fluoride is a semi-crystalline polymer, which has drawn both scientific and technological attention because of their useful pyroelectric, piezoelectric and ferroelectric properties. PVDF $[-\text{CH}_2-\text{CF}_2-]_n$ exhibits at least five different crystalline phases; these different crystal structures include non-polar α -phase, polar β -, γ -, δ - and ϵ -phases. α -Phase is more homogeneous. This enables it to be stable in nature and is non-polarized because of mixed positive and negative charges. The strong electric moment in the PVDF monomer unit arises because of strong electric negativity of fluorine atoms as compared to those of hydrogen and carbon atoms. Thus, each chain possesses a dipole moment perpendicular to the polymer chain. If the polymer chains pack in crystals to form parallel dipoles, the net dipole moment vanishes as in non polar α - and ϵ -phases¹. 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 conformation². Mixture of β and γ phases is formed in PVDF due to gamma irradiation³.

Swift heavy-ion (SHI) irradiation has been widely reported to produce remarkable changes in the physical and chemical properties of polymers. Permanent modifications in the molecular weight distribution and solubility, and electrical, optical and mechanical properties of polymers and other materials have been observed after ion irradiation⁴⁻⁹.

When an energetic ion traverses through a polymer, it loses its energy by interacting with target nuclei nuclear stopping and by interacting with target electrons electronic stopping processes. Nuclear stopping arises from collisions between the energetic ions and target nuclei that cause atomic displacement and chain scission. Electronic stopping is mainly determined by the charge state of the ion and its velocity as the orbital electrons of the moving ion are

stripped off to a varying degree depending upon the ion velocity. Crystallinity is also affected by ion irradiation and most semicrystalline polymers exhibit a decrease in the crystallinity at high-dose irradiation. Crystallinity plays a crucial role in almost all polymer properties such as mechanical, optical, electrical and thermal properties. The behaviour of PVDF under bombardment of different kinds of radiation¹⁰⁻¹¹, including ion beam of several different species in different energy regimes¹²⁻¹⁶ has been studied earlier. This paper reports on optical, chemical, structural and electrical changes in the α -phased PVDF due to 70 MeV carbon ions. The modifications have been examined using UV-Vis, FTIR, XRD and HFIA techniques.

2 Experimental Details

For swift heavy ion irradiation, PVDF samples in form of thin film (procured from Goodfellows, UK) of thickness 80 μm were irradiated using 15 MV Pelletron accelerator facility available at the Inter University Accelerator Centre, New Delhi, India. The samples were irradiated with 70-MeV: $^{12}\text{C}^{+5}$ beam of three different fluences: 1×10^{11} , 1×10^{12} , 3×10^{12} ions/ cm^2 . An energy of 70-MeV for the $^{12}\text{C}^{+5}$ ion beams has been chosen so that the samples would undergo uniform irradiation effects. The mean value of electronic stopping power of the beam, $(dE/dx)_e$, is 36.01 eV/ \AA . The samples were analyzed with UV-Visible spectrophotometer (UV 1601 PC) in the wavelength range (200-900 nm) to observe the absorption studies. Chemical modifications were evaluated using Fourier transform infrared spectroscopic technique (Perkin Elmer) in the range (4300-500 cm^{-1}) and structural aspects of PVDF were analysed using powder X-ray diffractometer (PW-1830) techniques. XRD measurements were taken by using monochromatic $\text{CuK}\alpha$ (8.04 keV and $\lambda = 0.154$ nm) radiation and wide range of Bragg angles 2θ ($5^\circ \leq 2\theta \leq 90^\circ$) at the scanning rate of $5^\circ/\text{min}$. The electrical properties of all samples (virgin and irradiated) were also studied. The *ac* conductivity, dielectric loss and dielectric constant measurements were carried out by using High Frequency Impedance Analyzer in the frequency range 1 MHz-10 MHz at room temperature.

3 Results and Discussion

All our experiments can be divided into four types of measurements: UV-Visible spectrophotometry, FTIR spectroscopy, X-ray diffraction and High

Frequency Impedance Analyzer of the virgin and irradiated samples. The projected range of 70 MeV $^{12}\text{C}^{+5}$ ions in PVDF is around 124 μm according to the stopping and ranges of ions in matter (SRIM code¹⁷, which is more than 1.5 times the thickness of the polymer. Under these conditions, ionization processes are very important and SRIM calculations indicate that 99.95% of energy lost by 70 MeV $^{12}\text{C}^{+5}$ ions in 80 μm is electronic in its nature.

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 displacement of target atoms. Displacement damage is usually considered to be the most cause of material modification in solids; however, in polymers, ionization processes are also highly important.

3.1 Optical response

The absorption of light energy by polymeric materials in ultraviolet and visible regions involves promotion of electrons in σ , π and n-orbitals from the ground state to the higher energy states which are described by molecular orbitals¹⁸. The electronic transitions that are involved in the ultraviolet and visible regions are of the following types $\sigma \rightarrow \sigma^*$, $\nu \rightarrow \sigma^*$, $\nu \rightarrow \pi^*$, $\pi \rightarrow \pi^*$. Many of the optical transitions which result from the presence of impurities have energies in the visible part of the spectrum, consequently the defects are referred to as colour centres.

The results of optical absorption studies with UV-Visible spectrophotometer carried out on virgin and irradiated samples are shown in Fig. 1. The optical absorption spectrum of virgin sample shows a

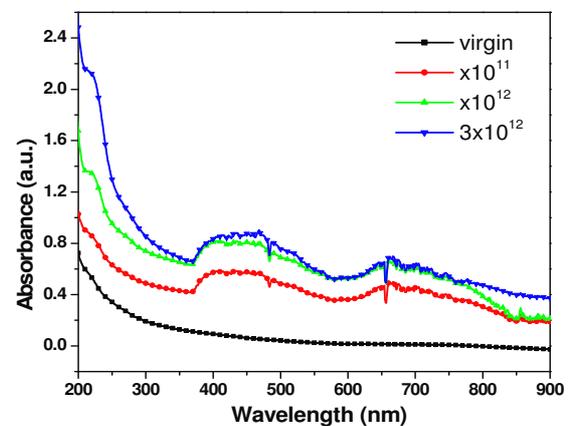


Fig. 1 — UV/VIS spectra of pristine and 70 MeV carbon ions-irradiated PVDF

sharp decrease with increasing wavelength up to 350 nm, followed by a plateau region. It is evident from Fig. 1 that the optical absorption is maximum at 200 nm and it increases with increasing fluence as observed in earlier results^{14,19}. This change is observed due to transition from $n \rightarrow \sigma^*$ orbitals. The spectra for irradiated samples show a significant change with increasing ion fluence. Two new dips at 482 nm and 654 nm have been appeared in the irradiated samples. It may be due to the breaking of chain and creation of new defects. These characteristics dips may be correlated with the transition occurring in fluorocarbons¹⁹. However, the destruction of original polymer structure upon irradiation leading to the formation of multiple bonds (C=C) due to the breaking of lateral bonds (C-F and C-H) and absorption of volatile species such as H₂, HF and F₂ for PVDF.

3.2 Chemical response

FTIR spectra of PVDF (virgin as well as irradiated) are shown in Fig. 2. Two characteristic absorption peaks at 3024 and 2985 cm⁻¹ of the asymmetric and symmetric vibration of CH₂ group are found to be assigned in the literature. Fluorine atoms attached to carbon double bonds have the effect of shifting the C=C stretching vibration to higher frequencies near 3000 cm⁻¹. Some of the observed minor peaks in the region 2800-1500 cm⁻¹ were found to remain unassigned in the literature of PVDF. However, the absorption is constant in the range (1500-1000 cm⁻¹) in virgin polymer [Fig. 2(a)]. Well known peaks of α -phase in fingerprint region located at 873, 763, 615, and 488 could be recognized very clearly.

The FTIR spectra of the irradiated PVDF sample (Fig. 2b) at 1×10^{11} ions/cm² produced no significant change in their peak positions. It is clear that the intensity of these peaks remains same as virgin sample but overall transmittance intensity decreases with increasing fluence. It may be due to the destruction of crystalline structure in the PVDF upon irradiation. Crystallization/amorphization ability of the polymer depends on the polarity also. The crystallizability of PVDF is attributable to the polar groups in the molecule (which leads to the formation of hydrogen bonds) increasing the interchain forces of attraction. The amorphization in the present case for polar polymer upon high linear energy transfer (LET) (i.e. the energy deposited per unit ion path length) irradiation seems to have occurred during secondary electron-phonon coupling, while transferring a huge

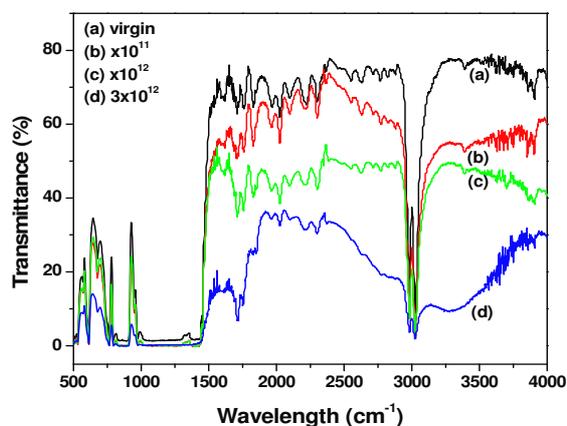


Fig. 2 — FTIR Spectra of Virgin and 70 MeV carbon ions irradiated PVDF with various doses (a) virgin (b) 10^{11} (c) 10^{12} (d) 3×10^{12}

amount of electronic energy into the lattice. This in turn might have destroyed the molecular dipoles into a more disorder one due to irradiation.

Further, the specific decrease in transmittance intensity of PVDF upon higher ion fluence 1×10^{12} (Fig. 2c) impact possibly indicates the realignment of the molecular dipoles into a highly ordered state of chain cross-linked molecules in the crystalline region of PVDF, creating volume element as crystallites¹⁵. It can be seen that increase in crystallization times results in decrease in intensity. Upon increasing ion fluence 3×10^{12} ions/cm² (Fig. 2d), transmittance intensity again decreases significantly. Some minor peaks at 2868, 2771, 2712, 2631 and 2543 cm⁻¹ have been disappeared in Fig. 2d which were present in Fig. 2c. In α -phased PVDF, higher electronic stopping power of 70 MeV carbon ions induces a significant increase of main chain scission, formation of alkynes, gas evolution, complex sequences of chemical reactions and marked increase in the yield of fluorinated defects ($-\text{CH}=\text{CF}_2$) end groups. The polymer destruction occurs simultaneously with an amorphization as revealed by XRD analysis.

3.3 XRD studies

X-ray diffractograms of virgin and C⁵⁺ ion-irradiated PVDF samples are shown in Fig. 3. In the Fig. 3a, X-ray diffraction from crystalline regions of PVDF gives sharp and well-defined peaks located at 2θ angular positions at 18°, 18.5° and 20°. From the Bragg's law, interplanar spacings of 0.492, 0.479 and 0.443 nm are obtained, correspondingly to the (100), (020), and (110) atomic planes²⁰ of PVDF, respectively.

In Fig. 3b, XRD spectrum of irradiated (1×10^{11} ions/cm²) sample is the same as that of virgin sample, showing that at lower fluence the crystallinity of irradiated sample is not modified. In the Fig. 3(c), peak intensities decrease at fluence 1×10^{12} ions/cm² as compared to earlier one. At low fluence ion irradiation ($\leq 10^{12}$ ions/cm²), crystallinity decreases due to breaking of bonds which amorphises the polymer sample, whereas at higher fluence of

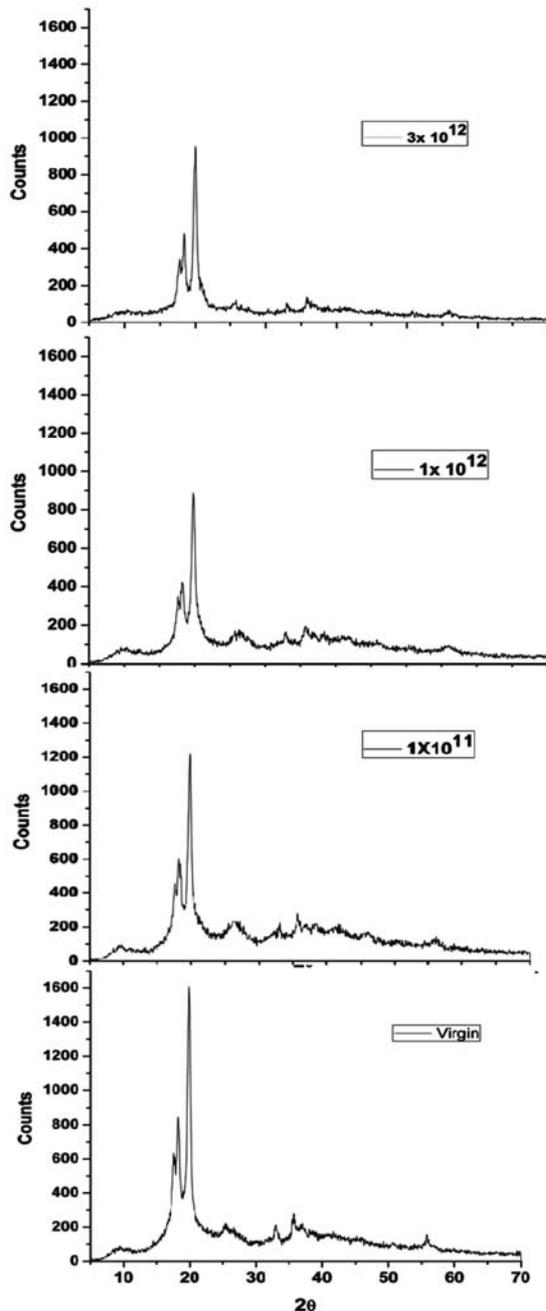


Fig. 3 — X-ray diffraction pattern of virgin and gamma irradiated PVDF at various fluence (10^{11} , 10^{12} , 3×10^{12})

10^{12} ions/cm² reordering and cross-linking of bonds take place, leading to formation of crystalline regions in the polymer. Further, upon increasing the ion fluence i.e. 3×10^{12} ions/cm² (Fig. 3d) the peak intensities again decrease suggesting a decrease in the degree of crystallinity. This interesting result could be attributed to the fact that for a particular ion beam with a given energy, a higher fluence provides critical activation energy for cross-linking and crystallization to occur, which results in the decrease in crystallinity²¹. The structure of polycrystalline materials has been investigated by means of Debye-Scherrer method. The Scherrer equation²² relates FWHM (β) of an XRD peak to the size of crystallites L as :

$$L = K\lambda/\beta \cos\theta \quad \dots (1)$$

where L is the average crystallite size, λ is the X-ray source wavelength (in Å), β is the full-width at half-maximum (FWHM), $K=0.89$ and θ is the diffraction angle. The values of FWHM (β) and corresponding results of crystallite size (L) for virgin as well as irradiated samples have been reported in Table 1. It has been observed that crystallite size increases with increasing ion fluence.

3.4 Electrical response of PVDF

The *ac* conductivity measurement was performed for virgin and irradiated PVDF samples and the result is shown in Fig. 4. A sharp increase in the conductivity at high frequencies was observed in virgin as well as irradiated PVDF samples with the increase of dose. The increase in conductivity at a given frequency due to irradiation may be attributed to scissioning of polymer chains and the migration of long lived radicals which are trapped mostly in crystalline region to amorphous region, resulting in an increase of free radicals, unsaturation, etc. An *ac* field of sufficiently high frequency may cause a net polarization, which is out of phase with the applied field. This results in *ac* conductivity and it appears at frequencies greater than that at which the traps are filled or emptied^{23,24}.

Table 1 — X-ray diffraction spectra of 70 MeV carbon ions irradiated PVDF at different fluences

S. No.	Angle of Peak (2θ)	Fluence (ions cm ⁻²)	FWHM (β)	Crystallite size (L) (Å)
1	20.215	0	0.600	150.00
2	20.010	1×10^{11}	0.420	216.90
3	20.030	1×10^{12}	0.360	249.19
4	20.085	3×10^{12}	0.360	252.29

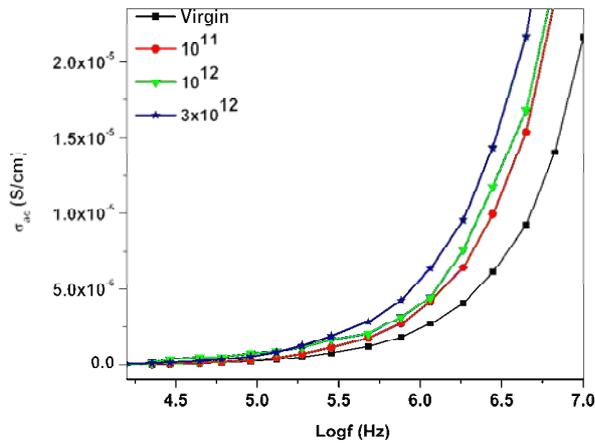


Fig. 4 — *ac* Conductivity versus log of frequency plot for virgin and irradiated PVDF

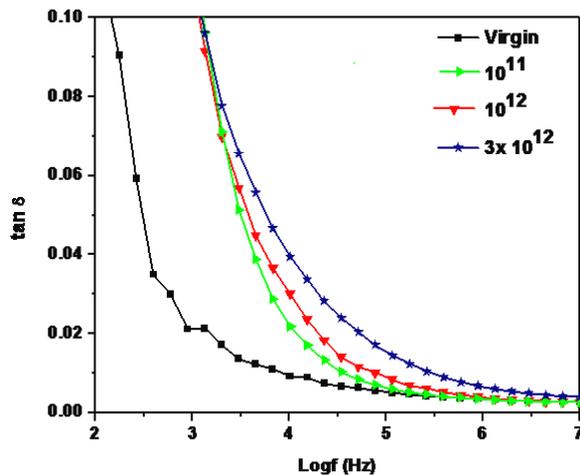


Fig. 5 — Variation of $\tan \delta$ with log of frequency for virgin and irradiated PVDF

Figure 5 shows a plot of $\tan \delta$ (dissipation factor) versus log frequency for virgin and irradiated PVDF samples. It is observed that loss factor decreases with increase of frequency moderately with ion fluence. The increase in loss factor with fluence may be due to accumulation of stable radiolytic products, resulting in an increase of free radicals unsaturation, etc.

Figure 6. shows a plot of dielectric constant (ϵ_r) versus log frequency at ambient temperature for both virgin and irradiated PVDF polymer samples. As evident from the graph, the dielectric constant slightly decreases with the increase of frequency. At lower frequencies, the mobility of the free charge carriers is found to be constant and thus the dielectric constant also remains constant in this region. As the frequency increases, the charge carriers migrate through the

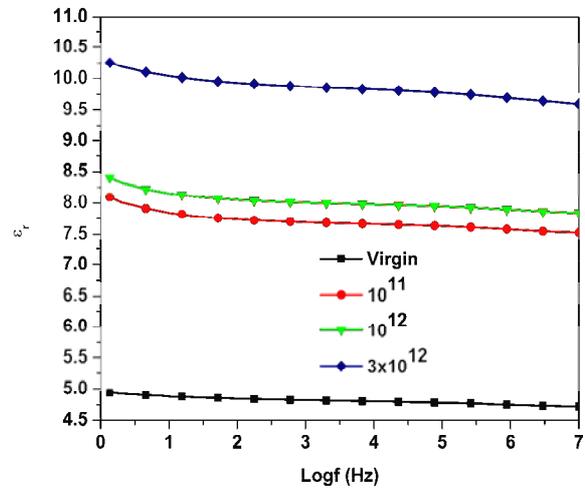


Fig. 6 — Plot of dielectric constant versus log of frequency for virgin and irradiated PVDF

dielectric and get trapped against defect sites and induce an opposite charge in its vicinity. At these frequencies, the polarization of trapped and bound charges cannot take place and hence, the dielectric constant decreases. The decrease in the dielectric constant at higher frequency can also be explained by Jonscher's power law²⁵.

Universal power law equation:

$$\sigma_{ac} = \sigma(0) + A\omega^s \quad \dots (2)$$

It can be seen that exposure to radiation leads to slight increase (at any given frequency) in the *ac* conductivity, dielectric constant and loss. Interestingly, the electromagnetic radiation blocking response is critically dependent on the above properties²⁶⁻³¹, exposed materials may be useful for low frequency electromagnetic wave shielding properties

4 Conclusions

Physico-chemical modifications induced by 70 MeV carbon ions in α -phased polyvinylidene fluoride (α -phased PVDF) have been studied by means of UV-Vis, FTIR, XRD and High Frequency Impedance Analyzer. The following conclusions are drawn:

The optical absorption increases with increasing ion fluence and maximum absorption at 200 nm is observed. Two new dips at 482 nm and 654 nm are appeared after irradiation which may be due to the fluorinated defects ($-\text{CH}=\text{CF}_2$) created due to carbon ion irradiation. An IR study shows that transmittance

intensity decreases with increasing ion fluence in the range 1500-4000 cm^{-1} . The decrease in transmittance or increase in absorbance may be due to cross-linking of polymeric chain in PVDF. The diffraction pattern of PVDF indicates that crystallinity decreases with increasing ion fluence which is also confirmed by the decrease of peak intensities but the crystallite size is found to increase due to carbon ion irradiation. At low fluence ion irradiation ($\leq 10^{12}$ ions/ cm^2) crystallinity decreases due to breaking of bonds which amorphises the polymer sample, whereas at higher fluence of 10^{12} ions/ cm^2 reordering and cross-linking of bonds take place, leading to formation of crystalline regions in the polymer. The remarkable increase is in the value of dielectric constant from 5 to 10 with increasing ion fluence and the *ac* conductivity also increases with increasing fluence.

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