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Morphology, crystalline structure, and chemical properties of 100 MeV Ag- ion beam irradiated polyvinylidene fluoride (PVDF) thin film

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Thin films (12 μm) of polyvinylidene fluoride (PVDF) were irradiated with 100 MeV Ag- ion beam at fluence $1.875X10^{11}$ ion/cm^2. The changes in physical, chemical, and surface morphological properties of irradiated films have been investigated using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy(FTIR), Field emission scanning electron microscopy (FESEM) and Energy Dispersive Analysis by X-ray (EDAX) techniques by taking unirradiated (pristine) film as reference. The diffraction pattern of PVDF films shows this polymer is in semi-crystalline form and posses crystalline α-, β-, and γ- phases. A decrease in the crystallinity and increase in crystallite size has been observed due to 100 MeV Ag - ion irradiation. Using XRD data, the degree of crystallinity, crystallite size and other structural parameters such as micro strain and dislocation density of pristine and irradiated films have been estimated. In the FTIR spectra, no appreciable change in characteristic bands has been observed after irradiation, indicating that PVDF is chemically stable. EDAX result shows that the relative chemical composition of PVDF is invariant under energetic heavy ion irradiation. FESEM analysis show granular microstructure with increase in grain size and porosity upon ion irradiation.

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Keywords: SHI, PVDF, FTIR, XRD, FWHM, EDAX, FESEM

1. Introduction

Polyvinylidene fluoride is a long chain semi-crystalline high-molecular weight polymer with repeat unit (CH2 - CF2), whose structure is essentially head-to-tail, i.e., CH2 - CF2 - (CH2-CF2) n - CH2 - CF2 and has acquired immense importance in scientific and technological research because of its unique mechanical, electrical, pyroelectric, ferroelectric, piezoelectric properties and exceptional biocompatibility[1]. It is also one of the rare polymer exhibit diverse crystalline forms, having at least five phases known as α, β, γ, δ and ε [2-4]. The alpha (α) phase assumes a distorted trans-gauche-trans-gauche' (TGTG') conformation. While there is a net dipole moment perpendicular to the chain due to the polar C-F bond, the unit cell is actually non polar. The beta phase (β) assumes a distorted planar zigzag, all-trans conformation, resulting in a polar unit cell. The γ- phase has a structure intermediate to the helical α - and zigzag β - phase [5]. The β - phase and sometimes the γ- phase can undergo reversible changes in polarization to create high piezoelectric and pyroelectric activity which makes this suitable polymeric material to be used in IR sensors, ultrasonic transducers, electromechanical, electro acoustic transducers [6] and micro-actuators development. The exceptional biocompatibility of PVDF film is used in the development of skin transducer, implantable medical devices and micro actuators [1].

In addition, light weight and chemical resistance of PVDF polymer promote their use for development of micro sensors and actuators for space applications. However, in space the performance of sensors and actuators may be affected due to the strong interaction of ultraviolet, γ-rays, X-rays, energetic ions and atomic oxygen exposure with the sensor material. The interaction of these radiations with PVDF may change its physical, chemical, optical, structural and morphological properties. The behavior of PVDF exposed to different kinds of radiation [7-15, 20] has been studied before. These studies reveal the enhancement in electrical conductivity and change in crystallinity of PVDF [11, 12]. The decrease in crystallinity has been reported under low-energy ion implantation [11, 12, and 15] whereas an increase in crystallinity has been reported under electron, X-ray and γ-ray irradiations [13, 16-18]. The crystallinity plays a crucial role in determining piezoelectric, mechanical, optical, electrical and even thermal properties of polymers [11].

Swift heavy ion (SHI) irradiation is a relatively new technique for modification of polymeric material properties to promote their use for the development of sensors and actuators to radiation environmental applications. In the present paper, we investigate the physical, structural, chemical, and morphological changes in PVDF films due to SHI irradiation through the XRD, FTIR, FESEM, and EDAX techniques. The transmission electron microscopy (TEM) and electron Scanning microscopy (SEM) are mainly used to examine surface structure and inside the object (<100nm). Augmenting the TEM method with high resolution FESEM provides the

opportunity to examine the overall particle shape, surface topography, and the side and termination (particle end) geometries. To the best of our knowledge, this is the first time a detailed and comprehensive FESEM morphological characterization method has been presented for supplementing TEM analyses.

2. Experimental details

The poly-vinylidene fluoride used in the present study was procured form DuPont in flat film forms of 12 μm thickness. The samples of size 1 sq. cm were irradiated with 100 MeV Ag- ion at fluence $1.875X10^{11}$ ions/cm^2 using the PELLETRON facility at Inter University Accelerator Centre, New Delhi. The pristine and SHI exposed PVDF films were later investigated using XRD, FTIR, FESEM, and EDAX techniques.

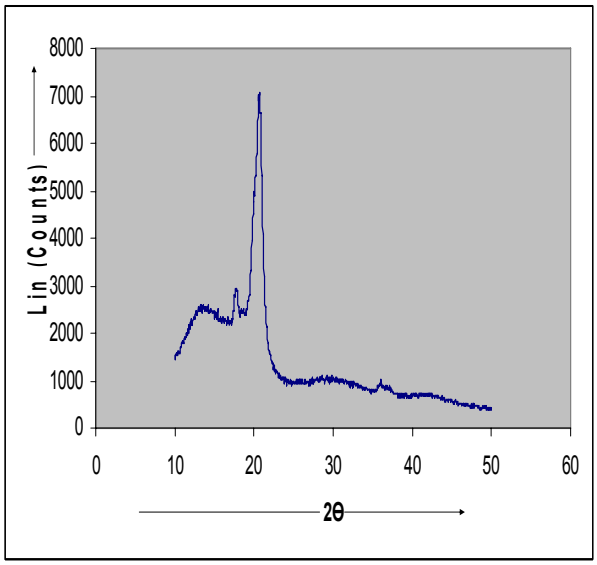
The XRD analysis has been done using Bruker AXS D8 Advance diffractometer with operating target voltage 40 KV and current 30mA. The XRD data were collected for angular position 2Θ in the interval 10 to 50^0, in steps of 0.05^0 in 3second, using Bruker AXS D8 powder diffractometer with copper Kα (λ=1.5406 Å) radiation source at the room temperature. The FTIR analysis of samples has been done using ABB Bomen spectrometer (MBIO4E) with the ATR (attenuated total reflection) in the range 650 -4000cm^{-1}. The samples were analyzed at 8 cm^{-1} resolution and 16 scans co-averaged using the Galactic spectra Calc software. Surface morphology of pristine and irradiated films has been investigated through TEM/FESEM using Quanta 200FEG instrument system having resolution of 2nm at accelerating voltage 30 KV with magnification; 1,000,000X. The chemical compositional identification is done by EDAX using EDX - INCA 350 Energy System (Energy Dispersive X-Ray System for SEM) attached to Quanta 200FEG instrument system.

3. Results and data analysis

3.1 X-ray diffraction analysis

X-ray diffraction technique has been utilized to detect changes in crystalline and amorphous regions along with the degree of crystallinity. It is used to measure crystal structure, grain size and residual stress of materials through interaction of X-ray beams with samples. As X-rays are predominantly diffracted by electron density, analysis of the diffraction angles can be used to produce an electron density map of a given crystal or crystalline structure. The polycrystallinity of the pristine and the irradiated PVDF films are investigated using X-ray diffraction analysis.

The X-ray diffraction spectra of pristine and Ag-ion irradiated PVDF films have been illustrated in figures 1a and 1b respectively. The diffraction patterns of pristine PVDF show its semi crystalline nature. The peak positions show crystalline α-, β-, and γ- phases and a broad background due to the scattering from amorphous regions of the polymer. The XRD data, i.e. angular positions (2Θ), peak intensity (I) and lattice spacing (d), corresponding to α-, β-, and γ- phases, of pristine and Ag-ion irradiated films are summarized in table1. In conformity with other workers [7, 11, 12, 15, 19-21] the X-ray diffraction data of pristine film (figures1, table1) show characteristic strong β-phase peak at $2\Theta \approx 20.63^0$, which is a reflection of (200) and (110) planes, characteristic strong α-phase peak at $2\Theta \approx 17.77^0$ from the reflection of (100) plane and very weak broader peak at $2\Theta \approx 36.06^0$ from the reflection plane (200) is correspond to the γ- phase. These observations (figures1a, table1) clearly indicate that PVDF thin films possess crystalline α-, β- and γ-phases.



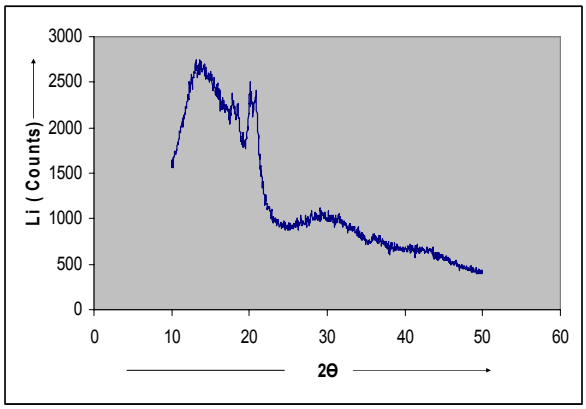


Fig. 1. XRD spectra of PVDF (a) Pristine (b) Ag-ion irradiated

In ion irradiated PVDF (Fig. 1b), the diffraction peaks corresponding to the crystalline α- and β- phases get converted into the two closely spaced peaks at $2\Theta \approx 17.85^0$ -18.48^0 with equal full width at half maxima (FWHM) and

peaks at 2Θ ≈ 20.10^0, 20.81^0 with equal FWHM (table1) respectively. Two smaller peaks at angular position 2Θ ≈ 28.00^0 with inter-planar spacing (d) 3.184 Å and at angular position 2Θ ≈ 38.29^0 with inter-planar spacing (d) 2.348 Å are also observed in the XRD spectra of irradiated film, which can be assigned to crystalline α (111) and γ (211) phases respectively. As compared to pristine film, the diffraction pattern of irradiated film not only shows a decrease in intensity but also shows the presence of kinks at crystalline α –, β- and γ- phases peaks. The decrease in peak intensity of diffraction peaks is usually related to the decrease in crystallinity [11, 12, and 15] and the occurrence of kinks can be associated with the increase in the mean crystallite size. The decrease in crystallinity on irradiation could be due to scission processes in the main chains of PVDF leading to the disruption in packing. The increase in mean crystallite size is due to the formation of some large size crystallites in the amorphous regions of films upon irradiation. The addition of these large size crystallites with the original crystallites causes the mean size of the crystallite to increase. From the table1, we further observe that on irradiation the angular positions of α- and γ- phases get shifted towards higher angles due to the decrease in lattice spacing (d) while the angular positions of β-phase get shifted towards higher and lower angles.

3.1.1 Crystallinity, crystallite size and other structural parameters

The degree (percentage) of crystallinity (K), mean crystallite size (D), micro strain (ε) and dislocation density (δ) have been be estimated from the XRD pattern of pristine and swift heavy ion irradiated samples. In order to determine the crystallinity of pristine and ion irradiated samples we obtained X-ray diffractogram from their respective XRD spectra and shown in figures 2a and 2b respectively. The X-ray diffractogram for pristine PVDF has two crystalline peaks with area A1, A2, superimposed on abroad amorphous hump of left over area A5 as shown in figure 2a. The percentage of crystallinity (*Kp*) can be calculated using following equation;

$$Kp = \frac{Kc(A1 + A2)}{Kc(A1 + A2) + Ka(A5)} \times 100 = \frac{(A1 + A2)}{(A1 + A2) + \frac{Ka}{Kc}(A5)} \times 100 \quad (1)$$

Here Ka and Kc are proportionality constant for amorphous and crystalline phases respectively. This polymer is known to have nearly 50% crystalline and 50% amorphous in pristine form and hence Ka is equal to Kc. The equation (1) becomes

$$Kp = \left(\frac{\Omega cp}{\Omega tp}\right) \times 100 \quad (2)$$

Here Ωcp denotes the total crystalline area and Ωtp denotes the total area under the diffractogram. The area Ωcp and Ωtp have been calculated by dividing the X-ray diffratogram into small square grids (0.5X0.5 mm^2) and counting the number of grids.

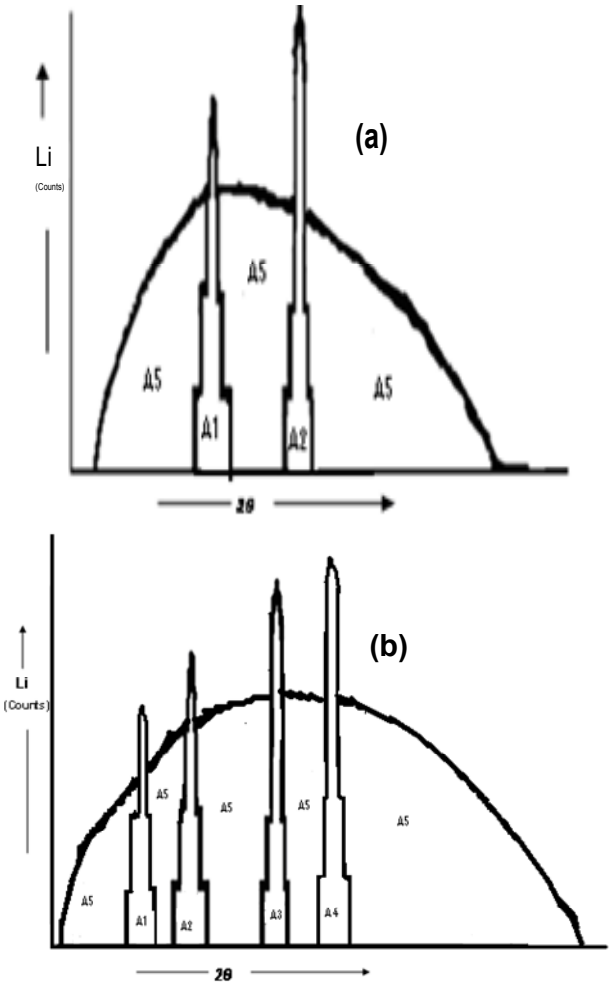


Fig. 2. XRD diffractograms for (a) Pristine, (b) Ion irradiated

For the irradiated film the X-ray diffractogram has Four crystalline peaks with area A1 ,A2, A3 and A4 superimposed on abroad amorphous hump of left over area A5 as shown in figure2b, then the percentage of crystallinity(Ki) can be calculated using following equation;

$$Ki = \frac{Kc(A1 + A2 + A3 + A4)}{Kc(A1 + A2 + A3 + A4) + Ka(A5)} \times 100 \quad (3)$$

$$= \frac{(A1+A2+A3+A4)}{(A1+A2+A3+A4)+\frac{Ka}{Kc}(A5)} \times 100$$

Here Ka and Kc are proportionality constant for amorphous and crystalline phases respectively. For Ka equal to Kc the equation (1) becomes

$$Ki = \left(\frac{\Omega ci}{\Omega ti}\right) \times 100 \quad (4)$$

Here Ωci denotes the total crystalline area and Ωti denotes the total area under the diffractogram. The degree (percentage) of crystallinity for pristine and irradiated films is found to be approximately 52.56% and 50.28% respectively.

We estimate the crystallite size (D) from the diffraction ray line broadening using Scherrer equation [19]:

$$D = \frac{C\lambda}{W \cos\theta} \quad (5)$$

here, C is a constant which depends on diffractometer setup, λ is wavelength of X-ray, θ is diffraction angle or Bragg's angle and W denotes FWHM. In the present setup C=0.9 and λ=1.5406 Å. The values of W and θ can be obtained from the diffraction pattern (figures1a and b).

The micro strain (Є) and dislocation density (δ) have been calculated using the following relations:

$$Є = \frac{1}{4} W \cos\Theta \quad (6)$$

and

$$\delta = \frac{1}{D^2} \quad (7)$$

The estimated structural parameters for pristine and irradiated PVDF films have been given in table2. We observe a significance enhancement in crystallite size in irradiated PVDF samples. This is in conformity with our interpretation of XRD spectra as discuss earlier. However we observe a decrease in micro strain (Є) and dislocation density (δ) in irradiation PVDF film.

Table1. XRD Data of pristine and irradiated PVDF film

Phase	Pristine film			Irradiated Film		
	2Θ	I	d(Å)	2Θ	I	d (Å)
α	17.77	2912	4.987	17.85	2385	4.963
				18.48	2243	4.796
β	20.63	6973	4.301	20.10	2511	4.422
				20.82	2354	4.263
γ	36.06	1005	2.488	38.29	702	2.348

Table 2. Structural parameter of pristine and irradiated PVDF film.

Sample	Phase	2Θ (deg)	Θ	Cos Θ	W (deg)	W (10^{-3} rad)	W Cos Θ (10^{-3})	D (nm)	Є (10^{-3})	δ (10^{15})
Pristine	α	17.77	8.880	0.9980	0.50	8.722	8.617	16.08	2.154	3.8667
	β	20.63	10.315	0.9838	1.10	19.190	18.879	7.43	4.719	8.1100
Ag –ion Irradiated	α_1	17.85	8.925	0.9878	0.25	4.363	4.311	32.15	1.077	0.9700
	α_2	18.48	9.240	0.9870	0.20	3.490	3.444	40.24	0.861	0.6170
	β_1	20.10	10.050	0.9846	0.35	6.108	6.014	23.05	1.500	1.8820
	β_2	20.82	10.410	0.9835	0.55	9.599	9.440	14.68	2.360	4.6400

3.2 FTIR analysis

The FTIR spectroscopy detects the transition between energy levels in molecules which results from vibrations of inter atomic bonds and hence provides precise information about orientations of specific functional groups within the polymer. In infrared spectroscopy, the frequency region 650-4000 cm^{-1} covers the absorption due to the fundamental vibration of almost all the common functional groups of organic compounds. The functional groups in polymers have absorption which are characteristic not only in position but also in intensity.

Table 3. Infrared absorption band frequencies (cm^{-1}) for pristine PVDF film.

Absorption bands (cm^{-1})	Source of origin
760	CF2 bending& Skeletal bending
837	CH2 out of plane wagging
874	CH2 rocking vibration
975	CH_2 bending
1067	CH2 rocking deformation
1167	CF2 Asymmetric stretching mode
1399	CH2 Scissoring deformation
2978,3029	CH2 symmetrical and asymmetrical vibration

The FTIR spectrum of pristine PVDF film is shown in figures 3. The infrared characteristic absorption band frequencies are given in table 3 along with their functional groups. The observed characteristic bands are in conformity with the results obtained by other groups [4, 11, 22-27]. The FTIR spectra of pristine film show characteristic absorption bands of crystalline α-phase at 975cm^{-1}, 760 cm^{-1} , the absorption band at 837 cm^{-1} corresponds to the crystalline β-phase. We have assigned the absorption band at 1167 cm^{-1} to CF_2 asymmetric stretching mode, since CF_2 group absorb strongly in the region 1120 -1350cm^{-1}. We observe weak bands at 2978 $cm^{-1}$and 3029cm^{-1} corresponding to symmetrical and asymmetrical stretching vibration of CH_2 group.

The FTIR spectra of 100 MeV Ag-ion irradiated film is illustrated in figure 4 along with the spectra of pristine film. The FTIR spectra of the irradiated film does not show any major change in main characteristic bands except some broadening and decrease in intensity of bands. The reduction in intensity of various characteristic bands for α- and β- phases indicates the marginal reduction in crystallinity. The positions of these characteristic bands do not change which show that the crystalline structure of PVDF is stable under ion irradiation. The weak bands at 1710 cm^{-1} and 1748 cm^{-1} present in pristine film disappear in irradiated sample and some new weak bands appear at 1652 cm^{-1} and 1688 cm^{-1} indicates the evolution of HF* due to C=C formation . The formation of C=C bond due to irradiation in certain polymer has been reported earliear [28].

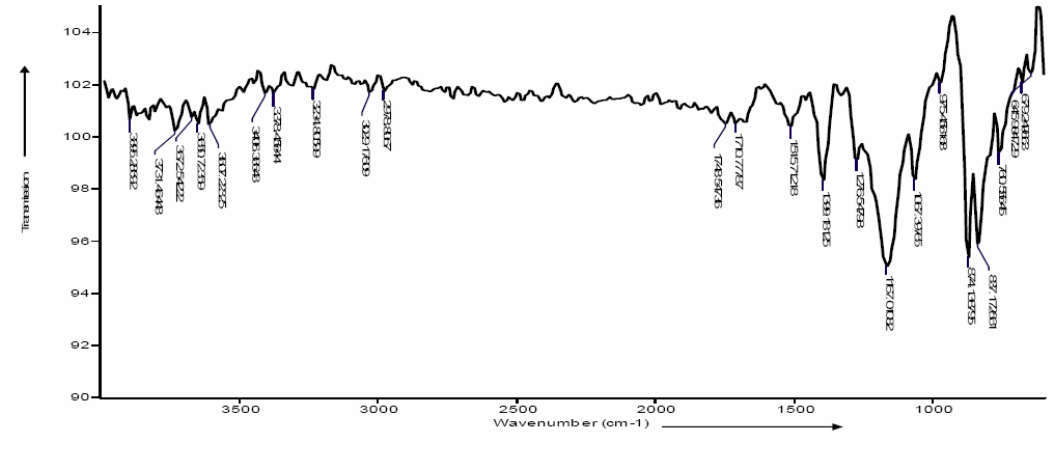


Fig. 3. FTIR spectra of pristine PVDF film.

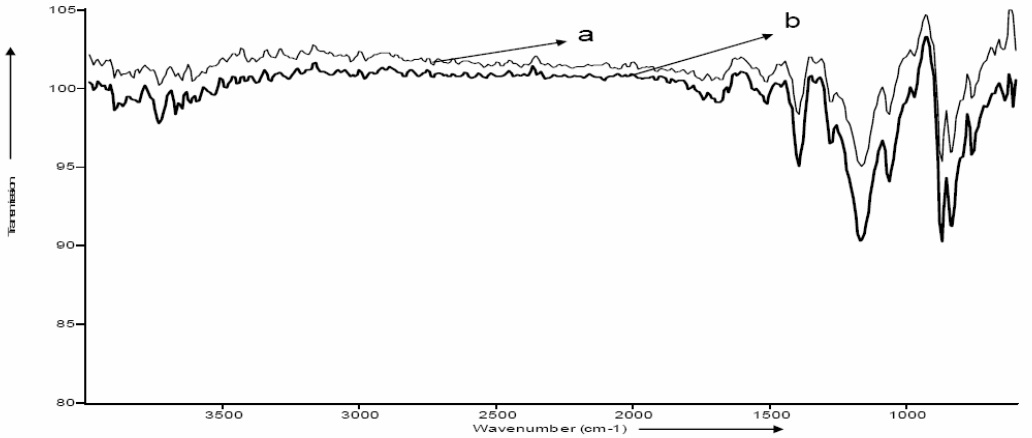
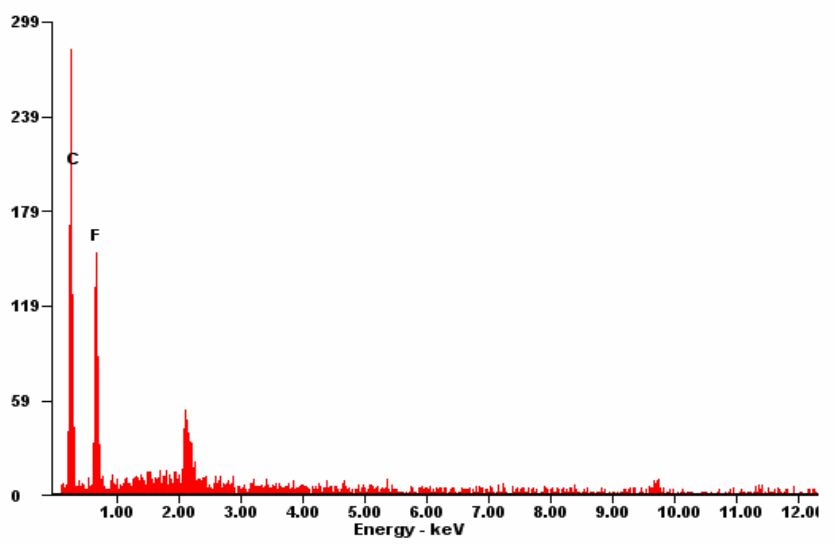


Fig. 4. FTIR spectra of PVDF (a) Pristine (b) 100 MeV Ag-ion Irradiated film.

3.3 Energy dispersive analysis by X-ray (EDAX)

The EDAX microscopy is an indispensable tool for identification and measuring element composition on the surface of thin film samples of interest. The peak intensity in the Energy dispersive x-ray (EDX) spectra represents a semi-quantitative relationship of the chemical elements present in the sample. EDAX microscopy cannot identify the chemical elements having atomic weight less than four and hence we can not find hydrogen in the EDX spectra. The EDX spectra of pristine and Ag-ion irradiated 12 µm PVDF films are illustrated in figure 5a and figure 5b respectively. Both spectra show only two peaks corresponding to main chemical elements carbon and fluorine originating from PVDF structure. We do not find any new peak in the EDX spectra of irradiated samples, which indicate that there is no formation of any new intermediate chemically distinct compound on irradiation which collaborate our FTIR findings. The appearance of third small peak in all EDX spectra represents the presence of gold electrode deposited on the films for EDAX.



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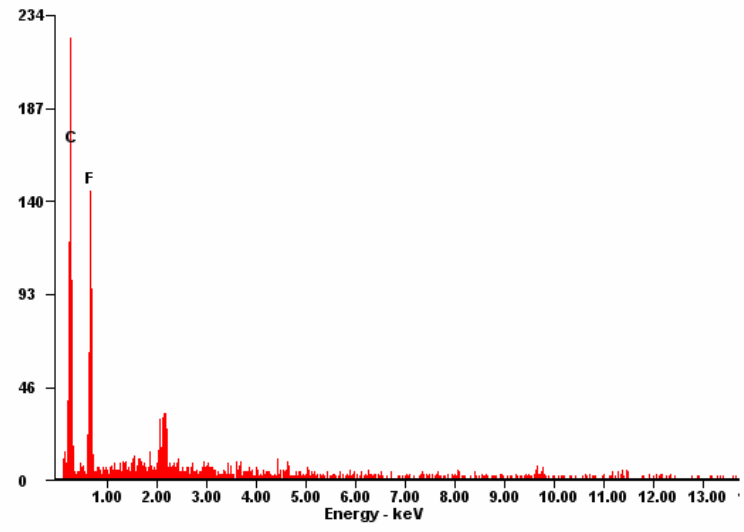


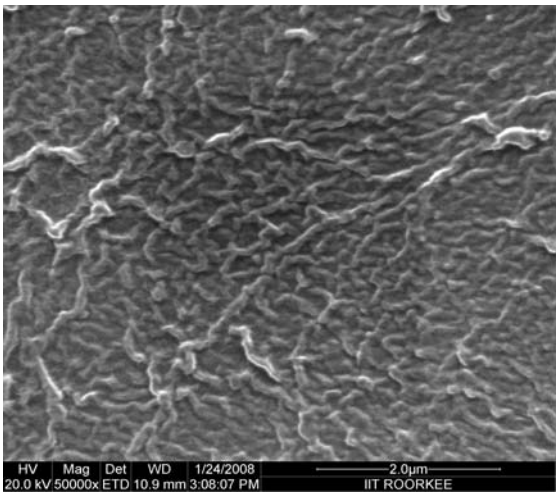
b

Fig. 5. EDX spectra of 12 µm PVDF films (a) Pristine (b) irradiated

3. 4 Field emission scanning electron microscopy (FESEM)

The FESEM is used for the investigation of topographic details on the surface and entire structure of the thin films. The field emission scanning electron microscopic (FESEM) micrographs (at magnification of 50000) of pristine and 100MeV Ag-ion irradiated PVDF films are shown in figure 6a and figure 6b respectively.

Fig. 6a shows that pristine PVDF film posses' long finger/fibers chain like structures on entire surface area with small protuberance at some places and show grains of different size and nano-porous regions in between. These fibers like structures probably may be correlated to random orientation of the β and α crystallites. On irradiation with swift heavy Ag-ion the surface morphological features such as distributions of grain shapes, size and porosity of the film changes and show increase in grain size and non uniform distribution of grains in the granular surface microstructure of the film. This change in grain shape and size is in line with our interpretation of XRD spectra and estimated crystallite size (table 2). Further, we also observe that the nanoporosity increases upon ion irradiation (figure 6b).



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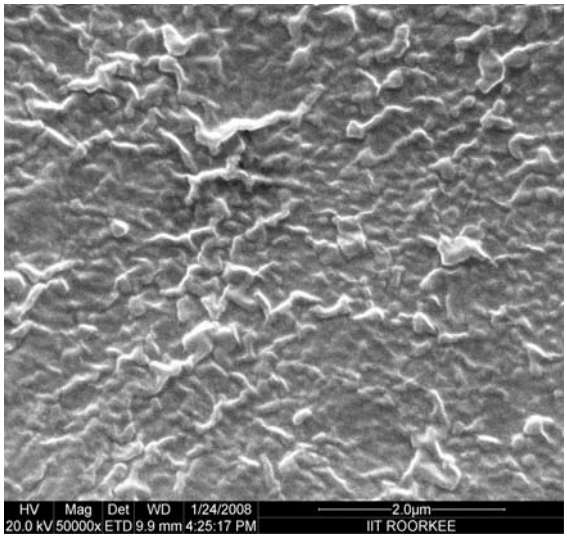

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Fig. 6. FESEM Micrographs of 12 µm PVDF films (a) Pristine, (b) Ag-ion irradiated.

4. Conclusions

We have investigated SHI irradiation induced changes in PVDF thin film using XRD, FTIR EDAX and FESEM techniques. The XRD spectra are used to estimate structural parameters such as degree of crystallinity, crystallite size, micro strain and dislocation density of pristine and irradiated samples. The XRD analysis shows that the size of crystallites is increased while the lattice spacing and the degree of crystallinity is decreased upon irradiation. The micro strain and dislocation density also decreases upon ion irradiation. The FTIR spectra of irradiated film do not show any prominent new bands, which indicates that there is no significant formation of intermediate chemically distinct material on irradiation. EDAX results show that the relative chemical composition of PVDF remains invariant under ion irradiation. FESEM micrographs show granular and porous surface morphology with adhesivity and increased grain size and porosity upon ion irradiation.

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