



Electrical Structural and SEM studies of 1.25Mev gamma irradiated poly vinylidene fluoride (PVDF) polymer

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Abstract

The gamma irradiated Polyvinylidene fluoride (PVDF) polymer samples of thickness 80 μ m and length (1*1cm²) have been studied for electrical, structural and morphological properties. These properties were examined using Impedance analyzer (PSM 1735), X-ray diffraction and Scanning Electron Microscope respectively. The variation of dielectric loss, dielectric constant and A.C. conductivity with frequency was carried out at room temperature. It has been found that the dielectric loss and dielectric permittivity shows significant changes due to irradiation. The XRD pattern of virgin sample shows that PVDF polymer is semi-crystalline but due to irradiation, a decrease in the peak intensity decreases up to the dose level 2000 kGy. The structural parameters such as degree of crystallinity, crystalline size, micro strain and dislocation density have also been estimated. The SEM analysis shows granular microstructure with small porosity with higher dose. The well-defined grain and grain boundary structure was identified from this studies.

Keywords: PVDF, Gamma irradiation, Impedance analyzer, XRD and SEM.

1. Introduction

The development of more advance materials is often one the driving forces behind innovation of this area. Polymers have attracted attention of the Scientific and technological researchers because of their wide applications. PVDF has a melting temperature approximately 170 °C and has a reasonable melt viscosity suitable for melt processing. Polyvinylidene fluoride (PDVF) a polycrystalline polymer drawing a scientific interest in the 17th century, because of its extraordinary pyro and piezo-electrics properties. This polymer has an exceptional structure which is able to crystallize to four different crystalline forms α , β , γ , and δ forms [1]. Polyvinylidene fluoride (PVDF) is a semi-crystalline thermoplastic having remarkable high piezoelectric

coefficient [2, 3]. It is also a non-toxic material, exhibiting resistance to heat and chemicals and low water absorption characteristics which make it more suitable for making electronic components. Moreover, PVDF is an attractive polymer matrix for micro and nanocomposites with superior mechanical and electrical properties [4–8]. This polymer is also distinguished from the other polymers on the basis of polymorphism [9].

The α phase is lowest energy conformation and is the non polar form. It is based on stretch trans-gauche, trans-gauche' (TGTG') chain conformation. While there is net dipole moment perpendicular to the chain due to the polar C-F bond, the unit cell is actually non polar. The dipole moment of the α -form is moderated, but the symmetric packing of these chains (TGTG) makes the overall dipole moment null of the unit cell.

The polar β phase is known for the crystalline phase for its ferroelectricity. The polymer chains are in a distorted, planer zigzag, all-trans (TTTT) conformation and the unit cell is polar. However, this conformation is thermodynamically unfavorable and therefore unstable. To overcome the energy barriers of TGTG-TTTT conversion many experimental techniques have been developed. Moreover, an increasing interest has been devoted to PVDF as electric or magnetic field sensors when filled with transition metal halides [10].

The dielectric studies were carried out by using High Frequency Impedance Analyzer (PSM 1735) over the frequency range (10 Hz–30 MHz) at ambient temperature. The data generated from the instrument were collected through an interface between instrument and the computer using software (developed in our laboratory). The dielectric permittivity was evaluated using the standard relation $\epsilon_r = C d/\epsilon_0 A$, where C = capacitance, d is the thickness of the sample, $\epsilon_0 = 8.854 \cdot 10^{-12}$ F/m and A is the effective area of the sample. The A.C. conductivity was calculated by using the equation.

Equation (1) alternatively identifies the kinds of charged particles by using their electric conductivities and analyzes the way in which the dielectric characteristics change with the dose rate. The high dielectric permittivity materials have been considered to be very good potential for electronic devices. Ceramics possessing very high dielectric permittivity are being used as voltage capacitors due to their high breakdown voltages. However, they are brittle, suffer from poor mechanical strength and hence cannot be exposed to high fields. Though polymers possess relatively low dielectric permittivity as compare to ceramics, they can withstand high fields, are flexible and easy to process. By combining the advantages of both, one can fabricate new hybrid materials with high dielectric permittivity, and high breakdown voltages to achieve high volume efficiency and energy storage density for applications in capacitors as electric energy storage devices [11–13]. In order to enhance the dielectric permittivity of the (PVDF) polymer, it irradiated with Gamma ray dose of 500 kGy, 1000 kGy, 1500 kGy and 2000kGy. The dielectric permittivity increases as the dose increases and decreases at higher frequency [14-15].

The microstructure and morphology of the samples were characterized by using scanning electron microscope (SEM).

In this paper we report about the investigations of structural electrical and morphological responses of 1.25MeV gamma irradiated (PVDF) polymer samples. We carried out these studies by using XRD, High Frequency Impedance Analyzer and SEM techniques.

2. Experimental Details

The semi-crystalline pure research grade Polyvinylidene fluoride (PVDF) sheet of thickness 80 μm was imported from MS Goodfellow (UK). The polymer samples of size ($1 \times 1 \text{ cm}^2$) were cut from the commercially available sheet. One sample was kept as virgin and the other four samples were subjected to irradiation. The samples were irradiated in vacuum at the atmospheric pressure of 10^{-3} torr in 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 4 kGy/h and source strength was 2 K Curie.

The four identical PVDF polymers samples were exposed with gamma radiation dose of 500 kGy, 1000 kGy, 1500 kGy and 2000 kGy respectively. The UV-visible and FTIR techniques were employed to study the gamma radiation induced changes in PVDF polymer samples. The samples were analyzed with XRD measurements were made on PW-1830 machine by using monochromatic CuK_α (8.04 keV and $\lambda = 0.154 \text{ nm}$). The scanning rate was set from 5° to 70° and a scanning rate of 2.5 step/s. The operating conditions were 25 kV and 30 mA, employing a 0.15-mm slit in front of the detector. The polymer samples were mounted one by one on a sample holder plate without using tape and the fitted profiles of the spectra were obtained by the software.

The dielectric studies were carried out by using High Frequency Impedance Analyzer (PSM 1735) over the frequency range (10 Hz–30 MHz) at ambient temperature. The impedance analyzer was equipped with a small furnace for high temperature measurements. The data generated from the instrument were collected through an interface between instrument and the computer using software (developed in our laboratory).

The morphological was carried out by scanning electron microscope (SEM) using (JEOL, Model No. 3300) operating at 30 kV accelerating voltage. Surface of the samples were coated a thin layer of gold by using the vacuum evaporation technique to minimize samples charging effects due to the electron beam of SEM.

3. Result and discussion

The structural study of poly vinylidene fluoride polymer samples was carried out in the dose range of 500 kGy, 1000 kGy, 1500 kGy and 2000 kGy. The results are interpreted in terms of existing theories. The X-ray diffraction pattern of virgin sample indicates the presence of semi crystalline structure. From this study we observed well defined peaks formed at $2\theta=18.29^\circ$, 19.89° , Which belong to α phase [16 & 17]. Therefore only α phase exist in PVDF polymer at room temperature as shown in figure 1(a). The β and γ phases are present along α phase however the presence of peaks at 20.7° and 20.8° conform the existence of maximum β phase in PVDF

polymer [18]. The diffraction pattern of unexposed PVDF polymer shows a large peak at 19.89^0 indicates the amorphous nature of the sample. The Gamma irradiated PVDF polymer samples shows no significant changes except decrease in the peaks intensities from 454 to 298 and decrease in the d-value is also observed from 5.62 to 2.03. From figure 1(b-e) the irradiated samples also shows an identical pattern in the XRD spectra, except that the width of large peak increases from **20.86 to 22.09** (slight broadening). The overall decrease in peaks intensity and broadening of peaks shows the amorphization of PVDF polymer samples after irradiation. This observed change in intensity of XRD spectra may be due to the destruction of original structure of PVDF polymer [19].

A change in the crystallite size was also observed after irradiation. The average crystallite size was calculated using the Scherrer formula [21]

The decrease in the intensity of peaks and change in the crystallite size due to irradiation from 500 kGy to 2000 kGy shows the formation of disordered system in the irradiated polymer samples. The various observed and calculated parameters, such as the peak intensity, crystallinity, FWHM, dislocation etc. with irradiation dose is provided in the Table (1).

3.1 Electrical study

The electrical study of virgin and gamma irradiated PVDF polymer samples was performed at room temperature and the corresponding graphs are shown in the figures (2, 3&4). From Figure (2) the plot of dielectric constant Vs log frequency indicate that the dielectric constant (ϵ_r) remain constant at lower frequency side and decreases at higher frequencies. From the constant portion of the graph at lower frequencies it shows that the mobility of free charge carrier is constant and thus the dielectric constant remains uniform at lower frequency range. Whereas at the higher side of the frequency the charge carriers moves from the dielectric sides and get trapped against defect sites and induce an opposite charge. The polarization of bound and trapped charges cannot take place at higher frequency and hence the dielectric constant decreases. Such type of decreasing behavior of the dielectric constant is due to the single cluster dipole moment relaxation which takes place at higher frequency [22]. Similar type of behavior was also reported in some other polymers [23]. It is also found that with increasing radiation dose the dielectric constant increases.

Figure (3) shows a plot of dissipation factor vs log frequency for virgin and gamma irradiated samples. From the graph it is observed that $\tan \delta$ factor decreases as the frequency increases. The increase in losses at low frequency could be associated with the polarization of the trapped charge carriers. With increase in frequency, polarization decreases and becomes vanishing small at high frequency range [24]. The increase in dielectric loss as the dose increases from 500 kGy to 2000 kGy attributed to chain scissioning. As for the pyroelectric materials, it is very important to reduce the dielectric constant and loss.

The a. c. conductivity measurement was also carried out at ambient temperature and the corresponding graph is shown in figure (4). The graph shows σ_{ac} a decreasing tendency towards the lower frequency range due to the formation of some defects in the energy gap as a result of v- irradiation. These defects (sometimes called traps or clusters) create barriers against the mobility of charge carriers (electrons) already existing in non-irradiated polymeric materials [25]. From the plot it is also observed that A. C. conductivity increases with the increase of frequency as well as with the increase of dose rate. The alternating current field of high frequency side may cause of net polarization, which is out of phase with the field. This results in increase of a c conductivity at higher frequency. The increases in σ_{ac} at higher frequency due to irradiation attributed to scissioning of polymer chains and the migration of long lived radicals which are trapped mostly in crystalline region to an amorphous region, resulting in an increase of free radicals, unsaturation.

Morphology of the PVDF

Scanning electron microscopy (SEM) was used to examine the changes in the surface texture of PVDF polymer samples before and after gamma irradiation. Figure 5(a-e) shows the SEM micrograph of (a) virgin and gamma irradiated (b) 500 kGy (c) 1000 kGy (d) 1500 kGy (e) 2000 kGy. The results indicated that no porous structure appeared on the surface of the pure PVDF polymer sample; only a raised structure was found, as shown in Figure 5(a). The raised structure might be related to the stacked crystalline lamellae in the polymer. With gamma irradiation the surface morphology of the samples changes, and show granular microstructure with increase in microporosity Fig. 5(b-e). The increase in porosity will enhance the ionic conduction in the irradiated polymer samples. The micrographs of PVDF polymer samples irradiated at different doses reveal the increase in grain shape and size in granular microstructure with decrease in porosity. These results are in agreement with the estimation of crystallite size given in Table (). The gamma irradiation appears to modify the polymer grain formation process, and altering the size and morphology of the pores. The colour of the polymer samples changes from white to near yellow and become brittle after 500 kGy.

The micrograph in Fig. 5a for pure PVDF is characterized by normal crystalline domains uniformly shaped with equal size. The gamma irradiated polymer samples leads to changes in the surface morphology (Fig. 5b–e). The morphology of Fig. 5b gave rise to crystalline domains with coarse spherulitic structure. From these micrographs it can be seen that the spherulites will increase with the increase gamma radiations which gives rise to extended crystalline regions, as shown in Fig. 5e. These spherulites are a very useful feature for piezoelectric and other applications.

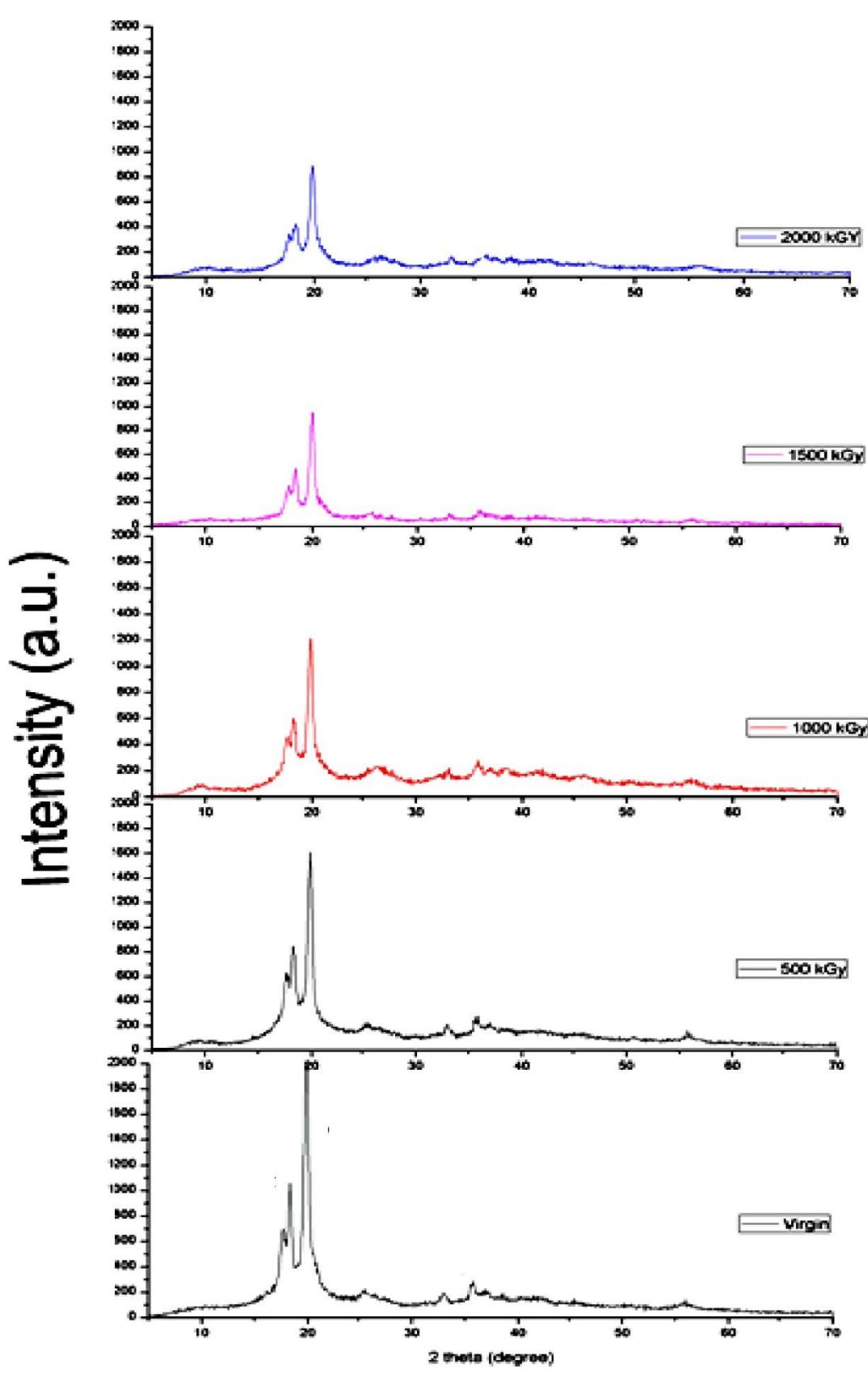


Figure 1

Figure 2

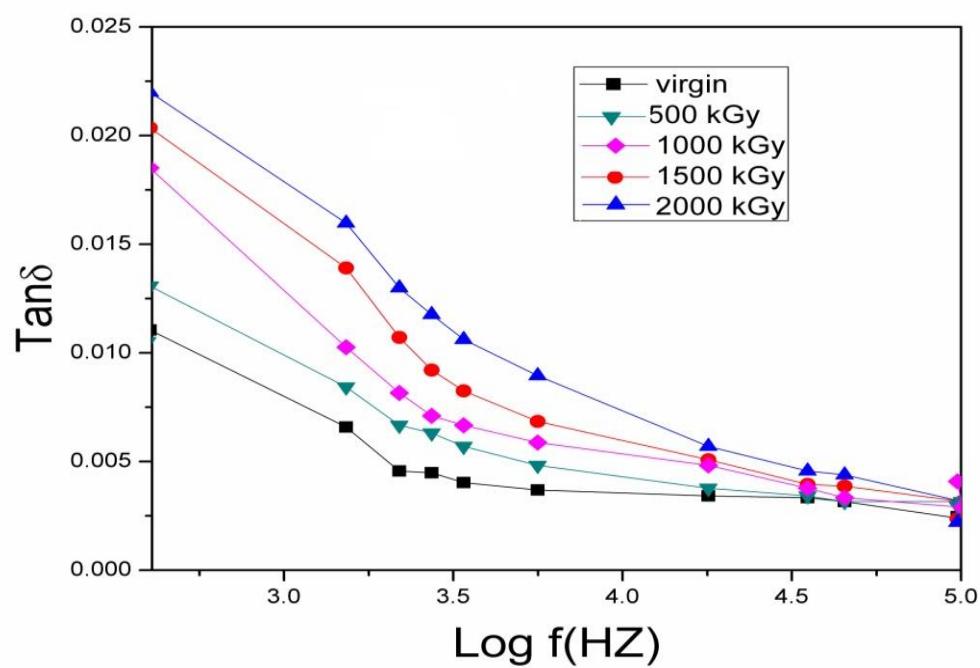
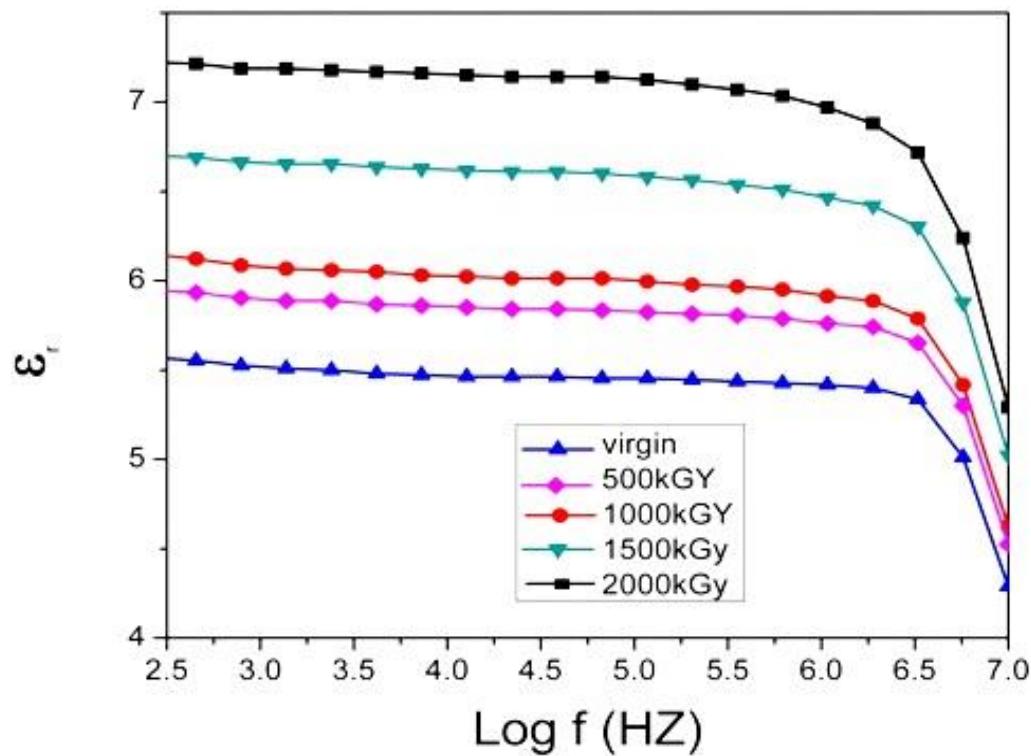


Figure 3

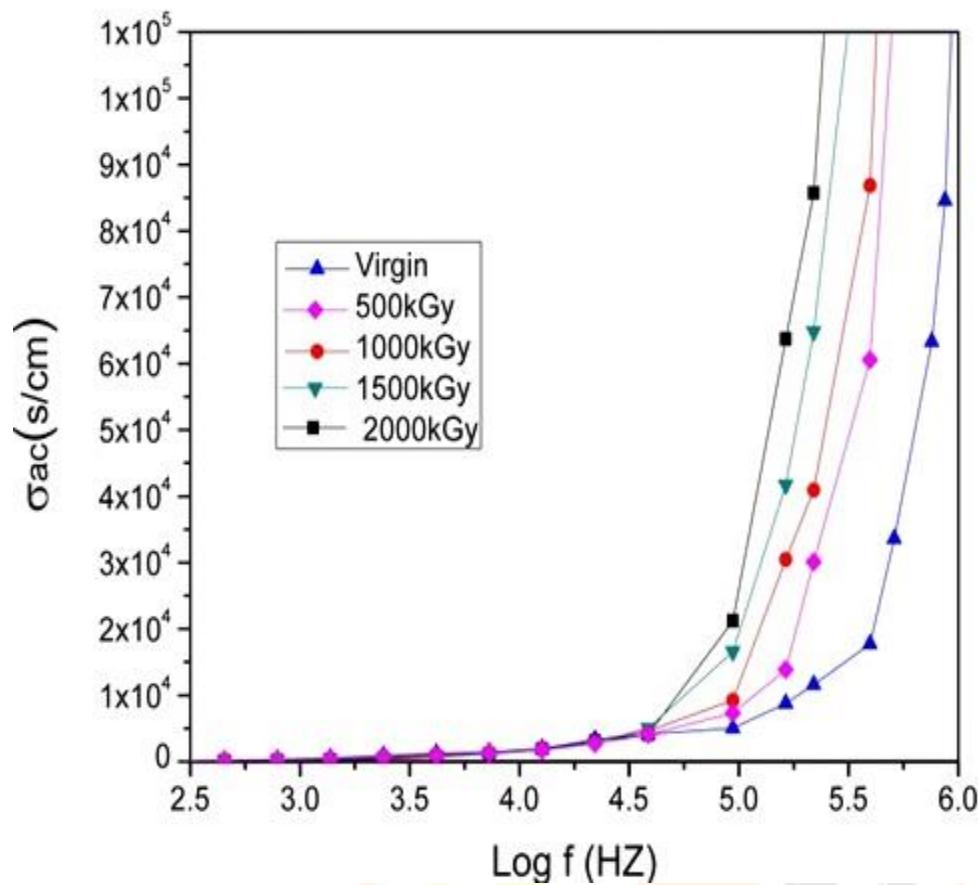
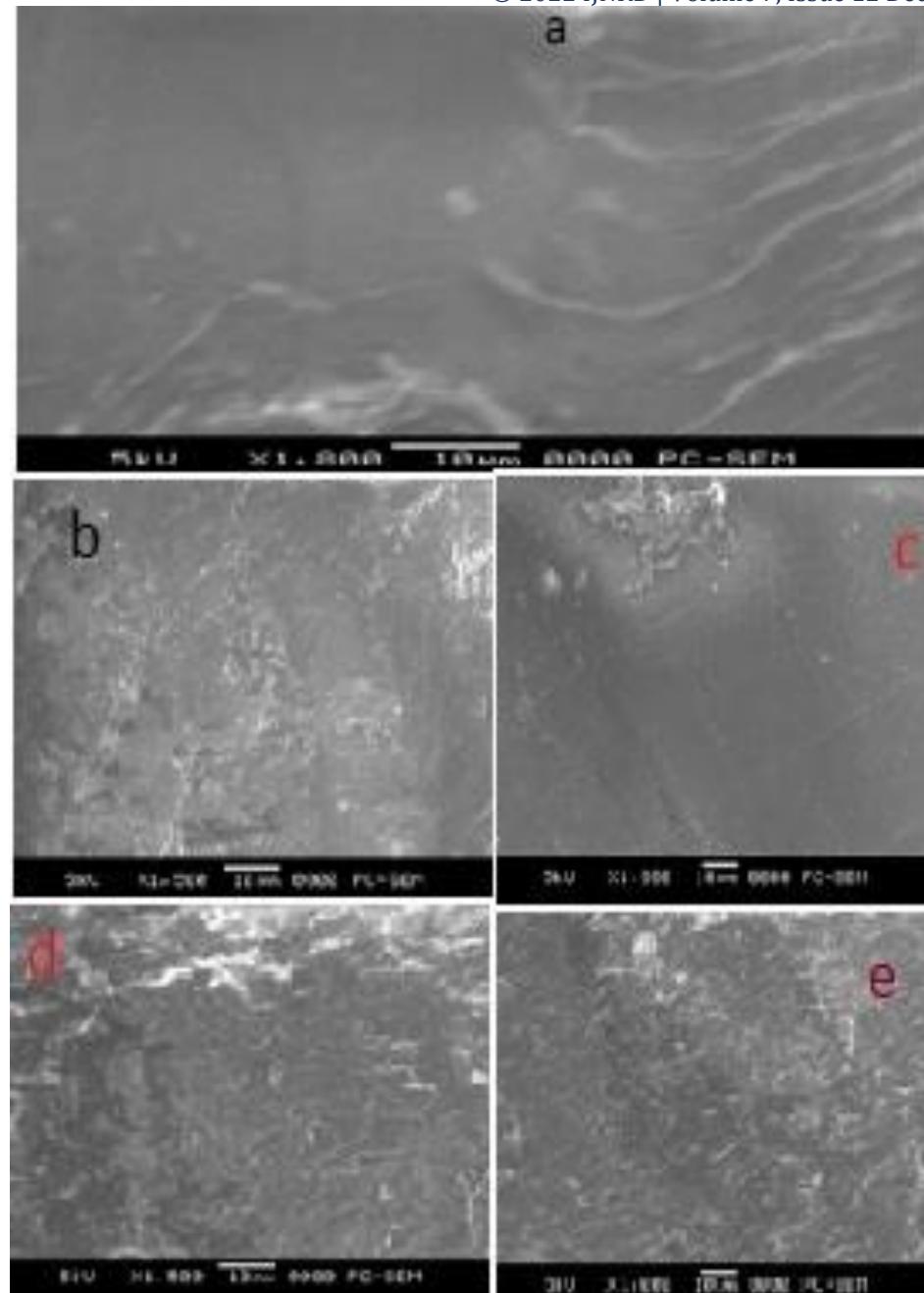


Figure 4

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Figure 5

S No	γ -adiation dose (kGy)	Angle of peak(2θ)	FWHM(β) (A 0)	Crystalline size(L)= $k\lambda/\beta\cos\theta$ (A 0)	Strain ε = $(\beta\cos\theta)/4$	Dislocation $\delta=15\varepsilon/(a^*L)$	d-value (A 0)
Peak 1st	virgin	18.28	0.062	24.86	0.024		5.62
2	500	18.28	0.063	24.44	0.017		4.08
3	1000	18.28	0.069	22.31	0.014		4.05
4	1500	18.28	0.073	21.28	0.013		3.94
5	2000	18.28	0.075	20.53	0.013		3.90
Peak 2nd	Virgin	19.91	0.018	96.20			5.19
2	500	19.91	0.029	57.03			4.70
3	1000	19.92	0.030	55.00			4.61
4	1500	19.91	0.018	55.00			3.60
5	2000	19.91	0.030	55.00			3.52
Peak 3rd	Virgin	32.97	0.018	102.60			3.15
2	500	32.97	0.029	64.16			2.83
3	1000	32.97	0.030	61.60			2.63
4	1500	32.97	0.018	61.60			2.20
5	2000	32.97	0.030	61.60			2.19

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