Effects of Gamma Irradiation on Polyvinylidene Fluoride Thin Films

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Abstract. Polyvinylidene fluoride thin films were synthesized by Sol-Gel method with spin rate of 3000 rpm for 30 sec on ITO glass substrates and were annealed at 170 C. The films were irradiated by Gamma radiation with different doses (10, 30, 40 and 50 kGy). XRD and FTIR spectra have been obtained to identify the presence of α / β phases. Mean crystallite size was calculated by Scherer’s equation. Different vibrational bands were identified and percentage of β phase was determined by FTIR analysis. Optical properties like band gap, refractive index, optical activation energy have been determined. Surface morphology and compositions of pristine and gamma irradiated PVDF thin films were confirmed respectively, by SEM and Energy dispersive X-ray analysis. The comparison of the structural and optical optical properties of pristine PVDF polymer film has been made with those of the Gamma irradiated films.

1. Introduction

Polyvinylidene fluoride (PVDF) is a ferroelectric semicrystalline polymer which exists in four different phases, namely α, β, γ and δ phases. The α-phase has helical structure whereas β-phase all-trans planar zigzag conformation with dipole moments perpendicular to the chain axis, and the γ-phase is intermediate between α and β phases. In recent years, many studies have focused on the crystalline structure of β and γ phases. PVDF has drawn much attention both in scientific and technological field due to its excellent mechanical, pyroelectric, piezoelectric and ferroelectric properties [1]. Only few studies have focused on optical properties of PVDF; there are no detailed studies on optical properties of PVDF films [2]. Irradiation plays an important role in the modification of the physical, chemical, structural, optical, mechanical and electrical properties of polymers by irreversible changes in their macromolecular structure that depends on dosage levels [3]. Gamma rays, X-rays, UV rays, electron beam or laser beams were employed to study the radiation response of polymeric materials. In the present study, PVDF thin films were irradiated by gamma radiation (60Co source) with different doses. Gamma ray interacts with polymers causing chain scission, cross linking and creation of free radicals. Chain scission process reduces tensile strength and elongation whereas crosslinkage increases tensile strength and decreases elongation, both processes occur simultaneously and free radicals may create double bonds by removing hydrogen atoms [4,5]. Batista et. al. [6] reported the effect of gamma irradiation on the crystalline structure of PVDF by differential scanning calorimetry, x-ray diffraction technique. Ribeiro et.al.[7] studied the properties of pristine and gamma irradiated PVDF thin films by infrared spectroscopy, thermal analysis and mechanical measurements. Raghu et.al.[8] investigated the physical and chemical properties of gamma irradiated polymer electrolyte films by FT-IR analysis, uv-vis spectroscopy, thermal analysis, optical micrograph image and DSC and TGA analysis.
PVDF is light in weight and resistant to chemical attack; this promotes the development of micro sensors and actuators for space research, electromechanical, electro acoustic transducers and structural health-monitoring systems[9].

The objective of present work was to identify the formation of α and β phases and to study the changes in structural and optical properties of gamma irradiated PVDF thin films with doses 10, 30, 40 and 50 kGy by XRD, FT-IR, UV-VIS, SEM and EDX techniques.

2. Experimental Details

Granular, AR grade PVDF was supplied by Himedia Laboratories Pvt. Ltd. The solvent N, N-dimethylformamide, (DMF, 99.5%) was purchased from S. D. Fine-Chem. Ltd. PVDF granules were dissolved in 10 ml DMF solution with continuous stirring with a magnetic stirrer for 2h. The obtained solution was spin-coated on ITO glass substrate at a spin rate of 3000 rpm for 30 sec. The obtained PVDF films were annealed at 170 °C for 2h. The films were then irradiated with gamma rays (60Co source) at room temperature using gamma cell at fixed dose rate of 4.918 kGy/hour and varying doses of 10, 30, 40 and 50 kGy. The irradiated films are labelled as 10-PVDF, 30-PVDF, 40-PVDF and 50-PVDF wherein the corresponding dosage is mentioned.

The phases of the obtained PVDF films were confirmed by x-ray diffraction technique using CuKα radiation using PHILIPS X pert PRO X-ray Diffractometer. FTIR spectra were obtained at room temperature using Bruker Tensor 27, Fourier Transform Infrared Spectrometer in the range of 4000-400 cm⁻¹ in transmission mode. UV-Vis absorption and transmission measurements were carried out using Analytical Technologies Ltd. UV/Vis spectrophotometer in the wavelength range 200-1000 nm. The surface morphology was obtained with a ZEISS Scanning Electron Microscope (SEM) and attached with EDX. Compositional analysis was done using EDX.

3. Results and Discussion

3.1. EDX Analysis

(a) pristine PVDF thin film
(b) 10-PVDF thin film
(c) 30-PVDF thin film
(d) 40-PVDF thin film
Figure 1. EDX spectra of pristine and gamma irradiated PVDF thin films. Energy dispersive X-ray analysis was done in order to determine the chemical composition of pristine and gamma irradiated PVDF thin films. The spectra (Figure 1) confirm the presence of elements in desired composition. EDX shows the presence of Carbon and Fluorine elements originating from PVDF structure [10]. Carbon and Fluorine weight percentage increased after gamma irradiation.

Table 1. EDX analysis of films.

|             | Pristine | 10-PVDF | 30-PVDF | 40-PVDF | 50-PVDF |
|-------------|----------|---------|---------|---------|---------|
| Carbon weight % | 26.40    | 29.29   | 27.49   | 28.78   | 26.80   |
| Fluorine Weight % | 52.35    | 70.98   | 72.58   | 71.58   | 72.57   |

3.2. XRD Analysis

XRD analysis gives the structural phase change of pristine and gamma irradiated PVDF thin films and is shown in Figure 2. The sharp narrow peaks at 2θ=30.24°, 35.14° and 50.53° are associated with (110), (200) and (221) reflections of β, α and β crystalline phases, respectively. Gamma irradiated PVDF thin films (30-PVDF, 50-PVDF) showed amorphous phase. The mean crystallite size, D of pristine and gamma irradiated PVDF thin films were obtained by Scherer’s equation:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where $\lambda= 1.54078$ Å, $\beta$ is the full width at half maximum of the diffraction peaks and $\theta$ is the corresponding diffraction angle. The mean crystallites size were 20.58 nm for pristine PVDF thin film, 30.85, 20.57 and 414.69 nm for 10-PVDF, 40-PVDF and 50-PVDF films. The changes in the structural parameters for pristine and gamma irradiated PVDF thin films are shown in the Table 2.
Figure 2. XRD patterns of pristine and gamma irradiated PVDF thin films.

Table 2. Structural parameters for pristine and gamma irradiated PVDF thin films.

| Films       | 2θ   | D (nm) | d (Å) |
|-------------|------|--------|-------|
| Pristine PVDF | 35.16| 20.58  | 2.55  |
| 10-PVDF     | 35.14| 30.85  | 2.55  |
| 40-PVDF     | 35.15| 20.57  | 2.55  |
| 50-PVDF     | 30.35| 460.23 | 2.94  |

3.3. FTIR Analysis

Figure 3. FT-IR transmission spectra of pristine and gamma irradiated PVDF thin films.
The FT-IR spectra of pristine and gamma irradiated PVDF thin films were recorded between 1600 and 600 cm\(^{-1}\) and are shown in Figure 3. The transmission bands at 744, 670, 674, 669 and 674 cm\(^{-1}\) represents the crystalline \(\alpha\)-phase, CF\(_2\) bending and skeletal bending vibrational mode. The transmission bands at 1253, 843, 846, 848 and 843 cm\(^{-1}\) were identified as crystalline \(\beta\)-phase, CH\(_2\) rocking and CF out of plane deformation mode [11]. Intensity of transmission bands reduced after gamma irradiation in all the irradiated films as compared to pristine PVDF thin film. The bands at 1004, 1042, 1034, 1038 and 1042 cm\(^{-1}\) were identified as C-C asymmetric stretching vibrations. After gamma irradiation, new transmission bands were formed at 1172 and 1168 cm\(^{-1}\) which indicates the CF\(_2\) symmetric stretching vibrations; these bands were absent in pristine PVDF thin films. The bands at 1406, 1403, 1405 and 1393 cm\(^{-1}\) were identified as CH\(_2\) wagging vibrational modes [12,13]. New broadened transmission bands were formed at 1532, 1545 and 1537 cm\(^{-1}\) which indicates CH\(_2\) bending vibrational modes and these bands were absent in pristine PVDF thin films [14].

3.4. **UV-Vis Spectroscopy**

![UV-Vis absorbance spectra of pristine and Gamma irradiate d PVDF thin films.](image)

**Figure 4.** UV-Vis absorbance spectra of pristine and Gamma irradiated PVDF thin films.

UV-Vis spectroscopy technique is used to find the optical properties of pristine and gamma irradiated PVDF thin films in the wavelength range 350-800 nm. Figure 4 represents the absorption spectra of pristine and gamma irradiated PVDF thin films. Absorption of light energy decreases from 350 – 800 nm. In between 400 - 600 nm, two distinct characteristic peaks were observed in pristine PVDF thin films and peaks gradually disappeared with the increase of irradiation dose.

3.4.1 **Optical Band Gap**

The optical band gap can be measured from its absorption spectra. The absorption coefficient was calculated using the following relation [15]:

\[
\alpha(\nu) = 2.303 \left( \frac{A}{l} \right)
\]

(2)

where A is the optical absorbance and \(l\) is the thickness of the PVDF thin films. The value and nature of the optical band gap depends on absorption coefficient. Optical band gap can be calculated using the following relation [16].
\[
(\alpha h^2) = B(hv - E_g)
\]  
(3)

where \(\alpha\) is absorption coefficient, \(h\) is Planck’s constant, \(\nu\) is the frequency, \(B\) is a constant which depends on the transition probability, \(E_g\) is the optical band gap and \(n\) is an index which indicates the optical absorption process. Theoretically, it is equal to 2 for direct allowed transition, 1/2 for indirect allowed transition, 2/3 for direct forbidden transition and 1/3 for indirect forbidden transition [17]. In the present case, we have calculated the direct band gap and indirect band gap of pristine and gamma irradiated PVDF thin films for \(n=2\) and \(n=1/2\) respectively using equation (3). For the determination of direct band gap, \((\alpha h\nu)^2\) was plotted as a function of photon energy, \(h\nu\). The value of direct band gap \((E_g)\) was calculated from the intersection of the extrapolated line with the photon energy axis \((\alpha h\nu)^2=0\) using the linear portion of absorption edge of the UV-Vis spectra. Figure 5 represents the direct optical band gap for pristine and gamma irradiated PVDF thin films. For the determination of indirect band gap, \((\alpha h\nu)^{1/2}\) was plotted as a function of photon energy, \(h\nu\). The value of indirect band gap \((E_g)\) was calculated from the intersection of the extrapolated line with the photon energy axis \((\alpha h\nu)^{1/2}=0\) using the linear portion of absorption edge of the UV-Vis spectra. Figure 6 represents the indirect band gap for pristine and gamma irradiated PVDF thin films. The value of direct and indirect band gap \((E_g)\) decreased with an increase of irradiation dose.

For a linear carbon chain structure, the number of carbon atoms \((N)\) in a cluster is related to the optical energy direct band gap and is given by the equation [18]:

\[
N = \frac{2\beta:\pi}{E_g}
\]  
(4)

where \(2\beta\) is the energy of a pair of adjacent \(\pi\) sites and \(\beta\) is taken to be 2.9 eV as it is associated with \(\pi \rightarrow \pi^*\) optical transition in the \(-C=\pi-\) structure [19]. The change in the number of carbon atoms in clusters as a function of irradiation dose for gamma irradiated PVDF thin films are shown in Table 3. The number of carbon atoms in cluster increased with increasing irradiation dose. This is due to the breakage of C–H bonds. The refractive index \((n)\) can be determined from the direct optical band gap using the relation proposed by Dimitrov and Sakka [20]:
Refractive index of gamma irradiated PVDF thin films increased due to the decrease of direct optical energy band gap hence, refractive index of thin film depends on the defects present in the gamma irradiated PVDF thin films.

3.4.2 Optical Activation Energy

The absorption coefficient near the optical band edge shown an exponential dependence on photon energy and this dependence is given as Urbach rule. The optical activation energy for pristine and gamma irradiated PVDF thin films were determined using Urbach rule [21]:

$$\alpha = C \exp \left( \frac{h \nu}{E_a} \right)$$  \hspace{1cm} (6)

where C is a constant and $E_a$ is the optical activation energy. The values of optical activation energy $E_a$ gives details about the optical behavior of the pristine and gamma irradiated PVDF thin films. Figure 7 shows the variation of ln($\alpha$) with the photon energy ($h \nu$) for pristine and gamma irradiated PVDF thin films. The values of the optical activation energy were determined by taking the reciprocal of the slopes of linear part of these plots. The values of optical activation energy for pristine and gamma irradiated PVDF thin films are presented in Table 3. The activation energy for gamma irradiated PVDF thin films increased with increasing irradiation dose except for 40-PVDF film. This is due to the formation of free radicals, breakage of C-H bonds and increase in the density of defects of gamma irradiated PVDF thin films [22,23].

![Figure 7. ln($\alpha$) Vs. ($h \nu$) for pristine and gamma irradiated PVDF thin films.](image-url)
**Table 3.** The values of optical band gap, number of carbon atoms in clusters, refractive index and optical activation energy.

| Films    | Direct band gap (eV) | Indirect band gap (eV) | N       | n       | E_a (eV) |
|----------|----------------------|------------------------|---------|---------|---------|
| Pristine | 2.85                 | 2.91                   | 6.39    | 2.44    | 0.90    |
| 10-PVDF  | 2.77                 | 2.50                   | 6.58    | 2.46    | 1.10    |
| 30-PVDF  | 2.51                 | 2.45                   | 7.26    | 2.54    | 1.65    |
| 40-PVDF  | 2.41                 | 2.31                   | 7.56    | 2.58    | 0.80    |
| 50-PVDF  | 2.15                 | 2.26                   | 8.48    | 2.67    | 7.42    |

**3.5 SEM Analysis**

![SEM images](image)

**Figure 8.** SEM morphology of pristine and gamma irradiated PVDF thin films (a) pristine PVDF (b) 10-PVDF (c) 30-PVDF (d) 40-PVDF and (e) 50-PVDF films.

Surface morphology of thin films was studied by SEM. Figure 8 shows the SEM images of pristine and gamma irradiated PVDF thin films. Figure 8(a) shows the formation of spherulite structure and white irregular shape particles dispersed on the dark field which indicates the surface roughness of the pristine PVDF thin film. Figure 8(b) shows the gamma irradiated 10-PVDF thin film which illustrates the spherulite structure originated from centre region and white irregular shape...
particles dispersed uniformly on spherulite structure [24]. 30-PVDF thin film exhibit the spherulite structure and white irregular shaped particles, while 40-PVDF thin film exhibit the dark smooth surface with the formation of pin holes. Similarly, 50-PVDF thin film exhibit the spherulite structure with dark smooth surface and spreading pin holes over the film [25].

4. Conclusions

Pristine PVDF and gamma irradiated PVDF thin films were synthesized on ITO glass substrate by Sol-Gel technique. EDX spectra confirmed the presence of Carbon and Fluorine elements in desired composition which were originating from PVDF structure. From the XRD analysis, it is clear that synthesized films have both α and β phases and crystallite size was in nano scale. Different modes of vibration, characteristic bands, and crystalline phases of prepared films were identified by FTIR analysis. Two distinct characteristics peaks were observed in pristine PVDF thin films and peaks gradually disappeared with an increase of irradiation dose. Transparency of gamma irradiated PVDF thin films reduced as compared to pristine PVDF thin films. The direct band gap, indirect band gap, number of carbon atoms, refractive index and optical activation energy were determined by uv-vis spectroscopy. Spherulite structure with a smooth surface, carbon clusters and pin holes were formed in PVDF thin films.

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