Optical properties and structural features of UV-C irradiated polyvinylidene chloride films

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Research Article

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Abstract:
The modifications caused in polyvinylidene chloride (PVDC) polymer films on exposure to ultra-violet light (UV-C light of wavelength 254 nm) in air for different exposure times varying from one hour up to six hours have been investigated by using ultraviolet - visible (UV-Vis) and Fourier transform infrared (FTIR) spectroscopic techniques, as well as powder X-ray diffraction (XRD) technique. XRD scans reveal that the degree of crystallinity ($X_c$) increased from 4.7% up to 28.6% on increasing the UV exposure time of PVDC from 1 hour up to 4 hours, and a further increase in the exposure time causes a decrease in the value of $X_c$. The FTIR scans reveal the formation of hydrogen bonded hydroxyl groups as well as conjugated alkene structures in the PVDC sample on exposure to UV-C radiation. For the study of modification in band structure of the UV irradiated PVDC films, the UV-Vis spectroscopy was used; it was found that the optical band gap decreases from 4.70 eV down to 3.92 eV, as obtained from the plot of $\sqrt{\varepsilon_i} \ h\nu$ versus $h\nu$, using linear fit method and the penetration depth ($\delta$) decreased from 0.0074 cm down to 0.0035 cm at 4.88eV, the energy corresponding to UV-C radiation. The calculation of percentage decrease in the value of $\delta$ with respect to wavelength and UV-C exposure time reveals that UV-C irradiated PVDC films are good radiation shields against both UV-A and UV-B EM radiation. The study of refractive index with respect to wavelength reveals that UV irradiation of PVDC films is an effective method to modify the refractive index of PVDC, thereby making the material suitable for use in different optical applications. The optical dielectric constant was studied systematically, which demonstrates that the energy storage properties of the PVDC films can be tuned and tailored by UV-C radiation. Details are discussed.

Keywords: Polyvinylidene Chloride; Optical Analysis; Penetration depth ; Optical band gap ; FTIR ; Degree of crystallinity; UV-C irradiation.

Introduction.

The effect of ultraviolet (UV) radiation on polymeric materials and composites is an area of rapidly increasing interest. Several high technology industries require special type of polymers that exhibit a specific response on exposure to UV radiation [1]. The UV photon absorption is “molecular site” specific, and often leads to electronically excited states. The effect of UV light in polymeric materials could involve either side group or main chain scission or/and crosslinking [2]. Even a small amount of radiation can induce significant changes in the physical or mechanical properties of a polymer, with the extent of these changes being dependent upon the chemical structure of a particular polymer and the ambient atmosphere. In some cases, even a few cross-links or scissions at different sites per polymer molecule can dramatically affect the strength or solubility of a polymer, which in turn determines a particular polymer application in a specific industry, like for example, microelectronics, radiation sterilization, modified polymeric materials and surface coatings [3-5].

The UV irradiation of polymers will frequently give rise to small molecular products, resulting from bond scission followed by abstraction or combination reactions. Information regarding such processes can give valuable insight into the mechanism of the radiation induced degradation process. The development of a particular color is a common manifestation of degradation of a polymeric sample on exposure to UV radiation [6-7]. In the area of microlithography, UV radiation is essential for the photolithographic process, a conventional technique used in the fabrication of integrated circuits (ICs). Microlithography is an essential process in the fabrication of silicon chip ICs
and involves modification of the solubility or volatility of thin polymer resist films by UV radiation [8]. Nowadays, almost all the commercial devices made by photolithographic techniques utilize UV radiation in the wavelength range 365-436 nm. The lithographic strategies which are alternatives to conventional photolithography involve deep-UV (in the wavelength range 240-260nm), scanning electron-beam and x-ray radiation for the lithography process [9].

Polymeric materials are used in a wide variety of applications, including space applications. However, the polymeric materials are subject to degradation in space by UV and high energy radiation, as well as oxygen atom bombardment. Materials used in space sometimes encounter harsh radiation environments, like for example, during solar flares. The study of the effects of radiation on polymer materials is of increased importance in the case of aerospace programs, as the design lifetime of satellites and other space vehicles has increased. Thus, the effects of radiation on the materials planned to be used for aerospace applications must be experimentally investigated. Such characterization would include an understanding of the immediate reactions taking place in these materials, on exposure to radiation, in addition to continued post-exposure degradation processes.

Radiation is being used increasingly for the sterilization of medical and pharmaceutical items, both for the convenience of this process, and also because of concerns about the toxicity of chemical sterilizing agents which are used alternatively for sterilization. The radiation sterilization of biomedical polymeric materials, particularly implantable surgical devices, raises significant concerns. Polymers typically undergo some radiation induced degradation leading to discoloration and associated deterioration in their properties. Knowledge of the relationship between the chemical composition of polymeric materials and their radiation sensitivity is necessary in order to enable the selection of appropriate materials for radiation sterilization. Information on the radiolysis products, from both natural and synthetic polymers, is also required by the food industry as the radiation sterilization of products related to this industry is a common procedure. Irradiation of polymers causes modification of properties of the polymeric material, which is currently the basis of major industries in heat shrinkable films and tubing, crosslinked polymers and grafted copolymers [10]. This area is now entering an era of new technology resulting from greater knowledge of the chemical processes. There are many applications of radiation modified polymers, including their use in the medical and healthcare fields. These materials may be used as implantable materials, controlled release drug preparations, and hydrophilic wound dressings. UV and high energy irradiation of polymer coatings on substrates such as metals, plastics and optical fibers is being developed industrially for a wide variety of purposes.

Ultraviolet-C (UV-C radiation of wavelength 254 nm) light can reduce bacteria levels on food contact surfaces. Several studies have focused on inactivating or reducing food borne pathogens on fresh meat and ready-to-eat meat products, and how these treatments could impact the quality attributes of the food. Color changes, texture deformation and the lipid oxidation are the most possible effects of UV-C treatment on the quality of ready-to-eat food products such as cured meat, frankfurters, bologna and cooked meat products [11]. There have been numerous studies on the changes of the spectral characteristics of high polymers when subjected to prolonged irradiation by UV light. Polymers are progressively replacing conventional materials in many engineering applications. Physical, mechanical and chemical properties of the polymeric materials are crucial in assessing their fields of applicability. For instance, the structural, thermal properties, optical properties and storage stability in air of PVDC films were rigorously studied in the sense of relating these properties to its internal structure. The action of ionizing radiation is known to be one of the major sources of altering the internal structure of polymers, leading to a wide span of inter-related changes in their properties. It may result in cross-linking of the molecular chains. [12-15]

In this paper, pure PVDC films, each of thickness 0.0016 cm were irradiated by UV-C light of wavelength 254 nm for different time of exposure, from one hour up to six hours. The color of the UV-C irradiated PVDC films gradually changed from transparent to orange as the exposure time (to UV-C radiation) increased, which give an indication that radiation induced degradation processes could have occurred in the irradiated polymeric films. The detailed structural studies were carried out by using the different analytical techniques, such as UV-visible spectroscopy, FTIR and XRD. From UV-visible spectroscopy, optical parameters like transmittance, reflectance, extinction coefficient, penetration depth, refractive index (RI) and optical dielectric constant were obtained, and the corresponding graphs were plotted for detailed analysis. The optical band gap (OBG or $E_g$) is obtained by using Tauc’s plot and Mott Davis relation, along with error estimation (by residual analysis). As the exposure of the PVDC films to UV-C radiation increased from one hour up to six hours, the OBG decreased. XRD analysis on the unirradiated and UV-C irradiated PVDC films was carried out, and the results revealed increase in the degree of crystallinity ($X_c$) of the UV-C irradiated PVDC films, for exposure times varying from one hour up to four hours;
but beyond the UV-C exposure time of four hours, the value of $X_C$ decreased. FTIR technique was used to analyze the chemical changes at the molecular level which are caused by UV-C irradiation on the PVDC films. The results obtained were compared with those of the unirradiated sample (that is, the PVDC film with UV-C exposure time of zero (0 hour)). The FTIR scans reveal the formation of hydrogen bonded hydroxyl groups as well as carbonyl groups in the UV-C irradiated PVDC sample; this could be due to the exposure of the PVDC sample to UV-C radiation, with air as the ambient atmosphere.

2. Experimental

2.1. Materials and instruments:

Pure PVDC thin films, each of thickness 0.0016 cm, were utilized for this study. The thickness was measured using a digital micrometer (Yuzuki™), and the optical spectra were recorded by using a UV-VIS spectrometer (JASCO; model 670-V), XRD data (40 kV, 30 mA, Cu k-α 1D), and FTIR spectra (NICOLET 6700) were recorded. The PVDC films were exposed to ultraviolet radiation of wavelength 254 nm, and the irradiance is 3.1 mW/cm$^{-2}$ (the films were kept at a fixed distance of 14 cm from the UV tube), using a germicidal tube (Philips TUV 15W/G15T8, Holland) at room temperature, the ambient atmosphere (for the composite sample) being air.

![Figure 1. Photographs of (I) UV-C irradiation set-up (II) PVDC films before (0hr) and after irradiated with UV-C from 1 hour up to 6 hours, changes (visible to the naked eye) are observed in color of the UV-C irradiated films (the films become orange in color)](image)

2.2. Analysis and Characterization:

The PVDC films of each thickness of 0.0016 cm were exposed to the UV radiation of 254 nm, for different intervals of time (from 1hr up to 6hr) using the UV-C source. Optical absorbance for these films was recorded in the wavelength range 200–800 nm by using a computerized UV-VIS spectrophotometer. Using the optical absorbance data, the optical parameters ($\alpha$, T, R, K, n, $\epsilon$ and $\delta$) were calculated by using the equations listed later in this paper (in section 3.1), and the corresponding graphs were plotted. FTIR data (in the wavenumber range 4000 cm$^{-1}$ - 500 cm$^{-1}$) was used to study the molecular chemical changes caused by UV irradiation on PVDC films. The XRD data was analyzed to determine micro-structural parameters of the composite films, like its degree of crystallinity, average crystallite size, average crystallite separation, dislocation density, number of crystallites per unit area, lattice strain and scattering function.

3. Results and Discussion

3.1. Optical properties:

From the UV-Vis spectra of PVDC films [shown in figure 2 (a)], which corresponds to unirradiated and UV-C irradiated PVDC films (at different exposure times to UV radiation), it is observed that the maximum absorbance peak appeared at 208 nm for all the PVDC films (for 0 hr to 6 hr irradiation exposures); this absorption is due to $\pi$
$\pi^*$ electronic transition. The main effects of UV-C irradiation are chain scission and cross linking, accompanied by the formation of unsaturated products in the polymer chain. Free radicals are produced in the polymer due to irradiation with UV-C radiation, and these radicals can react with oxygen in air and form carbonyl and hydroxyl groups. The change in absorbance of the polymeric material on UV-C irradiation is likely to be due to the formation of unsaturated groups and the presence of carbonyl and hydroxyl groups in it. It must be the carbon-chlorine bond which absorbs the incident radiation, as it is the photo-sensitive group [16]. As the exposure time of the PVDC film to UV-C radiation increases, a hyper-chromic (monotonically increased absorbance) effect is observed in the peak observed at 208 nm; this may due to absorption of radiation by the hydroxyl groups present in the sample because of reaction of polymer with oxygen present in air (irradiation effect). The change in the absorption intensity and the photo-degradation of the PVDC film (on exposure to UV-C radiation), with gradual change in color (from colorless to orange) of the polymeric film (which is originally transparent), seems to justify this conclusion.

![Figure 2](image_url)

**Figure 2.** [a] Variation of absorbance with wavelength of incident radiation (UV-Visible spectra) for unirradiated and UV irradiated PVDC films, for different exposure times, expressed in hours (hr), [b] The variation in the absorbance (relative to wavelength of incident UV-Visible radiation) caused by UV irradiation, obtained by subtracting the spectrum of the unirradiated PVDC film from the spectrum of each of the UV-C irradiated PVDC films, the exposure time of which varies from one hour up to six hours.

Referring the figure 2 [b], the absorption shoulder has a broad maximum at about 295 nm when the curve corresponding to the unirradiated sample (0 hour) is subtracted in each irradiated curve corresponding to PVDC films with UV exposure time varying from one hour up to six hours. The shape of the curve and the position of the maximum are maintained the same as the irradiation is continued. This indicates that progressively longer conjugated bond species are not being produced. After this maximum absorption at 296 nm, the absorption monotonically falls off gradually into the visible region. This long tail in visible region is due to carbonium ion formation which may arise as a consequence of the interaction of UV-induced free radicals with the chlorinated conjugated structure. A similar trend was observed in the study by Oster et al [15].

The band gap energy for direct and indirect forbidden and allowed transitions were determined by using Tauc’s plot (from the linear fit of data points in the high absorption edge of the UV-Visible spectra of the PVDC films) and Mott Davis relation (Eq.1) as shown in figure 3 [(a) to (d)]. The optical bandgap ($E_g$) decreases with an increase in the exposure time. Davis and Mott’s model infers that the localized states within the band structure are the reason for the reduction of the band gap. Thus, the obtained results seem to be in good agreement with Davis and Mott’s discussion. The value of $E_g$ obtained for direct forbidden transitions (DFT) for the unirradiated sample and those that are obtained for indirect allowed transitions (IAT) for the UV-C irradiated (from 1 hour up to 6 hours exposure time) PVDC films [Table 1] closely matched with the $E_g$ values obtained from the $\sqrt{\varepsilon \cdot hv}$ versus $hv$ plot (figure 3(e),
obtained by the linear fit method). The value of energy band gap $E_g$ determined from the plot of $\alpha$ Vs $hv$ (figure 3(f)) has also been listed in table 1.

The optical band gap is obtained by using Tauc’s plot and the Mott Davis relation, which follows.

$$\alpha hv = B(hv - E_g)^n \quad (1)$$

where $\alpha$ is the absorption coefficient, $h$ is the Planck’s constant, $v$ is the frequency of incident radiation, and $E_g$ is the optical band gap. The parameter $n$ can take values $\frac{1}{2}$, 2, $\frac{3}{2}$ and 3 for direct allowed transition (DAT), indirect allowed transition (IAT), direct forbidden transition (DFT) and indirect forbidden transition (IFT), respectively.

Figure 3. (a) $(\alpha hv)^2$ Vs $hv$; (b) $(\alpha hv)^{1/2}$ Vs $hv$; (c) $(\alpha hv)^{1/3}$ Vs $hv$; (d) $(\alpha hv)^{2/3}$ Vs $hv$; (e) $\sqrt{\epsilon_i}$ Vs $hv$; (f) $\alpha$ Vs $hv$
Table 1. The variation of $E_g$ with time exposure, where DAT = Direct allowed transition; IAT=Indirect allowed transition; DFT=Direct forbidden transition; IFT=Indirect forbidden transition.

<table>
<thead>
<tr>
<th>Exposure time to UV-C radiation $t$ (hour)</th>
<th>$E_g$ from $(\alpha h\nu)^{1/2}$ vs $h\nu$ (eV)</th>
<th>$E_g$ from $(\alpha h\nu)^{2/3}$ vs $h\nu$ (eV)</th>
<th>$E_g$ from $(\alpha h\nu)^{1/3}$ vs $h\nu$ (eV)</th>
<th>$E_g$ from $\alpha$ vs $h\nu$ (eV)</th>
<th>$E_g$ from $(\epsilon_i^{0.5} h\nu) vs h\nu$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.05±0.011</td>
<td>4.00±0.006</td>
<td>4.25±0.012</td>
<td>4.66±0.003</td>
<td>4.70±0.009</td>
</tr>
<tr>
<td>1</td>
<td>5.46±0.032</td>
<td>4.45±0.015</td>
<td>4.71±0.020</td>
<td>5.07±0.013</td>
<td>4.55±0.011</td>
</tr>
<tr>
<td>2</td>
<td>5.38±0.023</td>
<td>4.28±0.006</td>
<td>4.58±0.012</td>
<td>4.84±0.017</td>
<td>4.41±0.008</td>
</tr>
<tr>
<td>3</td>
<td>5.28±0.030</td>
<td>4.22±0.004</td>
<td>4.53±0.007</td>
<td>4.79±0.006</td>
<td>4.32±0.008</td>
</tr>
<tr>
<td>4</td>
<td>5.35±0.014</td>
<td>4.23±0.004</td>
<td>4.55±0.007</td>
<td>4.82±0.004</td>
<td>4.31±0.010</td>
</tr>
<tr>
<td>5</td>
<td>5.35±0.043</td>
<td>4.15±0.004</td>
<td>4.50±0.006</td>
<td>4.75±0.006</td>
<td>4.20±0.008</td>
</tr>
<tr>
<td>6</td>
<td>5.30±0.017</td>
<td>4.14±0.008</td>
<td>4.50±0.006</td>
<td>4.75±0.005</td>
<td>4.22±0.008</td>
</tr>
</tbody>
</table>

The corresponding variation in other optical parameters like absorption coefficient, reflectance, transmittance, refractive index, penetration depth and optical dielectric constants were observed as shown in figure 4[(i) to (xii)]. These parameters were calculated using Eqs. (2) to (8), respectively. The transmission is found to decrease, while the reflectance is gradually increasing (for wavelengths from 200 nm up to 450 nm), with an increase in exposure time of irradiation [figure 4 (ii and iii)]. This is due to the increase in the degree of crystallinity of the polymeric film as observed from the XRD study due to UV-C irradiation, thereby minimizing the crystal defects, which in turn leads to the increase in absorbance of the thin films. The films become more absorbing, due to which there is a decrease in the transmittance with an increase in exposure time to UV-C radiation. It is found that, with an increase in wavelength of EM radiation in UV-Visible range, the transmittance increases (significant change in transmittance is observed in the 210 nm to 500nm wavelength range), but above 500 nm wavelength, there is no identifiable difference found (although transmission is higher), and such materials with a high transmission (in the visible region) has a potential to be used in many applications, like optoelectronic sensors and photonic devices. In figure 4(iv), the gradual decrease in k (for all the different exposure time) with wavelength represents the light dispersion and drop in absorption, respectively. But, with an increase in exposure time of the PVDC film to UV-C radiation, the k value increased, which is due to a decrease in surface smoothness [R. Naik et al (17)] of the UV irradiated PVDC film.

Absorption coefficient, $\alpha = \frac{2.303 \times A}{t}$ (2)

where A is the absorbance and t is the thickness of the PVDC film (in cm).

Transmittance $T = 10^{-A}$ (3)

where A is the absorbance and T is the transmittance.

Extinction coefficient $K = \frac{\alpha \lambda}{4\pi}$ (5)
where $\lambda$ is the wavelength of incident Electro-magnetic radiation and $\alpha$ is the absorption coefficient.

Refractive index (RI), \[ n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \]  
where R is the reflectance.

Penetration Depth \[ \delta = \frac{1}{\alpha} \]  
where $\alpha$ is the absorption coefficient.

Optical Dielectric constant \[ \epsilon = n^2 - k^2 + 2nk \]  
Here, $n^2 - k^2$ is the real part of the optical dielectric constant, denoted by the symbol $\epsilon_r$, whereas $2nk$ is the imaginary part, denoted by the symbol $\epsilon_i$, whereas the symbol $n$ denoted the RI of the film and $k$ is the extinction coefficient.
The value of the $\varepsilon$ (optical dielectric constant) increases with an increasing UV-C exposure time, which demonstrates that the energy storage properties of the PVDC films can be tuned and tailored by the UV-C radiation [figure 4(vii)]. Both the values of real part ($\varepsilon_r$) and imaginary part ($\varepsilon_i$) of $\varepsilon$ increases with an increasing UV-C exposure time and decreases with increasing wavelength. The maximum value attained by $\varepsilon_r$ is equal to 7 and that of $\varepsilon_i$ is equal to 0.0065. At the photon energy of UV-C radiation of 254 nm wavelength is 4.88 eV, the value of $\varepsilon_r$ increases from 3.73 (for unirradiated PVDC film) up to 5.66 (for 6 hr irradiated PVDC film), and that of $\varepsilon_i$ increases from $11 \times 10^{-4}$ (for unirradiated PVDC film) up to $27 \times 10^{-4}$ (for 6 hr irradiated PVDC film). The dissipation factor (tanD) increases with increase in UV-C exposure time of PVDC films. The value of tanD varies from $2.84 \times 10^{-4}$ (for unirradiated PVDC film) to $4.8 \times 10^{-4}$ (for 6 hr irradiated PVDC film) [see figure 4 (vii) to (xii)]. Compared to the
value of \( \varepsilon_r \), the order of the values for \( \varepsilon_i \) and \( \tan \delta \) are too small. The low dissipation factors indicate the high-quality, high performance electrical or electronic systems. It is also important for plastic insulators in high-frequency applications such as radar equipment or microwave parts. Similarly, the high dissipation factors are important for polymers that are to be heated in a radio frequency or microwave oven for welding or drying etc. Increase in dielectric constant with increasing UV-C exposure time can be described based on increasing the density of states, because \( \varepsilon_i \) is directly correlated to the density of states within the solid polymer film’s forbidden gap. A higher dielectric constant is required for the electric applications where high capacitance is needed [18-20].

Penetration depth is basically the effective distance of penetration of electromagnetic (EM) wave into the material, and is defined as \( \delta = 1/\alpha \). The thickness of the sample (through which radiation penetrates) when optical intensity of the electromagnetic radiation (in the UV-Visible region of the EM spectrum) becomes 36.8% below its value at the surface of the thin film is called its penetration depth (\( \delta \)). The value of absorption coefficient (\( \alpha \)) of a medium for a particular wavelength of EM radiation is a measure of propagation and absorption of EM waves when it passes through the medium, and is dependent on dielectric loss and so, it shows the same trend as that of dielectric loss. As revealed by the graph [see figure 5 (a)], the value of \( \delta \) decreases on increasing the exposure time of the PVDC film to UV-C radiation. When \( \delta \) decreases, it implies that the material becomes more opaque to EM radiation. It is clear that the value of \( \alpha \) is low for unirradiated film, and the value of \( \delta \) for this film is high, as the penetration depth is inversely related to absorption coefficient. Since UV-radiation of wavelength 254 nm has been used (the corresponding photon energy is 4.88 eV), as seen from graph shown in Figure 5(b) and (c), the value of penetration depth gives a measure of the distance up to which UV light will travel through a film, corresponding to a particular time of exposure to the UV-C light. The penetration depth decreased from 0.0074 cm (for unirradiated sample) down to 0.0035 cm (for the sample exposed to UV-C radiation for six hours), on UV irradiation. The decrease in \( \delta \) and \( 5\delta \) was observed as the exposure time of UV-C radiation increased, whereas the values of \( \delta \) and \( 5\delta \) increased with an increase in wavelength [from 208 nm up to 750 nm, refer the Table 2, A and B]. The value of \( 5\delta \) is the thickness at which the incident radiation is absorbed up to 99.3% [Eqs.(9) and (10)] The percentage (%) decrease in the \( \delta \) (or \( 5\delta \)) were determined and it is observed that initially it shows an increasing trend and reaches its peak at 350 nm wavelength and then, it gradually decreases [figure 5 (d)]. The figure 5(d) represents the % decrease in the \( \delta \) with respective to wavelength; the graph is divided into four regions, corresponding to Ultraviolet-C (I), Ultraviolet-B (II), Ultraviolet-A (III) and visible regions (IV) of the electromagnetic (EM) spectrum. Here the % decrease in \( \delta \) with wavelength in UV-C region decreases up to 230 nm (reaches to minimum value of 33.8%), and above this wavelength, the value of % decrease in \( \delta \) increases and reaches its peak value at 350 nm (73%). This implies that the UV-C irradiated PVDC films are good radiation shields against UV-A and UV-B EM radiation. The UV-C radiation absorbed by PVDC films is capable of causing structural damage in the target material; so, the variation in the depth of penetration indicates the different depths of the material where damage is expected to occur (due to UV irradiation), starting from surface damage up to bulk degradation.

The decrease of the value of \( \alpha \) and \( n \) [figure 4 (i) and (v)] with wavelength indicates an increase in the transparency of the film at a higher wavelength, which becomes suitable for light waves to propagate easier. Moreover, the value of \( \alpha \) and \( n \) increased with increase of exposure time and therefore, the irradiated sample can be used as good absorber of the radiation in the lower wavelength region [200-400 nm], with a significantly lower thickness of the material being used. The value of \( n \) for the PVDC film at 254 nm (wavelength of UV-C radiation, corresponding to photon energy equal to 4.88 eV) increases with the increase in time of UV exposure from 1.45 (for unirradiated PVDC film) up to 2.4 (for 5 hr and 6 hr irradiation). Above the wavelength equal to 225 nm, the value of \( n \) increases with increase in the time of exposure, and it is observed that below this wavelength, the value of \( n \) decreases with UV exposure time. The refractive index of the sample film decreases with increasing wavelength and reaches a nearly constant value at long wavelength (above 500 nm) suggesting a normal dispersion, and the decrease in value of \( n \) with increasing wavelength indicates the best optical characteristic of UV-C irradiated PVDC films, with promising applications in the visible region. A deep and comprehensive understanding of the refractive index is vital for designing optoelectronic devices. High refractive index-based polymer materials are required for optical data...
storing, lenses, anti-reflective coatings and immersion lithography. In order to fabricate a material that is optically active, the refractive index has to be modified. The UV irradiation of PVDC films is an effective method to modify its refractive index, thereby making the material suitable for use in different applications, such as the optical devices, like mirrors, optical sensors, waveguide-based optical circuits, optical interference filters, solar cells, high performance eyeglass lenses, photo-optical switching and optical fibers demand high refractive index materials.

To quantify the illumination fraction transmitted through a material, Beer–Lambert established the relationship

\[
\frac{I_t}{I_o} = e^{-\alpha t}
\]

(9)

where the fraction of light incident and transmitted by the film are represented as \(I_o\) and \(I_t\), respectively. The ratio of incident to transmitted light is dependent upon the light path length \(t\) (here it equals to the thickness of the PVDC films), and the polymer material’s absorptivity or absorption coefficient (\(\alpha\)) at specified light wavelength. When \(\delta\) (penetration depth) equals 5\(\delta\), then Eq.17 can be used to obtain the following.

\[
\frac{I_t}{I_o} = e^{-5} = 0.0067 \quad \text{[Substituting } \alpha=1/\delta \text{ in (17)], from which } 1 - \frac{I_t}{I_o} = 0.9933 = 99.33%.
\]

(10)

Table 2. The variation of \(\delta\) (penetration depth) and 5\(\delta\) with wavelength for different UV-C exposure time of PVDC films [from unirradiated (0hr) up to 6 hr]

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
<th>208 nm</th>
<th>250 nm</th>
<th>300 nm</th>
<th>350 nm</th>
<th>400 nm</th>
<th>450 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (hour)</td>
<td>(\delta) (cm)</td>
<td>5(\delta) (cm)</td>
<td>(\delta) (cm)</td>
<td>5(\delta) (cm)</td>
<td>(\delta) (cm)</td>
<td>5(\delta) (cm)</td>
</tr>
<tr>
<td>0</td>
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<td>0.0090</td>
<td>0.0065</td>
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<td>0.0250</td>
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<td>0.0032</td>
<td>0.0160</td>
<td>0.0040</td>
<td>0.0200</td>
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<tr>
<td>6</td>
<td>0.0010</td>
<td>0.0050</td>
<td>0.0034</td>
<td>0.0170</td>
<td>0.0042</td>
<td>0.0210</td>
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<table>
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<th>(\lambda) (nm)</th>
<th>500 nm</th>
<th>550 nm</th>
<th>600 nm</th>
<th>650 nm</th>
<th>700 nm</th>
<th>750 nm</th>
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<td>Time (hour)</td>
<td>(\delta) (cm)</td>
<td>5(\delta) (cm)</td>
<td>(\delta) (cm)</td>
<td>5(\delta) (cm)</td>
<td>(\delta) (cm)</td>
<td>5(\delta) (cm)</td>
</tr>
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<td>0.220</td>
<td>0.048</td>
<td>0.240</td>
<td>0.051</td>
<td>0.255</td>
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<td>0.200</td>
<td>0.044</td>
<td>0.220</td>
<td>0.047</td>
<td>0.235</td>
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<td>0.023</td>
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<td>0.130</td>
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<tr>
<td>3</td>
<td>0.022</td>
<td>0.110</td>
<td>0.025</td>
<td>0.125</td>
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<td>0.135</td>
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<tr>
<td>4</td>
<td>0.021</td>
<td>0.105</td>
<td>0.024</td>
<td>0.120</td>
<td>0.027</td>
<td>0.135</td>
</tr>
<tr>
<td>5</td>
<td>0.017</td>
<td>0.085</td>
<td>0.020</td>
<td>0.100</td>
<td>0.022</td>
<td>0.110</td>
</tr>
<tr>
<td>6</td>
<td>0.018</td>
<td>0.090</td>
<td>0.022</td>
<td>0.110</td>
<td>0.024</td>
<td>0.120</td>
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3.2 Analysis of XRD:

The different parameters like degree of crystallinity ($X_c$), Average crystallite size ($C_r ave$), Average crystallite separation ($C_s ave$), Dislocation Density ($D$), Number of crystallites per unit surface area ($N$), Lattice strain ($L_s$) and Scattering function ($S$) were determined [using Eq.s (11) to (17)], by analyzing the XRD scans (see figure 6 (a)) of the PVDC films (unirradiated and UV-C irradiated, for different exposure times). The value of degree of crystallinity of PVDC films is found to increase on increased duration of exposure to UV-C radiation, that is, from $X_c = 4.7\%$ for unirradiated PVDC film up to $X_c = 28.6\%$ for UV-C irradiated PVDC film exposed to UV-C radiation for 4 hours [figure 6 (b)], but a further increase in the exposure time (for 5hr and 6hr) results in a decrease of the degree of crystallinity of the PVDC film. Referring to the table 3, there is a decrease in strain and dislocation density of the PVDC films with increase in the exposure time to UV-C radiation, which ensures the increase in the degree of crystallinity of the PVDC films with increase in time of irradiation. At the point of four hours exposure time of UV-C radiation, the degree of crystallinity is maximum; here, the average crystallite size and scattering functions are maximum whereas the other parameters [(C_s)ave, D,N and L_s] are minimum.

\[
X_c = \frac{A_c}{A_c + A_A} \times 100 \tag{11}
\]

where $A_c$ and $A_A$ are the area under the crystalline peaks and amorphous profiles, respectively.

The Scherrer equation for average crystallite size

\[
(C_r)_{ave} = \frac{\kappa \lambda}{\beta \cos \theta} \tag{12}
\]
Average crystallite separation \((Cs)_{ave}\) \(\quad (Cs)_{ave} = \frac{5\lambda}{8 \sin \theta}\) \hspace{1cm} (13)

In equations (10) and (11), \(\lambda\) is wavelength of incident X-rays \((\text{Copper } K_\alpha, \lambda=1.5406 \text{ Å})\), \(\theta\) is the Bragg angle or scattering angle in radian and in Eq (10), \(\beta\) refers to full width at half maximum (FWHM) in radians, and \(k\) is the shape factor which is typically equal to 0.9 for FWHM \((\beta)\).

\[
\text{Dislocation Density} \quad D = \frac{1}{[(Cs)_{ave}]^2} \hspace{1cm} (14)
\]

\[
\text{Scattering function} \quad S = \frac{1}{d} \hspace{1cm} (17)
\]

where \(d\) is interplanar spacing

Figure 6. a) X-ray diffraction pattern of UV-C treated PVDC films; b) Degree of crystallinity Vs exposure time.

Table 3. Variation of the XRD parameters of the PVDC film, relative to the exposure time to UV-C radiation

<table>
<thead>
<tr>
<th>Time of exposure (hour)</th>
<th>Degree of crystallinity (%)</th>
<th>Average crystallite size ((C_R)_{ave}) (nm)</th>
<th>Average crystallite separation ((C_S)_{ave}) (Å)</th>
<th>Dislocation Density (D \times 10^{16}) (m(^{-2}))</th>
<th>Number of crystallites per unit surface area (N \times 10^{19}) (m(^{-2}))</th>
<th>Lattice strain (L_s)</th>
<th>Scattering function (S \times 10^{10}) (m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>04.66±0.064</td>
<td>5.30</td>
<td>7.06</td>
<td>3.56</td>
<td>10.70</td>
<td>0.048</td>
<td>0.177</td>
</tr>
<tr>
<td>1</td>
<td>13.67±0.107</td>
<td>8.14</td>
<td>7.10</td>
<td>1.51</td>
<td>2.97</td>
<td>0.031</td>
<td>0.176</td>
</tr>
<tr>
<td>2</td>
<td>16.21±0.008</td>
<td>8.33</td>
<td>7.10</td>
<td>1.44</td>
<td>2.77</td>
<td>0.029</td>
<td>0.175</td>
</tr>
<tr>
<td>3</td>
<td>14.87±0.086</td>
<td>8.06</td>
<td>7.03</td>
<td>1.54</td>
<td>3.05</td>
<td>0.030</td>
<td>0.177</td>
</tr>
<tr>
<td>4</td>
<td>28.58±0.082</td>
<td>8.88</td>
<td>6.99</td>
<td>1.27</td>
<td>2.30</td>
<td>0.028</td>
<td>0.178</td>
</tr>
<tr>
<td>5</td>
<td>13.70±0.008</td>
<td>8.44</td>
<td>7.10</td>
<td>1.40</td>
<td>2.66</td>
<td>0.030</td>
<td>0.176</td>
</tr>
<tr>
<td>6</td>
<td>03.97±0.031</td>
<td>7.46</td>
<td>7.07</td>
<td>1.79</td>
<td>3.84</td>
<td>0.034</td>
<td>0.176</td>
</tr>
</tbody>
</table>

Number of crystallites per unit surface area \(N = \frac{t}{[(C_R)_{ave}]^3}\) \hspace{1cm} (15)

where \(t\) is thickness of the film

Lattice strain \((L_s)\), \(L_s = \frac{\beta}{4 \tan \theta}\) \hspace{1cm} (16)

where \(\beta\) is full width at half maximum (FWHM)
3.3 Analysis of FTIR spectra

The FTIR spectra of un-irradiated and UV-C irradiated (at different exposure times) PVDC film are shown in figure 7. The broad vibrational band around 3400 cm$^{-1}$ in the FTIR spectrum corresponds to –OH group. The broad vibrational peak around 3400 cm$^{-1}$ pertains to the water (the physically adsorbed water molecules) or moisture absorption of -OH group, which is not present in un-irradiated (0 hr) film, followed by gradual broadening of the peak as irradiation exposure time (to UV-C) increases.

![FTIR spectra of UV-C irradiated PVDC films.](image)

**Figure 7.** FTIR spectra of UV-C irradiated PVDC films.

**Table 4.** Assignments for the absorption bands in the FTIR spectra of UV-C irradiated PVDC films.

<table>
<thead>
<tr>
<th>Wavenumber corresponding to peak of the absorption band (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3419.2, 3416.6, 3399.8, 3398.9, 3400.2, 3340</td>
<td>-OH group (hydrogen bonded)</td>
</tr>
<tr>
<td>3227, 3244.5</td>
<td>-OH group</td>
</tr>
<tr>
<td>2985.1, 2986, 2985.2, 2981.3</td>
<td>CH$_2$-symmetric stretching</td>
</tr>
<tr>
<td>2918.2, 2918, 2918.3, 2917.1, 2917</td>
<td>CH$_2$-asymmetric stretching</td>
</tr>
<tr>
<td>2852.4, 2853.5, 2853, 2852.4, 2852.4</td>
<td>C=O stretching</td>
</tr>
<tr>
<td>1738.6, 1738.4, 1736</td>
<td>C=O stretching, C=C stretching</td>
</tr>
<tr>
<td>1650.5, 1652, 1636.7, 1635.7, 1635.7, 1635.7</td>
<td>CH$_2$-bending</td>
</tr>
<tr>
<td>1408.3, 1407.5</td>
<td>CH$_2$-wagging</td>
</tr>
<tr>
<td>1356.4, 1358.4, 1358.7, 1356.4</td>
<td>skeletal stretching</td>
</tr>
<tr>
<td>1069.7, 1069.6</td>
<td></td>
</tr>
<tr>
<td>655, 655.1, 654.6</td>
<td></td>
</tr>
<tr>
<td>597.8, 598, 598.5</td>
<td></td>
</tr>
<tr>
<td>529.4, 529.7</td>
<td></td>
</tr>
</tbody>
</table>

The conspicuous absorption band around 1636 cm$^{-1}$ due to irradiation effect (which is not present in unirradiated PVDC film) is due to conjugated alkene, that is, due to C=C stretching vibration as a result of an increase in un-
saturation, or the generation of C=C bond could be a result of cross-linking between the radicals after the initial chain scission. The variation in the absorption bands of C–Cl stretch vibrations at 529.4 cm⁻¹, 597.8 cm⁻¹, and 659.5 cm⁻¹, as well as C=O stretching (of acetyl groups) at 1738 cm⁻¹ and C–C at ~1070 cm⁻¹ and CH₂ stretch vibrations at ~2853 cm⁻¹, 2918 cm⁻¹, 2985 cm⁻¹, 1408 cm⁻¹ and 1356 cm⁻¹ cannot be discerned, as UV-C irradiation has apparently no effect on these bands for exposure times varying from 0 hr (unirradiated sample) to 6 hr; only a small amount of intensity (negligible) variation was observed (figure 6). The band at ~1070 cm⁻¹ is assigned to the skeletal stretching mode (due to the stretching of the main chain skeleton of the polymer molecules). The 1357 cm⁻¹ band is assigned to the CH₂-wagging mode and the 1408 cm⁻¹ band is assigned to the CH₂-bending mode and the polarization of the band. In analogy with the discussion regarding the CH₂-stretching modes of polyvinyl chloride [21- 22], the 2985 cm⁻¹ is assigned to the CH₂-symmetric stretching mode and the bands at 2918 cm⁻¹ and 2852 cm⁻¹ are due to the CH₂ anti-symmetric stretching modes. The band at 1408 cm⁻¹ in the FTIR spectrum is assigned to the CH₂-bending mode. These results were confirmed by taking the standard spectrum and analyzing twice.

4. Conclusions

The effect of UV-C radiation on PVDC films, for different exposure times varying from 1 hour up to 6 hours was investigated using UV-Visible and FTIR spectroscopy as well as XRD scans. The change in absorbance in UV-Visible spectra is due to the formation of unsaturated groups and presence of carbonyl and hydroxyl groups. The photo-degradation of the polymeric films (which is originally transparent) occurred. The broad maximum of absorption shoulder at about 295 nm indicates that progressively longer conjugated bond species are not being produced. The long tail in visible region is a consequence of free radical interaction with the chlorinated conjugated structure, and due to carbonium ion formation. The optical bandgap decreases with increased exposure time and the value of bandgap obtained from DFT for unirradiated PVDC film and that obtained from IAT for irradiated (for 1 hour up to 6 hours exposure time to UV-C radiation) PVDC films closely matched with the values obtained by √εᵣhv versus hv plot. The decrease in transmittance and the increase in reflectance with an increase in exposure time of irradiation indicate the improved film crystallinity and minimized crystal defects. The detailed study of penetration depth (δ) and the percentage decrease in δ with UV exposure time revealed that the UV-C irradiated PVDC films are good radiation shields against UV-A and UV-B EM radiation. The UV irradiation of PVDC films is an effective method to modify its refractive index, thereby making the material suitable for use in different applications, say in optical devices. The study of ε (optical dielectric constant) reveals the energy storage properties of the PVDC films can be tuned and monitored by UV-C irradiation. The degree of crystallinity of the PVDC film increased from 4.66% to 28.58% due to UV-C irradiation, for exposure time varying from 0 hour to 4 hours, but for a further increase in the irradiation time (for 5hrs and 6hrs), it is found that the degree of crystallinity is reduced. The FTIR studies reveals the formation of broad vibrational peak around 3400 cm⁻¹ which is due to the moisture absorption of -OH group, which is not present in un-irradiated PVDC film, followed by gradual broadening of the peak as irradiation exposure time (to UV-C) increases, indicating hydrogen bond formation. The conspicuous absorption band around 1636 cm⁻¹ is observed due to irradiation effect (which is not present in unirradiated PVDC film) and is due to conjugated alkene, that is, due to C=C stretching vibration, which is a result of an increase in un-saturation or else, the generation of C=C bond maybe as a result of cross-linking between the radicals formed after the initial chain scission of polymer molecules on UV-C irradiation.

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Corresponding Author: Conceptualization, Supervision, Reviewing and Editing, Visualization, Validation.
All authors have read and agreed to the published version of the manuscript and there are no other persons who satisfied the criteria for authorship, but are not listed.

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References


