Effect of Gamma Irradiation on the Physical Properties of PVA Polymer

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Abstract
Polyvinyl alcohol (PVA) films were prepared by casting method. The optical properties was measured in the wavelength rang of (200–900) nm, by using UV-visible spectroscopy. The effect of irradiation lead to degradation on the physical properties such as absorbance, transmittance, refractive index, extinction coefficient in addition of the real and imaginary part of dielectric constant was studied. This study reveals that all these parameters affected by the increasing of them irradiation, and also found that the optical energy gap has been increased with the increasing of the irradiation. The structural properties are studied by using XRD, FTIR spectrum, and FESEM.

Key Words: optical properties, structural properties, effect of gamma irradiation, PVA polymer.

1. Introduction
Polymers are important materials that having wide applications in the fields of science. There is great importance for studying the effect of radiation on the physical and chemical properties of the polymer because of it is wide use in radiation environment such as, nuclear power plants, spacecraft [1]. Exposure of the polymer to radiation can lead to numerous changes in the polymer structure, which in turn changes the physical and chemical properties of the polymer. The changes in the polymer structure depend on the type of radiation, the polymer composition, the dose amount, and the irradiance conditions [2]. PVA is non-toxic, water-soluble synthetic polymer, which is widely used due to it has good physical and chemical properties [3], it has been used in many industrial application commercial, medical, and food sectors and has been used to produce many end products, such as lacquers, resins, surgical threads, and food packaging materials that are often in contact with food [4].

A. J. Almusawe, et al [5]. Studied Gamma irradiation effect on the optical properties of Bromocresol Green dye doped polymethylyl
methacrylate (PMMA) thin films, showed the transmission relationship with absorption is a logarithmic relationship.

Islam Shukri Elashmawi et al (2019)[6], studied the effect of irradiation at different time's Nd:YAG laser on optical properties of PVA/Ag, the absorbance spectra is increase with increase times of irradiated (5, 10 and 15) min, and the energy gap before irradiation for PVA and PVA/Ag nanocomposite are(3.96 eV, 3.33 eV), but for irradiation the energy gap for PVA is (3.96 eV) and for PVA/Ag the energy gap are (3.01, 2.19 and 1.94) eV at different irradiation of time's (5, 10 and 15) min respectively. It is clear the energy gap is decrease with increase irradiation times.

F.M. Alia et al (2019) [7], studied the optical properties of PVA films doped with methyl violet-6B (MV-6B) which are prepared by casting method, show the addition MV-6B to PVA has a strong effect on the optical properties, and energy gap is decrease with increase concentration of PVA.

The aim of the present work is to prepare PVA films using casting method. PVA thin film will be irradiated by γ-rays and physical properties will be tested before and after irradiation.

2. Theoretical Part

The relationship between the intensity of incident and transmitted light is given by the equation (1) [8]

\[ I = I_0 e^{-\alpha t} \]  

Where (I₀) and (I) are the intensities of the incident and transmitted light, respectively, (α) is the optical absorption coefficient; (t) is the thickness of film and absorbance is defined by \( A = \log \left( \frac{I_0}{I} \right) \).

The optical absorption coefficient (α) can be calculated from the optical absorbance spectra by using the relation (2) [8]:

\[ \alpha t = \log \left( \frac{I_0}{I} \right) = 2.303A \]  

The extinction coefficient (K) is related to absorption coefficient (α), by the following equation [9]:

\[ K = \frac{\alpha \lambda}{4\pi} \]  

Where, \( \lambda \) is the wavelength of incident light.
The reflectance (R) can be calculated from the values of the absorbance and transmission coefficient from the equation:

\[ R = 1 - (A + T) \]  \hspace{1cm} (4)

The refractive index (n) depends on the reflectance (R) and extinction coefficient (K) and it can be calculated from the following equation[10]:

\[ n = \sqrt{\frac{4R}{(R-1)^2} - K^2 - \frac{R+1}{(R-1)}} \]  \hspace{1cm} (5)

The absorption edge for direct and indirect transition can be obtained in the view of the proposed by Tauc et al. [11]

\[ \alpha h\nu = A(h\nu - E_g)^r \]  \hspace{1cm} (6)

Where \((h\nu)\) is the energy of photon, \((A)\) is the proportional constant, \((E_g)\) is the allowed or forbidden energy gap of direct and indirect transition and \((r)\) is constant depended on the electronic transition, \(r=1/2, 3/2, 2\) or \(3\) for allow direct, forbidden direct, allow indirect and forbidden indirect transition, respectively.

The Dielectric constant clarified the ability of material to polarization and can be express by the following equation:

\[ \varepsilon = \varepsilon_r - \varepsilon_i \]  \hspace{1cm} (7)

The dielectric constant is divided into two parts real \((\varepsilon_r)\) and imaginary \((\varepsilon_i)\) and described by the following equations:

\[ \varepsilon_r = n^2 - K^2 \]  \hspace{1cm} (8)

\[ \varepsilon_i = 2nK \]  \hspace{1cm} (9)

2. Experimental Work

Polyvinyl alcohol (PVA) is a light, white, powdery solid polymer when it is pure. The structure of PVA is shown in figure (1) [12]. PVA solution was prepared by taking certain amount of PVA powder (0.5) g in 15 ml distilled water, stirred for 3 to 4 hours at room temperature by magnetic stirrer (hot plate) in (25 – 35) °C to ensure for fully dissolving. Forming the PVA films by pouring out the solution in glass plates with diameter (5) cm and allowed it to evaporate slowly at room temperature for (3 to 4) days to get homogeneous films.

The samples were irradiated with irradiation dose(1, 3, 5, 8, 10 and 15) kGy, using \textsuperscript{60} Co Gamma Cell-900, of strength rate 3.7 Ci and dose rate 53 Gy/h, which emits mono-energetic 1.17 and 1.33 MeV, and a half-
life of 5.3 years. The source used has been built into a lead container with facilities for interesting chemicals without exposing the operator to the radiation, installed at the physics department, university of Baghdad.

Figure (1): The Chemical structure of polyvinyl alcohol [12]

3. Result and Discussion
3.1 Absorption Spectrum for pure PVA
Figure (2), shows the UV/Vis absorption spectra of unirradiated and irradiated PVA films. The results from figure (2) shows the absorbance spectra as a function of the wavelength of the incident light for PVA film. As it is clear in figure (2), shows absorption spectrum is increase with increase in irradiation dose but we note full of some absorption spectra at (3, 8 and 10) kGy because of during irradiation process increase in the movement energy of the molecules in the polymeric chain with increase in the irradiation doses, which lead to a weakening of the bonding forces between the partial chains of the polymer. This result corresponds to A.H. R.H. Al-Azzawi [13].

Figure (2): Absorption spectrum for PVA polymer at different irradiation doses
Table (1) shows the highest peak of the absorption spectrum at different irradiation doses

| Wavelength (nm) | Dose (kGy) | Abs  |
|-----------------|------------|------|
| 280             | 0          | 0.198|
| 280             | 1          | 0.259|
| 280             | 3          | 0.248|
| 280             | 5          | 0.285|
| 280             | 8          | 0.228|
| 280             | 10         | 0.183|
| 280             | 15         | 0.288|

3.2 Transmission Spectrum
The transmittance spectrum for irradiated PVA films with different irradiation doses exhibit opposite behavior in absorbance spectra as shown in figure (3) because the transmission relationship with absorption is a logarithmic relationship. These results are in agreement with A.J. Almusawe, et al [5].

3.3 Reflection Spectrum
The reflection spectra after irradiation by Gamma ray for pure PVA is showed in figure (4). The reflection spectrum is calculated from absorption and transmission spectrum according to equation (4).
Figure (4): The reflection spectrum for PVA films at different irradiation doses

Figure (5) shows the refractive index for pure PVA films after irradiated by gamma ray. The refractive index like reflection spectrum where the refractive index for pure PVA increased after irradiated, but it is decreased at (8 and 10) kGy. These changes in the refractive index and reflection spectrum of irradiated PVA may be due to degradation process that is predominant [14].

3.4 Absorption Coefficient

The absorption coefficient is defined as the ability of material to absorption light with a limited wavelength per unit length and it is a characteristic property for every absorber molecule or ion [15]. The value of absorption coefficient (α) is calculated from equation (2) for all samples. The absorption coefficient helps to deduce the nature of electronic transition. Figure (6) showed the absorption coefficient (α) for pure PVA polymer for different radiation dose. When the high absorption
coefficient values \((\alpha > 10^4 \text{cm}^{-1})\) at higher energies, direct electronic transitions have been expected and the energy momentum preserve of the electron and photon. Whereas the values of absorption coefficients low \((\alpha < 10^4 \text{cm}^{-1})\) at low energies, indirect electronic transitions have been deduced. In this work the values of absorption coefficients were low energies and indirect electronic transitions have been deduced.

![Absorption coefficient for PVA films at different irradiation doses](image)

**Figure (6): Absorption coefficient for PVA films at different irradiation doses**

### 3.5 Optical Energy Gap

The optical energy gap is the value of optical energy gap that is necessary to develop the electronic band structure of film material [16]. Figure (7) show the relationship between absorption edge \((\alpha h\nu)^{1/m}\) and energy of photon for the pure PVA film. It can be noted that the energy gap for pure PVA film can be measured and equal to \((4.66 \text{ eV})\) at 0kGy, for allowed and forbidden transition. When irradiated PVA polymer with different radiation dose, the value of energy gap for PVA increase with increasing radiation dose to become \((4.88 \text{ eV})\) at 10kGy and \((5 \text{ eV})\) at 15kGy. These different changes in energy gap occurred for PVA illustrated in table (2).

| Dose (kGy) | 0  | 1  | 3  | 5  | 8  | 10 | 15 |
|------------|----|----|----|----|----|----|----|
| Energy gap(eV) | 4.66 | 4.68 | 4.78 | 4.74 | 4.84 | 4.88 | 5  |

**Table (2): Indirect band gap \((E_g)\) values for irradiated PVA films by Gamma irradiation**
3.6 Extinction coefficient

The extinction coefficient depends on absorbance so that the behavior of extinction coefficient is similar to the absorption spectrum for all samples. Figure (8) illustrates the extinction coefficient for irradiated pure PVA films at different radiation doses.

3.7 Dielectric constants

The optical constants are very important for the quantitative determination of the electronic band structure of solids from information of optical reflectivity; transmission and refraction provide the way to determine the dielectric constants of solid, which is related to the band structure. Equations (8) and (9) represent the real and imaginary parts of...
dielectric constants, respectively. The real part of dielectric constants for pure PVA films at different radiation dose which showed in figure (9). The real dielectric constant increases with increasing radiation dose that mean the real dielectric constant depend on the square of refractive index and the square of extinction coefficient. The behavior of these figures is similar to refractive index because of the smaller value of $k^2$ compared to $n^2$.

![Figure (9): real dielectric constant for PVA films at different irradiation doses](image)

The imaginary part of dielectric constants for pure PVA films at different irradiation doses in figure (10). Imaginary dielectric constant for pure PVA film films increased with increasing radiation dose, and this constant depends on the $k$ value, which is related to the variation of the absorption coefficient.

![Figure (10): imaginary dielectric constant spectrum for PVA films at different irradiation doses](image)
4. X-ray Diffraction

The XRD shall provide information on the crystallinity of the materials for unirradiated and irradiated samples. The XRD pattern for pure PVA film exhibited one broad peak with $2\theta = 19.4174^\circ$, intensity is 1735.25, this means the semi crystalline nature of pure PVA film; this result correspond with the research [17].

![X-ray diffraction pattern of un-irradiated pure PVA](image)

Figure (11): X-ray diffraction pattern of un-irradiated pure PVA

The XRD pattern for irradiated pure PVA by Gamma radiation at irradiation dose (3kGy), the intensity that equal (1952.05) and $2\theta = 19.4005^\circ$ clear in figure (12).

The XRD pattern for irradiated PVA film shows the intensity is equal (880.56) and $2\theta = (19.3544)$. Figure (13) illustrates the XRD pattern for irradiated PVA films by gamma ray at irradiation dose (15kGy). It is clear the intensity is increase with increase irradiation dose [18].
5. FTIR Characterization

The FTIR spectroscopy has real important because it has given the main characteristics peaks of pure PVA. All (FTIR) spectra are taken in transmittance mode.

Figure (14) shows the FTIR spectrum for pure PVA polymer. The many bands are listed in the table (3). The peaks appear between (625-970) cm\(^{-1}\) refers to C-H out of plane bending. The peak (1047) cm\(^{-1}\) refer to C-O stretching vibration is disappear. The peaks appeared at 1328.29 cm\(^{-1}\) and 1373.64 cm\(^{-1}\) refers to C-(CH\(_3\)) symmetric bending vibration. The peak appeared between (1550-1780) cm\(^{-1}\) refers to carbonyl stretching vibration (C=O). The two peaks appeared at 2912.57 cm\(^{-1}\) and 2939.54 cm\(^{-1}\) refer to symmetric and asymmetric CH\(_3\) stretching vibration respectively, the broad band at 3231.73cm\(^{-1}\) refer to O-H hydrogen-bonded alcohols.
The effect of gamma irradiation to PVA polymer on FTIR spectrum is shown in figure (15) and these bands are listed in the table (3) for different irradiation doses (1, 3, 5, 8, 10 and 15). In irradiation the band at (919 cm\(^{-1}\)) refer to C-H out phase bend for (15 kGy) is disappear , and the band at (1024) cm\(^{-1}\) at irradiation dose (8 kGy), and the band at (1243) cm\(^{-1}\) at irradiation doses (5, 8 and 10) kGy respectively refers to C-O stretch are disappeared , and the band at (1328 cm\(^{-1}\)) refers to CH\(_2\) bending is disappeared at irradiation dose ( 3 kGy), the new peak at (1579.50 cm\(^{-1}\)) is appeared for PVA-pure refer to the C=O stretch irradiation dose 8 kGy. The peaks appeared between (2800-3000) cm\(^{-1}\) refer to stretch aliphatic. The broad band between (3265-3282) cm\(^{-1}\) refers to O-H hydrogen- bonded alcohols. The FT-IR analysis of PVA polymer after exposure to gamma irradiation showed approximately the same spectrum for pure polymer, before irradiation with no shift in the peak positions. These findings suggest that gamma irradiation did not cause structural changes in the polymer chains [19].
Table (3): FTIR-characteristic of pure PVA film for different irradiation doses

| Bands                        | PVA before irradiation | PVA after 1kGy | PVA after 3kGy | PVA after 5kGy | PVA after 8kGy | PVA after 10kGy | PVA after 15kGy |
|------------------------------|------------------------|----------------|----------------|----------------|----------------|----------------|-----------------|
| C-H out phase bend (625-970)cm⁻¹ |                        |                |                |                |                |                |                 |
| 835.20, 918.88, 945.15       | 834.90                 | 835.14         | 834.30         | 835.29         | 835.02         | 835.65         |                 |
| C-O stretch (1015-1300)cm⁻¹  | 1024                   | 1023.89        | 1023.93        | 1023.85        | 1046.85        | 1023.88        | 1023.84         |
| 1087.56, 1242.90             | 1087.68                | 1087.70        | 1087.38        | 1087.61        | 1087.42        | 1087.40        |                 |
| CH₂ bending (1300-1380)cm⁻¹  | 1328.29                | 1328.19        | 1328.17        | 1328.31        | 1328.32        | 1328.34        |                 |
| 1373.64                      | 1373.68                | 1373.70        | 1373.69        | 1373.75        | 1373.64        |                 |                 |
| C=O stretch (1550-1780)cm⁻¹  | 1714.53                | 1714.19        | 1714.38        | 1714.37        | 1579.50        | 1714.17        | 1714.34         |
| 1732.00                      | 1731.95                | 1731.89        | 1731.89        | 1714.46        | 1731.95        |                 |                 |
| 1731.77                      |                         |                |                |                |                |                 |                 |
| stretch aliphatic (2800-3000)cm⁻¹ | 2912.57                | 2913.37        | 2913.05        | 2913.53        | 2914.94        | 2912.65        | 2913.35         |
| 2939.54                      | 2939.36                | 2939.57        | 2939.57        | 2939.38        | 2939.81        |                 |                 |
|                               |                        |                |                |                |                |                 |                 |

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Figure (15): The FTIR spectra of PVA films before and after $\gamma$-irradiation at different doses (0, 1, 3, 5, 8, 10 and 15) kGy
6. FESEM Results

The FESEM image for un-irradiated PVA films show in the figure (16), the surface is rough until after irradiation dose (3kGy), after irradiation dose (8kGy) the roughness is decreased to that disappear at irradiation dose (15kGy).

![FESEM micrographs](image)

**Figure (16): FESEM micrographs of PVA films before and after γ-irradiation at different doses (0, 3, 8 and 15) kGy**

7. Conclusions

UV–VIS spectrophotometric studies optical properties for irradiated pure PVA films with different irradiation doses, gamma ray lead to degradation in polymer chains, and indirect bandgap increase with increase irradiation dose, and each optical constants have changed value after irradiation. The XRD show the polymer (PVA) is semi crystalline and the intensity is increase with increase irradiation dose, FTIR spectrophotometric studied the effect of irradiation on the chemical bond of the materials, we show the irradiation doesn’t effect on the bond of polymer, but FESEM results show the polymer surface is rough, and it is continuously reduces irradiation until it disappear.

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