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The influence of gamma rays on the physical properties of polyvinyl chloride

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Abstract:

Polyvinyl chloride (PVC) is the most widely product used in a range of industrial and commercial applications due to its high chemical resistance, properties, and low cost. Thin films of polyvinyl chloride were produced using a casting process. Cobalt (^{60}Co) source and radiation doses of (1, 5, 10, 15, and 20) kGy were used for gamma irradiation. According to the X-ray diffraction (XRD) results, the PVC films had an amorphous structure. Before irradiation, the surface PVC did not have a porous structure, but after irradiation, porous PVC formed, according to field emission scanning electron microscopy (FESEM) photographs. The polymer chains exposed to gamma radiation showed no structural alterations according to the Fourier-transform infrared spectrometer FTIR measurements. The effect of radiation on optical characteristics was determined using the UV-VIS spectrophotometer. The results demonstrate that the absorption spectrum increases, and transmission decreases with the increase in the dose of irradiation and indicated that indirect transition was allowed and the energy gap of PVC films decreased when irradiated with a radiation dose from (4.95 eV – 4.48 eV). The purpose of gamma irradiation is to improve the specifications and properties of the polymer for use in other application areas.

Keywords: Gamma irradiation; Polyvinyl chloride; Physical properties; XRD; FESEM; FTIR; UV-VIS

1. Introduction

Polymers are widely used in the fields of science because they have several applications. It is well known that radiation affects polymers' chemical and physical properties. Therefore, it is widely used in radiation environments, including spacecraft and nuclear power plants [1]. In recent years, polyvinyl chloride (PVC) polymers have become one of the most versatile and practical materials. In a variety of applications, they have been used as composites, mixes, and copolymers [2]. Radiation has a crucial impact on polymeric materials because it alters and improves their physical properties. Free radicals are produced when polymeric materials are exposed to X-rays, electrons, gamma rays, or ion beams, for example, resulting in degradation or cross-linking. This interaction is controlled by the dose of radiation [3]. Depending on the polymer's chemical structure, various polymers react differently to radiation doses. Therefore, polymer properties are modified, including optical, electric, mechanical, and chemical properties [4].
H. R. Ravi et al., this study investigates gamma radiation affects the structural characteristics and dielectric constant of polyvinyl chloride [5]. PVC film was exposed to varying doses of radiation from a ^{60}Co source was investigated. Measurements of PVC structural characteristics were made using XRD, FTIR, and the dielectric constant.
D.P. Gupta et al., a study of the chemical, optical, and structural characteristics of PVC polymers exposed to gamma rays used ultraviolet-visible and Fourier transform infrared spectrometry [6].
P. Oberoi et al., studied gamma radiation's impact on dimethyl yellow blended PVC dyed film to observe color change [7]. After gamma irradiation, a yellow-to-red color change was found, which can be determined by color spectroscopy and absorbance. With an increase in absorbed dose, as shown by a UV-Vis spectrophotometer, the absorbance increased. FTIR analysis reveals structural group changes.
C. Paun et al. studied the changes gamma radiation brings on some PVC plates [8]. Gamma irradiation was applied to the samples at varying dosages. UV-Vis, electrical tests, and SE-M analysis were used on both irradiated and non-

irradiated samples, and the changes in the characteristics of the irradiated PVC plates were investigated. It is evident from the findings that PVC plates are impacted by gamma irradiation.
The current project intends to prepare PVC films utilizing the casting method. PVC thin films before and after gamma radiation exposure were examined for their physical properties.

2. Theoretical part

Absorbance refers to the relationship between the intensity of the material's absorbed light (I_A) and the intensity of incident light (I_o) [9].

$$A = \frac{I_A}{I_o} \quad (1)$$

Using the optical absorption spectrum, the absorption coefficient (α) can be calculated from Equation (2) [10].

$$\alpha = 2.303 \frac{A}{d} \quad (2)$$

where d is stands for sample thickness.
The extinction coefficient (k) represents the extinction caused by electromagnetic waves within a material that can be determined in Equation (3) [11].

$$k = \frac{\lambda \alpha}{4\pi} \quad (3)$$

and λ is the incident light wavelength.
The energy band gap was determined using Equation (4) [12].

$$\alpha h\nu = B(h\nu - E_g)^r \quad (4)$$

where $h\nu$, it is the energy of the photon, B, a constant whose value depends on the conduction and valence band properties, E_g: direct or indirect transition's energy gap, and r: constant whose value depends on the type of transition. r is equal to 1/2, 3/2, 2, 3 for allowing direct, forbidden direct, allow indirect, and forbidden indirect transition, respectively.

3. Experimental work

In this work, a casting technique was used to prepare PVC films. Sabic company supplies Poly Vinyl Chloride (PVC) powder. It has a molecular weight of (6000 g. mole^{-1}) and a chemical formula $(C_2H_2Cl)_n$. Tetra hydro furan (THF) with a purity of 99.8% from (LOBA CHEMIE) was applied as a solvent. To make pure PVC films, mix 0.5 g of PVC in 15 mL of THF. The solution was thoroughly stirred using a magnetic stirrer, to produce a homogeneous mixture. After allowing it to dissolve completely, pour this mixture onto previously cleaned and dried Petri dishes (5 cm diameter) and leave to dry for 24 hr. Films are formed by evaporating the solvent at room temperature. These films were peeled from Petri dishes. Films produced were semi-transparent, uniform in thickness, and airless. The thickness of the PVC films produced is (0.15425 mm), measured using a digital micrometer (0.001 mm), and the measurement accuracy is in the measuring range of (0 - 150) mm, manufactured in Japan and employed a ^{60}Co-Gamma Cell-900 of 3.7Ci strength and 1.17 MeV and dose rate 12 Gy/h with a half-life of 5.3 years to irradiate samples at doses of (5 and 20) kGy. In the Department of Physics, the University of Baghdad, the radiation source was built into a lead container containing chemicals of interest. The UV-visible spectrophotometer (T70/T80) series measures absorption and transmission spectra ranging from 200 nm to 900 nm wavelengths. FTIR spectroscopy was conducted on all films using the (Bruker-Tensor 27 with an ATR unit), in the wavenumber range (400 - 4000) cm^{-1}. The structure of PVC films was investigated by computerized XRD (XRD; X'Pert PRO, PANalytical, Netherlands). High-resolution FESEM image (FEI Company, Dutch origin) characterized PVC films' surface composition.

4. Results and discussions

4.1 XRD analysis

Un-irradiated and irradiated PVC films can be analyzed using a technique of X-ray diffraction (XRD). An XRD analysis of PVC films without irradiation is shown in Fig. 1 (a). It exhibits two large amorphous peaks at 2θ = (7.4264° and 18.8680°), showing that the structure is amorphous, which agrees with [13]. XRD analysis of pure PVC exposed to gamma radiation at a radiation dose 5 kGy displays the different amorphous peaks in 2θ = (18.9215°, 24.4915°, and 39.4300°) as illustrated in Fig. 1 (b). XRD pattern for gamma-irradiated PVC film at a dose of 20 kGy. Irradiated PVC film displays amorphous peaks at 2θ = (17.8362°, 24.3479°, and 39.7013°) as shown in Fig. 1 (c). As a result, it has been shown that the shape of the spectrum, the width of the peaks, and their intensity become less after exposure to gamma rays. Because long exposure to gamma rays, breaks the connections between the films and increases surface roughness.

4.2 FESEM analysis

Field emission scanning electron microscopy (FESEM) investigated PVC film surfaces before and after irradiation. Fig. 2 (a) displays the FESEM image of a PVC film without irradiation. The surface is smooth and free of holes or pores. But after irradiation with doses of 5 and 20 kGy, as shown in Fig. 2 (b, c). Damage appears on the PVC surface and Small cracks at dose 5 kGy, but increased roughness and more cracks are formed at dose 20 kGy. As a result of the photo-degradation of the polymer chain, due to the effect of gamma rays. As a result, before irradiation, PVC did not have a porous structure, but after irradiation, porous PVC formed, this agree with [14, 15].

4.3 FTIR analysis

A Fourier-transform infrared spectrometer is used to determine the main characteristic peaks in pure PVC films and demonstrate their response to irradiation. FTIR spectrum of un-irradiated pure PVC films is displayed in Fig. 3. Un-irradiated pure PVC showed a large number of bands in Table 1. Peaks between (600 - 800) cm^{-1} suggest (C-Cl) stretching overlaps on the (C-H) stretching bands at 635.09 cm^{-1}, and peaks between (625 - 970) cm^{-1} indicate C-H

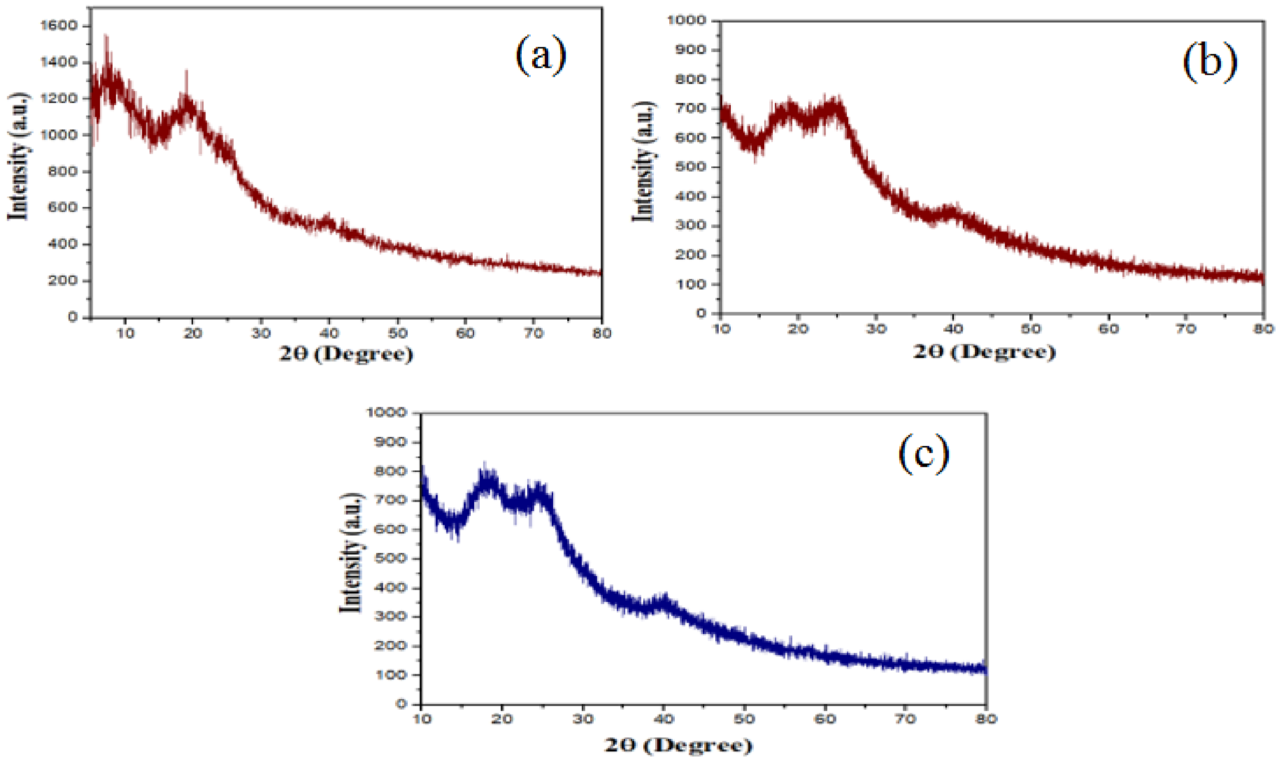

Figure 1. The XRD analysis of (a) pure PVC un-irradiated, (b) PVC irradiated at does (5 kGy), (c) PVC irradiated at does (20 kGy).

bending of the plane. Peaks between (1015 and 1300) cm^{-1} indicate C-O stretching vibration, while (1300 – 1380) cm^{-1} indicates CH_2 bending vibration. Peaks between (1550 - 1780) cm^{-1} indicate carbonyl stretching vibration (C=O). Two peaks, formed at (2908.33) cm^{-1} and (2962.65) cm^{-1}, respectively, indicate C-H stretch aliphatic vibration; this agrees with [16].
FTIR spectra of PVC polymer for different gamma irradiation doses (1, 5, 10, 15, and 20) kGy are shown in Fig. 4. In irradiation, disappeared the peak at (635.09) cm^{-1} indicates C-CL for doses (1, 5, 10, 15, and 20) kGy, and also the peak at (753.78) cm^{-1} for irradiation doses (1 and 20) kGy. A peak at (844.20) cm^{-1} bend for doses (10 and 20) kGy, and the peak at (925.07) cm^{-1} at irradiation doses (5, 10, 15, and 20) kGy, respectively, indicates C-H out phase has disappeared. The peak at (1456.46) cm^{-1} at irradiation doses

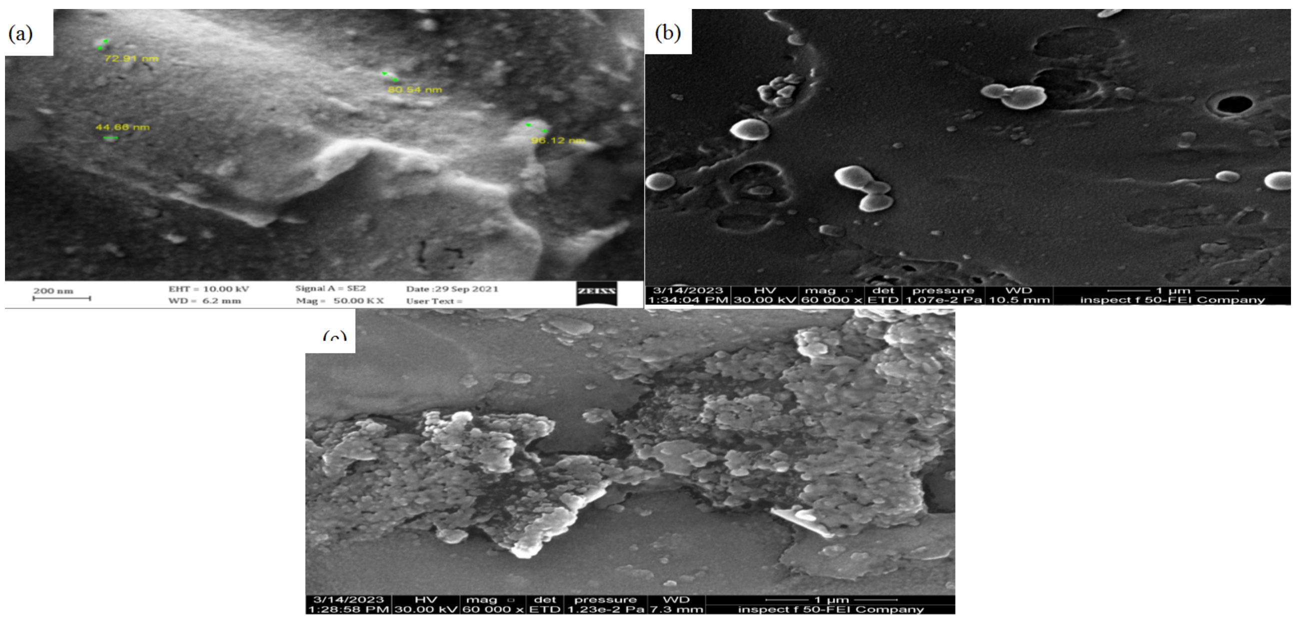

Figure 2. The FESEM patterns of (a) pure PVC un-irradiated, (b) PVC irradiated at does (5 kGy), (c) PVC irradiated at does (20 kGy).

Table 1. FTIR-characteristic of pure PVC films before and after gamma-irradiated for different irradiation dose.

Bands	PVC un-irradiation	PVC 1 kGy	PVC 5 kGy	PVC 10 kGy	PVC 15 kGy	PVC 20 kGy
	608.80	610.32	610.83	610.46	610.10	610.45
C-CL	635.09	—	—	633.27	635.19	—
(600-800) cm^{-1}	690.42	683.17	682.07	682.54	686.78	680.68
	753.78	—	761.49	671.56	759.87	—
C-H	844.20	851.32	851.93	—	856.93	—
Out phase bend	925.07	—	—	—	—	—
(625-970) cm^{-1}	958.03	958.71	957.52	957.62	957.75	958.68
C-O stretch	1035.87	1035.79	1035.82	1036.01	1035.95	1036.08
	1062.45	1065.55	1066.86	1067.78	1067.96	1068.92
(1015-1300) cm^{-1}	1191.53	1194.90	1194.78	1193.99	1193.78	1193.81
	1253.11	1251.97	1251.69	1251.89	1251.87	1251.51
CH_2 bending (1300-1380)cm^{-1}	1335.17	1328.89	1328.80	1329.05	1329.57	1328.74
C=C stretch	1456.46	—	—	—	1456.28	1508.01
(1430-1600) cm^{-1}	1541.34	—	—	1541.44	1541.35	1541.48
		1540.99				
C=O stretch	1647.52	—	—	—	—	1647.79
	1698.72	—	—	—	—	1670.81
(1550-1780) cm^{-1}	1716.75	1717.44	1717.20	1717.01	1717.22	1716.78
	—	—	—	1771.28	1771.09	—
C-H stretch Aliphatic	2908.33	2910.90	2909.59	2909.73	2910.73	2910.24
(2800-3000) cm^{-1}	2962.65	2965.78	2967.63	2966.59	2966.21	2965.12

(1, 5, and 10) kGy, and a peak at (1541.34) cm^{-1} indicates that the C=C stretch also disappeared. Peaks at (1647.52 and 1698.72) cm^{-1} indicate C=O stretch for (1, 5, 10, and 15) kGy disappeared, but appeared two peaks at (1771.28 and 1771.09) cm^{-1}, respectively, at irradiation doses (10 and 15) kGy, this agrees with [17]. These bands are listed in the Table 1.

4.4 Optical properties

Fig. 5 displays the UV/VIS absorption spectra of radiation-exposed and unirradiated PVC films. The figure illustrated a PVC film absorbance spectrum as a function of incident light wavelength. Before irradiation, PVC had no peak, but after irradiation at doses (1, 5, 10, 15, and 20) kGy peak appeared, as shown in Table 2. Due to this, the absorption spectra increase with increasing irradiation dose. This agree with [6, 18].

In Fig. 6, the transmission (T) for PVC films is shown before and after gamma irradiation, defined as the ratio between transmitted and incident radiation. These spectra behaved inversely to the absorption spectrum. As a result, the transmittance spectra decreased with an increase in irradiation dose.

Each absorber molecule or ion has an absorption coefficient (α) attribute. It is described as the substance's capacity to absorb light with a specific range of wavelengths per unit length. Equation (2) could be used to calculate the absorption coefficient. Electronic transitions can be determined by the absorption coefficient. Fig. 7 shows un-irradiated and irradiated PVC films' absorption coefficient (α). At higher energies, the electron and photon are expected to undergo direct electron transformations while conserving energy and momentum. While indirect electronic transitions allowed are assumed at lower energies, absorption coefficients are low ($\alpha < 10^4$ cm^{-1}). This work involved the calculation of indirect electronic transitions permitted as well as absorption coefficients at low energies, which agrees with [19].

This property can be specified as the value related to the op-

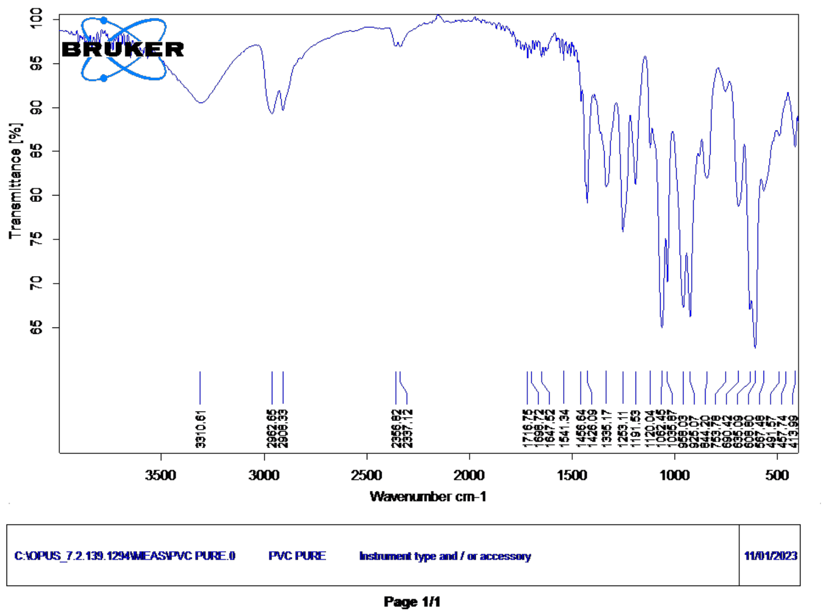

Figure 3. FTIR spectrum for pure PVC Film before gamma-irradiated.

tical energy gap required for developing the film material's electronic band structure.

Fig. 8 shows the relationship between absorption edge $(\alpha h\nu)^{1/2}$ and photon energy for pure PVC film. For indirect electronic transitions allowed, a pure PVC film had an energy gap of (4.95 eV) before irradiation. When irradiated PVC polymer with various radiation doses, the value related to the energy gap for PVC will decrease with the increase in radiation dose to be (4.48 eV) at 20 kGy; this agrees with [6]. The various changes in the energy gap that occur for PVC are shown in the Table. 3.

According to Equation (3), the extinction coefficient varies with absorbance. Figure 9 shows the extinction coefficients of unirradiated and irradiated pure PVC films.

5. Conclusion

The present study examines the impact of gamma irradiation on PVC pure film's optical and structural characteristics. The films were exposed to varying doses of gamma radiation (1, 5, 10, 15, and 20) kGy, and the effects were analyzed. According to the XRD results, the polymer (PVC) displayed an amorphous structure, and its intensity decreased when exposed to gamma radiation. FESEM images showed that the PVC surface was smooth before irradiation, but after irradiation, it appeared porous. FTIR spectrophotometer was used to study gamma radiation effects on chemical bonding in polymers, and we found that irradiation did not affect the structure of the polymers. A spectrophotometer for UV-VIS is used to investigate the optical properties of PVC films exposed to different doses of radiation. After irradiation, gamma rays degrade polymer chains, the energy gap decreases with increasing radiation dose, and optical constants change.

Table 2. The highest peaks of the absorption spectrum of PVC Films before and after gamma irradiated.

Samples	Wavelength (nm)	Absorbance
un-irradiated PVC	—	—
PVC(1 kGy)	365	0.694
	280	1.058
PVC(5 kGy)	365	0.904
PVC(10 kGy)	365	1.03
PVC(15 kGy)	365	1.298
	280	1.398
PVC(20 kGy)	365	1.267

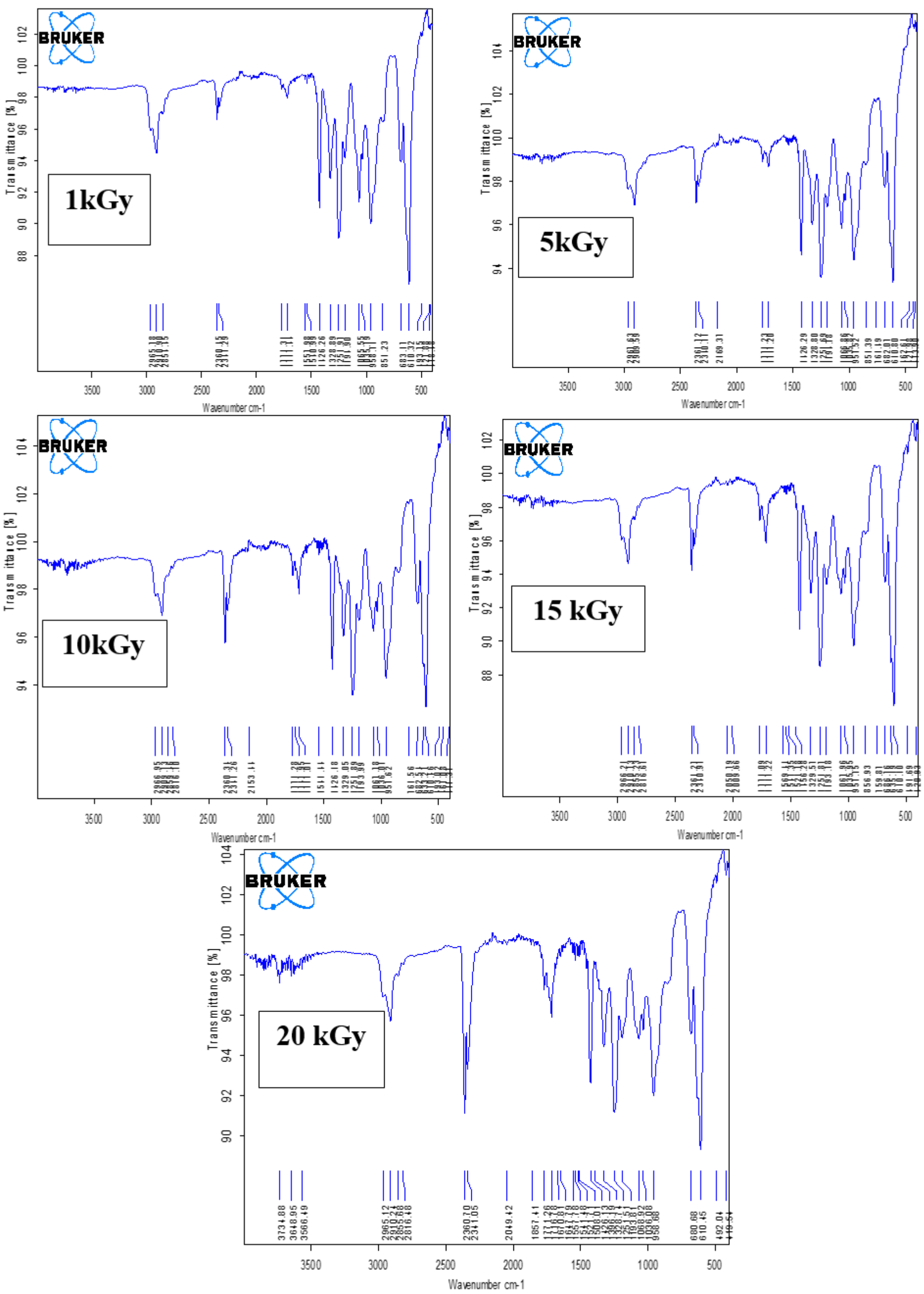

Figure 4. FTIR spectra for PVC film after gamma-irradiated at different doses (1, 5, 10, 15, and 20) kGy.

Table 3. The energy gap (E_g) for pure PVC before and after gamma irradiation.

Dose	Energy gap (eV)
PVC(0 kGy)	4.95
PVC(1 kGy)	4.7
PVC(5 kGy)	4.68
PVC(10 kGy)	4.6
PVC(15 kGy)	4.5
PVC(20 kGy)	4.48

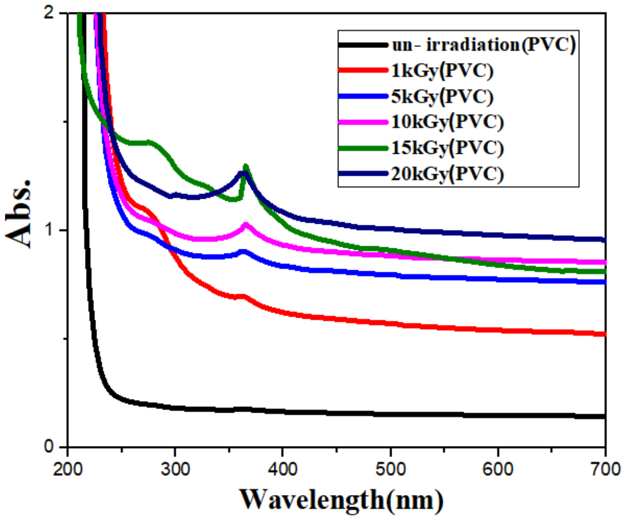

Figure 5. The absorption spectra for pure PVC before and after gamma irradiation.

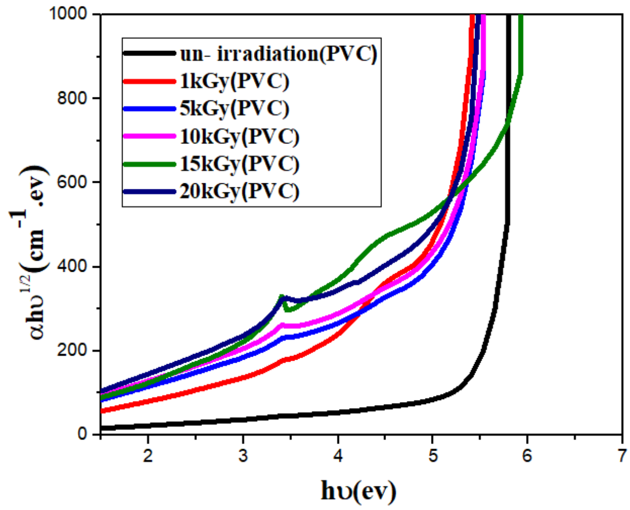

Figure 8. Optical energy gap for pure PVC before and after gamma irradiation.

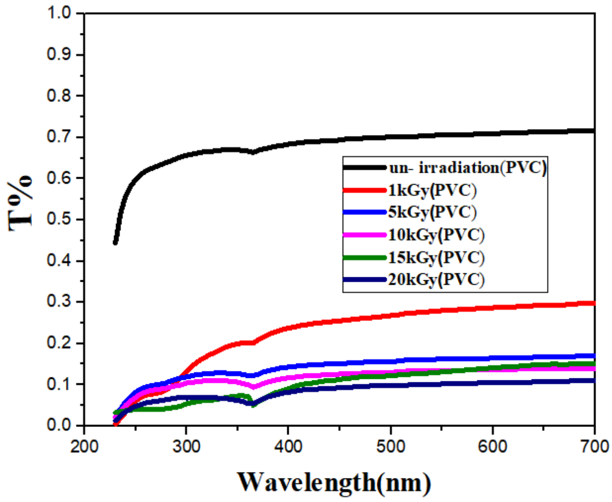

Figure 6. Transmittance spectra for pure PVC before and after gamma irradiation.

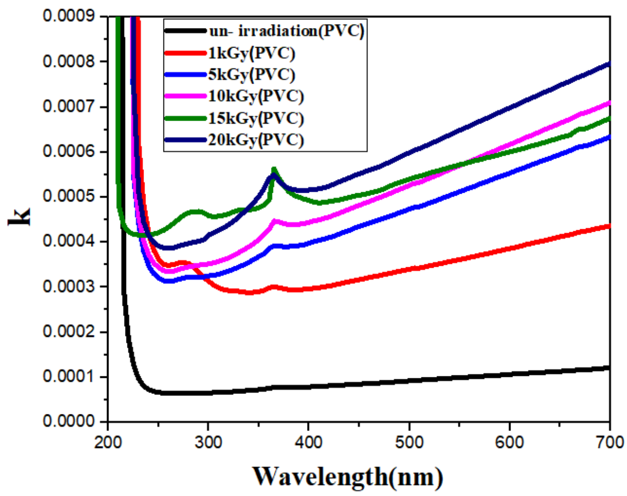

Figure 9. Extinction Coefficient for pure PVC before and after gamma irradiation.

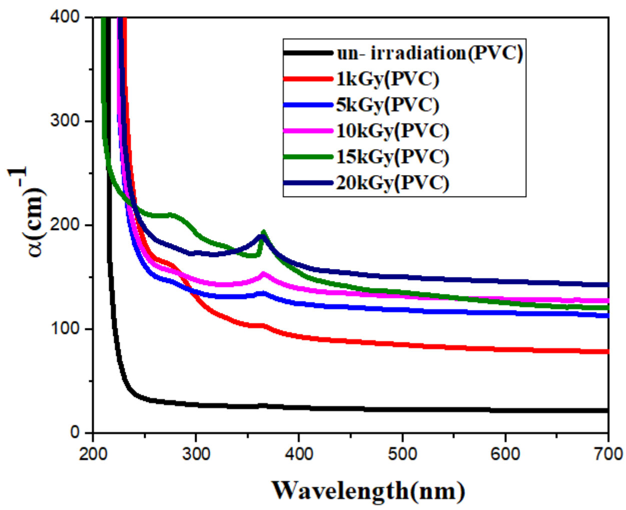

Figure 7. The absorption coefficient for pure PVC before and after gamma irradiation.

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Ethical approval
This manuscript does not report on or involve the use of any animal or human data or tissue. So the ethical approval is not applicable.

Authors Contributions
All the authors have participated sufficiently in the intellectual content, conception and design of this work or the analysis and interpretation of the data (when applicable), as well as the writing of the manuscript.

Availability of data and materials
The datasets generated and analyzed during the current study are available from the corresponding author upon reasonable request.

Conflict of Interests
The author declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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