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Influence of Gamma irradiation on the structural and optical characteristics of Li ion-doped PVA/PVP solid polymer electrolytes

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Abstract: Lithium ions-doped polyvinyl alcohol/polyvinyl pyrrolidone (PVA/PVP) films were prepared by solution casting technique and exposed to 100 kGy gamma radiation. The structural modifications in the samples before and after irradiation were studied using X-ray diffraction XRD and UV–Vis spectroscopy. The results indicated that absorbance $A(\lambda)$ and absorption index (k) increased, while semicrystalline nature of the blend decreased due to the addition of Li_2SO_4 and irradiation. The optical band gap E_g^{opt} of the composites showed significant decrease from 2.98 to 2.196 eV by adding Li_2SO_4 and from 2.83 to 2.08 eV after irradiation due to cross-linking. The Tauc's relation indicated that allowed transitions are indirect for both irradiated and unirradiated samples. The Urbach energy (E_u) increased with increasing Li ion content and exposure to γ irradiation. The dependence of dielectric permittivity ε_1, dielectric loss ε_2 and optical conductivity σ_{opt} on photon energy $h\nu$ was also studied.

1. Introduction

Polymer blending is a commonly used process to form new materials with improved physical properties compared to its constituents [1]. Polyvinyl alcohol (PVA) has a semicrystalline structure and contains hydroxyl groups (O–H) responsible for hydrogen bonding with other polymers. However, polyvinyl pyrrolidone (PVP) is a conjugated polymer characterized by the presence of proton-accepting carbonyl group (C=O) that facilitates its complexation with various inorganic salts. PVP has many advantages such as its high of mechanical strength and thermal stability [2]. PVA and PVP polymers are soluble in water and miscible in all ratios. PVA/PVP blend matrix can be used in several applications due to its optical and dielectric properties. The semicrystalline nature of both polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP), homogenous film forming ability with high transparency and controllable electrical and optical properties by various types of dopants became now of considerable significance in several optical and

optoelectronic applications [3, 4]. Mixing polymer blends with inorganic metal salts to form solid polymer electrolytes has many important applications in the field of high-energy electrochemical devices, photocells and electrochemical displays. Addition of Li ion salts such as lithium sulfate (Li_2SO_4) to PVA/PVP blend can control the optical density, thermal conductivity, thermal expansion and electrical properties of the blend [5]. Optical properties of polymer electrolytes used in various optoelectronic applications have an important role on the performances of these applications. UV–Vis spectroscopy is the simplest way for determining the optical parameters of the material such as absorption coefficient, band gap and refractive index. These fundamental optical parameters are closely related to the electronic properties of the material and help in estimating the dielectric parameters of the polymer and its optical conductivity [6, 7].

On the other hand, radiation induces modifications in the chemical and physical properties of the polymer. Molecular chain scission, formation of new bonds, rearrangement of bonding and formation of carbon-rich clusters are some structural deformations in the irradiated polymer that direct to modify the structural and optical properties of the material [8]. The main physical interaction of radiations

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with the polymers creates particular damage identified as chemical bond scission, free radicals and new covalent bonds formation [9]. The aim of the present study is to investigate the structural and optical properties of PVA/PVP blend and their complexes doped with various concentrations of Li_2SO_4 before and after gamma irradiation dose 100 kGy (to ensure the breaking of bonds) to be used in several electrochemical and optical applications.

2. Experimental details

2.1. Preparation of the polymeric composite films

PVA $[CH_2CH(OH)]_n$ (M.W. 125000) supplied from Alpha Chemica, PVP $[C_6H_9ON]_n$ (M.W. 40000) supplied from Research-lab Fine Chem. Industries (India) and Li_2SO_4 (m.p. 845 °C and density 2.22 g/mL) purchased from Sigma-Aldrich were used as raw materials. PVA/PVP (70/30) by weights was added to deionized water and stirred at 60 °C using a stable temperature magnetic stirring. Li_2SO_4 was added to the prepared solution with certain variable amounts (0–2 wt.%). The samples with different Li_2SO_4 content were distributed in Petri dishes and then dried in an oven at 65 °C for three days. After that, samples were husked from Petri dishes and preserved under vacuum.

2.2. Irradiation facilities

Indian gamma cell (type 4000A) at the Atomic Energy Authority in Egypt (AEA) was used for γ-irradiation using a ^{60}Co source. The irradiation procedure was accomplished within the air, at room temperature and in ambient humidity. The PVA/PVP/Li_2SO_4 composites were exposed to a gamma irradiation dose of 100 kGy at a dose rate of 1.774 kGy/h.

2.3. Measurements

XRD patterns were measured by using Diano USA X-ray diffractometer using Cu Kα radiation with $\lambda = 1.54$ Å, and H.V. 30 kV. The measured range of Bragg's angle 2θ is (5°–80°). V-570 UV/Vis/NIR, JASCO, (Japan) spectrophotometer was used to measure the UV/Vis spectra in the range of wavelength 200–850 nm.

3. Results and discussion

3.1. XRD studies

To get information about the structure of the investigated samples, XRD analysis was performed. Figure 1 shows the
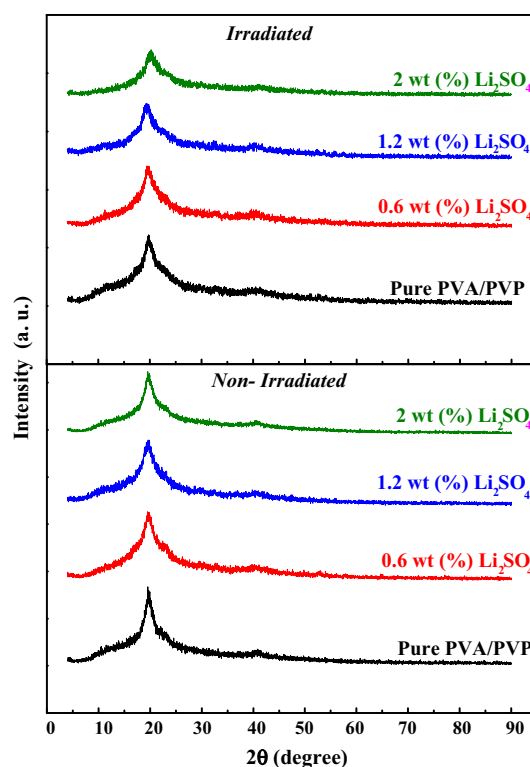

Fig. 1 XRD scans of PVA/PVP blend, PVA/PVP/Li_2SO_4 composites before and after γ-irradiation

XRD pattern of the pure PVA/PVP blend and doped with 0.6, 1.2 and 2 wt.% of Li_2SO_4 before and after gamma irradiation. All patterns are characterized by a diffraction peak nearly at $2\theta \approx 19.54°$ indicating the semicrystalline nature of the composite. The area under the main diffraction peak (integral intensity) is proportional to the mass fraction of the amorphous phase. To get insight into these patterns, the values of peaks' positions 2θ, their intensities I, full width at half maximum FWHM and areas under each peak A for the investigated samples are given in Table 1. From this table, it is observed that the area (A) and its intensity (I) decrease with adding Li_2SO_4 indicating an increase in the amorphous phase. This suggests that the complexation between Li_2SO_4 and the polymer matrix tends to reduce the intermolecular interaction between polymeric chain segments and increases the amorphicity of the investigated samples [10]. The increase in FWHM with increasing Li_2SO_4 content refers to a decrease in the polymer crystallite size. The absence of additional sharp peaks in the XRD patterns in the samples containing Li_2SO_4 is an evidence of the complete dissolution of Li_2SO_4 in the PVA/PVP polymer blend [11, 12]. The areas under diffraction peaks of the composites after irradiation are less than that of pristine samples. This indicates that γ-irradiation reduces the sample crystallinity by creating active polymeric free radicals and allows the formation of

Table 1 Values of Bragg's angle 2θ, full width at half maximum FWHM, peak intensity I, relative intensity RI of each sample peak with respect to pure non-irradiated PVA-PVP blend peak and peak area A (sum of counts under peak) of non-irradiated and irradiated PVA/PVP with different content of Li_2SO_4

Li_2SO_4 wt (%)	Non-irradiated					Irradiated				
	2θ (degree)	FWHM (degree)	I (counts)	RI (%)	A (a.u.)	2θ (degree)	FWHM (degree)	I (counts)	RI (%)	A (a.u.)
0	19.54	5.42	401	100	2046	19.62	5.88	303	75.5	1876
0.6	19.52	6.35	357	89.0	2120	19.56	6.76	267	66.6	1543
1.2	19.62	7.23	344	85.7	1964	19.54	7.59	245	61.1	1388
2	19.58	7.72	326	81.3	1743	19.73	8.63	198	49.3	1029

new covalent bonds between the polymer and Li_2SO_4 resulting in an increase in the cross-linking of the polymer electrolyte [13–15].

3.2. Optical properties

Transmission spectrum $T(\lambda)$ of the unirradiated and irradiated PVA/PVP composites with different content of Li_2SO_4 (0–2 wt.%) were measured in the wavelength range (200–800 nm) and is shown in Fig. 2. It is seen from the figure that the pure PVA/PVP has a high transmission ($\sim 82\%$) which decreases to ($\sim 45\%$) with increasing Li_2SO_4 concentration up to 2 wt.% in doped samples. The

Fig. 2 Dependence of the transmittance percentage on the wavelength for unirradiated and irradiated PVA/PVP/Li_2SO_4 films

reduction in the transmission of PVA/PVP/Li_2SO_4 samples by increasing Li_2SO_4 content leads to a decrease in E_g^{opt} due the structural changes in the polymer as a result of the inter- and intra-molecular interactions between polymeric chain segments (PVA/PVP) and dopant chemical species (Li_2SO_4) in the polymer blend. These interactions arise between PVA hydroxyl group, PVP unsaturated carbonyl group and the interactions of cations (Li^+) and anions (SO_4^{-2}) with electro-negative/positive constituents in PVA/PVP matrix. A small transmission band is detected at about 274 nm; this band seems to disappear by adding Li ions and also by irradiation which can be attributed to the interaction between Li ions and the polymer chains leading to π–π^* transitions [2]. The decrease in transmission after irradiation is due to the cross-linking of polymer chains that introduces new defects and light traps [16].

Absorption spectra $A(\lambda)$ of unirradiated and γ-irradiated samples are shown in Fig. 3. It is clear that, the sample absorbance increases with increasing doping level as a result of the complexation between Li_2SO_4 and the polymer matrix and the ability of Li ions to absorb more incident photons by their free electrons [2]. Irradiation with γ-rays also increases the absorption of light in the investigated polymer composites due to chain scission, cross-linking, etc., resulting in the change in molecular weight distribution, entanglements and packing density which in turn further increases the refractive index of the investigated composites after irradiation. The optical energy band gap E_g^{opt} can be estimated as follows [17–19]:

$$\alpha h v = B(h v - E_g^{opt})^r$$

where α is the absorption coefficient, B is a constant, hv is the incident photon energy and the index $r = 0.5$ for *direct* transitions and $r = 2$ for *indirect* transitions. The value of α can be calculated by Beer–Lambert's equation [20–22]:

$$\alpha(v) = \frac{2.303 A(\lambda)}{L}$$
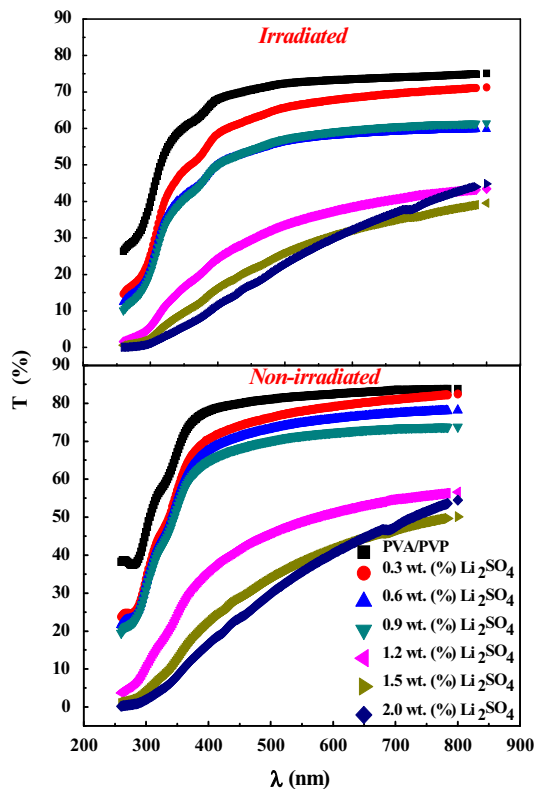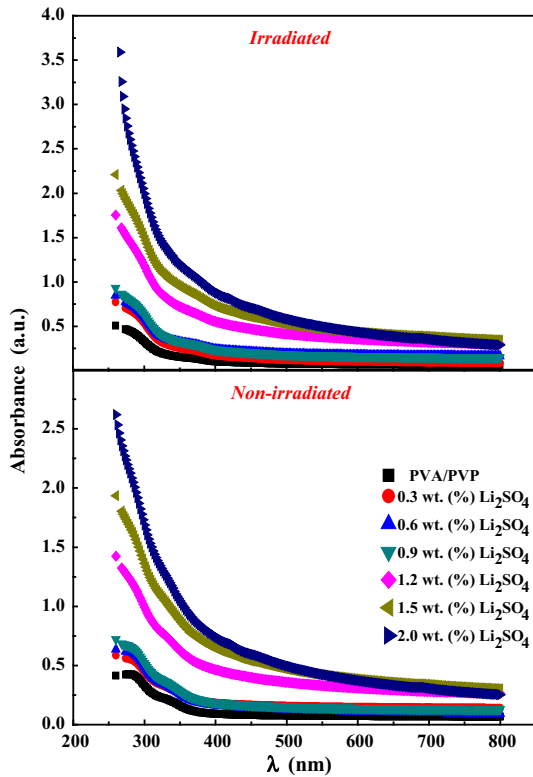
where L is the thickness of the sample.

Fig. 3 UV/Vis absorbance spectra for unirradiated and γ-irradiated PVA/PVP/Li$_2$SO$_4$ films

Fig. 4 Indirect optical energy band gap of unirradiated and irradiated PVA/PVP film loaded with different content of Li$_2$SO$_4$

Mott and Davis [22] suggested that *indirect* transition occurs near the edge of the fundamental band and estimated the indirect band gap from the plot of $(\alpha h v)^{1/2}$ versus $(h v)$ as presented in Fig. 4. It is obvious that the allowed transitions in the investigated samples are *indirect*. Extrapolation of the straight line parts of these curves to $(\alpha h v)^{1/2} = 0$ gives the values of E_g^{opt} which are listed in Table 2 for both pristine and irradiated samples. It is observed that E_g^{opt} decreases with the addition of Li$_2$SO$_4$, which indicates the significant effects of Li$_2$SO$_4$ on the optical band gap. The decrease in E_g^{opt} values can be explained by the charge transport complexes that occur between the LUMO (lowest unoccupied molecular orbital) and HOMO (the highest occupied molecular orbital) energy bands. The changes in E_g^{opt} can be also illustrated by the occurrence of local cross-linking in the amorphous region of the polymer resulting in the formation of localized states [23, 24]. This behavior is in agreement with the enhanced disordering degree which is confirmed by XRD. In irradiated samples, the values of E_g^{opt} are shown to be lower than that of unirradiated samples, see Table 2. The gamma irradiation offers new bonds and cross-links between polymer chain segments leading to a decrease in E_g^{opt}. A similar behavior is observed in some polymers irradiated with γ-rays [25–27]. For optical transitions resulting from photons of energy $h v < E_g^{opt}$, photons
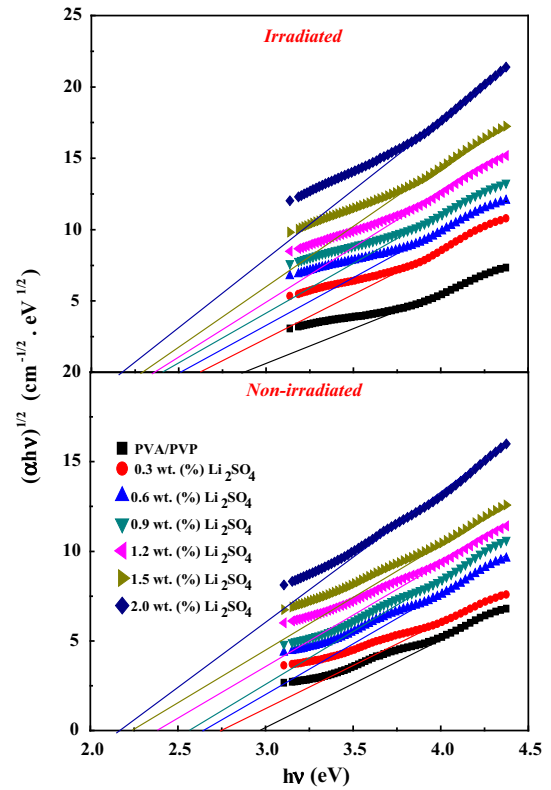
absorption is relevant to the existence of tail-localized states inside the forbidden band which is called Urbach tail. The energy of Urbach tail E_u can be calculated from the equation [28–30]:

$$\alpha(v) = \alpha_o e^{h v / Eu}$$

where α_o is constant. The plot of $\ln \alpha(v)$ versus hv for the investigated samples before and after irradiation shown in Fig. 5 are used to estimate the values of E_u, see Table 2. It is clear that E_u increases from 0.77 to 1.37 eV by the addition of 2 wt.% of Li$_2$SO$_4$. However, for irradiated samples, E_u has lower values ranging from 0.75 to 1.23 eV. The increase in E_u with Li ion content is consistent with the decrease in E_g^{opt} as a result of localized states formation. The lower values of E_u obtained after γ-radiation are due to the increase in the number of traps [28]. Figure 6 demonstrates the absorption index k distributions of the unirradiated and γ-rays-irradiated PVA/PVP composites loaded with different content of Li$_2$SO$_4$. From this figure, it is clear that the absorption index k increases by adding Li$_2$SO$_4$ and decreases with incident photons wavelength till $\lambda = 550$ nm, after that k values appear to be wavelength independent. Moreover, the values of k for each sample increase after irradiation. The variation in optical parameters of the studied composites is affected by the changes in

Table 2 Variation of the optical band gap, E_g^{opt}, Urbach energy E_u, refractive index at infinite wavelength n_∞, the average oscillator strength S_0, and average oscillator wavelength λ_0, high-frequency dielectric constant ε_∞, free carriers ratio (N/m^*) for non-irradiated and irradiated PVA/PVP with different content of Li_2SO_4

Li_2SO_4 wt (%)	Non-irradiated							Irradiated						
	E_g^{opt} eV	E_u eV	n_∞	$S_0 \times 10^{12}$ m^{-2}	λ_0 nm	ε_∞	$N/m^* \times 10^{43}$ m^{-3}	E_g^{opt} eV	E_u eV	n_∞	$S_0 \times 10^{12}$ m^{-2}	λ_0 nm	ε_∞	$N/m^* \times 10^{43}$ m^{-3}
0	2.98	0.76	1.08	2.68	144.1	1.19	0.074	2.83	0.75	1.72	11.85	246.4	1.86	0.381
0.3	2.79	0.91	1.20	15.70	151.2	1.49	.541 0	2.62	0.82	1.50	21.69	239.9	2.44	0.590
0.6	2.66	0.96	1.33	33.56	166.3	1.75	1.488	2.46	0.93	1.68	29.94	246.4	3.22	3.010
0.9	2.58	1.01	1.50	38.91	178.9	2.44	2.054	2.36	1.01	1.87	37.59	257.9	4.13	3.493
1.2	2.40	1.19	1.65	44.84	195.9	2.98	3.874	2.27	1.12	2.12	40.82	293.2	6.02	22.25
1.5	2.30	1.26	1.81	51.81	209.5	3.76	5.928	2.18	1.21	2.38	43.29	327.8	8.67	50.55
2	2.20	1.37	2.24	81.97	221.1	5.87	9.913	2.08	1.23	2.73	48.08	366.3	14.7	129.41

the internal structure after irradiation, such as molecular weight, defect distributions, cross-linking, etc. As a result of exposure to gamma rays, degradation of polymer chains creates excited states and free radicals with high mobility which then leads to increase in cross-linking. Therefore, an increase in the absorption index is obtained [31–33].

Refractive index n is the real part of the complex refractive index $\hat{n} = n + ik$ and considered one of the most important factors in manufacturing optical and optoelectronic materials. The refractive index n can be calculated using the reflectance $R = 1 - \sqrt{Te^A}$ and the absorption index k from the relation [30]:

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{(1-R)^2} - k^2}$$

Figure 7 shows the distributions of n for the unirradiated and irradiated PVA/PVP samples doped with different amounts of Li_2SO_4. At low-wavelength region (up to 400 nm) n shows a gradual decrease with increasing λ and a slight dependence of n on the wavelength is observed at higher wavelengths ($\lambda > 400$ nm). One can also notice that the refractive index n increases to considerable values by increasing the concentration of Li ions. This increase may be explained by the increment of the PVA/PVP/Li_2SO_4 composites density as a result of incorporating Li ions in the main chain of the polymer blend. Doping Li ions in the blend matrix can devastate the chains ordering of PVA/PVP blend and increase the amorphous domains as confirmed before by XRD. The presence of the amorphous domains induces the light interference phenomenon throughout the polymer matrix leading to the observed increase in n values [34]. Exposure of the investigated polymer electrolyte samples to γ-rays destroys the initial structure of the matrix via bond cleavages and free radicals formation. The increments of the refractive index after irradiation can be explained in terms of the cross-linking process at which covalent bonds are formed between free radicals and polymeric chains. This cross-linking process introduces the disordered regions and defects inside the material that are responsible for the increase in the refractive index [32].

In the transparent region, the dispersion of n can be analyzed by the model of single oscillator. The linear relation between $(n^2 - 1)^{-1}$ and λ^{-2} shown in Fig. 8 suggested that the refractive index of the investigated composites follow the classical dispersion relations [35, 36]:

$$\frac{(n_\infty^2 - 1)}{(n^2 - 1)} = 1 - (\lambda_0/\lambda)^2$$

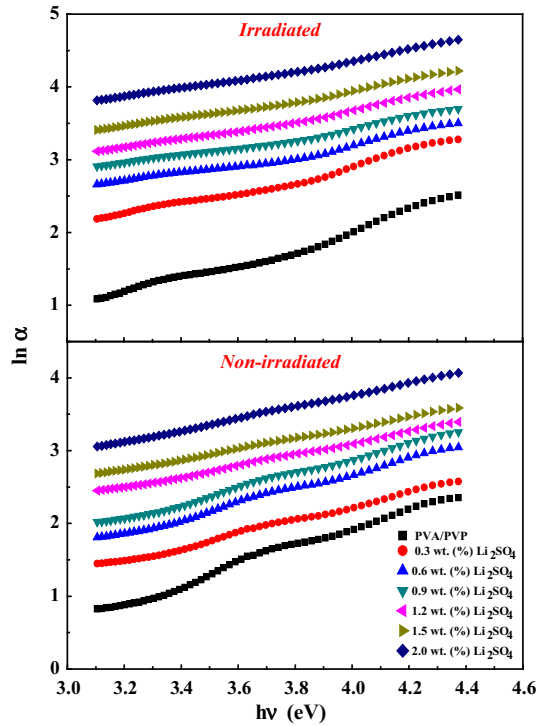$$[n^2 - 1]^{-1} = \frac{1 - (\lambda_0/\lambda)^2}{S_0 \lambda_0^2}$$

Fig. 5 Plots of ln (α) versus photon energy for the unirradiated and γ-irradiated PVA/PVP films loaded with different contents of Li_2SO_4
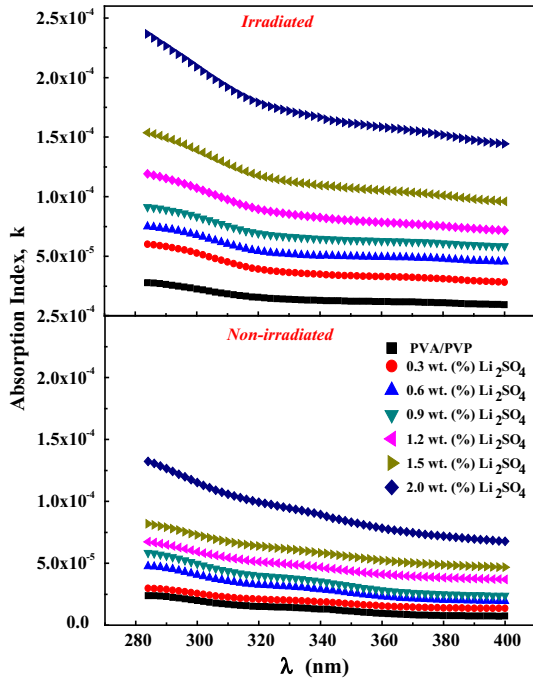

Fig. 6 Absorption index distributions of unirradiated and irradiated PVA/PVP films loaded with different contents of Li_2SO_4

where $n_\infty^2 = 1 + S_0\lambda_0^2$ and n_∞ are the refractive index at infinite wavelength, λ_o and S_o are the average oscillator wavelength and strength, respectively. The optical

parameters n_∞, S_0 and λ_0 which calculated for unirradiated and irradiated samples are listed in Table 2. It is clear that both of n_∞ and S_0 increase with increasing Li_2SO_4 content. This can be ascribed to the complexation between Li ions and PVA/PVP polymer matrix which lead to the changes in n values [36]. However, the values of λ_0 is decreased with dopant up to 0.6 wt.(%) and then increased till the Li_2SO_4 content reaches 2 wt.(%). This behavior observed in both irradiated and unirradiated samples.

Elicitation of the dielectric properties from the optical measurements helps not only in assessing their insulating character, but also in understanding the structure of the investigated composites to some extent. The real ε_1 and imaginary ε_2 parts of dielectric constant were determined from the following equations [37]

$$\varepsilon_1 = n^2 - k^2 = \varepsilon_\infty - \left(\frac{e^2 N}{4\pi^2 c^2 \varepsilon_0 m^*}\right)\lambda^2, \quad \varepsilon_2 = 2nk$$

where ε_o is the free space permittivity, ε_∞ is the high-frequency dielectric constant, e is electron charge of the, N is the concentration of free charge carriers, m^* the charge carriers effective mass and c is the speed of light in free space.

By plotting the relation between ε_1 and λ^2 as shown in Fig. 9 for unirradiated and irradiated samples, we can calculate (N/m^*) and ε_∞ from the slopes and intersections
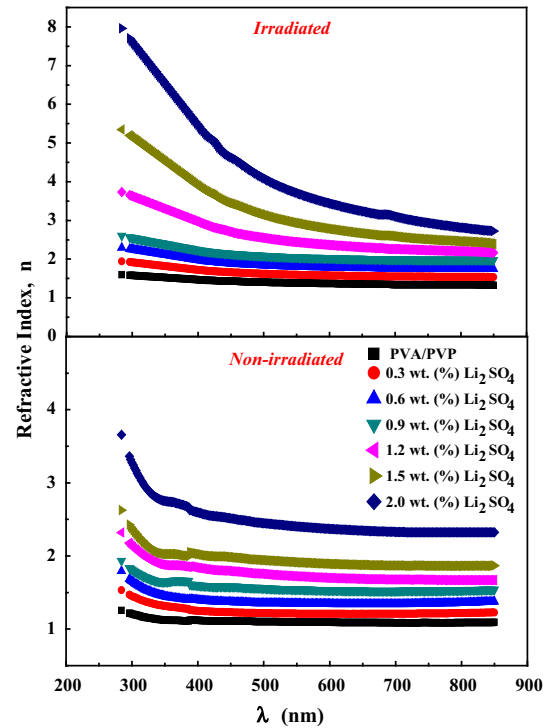

Fig. 7 Dependence of the refractive index n on the wavelength for unirradiated and irradiated PVA/PVP films loaded with different contents of Li_2SO_4
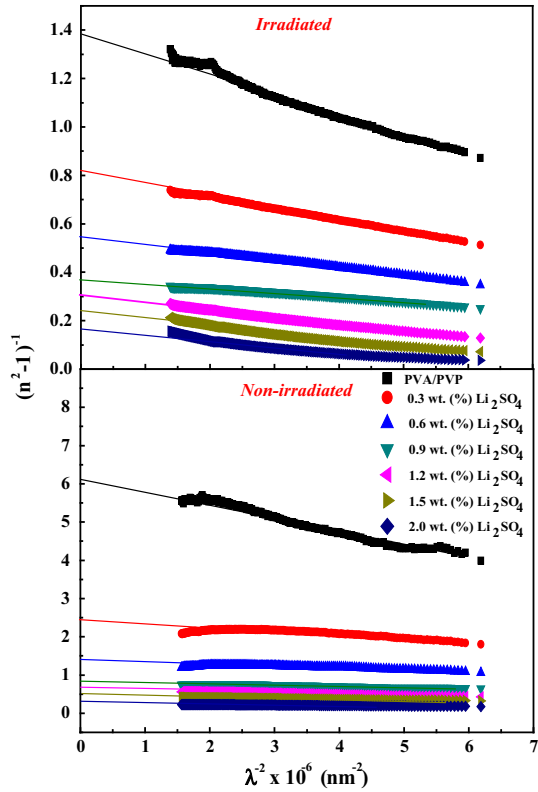
Fig. 8 Plot of $(n^2 - 1)^{-1}$ versus λ^{-2} for PVA/PVP loaded with different contents of Li_2SO_4 before and after irradiation

Fig. 9 Plot of n^2 versus λ^2 for PVA/PVP loaded with different contents of Li_2SO_4 before and after irradiation

of the linear parts of these curves. Also, it is noticed that the free carriers increase the ratio (N/m^*) of the samples with increasing of Li_2SO_4 before and after irradiation as shown in Table 2. Furthermore, the high-frequency dielectric constant ε_∞ increases with increasing Li_2SO_4 content and exposure to gamma rays. From these results, one can conclude that, the optical and dielectric parameters of these samples are controlled by the addition of Li_2SO_4 as well as the gamma irradiation. The measurements of these parameters can probably help in the manufacture and designing of such samples for use in optoelectronic applications. The plots of real ε_1 and imaginary ε_2 parts of dielectric constant versus $h\nu$ are shown in Figs. 10 and 11, respectively. It can be observed from these figures that the values of ε_1 and ε_2 are slightly dependent on the photon energy up to ~ 3.8 eV followed by a sharp increase at higher photon energy. The values of both ε_1 and ε_2 for irradiated samples are higher than those of unirradiated. This may be explained by the change in stoichiometry and internal strain of irradiated samples [8]. The behavior of ε_1 similar to the behavior of the refractive index n, because k^2 is very small compared to n^2, but the behavior of ε_2 depends mainly on the variation of the absorption index k, and therefore, ε_1 is larger than ε_2.
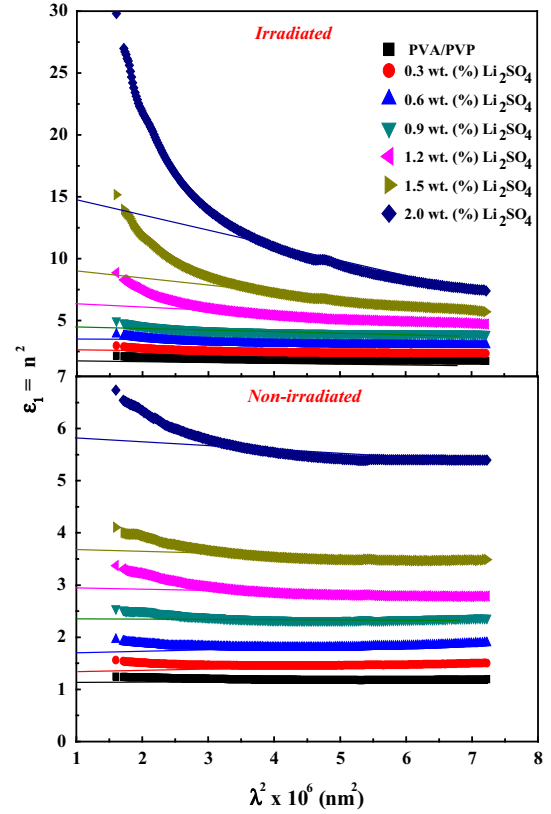
The optical conductivity σ_{opt} of a material arises from the motion of charge carriers which exposed to the light wave electric field. Optical conductivity σ_{opt} is related to the refractive index (n), speed of light (c) and absorption coefficient (α) by the following equation [37]:

$$\sigma_{opt} = \frac{nc\alpha}{4\pi}$$

Figure 12 depicts the relation between σ_{opt} and $h\nu$ for the unirradiated and irradiated PVA/PVP samples loaded with different contents of Li_2SO_4. From this figure, it is clear that both increasing Li_2SO_4 content and gamma irradiation provide some new energy levels in the band gap [38] helping to ease the flow of electrons from the V.B to the C.B resulting in the decrease in the band gap and consequently increase in σ_{opt}.

4. Conclusions

PVA/PVP/Li_2SO_4 polymer electrolyte was prepared by casting technique. The degree of crystallinity as well as the optical parameters was affected by the addition of Li_2SO_4 to the polymer matrix and also by γ-irradiation as confirmed by XRD and UV/Vis spectroscopy. The optical
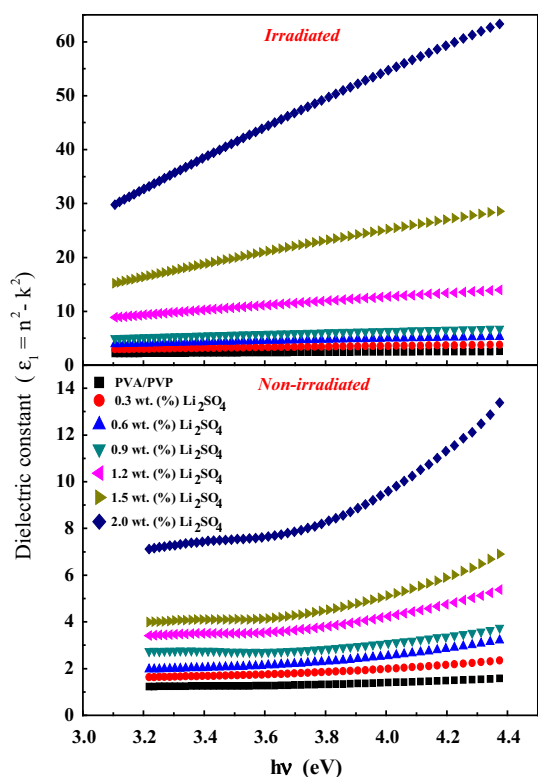
Fig. 10 Relation between real part of dielectric constant (ε_1) and photon energy for PVA/PVP loaded with different contents of Li$_2$SO$_4$ before and after irradiation
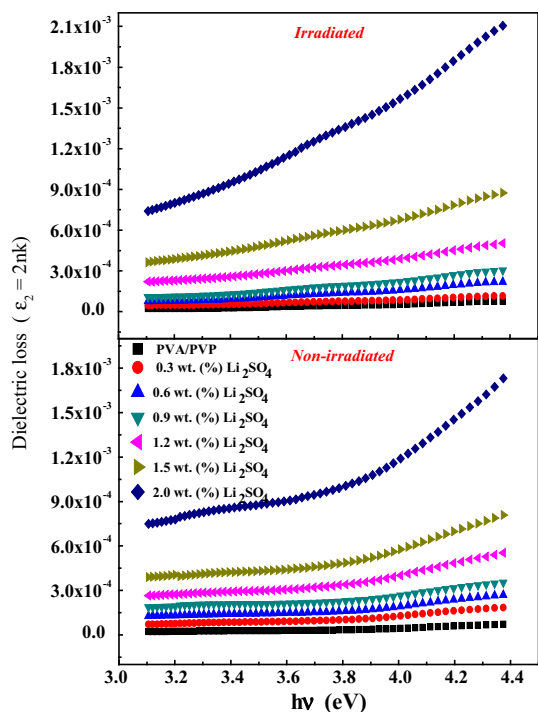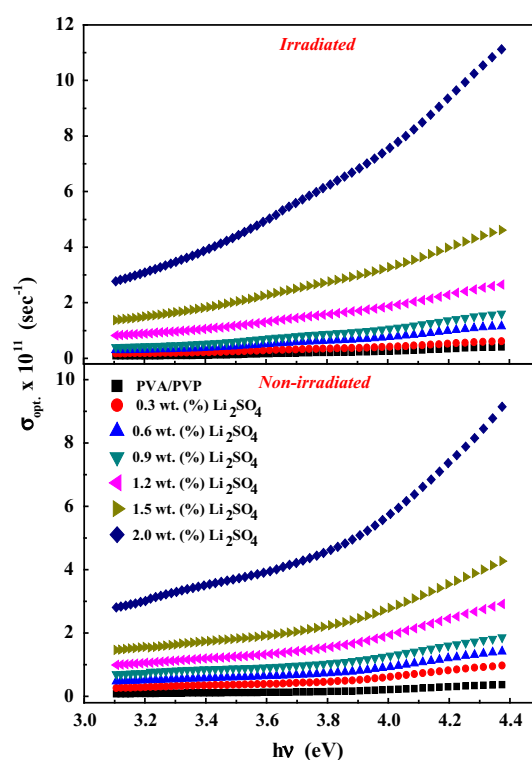

Fig. 12 Dependence of the optical conductivity of PVA/PVP loaded with different content of Li$_2$SO$_4$ on the photon energy before and after irradiation

band gap shows significant decrease from 2.83 to 2.08 eV after irradiation due to cross-linking. The indirect optical gap of the doped blend refers to the existence of charge transfers complexes in the host polymer by the addition of small amounts of Li ions. The determined parameters: N/m^*, S_0 and ε_∞ increase with increasing Li$_2$SO$_4$ content and exposure to gamma irradiation.

Fig. 11 Relation between imaginary part of dielectric constant (ε_2) and photon energy for PVA/PVP loaded with different content of Li$_2$SO$_4$ before and after irradiation

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