



Effect of Gamma Irradiation on the Physical and Chemical Properties of Copper-Poly Vinyl Pyrrolidone Composite Films

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Polymer composite films based on poly-vinylpyrrolidone (PVP) doped with different copper concentrations in 1 % HNO₃ were prepared using the solution cast technique. The polymer films were subjected to ⁶⁰Co γ -ray source at various doses ranging between 100 and 400 kGy. The effect of Cu ions concentration and γ -irradiation doses on the physico-chemical properties have been investigated. FTIR spectra gave information about vibration changes that occurred due to copper dopant and γ -irradiation doses. XRD results indicated that the amorphous domain of the PVP polymer matrix was increased with increasing of the dopant concentration. The surface morphology was examined (SEM). The electrical conductivity was increased with the increase of the Cu dopant concentration and γ -irradiation dose. The direct and indirect optical band gap values were decreased to 3.09 and 2.84 eV respectively as the irradiation dose was increased to 400 kGy.

Keywords: Cast technique/ Gamma irradiation/ Poly-vinyl pyrrolidone (PVP)/ FTIR/ XRD/ SEM, Ionic conductivity/ Optical band gaps

Introduction

In the recent years, solid polymer electrolytes (SPE) have attracted more attention due to their various advantageous properties. Mechanically, they behave as solids, while their internal structure, and consequently their conductivity behavior closely resemble the liquid state [1, 2]. Accordingly, it is important to develop these polymer electrolytes to be used in various applications, such as high energy batteries, fuel cells, sensors, display devices. The advantages of these materials are their flexibility, lightweight, elasticity, ability to form thin films and high energy density which make them suitable for many electrochemical devices such as solid state batteries, super capacitors and dye sensitized solar cells [3–6]. SPE complexes with inorganic metal

salt were first introduced by Weston and Steele in 1982. These complexes improve the electrical and mechanical properties of the polymer. Several polymers such as PVA, PVC, PAN, PMMA, PVP complexes with different metal salts have been reported [7]. Among these polymers PVP showed several interesting physico-chemical properties. This includes good environmental stability, excellent wet, readily film forming [8], toxicological safety, excellent transparency and gloss. PVP has also a good charge storage capacity and dopant dependent electrical and optical properties [9]. Furthermore, the amorphous nature of PVP-complexes has a low scattering loss, which is useful for optical applications. Accordingly, PVP is suitable for use in a wide variety of

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applications in medicine, pharmacy, cosmetics and industry [10].

The physical and chemical properties of SPE are controlled by many factors such as structure, nature of complex salt and preparation method. The interaction of γ -irradiation with the polymers led to different structural modification, while affecting their physico-chemical properties. These effects lead to modification of the electrical, optical, thermal, morphology and track properties [11-20].

The present study focuses on synthesis and characterization of SPE films based on Polyvinylpyrrolidone (PVP) complexed with Cu ion in 1% of HNO_3 . The effect of doping Cu and γ -irradiation doses on the physico-chemical properties of the composite polymer films were investigated. This may include either new or improved physio-chemical properties of Cu-PVP composite films suitable for electronic, optical and/or electrochemical device applications.

Experimental

Materials

Poly vinyl pyrrolidone (PVP) with a molecular weight of $\sim 400,000$ g/mol was purchased from Merck and used without further purification. Cu standard solution (1g/L) in 1 % HNO_3 from sigma was used as a dopant solution.

Method

Films of pure PVP and various concentrations of Cu doped-PVP were prepared. 0.5 g PVP (AR grade) was dissolved in 50 ml of deionized water. 10 mg, 15 mg, 20 mg, 30 mg of Cu (standard solution Sigma) in 1 % HNO_3 were added into 50 ml each PVP solutions drop wise. These resulting solutions were stirred for 10–12 h at 70 $^{\circ}\text{C}$ to get a homogeneous mixture and then cast onto polypropylene dishes and allowed to evaporate slowly at room temperature. The resultant thin film (0.1 mm) was carefully removed from the molds. The films were irradiated with ^{60}Co γ -ray source at various doses between 100 and 400 kGy.

Characterization

XRD patterns of the polymer films were recorded using Shimadzu XRD-6000 with $\text{CuK}\alpha$ radiation of wavelength $\lambda=1.54056$ Å. The surface morphology of the polymer films have been examined using SEM (JEOL JSM 840A). The

samples were coated with gold using the sputter coater on SC 7610 at 10 mA current under 10^{-2} torr vacuum for 6 minutes before imaging. FT-IR spectra of these films were recorded using EOSXBIR spectrometer in the wave number range of 400–4000 cm^{-1} . The electrical conductivity was measured using two- point probe method, coplanar silver electrodes separated by gap of width about 1 cm were deposited onto the samples. Optical absorption spectra were recorded at room temperature in the wavelength range 200–800 nm using Shimadzu UV-VIS-NIR (model-UV-3100) spectrophotometer.

Results and Discussion

PVP contains a pendant lactam ring which is a part of monomeric repeat unit structure. The high polarity of the ring can be attributed to strong resonance stabilization facilitated by a near planar ring geometry. Poly-vinylpyrrolidone polymer can form complexes with metals via oxygen and nitrogen. The interaction between PVP and metal ions are represented schematically in scheme 1, which show that copper ions are bound by the strong ionic bonds between the metallic ions and the amide group in a polymeric chain or between the polymeric chains. The solution of PVP in water can be attributed to its hydrophilic property [21-23]. Metal bonding mechanisms of PVP may be described as follows:

Cu doped-PVP polymer films were subjected to ^{60}Co γ -ray's source at various doses between 100 and 400 kGy at room temperature in atmospheric air. These composite polymer films were characterized by the following techniques:

FTIR analysis

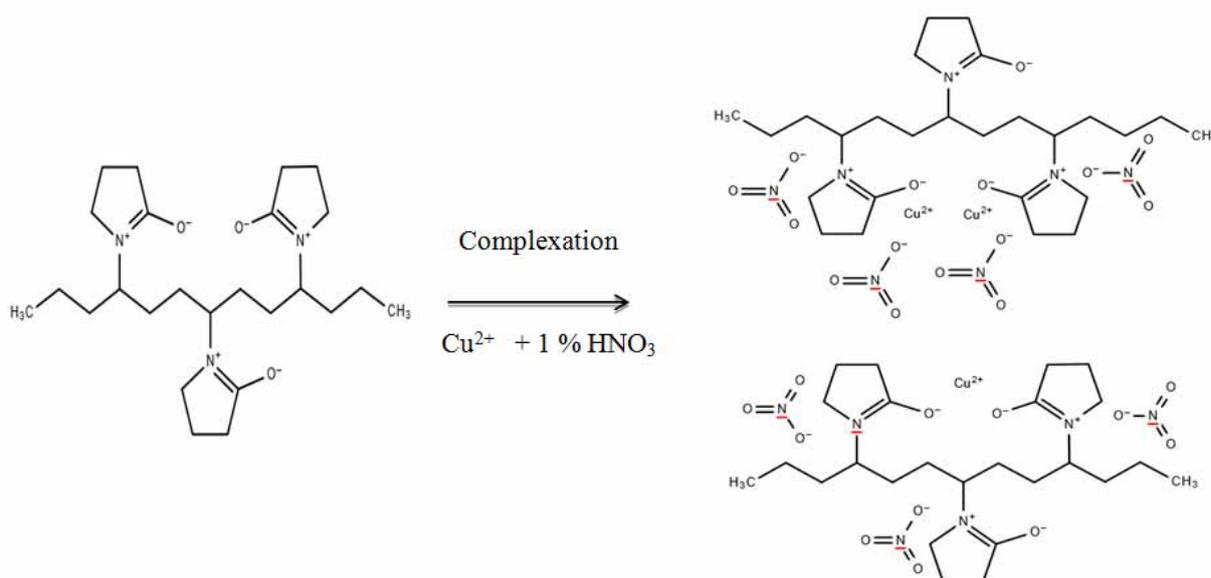
FTIR is an effective and essential characterization technique that determines the chemical compositions, chemical interaction and it also follows the variation in functional group during reaction [24]. IR transmittance spectra of pure PVP, Cu-PVP and irradiated Cu-PVP polymer films were recorded in 4000-400 cm^{-1} region at ambient of temperature. The results obtained are shown in Figure. (1) (a and b). Fig. (1a) represents FT-IR spectra of PVP powder and pure PVP film. It is clear that, both the PVP powder and pure PVP films have exhibited similar characteristic FTIR bands and the broad bands become narrow for PVP films and the obtained results are in good

agreement with the earlier reports in literature [25-27]. The peak at 1376 cm^{-1} represents the functional unit C-N present in PVP powder and pure PVP polymer films while disappeared in Cu-PVP and irradiated Cu-PVP as shown in Fig. (1b). This suggests that there may be an interaction between copper or nitrate ions and the N- atom of the heterocyclic ring of the polymer [21, 22]. However, another characteristic peak at 1659 cm^{-1} in pure PVP due to C=O stretching of the pyrrolidone ring was also found. A blue shift of the C=O group in PVP is attributed to the change of $\pi \rightarrow \pi$ conjugation associated with the amide group of PVP arising from the dissociation of PVP chains due to the incorporation of Cu. The interaction between the Cu and PVP leads to the dissociation of aggregated PVP chains, resulting in the blue shift of the C=O vibration band. The C-H asymmetric stretching of CH_2 absorption band located at 2959 cm^{-1} become narrow for pure PVP film than PVP powder. In addition to this, the C-H stretching of CH_2 exhibited at 2959 cm^{-1} in pure PVP is shifted to 2965 and 2970 cm^{-1} , respectively for Cu-PVP and irradiated Cu-PVP at dose 400. It must be mentioned that the absorption peak of the nitrate anion overlaps with vibration of C-H at 1230 and 1430 cm^{-1} [21].

The hydrogen bonded O-H stretching mode of pure PVP films appeared in $3500\text{-}3200\text{ cm}^{-1}$ region, and it is shifted to lower wave number with irradiated Cu-PVP films. The changes in the FTIR spectra are clear indications for the effect of complexation of PVP with Cu.

XRD analysis

XRD studies provided a wide range of information on crystal structure, orientation, and crystallinity and phase changes of materials. XRD patterns for pure PVP and Cu-PVP composite films are shown in Fig. (2a). The XRD of pure PVP shows a characteristic broad diffraction peaks for an orthorhombic lattice centered at 2θ value 10° and 20° indicating its amorphous nature of the prepared polymer films [26, 27]. It also indicates that there is no diffraction peaks from copper doping. This may be attributed to that Cu^{2+} ions are dispersed into the PVP lattices [28]. The XRD of 30 mg Cu doped-PVP films irradiated with different doses namely, 100, 200 and 400 kGy are shown in Fig. (2b). The patterns revealed that there are no sharp diffraction lines indicating that the amorphous phase was dominant. This amorphous nature results in greater ionic diffusivity with a high ionic conductivity, which can be obtained in amorphous polymers that have flexible back bone [33].



Scheme (1): A proposed mechanism of interactions between PVP and Cu in presence of 1% HNO_3 [21-23]

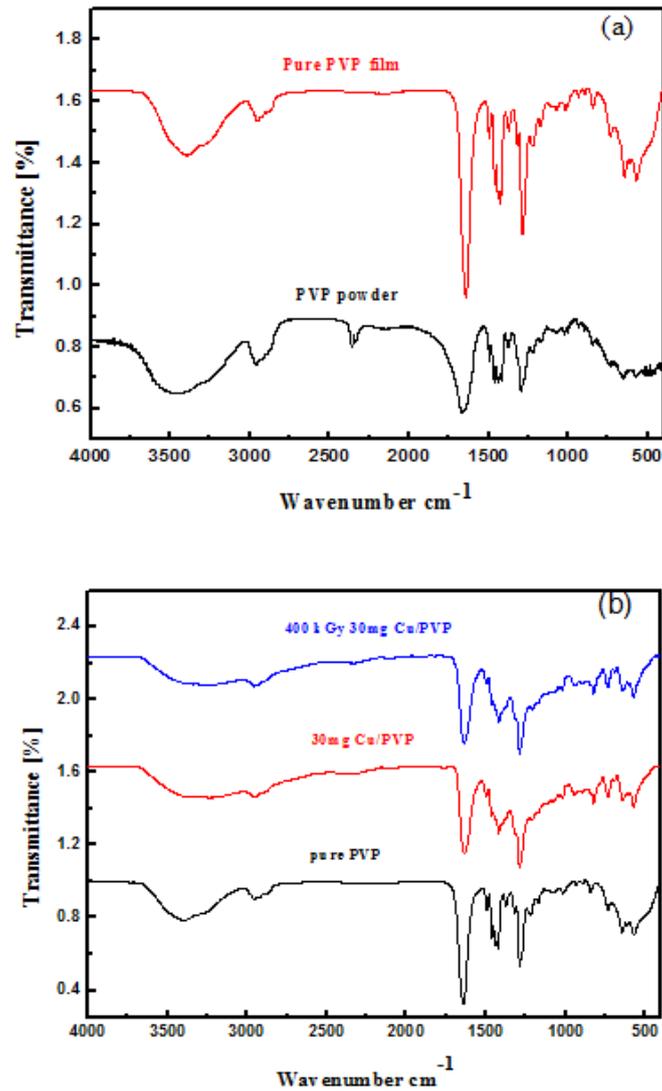


Figure (1): FT-IR spectra of: (a) PVP powder and pure PVP polymer film, (b) Pure PVP, 30 mg Cu-PVP and 30 mg irradiated Cu-PVP at 400 kGy

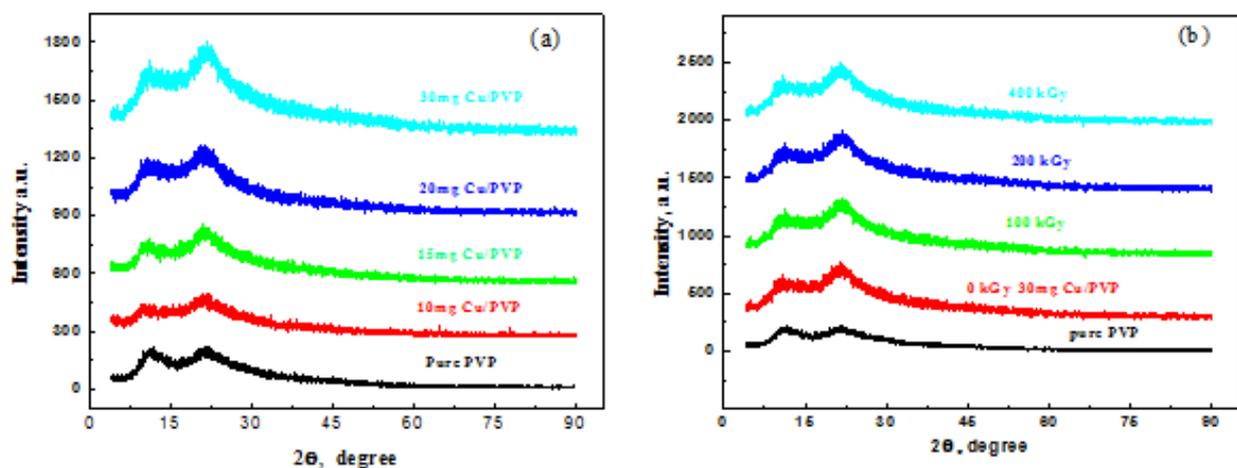


Figure (2): XRD patterns of: (a)-pure PVP and different concentrations of Cu-PVP (b)-pure PVP and 30 mg Cu-PVP irradiated with different doses

Morphological studies

SEM is often used to study the compatibility between various components of the polymer film through the detection of phase separations and interfaces. The compatibility between the polymer matrix and the inorganic fillers has great influence on the properties (mechanical, thermal, ionic conductivity) of the polymer electrolytes [29]. SEM images of pure PVP and Cu-PVP polymer film clearly indicate that the morphology of the particles are nearly spherical and homogeneous as shown in Figure. (3). The surface of the film is smooth, uniform and no crack can be observed.

From Figure (3 b and c), it is observed that the average size is about 150 and 200 nm respectively. The size of the particle is increased as the doping concentration increases due to the agglomeration of the particle.

Electrical properties

Conductivity of polymer electrolyte films depends on the actual concentration of conducting species, morphology, and their mobility. The variation of voltage with the current for pure PVP, Cu-PVP and γ -irradiated Cu-PVP composite films was recorded at room temperature and shown in Figure. (8) (a and b).

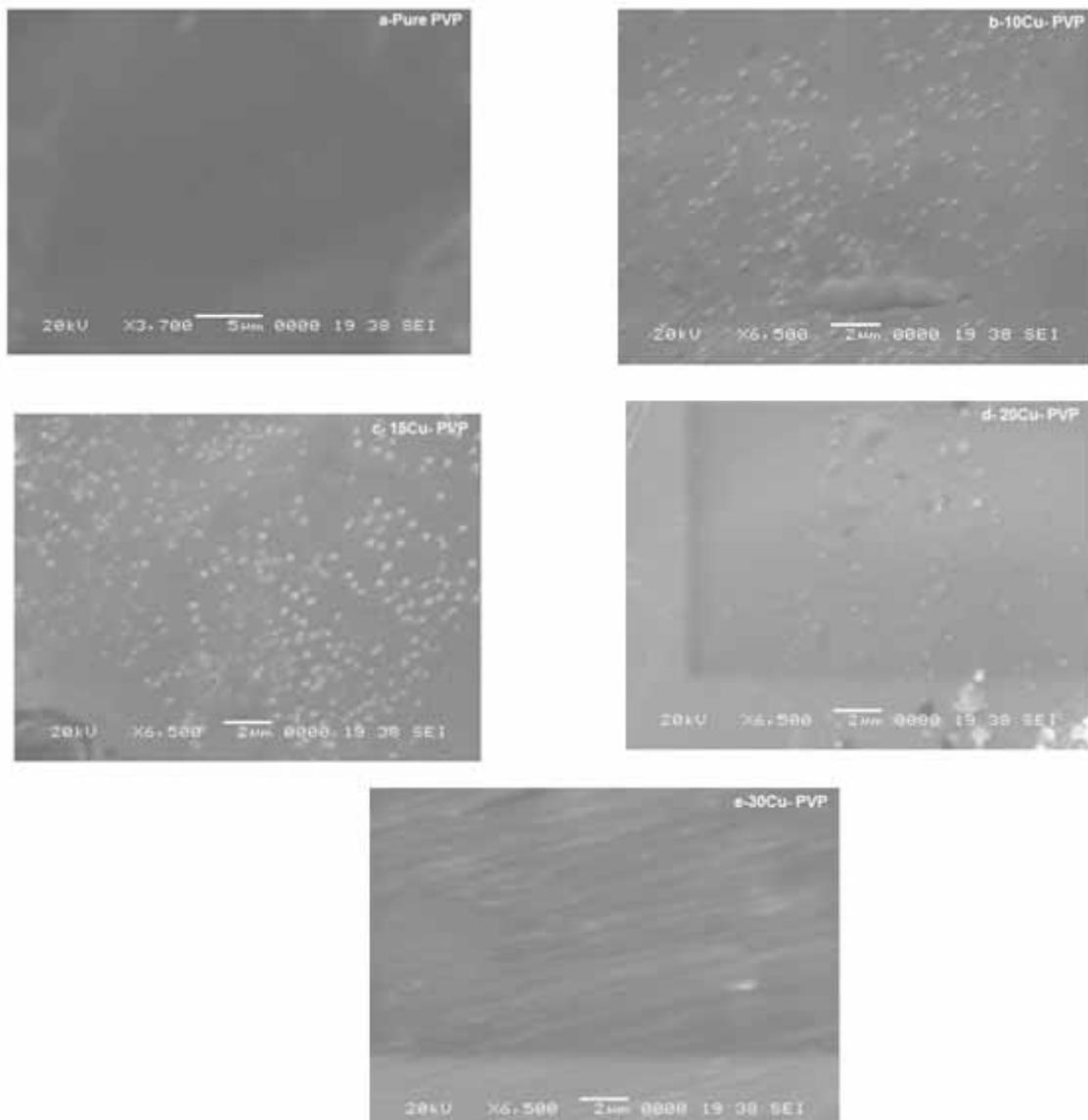


Figure (3): SEM images of : (a) pure PVP (b) PVP -10 mg of Cu (c) PVP-15 mg Cu (d) PVP-20 mg Cu (e) PVP- 30 mg Cu polymer films

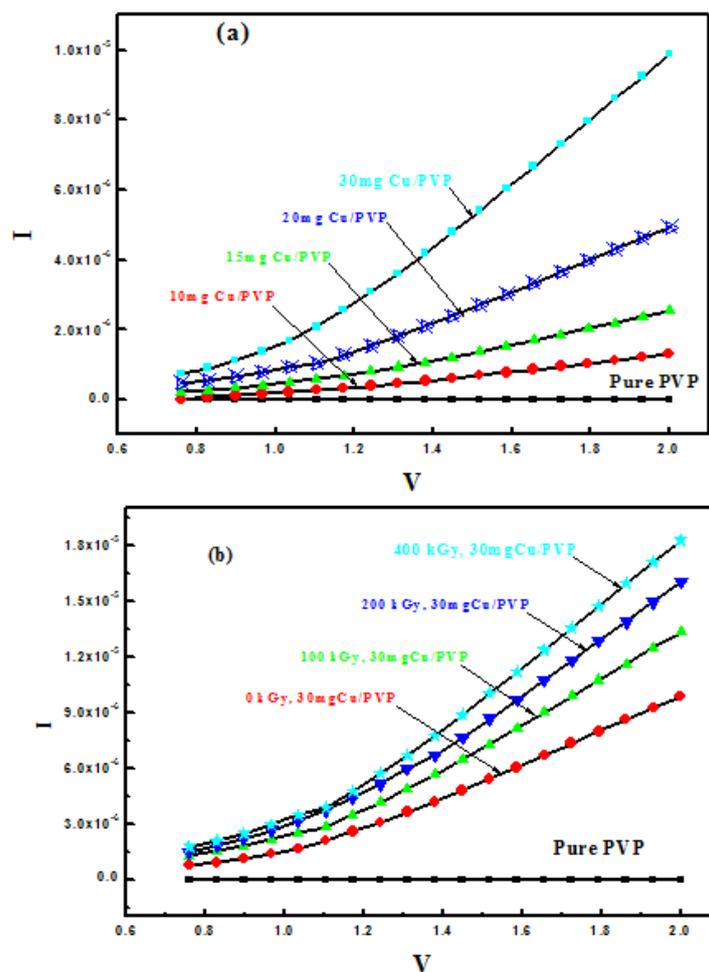


Figure (4): Current vs. voltage plots for (a) Pure PVP and Cu-PVP polymer films. (b) Pure PVP and 30 mg irradiated Cu-PVP film at different irradiation doses

The electrical conductivity was increased with increasing the concentration of Cu dopant as shown in Figure. (4a). This enhancement may be due to the increase of doping concentration of Cu in the composite polymer films which interacts with either anion or cation there by reduces the ion pair formation and increases the charge carriers [3].

Figure (4b) illustrates that as the γ -irradiation dose increased the electric conductivity of composite film increased. This may be due to the rupture of the ionic bond caused by γ -irradiation, electrons and free radicals which move freely in the polymer causing change in the electrical properties. It is clear that the conductivity increases with increase of precursor concentration and the dose of γ -irradiation.

Optical properties

Study of the optical absorption gives information about the band structure. The optical absorbance as a function of the wavelength (200-800 nm) of pure PVP and Cu-PVP films at various concentrations is shown in Figure. (5). It is shown that there is a simple shift in the intensity of the peak. The absorbance increases with increasing doping concentration. This is due to the filling of Cu ions combined with the polymer chains which absorb the incident radiation at the shortest wavelengths greater than 190 nm by the free electrons.

As shown in Figure. (6). It is clear that increasing the irradiated dose from 100-400 kGy leads to an increase of the absorbance due to increase of polarons formation at higher doses.

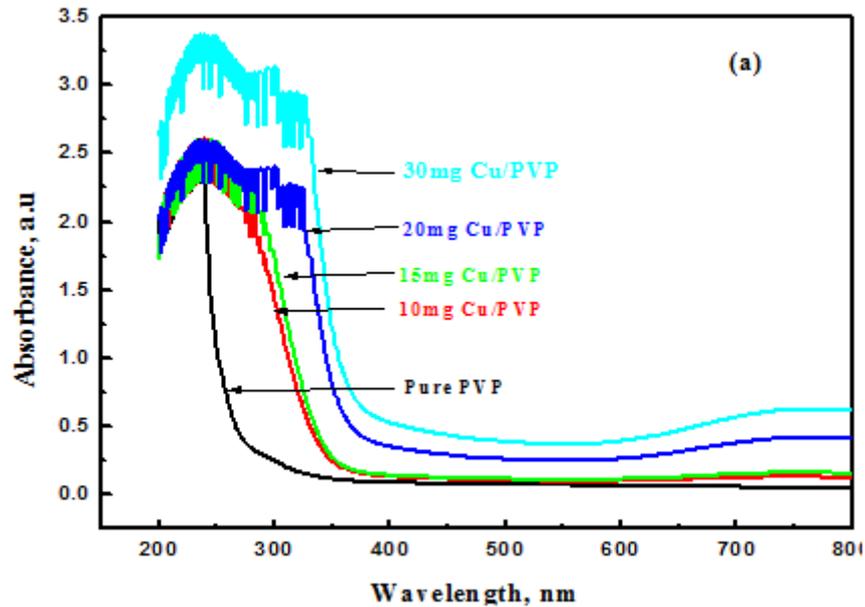


Figure (5): The optical absorbance spectrum for pure PVP and various concentrations of Cu-PVP polymer films

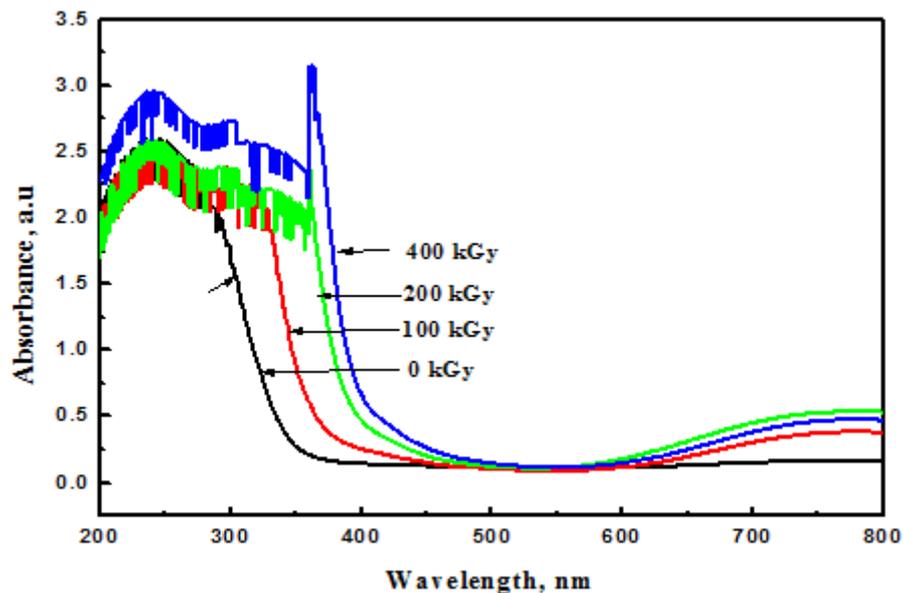


Figure (6): The optical absorbance spectrum of 15 mg Cu-PVP at different gamma irradiation doses

The observed shift in the fundamental absorption edge of UV-visible spectra can be correlated with optical band gap E_g [30-32]. For the determination of direct and indirect energy band gap, $(h\nu\alpha)^2$ and $(h\nu\alpha)^{1/2}$ they were plotted separately as a function of photon energy ($h\nu$). From the extrapolation of the linear section of the curves to x-axis, direct and indirect energy band gaps have been determined

for pure PVP and Cu-PVP with different concentration as represented in Figure. (7). For pure PVP film the direct band gap and indirect band gap were observed to be 4.95 eV and 4.40 eV respectively, while for doped films the values decrease with the increase of dopant concentration as shown in Table (1).

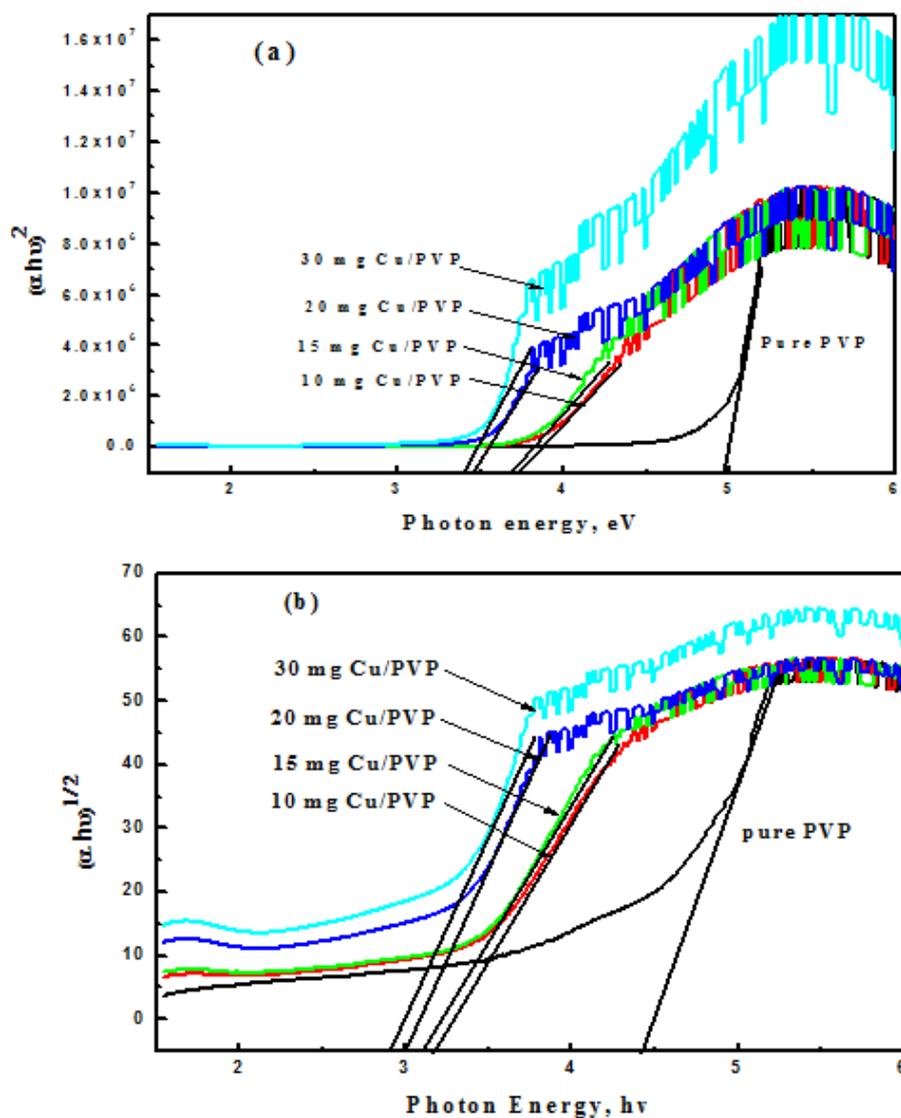


Figure (7): Effect of doping concentrations on a) direct and b) indirect band gap for pure PVP and Cu-PVP polymer films

Table (1): Direct and indirect band gap of pure PVP and Cu-PVP polymer films

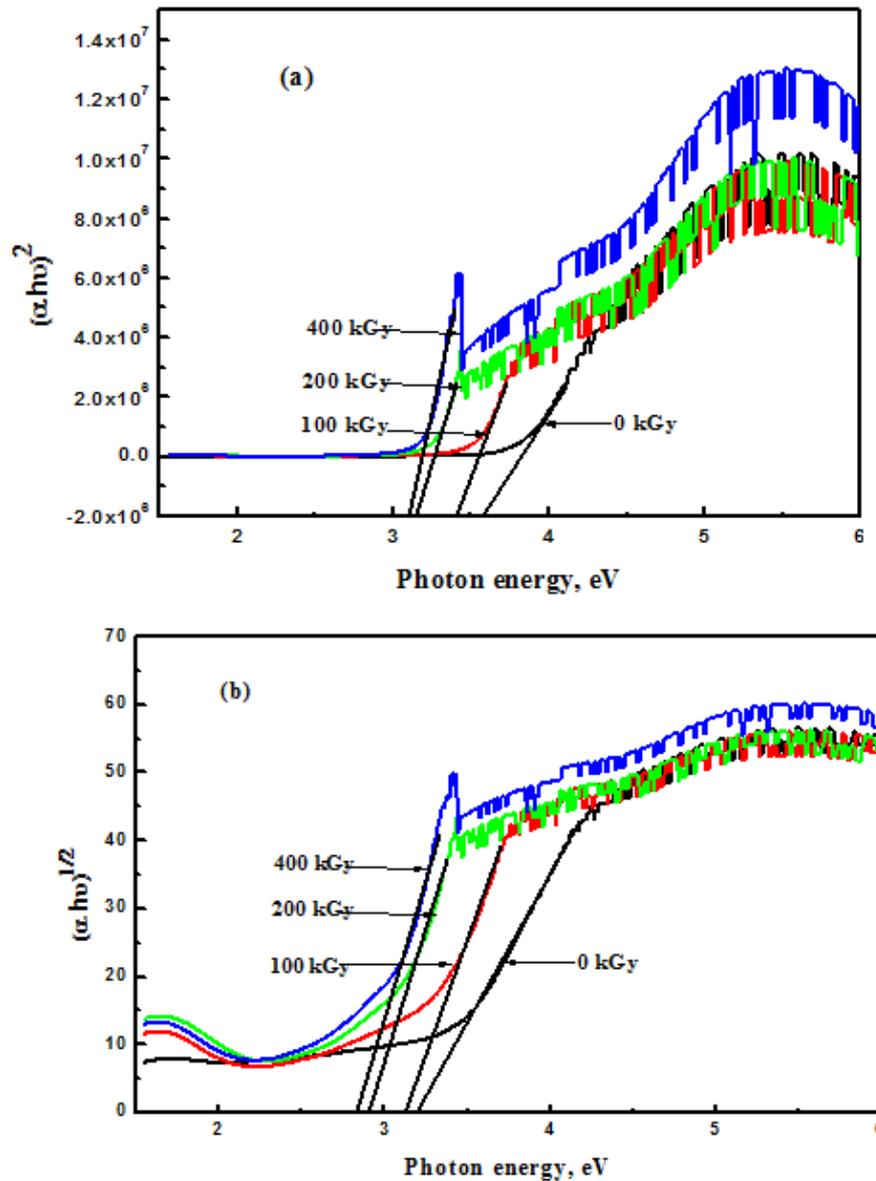
| Cu concentration | Direct band gap (eV) | Indirect band gap (eV) |
|------------------|----------------------|------------------------|
| 0 | 4.95 | 4.4 |
| 10 mg | 3.70 | 3.2 |
| 15 mg | 3.60 | 3.17 |
| 20 mg | 3.45 | 3.0 |
| 30 mg | 3.35 | 2.90 |

The direct allowed band gap of the irradiated 15 mg Cu-PVP films at different irradiation doses was evaluated as shown in Figure. (8). The band gap decreased with increasing of irradiation dose due to increase of polarons with increasing dose. The

effect of irradiation dose on the optical band gap represents in Table (2). The values of direct and indirect band gap decreased to 3.09 and 2.84 eV respectively as the irradiation dose increased to 400 kGy.

Table (2): Direct and indirect band gap of the irradiated 15 mg Cu doped-PVP film at different irradiation doses

| Irradiation dose (kGy) | Direct band gap (eV) | Indirect band gap (eV) |
|------------------------|----------------------|------------------------|
| 0 | 3.60 | 3.17 |
| 100 | 3.40 | 3.10 |
| 200 | 3.15 | 2.91 |
| 400 | 3.09 | 2.84 |

**Figure (8): Effect of irradiation dose on a) direct and b) indirect band gap for Cu-PVP films**

Conclusion

In this study, synthesis and characterization of solid polymer electrolyte films based on polyvinylpyrrolidone (PVP) complexed with Cu in 1% of HNO₃ were carried out. The effect of doping and γ -irradiation on the physico-chemical properties of the composite polymer films was investigated. Complexation of Cu with the polymer was confirmed by FTIR and XRD studies. The surface morphology of pure PVP and Cu-PVP polymer films was studied using SEM. The marked increase in the electrical conductivity with increasing concentration of dopant and γ -irradiation makes this electrolyte system suitable for electrochemical device applications. Irradiation by γ -ray is an effective technique to improve the optical properties of Cu-PVP composite films. The decrease in the energy gap of the composite film with increasing irradiation dose may be attributed to the increase in the structural disorder or the formation of π -electron clouds with the polarization aligned in the direction of the molecular chains.

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