Influence of Gamma Radiation on Optical Properties and the surface, volume energy loss function of (PHHP) films

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ABSTRACT

Thin films of (PHHP) were investigated for gamma – irradiation samples were fabricated using cast method. Thin films of (PHHP) were exposed to Cs-137 gamma – irradiation source at a dose rate 0.5 Gy/min at room temperature. Absorption spectra for(PHHP) films were recorder and values of the optical properties (energy gap, interband transition ((real and imaginary)) strength and surface energy loss function SELF and volume energy loss function VELF and optical constant (n, k))for no irradiation and gamma- irradiated samples were calculated. It was found that the optical absorption spectral distribution is sensitive to the radiation influence at the wave length 350 nm.

Keywords: PHHP, optical properties, gamma radiation, interband transition strength, SELF and VELF
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INTRODUCTION

In recent year, the azo dye has become an attractive due to its optical properties. It has been applied in divers applications such as the polarized photo induced anisotropy[1]. The polymers with different optical properties have been attracted much attentions due to their applications in sensors[2], light- emitting diodes[3-5], and others[6,7].

In the irradiation of polymers, it is the ratio of cross linking to chain scission which determines the kind and extent of changes take place. Although many reactions occur during the irradiation of polymers (eg. cross linking , chain scission , formation of unsaturation).Ionization radiation is not absorbed selectively like ultraviolet. Instead , the absorption of gamma rays is a function of electron density in the path of the radiation after a random ray strikes an atom . However, the energy transfer occurs, free radiation many form and subsequent reactions like oxidation and chain reactions, may proceed in the same manner as after uv light irradiation .[8,9]

High energy radiations, such as gamma rays change physical properties of the material, the changes are strongly depend on the internal structure of the absorbed substances , it is believed that radiation causes structural defects called color centers or oxygen vacancies leading to their density change on the exposure to gamma rays[10,11].

This paper reports the results of some optical properties of (PHHP) film with   (60 μm) thickness in the wavelength (300-900)*nm* and the effect of gamma rays on these properties.

MATERIALS AND METHODS

2-1 Synthesis of azo dye polymer compound
The azo dyes compound of (poly (6,6'-(2-hydroxy-5-(3-hydroxyphenyl) -1,3-phenylene) bis (methylene) bis(2-ethylphenol)) PHHP prepares using the Fox method *P* [12] (0.545g ,0.005 mole) of aniline was dissolved in 2 ml of Cone. HCl and then (10 ml) of dionized water were add . The solution was then cooled to 5°C in an ice - bath and maintained at this temperature . Sodium nitrite (0.36g) solution in water (5 ml) was then added dropwise . Stirring

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was continued to produce diazonium salt at the same temperature . The diazonium solution was added portion wise to the coupling component solution prepared by mixing of novolac (0.545g, 0.005 mole) in ethanol /water ratio (1:3)   with sodium hydroxide (2 gm) dissolves in (100 ml) of water. During the procedure. The pH value was maintained with 9 – 10 , and the temperature at 5°C . The mixture was stirred for 30 min, and then the pH value was decreased to ~ 6. The mixture was left overnight . The precipitated crude dyes were collected by filtration , and washed with water , ethanol and acetone .

The structure and some physical properties of azo dyes compounds of (poly (6,6'-(2-hydroxy-5-(3-hydroxyphenyl) - 1,3-phenylene) bis (methylene) bis(2-ethylphenol)) PHHP were given in Fig.(1).
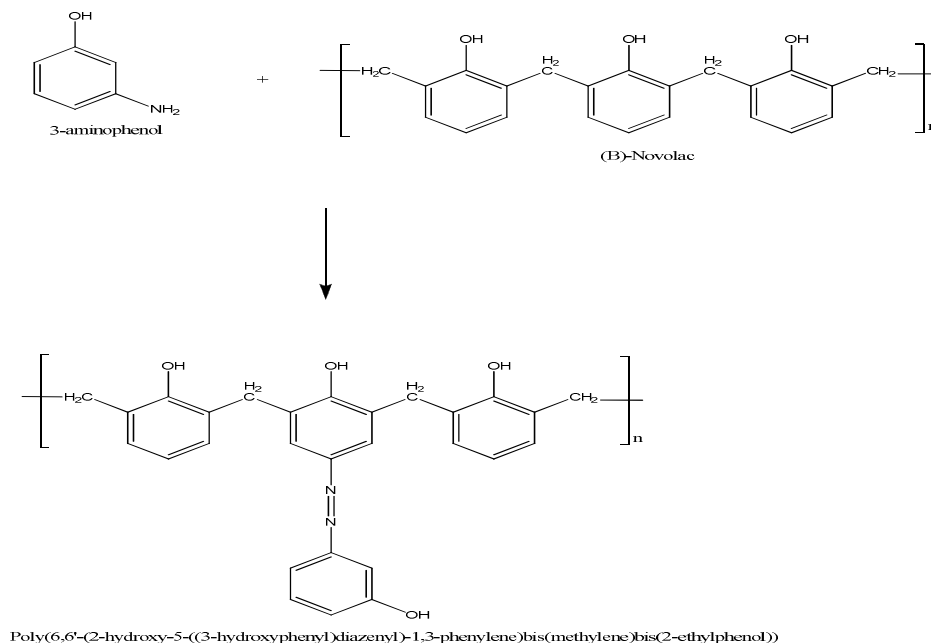

Fig.(1) The chemical structure of the azo dye compounds (poly (6,6'-(2-hydroxy-5-(3-hydroxyphenyl)-1,3-phenylene) bis (methylene) bis(2-ethylphenol)) PHHP

2-2 Preparation of the thin Film
A thin film of azo dye-polymer compound PHHP was prepared on glass substrate that has dimension (1.4 × 2 cm) using solvent casting method. The thickness of PHHP film kept around (60µm). The thickness of the film was measured by digital micrometers. Finally, the film was heated at $80\,^{0}C$ for 1hr to evaporate the of solvent used.

2-3 Gamma irradiation
(PHHP) thin film were irradiation with Cs – 137 gamma- source with the activity of the source an exposure rate 0.5 Gy/min. The optical absorption spectra were recorded using a. spectrophotomer Mark (   ). It is supplied from (   ). Which is measure for the interval wavelength from (300 900) *nm*. During gamma –ray radiation 3 mm thick plexglas was used with sample in order to attain electronic equilibrium [13].

RESULTS AND DISCUSSION

The optical properties of material are important, as they provide information on the electric band structures, localized states and types of optical transitions.

Typical optical absorption spectra plots against wavelength of (PHHP) thin films of irradiation at (5 Ky) are shown in fig. (2). From this it is evident that optical absorption spectral distribution is sensitive to the radiation influence at the wavelength 350 *nm*, it is believed that ionizing radiation causes structural defects (called color center) leading their density change on the exposure to gamma- irradiation[14].
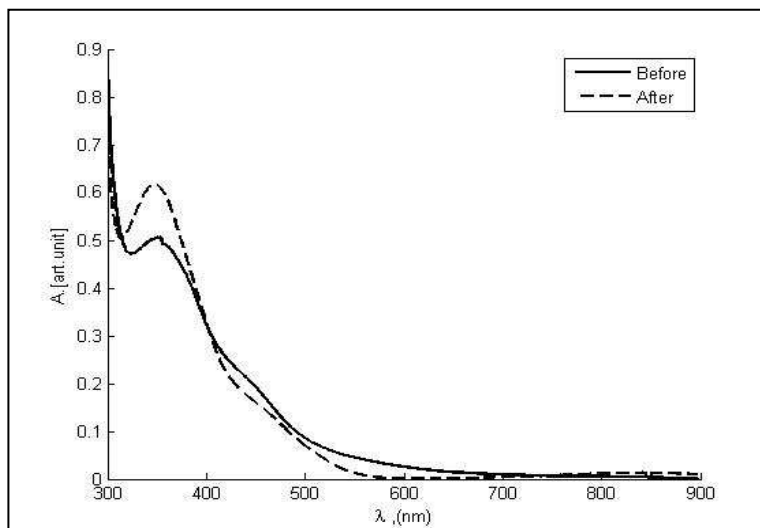
Fig.(2): The spectrum absorbance (A′) as a function the wavelength (λ) of PHHP film before and after irradiation .
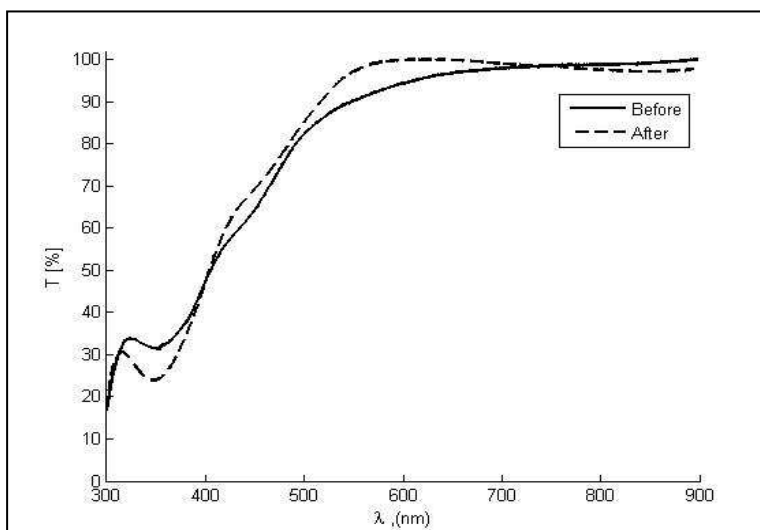

Fig.(3): The spectrum transmittance(T) as a function the wavelength (λ) of PHHP film before and after irradiation .
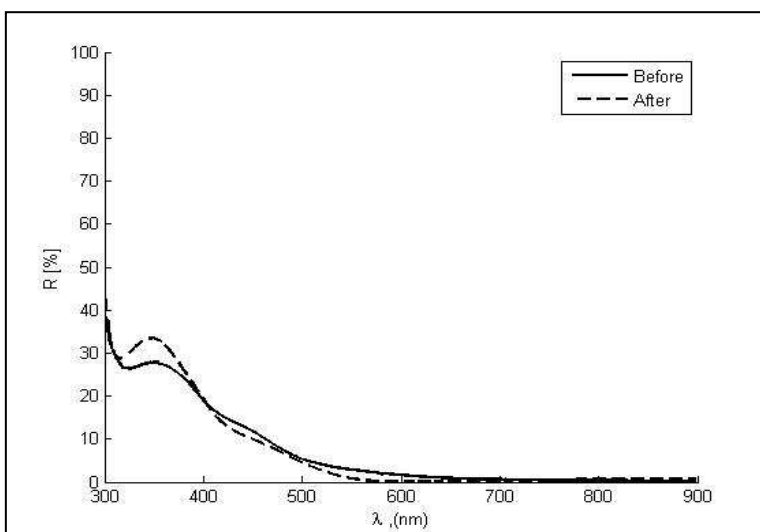

Fig.(4): The Reflectance (R) as a function the wavelength (λ) of PHHP film before and after irradiation .

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Fig. (3) shows the variation of transmittance with wavelength for fig.(3) before and after irradiation. Transmittance after irradiation film is higher than that before irradiated,

The *uv- visible* diffused reflectance spectra of (PHHP) as a function of wavelength are shown in fig.(4)

The energy band gaps of this films were calculated with the help of the absorption spectra. To determinate of the energy band gap $(\alpha h v)^{1/2}$ is plotted versus (photon energy) using the relation [15,16] :

$$\alpha h v = B(h v - E_g^{opt})^r \tag{1}$$

where B is the characteristic parameter (independent of photon energy) for respective transitions and inversely proportional to amorphousity , $h v$ denotes photon energy , E_g^{opt} band gap energy and r is the number which characterizes the transition process, and is theoretically equal to 1/2, 2, 3/2 or 3 for direct allowed ($\alpha \geq 10^4$cm^{-1}) indirect allowed, direct forbidden and indirect forbidden transition, respectively [17].

We obtained energy gap before irradiation $E_g^{ind} = 1.9944\ eV$ and after irradiation $E_g^{ind} = 2.0856\ eV$ in general optical band gaps increase with irradiation as shown in fig.(5).
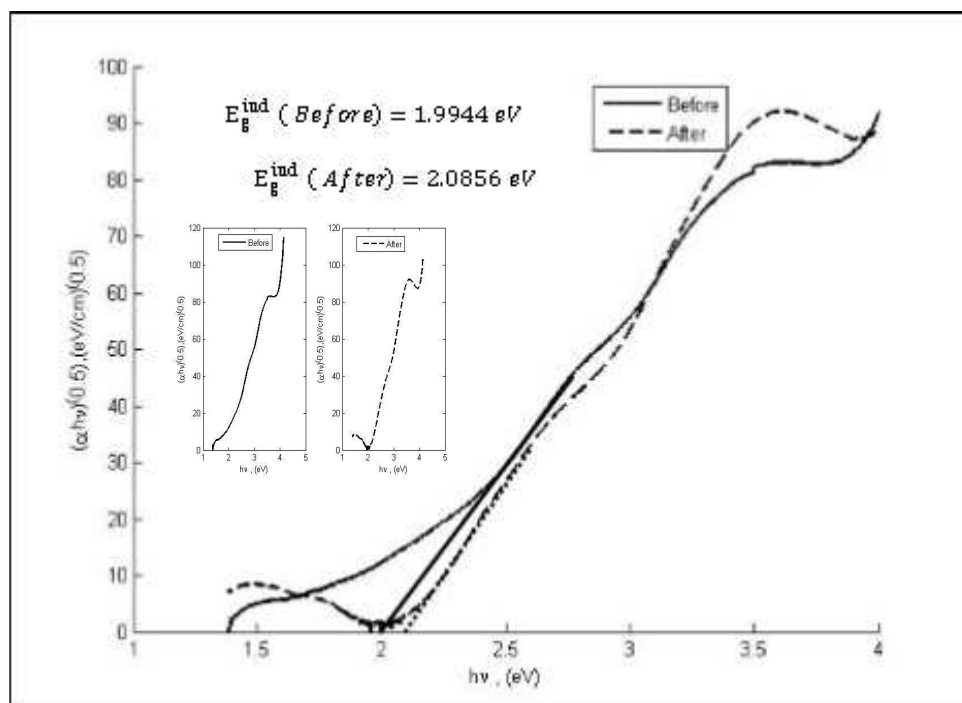

Fig.(5) Dependence of $(\alpha h v)^{1/2}$ on the photon energy for PHHP film before and after irradiation .

The refractive index of the films was calculated by the following equation [18]:

$$n = \frac{(1 + R^{1/2})}{(1 - R^{1/2})} \tag{2}$$

Fig.(6) shows the spectral dependence of refractive index (*n*). It is clear from the figure that refractive index decrease after irradiation which can be attributed to change in the film structure and in the chemical band distribution.
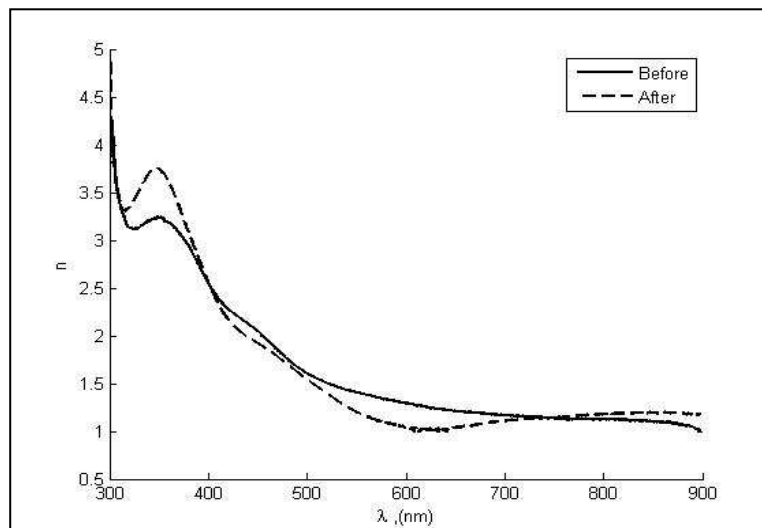
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Fig.(6): The refractive index (*n*) as a function the wavelength (λ) of PHHP film before and after irradiation .

The extinction coefficient (k) can be obtained from the relation [19]:

$$k = \frac{\alpha\lambda}{4\pi}$$

(3)

Where α : is absorption coefficient . from fig. (7) one can notice that The extinction coefficient (k) decease after irradiation.
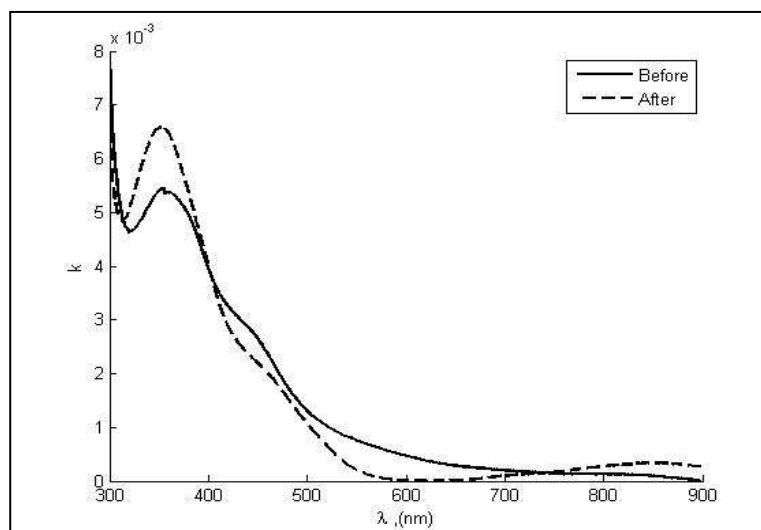

Fig.(7): The extinction coefficient (k)as a function the wavelength (λ) of PHHP film before and after irradiation .

The variation of ε_1 as a function of photon energy ($h\nu$) is shown in fig. (8)this increase of real part of dielectric constant ($\varepsilon_1 = n^2 - k^2$) after irradiation can be cross linking [20].

Fig.(9) shown the relationship between imaginary part of dielectric constant $\varepsilon_2 = 2nk$ after irradiation imaginary part of dielectric constant ε_2 increase because $\varepsilon_2$mainly depend an (k) values which are related of the variation of absorption spectra [21].
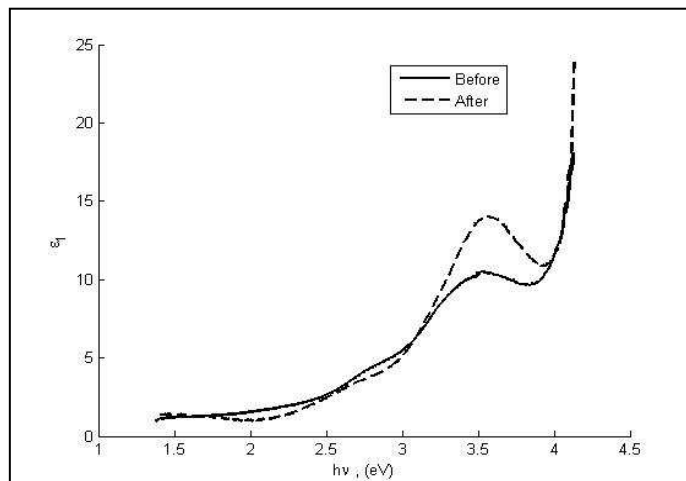
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Fig.(8): The real part(ε_1) of the dielectric constantas a function of photon energy ($h\nu$)of PHHP film before and after irradiation .
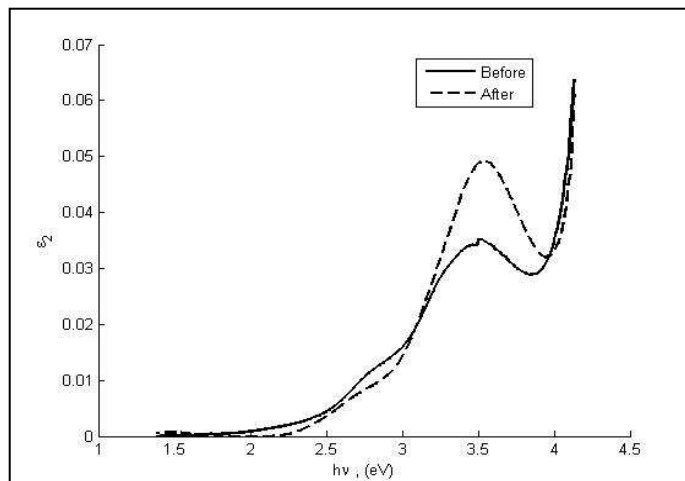

Fig.(9): The imaginary part (ε_2) of the dielectricconstant as a function of photon energy (hν)of PHHP film before and after irradiation .

From the real and imaginary parts of the dielectric constant the complex interband transition strength [22] can be calculated as :

$$J_{cv} = J_{cv1} + J_{cv2} = \frac{m_o^2 \, 4\pi^2}{e^2 h^2} \frac{(h\nu)^2}{2} (\varepsilon_2 + i \, \varepsilon_1) \qquad (4)$$

where m_o is the mass of the electron, h is Plank's constant , e is the charge of electron and$(h\nu)$ is the photon energy . The real part of interband transition strength J_{cv1} is proportional to the imaginary part of the dielectric function . the imaginary part of interband transition strength J_{cv2} is proportional to the real part of the dielectric function ε For computational convenience we take the prefactor $(\frac{m_o^2 \, 4\pi^2}{e^2 h^2})$ in Eq.(4) , whose value in cgs units is $8.289 \times 10^{-6} \, g \, cm^{-3} eV^{-2}$, therefore, the J_{cv} calculated from is Eq.(4) is shown in the Figs.(10) and (11).
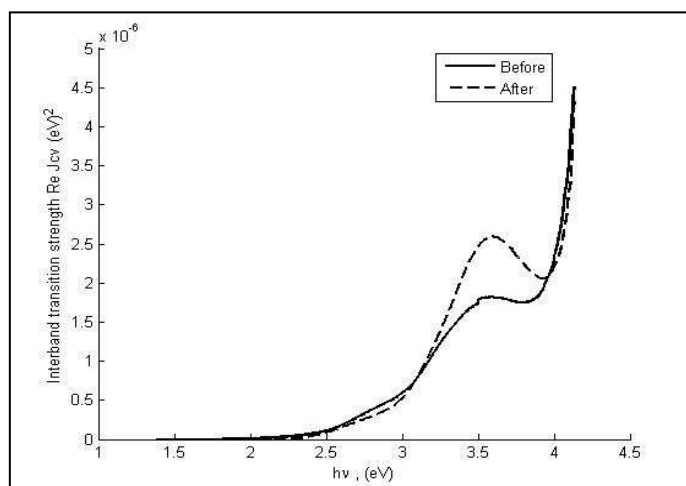

Fig.(10): The real part(J_{cv}) as a function of photon energy ($h\nu$)of PHHP film before and after irradiation .
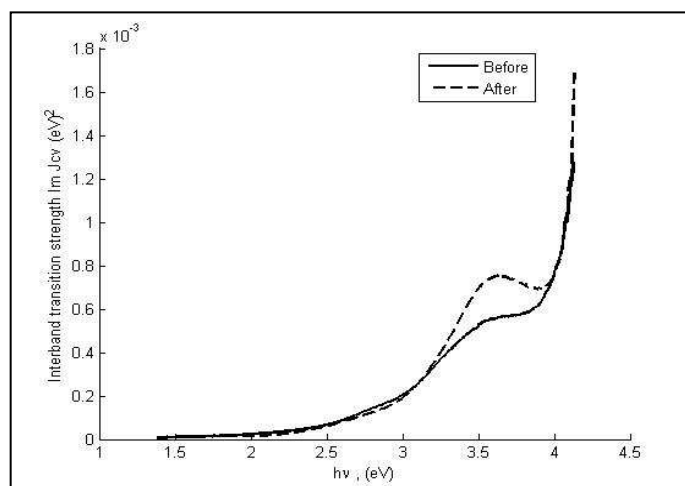

Fig.(11): The imaginary part (J_{cv}) as a function of photon energy ($h\nu$)of PHHP film before and after irradiation .

In these figs. Illustrated Interband transition strength J_{cv} as a function of the photon energy$(h\nu)$. It increases with increasing photon energy and this denotes that the probability of electronic transition makes increase with increasing photon energy. These Figures also show that the interband transition strength J_{cv}grows significantly when the photon energy is higher than 2.5eV . This means that most of the high absorption happens which increases the excitation of the electrons and moving it from the valence band to the conduction band.

It is also possible to calculate the surface $- Im (\frac{1}{1+\varepsilon})$ and volume (bulk) $- Im (\frac{1}{\varepsilon})$ energy loss functions (SELF and VELF) related to the real and imaginary parts of the dielectric constant as [23,24]:

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$$Surface - Im\left(\frac{1}{1+\varepsilon}\right) = \frac{\varepsilon_2}{((\varepsilon_1+1)^2+\varepsilon_2^2)} \tag{5}$$

$$Volume - Im\left(\frac{1}{\varepsilon}\right) = \frac{\varepsilon_2}{(\varepsilon_1 + \varepsilon_2)^2}$$

The behavior of both surface and volumeenergy loss function as a function of photon energy isshown in the Fig.(12) and Fig.(13). It is clearthat the volume energy loss is greater than surface energy loss at incident photon energies. It is also clear that the maximum of SELF and VELF correspond to the absorption energy due to the interband transition that occurs at [before irradiation at 2.7623eV and after irradiation at 2.7642 eVfor SELF] and [before irradiation at 2.5205 eV and after irradiation at 2.5205 eV for VELF). Roth the energy losses are when the fastsingle electrons traverses from valance band toconduction band in the PHPP film. The surface energy loss function (SELF) and volume energy loss function (VELF) before irradiation film are higher than that after irradiation.
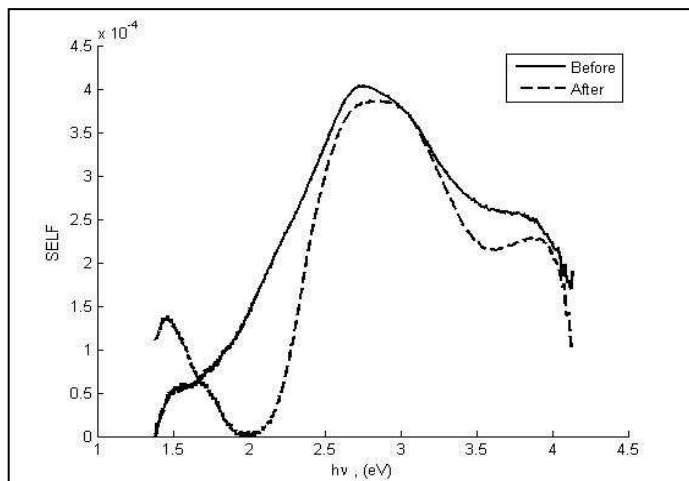

Fig.(12): Surface energy loss function (SELF)as a function of photon energy ($h\nu$)of PHHP film before and after irradiation .
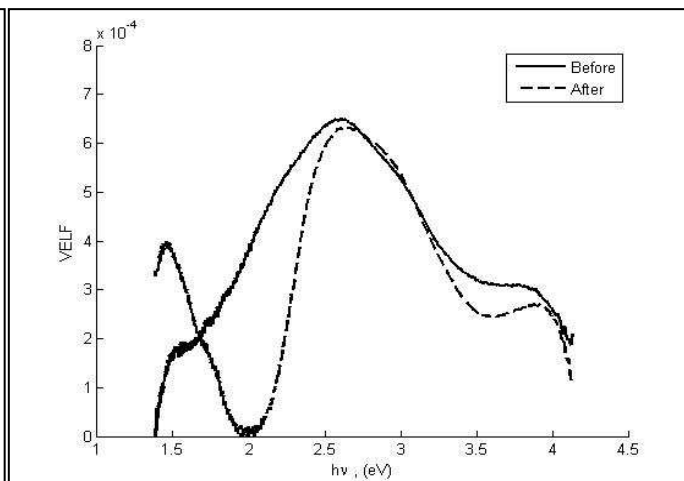
Fig.(13): Volume energy loss function(VELF)as a function of photon energy ($h\nu$)of PHHP film before and after irradiation .

CONCLUSION

From the study of the absorbance as a function of wavelength for un irradiated samples as well as samples exposed to gamma – dose, we come out with the following conclusion:-

1- The absorbance increases with increasing absorbed gamma – dose.

2- The optical gap energy increases with increasing absorbed gamma – dose.

3- The reflectance, refractive index, extinction coefficient, dielectric constant(ε_1 , ε_2)and interband transition strength (read and imaginary) are increases with increasing absorbance gamma – dose.

4- The spectrum transmittance and the surface and volume energy loss function (SELF and VELF) are increases with increasing absorbance gamma – dose.

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