European Journal of Material Sciences
Vol.3, No.3, pp.1-11, September 2016
Published by European Centre for Research Training and Development UK (www.eajournals.org)

STUDY OF THE OPTICAL PROPERTIES OF POLY FURFUYL ALCOHOL (PFA) DOPED WITH CRYSTAL VIOLET

Samah Hussein Kadhim[1], Anis A. Al-Najar [2], Ali H. Al-Mowali [2]

[1]Department of Chemistry, College of Science, University of Thi-Qar, Iraq
[2]Department of Chemistry, College of Science, University of Basrah, Iraq

ABSTRACT: *Films of Poly Furfuryl Alcohol (PFA) doped by crystal violet have been prepared using casting method, different ratios of (0.01, 0.03, 0.05, 0.07, 0.1)%wt of crystal violet at room temperature (298) K, the optical absorption spectra of these films in the wavelength range from 200-800 nm. The result showed that the optical absorption is due to indirect allowed transitions for pure PFA and different doping ratios, while the Energy gap* E_g *of the composite films decreases with increasing doping ratios. The absorption coefficient (*α*), real and imaginary parts (*$\varepsilon_r,\varepsilon_i$*), and optical conductivity (*σ_{opt}*) were found to be increased with increasing the doping ratios.*

KEYWORDS: Poly Furfuryl Alcohol, Crystal Violet, Absorption Coefficient, Optical Conductivity.

INTRODUCTION

The optical investigation of polymers constitutes an important tool to enhance its application in solar energy conversion as a cover in solar collector [1], green house and optical filter [2] and in manufacturing the compact discs (CDs) and Digital Versatile discs DVDs [3]. Among the new classes of materials, polymers are especially interesting because they combine the optical and electronic properties of semiconductors with processing advantages and mechanical properties of polymers [4]. Polymers offer several advantages in optical applications. For example, their manufacturing costs are low because the precision of injection and molding produces a product that needs no finishing operation and no grinding or polishing. The absorption coefficient near fundamental absorption edge in both of crystalline and amorphous semiconductors, is dependent on the photon energy . For direct transitions, the absorption coefficient was taken on the following more general form as a function of photon energy [5,6].

$$\alpha h \upsilon = A (\alpha h \upsilon - E g)^n \qquad (1)$$

and for indirect transition

$$\alpha h \upsilon = B (\alpha h \upsilon - E g)^n \qquad (2)$$

where υ is the frequency of the incident photon , n is the number which characterizes the optical processes .n has the value 1/2 for the direct allowed transition , 3/2 for a forbidden direct allowed transition and 2 for the indirect allowed transition , A and B are constants and Eg is the optical energy gap. When the straight portion of the graph of $(\alpha h\upsilon)^n$ against $h\upsilon$ is extrapolated to $\alpha = 0$,the intercept gives the transition band gap [7].

The optical absorption coefficient α (cm^{-1}) which is a function of wavelength can be calculated from the optical absorbance spectra by using the relations [8]:

$$I = I_0 \, e^{-\alpha t} \qquad (3)$$

Where I is the incident intensity and I_0 is the penetrating light intensity, and t is the thicknesses of matter (cm) and a is the absorption coefficient $(cm)^{-1}$.

Where the amount of log I/I_0 represents the absorbance (A).

The absorption coefficient can be calculated by:

$$\alpha = 2.303(A/t) \qquad (4)$$

The refractive index n can be expressed by:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \qquad (5)$$

The extinction coefficient can be calculated by:

$$k = \frac{\alpha\lambda}{4\pi} \qquad (6)$$

Where λ is the wavelength of the incident ray.

The relation between the complex dielectric constant and the complex refractive index *N* is expressed by:

$$\varepsilon = N^2 \qquad (7)$$

It can be concluded that:

$$(n-ik)^2 = \varepsilon' - \varepsilon'' \qquad (8)$$

The real and imaginary complex dielectric constants can be expressed by Equation 9 and 10, respectively:

$$\varepsilon' = n^2 - k^2 \qquad (9)$$

$$\varepsilon'' = 2nk \qquad (10)$$

The optical conductivity, σ_{opt} ,is related to light speed and can be expressed by the following equation:

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \qquad (11)$$

EXPERIMENT

Materials

The materials tested in this study were Furfuryl alcohol, dimethyl formamide, Sulfuric acid and crystal violet .

Prepration of poly Furfuryl alcohol (PFA)

PFA has been prepared from the distillated liquid monomer FA (25 ml) via drops of acid catalysis H2SO4 (1M) and heated at 60°C for 1 hour to yield viscose colored polymer [9-12].

Doping of PFA

Doping PFA with dye crystal violet is carried out by adding the weighed dye to the appropriate weight of polymer (1g) then the mixture was dissolved in dimethyl formamide DMF after the prepared directly to give a polymer / dye system containing (0.01, 0.03, 0.05, 0.07 and 0.1) g wt% of doping reagent Crystal violet [13]. The mixture was stirred well for 15 minutes to guarantee that the homogenous distribution of dye in the polymer matrix , and then coated on a glass substrate (with certain dimensions) by casting method at room temperature (RT). The thickness of the films were measured using Micrometer. The spectra of absorption was recorded for wavelengths 200-800 nm using UV-visible spectrophotometer model (U-V-25400-38) by SHIMADZU Co.

RESULTS AND DISCUSSION

Figure (1) shows the optical absorbance curve versus wavelength with a range of (200-800) nm at room temperature for PFA and with different ratios of dye crystal violet (CV) thin films. There is one peak that can be seen for pure PFA at 332 nm related to π-π^*, while there are two peaks that can be observed for the doping ratios, one at about 336-342 nm related to π-π^* and the other at around 588-598 nm related to crystal violet [13,14].

Figure (2) shows a plot of absorption coefficient versus photon energy for PFA with different doping ratios . The absorption coefficient of film was calculated after correction for the reflection losses according to equation (2).The value of absorption coefficient plays an important role to the limitation of the type of transition. It is obvious from the same figure that the value of (α) is lower than 10^4 cm^{-1} , indicating that the transition was an indirect electron transmission in pure PFA and ratios.

According to equation (2), the plots of $(\alpha h\upsilon)^{1/2}$ versus photon energy are shown in figures (3)-(8) . There are two straight line portions that are clearly seen in these curves. The lower energy line corresponds to the phonon absorption processes, while the photon energy intercepts at (E_g+E_p). The other line corresponds to the phonon emission processes and photon energy intercept at (E_g-E_p).

The energy gap of the PFA films decreases with increasing doping ratio and the values of indirect band gap energy (E_g) and the phonon energy (E_p) are tabulated in table (1).

The calculated Ep is too high to be considered a lattice phonon and it may be suggested that the tail states or defect in energy gap is present. This result is in agreement with other research work accomplished [15].

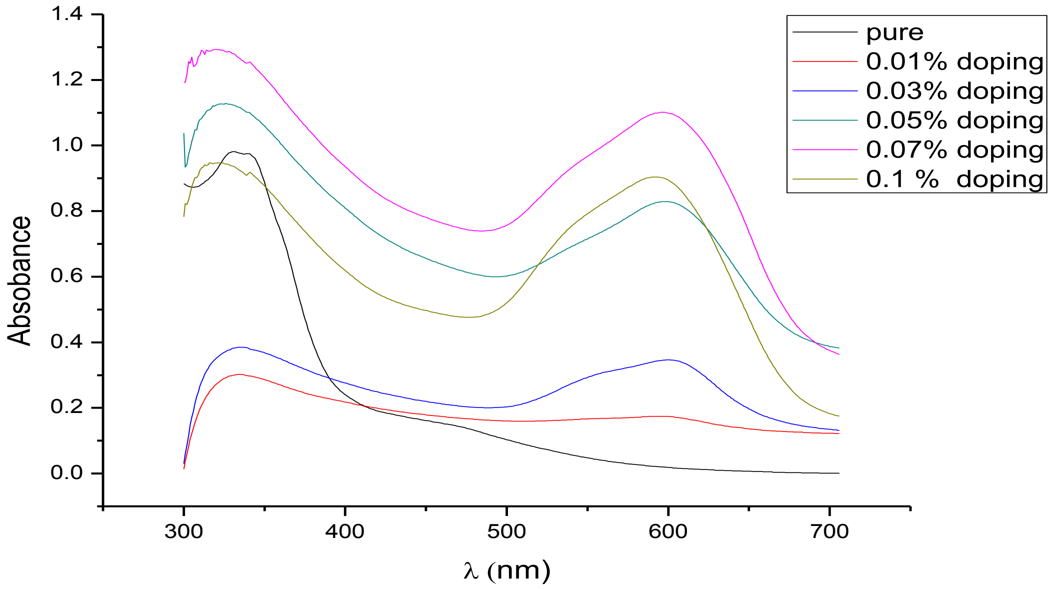

Figure (1): The relationship between absorption and wavelength for PFA with different doping ratios.

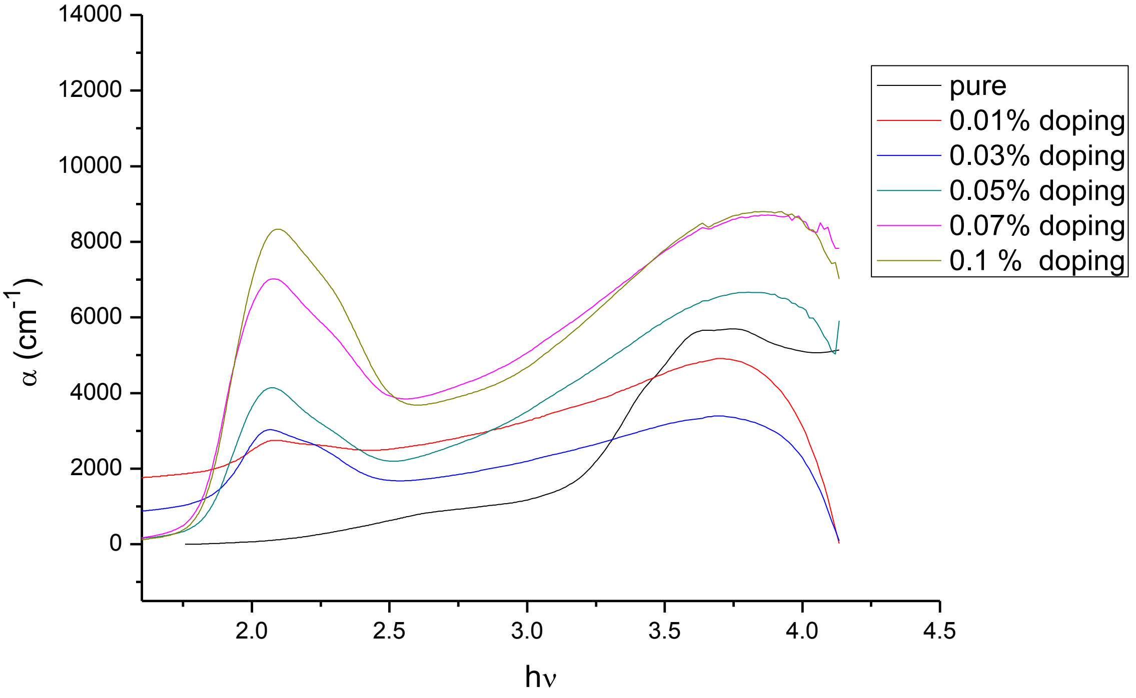

Figure (2): The relationship between absorption coefficient and photon energy for PFA with different doping ratios.

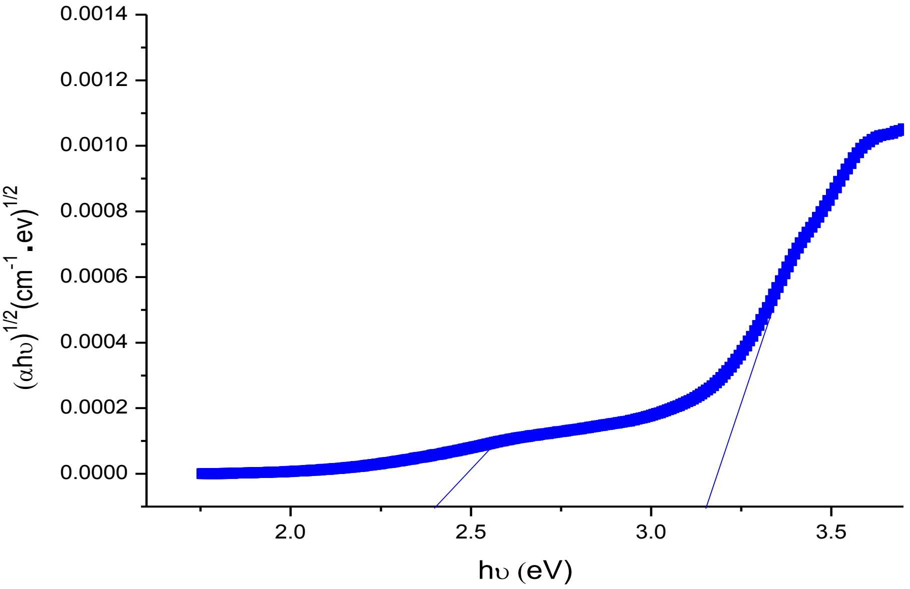

Figure (3): The relationship between $(\alpha h\upsilon)^{1/2}$and photon energy for PFA .

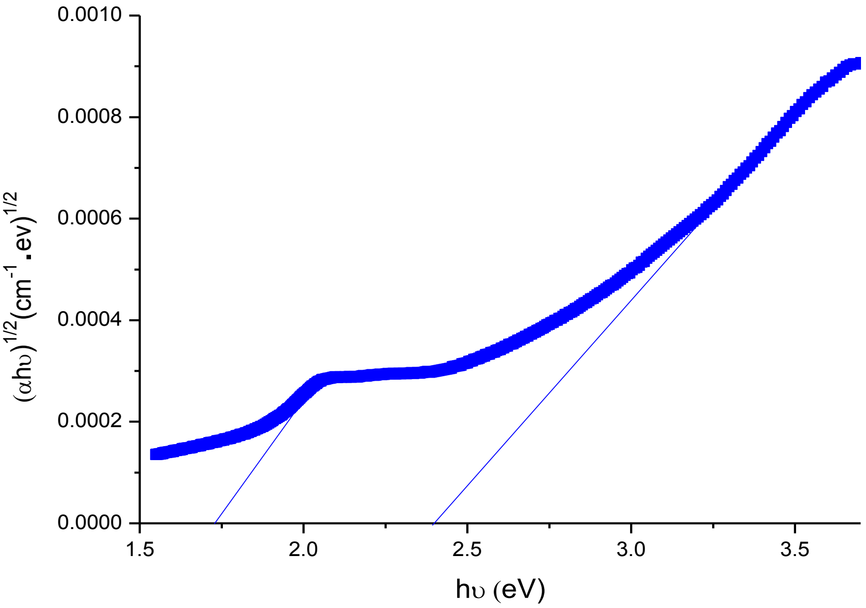

Figure (4): The relationship between $(\alpha h\upsilon)^{1/2}$and photon energy for (0.01%) of doping PFA .

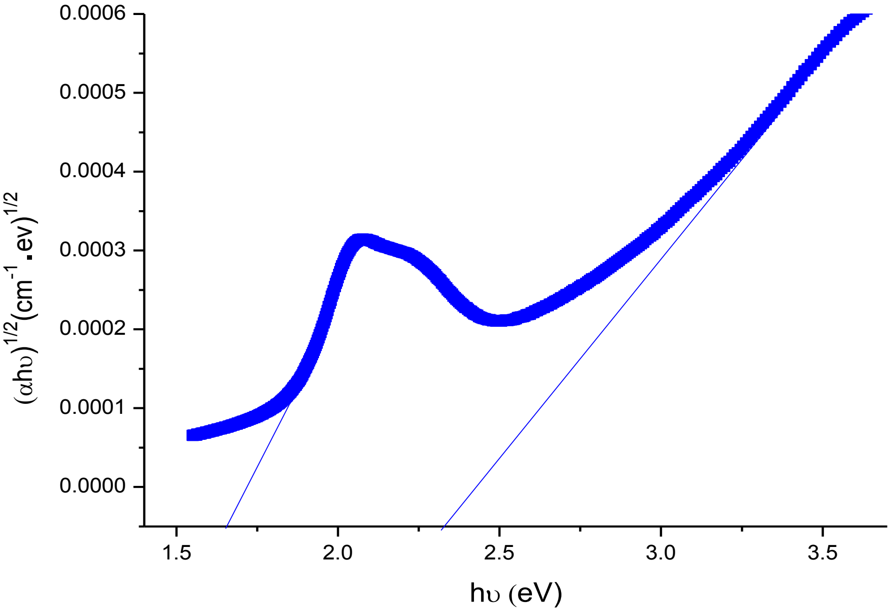

Figure (5): The relationship between $(\alpha h\upsilon)^{1/2}$and photon energy for (0.03%) of doping PFA .

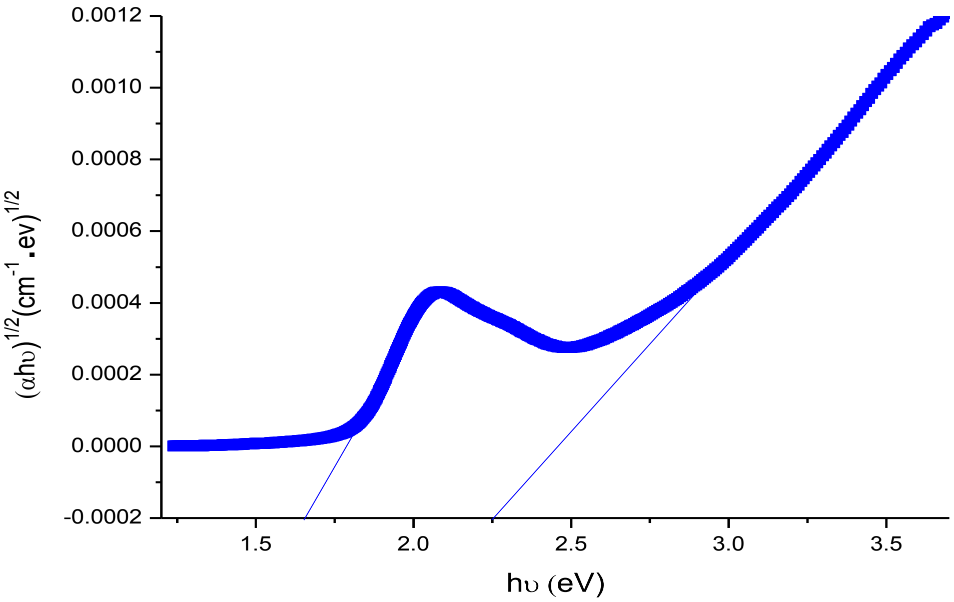

Figure (6): The relationship between $(\alpha h\upsilon)^{1/2}$and photon energy for (0.05%) of doping PFA .

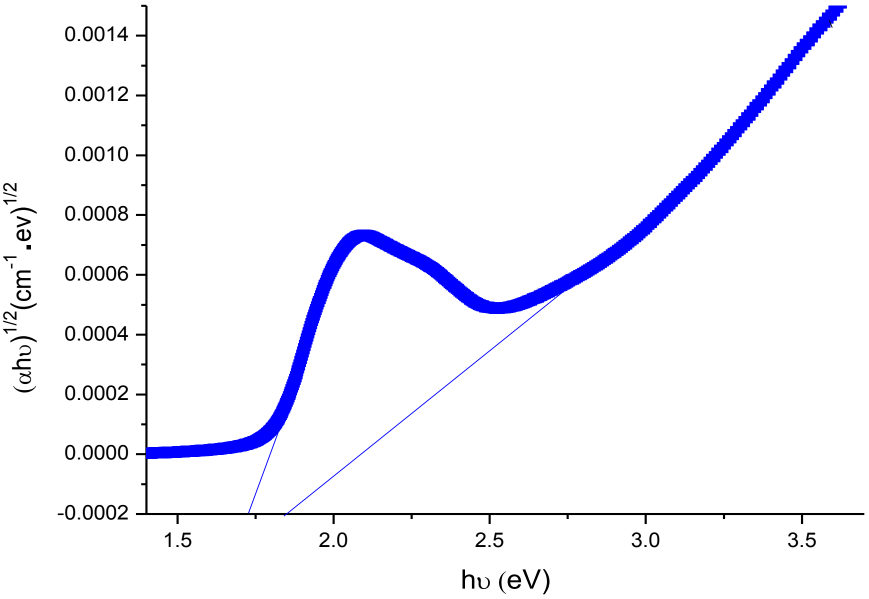

Figure (7): The relationship between $(\alpha h\upsilon)^{1/2}$and photon energy for (0.07%) of doping PFA .

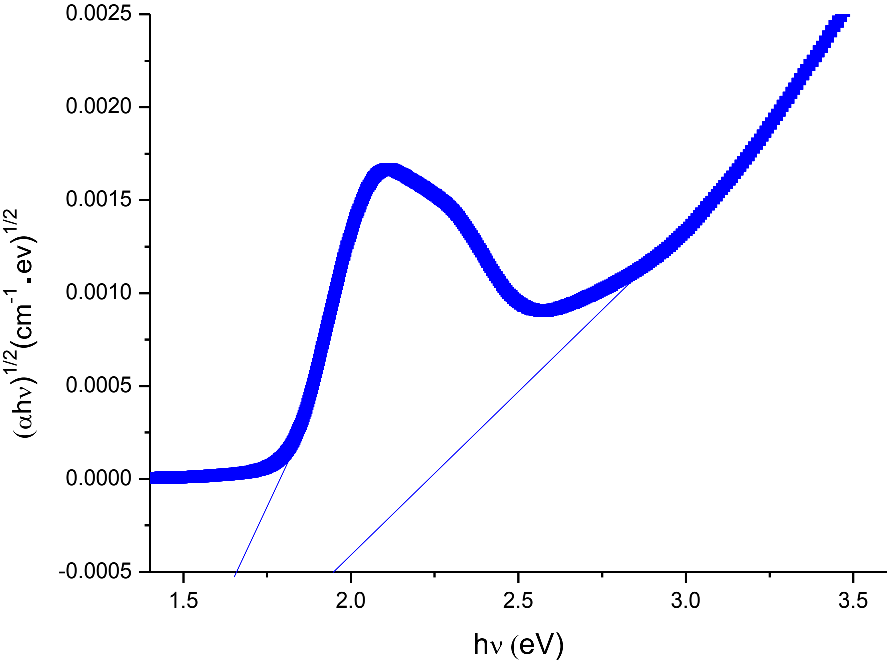

Figure (8): The relationship between $(\alpha h\upsilon)^{1/2}$and photon energy for (0.1%) of doping PFA .

Table (1): Indirect band gap energy (E_g) and the phonon energy (E_p) values for doping PFA film with different doping ratios.

Doping ratio%	E_g^{ind}	E_p
0	2.8	0.4
0.01	2.05	0.35
0.03	1.97	0.32
0.05	1.95	0.3
0.07	1.75	0.1
0.1	1.8	0.15

Figures (9) and (10) show the relationship between real part (ε_r) and imaginary part (ε_i) of dielectric constant with photon energy for pure PFA and those doped with different ratios of dye. The real and imaginary parts were computed from equations (9) and (10), respectively. The real part is associated with how much it will slow down the speed of light in the material and the imaginary part illustrates that how a dielectric constant absorbs energy from electric field due to dipole motion. It is clearly obvious, for both (ε_r) and (ε_i), that the value of each of them increases as the percentage of doping increased. Similar behavior was observed by others [16].

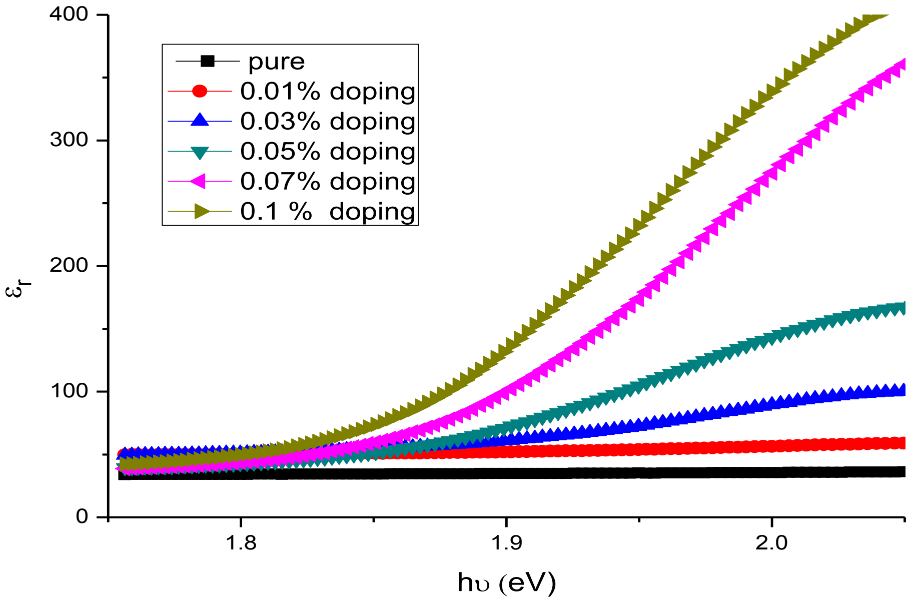

Figure (9): The relationship between real part and photon energy for PFA with different doping ratios.

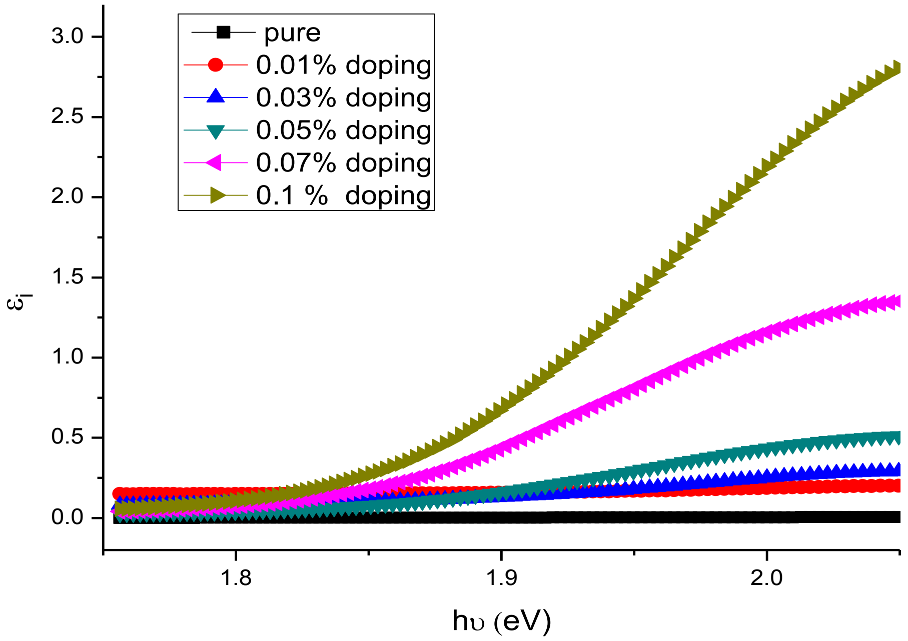

Figure (10): The relationship between imaginary part and photon energy for PFA with different doping ratios.

Figure (11) shows the relationship between optical conductivity and photon energy for pure PFA and its doping ratios. The optical conductivity was determined using equation (11). It is clear that there is an increase in optical conductivity as increasing in doping percentage increases. The increase in optical conductivity is due to the high absorbance of (PFA) doped with different ratios of crystal violet dye thin film or may be due to electron excited by photon energy. Also, it may be caused by the hopping of the charge carriers between the localized states as well as due to the excitation of the charge carriers to the states in the conduction band. Similar behavior was observed with many polymers such as poly (p-amino benzaldehyde) terminater by phenylene diamine thin film [17].

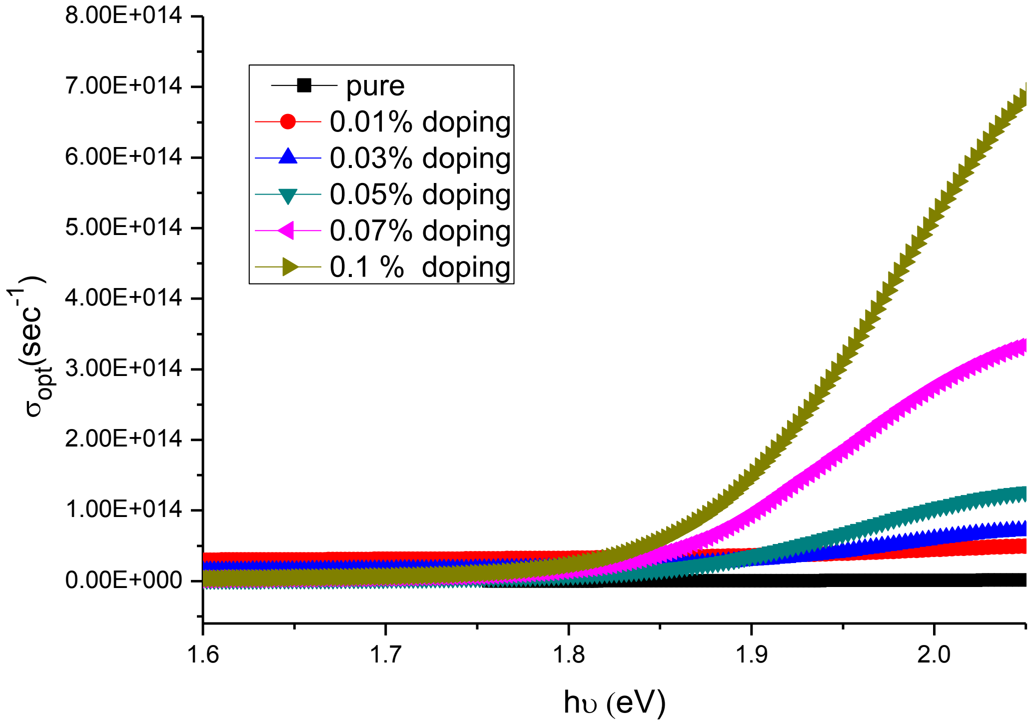

Figure (11): The relationship between optical conductivity and photon energy for PFA with different doping ratios.

CONCLUSION

Poly Furfuryl Alcohol doped with Crystal Violet thin films have been prepared by cast method technique. The optical transmission spectrum is used to calculate the optical Parameters such as absorption coefficient, real and imaginary parts and optical conductivity where found to be increasing with increasing of doping ratios. The energy gap of indirect transition decreases with increasing doping ratios.

REFERENCES

[1] F.P.Schafer."Dye Laser",N.Y.,Springer Verlage, 1(8) (1990).
[2] A.Q.Abdullah, Basrah J. Sci., 22 (1), (2004) 136-165 .
[3] A.S.Ali Al-Temimi, M.Sc. Thesis, University of Basrah, College of Science, (2007).
[4] L.Ma, Y.Zhang and N.Wang, Chinese optic Letter, 5 (10), (2007).
[5] T. M. Tsidilkovsk , Band structure of Semiconductors , Pergamon Press oxford (1982).
[6] H. N. Najeeb, A.A. Balakit, G. A. Wahab3, A. K. Kodeary, Academic Research International, Vol. 5 No. 1 (2014).
[7] F.I. Ezema , Turk J. PHYS.29 (2005) 105 – 114.

[8] A. Fassel, Physical Science Research International, (2013).
[9] S. C. Moldovenu, "Analytical Pyrolysis of Synthetic Organic Polymers" Vol. 25, 1st edition, Ch. 15 (2005).
[10] C. D. A. Almeida and A. J. G. Zaribin, J. Brazi. Chem. Soc., 17(6) (2006) 1151-1157.
[11] C. O. Nwokem and N. C. Nwokem , Zaria, Nigeria (2010).
[12] R. Gonzalez, J. M. Figueroa, H. Gonzalez, European polymer Journal 38 (2002) 287-297.
[13] E. Amir, P. Antoni, L. M. Campos, D, Damiron, N. Gupta, R. J. Amir, N. Pesika, E. Drockenmuller and C. J. Hawker, Electronic Supplementary Material (ESI), The Royal Society of Chemistry Journal (2012).
[14] H.R.Friend and J.R.M.Giles, Chem.Soc.Chem.Commun., (1984) 1101-1103 .
[15] Z.R.Ali, M.Sc. Thesis, University of Basrah, College of Science, (2007).
[16] H.K.Ibrahim and R.D.Salem, Journal of kufa Phys.,4 (1), (2012) 11-12.
[17] F.I.Ezema,Turk J.Phys.,29, (2005) 105-114.