Engineering and Technology Journal e-ISSN: 2456-3358

Volume 09 Issue 09 September-2024, Page No.-5131-5139

DOI: 10.47191/etj/v9i09.15, I.F. – 8.227

Investigation of Optical Properties of Polymeric Composite (PVA/PVP) Doped by Potassium Chromate

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ABSTRACT: The practical out comes of the present study involves preparation of [Poly (vinyl) alcohol (PVA)]/[pyrrolidone (PVP)] (50:25 wt%) composites doped by Potassium Chromate (K_2CrO_4) purity of 99% with different volume concentration (1.6% up to 7.7%) by simple solution casting method. The optical properties of the films were verified using UV-Vis-NIR spectroscopic analysis. The optical constants such as absorption coefficient, refractive index,Extinction coefficient real and imaginary parts of dielectric constant have been investigated, results show that the optical constants are affected by concentration of Potassium Chromate addition in the (PVA:PVP) blend .

The optical gap decreased from 3.5 eV for pure (PVA:PVP) polymer blend to 2.5 eV for [(PVA:PVP)/ Potassium Chromate 7.7 wt%] while the refractive index increased from 2.43 to 2.74 depended on Potassium Chromate additive.Hybrid polymeric composites of Potassium Chromate additive in (PVA:PVP) can be considered as a promising material for different electronic application.

KEYWORDS: Potassium Chromate, polymeric Composite, blend, UV-Vis spectroscopy, Optical band gap, refractive index.

INTRODUCTION

For many years, polymeric composites have received more focus due to their unusual mix of features and adaptability, especially in the production of economical devices, such as light weight and flexible electronic devices. This great deal is considered to investigate the polymeric films doped with various materials to get composites for wide range of applications [1-5]. The polymeric composites are a distinctive type of material that depending on a number of factors including an organic or inorganic status, concentrations ,types of interaction with the polymer matrix as well as the outstanding of the convenient characteristics. Recently the composites attracted serious research according to their concerned potential for a several assortment of applications in environmental solution. In addition to the polymers blending introduce a lot of useful characteristics depend on thier miscibility and degree of compatibility interaction between the various polymers to get simple and low cost technique for materials to enhance structures and characteristics different from the pristine polymer [6-8].

There are many fabrication of various optoelectronic devices, preparing by composed from different blending polymers such as (PVA) $[C_2H_4O]n$, (PVP) $[C_6H_9ON]n$, doped with different inorganic materials have been fabricated by the researchers and technical workers [9-11]. PVA considered as one of synthetic polymers, which used to synthesis many polymer composites since it has excellent properties such as water soluble, semi crystallinity, high quality film can be formed with various containing materials and non-toxicity [9, 10, 12-15].

PVP is also water soluble amorphous polymer which has a high glass transition temperature Tg due to the presence of rigid pyrrolidone group, so it can be used as good additive in fiber glass, ceramics and batteries [16, 17]. The miscibility and degree of compatibility for PVA and PVP get via the hydrogen bond interactions between the -OH groups of PVA and -CO groups of PVP to get polymer blend of (PVA/PVP). There are many researchers have looked at the different polymeric composites based on PVA and PVP such as silver sulfide (Ag_2S) [18], ZnO [19], CdS [20], MnO_2 [21], CuO [22], MgO[23] and TiO_2 [24] as well as Fe_2O_3 and Fe_3O_4 [25] for various optoelectronics applications. The present research aims is synthesised polymeric composites of (PVA: PVP) using simple solution casting method with variety concentration percentage of Potassium Chromate to investigate the optical characteristics to the composites in detail.

2. PRACTICAL PROCEDURE

2.1. Materials

1- Polyvinyl alcohol [-CH2CH(OH)-]n, Mw:14,000, Thomas Baker, CAS-No.:9002-89-5, Degree Hydrolysis (98%), India.

2- Polyvinyl pyrrolidone $C_6H_9NO)n$, K-30 (PVP): CAS-No.: 9003-39-8, Mw:4000, India.
3- Potassium Chromate (K_2CrO_4), Purity: 99%, Analytical Reagent Grad, CAS-No.:7789-00-6, India.

2.2. Preparation of (PVA)[Poly(vinyl)/ (PVP) composite

The polymeric materials was used to prepare (50:25 wt%) (PVA:PVP) polymer blend films. The amount of Potassium Chromate (K_2CrO_4) purity of 99% was employed without more purification. Figure (1) illustrates the molecular structure of PVA and PVP respectively.

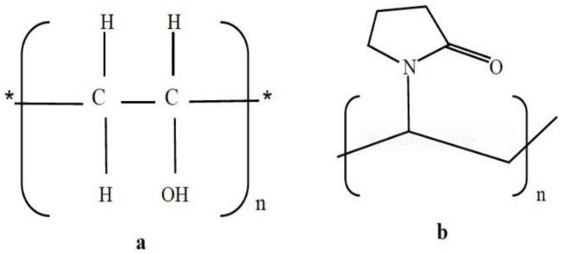

Figure (1): shown the molecular structure of a) PVA and b) PVP.

The polymeric composite films were synthesised employing the simple casting method. The polymeric solutions were synthesised initially by dissolving a quantity of PVA (0.5gm.) and PVP (0.25gm.) composites in 10ml of distilled water (stirred in 80ºC for 2 hours). All solutions were filtered by using a 0.45 micrometer syringe filter. Then amount of Potassium chromate: (0.5gm.) was dissolved in 10 ml of distilled water (stirred in 40ºC for 15 min).

A constant volume amount (3ml) of PVA/PVP blend was doped of Potassium Chromate solution with different volume addition (0.05ml, 0.1ml, 0.15ml, 0.2 ml, and 0.25 ml), as in table (1). Finally, the solutions were mixed and stirred continuously to get a homogeneous viscous liquids. This resultant solution were deposited by casting method on glass substrates, and left at room temperature for one day for drying to obtain a homogenous and bubble free of [(PVA:PVP)- K_2CrO_4] composite films. After 24 hours the films annealed in temperature of 50ºC for 2 hours.

Table (1): K_2CrO_4 doping amounts of PVA:PVP blend.

10031S. NO.	(PVA:PVP) blend	Potassium chromate	thickness cm
1	3 ml	0	0.006
2	2.95ml	0.05ml	0.0065
3	2.9 ml	0.1 ml	0.0125
4	2.85 ml	0.15ml	0.0085
5	2.8 ml	0.2 ml	0.0065
6	2.75 ml	0.25 ml	0.0045

The optical parameters of (PVA:PVP) composites doped by (K_2CrO_4) were studied by used UV-Vis spectroscopy (UV-1800, SHIMADZU CO., Japan) with the wavelength range of (200–1000 nm) for the prepared films. (0.05ml, 0.1ml, 0.15ml, 0.2 ml, and 0.25 ml) .

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3. RESULTS AND DISCUSSION

3.1 Analysis of Optical Spectra

The optical parameters of the prepared films were investigated via recording the absorption spectroscopy by using UV-VIS spectroscopy (UV-1800, SHIMADZU CO., as increasing the volume ratio (0.05,0.1,0.15,02, and 0.25) ml of Potassium Chromate (K_2CrO_4). This increase is due to the additive added of Potassium Chromate to the blend (PVA:PVP).The absorption coefficient of PVA:PVP blend doped with a volume of Potassium Chromate solution with different concentration (0.05,0.1,0.15,02,and 0.25ml) as a Japan) in the wavelength range 200-1000 nm. The the Optical absorption (UV-Visible) spectra were recorded at room temperature and analyzed to extract optical parameters like the absorption coefficient and , the refraction index (n), extinction coefficient (k), activation energy and optical band gap.

Figure (2) illustrates the relationship between absorbance at different wavelength for blend sample (PVA/PVP) as well as for the added volume ratio (0.05, 0.1, 0.15, 0.2, and 0.25) ml of Potassium Chromate (K_2CrO_4). It indicated that, the absorbance increases gradually

function of photon energy are shown in Figure (3) . From the figure, It can be observed that PVA:PVP blend added with a volume of Potassium Chromate with different concentration (0.05-0.25) ml obeys Mott-Davis model [30]. The theory of optical absorption assumed that the absorption coefficient (α) near the band edge illustrates anexponential dependence on the photon energy that given for a lot of materials [31]. This dependence, can be obtained the optical band gap Eg of materials given by equation (1). Additionally, the optical band gap energy (Eg) of the prepared thin films is obtained using the fundamental law [32].

$\alpha h\upsilon = A (h\upsilon - Eg)^n$ -------------- (1)

(α) represent the absorption coefficient, A is a proportional constant ، hυ is the photon energy, and the value of n is an index depends on the kind of the electronic transition.It is equal to 1/2 and 3/2, for direct allowed transition and direct forbidden transition respectively .While it is equal 2 and 3 for indirect allowed transition and indirect forbidden transition respectively. For our prepared samples, the value of n was estimated from the slope of the (log α) vs. (log hυ) equals to (0.5). The results of optical transitions were indicated as indirect allowed type.

Figure.4 implies to the relationship between $(\alpha h\upsilon)^{0.5}$ and (hυ) .Its noticed that the values of the energy gap (Eg) decrease with the increasing the concentration of of Potassium Chromate solution (0.05, 0.1, 0.15, 02, and 0.25)ml with (PVA:PVP) blend . The results of band gaps (Eg) estimated via the figure.4 are listed in the Table (2). The band gaps (Eg) for optical transitions Eg can be estimated from the extrapolating the straight portion of the curve on (hυ) axis at α =0. The bandgap values lie in the range(3.5-2.5) eV.

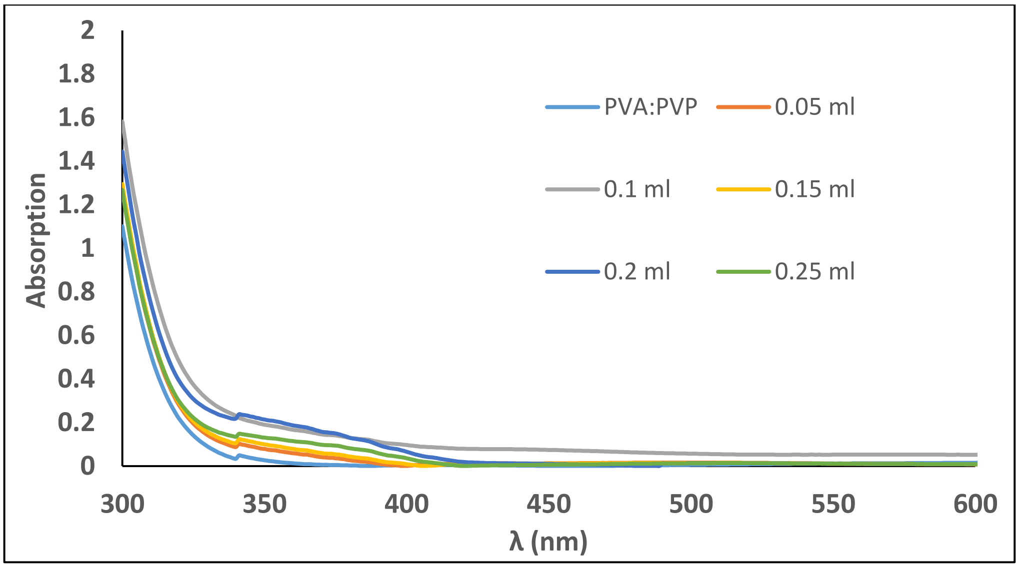


Figure (2): illustrates the relationship between absorbance as a function of wavelength for blend sample (PVA:PVP) as well as for the added the volume ratio (0.05, 0.1, 0.15,02, and 0.25)ml of (K_2CrO_4).

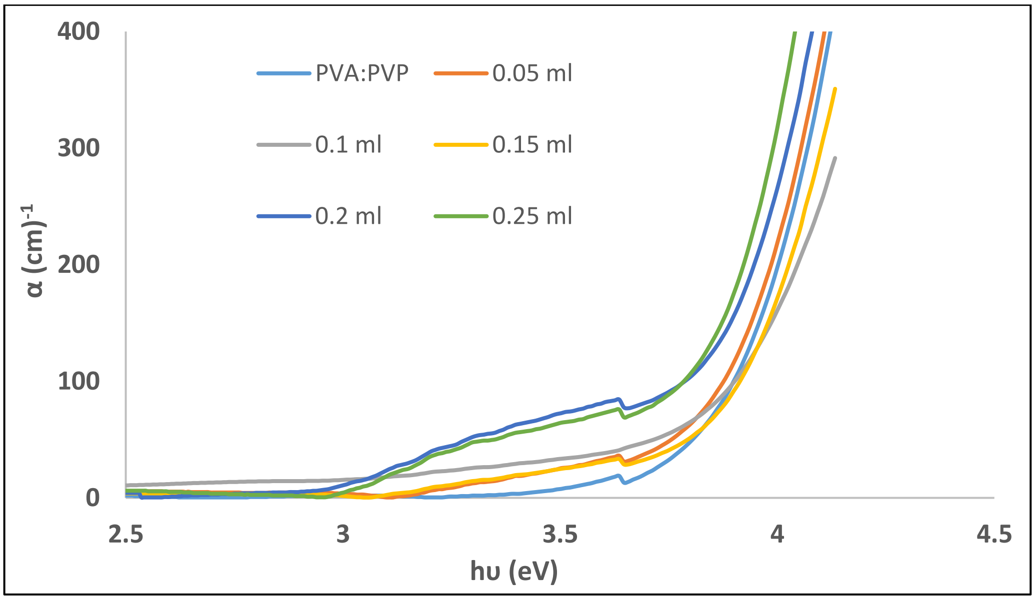


Figure (3): illustrates the relationship between Absorption coefficient as a function of Photon energy for blend sample (PVA:PVP) as well as for the added the volume ratio (0.05, 0.1, 0.15,02, and 0.25)ml of (K_2CrO_4).

Table (2): the energy gap for pure and doped (PVA:PVP) blend.

S. NO.	E_g (eV)
1	3.5
2	3.1
3	2.85
4	2.8
5	2.7
6	2.5

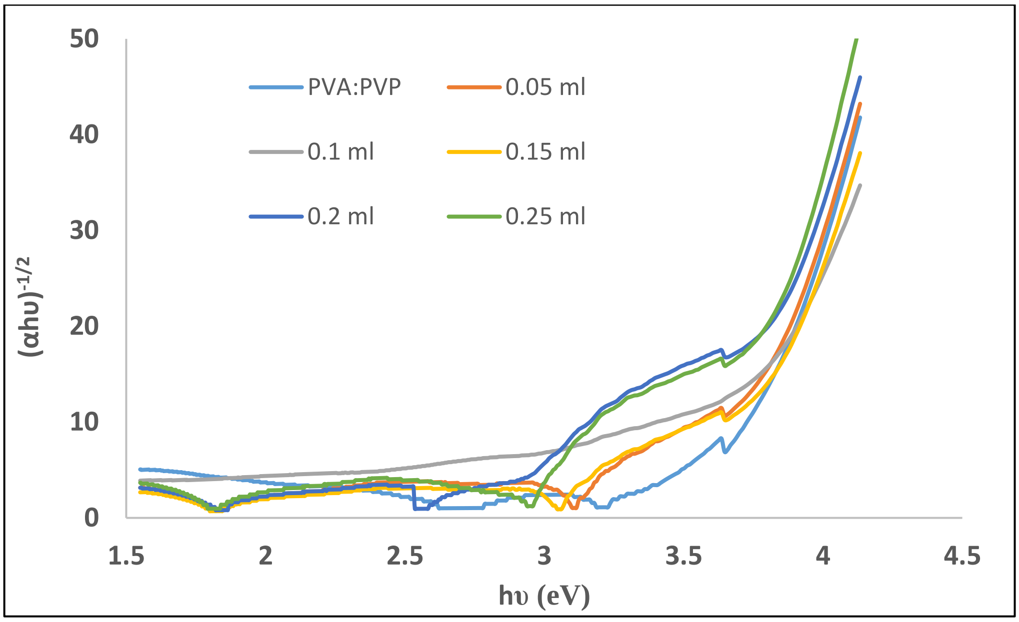


Figure (4): shows the relationship between $(\alpha h\nu)^{1/2}$ as a function of Photon energy for blend sample (PVA:PVP) as well as for the added the volume ratio (0.05, 0.1, 0.15, 02, and 0.25)ml of (K_2CrO_4).

3-2 The refractive index

The optical properties of the prepared films depend effectively on the fabricating technique.Two of the most important optical properties, refractive index and extinction coefficient are generally called optical constants.

The refractive index n(λ) is considered as important parameter of materials in optoelectronic devices [33]. Thus, getting a convenient refractive index of optical materials makes them suitable for many optoelectronic applications such as organic solar cells (OSCs), organic light-emitting diodes (OLEDs), optical communications, and design of polymer lens [34-36]. It is noticed that,the refractive indices values for (0.05, 0.1, 0.15, 02, and 0.25)ml (K_2CrO_4) ratio volume are more effective than the pure PVA/PVP. These effective may be according to increase in the reflection which causes by the effect of free carriers which result to increase the refractive index. As well as a high correlation is noticed between the band gap and refractive index .i.e when the optical band gap decreased with increasing the Potassium Chromate concentration, the refractive index increases. There is a certain difference between the values of the optical gap and refractive index of pure (PVA:PVP) blend and the [(PVA:PVP/(K_2CrO_4)] sample. It was observed that the refractive index spectrum behaves like a reflectivity spectrum and that the general was calculated based on the equation behavior of the refractive index curves was increasing with the energy of the incident photon (hv), the refractive index values of the films is determind using the following equation[37-38]:

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

R indicates to the Reflection.

The relationship between the values of refractive index and wavelength for different the volume ratio (0.05,0.1,0.15,02, and 0.25ml) of (K_2CrO_4) with (PVA:PVP) are illustrated in Figure (5). It can be noticed from the figure that the values of refractive index increase as the concentration increased.

The extinction coefficient is given by: K = $(\alpha\ \lambda/\ 4\pi)$

Figure (6) shows the relationship between the extinction coefficient and wavelength for different the volume ratio (0.05, 0.1, 0.15, 02, and 0.25ml) of (K_2CrO_4) with (PVA:PVP). It can be observed from the figure that the values of (K) increase with increasing concentration. It was also observed that the refractive index (n) and extinction coefficient (K) values are influenced by the increasing concentrations and decrease with increasing the wavelength.

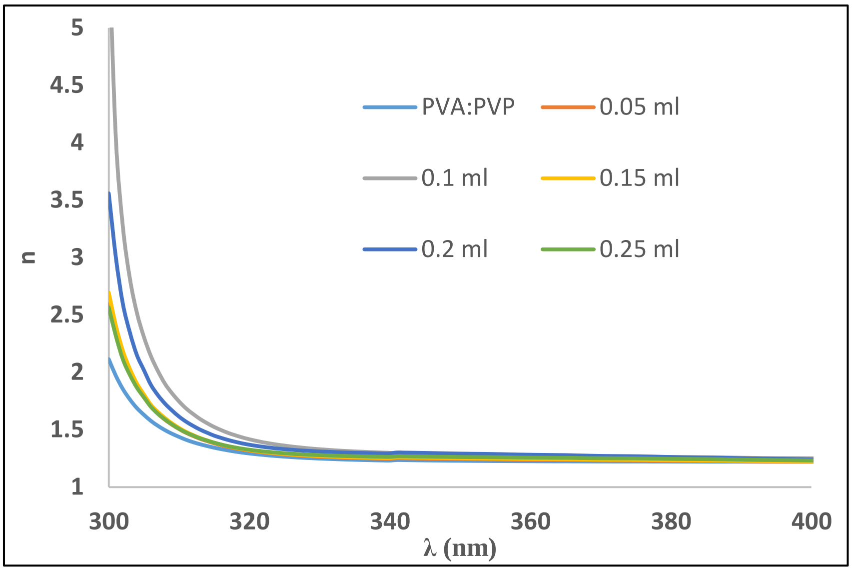
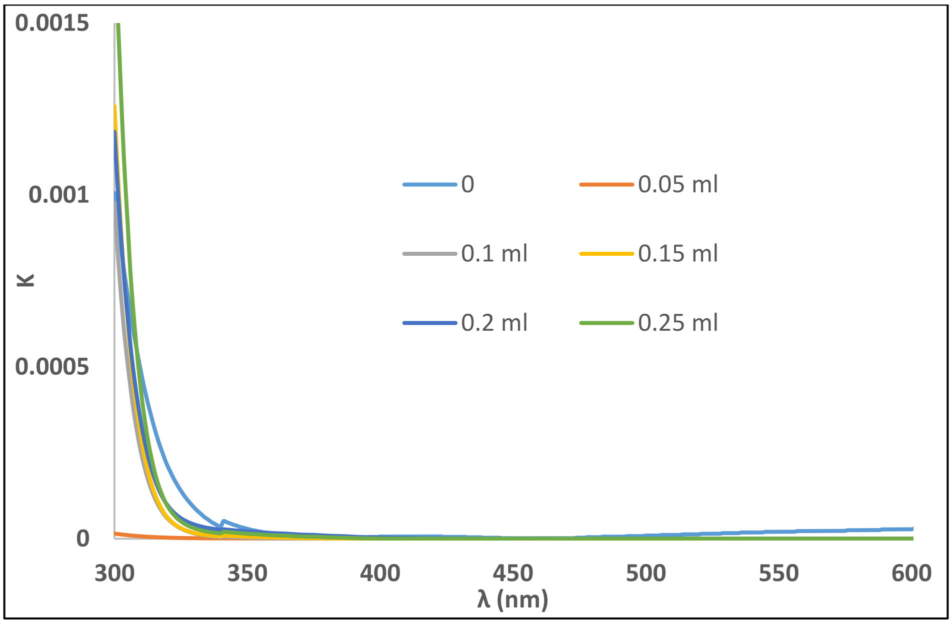


Figure (5): The relationship between refractive index as a function of wave length for blend sample (PVA:PVP) as well as for the added the volume ratio (0.05,0.1,0.15,02,and 0.25)ml of (K_2CrO_4).



Figure(6): The relationship between extinction coefficient (K) as a function of wavelength for blend sample (PVA:PVP) as well as for the added the volume ratio (0.05,0.1,0.15,02,and 0.25)ml of (K_2CrO_4).

3-Dielecrtic characteristics

The dielectric constant ($\mathcal{E}_r$) and dielectric loss ($\mathcal{E}_i$) are calculated from equations (4), and (5). Figures (7) and (8) shows the relationship between the real and imaginary dielectric constant at various of wavelength for different volume ratio (0.05,0.1,0.15,02,and 0.25ml)of (K_2CrO_4) added to (PVA:PVP) polymer blend at enviroment temperature. The polarization can be studied via the dielectric properties [39-42].The dielectric constant (ϵ') and dielectric loss (ϵ'') can get large value according to the fact of composite under the electric field acts as a dipole when have a sufficient time to orient themselves in the direction of the applied electric field.

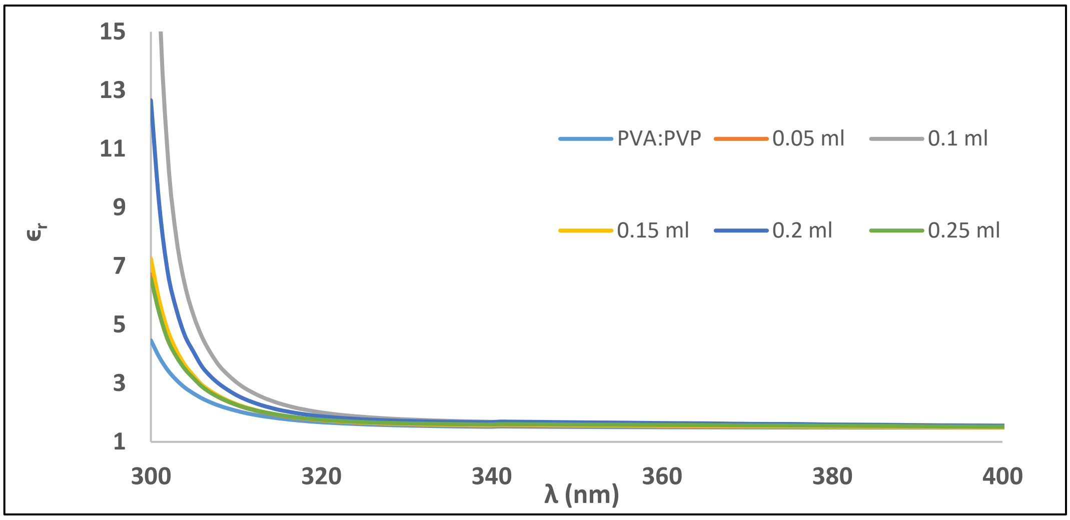
It can be noticed from the dielectric analysis that, the dielectric constant increases hence the dipole moment per unit volume increases and the dipoles move to the higher region, to get the steady state. This is give an indication of very well interfacial adhesion between the dopant Potassium Chromate material and the host polymer blend.

The dielectric constant describes the response of electrons to the electromagnetic field and the dielectric constant is represented by its real and imaginary parts and is given by the equation [43-45]:

$\mathcal{E}_r = -k^2$ ---------------- (3)

$\mathcal{E}_i = 2nk$ ----------------- (4)

It can be seen from figures 7 and 8 that show the relationship between the real and imaginary dielectric constant with the energy of the incident photon respectively. One can be noticed that the real dielectric constant behaves like a refractive index, while the imaginary dielectric constant behaves like extinction coefficient.



Figure(7): illustrates the relationship between real dielectric constant as a function of wave length for blend sample (PVA:PVP) as well as for the added the volume ratio (0.05,0.1,0.15,02,and 0.25)ml of (K_2CrO_4).

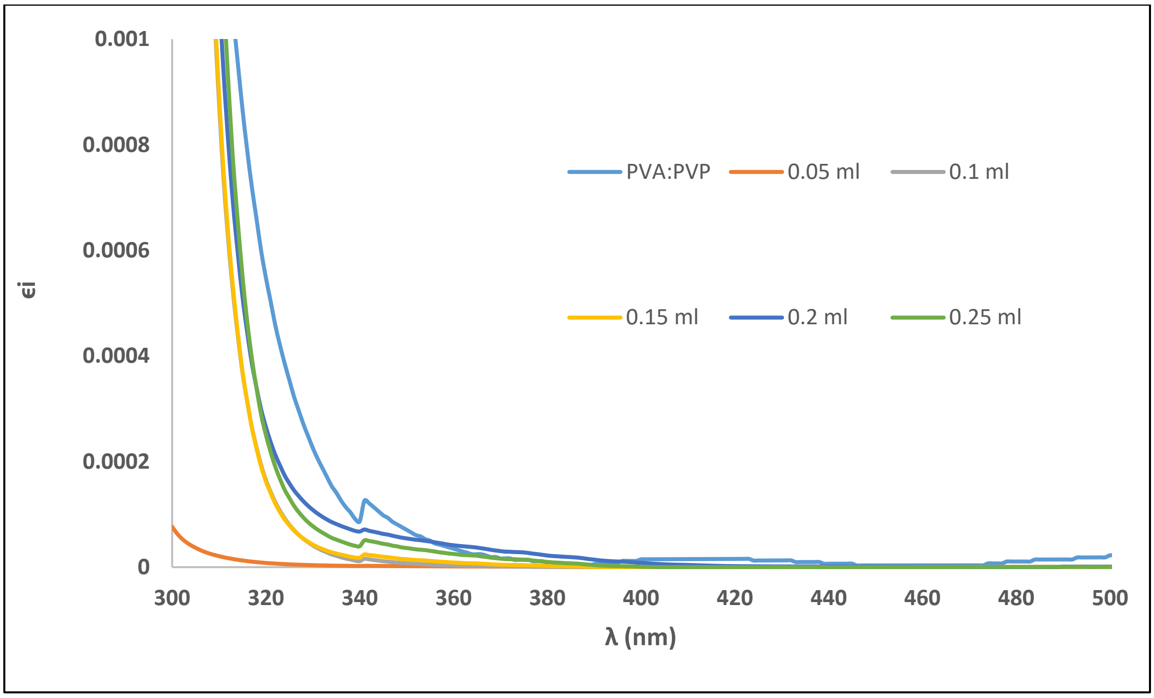


Figure (8): shows the relationship between dielectric loss ($\mathcal{E}_i$) and wave length for pure and dopped (PVA:PVP) blend with amounts of K_2CrO_4).

3-5 Optical conductivity

Optical conductivity (σ_{op}) is a property that deals with the lost power in insulators and semiconductors, and is connecting (electron - hole) at the edge of absorption. It also means connecting the charge carriers in matter Because of the generating an electron pair, its value depends on the strength of the irradiation light (the energy of photons falling on the material medium). Optical conductivity is related between, the coefficient of absorption, and the velocity of light in a vacuum with the following relationship [44]

$$\sigma_{op} = \frac{\alpha nc}{4\pi} \quad ....(3)$$

Figure (9) shows the relationship between the optical conductivity as a function of the photon energy. It can be observed the increase in optical conductivity with increasing concentration of potassium chromate to the polymer.This due to a result of the creation of local levels between the valence band and conduction bands. Thus increasing the absorption coefficient leads to increase the optical conductivity for prepared samples.

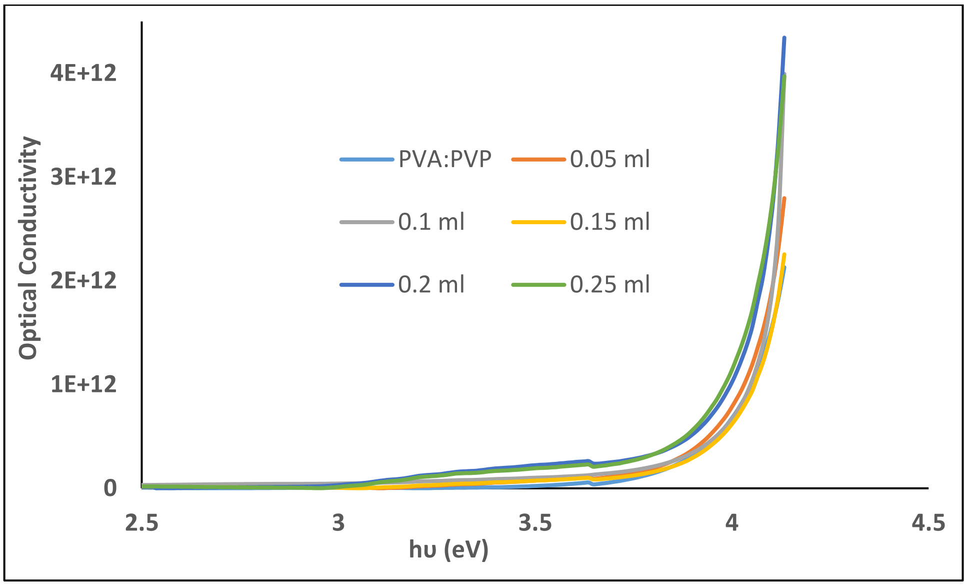


Figure (9): illustrates the relationship between optical conductivity as a function of photon energy.

CONCLUSIONS

High quality blend type of polymer (PVA: PVP) (50:25 wt%) (3ml) doped by Potassium Chromate (K_2CrO_4) with different volume adding (0.05,0.1,0.15,02,and 0.25ml) were synthesized using a simple solution casting method. Homogeneous surface with less porous structure has been observed. The optical properties were studied. The analysis of optical data indicates the formation of allowed energy bands within the forbidden optical gap of the polymer blend.The energy gap decreased from 3.5 eV for pure PVA-PVP to 2.5 eV for [(PVA:PVP):Potassium Chromate 7.7 wt%]. While the refractive index increased from 2.43 to 2.74 depend on the amount of the percentage of Potassium Chromate additive. Depending on the results of studies can be suggested that the prepared (PVA: PVP)/K_2CrO_4 are a promised material for different opto- electronic device applications.

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