

Optical properties of polyvinyl alcohol (PVA) films doped with CoCH_3COOH salt.

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Abstract

The optical characteristics of polyvinyl alcohol (PVA) films doped with different concentrations (0, 1, 3, 5, 7 and 10 wt%) of CoCH_3COOH salt powder were studied. The optical transmittance (T%) in the wavelength range (190-1100) nm of films deposited by using solvent casting method was measured. The results show indirect allowed transitions, and the optical band gap of the films decreases with increasing CoCH_3COOH content. Optical parameters such as absorption coefficient, refractive index, extinction coefficient and the real and imaginary parts of the dielectric constant of the films were calculated as a function of doping .

Keywords: Poly(vinyl alcohol), casting method, optical Properties, doping. effect.

الخصائص البصرية لأغشية بولي فنانيل الكحول المشوبة بملح خلات الكوبلت

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الخلاصة

تم في هذا البحث دراسة الخصائص البصرية لأغشية بولي فنانيل الكحول (PVA) المشوبة بتركيزات مختلفة (0, 1, 3, 5, 7 and 10 wt%) من مسحوق ملح خلات الكوبلت CoCH_3COOH . قيسَت النفاذية البصرية (T%) بمدى الأطوال الموجية (190-1100) nm للأغشية المرسبة بطريقة الصب. أظهرت النتائج انتقالات غير مباشرة مسموحة وان فجوة الطاقة البصرية للأغشية قد قلت بزيادة تركيز خلات الكوبالت. المعلمات البصرية مثل معامل الامتصاص، معامل الانكسار، معامل الخمود، ثابت العزل بجزئيه الحقيقي والخيالي قد حسبت كدالة للاشابة.

الكلمات الدالة : بولي فنانيل الكحول، طريقة الصب، الخصائص البصرية، تأثير التشويب.

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Introduction

Conductive polymers are organic compounds that conduct electricity. Such compounds may be true metallic conductors or semiconductors. It is generally accepted that metals conduct electricity well and that organic compounds are insulating, but this class of materials combines the properties of both. The biggest advantage of conductive polymers is their processibility. Conductive polymers are also plastics (which are organic polymers) and therefore can combine the mechanical properties (flexibility, toughness, malleability, elasticity, etc.) of plastics with high electrical conductivities. Their properties can be fine-tuned using the exquisite methods of organic synthesis [1]. Different additives are usually added to polymer in order to modify and improve its properties. Inorganic additives such as transition metal salts have considerable effect on the optical and electrical properties of PVA (polyvinyl alcohol) polymer [2,3].

A polyvinyl polymer, namely polyvinyl alcohol (PVA) has several interesting physical properties, which are very useful in material science and technical applications. (PVA), as semi crystalline water soluble material exhibits certain physical properties resulting from crystal-amorphous interfacial effects [4].

(PVA) is a polymer with carbon chain backbone with hydroxyl groups attached to methane carbons. These OH- groups can be a source of hydrogen bonding and hence assist in the formation of polymer [5].

Experimental

The materials used in this work were as a powder of commercial polyvinyl alcohol (PVA) doped by Cobalt acetate (CoCH_3COOH) salt with weight percent (0, 1, 3, 5, 7 and 10 wt%). It was dissolved in glass beaker (10 ml) by distilled water using magnetic stirrer about (1hr) and placed in Petri dish (5 cm diameter) using casting technique to prepare the films. The thickness of the dried samples is (0.045) cm by using micrometer. The spectrum of absorption and transmission were recorded for wavelengths (190-1100)nm at room temperature by using double beam spectrophotometer (shimadzu, UV-210 Å) provided by optima 300 plus company.

Results and discussions

The optical transmission spectra as a function of wavelength in the range of (190-1100) nm is shown in fig. (1). All the films showing the same behavior but the transmittance decreases as the doping percentage increases.

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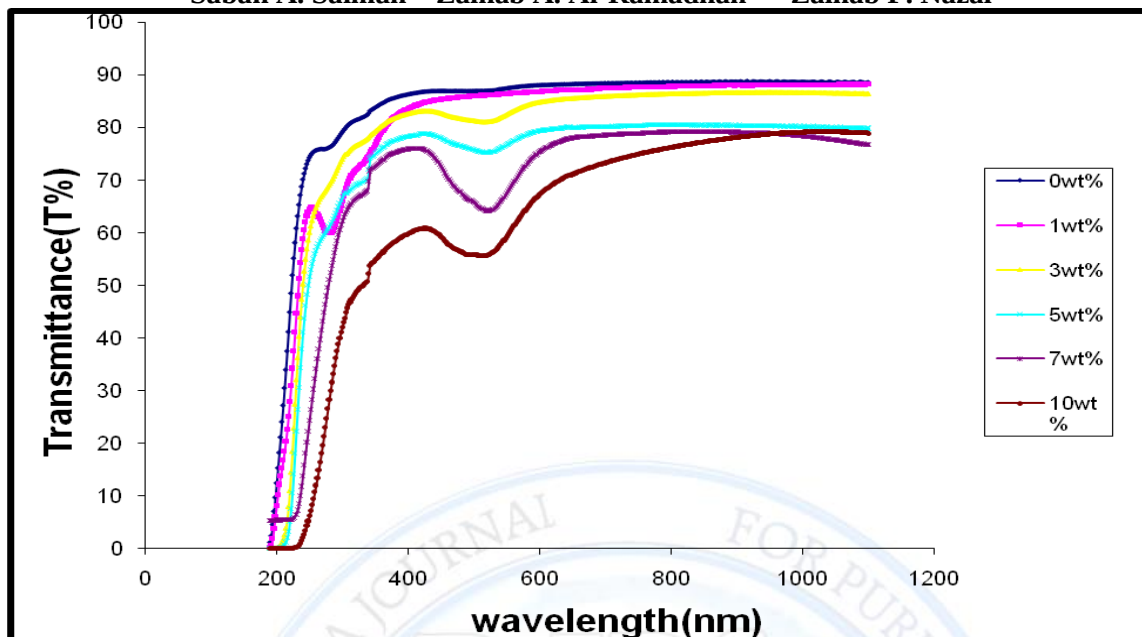


Fig. (1): Transmission Spectra of (PVA: CoCH_3COOH).

The behavior of Absorbance curves of all samples are shown in fig. (2), It is obvious that its behavior is opposite to that of the transmission spectrum. and was it found that the absorption edge shifts towards lower energies due to doping (red shift).

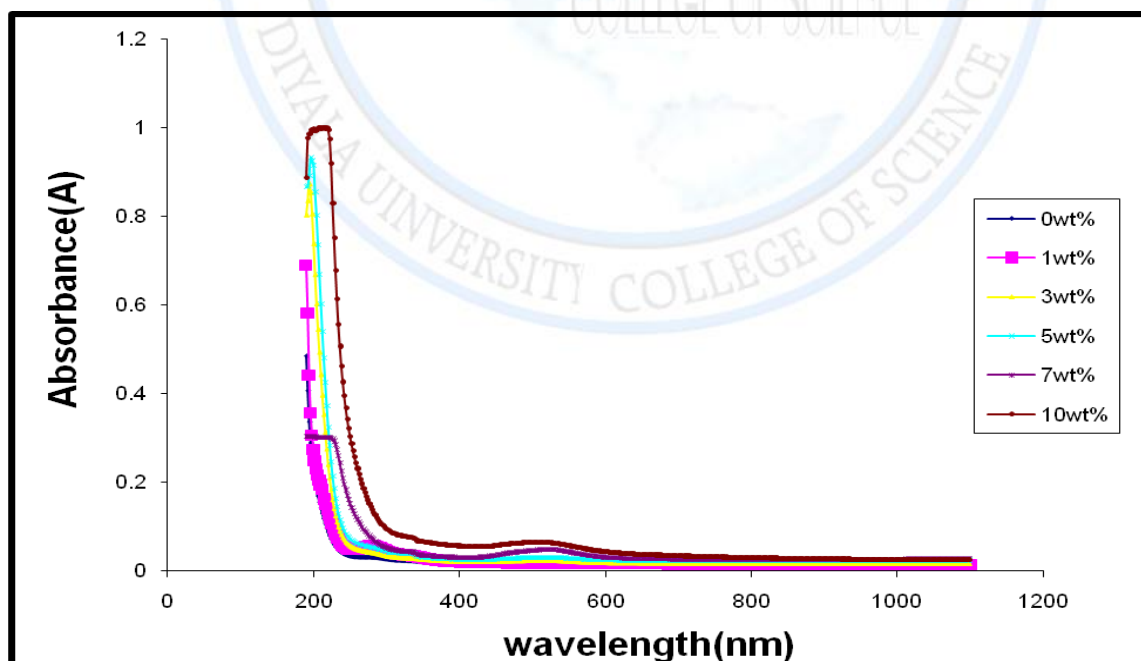


Fig. (2): Absorption Spectra of (PVA: CoCH_3COOH).

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The following relation could be used for calculating the absorption coefficient (α) [6]:

$$\alpha = \frac{2.303A}{t} \quad \text{----- (1)}$$

Where (A) is the absorbance and (t) is the film thickness.

From fig. (3) absorption coefficient increases with doping, at short wavelength (α) have higher values ($\alpha < 10^4 \text{cm}^{-1}$). The marked increase of the absorption coefficient at higher energies may be attributed to extra transition from the bonding molecular orbit to anti bonding molecular orbit [7].

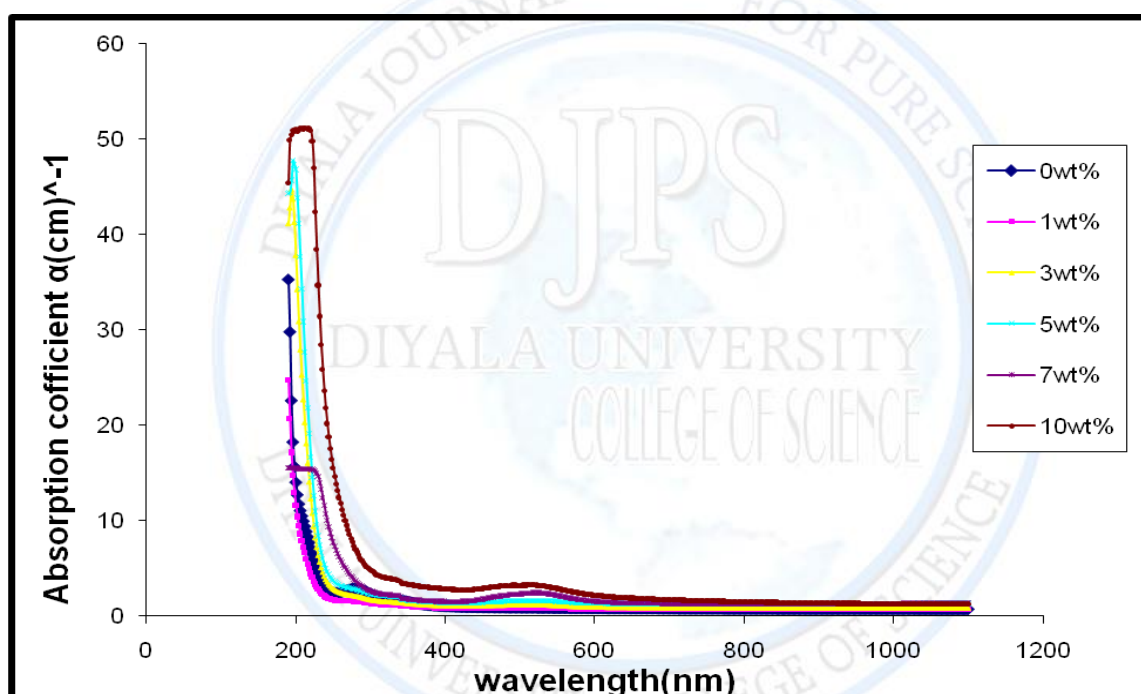


Fig. (3): Absorption Coefficient of (PVA:CoCH₃COOH).

The plot of the square root of product of absorption coefficient and photon energy ($\alpha h\nu$)^{1/2} versus the photon energy at room temperature shows a linear behavior, which can be considered as an evidence for indirect allowed transition. Extrapolation of the linear portion of this curve to a point ($\alpha h\nu$)^{1/2} = 0 gives the energy band gap (E_g) for the films as shown in fig.(4). The existence and variation of energy band gap with the photon energy, as the Cobalt acetate increased from (1-10)% we obtained energy band gap of (5.5-3.9) eV, respectively, may be explained by invoking the occurrence of local cross linking within the amorphous phase of the polymer, in such a way as to decrease the degree of ordering in these parts [8]. In general energy band gap decreases with doping percentages.

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Table (1). Shows the values of optical energy gap for (PVA: CoCH_3COOH) for different doping percentages.

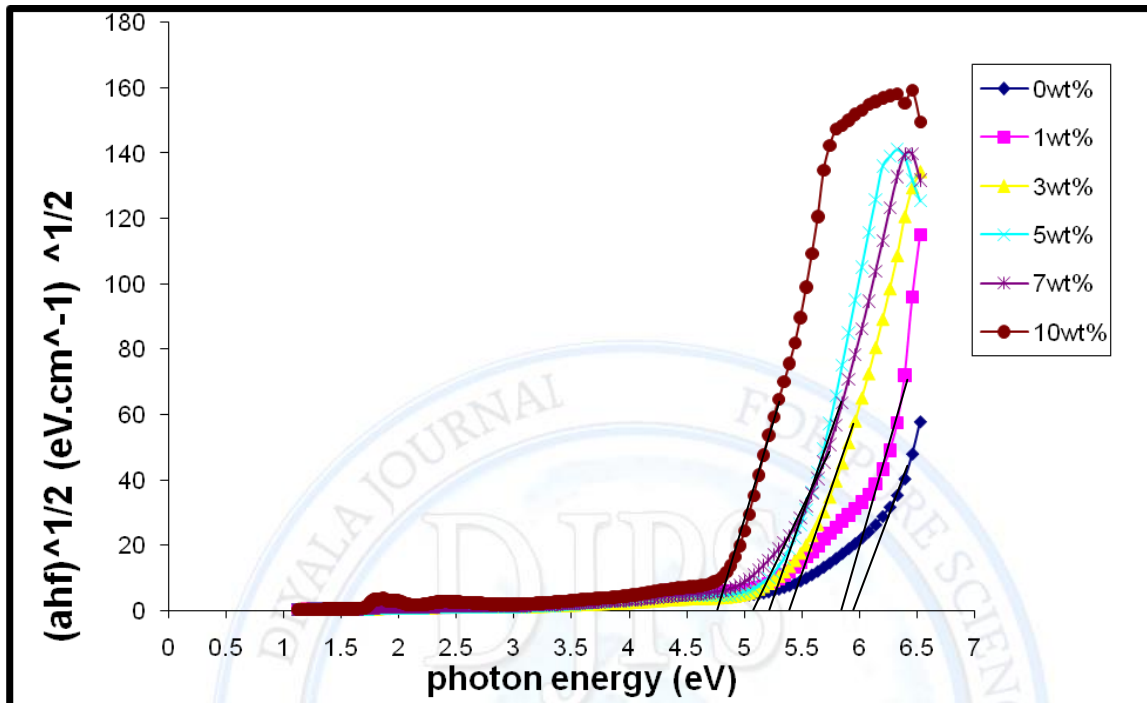


Fig. (4): $(\alpha hf)^{1/2}$ as a Function of the Photon Energy of (PVA: CoCH_3COOH).

Table (1): The Values of Optical Energy Gap for different doping percentages.

CoCH_3COOH wt%	$E_g(\text{eV})$ allowed
(PVA)pure	5.9
1%	5.7
3%	5.4
5%	5.3
7%	5.1
10%	4.7

The refractive index (n_o) is a suitable state parameter directly correlated to the material density. The refractive index (n_o) can be determined from the reflectance (R) using the relation [9].

$$n_o = \left(\left[\frac{4R}{(R-1)^2} - K_o \right]^{1/2} - \frac{R+1}{R-1} \right) \text{-----} (2)$$

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Where (k_o) is the extinction coefficient.

Fig. (5) Shows the variation of the refractive index (n_o) with the wavelength. The refractive index of these films increases with doping percentages.

The selective absorption of the photon energies of the incident light indicates that such energy is devoted to breaking up and hence deforming the partially crystalline structure of the polymers. Since the refractive index depends on the strength of the bonds, density and molecular weight, increasing the doping may alter all these parameters in a manner which increases the corresponding refractive index [10].

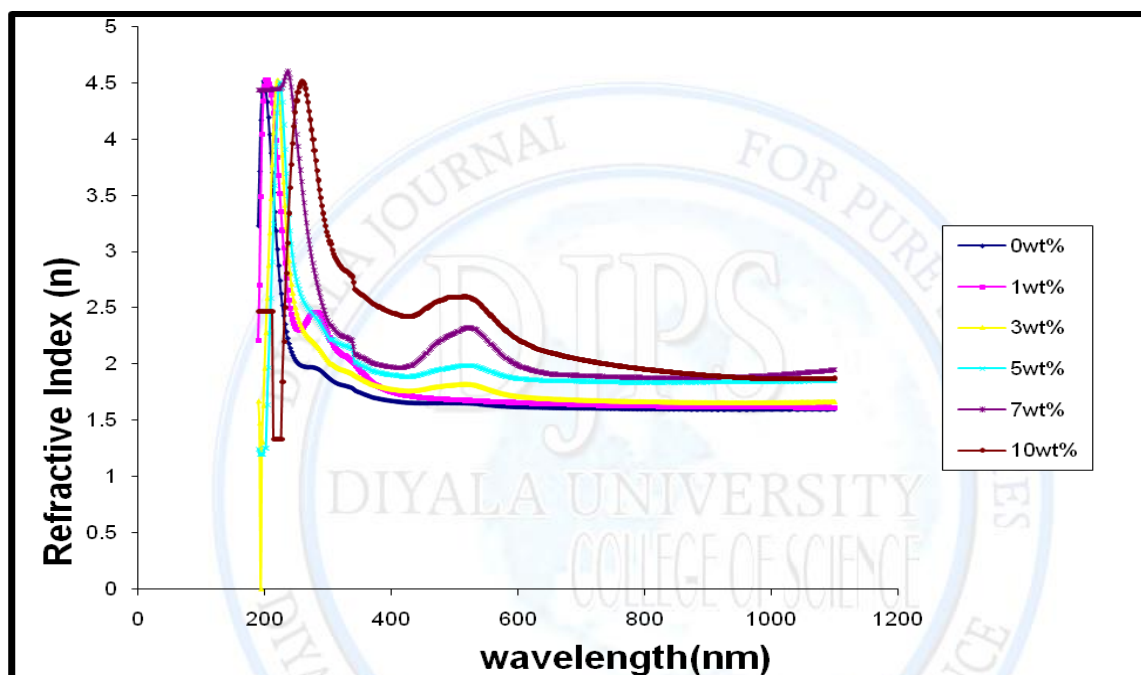


Fig. (5): Refractive Index of (PVA: CoCH_3COOH).

Extinction Coefficient (k_o) represents the imaginary part of complex refractive index and it can be defined as the amount of energy lose as a result of interaction between the light and the charge of medium [11]. The extinction coefficient (k_o) is directly proportional to the absorption coefficient (α) as seen in relation [12]:

$$k_o = \frac{\alpha \lambda}{4 \pi} \quad \text{----- (3)}$$

Where (λ) is the wavelength of the incident photon. Fig. (6) Shows the variation in extinction coefficient (k_o) as a function of the wavelength. The behavior of the pure (PVA) is different in comparison with doping films, for (PVA) it seems that the extinction coefficient remains nearly constant (at long wavelength) but for doped films, the extinction coefficient increases in comparison with the undoped one.

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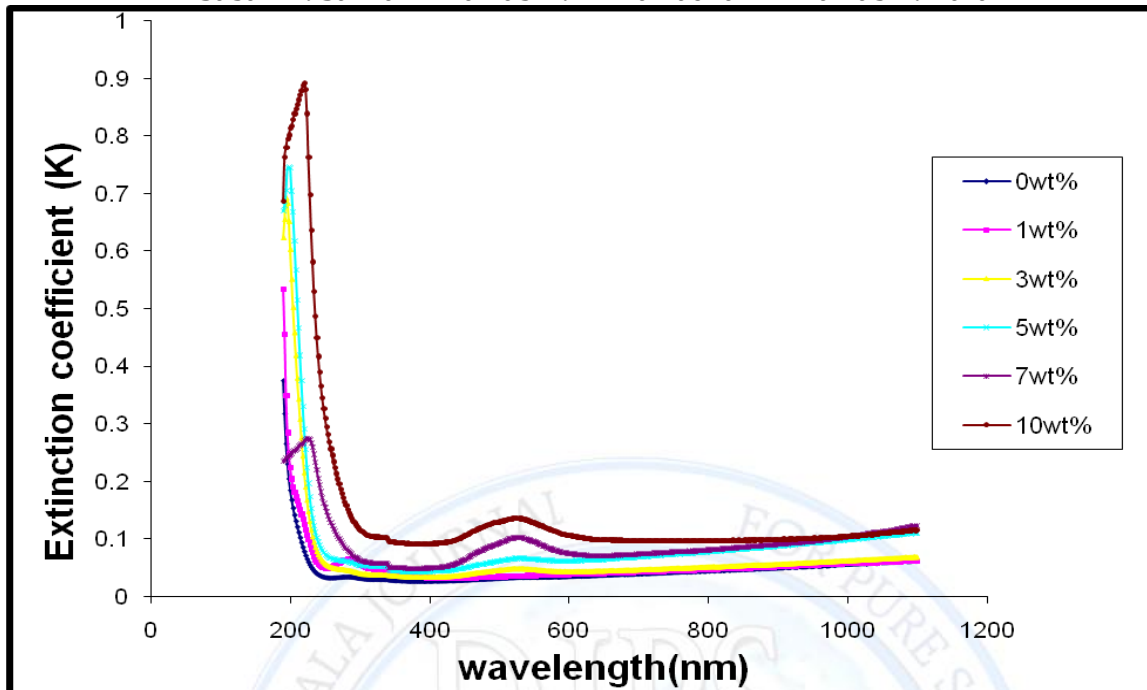


Fig. (6): Extinction Coefficient of (PVA:CoCH₃COOH).

The variation of the real (ϵ_r) and imaginary (ϵ_i) parts of the dielectric constant values versus wavelength in the range (190–1100) nm are shown in figs.(7 and 8). The behavior of (ϵ_r) is similar to that of (n_o) because the smaller value of (k_o^2) compared with (n_o^2) [13]:

$$\epsilon_r = n_o^2 - k_o^2 \quad \text{----- (4)}$$

while the (ϵ_i) is mainly depends on the (k_o) values, which are related to the variation of absorption coefficient [13]:

$$\epsilon_i = 2 n_o k_o \quad \text{----- (5)}$$

It is found that (ϵ_r) and (ϵ_i) increase with increasing of doping . The real and imaginary parts of the dielectric constant indicate the same pattern and the values of real part are higher than imaginary part [14] .

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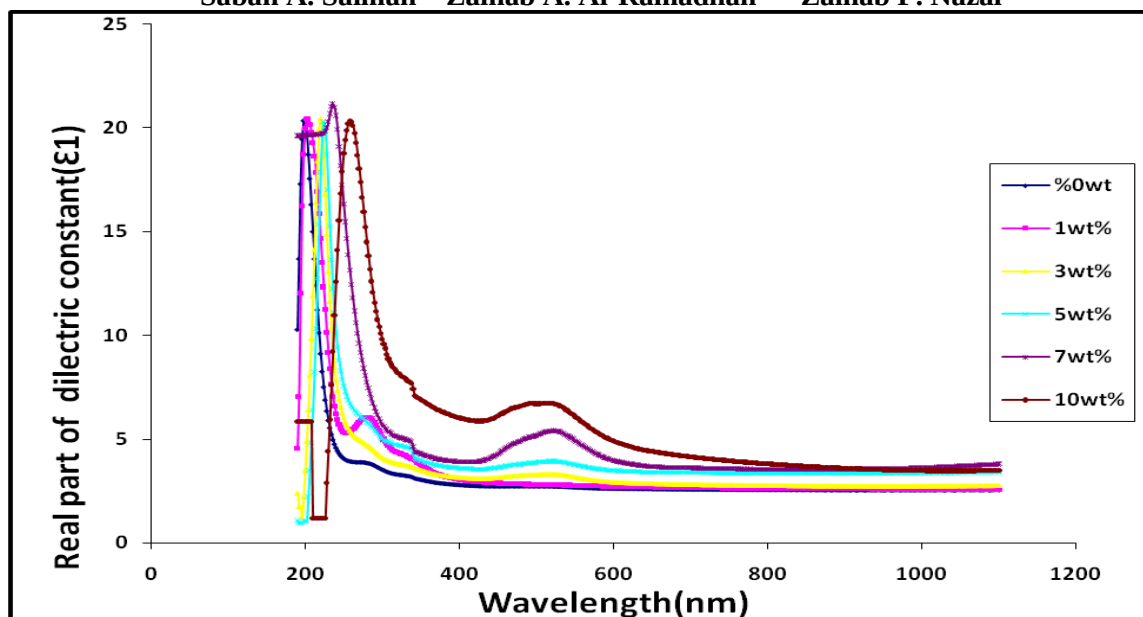


Fig.(7): Real Part of the Dielectric Constant of (PVA:CoCH₃COOH).

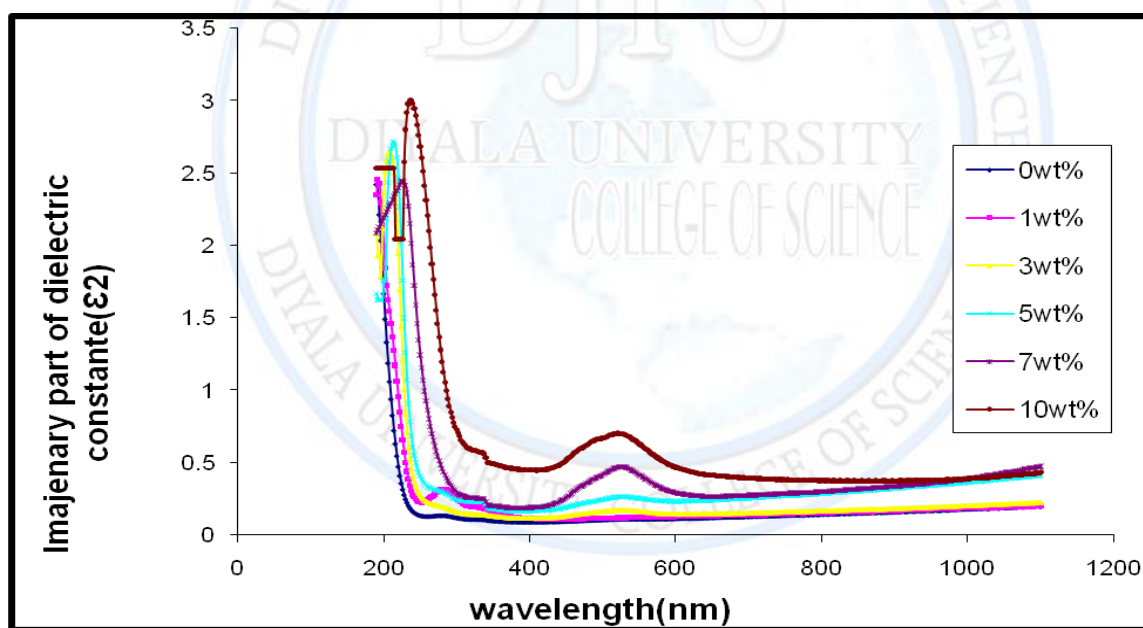


Fig. (8): Imaginary Part of the Dielectric Constant of (PVA:CoCH₃COOH).

Conclusions

Based on the experimental results the following conclusions can be drawn:

- 1- The doping process decreases the transmittance.
- 2- The type of electronic transition was indirect allowed transition.
- 3- In general energy band gap (E_g) decreases with doping.
- 4- Refractive index (n_o), extinction coefficient (k_o), real (ϵ_r) and imaginary (ϵ_i) parts of the dielectric constant increase with doping .

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