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Ministry of Higher Education  
& Scientific Research  
University of Diyala  
College of Sciences  
Department of Physics*



# **Physical properties of polymer(PVA) doped with Cobalt salts**

A Thesis

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of Diyala in Partial Fulfillment of the Requirements for the  
Degree of Master of sciences in Physics

by

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جامعة ديالى  
كلية العلوم / قسم الفيزياء

# الخصائص الفيزيائية لبوليمر (PVA) المشوب بأملاح الكوبلت

رسالة مقدمة الى

مجلس كلية العلوم - جامعة ديالى وهي جزء من  
متطلبات نيل درجة الماجستير علوم في الفيزياء

تقدمها

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2013م

1434هـ

# ***Dedication***

***To..***

***My Mother...***

***To..***

***My Husband...***

***To...***

***My Sisters...***

***For their kindness attention  
and encouragement...***

***Zainab***

## **ACKNOWLEDGEMENTS**

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## **Accepted articles in peer reviewed journals**

1- Sabah A. Salman , Zainab A. Al-Ramadhan and Zainab F.Nazal , ” **Optical properties of polyvinyl alcohol (PVA) films doped with  $\text{CoCH}_3\text{COOH}$  salt**”, accepted in Diyala University journal for pure Sciences No.380, 4/9/2013.

## Abstract

We prepared the pure films of polymer polyvinyl alcohol (PVA) and doped them with Cobalt salts ( $\text{CoCl}_2$ ,  $\text{CoNO}_3$  and  $\text{CoCH}_3\text{COOH}$ ) with different concentrations (1,3,5,7 and 10) wt% by using casting technique, and the glass basins made for this purpose .

The optical and the D.C. electrical properties of pure and doped (with Cobalt salts) films of polymer Polyvinyl alcohol (PVA) were studied.

The effect change of Cobalt salts concentration on the optical parameters such as absorbance, transmittance, absorption coefficient, refractive index, extinction coefficient and real and imaginary parts of dielectric constant for (PVA-( $\text{CoCl}_2$ ,  $\text{CoNO}_3$  and  $\text{CoCH}_3\text{COOH}$ )) films were calculated.

The effect of Cobalt salts concentration and change of temperature on the D.C electrical properties for (PVA-( $\text{CoCl}_2$ ,  $\text{CoNO}_3$  and  $\text{CoCH}_3\text{COOH}$ )) films have been investigated .

The experimental results for (PVA-( $\text{CoCl}_2$ ,  $\text{CoNO}_3$  and  $\text{CoCH}_3\text{COOH}$ )) films show that the absorbance increased with increasing the filler content, and the transmittance decreased with increasing the filler content. And the absorption coefficient, refractive index, extinction coefficient and real and imaginary parts of dielectric constant were found to be increased with increasing the filler content. Moreover the results show that allowed and forbidden indirect transitions, and the energy band gap decreases with

increasing the filler content. The experimental results for (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films show that the D.C. electrical conductivity increased with increasing the filler content and the temperature, and the activation energy was decreased with increasing the filler content.

We found that the best of Cobalt salts is Cobalt acetate (CoCH<sub>3</sub>COOH) because it has the less energy gap, high absorption coefficient, high refractive index, high extinction coefficient and high real and imaginary parts of dielectric constant and less activation energy in most concentrations, then we can use this salt in more scientific applications.



## الخلاصة

تم تحضير اغشية البوليمر (بولي فنايل الكحول) (PVA) النقية والمشوبة بأملاح الكوبلت ( $\text{CoCl}_2$ ,  $\text{CoNO}_3$  and  $\text{CoCH}_3\text{COOH}$ ) بتركيز مختلفة wt% (1,3,5,7 and 10) بطريقة الصب باستخدام قوالب زجاجية خاصة تم اعدادها لهذا الغرض.

لقد تمت دراسة الخصائص البصرية والكهربائية المستمرة لأغشية البوليمر (بولي فنايل الكحول) النقية والمشوبة بأملاح الكوبلت. تم دراسة تأثير تغير تركيز أملاح الكوبلت على المعلمات البصرية (الامتصاصية، النفاذية، معامل الامتصاص، معامل الانكسار، معامل الخمود وثابت العزل بجزيئه الحقيقي والخيالي) لأغشية ((PVA-( $\text{CoCl}_2$ ,  $\text{CoNO}_3$  and  $\text{CoCH}_3\text{COOH}$ )). وكذلك تم دراسة تأثير تغير تركيز أملاح الكوبلت وتغير درجة الحرارة على التوصيلية الكهربائية المستمرة لأغشية ((PVA-( $\text{CoCl}_2$ ,  $\text{CoNO}_3$  and  $\text{CoCH}_3\text{COOH}$ )).

لقد أظهرت النتائج العملية لأغشية ((PVA-( $\text{CoCl}_2$ ,  $\text{CoNO}_3$  and  $\text{CoCH}_3\text{COOH}$ )) بأن الامتصاصية تزداد مع زيادة نسب التشويب وأملاح الكوبلت وأن النفاذية تقل مع زيادة نسب التشويب وأملاح الكوبلت، وأن معامل الامتصاص، معامل الانكسار، معامل الخمود وثابت العزل بجزيئه الحقيقي والخيالي يزداد بزيادة نسب التشويب وأملاح الكوبلت، وكذلك اظهرت النتائج بأن الانتقالات الألكترونية هي انتقالات غير مباشرة وان فجوة الطاقة تقل بزيادة نسب التشويب وأملاح الكوبلت.

كذلك أظهرت النتائج العملية لأغشية ((PVA-( $\text{CoCl}_2$ ,  $\text{CoNO}_3$  and  $\text{CoCH}_3\text{COOH}$ )) بأن التوصيلية الكهربائية المستمرة تزداد مع زيادة نسب التشويب وأملاح الكوبلت و درجة الحرارة، كما ان طاقة التنشيط تقل مع زيادة نسب التشويب وأملاح الكوبلت.

لقد وجدنا بان أفضل ملح من أملاح الكوبلت هو خلات الكوبلت ( $\text{CoCH}_3\text{COOH}$ ) وذلك لكونه يمتلك اقل فجوة طاقة, معامل امتصاص عالي, معامل انكسار عالي, معامل خمود عالي, ثابت عزل

عالي بجزئيه الحقيقي والخيالي و اقل طاقة تنشيط في معظم تراكيزه لذلك بالأمكان استخدام هذا الملح في كثير من التطبيقات العلمية.



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## LIST OF SYMBOLS

Symbol	Definition
<b>PVA</b>	<b>poly (vinyl alcohol)</b>
<b><math>E_g</math></b>	<b>energy gap</b>
<b>n</b>	<b>Degree of polymerization</b>
<b><math>\mu</math></b>	<b>Mobility</b>
<b>V</b>	<b>applied potential</b>
<b><math>R_v</math></b>	<b>electrical resistance</b>
<b>L</b>	<b>Length</b>
<b><math>\rho_v</math></b>	<b>volume resistivity</b>
<b><math>\sigma_v</math></b>	<b>volume conductivity</b>
<b><math>\sigma</math></b>	<b>electrical conductivity</b>
<b><math>\sigma_0</math></b>	<b>electrical conductivity at absolute zero of temperature</b>
<b><math>k_B</math></b>	<b>Boltzmann constant</b>
<b><math>E_{act}</math></b>	<b>activation energy</b>
<b>R</b>	<b>Resistance</b>
<b><math>E_{ele}</math></b>	<b>the electronic energy</b>
<b><math>E_{vib}</math></b>	<b>vibration energy</b>
<b><math>E_{rot}</math></b>	<b>rotational energy</b>
<b><math>E_{trans}</math></b>	<b>translational energy</b>
<b><math>E_p</math></b>	<b>energy of phonon</b>

$\alpha$	the absorption coefficient
$I_0$	the incident light intensity
$I$	the penetrating light intensity
$t$	the thickness of the matter
$h\nu$	the photon energy
$n$	the refractive index
$C$	the light speed in vacuum
$v$	the light speed in matter
$k$	the Extinction Coefficient
$R$	the reflectance
$A$	The absorbance
$T$	The transmittance
$\lambda$	the wavelength
$\epsilon$	the complex dielectric constant
$\epsilon_1$	the real parts of the dielectric constant
$\epsilon_2$	The imaginary parts of the dielectric constant
$CoCl_2$	Cobalt chloride
$CoNO_3$	Cobalt Nitrate
$CoCH_3COOH$	Cobalt acetate

# CERTIFICATION

We certify that this thesis has been prepared under our supervision at the University of Diyala / College of Sciences / Department of Physics as a partial fulfillment of the requirements for the Degree of Master of sciences in Physics.

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## **Head of the Physics Department**

In view of the available recommendation, I forward this thesis for debate by the examining committee.

**Signature:**

**Name: prof. Sabah Anwer Salman**

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**Date: / / 2013**

*Chapter One*



**Introduction  
and  
Previous Studies**

*Chapter Two*



**Theoretical Part**





## *Chapter Three*

# **Experimental Work**

*Chapter Four*



**Results**  
,  
**Discussion**  
**and**  
**Conclusions**  
**and**  
*Future Work*

# References



## **1-1 General Introduction**

Generally, the use of most polymers was limited to the manufacture of cheap products which were used for simple purposes. However, the speedy technical development has required the replacement of some materials being used in industry with others having better specifications. Consequently, polymers have replaced Aluminum and Iron for some purposes that require stress and high temperature [1,2]. Later, the development of polymer science has started to increase by leaps and bounds. Nowadays, scientists seek to produce, cheap, flexible and multi-purpose polymers. They are used in housing, automobiles and they can be used for different industrial applications.

Plastics are the most versatile materials used in different industries, such as aircraft, packaging, electrical equipment and as electrical insulators. They have increasingly an important role in the manufacture of satellites, space researches and thermal barriers [1,2].

Plastics have replaced metals in many applications. They have superseded steel and many other metals in being erosion resistant and chemically inert. Having higher temperature extension and specific heat than metals, plastics have been used for constructing and lining of reactors, absorption towers and the manufacture of pipes and valves.

Most of plastics are currently manufactured as light, rigid and foamy materials and used as insulators due to their low thermal and electrical conductivity. Plastics have almost no free electrons but recent scientific and technical break-throughs have succeeded in making some modifications on regular plastics and brought into existence a new generation of plastics that combine the electrical features of the conductive and semi-conductive materials and the mechanical and chemical features of plastics [2,3] .

## **1-2 Polymer Structure**

A polymer consists of large organic molecules (macromolecules) of repeating small structural units (monomers) connected together in a process called polymerization [2,4]. Each molecule is composed of thousands of atoms connected by covalent chemical bonds. Molecules in a polymer attract each other by forces that depend on the type of the polymer.

As polymers consist of huge combined molecules which are hard to control, limited crystal connections can be seen in polymers associated with its low temperature. It is only in limited regions that a linear chain of molecules can arrange themselves in an organized form. In the solid state, polymers consist of crystalline and non-crystalline regions. Crystalline polymers consist of 90% of crystalline regions, while the non-crystalline polymers are almost entirely non-crystalline [5].

## **1-3 Classification of Polymers**

### **1-3-1 Thermal Classification of Polymers:**

Polymers are classified according to the effect of temperature to:

#### **1-Thermoplastic Polymers**

The properties of these polymers are changed by the effect of temperature. When the temperature increases, they become flexible and sticky. By lowering the temperature, these polymers return to their original solid state. This is because the molecules in a thermoplastic polymer are connected by relatively weak intermolecular forces (Van der Waals forces). When heated, these molecules can slide over each other as in polystyrene, polyethylene, polypropylene, poly (vinyl alcohol) and polyvinyl chloride [6].

## **2-Thermoset Polymers**

These polymers are chemically changed when heated. Thermosets are usually three-dimensional networked polymers in which there is a high degree of cross-linking between polymer chains. After being heated, these polymers become insoluble, non-conductive of heat and electricity and hard because molecules of these polymers are connected by strong covalent chemical bonds. Phenol formaldehyde resin and urea-formaldehyde resin are examples of this type of polymers [7,8,9].

### **1-3-2 Chemical Classification of Polymers**

Polymers are classified depending on the structural composition to:

#### **1- Linear Polymers**

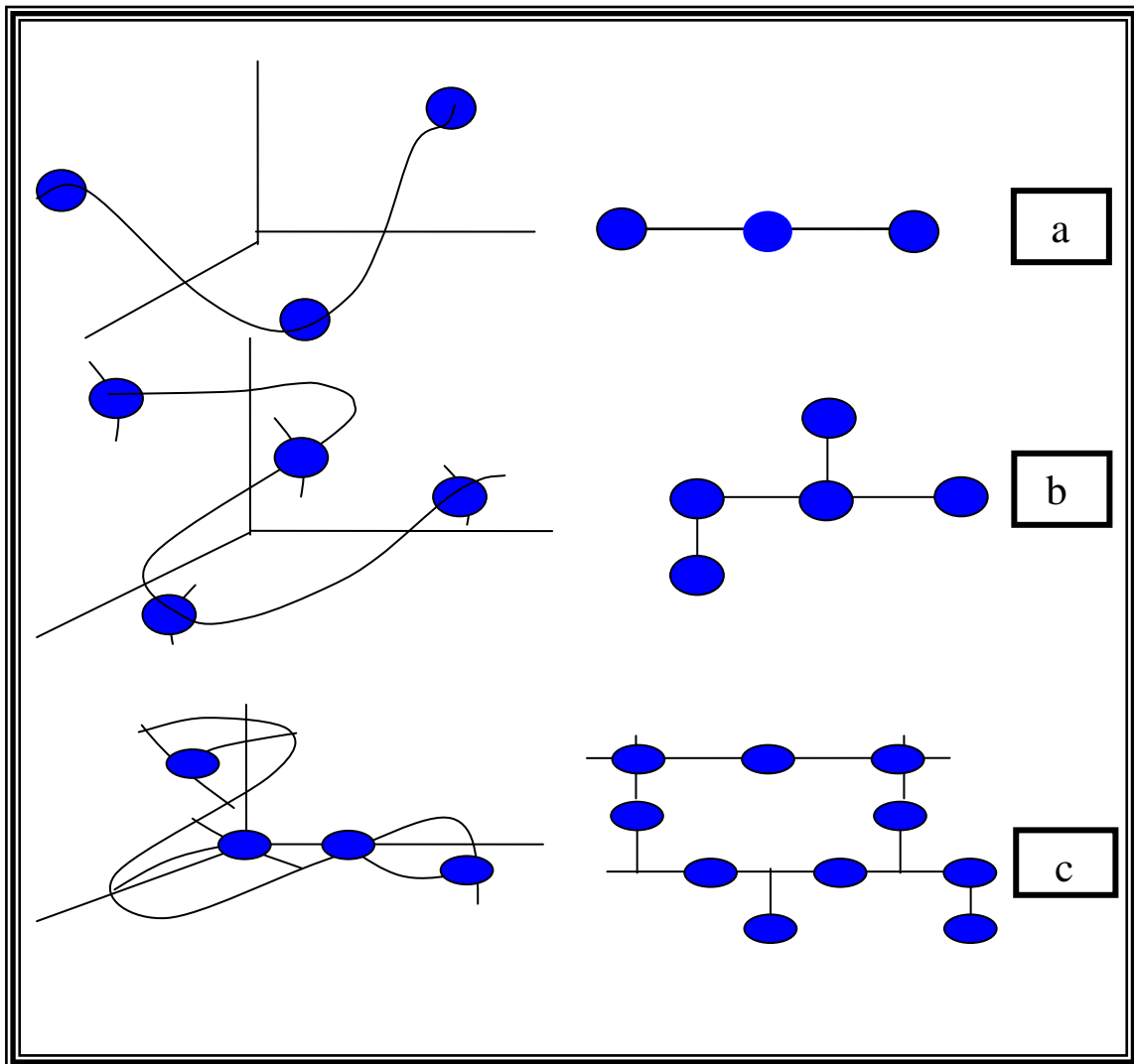
The essential structural unit for these polymers is one molecular series of certain length connected with each other in a linear shape, it does not contain the branch except the totals twisted which are part of monomer, as in figure (1-1-a).

#### **2- Branched Polymers**

Here the long chain is branching and it is characterized by this type of installation that the branches are as a Ladder or a Comb or as a Crusader. The branches have different lengths, as in figure (1-1-b).

#### **3- Cross Linked Polymers**

In this type, the chemical bonds are interwoven with each other in a complex way. The format string consists of three dimensional polymer chains linked together by more than one site, or when we use monomers containing effective totals rather than being included in two effective totals, as in the figure (1-1-c) [10,11].



**Figure (1-1): The different types of polymeric chains [12]**

### 1-3-3 Polymers Dependence on Homogeneity

Polymers are classified depending on the homogeneity of repeating units into:

#### 1- Homo Polymers

Where the building blocks of a polymer are of one type, as in polyterphethals ethylene.

## **2- Copolymers**

Where the building blocks of a polymer are more than one type, as in the polymer (styrene - butadiene).

## **3- Composite Polymers**

It is adding some material to homogeneous polymers in order to make change in some of its characteristics and the entering of new recipes on it[9,13].

## **1-3-4 Polymers Dependence on the Chains Lengths and Molecular Weights**

### **1- Mono Disperse Polymers**

All particles in this case are of equal size and have the same weight, this type of polymers is not common.

### **2- Poly Disperse Polymers**

Polymers resulting from polymerization consist of a wide range of molecular weights, i.e, different chains in length, where all chains do not grow during the polymerization process to the length itself. This means that the existence of a diverse distribution of the lengths of the chains and thus there is a multiplicity of molecular weights [3].

## **1-4 Polymers Sources**

Polymers are of two main sources:

### **1- Natural Polymers**

They are compounds which come from plant or animal such as timber, cotton, natural rubber, wool and silk. The natural food which is the natural polymer is starch, protein or cellulose [9] .



## **2- Synthetic Polymers**

Polymers which are prepared from simple chemical compounds and represent the most industrial important polymers, include plastics, synthetic leather, nylon fabrics and some other dyes [9,4].

### **1-5 Polymerization Process**

Polymerization is the process of transforming low molecular weight (monomers) to high molecular weight matters without making any change in the basic structure of molecules. Carthers (1940) and Flory (1953) divided polymerization processes into two groups:

#### **1- Additional Polymerization**

It is also called chain growth polymerization. The bearer of the chain is an ion or a substance that is charged with a single electron called free radical. A free radical is formed by the decomposition of an unstable molecule of a matter (initiator). A free radical can react by opening the double bond to form another molecule that contains a single electron. In a very short time monomer molecules are added to the second chain. The process ends with the formation of two free radicals that eradicate each other, resulting in the formation of one molecule or more of the polymer. In this process, a polymer is formed at the first stages. An example of this type of polymerization is the polyethylene. The following mechanism shows the polymerization of ethylene to form the polyethylene [9]:



#### **2- Condensation Polymerization**

It is also called step growth polymerization. It takes place in compounds with low molecular weight. In this type of polymerization, two molecules that contain multi-functional groups react with each other, resulting in a bigger

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molecule that also contains multi-functional groups. In this process, a molecule of water may be eliminated. This process continues until the entire depletion of one of the reactants. In contrast with the additional polymerization, the polymer in the condensation polymerization is formed at the last stages of the polymerization process. Examples of such type of condensation polymers are polyesters and polyurethanes [14].

### **1-6 Degree of Polymerization**

The length of a polymer chain can be measured by the number of repeating units in the long chain. This is called the degree of polymerization (n), from which the molecular weight of a polymer can be calculated as follows:

Polymer Molecular Weight = Degree of Polymerization (n) x Molecular Weight of the Repeating Unit.

Polymers of high degree of polymerization (ten thousand or more in some cases) are called high molecular weight polymers (molecular weight ranges from  $10^4 - 10^6$  g/mol). Polymers with low degree of polymerization ( $n \approx 1-50$ ) are called oligomers [15].

### **1-7 Composite Materials**

Composite materials are material system composed of a combination of two or more materials that differ in form on material composition. The properties of a composite are different from those of its materials [5,16]. It is also cohesive in structure.

The composite comprises two major components: the matrix (the basic material) and the additives. The matrix is the basic material, serving to enclose the composite and give it bulk form. It surrounds other constituents and makes them more cohesive to form a "compact system". Additives are constituents added to polymers to provide them with specific properties and improve basic

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properties. These constituents are added in a granular form or as small particles. Additives can increase the overall conductivity, reduce porosity, improve friction and some magnetic properties ...etc. [3,17,18].

## **1-8 Preparation Methods of Polymer Films**

### **1- Casting Method**

To prepare thin film in the casting method, a certain amount of polymer material is dissolved in a suitable organic solvent. The polymer solution is applied to a horizontal rotating disc set at a suitable temperature, to obtain a homogenous solution, the speed of solvent evaporation must be reduced and the preparation time must be long [15].

### **2- Spin Casting Method**

In this method, little amount of polymer solution is precipitated on the center of the rotating disc or nearby. It is rotating electrically operating in high speed where the acceleration of disc centrifuging diffuses the polymer solution over the rotating disc forming a thin film. The thickness of the prepared film in this method depends on the viscosity of the polymer solution, rotation speed and spin time. To obtain a very thin film, the polymer solution must be diluted and rotation speed must be increased [15].

### **3- Dip Coating Method**

In this method the rotating disc is dipped in already prepared polymer solution. Then, the rotating disc is removed and put on a balanced horizontal surface to obtain a homogenous thickness for the film. The thickness of the film can be controlled by the concentration of the polymer solution and the time of dipping. The dip coating method is effective in the preparation of metal-oxide-film where the polymer material is oxidized immediately after being removed from the solution [15].

#### **4- Sol-gel Method**

This method is similar to the dip coating method, but the rotating disc in this method is moving upward and downward in a constant speed. The movement of the rotating disc depends on the type of the prepared solution. For example, when a transparent film of SnO<sub>2</sub> is prepared, the dipping speed and removal of the glass disc is about (1.5 cm/min) [15].

After preparation, the film is dried at a temperature that depends on the type of used solvent in the preparation of the solution.

#### **5- Languimer-Blodgett (LB) Method**

This is one of the important methods of preparing homogenous thin films of very low thickness of one nanometer (1nm), known as molecular structures. Molecular structures thickness can be controlled by increasing film layers. The latter can be used in the Field Effect Transistors (FET), Light Emitting Diode (LED), Light Sensors,.. etc [15].

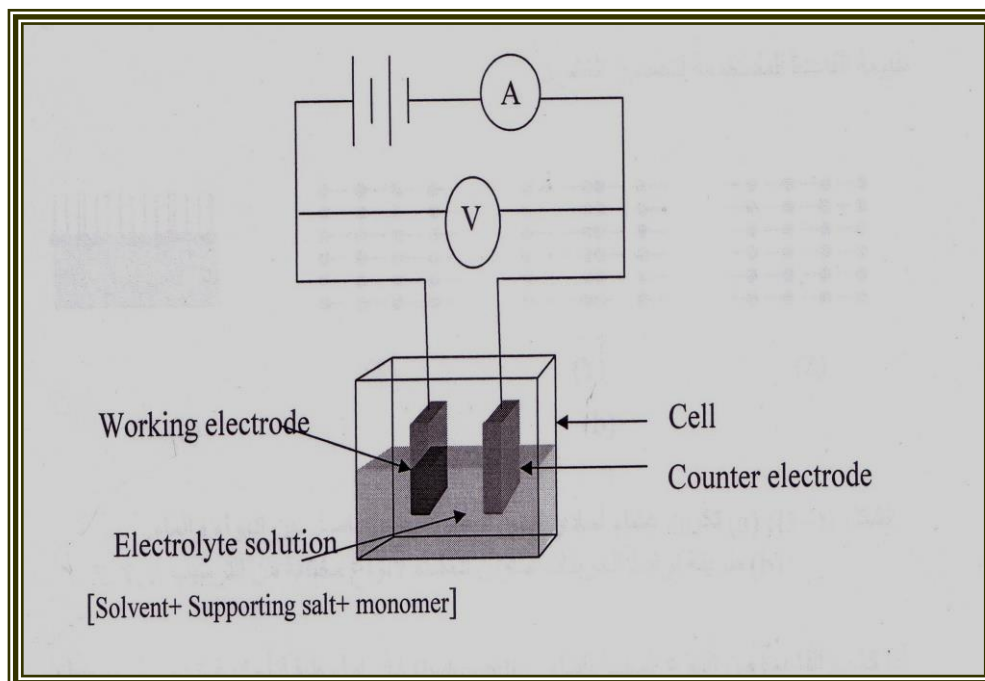
#### **6- Electrochemical Method**

Electrochemical method in non-organic matter takes place in a simple cell containing two electrodes-an anode and cathode-as well as electrolyte solution. The cell is provided with the required voltage to carry out the oxidation and reduction processes. This process is performed by power supply connected to the electrodes of the cell which are coated with the polymer material after a certain period of time. The type of the polymer material depends on the type of the electrolyte solution inside the cell. The electrolyte solution consists of monomer, salt, and solvent [19]. Figure (1-2) shows the main parts of an electrochemical cell:

1-cell

2-Electrodes

## 3-Electrolyte solution.



**Figure (1-2) : The main parts of electrochemical cell [19].**

### 1-9 Literature Survey

Abdul Muniam (2000) [20] studied the effect of the addition of Antimony compounds  $ET_4N(ETsbCl_2Br)$  and  $ET_4N(ETsbBr_2Cl)$  on polystyrene. The results showed that D.C electric conductivity increases and activation energy decreases with the increase of rates of added complexes. The results also showed that A.C electric conductivity increases with the increase of added material rates and slightly increases with the temperature.

Abd El-Kader and orabi (2002) [21] studied the effect of the molecular weights on the optical and mechanical properties of Pure Poly (vinylalcohol) (PVA) films with molecular weights (5000, 17000, 72000, 125000) g/mol which were prepared by a casting technique. The thickness of the prepared films was (0.21 mm). Optical absorption and mechanical properties were measured. The

UV–VIS–NIR absorption spectra gave the same band positions but the absorption intensity varies in a reverse trend with increasing molecular weight. The dependence of the absorption coefficient, on the photon energy, ( $h\nu$ ), has been determined and the band tails and energy gaps were calculated. It was found that the band tail increases, while the optical gaps decreased with increasing molecular weight, Young's modulus and the strength at the break for (PVA) films decrease as the molecular weight is increased.

Khaleel (2004) [22] studied the modification of the electrical and optical properties of polyvinyl chloride by Zinc, Copper, and Nickel EthylXanthate chelate complexes. She found that the D.C electrical conductivity increases several decimals with the increase of the concentration of the salt additive and temperature, while, the activation energy decreased with the increase of the concentration. The study revealed that the A.C electrical conductivity increases by increasing frequency from ( $10^2$ - $10^6$ ) Hz, while both the dielectric constant and the lost tangent angle increase with the increase of concentration.

Horibe, Amimura and Yoshido (2006) [23] studied the effect of adding the black carbon to high density polyethylene on electric resistibility. They found that resistibility decreases by increasing the rate of the additive (CB). Resistibility decreases even more when the size of a black carbon particle is less.

Hamzah et. al.(2009) [24] prepared (PVA-PPY) composites and studied the dielectric properties. They found that dielectric constant is decreasing with increasing frequency and become constant at high frequencies. While they are studying the change of dielectric loss with frequency, they found that dielectric loss is decreasing with increasing of frequency.

Alwash (2010) [25] studied the change in the optical band gap and optical activation energy for (PVA) doped with aluminum sulphate. They found that the optical band gap for allowed direct transition decreases with the increase of the concentration of aluminum sulphate.

Abdul Salam, Hashim and Abdul-Muhsien . (2010) [26] studied the effect of adding ( $\text{TiO}_2$ ) on the D.C. electric conductivity of polystyrene. They found that the electric conductivity of polystyrene increase with increased rate of ( $\text{TiO}_2$ ) and temperature. The composite activation energy decreases with increased rate of ( $\text{TiO}_2$ ).

Mahdy, Hashim, Abdul Muhsien and Aboud (2010) [27] studied the effect of adding ( $\text{Al}_2\text{O}_3$ ) on some optical properties of polystyrene. Transmittance and absorbance spectrum of (300-900) nm wavelength was recorded. Absorption coefficient and energy gap of allowed and forbidden transition were calculated. They found that absorption coefficient increases with increased rates of added material, while the energy gap decreases.

Al-Taay, Abdul Nabi and Al-Rawi (2011) [28] studied the optical properties of pure (PVA) and (PVA) doped with MR. They studied different percentage prepared with constant thickness using casting technique. They found that the optical properties of (PVA) are affected by increasing the impurity concentration.

Chiad, Habubi, Oboudi and Hameed (2011) [29] studied the effect of thickness on the optical parameters of (PVA) doped (Ag) films with different thicknesses were prepared by casting method. They founded that all the parameters affected by increasing the thickness.

Al-Rawi, Ali and Al-Jobory (2011) [30] studied the effect of additive (PVA) on cement \_silica. They found that increasing on compression resistance with increase of (PVA) and decreasing of thermal conductivity with increasing (PVA) solution ratio.

Hashim, Abdul-Muhsien and Hakim (2012) [31] studied the electrical properties of (PVA-CuCl<sub>2</sub>.2H<sub>2</sub>O) composites were studied. The effect of CuCl<sub>2</sub>.2H<sub>2</sub>O content and temperature on the D.C. electrical conductivity have been investigated. Results showed that the D.C. electrical conductivity increased with increasing the CuCl<sub>2</sub>.2H<sub>2</sub>O concentrations and temperature. Also the activation energy change with the increase of additional CuCl<sub>2</sub>.2H<sub>2</sub>O.

Ahmad, Sabeeh and Hussien (2012) [ 32 ] studied (PVA) which has been doped by different percentage of Lithium Iodide (LiI), and electrical and optical properties of polymer electrolytes have been investigated. At low frequency, the variation of dielectric constant and dielectric loss with frequency shows the presence of material electrode inter-face polarization processes. The exponent factor found is between (0.98) and (0.442) and obeys the universal power law. The absorption of pure and doped films have been studied in the visible and ultra-violet wavelength regions. It has been observed that the new absorption peaks at (290) and (375) nm are due to the formation of charge transfer complex. From direct allowed transition, the optical energy gap decreases from (5.56 eV) (for pure PVA) to (4.95 eV) for( PVA+20%LiI).

Ali Abid and Ali Habeb (2013) [33] studied many samples which have been prepared by adding CoCl<sub>2</sub> to the poly vinyl alcohol and poly vinyl pyrrolidon with different weight percentages (0, 3, 6 and 9)wt%. The effect of cobalt chloride concentration on the D.C. electrical properties has been investigated. Results showed that the D.C. electrical conductivity of such



composites increased with increasing the weight percentages of  $\text{CoCl}_2$ , and the activation energy changed with increasing the filler concentration.

Abdallh, Hamood and Yousif (2013) [ 34 ] studied the optical properties for poly (vinyl alcohol ). Films doped by copper chloride with the wave length rang from (200-800) nm at room temperature. They found that the optical band gap ( $E_g$ ) for allowed direct transition decrease with increasing of copper chloride concentration.

### **1-10 Aim of The Research**

Because of the rapid development in the science and applications of polymers in every part of our life (scientific, industrial, domestic, ...etc), it has become important to fulfill the growing needs and requirements of these applications.

In this research an important polymer has been used from the (PVA) films and doped by cobalt salts. Electrical and optical properties of films of this material have been studied. A new specifications are found that offer potential possibility of usage in the field of electronic component industry such as transistors, capacitors, ...,etc.

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## 2-1 Introduction

Polymers are weak conductors, hence they are used as electrical insulators in condensers where great amount of energy is stored in the insulator. Though polymers are inactive electrical insulators, the existence of impurities enables them to be electric conductors because of the free movement of the ions of impurities through them [2,3]. This chapter represents theoretical introduction to the electrical and optical properties of polymers.

## 2-2 Electrical Properties of Material

Electricity is the movement of charged units called charge carriers, that are subject to the effect of potential difference. These units are the electrons and holes of the matter in the solid state or its ions in the liquid and gas state. As electricity is transferring in solid matters via the movement of electrons, it is expected that the electrical properties of matters are fundamentally dependent on the electronic configuration of the matter [35].

Materials are classified according to their electrical conductivity to:

- 1- Insulators: its conductivity ranges from  $(10^{-22}-10^{-12}) (\Omega.cm)^{-1}$ .
- 2- Semiconductors: its conductivity ranges from  $(10^{-13}-10^{-3}) (\Omega.cm)^{-1}$ .
- 3- Conductors (metals): its conductivity is more than  $(10^{-3}) (\Omega.cm)^{-1}$ .
- 4- Superconductive matters: its conductivity is  $(10^{20}) (\Omega.cm)^{-1}$ .

To understand the electrical properties of the materials and how electrical conductivity takes place, it is necessary to know more about the energy levels of atom and the electronic distribution in these levels. Electrons are distributed in an atom in different energy levels, electrons closer to the nucleus are closely connected to the atom, the more distanced the electrons from the nucleus, The less is the connection of electrons to the nucleus. Consequently, electrons that occupy the orbital which is the most distant from

the nucleus are the least connected to the nucleus. These electrons are called valence electrons. Valence electrons are distributed among many levels of energy which are called valence band [36].

Though the electrons that occupy the valence band are weakly connected to the nucleus, this connection is making them unable to move. By gaining certain energy, valence electrons can transfer to higher levels, called the conduction band. The difference in energy between the conduction band and valence band is called energy gap ( $E_g$ ).

Electrons of the conduction band are very weakly connected to the nucleus and that makes them easily move by the influence of external effects such as the exertion of electrical field. The difference of energy ( $\Delta E$ ) determines the electrical properties of matter [37].

### **2-2-1 Metals**

One of the most important properties of metals is their good electrical conductivity, which is attributed to their electronic configuration. Electrons are equally distributed between the conduction band and the valence band so that the last band is occupied with a large number of electrons in nearly normal temperature, ensuring effective transfer of electric current. In metals, the energy gap ( $E_g$ ) is very small, conductivity in metals does not depend on temperature, on the contrary, increased temperature in metals (conductors) decreases electrical conductivity. Resistance in metals is caused by two reasons:

First, nucleus constituting the metal crystal has vibrating movement which is called phonon. This movement influences the movement of electrons or charges that transfer the current, it scatters and deviates them from their

trajectory. Increased temperature decreases electrical conductivity in metal conduction .

Second, the resistance resulting from the defect in the metal crystal lattice (crystal defect), is not influenced by temperatures, this defect cuts off the trajectory of electrons and charges that transfer the electric current [35].

### **2-2-2 Semiconductors**

Many solid elements have the properties of conductors and insulators, such as Silicon and Germanium. Such elements are called semiconductors. They are different in their electronic configuration from that of metals, the number of electrons in the valence band is greater than that in the conduction band because the energy gap is bigger in semiconductors, the electrons in the valence band need greater energy to transfer to the conduction band [38].

Since the number of excited electrons is increased by temperature, semiconductor conductivity increases with increased temperature. This is exactly the opposite in metals [7].

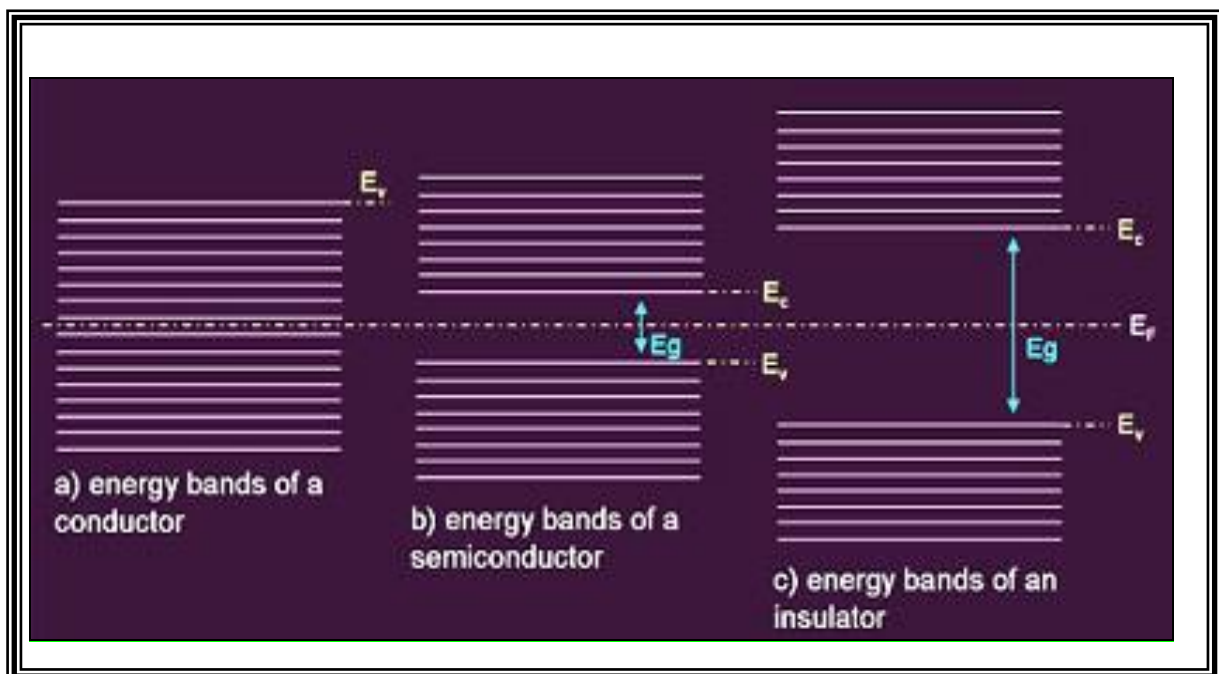
Electrical conductivity can be increased in elements such as Silicon and Germanium by adding small amounts of impurities. For instance, though there is a wide energy gap in Silicon, it is possible to make it effectively narrow by adding impurities such as Boron or Phosphorous to Silicon crystals. Very little amount of Boron or Phosphorous (parts per million) can be added to the crystal structure of Silicon. Phosphorous has five valence electrons, four of which bind with Silicon leaving the fifth electron free. This electron assumes a higher energy level than that possessed by the valence electrons of Silicon. Consequently, the value of ( $E_g$ ) decreases and the conductivity of the Silicon with impurities increases.

When little amounts of Boron is added to Silicon, three of its valence electrons share the three electrons of Silicon to make three bonds, leaving a

gap in the tetrahedral structure. Consequently, a new energy level closer to the valence band is formed, where electrons occupy such level, leaving an electronic gap filled with neighboring electrons. The end result of such process is decreased energy gap ( $E_g$ ) and increased electronic conductivity of Silicon [35].

### 2-2-3 Insulators

The energy gap ( $E_g$ ) is very much greater in insulators than in conductors and semiconductors, and the conduction band is empty of electrons, which are distributed in insulators at lower energy levels of the valence band, making them strongly bound to the atom with little movement, to be released, these electrons need high energy to enable them transferring to a higher energy level weaken their binding to the atom and facilitate their movement among atoms [35]. Figure (2-1) shows energy gap in metals, semiconductors and insulators.



**Figure (2-1):The energy gap and distances among the conductor, semiconductor and insulator materials [39].**

### 2-3 Optical Properties of Polymers

The study of the optical properties of polymers increases our knowledge of the type of polymer internal structure, nature of the bonds and expands the potential scope of polymer application.

Knowing the spectrums of absorbance and transmittance of a polymer assists in identifying many optical properties in different ranges of wavelengths. Conducting examination at the ultraviolet spectrum range enables us to know the type of the bonds, orbital and energy beams. The study at the visible spectrum range provides sufficient information about the behavior of a matter to solar applications. The study at the infrared range is very important in knowing the general structure of a polymer and the elements consisting its chemical structure [40].

### 2-4 Light Absorbance and Electronic Transitions

The total molecular energy is divided into the electronic energy ( $E_{\text{ele}}$ ), vibration energy ( $E_{\text{vib}}$ ), rotational energy ( $E_{\text{rot}}$ ) and translational energy ( $E_{\text{trans}}$ ). The absorbance of electromagnetic wave results in a change in the energy of the molecule due to the change in the different energies [41]:

$$\Delta E = \Delta E_{\text{ele}} + \Delta E_{\text{vib}} + \Delta E_{\text{rot}} + \Delta E_{\text{trans}} \quad \dots\dots\dots(2-1)$$

It is to be noted that the visible and ultraviolet spectrums are the spectrums of electronic absorbance, the remaining is the spectrum of other absorbance. The ( $E_{\text{ele}}$ ) is the clearest in the absorbance spectrum.

The reaction of the photon with the molecule makes the electrical field of the photon works in a manner that agitates the electronic structure of the molecule to the point that makes the photon disappears and its energy transferrs

to the molecule whose state has been changed to an excited state [10].Figure (2-2) shows the electromagnetic spectrum region.

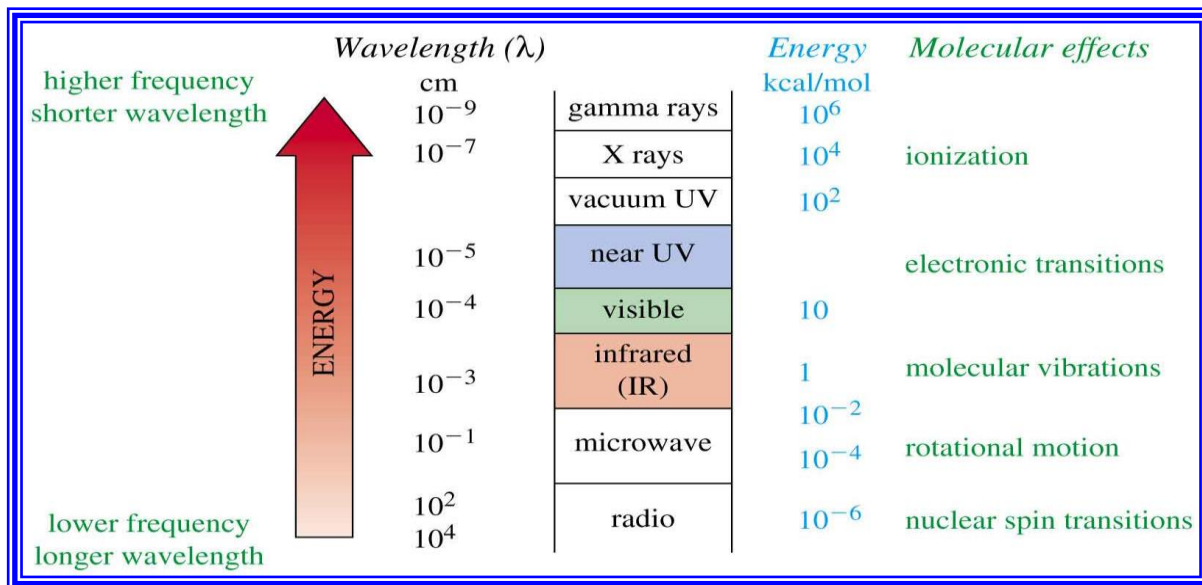


Figure (2-2) : The electromagnetic spectrum region [42].

### 2-4-1 Direct Transitions

In general, the direct transition occurs between top of valence band and bottom of conduction band (vertical transition) at the same wave vector  $\Delta k = 0$  for conservation of momentum. The allowed direct transition refers to that transition which occurs between top of the valence band and bottom of the conduction band when the wave vector is equal to zero as shown in Fig. (2-3a). This transition is described by the following relation [43].

$$\dots\dots\dots (2-2) \alpha h\nu = B(h\nu - E_g)^{1/2}$$

Where B is inversely proportional to amorphousity.

If the transition occurs between states of the same wave vector, (but the wave vector does not equal to zero), the transition is called forbidden direct transition as shown in Fig. (2-3b). It obeys the following relation [43].

$$\dots\dots\dots (2-3) \alpha h\nu = B(h\nu - E_g)^{3/2}$$

**2-4-2 Indirect Transitions**

In indirect transition there is a large momentum difference between the points to which the transition takes place in valence and conduction bands. This means that the conduction band minima are not at the same value of *k* as the valence band maxima, then, assistance of a phonon is necessary to conserve the momentum, therefore :

$$h\nu = E_g \pm E_p \dots\dots\dots (2-4)$$

Where *E<sub>p</sub>* is the energy of an absorbed or emitted phonon [44].

For an allowed indirect transition, the transition occurs from the top of the valence band to the bottom of the conduction band as shown in Fig.(2-3c) so that [44].

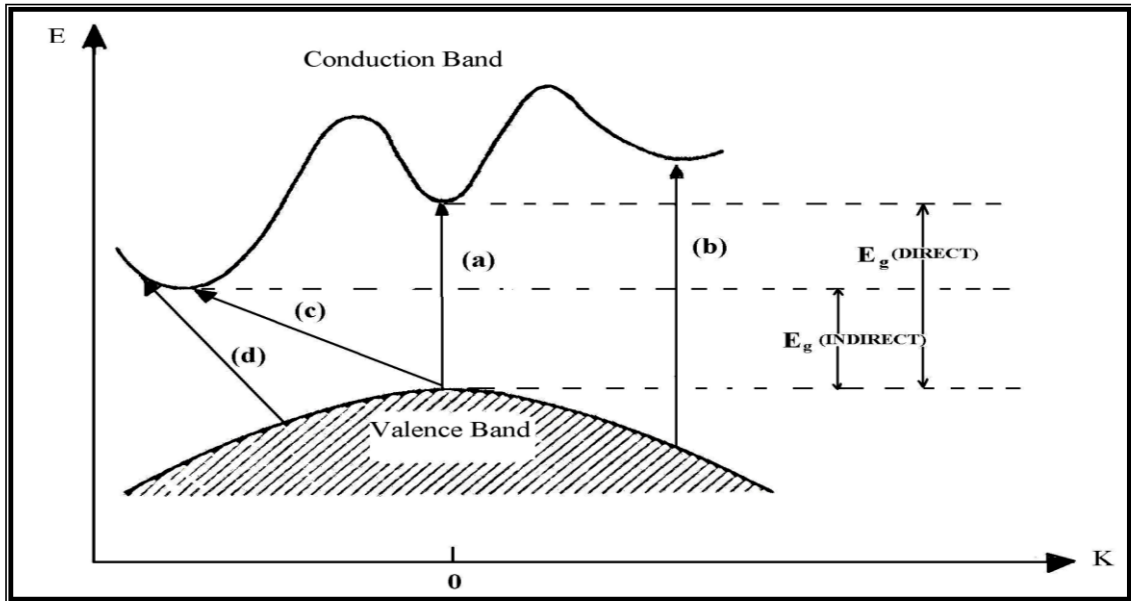
$$\dots\dots\dots (2-5) \alpha h\nu = B(h\nu - E_g)^2$$

While, the forbidden indirect transitions occur from any point near the top of V.B to any point other than the bottom of the C.B, as shown in Fig. (2-3d), then we have [44].

$$\dots\dots\dots (2-6) \quad \alpha h\nu = B(h\nu - E_g)^3$$



Experimentally, it is possible to differentiate between direct and indirect processes by the level of the absorption coefficient ( $\alpha$ );  $\alpha$  takes values from  $(10^4 \text{ to } 10^5) \text{ cm}^{-1}$  for direct transitions and  $(10 \text{ to } 10^3) \text{ cm}^{-1}$  for indirect transitions at the absorption edge[10].



**Figure.(2-3):The optical transitions (a) Allowed direct, (b) Forbidden direct; (c) Allowed indirect, (d) Forbidden indirect [45]**

## 2-5 Absorption Coefficient

The absorption coefficient ( $\alpha$ ) is defined as the gradual reduction of the flow of incident ray energy on a unit area along the direction of wave diffusion inside a medium. The absorption coefficient depends on the photon energy and properties of the semiconductor regarding the gap energy of the semiconductor and the type of electronic transitions [43,46].

From the equation related to the absorption of ray, the relation between the incident light intensity ( $I_0$ ) and the penetrating light intensity ( $I$ ) is described in the following equation [10]:

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$$I = I_0 e^{-\alpha t} \quad \dots\dots\dots(2-7)$$

where (t) is the thickness of the matter and ( $\alpha$ ) is the absorption coefficient, it is measured by  $\text{cm}^{-1}$ .

$$\alpha t = 2.303 \log I/I_0 \quad \dots\dots\dots(2-8)$$

where the amount of ( $\log I/I_0$ ) represents the absorbance (A). The absorption coefficient can be calculated as follows:

$$\alpha = 2.303(A/t) \quad \dots\dots\dots(2-9)$$

## 2-6 Fundamental Absorption Edge

The fast increase in absorption of the ray energy is proportional to the energy gap of the absorbing material. The fundamental absorption edge represents the lowest difference in energy between the highest point in the valence band and lowest point in the conduction band [47]. Absorption regions are divided into three regions:

### 2-6-1 High Absorption Region

This region is represented by the part (A) in figure (2-4). The amount of absorption is ( $\alpha \geq 10^4 \text{ cm}^{-1}$ ), thus, the electronic transitions are direct. Furthermore, it is easy to know the amount of optical energy gap from this region ( $E_g$ ) by using the following relation [40,48]:

$$\alpha h\nu = A(h\nu - E_g)^m \quad \dots\dots\dots(2-10)$$

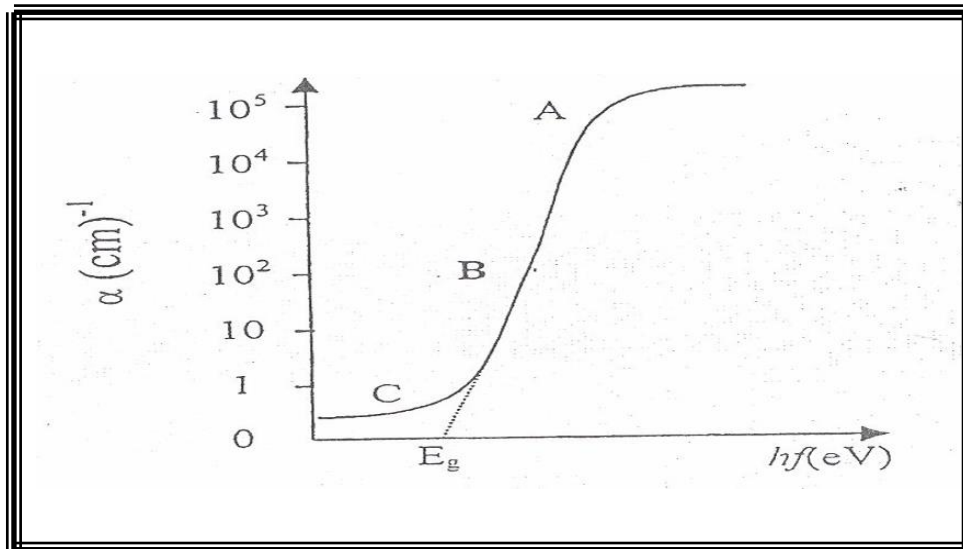
where  $(h\nu)$  is the photon energy,  $(A)$  is a proportional constant and  $(E_g)$  is the forbidden energy gap of direct transition.

### 2-6-2 Exponential Region

This region is shown by the part (B) in figure (2-4). Absorption coefficient in this region ranges from  $(1 < \alpha < 10^4) \text{ cm}^{-1}$ . It represents the transitions among the levels expanding from the valence band to the level in the conduction band. It also represents the levels at the top of the valence band to the level expanding at the bottom of the conduction band [48,49].

### 2-6-3 Low Absorption Region

The absorption coefficient in this region is very small  $(\alpha < 1 \text{ cm}^{-1})$ . The transitions between regions are attributed to the density of states in the mobile space resulting from structural defects, as shown in the part (C) in figure (2-4) [50].



**Figure (2-4): The absorption edge and the main absorption region [10].**

## 2-7 Optical Constants

The optical properties of homogenous materials (absorbance, transmittance and reflectance) are described by two parameters:

### 2-7-1 Refractive Index

It is the ratio of light speed in vacuum to its speed in a medium. This index shows how far a matter is affected by the electromagnetic waves. The refractive index consists of two parts: real and imaginary. It can be expressed by the following equation [51]:

$$n = \frac{c}{v} \quad \dots\dots\dots(2-11)$$

where (n) is the refractive index, (C) is the light speed in vacuum and (v) is the light speed in matter.

The relation between reflectance and refractive index is given in the following equation:

$$R = (n-1)^2 + k^2 / (n+1)^2 + k^2 \quad \dots\dots\dots(2-12)$$

where (k) is the Extinction Coefficient. R is the reflectance.

The absorbance (A) and transmittance (T) can also be calculated as in the following equation (44):

$$R + A + T = 1 \quad \dots\dots\dots(2-13)$$

Refractive index can be expressed by the following equation [52]:

$$n = \sqrt{\frac{4R - k^2}{(R-1)^2}} - \frac{(R+1)}{(R-1)} \quad \dots\dots\dots(2-14)$$

### 2-7-2 Extinction Coefficient

The imaginary part of the complex refractive index ( $N$ ) is called the extinction coefficient, as shown in the following equation:

$$N = n - ik \quad \dots\dots\dots (2-15)$$

where ( $n$ ) is the real part of the refractive index. The extinction coefficient can be calculated by using the following equation [43]:

$$k = \alpha\lambda/4\pi \quad \dots\dots\dots(2-16)$$

where ( $\lambda$ ) is the wavelength of incident ray.

### 2-8 Dielectric Constant

The dielectric constant represents the ability of a matter for polarization. The matter can respond to different frequencies in a complex manner, at optical frequencies represented by light waves the electronic polarity is dominating above other remaining types of polarization [10]. The real and imaginary dielectric constants can be calculated by the following equation [53]:

$$\epsilon = \epsilon_1 - i\epsilon_2 \quad \dots\dots\dots(2-17)$$

where ( $\epsilon$ ) is the complex dielectric constant, ( $\epsilon_1, \epsilon_2$ ) are the real and imaginary parts of the dielectric constant, respectively.

The dielectric constant can be calculated by calculating the refractive index. The relation between the complex dielectric constant and the complex refractive index is expressed in the following equation:

$$\varepsilon = N^2 \quad \dots\dots\dots(2-18)$$

From the equations (2-15), (2-17), and (2-18), it can be concluded that [49]:

$$(n - ik)^2 = \varepsilon_1 - i\varepsilon_2 \quad \dots\dots\dots(2-19)$$

From the equation (2-19), the real and imaginary parts of dielectric constant can be expressed by the following equation:

$$\varepsilon_1 = n^2 - k^2 \quad \dots\dots\dots(2-20)$$

$$\varepsilon_2 = 2nk \quad \dots\dots\dots(2-21)$$

## 2-9 Electrical Properties of Polymers

There are many electrical properties that determine the properties of polymers during application. Prominent among these properties are: electrical conduction and the activation energies.

### 2-9-1 Electrical Conduction

It has been mentioned that electrical conduction is the process of the transfer of electric charges through a medium from one place to another under the influence of electric field. Electrical conduction depends on two factors: First: The type of charge carriers (n). It can be electrons, holes or ions automatically generated due to the addition of impurities.

Second: Mobility ( $\mu$ ). It depends on temperature (T) and the applied potential (V).

Polymers of special structure (alternating) have the properties of semi conductors, whereas most commercial polymers are insulators. Given that polymers are easily formed, chemists and physicists started mid the twentieth century to conduct studies designed to develop conductor polymers characterized by alternating double bonds [35].

In its stable state, alternating polymers are insulators or semiconductors because it is not easy for electrons to transfer from one chain to another. These insulator polymers can be transformed into conductors by adding small molecules that have certain properties among polymer chains, these molecules are called dopants and the process of adding impurities is called Doping.

Dopants can operate as oxidizing or reducing factors. Charge transfer complexes can be created between dopants and polymers that make these polymers conductors [35].

### 2-9-2 The D.C. Electrical Conductivity

The electrical conductivity of polymers depends on the free ions which are not chemically connected to the large molecules. The volumetric electrical resistance ( $R_v$ ) can be calculated for a regular body with a section having a constant area (A) along the length (L), using the relation [54]:

$$R_v = \rho_v \frac{L}{A} \dots\dots\dots(2-22)$$

where ( $\rho_v$ ) is the volume resistivity that is different according to the substance, it equals to the inverse of the volume conductivity. This means that volume conductivity ( $\sigma_v$ ) is [54]:

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$$\sigma_v = \frac{1}{\rho_v} = \frac{L}{R_v A} \dots\dots\dots(2-23)$$

The conductivity increases exponentially in polymers with the increase of temperature according to the relation:

$$\sigma = \sigma_0 \exp(-E_{act}/k_B T) \dots\dots\dots(2-24)$$

where ( $\sigma$ ) is electrical conductivity at temperature ( $T$ ), ( $\sigma_0$ ) is electrical conductivity at absolute zero temperature, ( $k_B$ ) is Boltzmann constant and ( $E_{act}$ ) is activation energy.



### **3-1 Introduction**

This chapter includes the stages of samples preparation and testing measurement stages in addition to description of equipment and tools used in the preparation and measurement processes.

### **3-2 The Utilized Materials**

The materials used in this study are:

#### **3-2-1 poly (vinyl alcohol) PVA**

Poly (vinyl alcohol) (PVA) is the largest volume, synthetic, water – soluble produced in the world. It is commercially produced by the hydrolysis of poly(vinyl acetate), as the vinyl alcohol monomer does not exist in the free state, although traces have been detected [55,56]. The first scientific reports on (PVA) were published in (1927) [57].

##### **3-2-1-a Physical Properties of (PVA)**

The physical properties of poly(vinyl alcohol) depend on the method of preparation, as in the case of other polymers. The final properties are affected by the polymerisation conditions of parent poly(vinyl acetate) used as well as the hydrolysis conditions, drying, and grinding .

##### **3-2-1-b Solution Viscosity**

The viscosities of (PVA) solutions are mainly dependent on molecular weight, concentration, hydrolysis, and temperature. Materials with a high degree of hydrolysis increases in viscosity on standing and may even be gel [58,59]. The viscosity of solutions of partially hydrolysed (PVA) grades are stable.

### 3-2-1-c Crystallisation and Melting Point

The degree of crystallization has a pronounced effect on solubility, water sensitivity, tensile strength, oxygen barrier, and thermoplastic properties. The melting point of crystal depends on perfectness and size. Various experimental values of the melting point of poly (vinyl alcohol) have been reported [60,61], range is between (220°C) and (267°C) for fully hydrolysed (PVA). Exdetermination of the crystalline melting point using a normal differential thermal analysis technique (DTA) is different in melting point which may be due to decomposition.

### 3-2-1-d Glass- Transition Temperature (T<sub>g</sub>)

The glass transition temperature of fully hydrolysed (PVA) has been determined to be (85°C) for a high molecular weight material. The (T<sub>g</sub>) for (87-89)% hydrolysed (PVA) is (87°C). It is dependent on the degree of polymerization [9].

(PVA) used in this study was (99%) hydrolyzed batch no (6909/1) man date (9/2007) Gerhard Bachmann kG Tuttlingen / Germann .

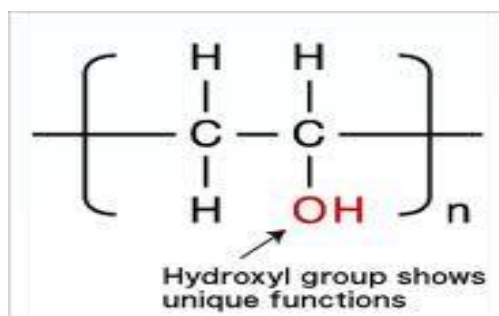


Figure (3-1): Chemical starchier of (PVA) [55] .

### 3-2-2 Additive Material ( Cobalt Salts )

There is a wide range of Cobalt Salts that is formulated using superior quality raw material. Used across diverse range of industries such as chemical, pharmaceutical, drug and others. Cobalt salts includes cobalt salt powder; cobalt acetate, cobalt chloride and cobalt nitrate [62].

#### 3-2-2-a Cobalt Acetate (CoCH<sub>3</sub>COOH)

Cobalt acetate used as paint drier, feed additive, Cobalt acetate is formulated using superior quality raw material. Table (3-1) show The physical and chemical properties of Cobalt acetate .

**Table (3-1) The physical and chemical properties of Cobalt acetate**

<b>Chemical name</b>	<b>Cobalt acetate</b>
<b>Molecular formula</b>	<b>CoCH<sub>3</sub>COOH</b>
<b>Molecular weight</b>	<b>249.08</b>
<b>Color</b>	<b>Red</b>
<b>Specific gravity</b>	<b>1.71</b>
<b>Solubility</b>	<b>In water and ethanol</b>

**3-2-2-b Cobalt Chloride (CoCl<sub>2</sub>)**

Cobalt (II) chloride with the chemical formula (CoCl<sub>2</sub>). This cobalt chloride is widely used for hydration and dehydration reaction and other chemical synthesis processes [62]. Table (3-2) show The Physical and chemical properties of Cobalt Chloride.

**Table (3-2) The Physical and chemical properties of Cobalt Chloride**

<b>Chemical name</b>	<b>Cobalt Chloride</b>
<b>Molecular formula</b>	<b>CoCl<sub>2</sub></b>
<b>Molar mass</b>	<b>129.84 g/mol</b>
<b>Anhydrous</b>	
<b>Hexa hedrate</b>	<b>237.93 g/mol</b>
<b>Density</b>	<b>3.356 g/cm<sup>3</sup></b>
<b>Melting point</b>	<b>735°C</b>
<b>Boiling point</b>	<b>1049°C</b>
<b>Solubility</b>	<b>In water 45g/100mol (7°C)</b>

**3-2-2-C Cobalt Nitrate (CoNO<sub>3</sub>)**

Superior quality cobalt nitrate which is derived from reacting metallic cobalt or one of its oxides, hydroxides, or carbonate with nitric acid. This cobalt nitrate is commonly used in dyes and inks as well as a common source of cobalt in metal organic frameworks and polymers [62]. Table (3-3) shows the physical and chemical properties of Cobalt nitrate.

**Table (3-3) The physical and chemical properties of Cobalt nitrate**

<b>Chemical name</b>	<b>Cobalt Nitrate</b>
<b>Molecular formula</b>	<b>CoNO<sub>3</sub></b>
<b>Molar mass</b>	<b>182.94 g/mol</b>
<b>Color</b>	<b>Red</b>
<b>Density</b>	<b>1.87 g/cm<sup>3</sup></b>
<b>Melting point</b>	<b>55°C</b>
<b>Boiling point</b>	<b>75° C</b>
<b>Solubility</b>	<b>In water 134 g/100mol(°C)</b>

### **3-3 Preparation of dopped polymer**

(PVA) was dissolved in distilled water and heated gently in water bath to prevents thermal decomposition of polymer, and doped with Cobalt salts (1,3,5,7 and 10)wt% were prepared by using the following:

1- The polymer (PVA) films with different weight of Cobalt salts were prepared by dissolving (PVA) and Cobalt salts in (10)ml distilled water and with stirring the solution by using magnetic stirrer for about (1hour) for complete dissolution.

2- Glass basin was made and divided into a number of small square basins, the side of each small square basin was (5cm) .

3- Casting method was used for the preparation of the films. Each sample was poured in (5×5 cm<sup>2</sup>) glass basin after being cleaned with water and acetone and kept till dried (24 hours) at (30 °C). The obtained films have almost transparent colors, some of them were yellowish, red. They were kept in a special place to investigate their optical and electrical properties.

4-The Thickness measurements were made by using micrometer. The thickness of the films were in the rang of (45-50) μm.

### **3-4 Measurement of Optical Properties**

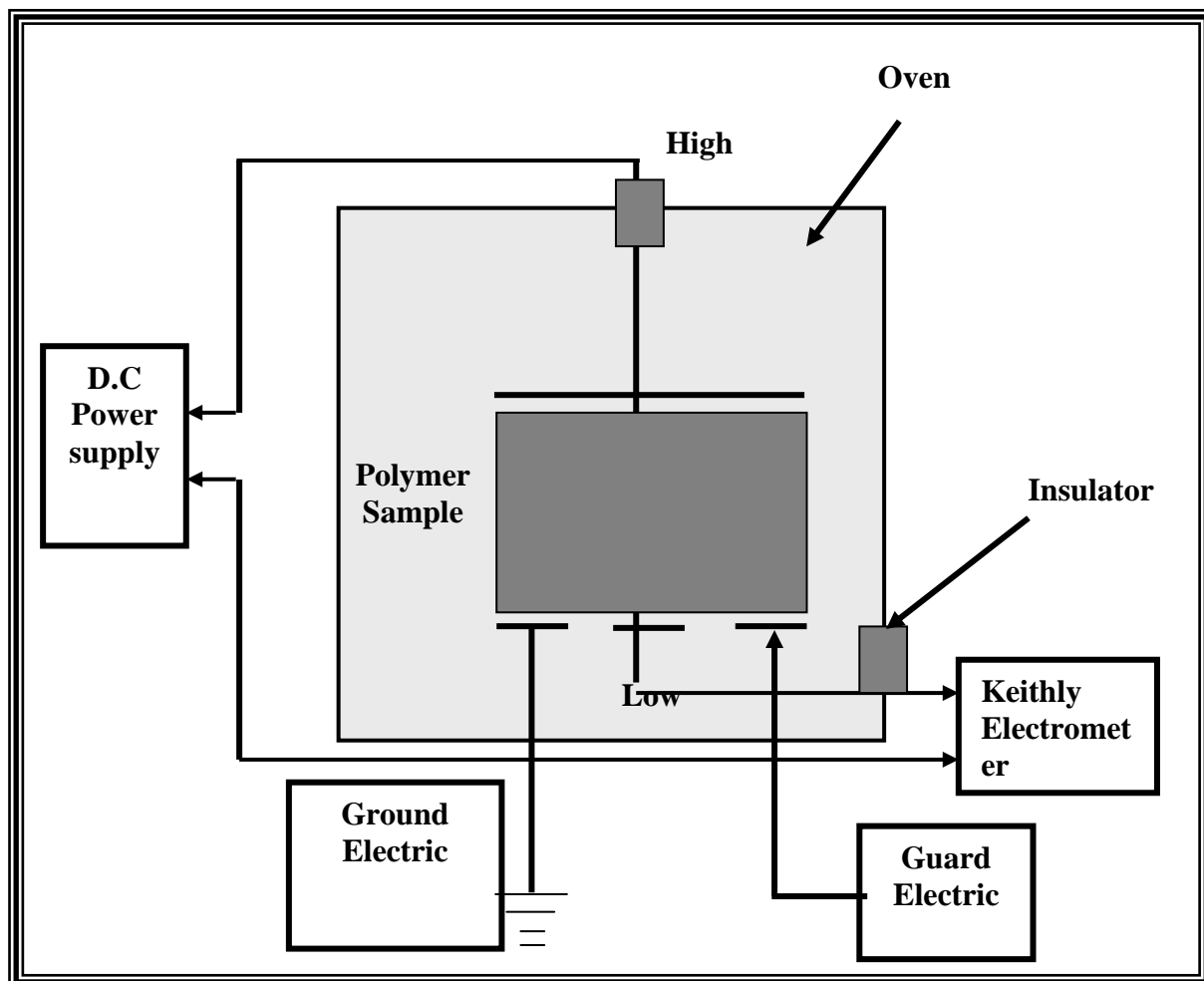
The spectra of absorption and transmittance for the (PVA-cobalt salts) composites have been recorded for the wavelengths (190-1100) nm by using the double beam spectrophotometer (shimadzu, UV-210 °A) provided by optima (300) plus company. The two spectra have been recorded at room temperature.

### **3-5 Measurement of D.C. Electric Conductivity**

The method of the three-electrode cell (the method of Teflon-isolated circular electrodes) was used according to ASTM D66-257 recommendations to study the effect of additives and temperature on the volumetric conductivity of polymeric systems. The volume conductivity is calculated by using equation (2-23).

Figure (3-6) shows a diagram of D.C. circuit. The devices and used materials in this research are locally manufactured with careful attention to the origin of the materials. The copper electrodes were fixed inside a cylindrical piece of Teflon for dielectric insulation.

The input electrical power was regulated by using a D.C. power supply of Phillips Harris Limited type having a voltage of (3-7) KV. The highest voltage used in this research was (1000) V. The current was measured by a Digital Solid State Electrometer 616 with sensitivity of ( $10^{-15}$ ) and full gradation. The temperature was changed by using an electrical oven of Yamato DP61 Japans type.



Figure(3-2) : A diagram of D.C. circuit



## **4-1 Introduction**

This chapter includes the results of the optical and (D.C.) electrical measurements for (PVA- (CoCl<sub>2</sub>, CoNO<sub>3</sub>, CoCH<sub>3</sub>COOH) films. It will also discuss the effect of different concentrations additives from these salts on the electrical and optical properties of poly(vinyl alcohol) .

## **4-2 Optical Measurements**

The main purpose of studying the optical properties of the (PVA-(Cobalt chloride, Cobalt nitrate and Cobalt acetate)) films is to identify the effect of adding the (Cobalt chloride, Cobalt nitrate and Cobalt acetate) on the optical properties of poly(vinyl alcohol) . The research covers the recording of the spectra of absorbance and transmittance for the (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films at room temperature and calculating the optical constants, as well as identifying the types of electronic transitions and calculating the energy gaps.

### **4-2-1 Absorption Spectrum**

Figures (4-(1-3)) shows the absorption spectrum of (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films with different concentrations of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) salts as a function of the wavelength. It is shown that the adding of the filler to the polymer leads to increase the intensity of the absorbance peak. So, there is shifting in the position of the peaks for all amounts of filler adding to the polymer towards red wave lengths. The increase of absorbance with the increase of the weight percentage of the added (Cobalt chloride, Cobalt nitrate and Cobalt acetate) can be explained by the fact that (Cobalt chloride, Cobalt nitrate and Cobalt acetate) ions absorbed the incident light on them. In other words ions absorb the incident light by the free electrons. Consequently, by increasing the weight percentage

of added (Cobalt chloride, Cobalt nitrate and Cobalt acetate) absorbance increases [3,10,63].

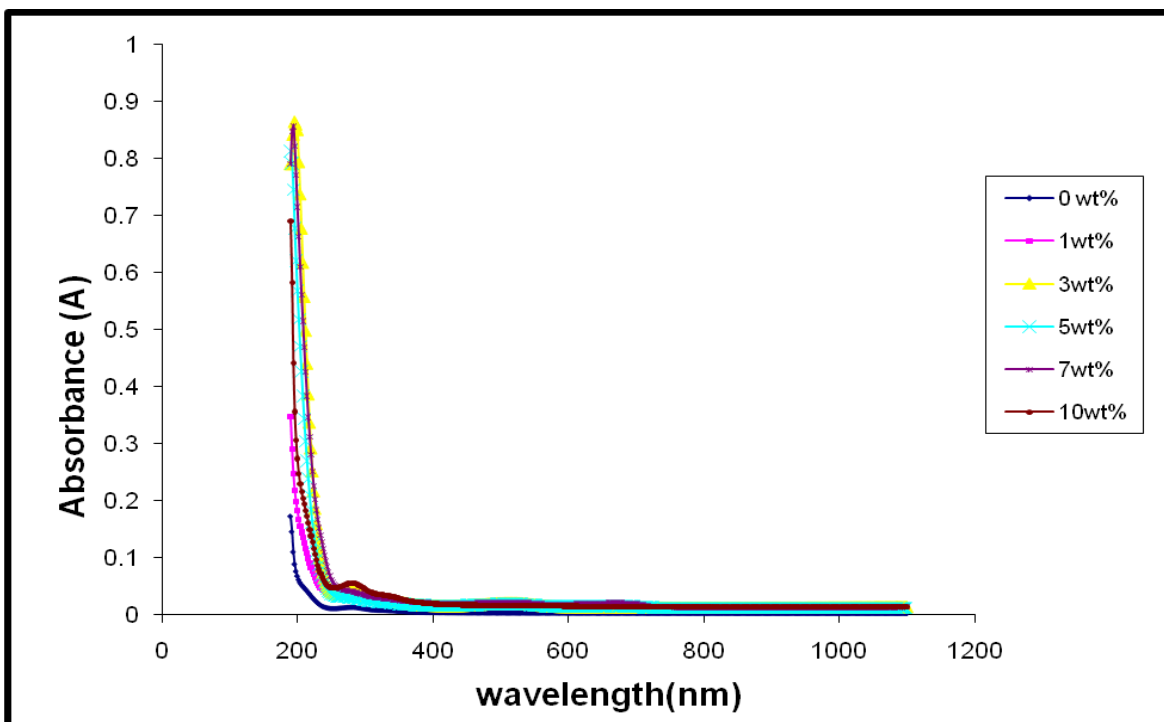


Figure (4-1) : The absorbance for (PVA-CoCl<sub>2</sub>) films as a function of the wavelength.

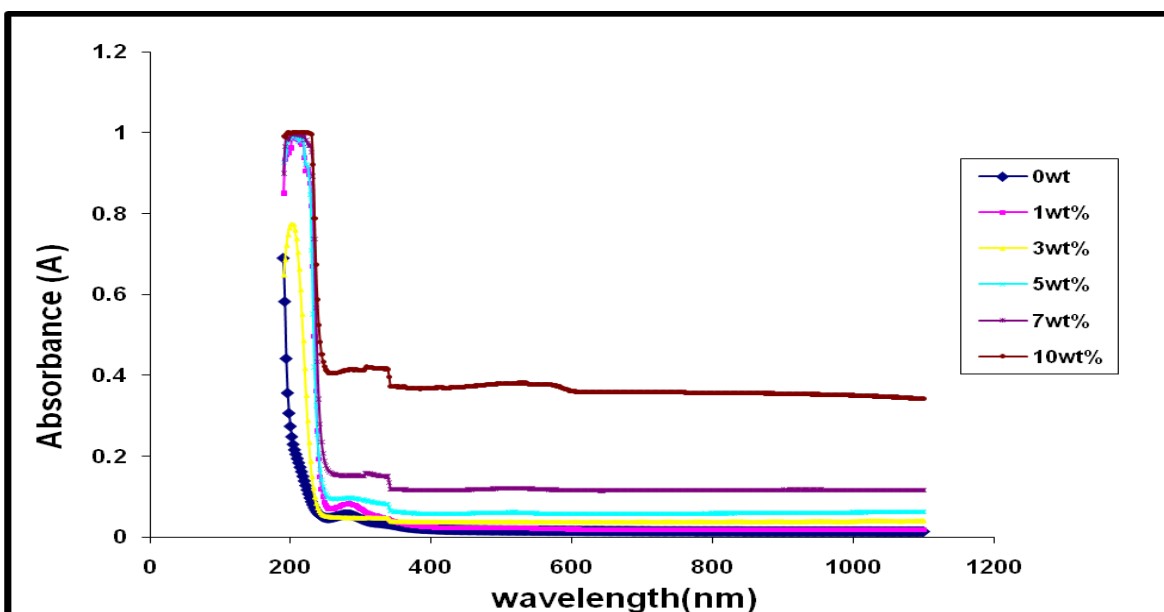
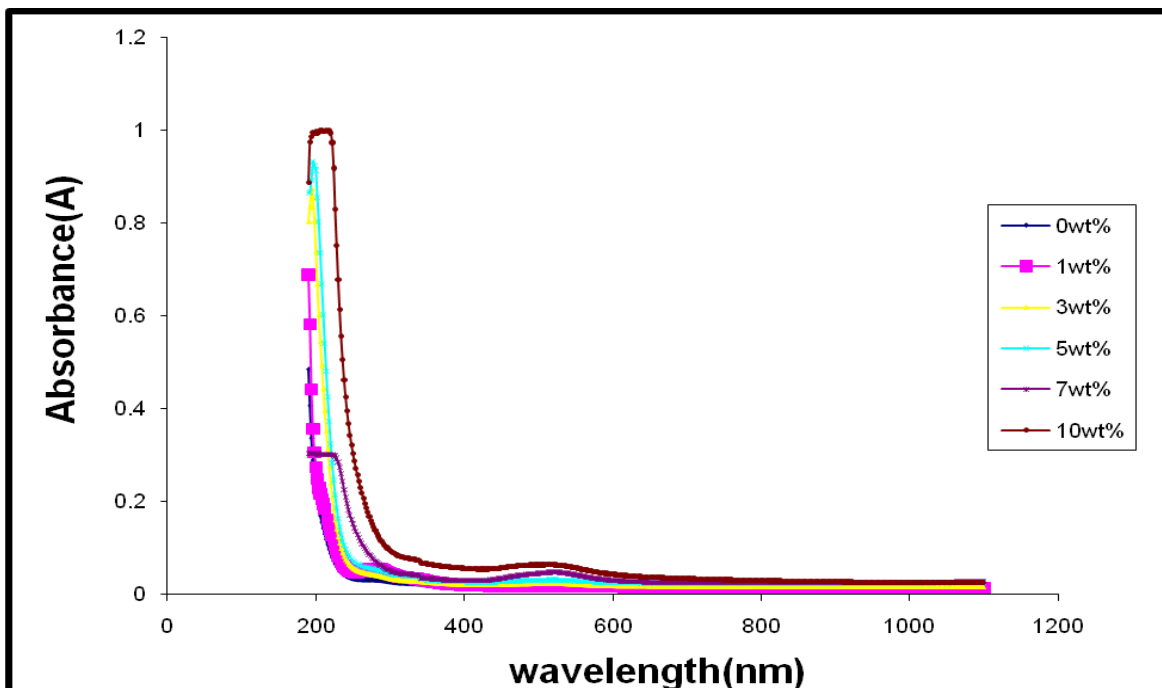


Figure (4-2) : The absorbance for (PVA-CoNO<sub>3</sub>) films as a function of the wavelength.

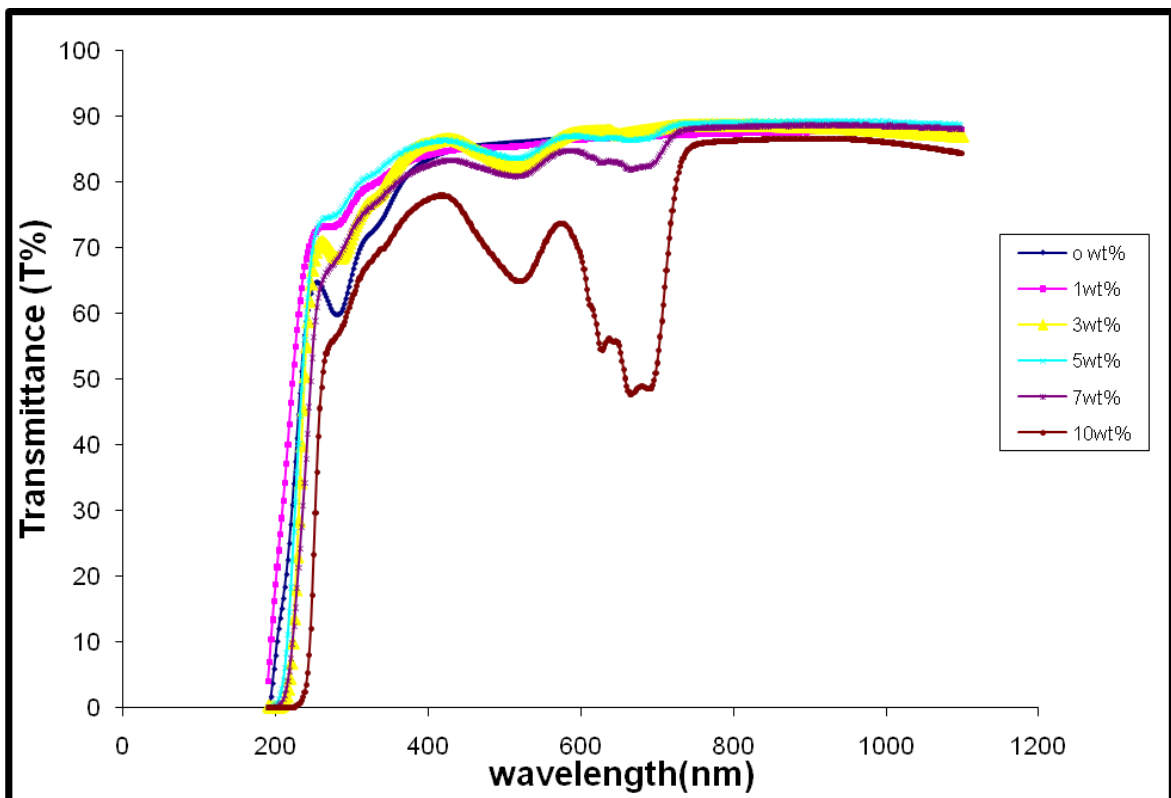


**Figure (4-3) : The absorbance for (PVA-CoCH<sub>3</sub>COOH) films as a function of the wavelength.**

#### 4-2-2 Transmission Spectrum

Figures (4-(4-6)) shows the optical transmission spectrum of (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films with different concentrations of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) salts as a function of the wavelength. The figures show that transmittance decreases with the increase of the weight percentage of the added (Cobalt chloride, Cobalt nitrate and Cobalt acetate). This is caused by the added (Cobalt chloride, Cobalt nitrate and Cobalt acetate) which contains electrons in its outer orbits which can absorb the electromagnetic energy of the incident light and electrons travel to higher energy levels. This process is not accompanied by emission of radiation because the traveled electron to higher levels have occupied vacant positions of energy bands, thus part of the incident light is absorbed by the substance and does not penetrate through it. On the other hand, the pure poly(vinyl

alcohol) has high transmittance because there are no free electrons (i.e. electrons are linked to atoms by covalent bonds). This is because the breaking of electron linkage and moving it to the conduction band need to photon with high energy [3].



**Figure (4-4): The transmittance for (PVA-CoCl<sub>2</sub>) films as a function of the wavelength.**

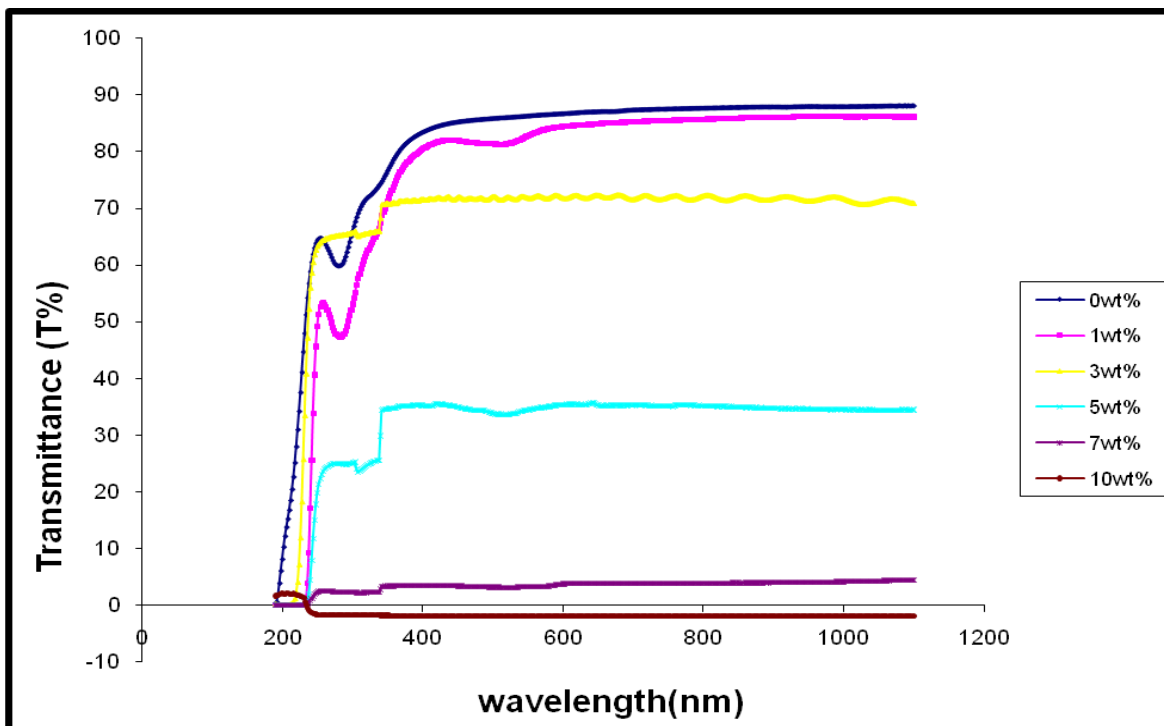


Figure (4-5): The transmittance for (PVA-CoNO<sub>3</sub>) films as a function of the wavelength.

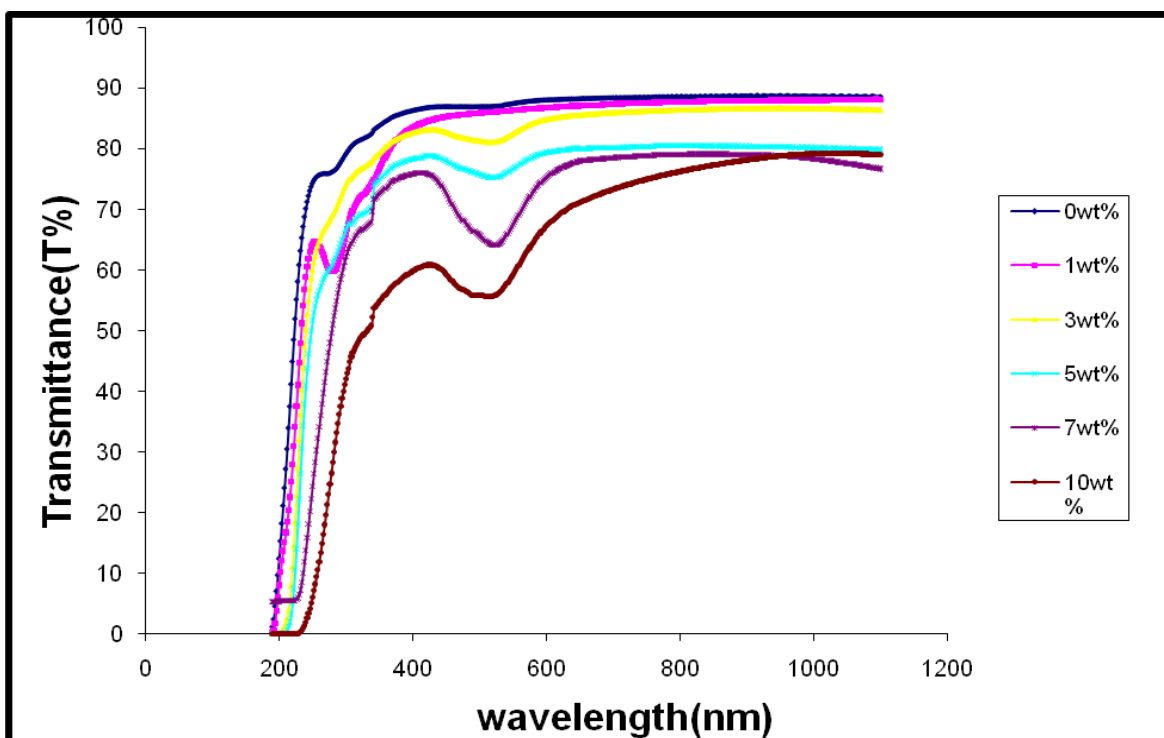


Figure (4-6): The transmittance for (PVA-CoCH<sub>3</sub>COOH) films as a function of the wavelength.

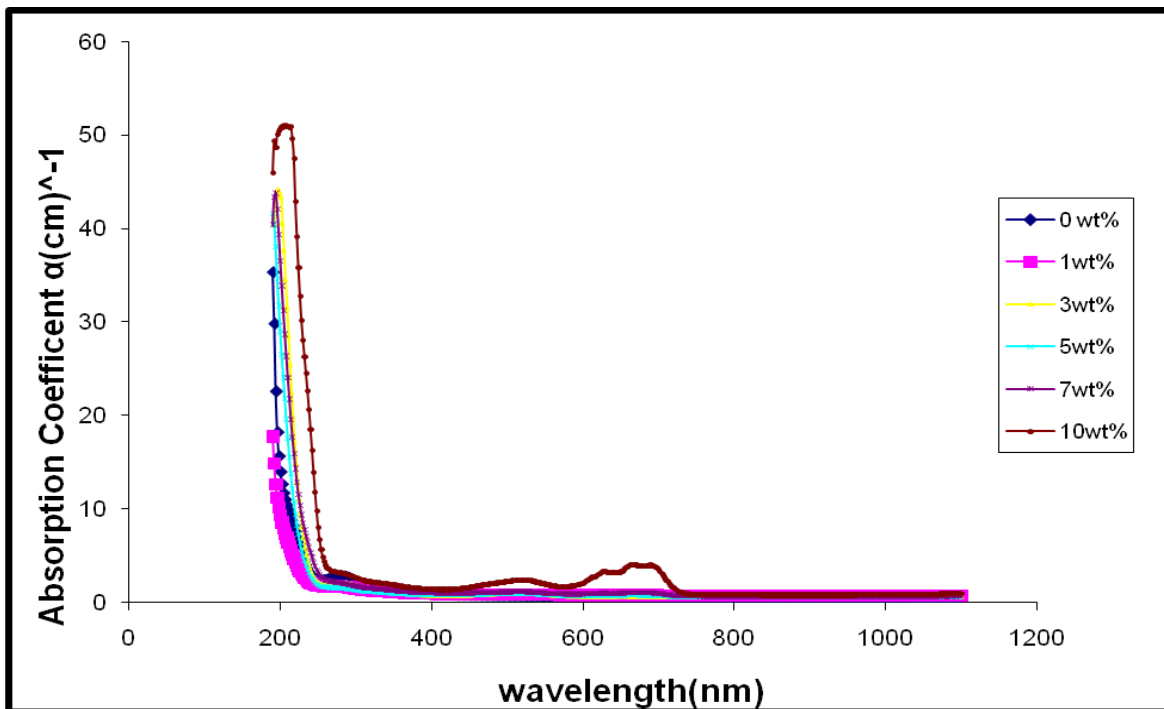
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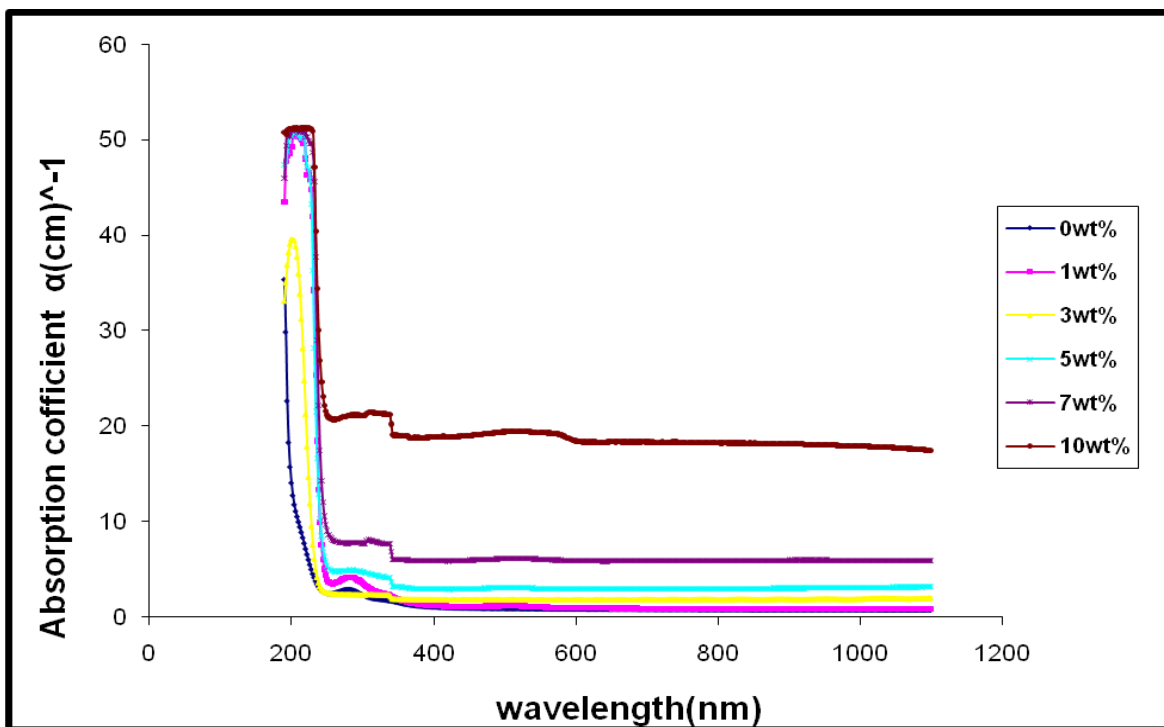
### 4-2-3 Absorption Coefficient

The absorption coefficient  $\alpha(\text{cm})^{-1}$  is calculated by using equation (2-9). Figures (4-(7-9)) show the absorption coefficient  $\alpha(\text{cm})^{-1}$  of (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films with different concentrations of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) salts as a function of the wavelength. It can be seen that the absorption is smallest at low energy. This means that the possibility of electron transition is low because the energy of the incident photon is not sufficient to move the electron from the valence band to the conduction band ( $h\nu < E_g$ ).

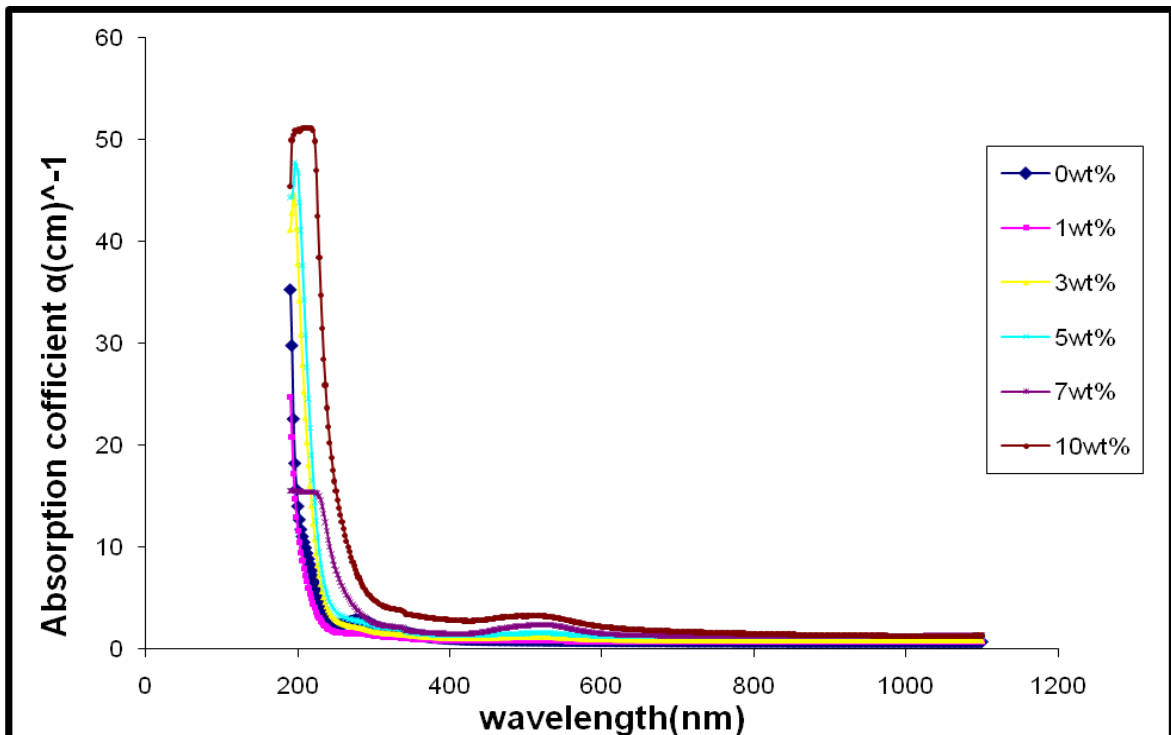
At high energies, absorption is high. This means that there is a high possibility for electron transition. Consequently, the energy of incident photon is enough to move the electron from the valence band to the conduction band, the energy of the incident photon is greater than the energy gap [3]. This shows that the absorption coefficient assists in figuring out the nature of electron transition, when the values of the absorption coefficient is high ( $\alpha > 10^4$ )  $\text{cm}^{-1}$ , it is expected that direct transition of electron occur, the energy and momentum are maintained by the electrons and photons. While, when the values of the absorption coefficient is low ( $\alpha < 10^4$ )  $\text{cm}^{-1}$ , it is expected that indirect transition of electron occurs, and the electronic momentum is maintained with the assistance of the phonon [46]. Among other results the absorption coefficient for the (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films is less than ( $10^4 \text{ cm}^{-1}$ ). This explains that the electron transition is indirect. We can also see from the figures (4-(7-9)) that the absorption coefficient increases with increasing the weight percentage of the added (Cobalt chloride, Cobalt nitrate and Cobalt acetate).



**Figure (4-7): The absorption coefficient  $\alpha(\text{cm})^{-1}$  for (PVA- $\text{CoCl}_2$ ) films as a function of the wavelength.**



**Figure (4-8): The absorption coefficient  $\alpha(\text{cm})^{-1}$  for (PVA- $\text{CoNO}_3$ ) films as a function of the wavelength.**



**Figure (4-9): The absorption coefficient  $\alpha(\text{cm})^{-1}$  for (PVA-CoCH<sub>3</sub>COOH) films as a function of the wavelength.**

#### **4-2-4 Energy gaps of the indirect (allowed and forbidden Transition )**

Both the allowed and forbidden indirect transition energy gap have been calculated by using equation (2-10). When the value of ( $m = 2$ ), the allowed indirect transition energy gap is calculated, and when the value of ( $m = 3$ ), the forbidden indirect transition energy gap is calculated.

Figures (4-(10-25)) show the relation between  $(\alpha h\nu)^{1/2}$  for (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films with different concentrations of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) salts as a function of the photon energy. On drawing a straight line from the upper part of the curve toward the (x) axis at



the value  $(\alpha h\nu)^{1/2} = 0$  we get the energy gap for the allowed indirect transition. The obtained values are shown in tables (4-(1-3)).

We can see that the values of energy gap decrease with the increase of the weight percentage of the added (Cobalt chloride, Cobalt nitrate and Cobalt acetate). This is attributed to the creation of on site levels in the energy gap, the transition in this case is conducted in two stages that involve the transition of electron from the valence band to the local levels and to the conduction band as a result of increasing the added weight percentage. This behavior is attributed to the fact that composites are of heterogeneous type (i.e. the electronic conduction depends on added impurities). The increase of the added rate provides electronic paths in the polymer which facilitate the crossing of electron from the valence band to the conduction band. This explains the decrease of energy gap with the increase of the weight percentage of the add (Cobalt chloride, Cobalt nitrate and Cobalt acetate) [3,10], our results are nearly in agreement with the results obtained by Abd allh et al. [34] .

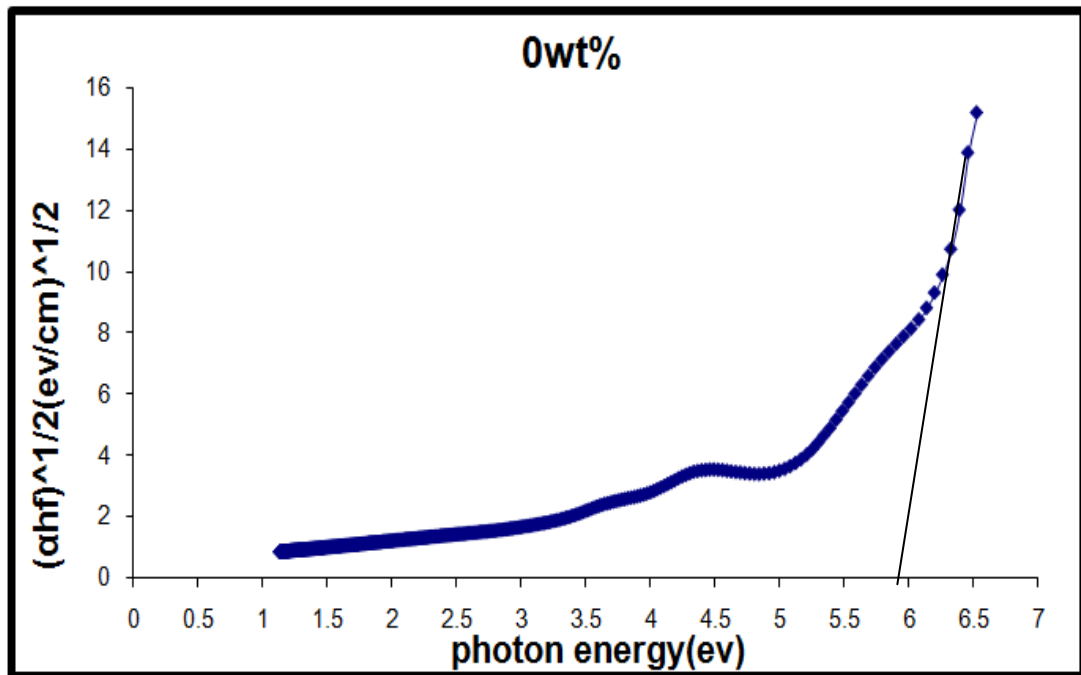


Figure (4-10) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA) film.

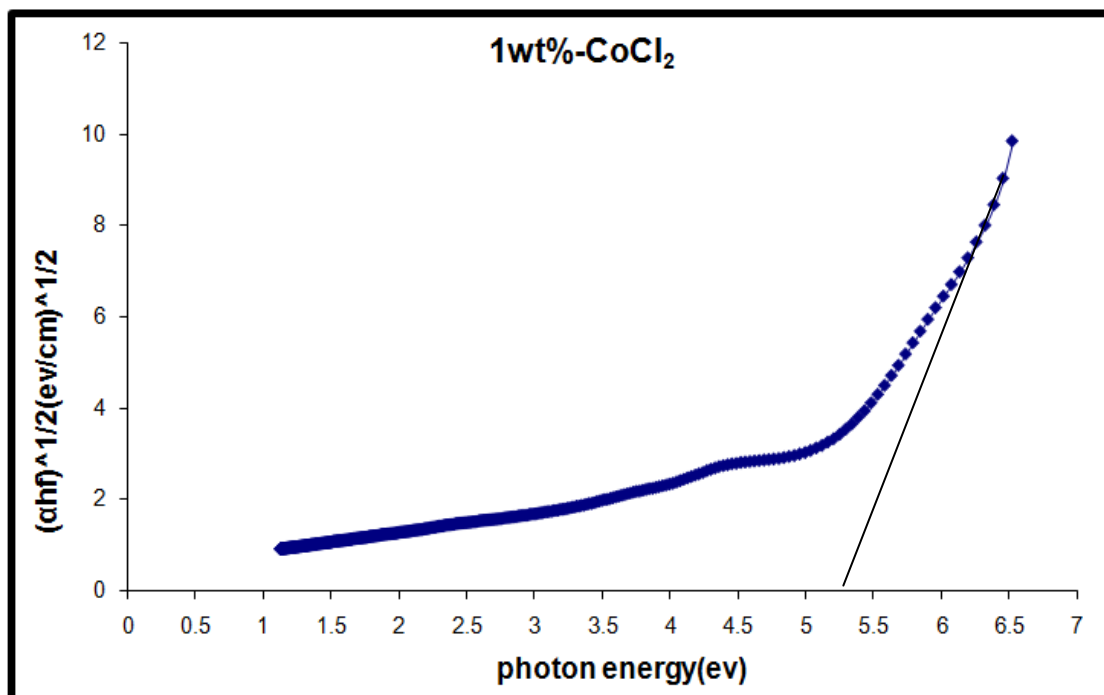


Figure (4-11) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoCl}_2$ ) film (1wt%).

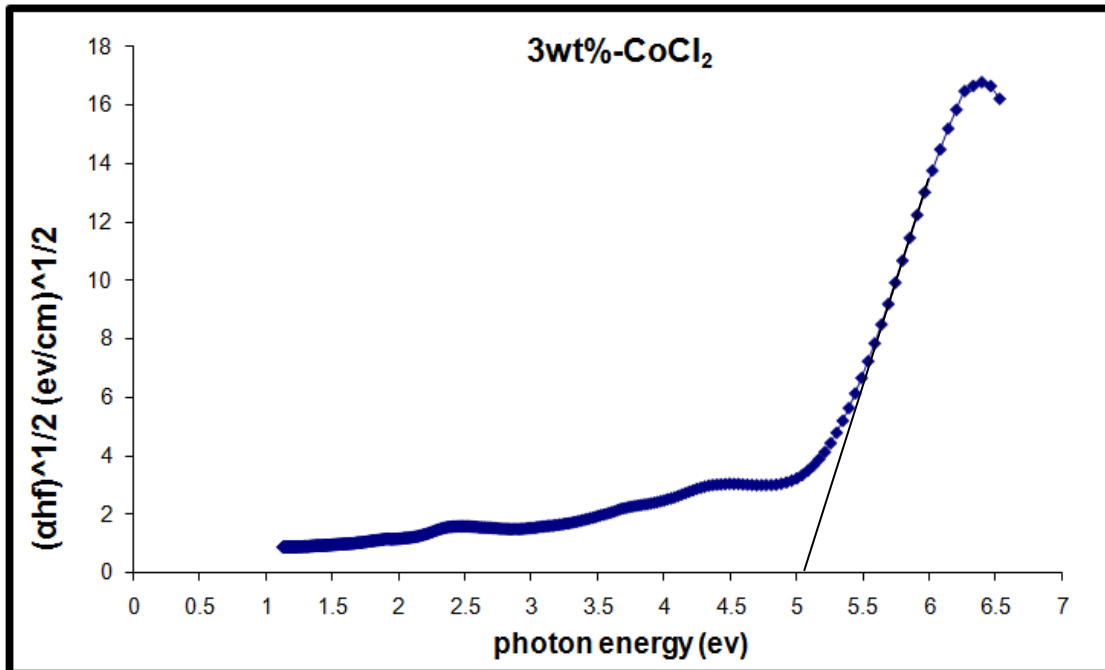


Figure (4-12) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoCl}_2$ ) film (3wt%).

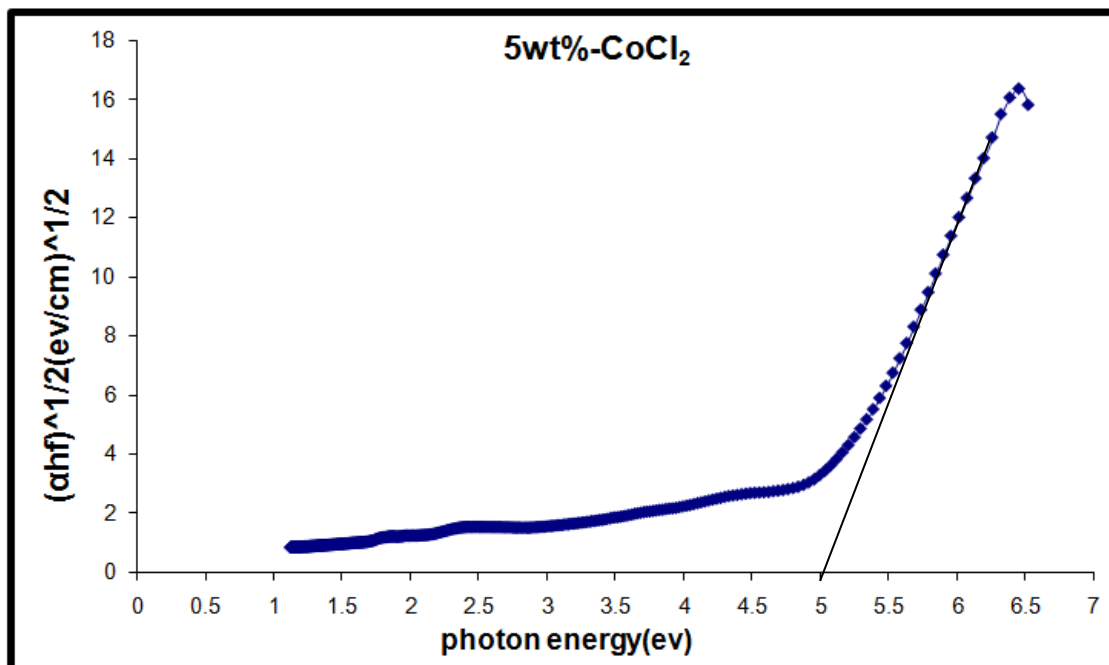


Figure (4-13) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoCl}_2$ ) film (5wt%).

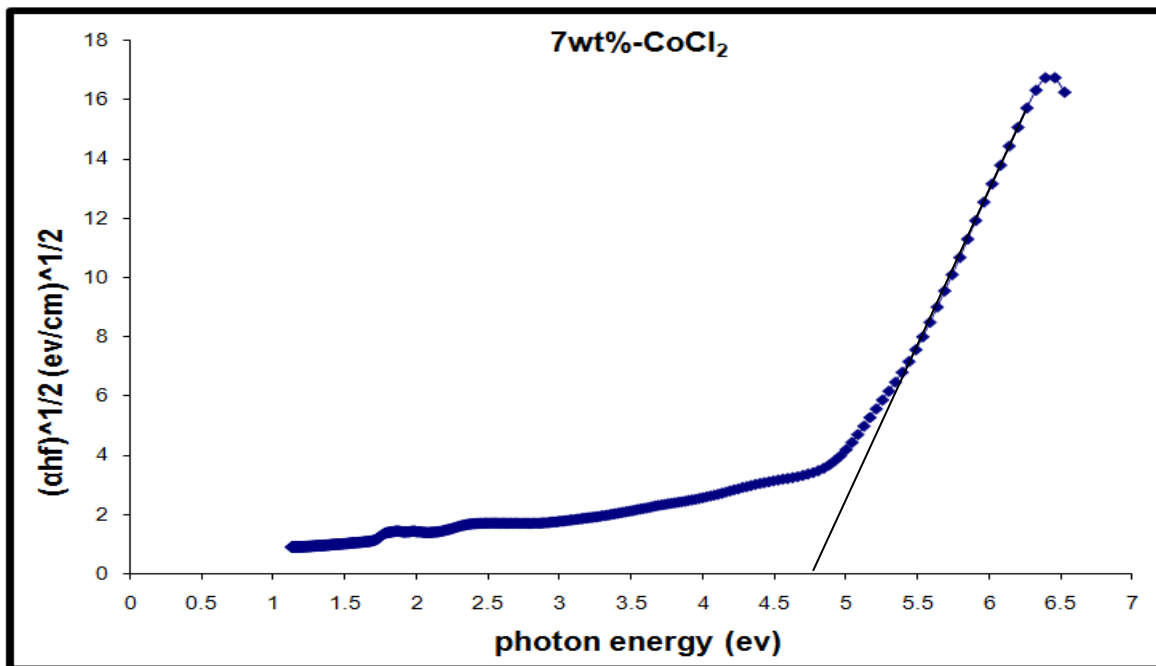


Figure (4-14) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoCl}_2$ ) film (7wt%).

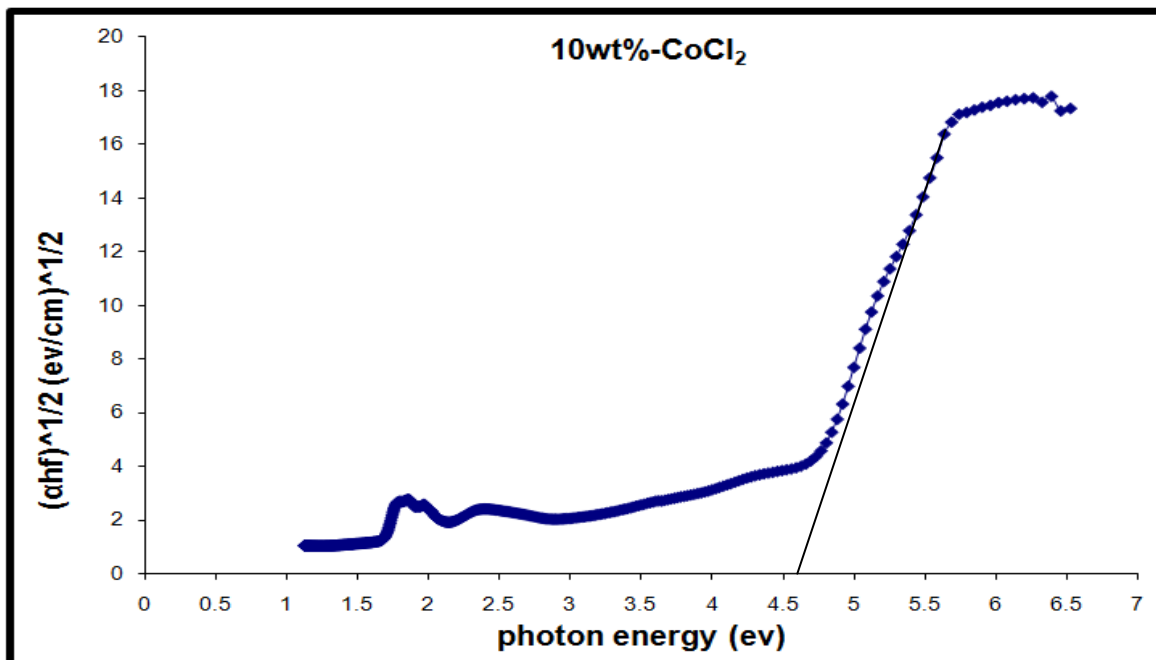


Figure (4-15) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoCl}_2$ ) film (10wt%).

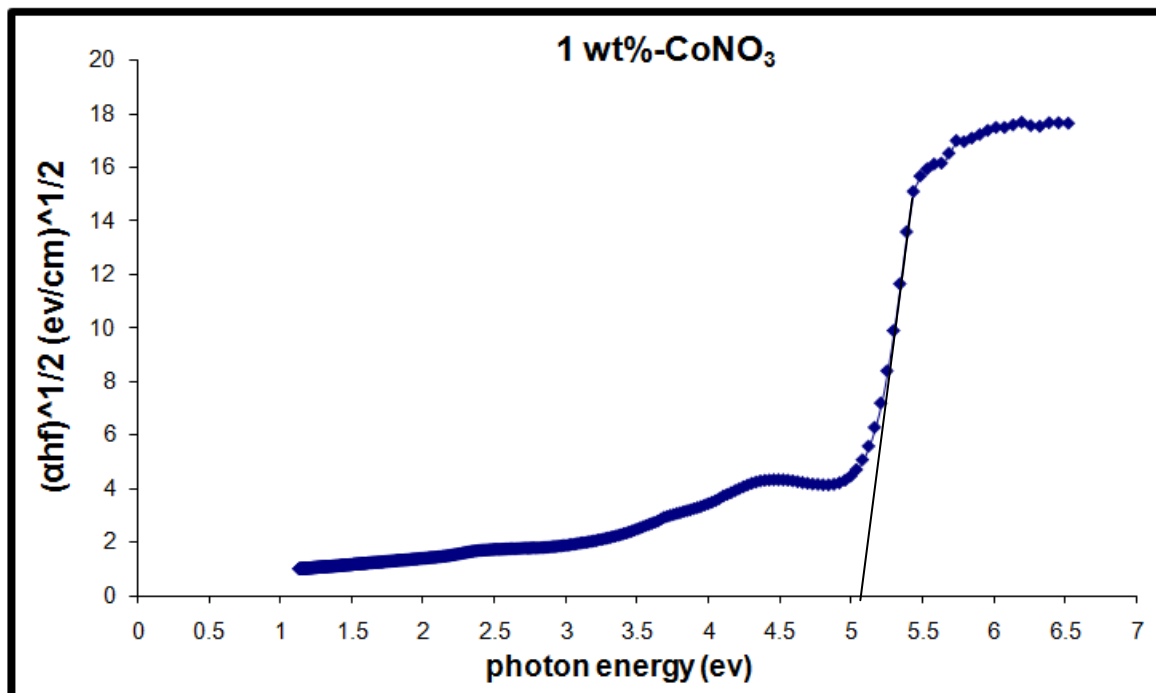


Figure (4-16) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoNO}_3$ ) film (1wt%).

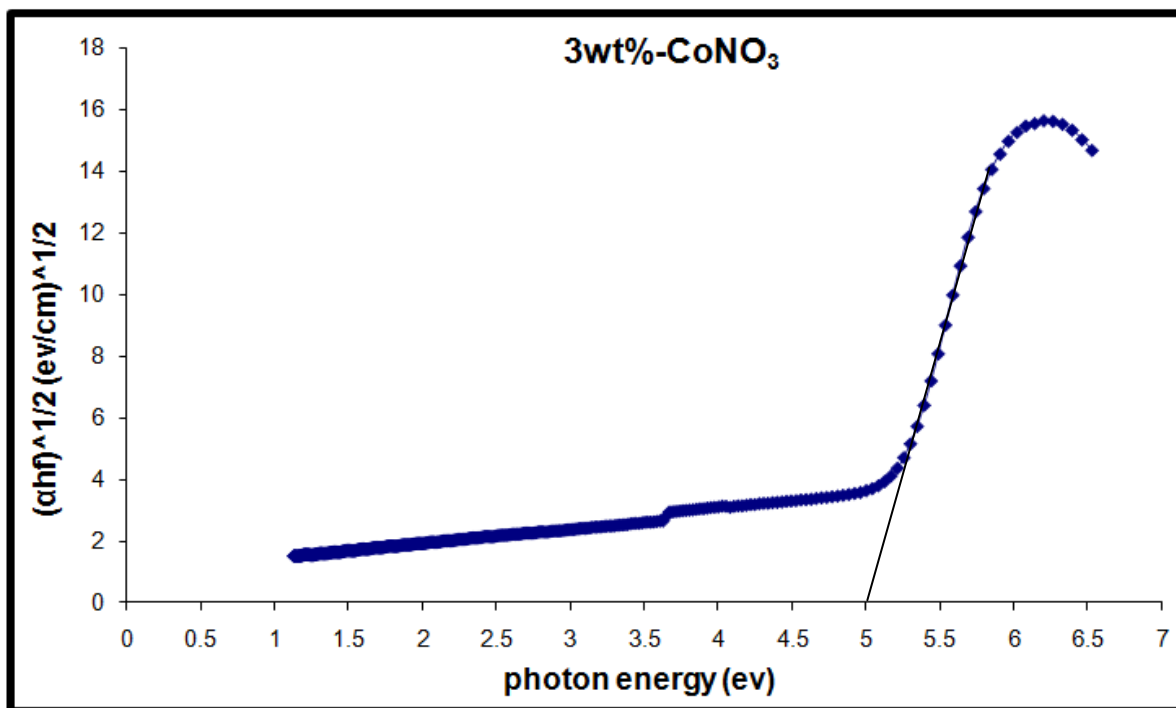


Figure (4-17) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoNO}_3$ ) film (3wt%).

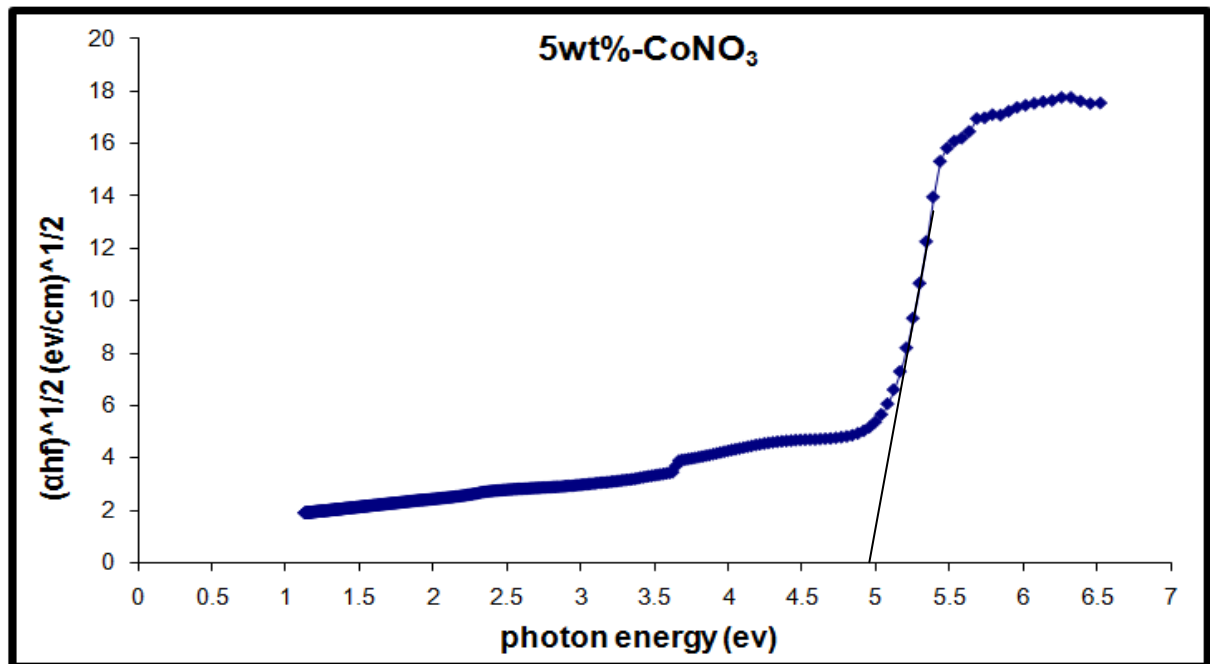


Figure (4-18) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoNO}_3$ ) film (5wt%).

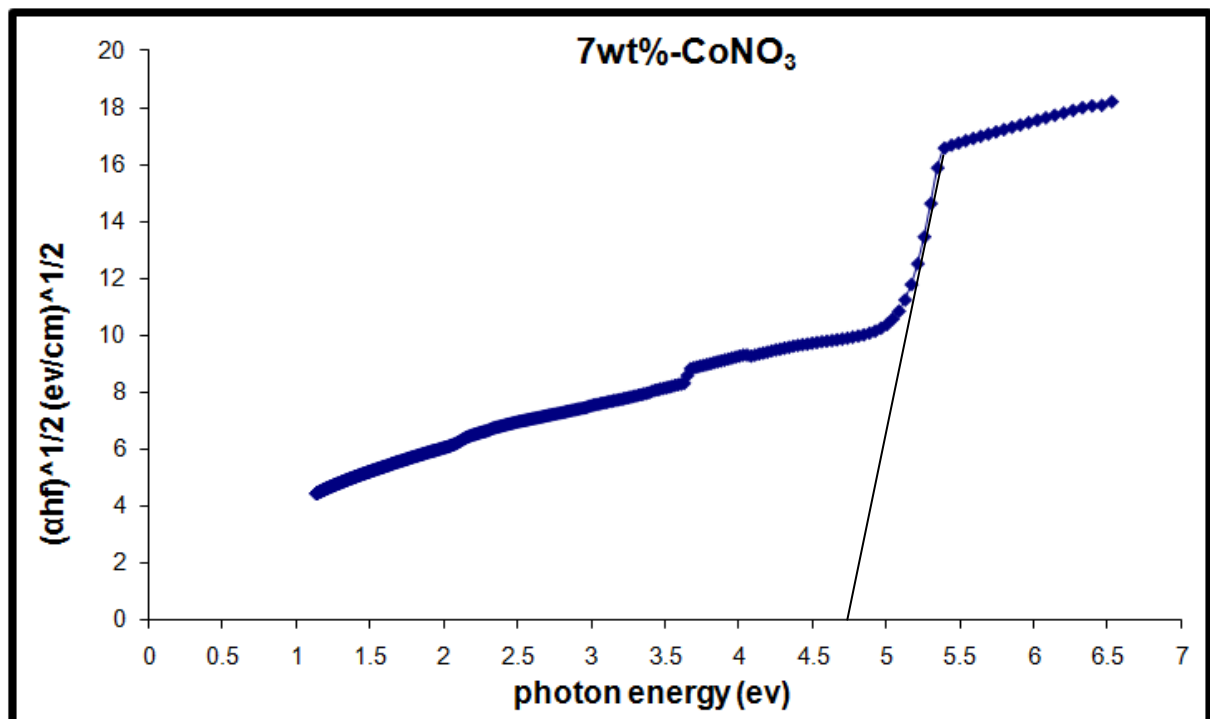


Figure (4-19) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoNO}_3$ ) film (7wt%).

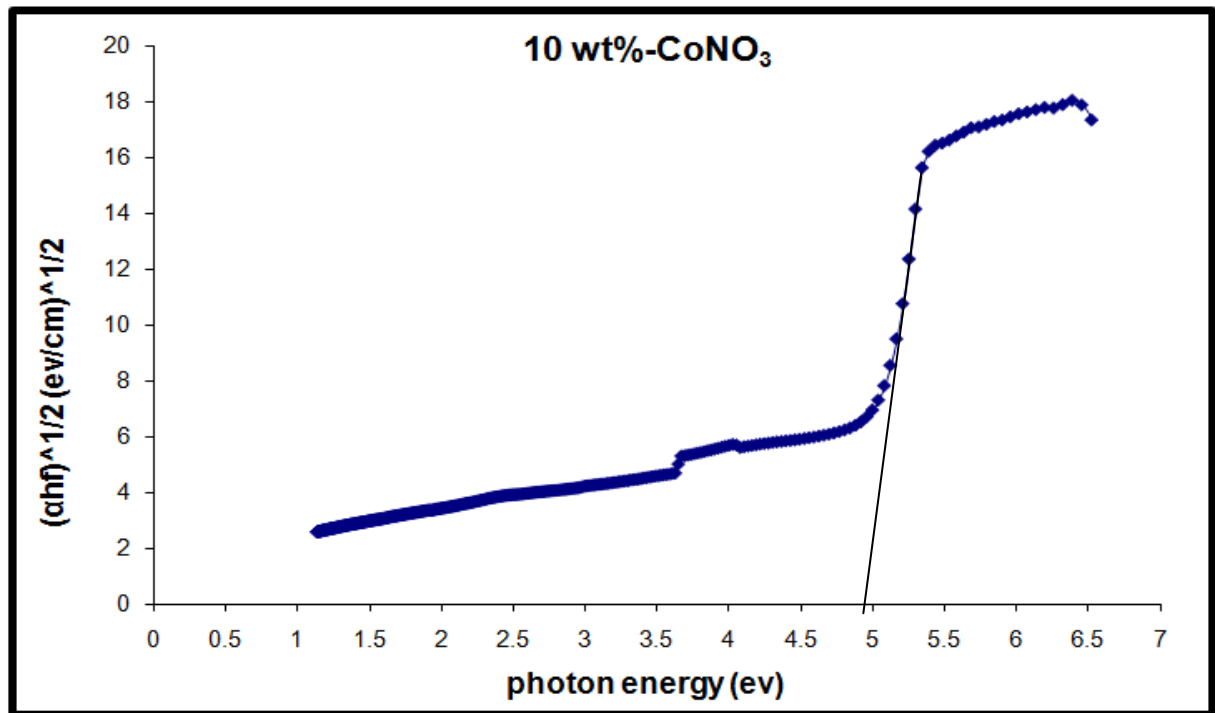


Figure (4-20) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoNO}_3$ ) film (10wt%).

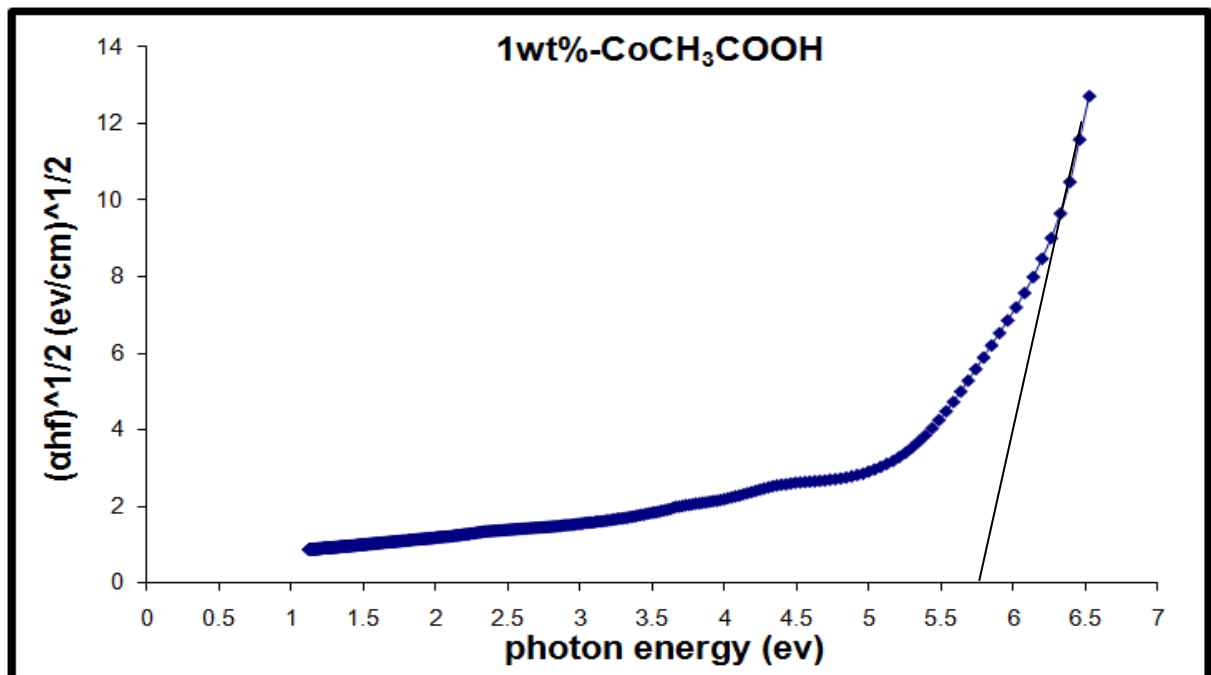


Figure (4-21) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoCH}_3\text{COOH}$ ) film (1wt%).

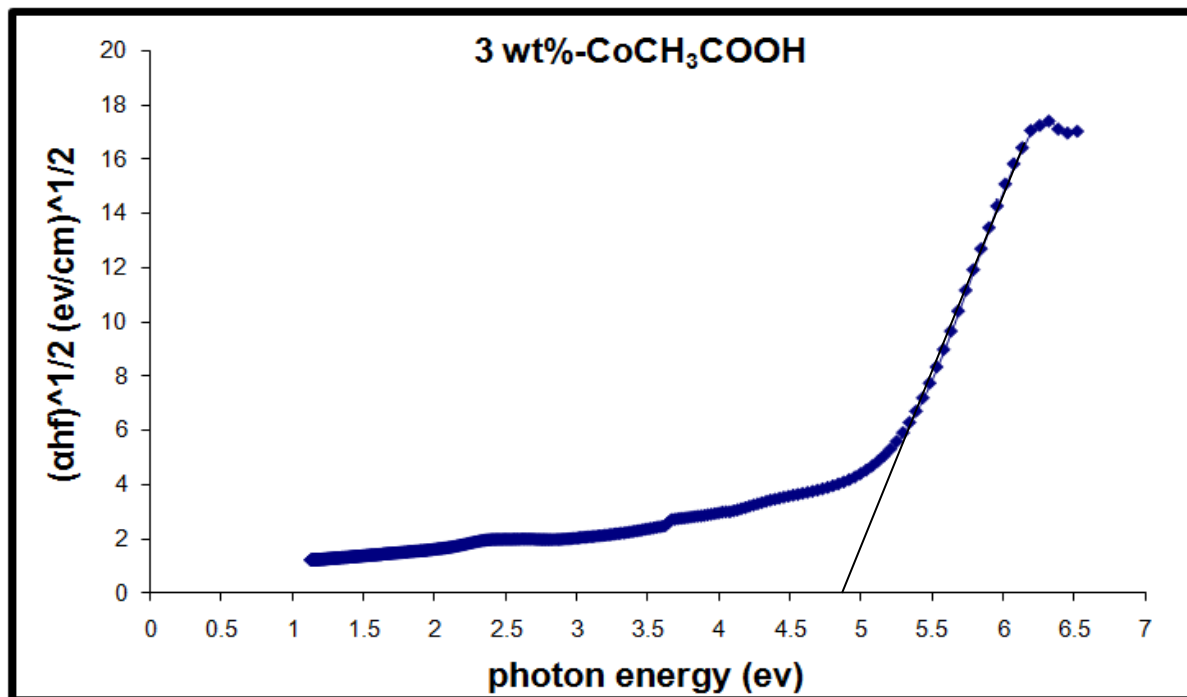


Figure (4-22) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoCH}_3\text{COOH}$ ) film (3wt%).

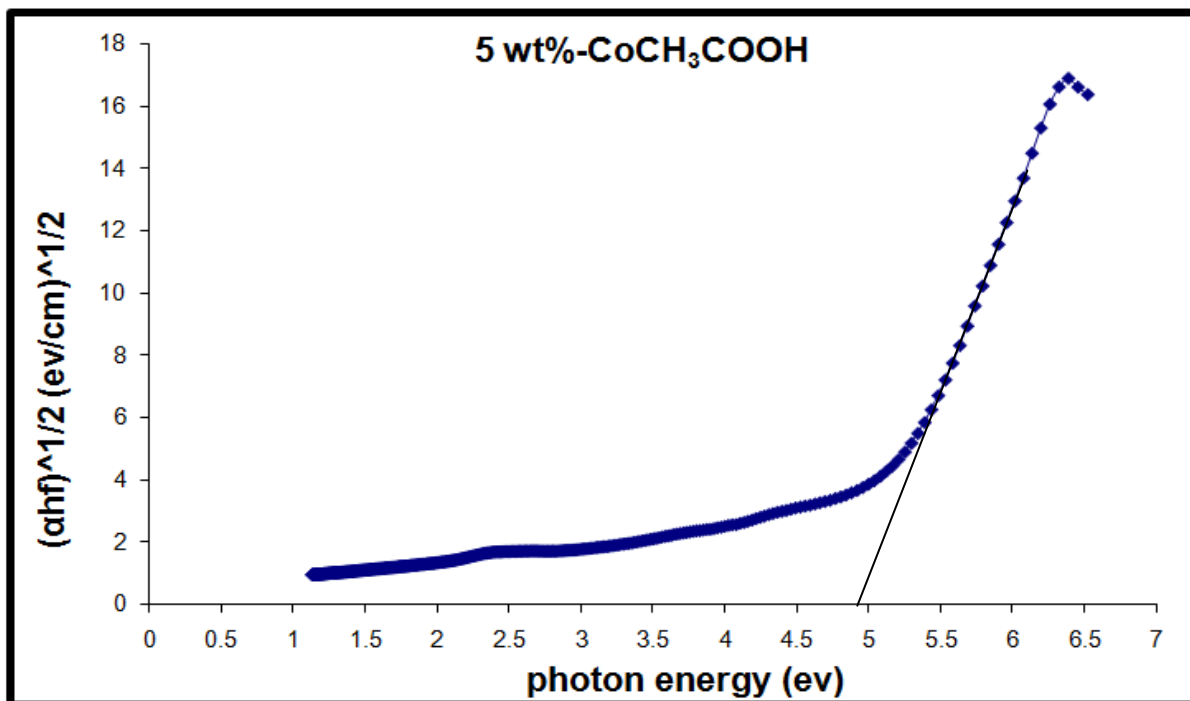


Figure (4-23) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoCH}_3\text{COOH}$ ) film (5wt%).



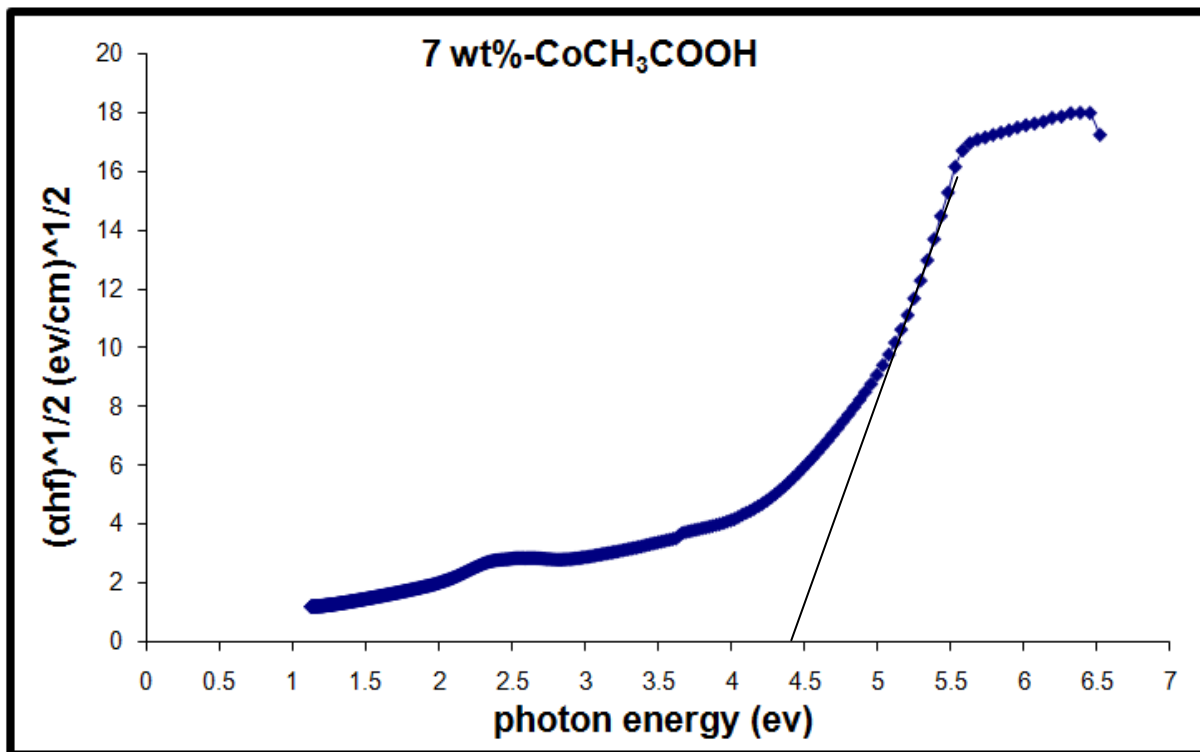


Figure (4-24) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoCH}_3\text{COOH}$ ) film (7wt%).

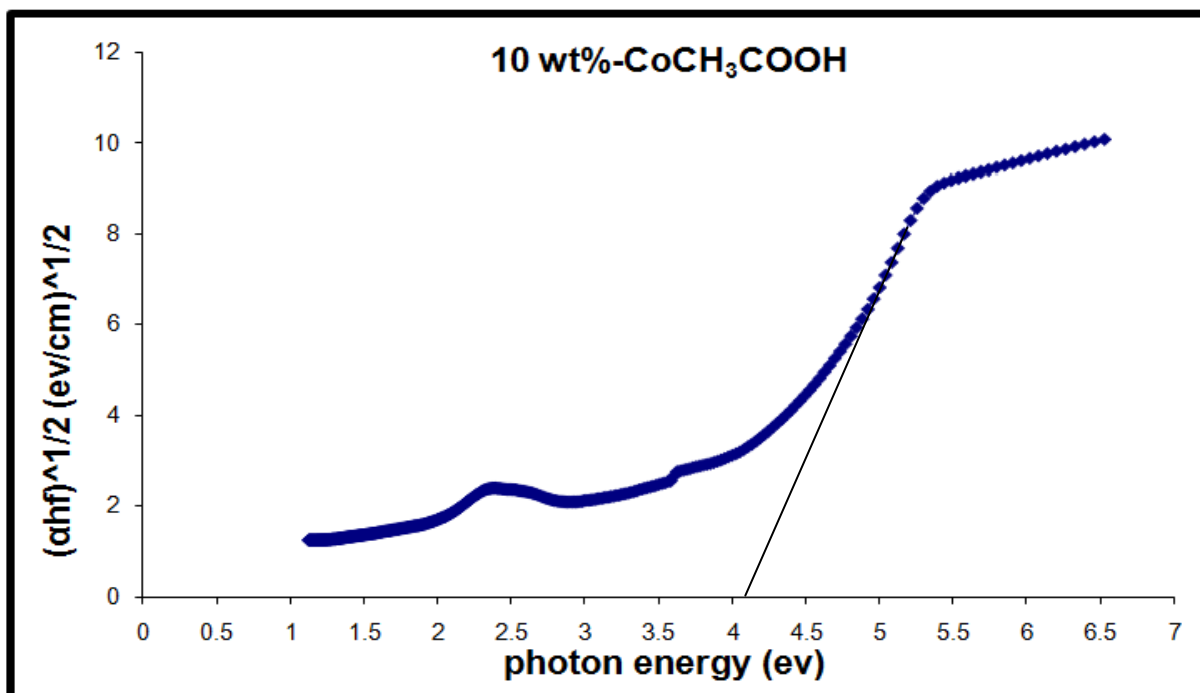


Figure (4-25) : The energy gap for the allowed indirect transition as a function of the photon energy for (PVA- $\text{CoCH}_3\text{COOH}$ ) film (10wt%).

Table (4-1)

The values of energy gap for the allowed indirect transition for (PVA-CoCl<sub>2</sub>) films.

CoCl <sub>2</sub> wt%	E <sub>g</sub> (eV)
	Allowed
Pure (PVA)	5.9
1	5.4
3	5.1
5	4.9
7	4.7
10	4.5

Table (4-2)

The values of energy gap for the allowed indirect transition for (PVA-CoNO<sub>3</sub>) films.

CoNO <sub>3</sub> wt%	E <sub>g</sub> (eV)
	Allowed
Pure (PVA)	5.9
1	5.1
3	5
5	4.9
7	4.7
10	4.9

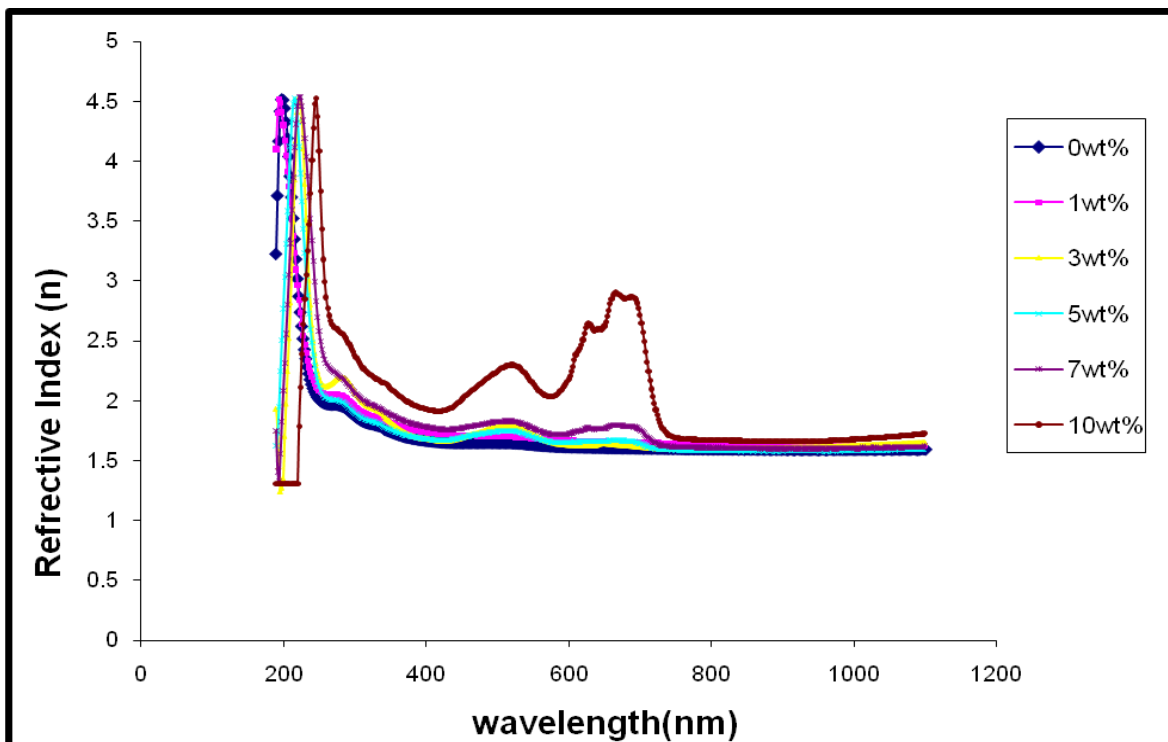
**Table (4-3)**

**The values of energy gap for the allowed indirect transition for (PVA-  
CoCH<sub>3</sub>COOH) films.**

<b>CoCH<sub>3</sub>COOH wt%</b>	<b>E<sub>g</sub>(eV)</b>
	<b>Allowed</b>
<b>Pure (PVA)</b>	<b>5.9</b>
<b>1</b>	<b>5.7</b>
<b>3</b>	<b>4.9</b>
<b>5</b>	<b>4.8</b>
<b>7</b>	<b>4.4</b>
<b>10</b>	<b>4.2</b>

#### 4-2-5 Refractive Index

The refractive index ( $n$ ) is calculated from equation (2-14). Figures (4-26-28) which show the change of refractive index for (PVA- ( $\text{CoCl}_2$ ,  $\text{CoNO}_3$  and  $\text{CoCH}_3\text{COOH}$ )) films with different concentrations of ( $\text{CoCl}_2$ ,  $\text{CoNO}_3$  and  $\text{CoCH}_3\text{COOH}$ ) salts as a function of the wavelength. From the figures we can see that the refractive index increases with increasing the weight percentage of the added (Cobalt chloride, Cobalt nitrate and Cobalt acetate). The reason for this result is increase of the number of free electrons [25].



**Figure (4-26) : The refractive index for (PVA- $\text{CoCl}_2$ ) films as a function of the wavelength.**

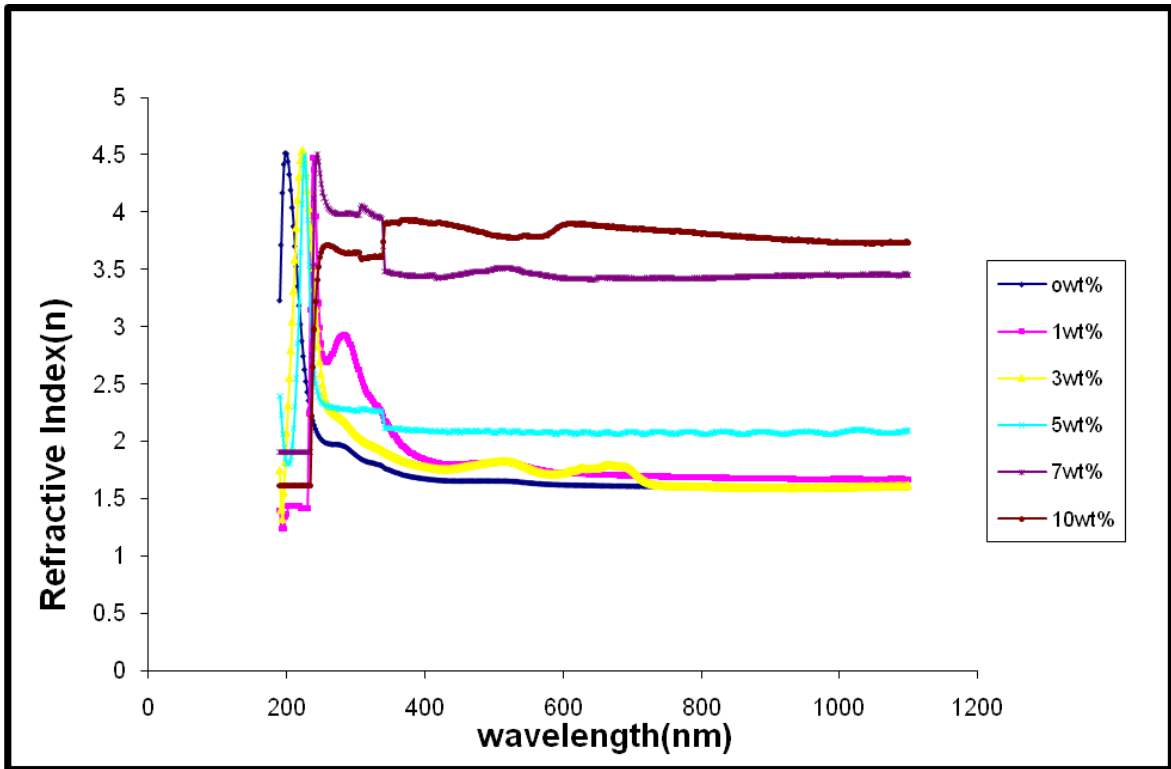


Figure (4-27) : The refractive index for (PVA-CoNO<sub>3</sub>) films as a function of the wavelength.

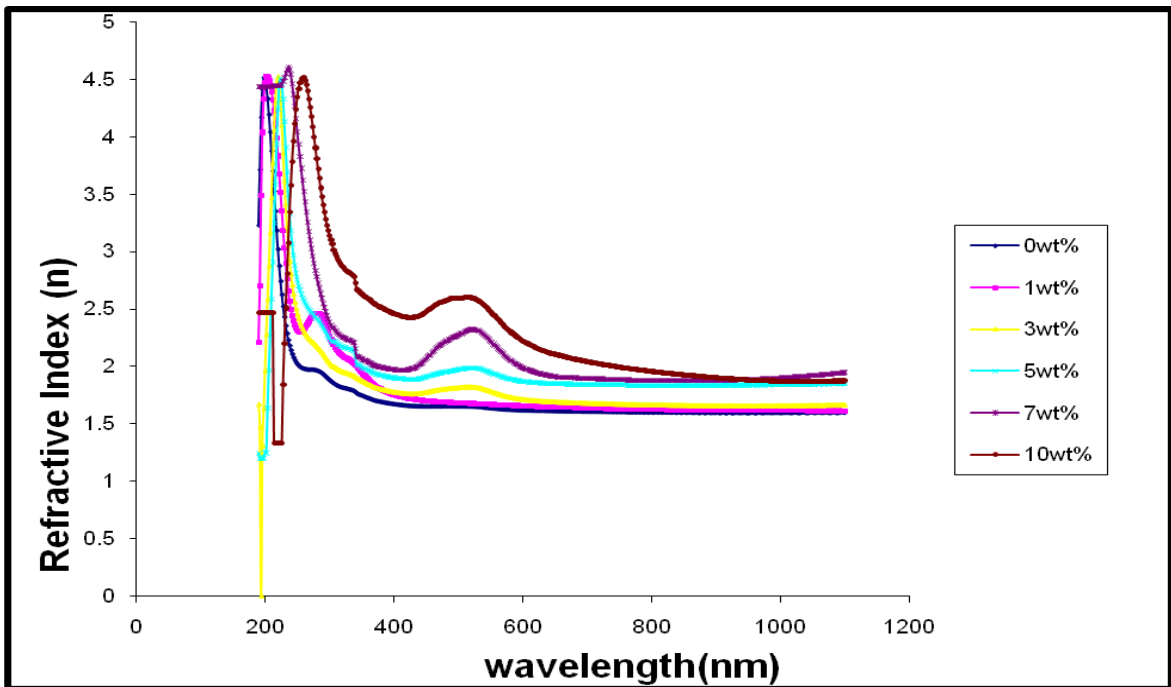


Figure (4-28) : The refractive index for (PVA-CoCH<sub>3</sub>COOH) films as a function of the wavelength.

#### 4-2-6 Extinction Coefficient

Extinction coefficient ( $k$ ) is calculated by using equation (2-16). The change of the extinction coefficient for (PVA-(CoCl<sub>2</sub>,CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films with different concentrations of (CoCl<sub>2</sub>,CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) salts as a function of the wavelength is shown in figures (4-(29-31)). It can be noted that extinction coefficient is of lowering values at low concentrations, but it increases with increasing the weight percentage of the added (Cobalt chloride, Cobalt nitrate and Cobalt acetate). This is attributed to increased absorption coefficient with increased percentage of added (Cobalt chloride, Cobalt nitrate and Cobalt acetate) .

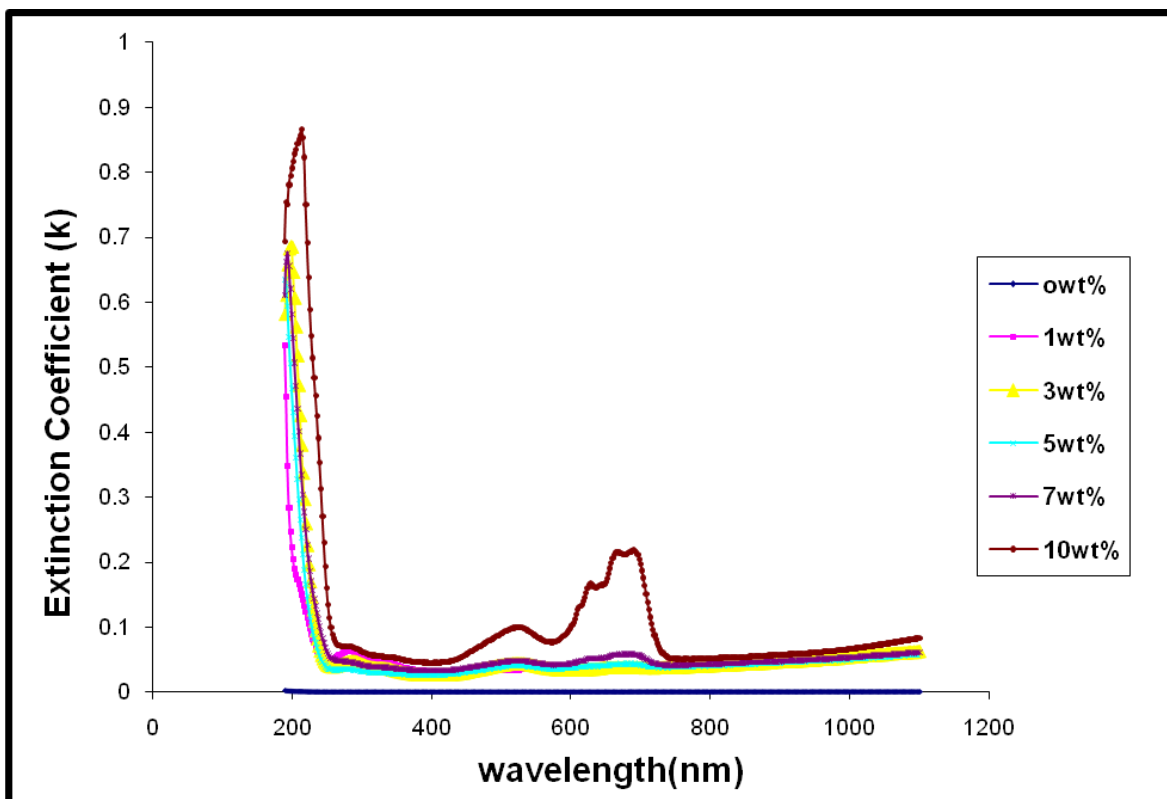


Figure (4-29) :The Extinction coefficient for (PVA-CoCl<sub>2</sub>) films as a function of the wavelength.

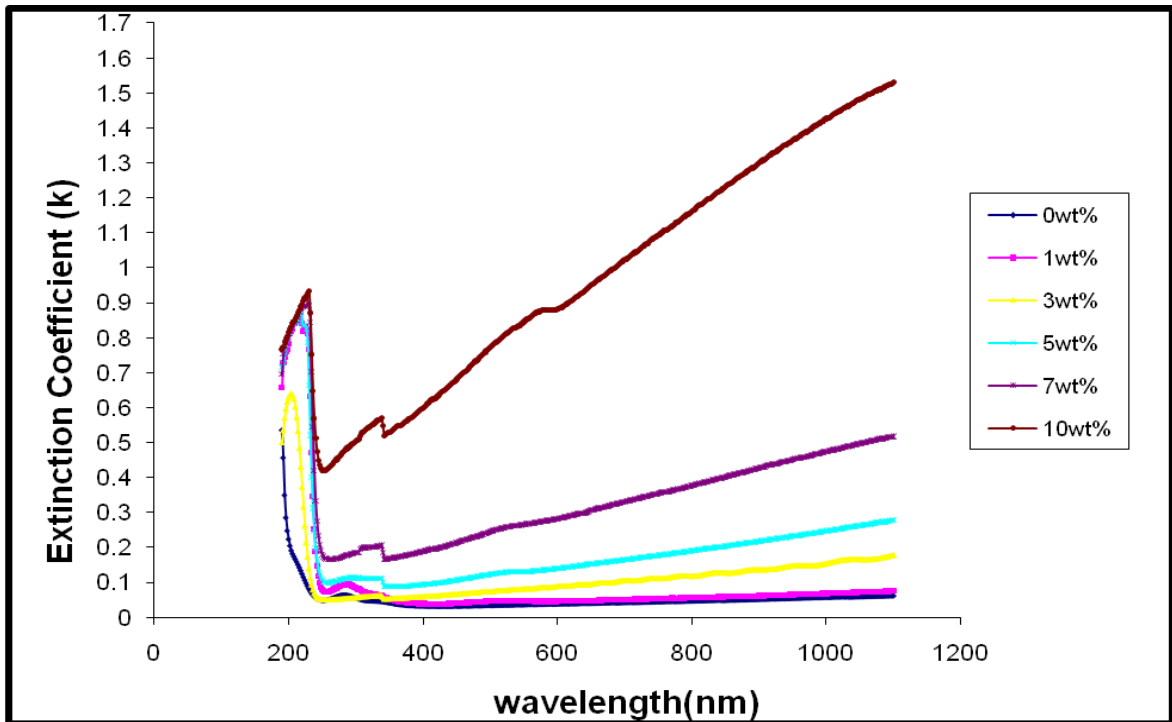


Figure (4-30) :The Extinction coefficient for (PVA-CoNO<sub>3</sub>) films as a function of the wavelength.

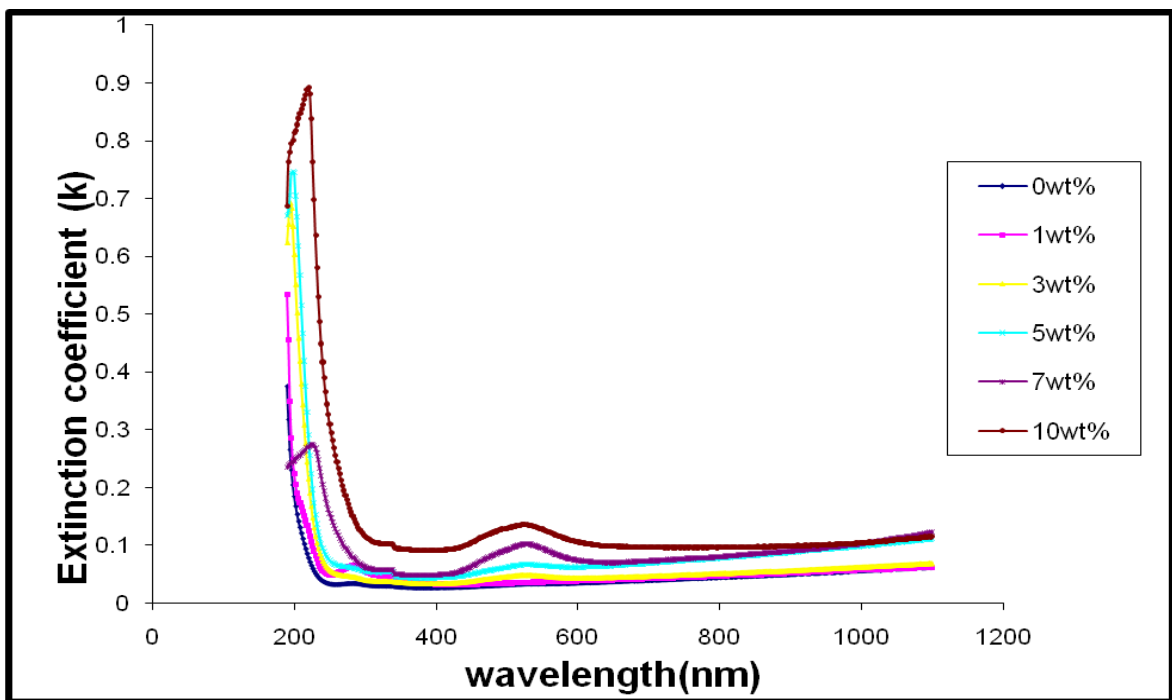


Figure (4-31) :The Extinction coefficient for (PVA-CoCH<sub>3</sub>COOH) films as a function of the wavelength.

#### 4-2-7 Real and Imaginary Part of Dielectric Constant

The real and imaginary part of dielectric constant ( $\epsilon_1, \epsilon_2$ ) for (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films with different concentrations of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) salts have been calculated by using equations (2-20) and (2-21), respectively. Figures (4-(32-37)) show the change of ( $\epsilon_1, \epsilon_2$ ) as a function of the wavelength. It can be seen that ( $\epsilon_1$ ) and ( $\epsilon_2$ ) increase with increasing the weight percentage of the added (Cobalt chloride, Cobalt nitrate and Cobalt acetate), and this behavior is similar to ( $n$ ) and ( $k$ ) because ( $\epsilon_1$ ) depends on ( $n^2$ ) due to low value of ( $k^2$ ), while ( $\epsilon_2$ ) is dependent on ( $k$ ) value that change with the change of the absorption coefficient due to the relation between ( $\alpha$ ) and ( $k$ ).

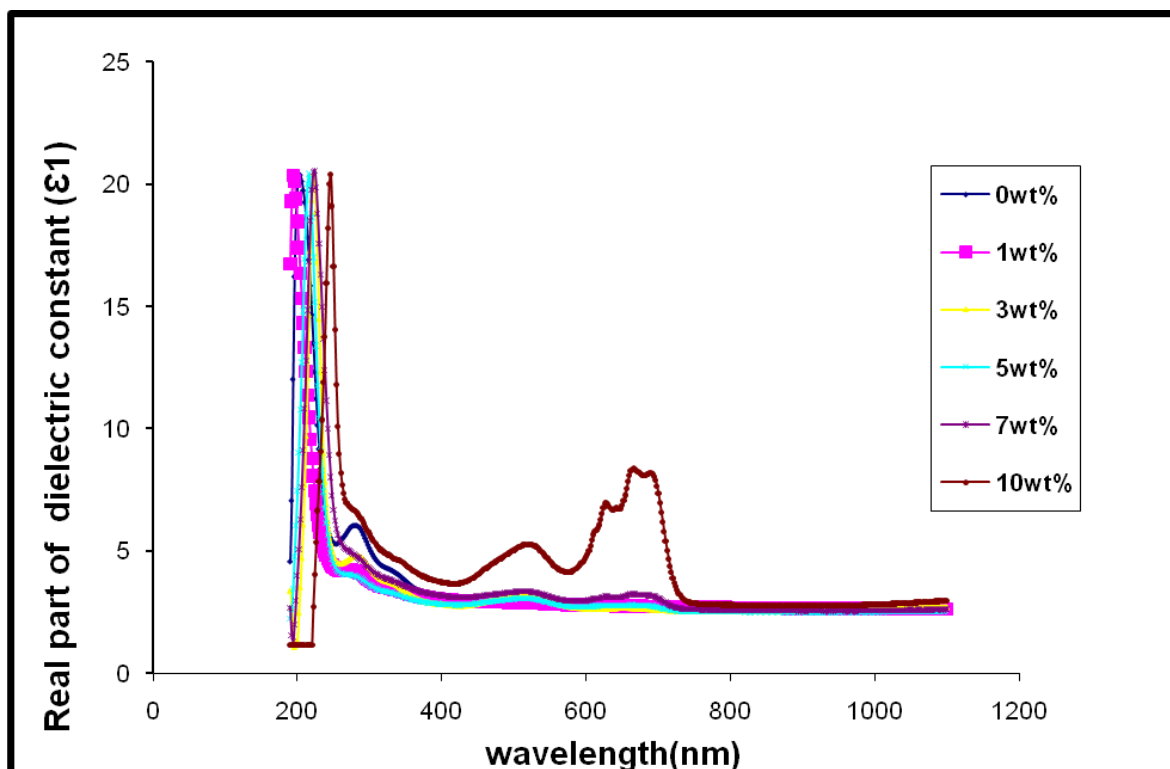


Figure (4-32): The real part of dielectric constant for (PVA-CoCl<sub>2</sub>) films as a function of the wavelength.



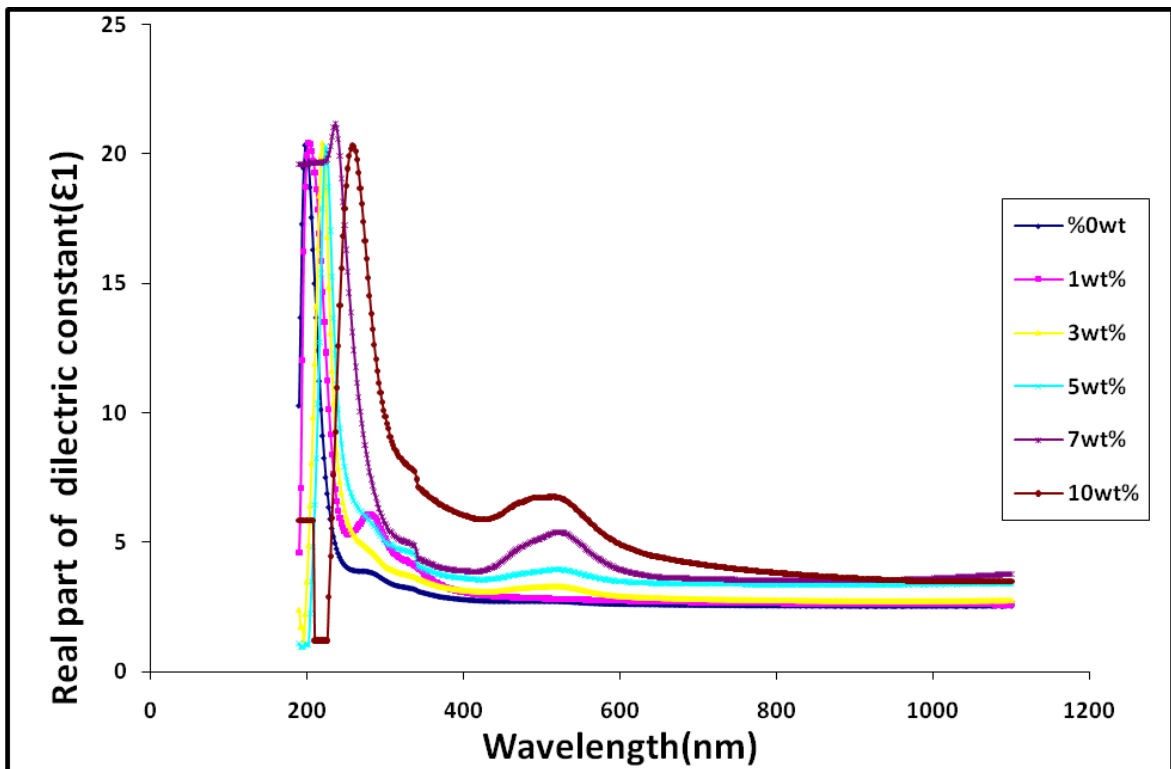


Figure (4-33): The real part of dielectric constant for (PVA- $\text{CoNO}_3$ ) films as a function of the wavelength.

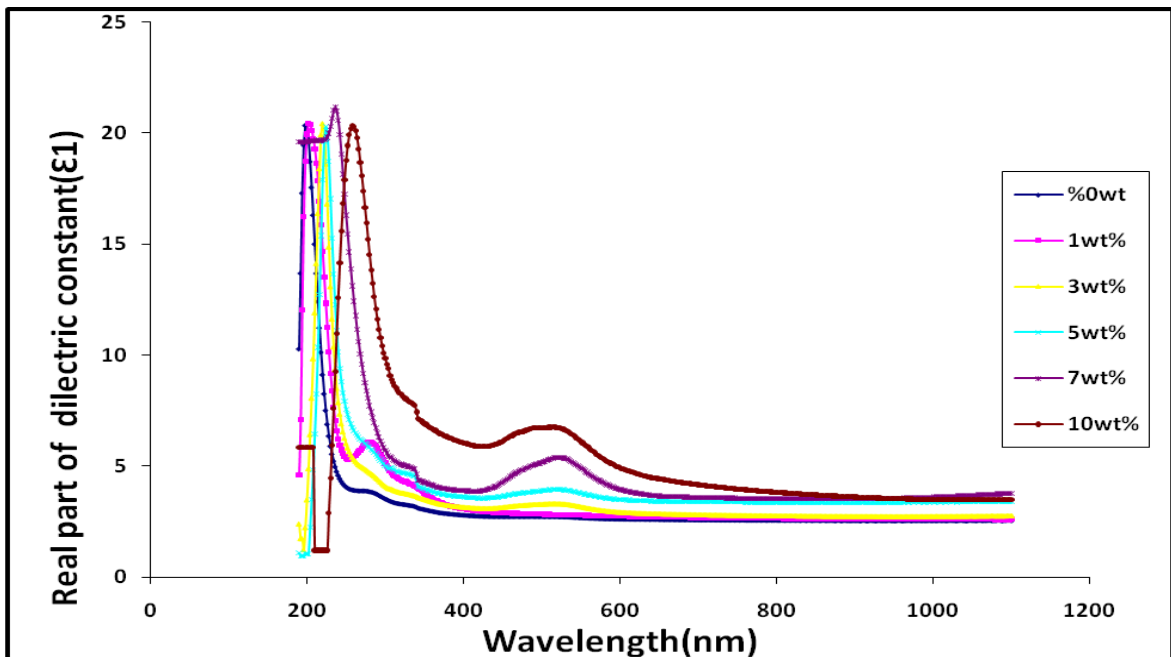


Figure (4-34): The real part of dielectric constant for (PVA- $\text{CoCH}_3\text{COOH}$ ) films as a function of the wavelength.

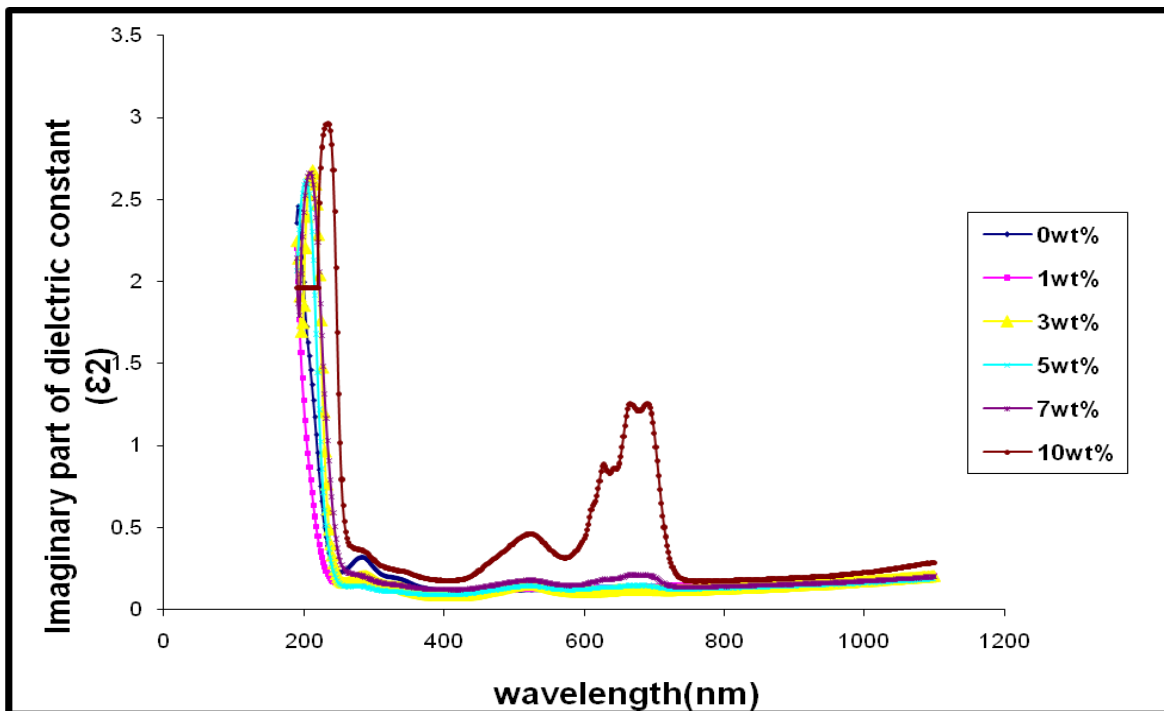


Figure (4-35): The imaginary part of dielectric constant for (PVA-CoCl<sub>2</sub>) films as a function of the wavelength.

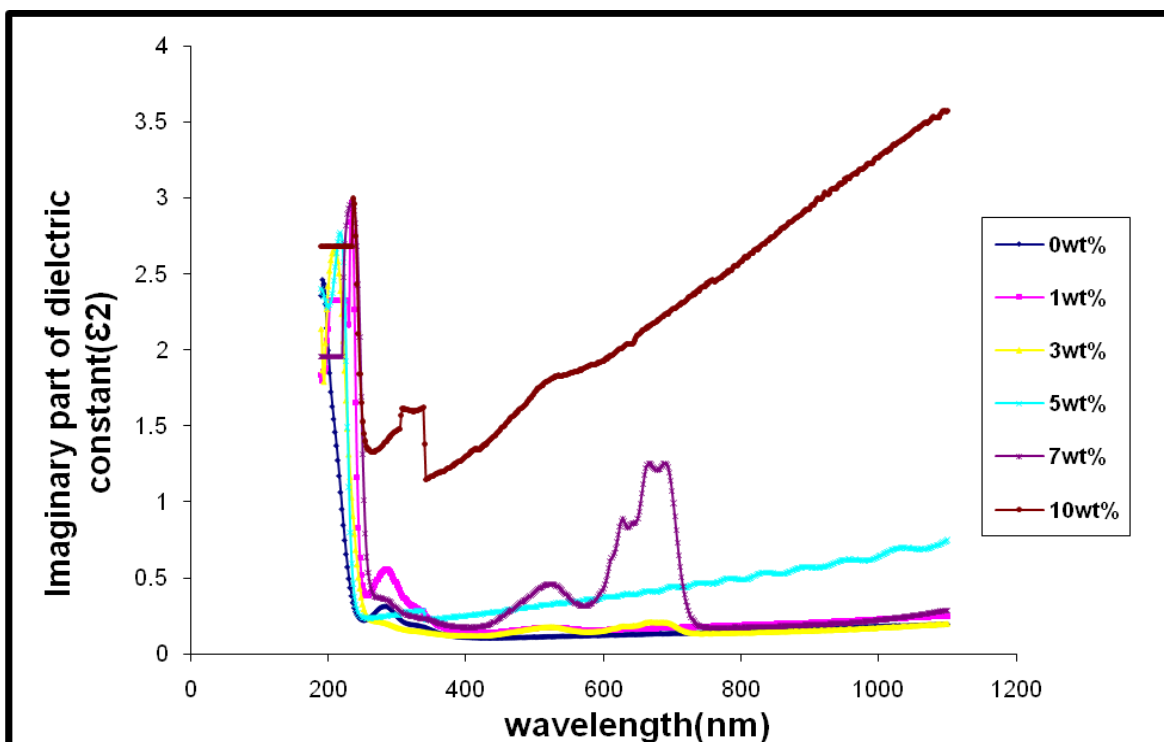
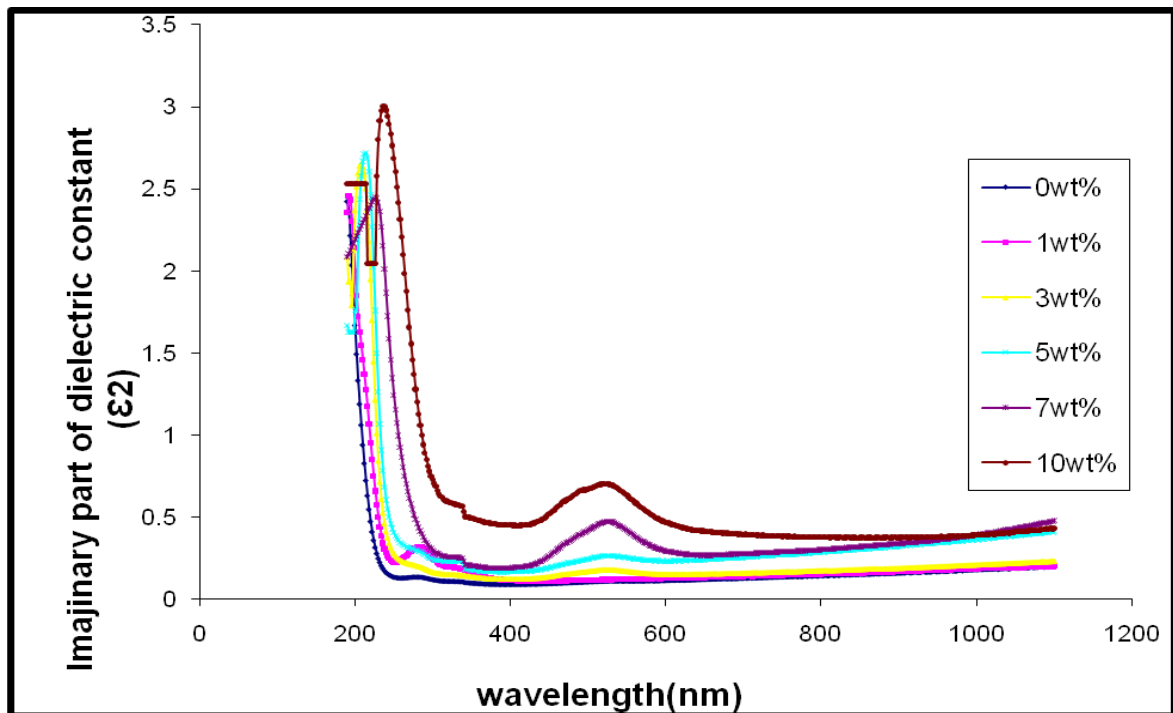


Figure (4-36): The imaginary part of dielectric constant for(PVA-CoNO<sub>3</sub>) films as a function of the wavelength.



**Figure (4-37): The imaginary part of dielectric constant for (PVA-CoCH<sub>3</sub>COOH) films as a function of the wavelength.**

### 4-3 Electrical Measurements

#### 4-3-1 D.C. Electrical Measurements

The volume electrical conductivity  $\sigma_v$  is calculated from the prepared films using equation (2-24). Below detailed results of these properties:

##### 4-3-1-1 The Effect of the (Cobalt chloride, Cobalt nitrate and Cobalt acetate ) salts Concentration .

Figures (4-(38-40)) show the volume electrical conductivity  $\sigma_v (\Omega.cm)^{-1}$  for (PVA-(CoCl<sub>2</sub>,CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films as a function of the concentration of (Cobalt chloride, Cobalt nitrate and Cobalt acetate ) at a temperature of (30°C). The figures show that the electrical conductivity is slightly increasing with the increase of the concentration of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) up to (1wt%). When increasing the concentration more is than

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that, the electrical conductivity increases to the large value ( $2.46 \times 10^{-14}$  ,  $6.40 \times 10^{-14}$  and  $5.97 \times 10^{-13}$ ) ( $\Omega \cdot \text{cm}$ )<sup>-1</sup> respectively at the concentration (5wt%) of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) and an increase in the concentration of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) to (10wt%), the conductivity reaches to ( $4.05 \times 10^{-13}$ ,  $3.22 \times 10^{-12}$  ,  $3.48 \times 10^{-12}$ ) ( $\Omega \cdot \text{cm}$ )<sup>-1</sup> respectively.

The increase of electrical conductivity with increasing concentration of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) is caused by the increase of the charge carriers ions in which they increased with increasing filler content when the (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) ions few at low concentrations and become more when the (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) content increases. But when the concentration of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) reaches to (10wt%), the network will be connected to each other containing the overlapping paths to allow the charge carriers to pass through, where the charge carriers with routes through which the electrical resistance is less [64,65]. Tables (4-(4-6)) show the values of electrical conductivity in ( $\Omega \cdot \text{cm}$ )<sup>-1</sup> with concentration of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) at (30°C) .

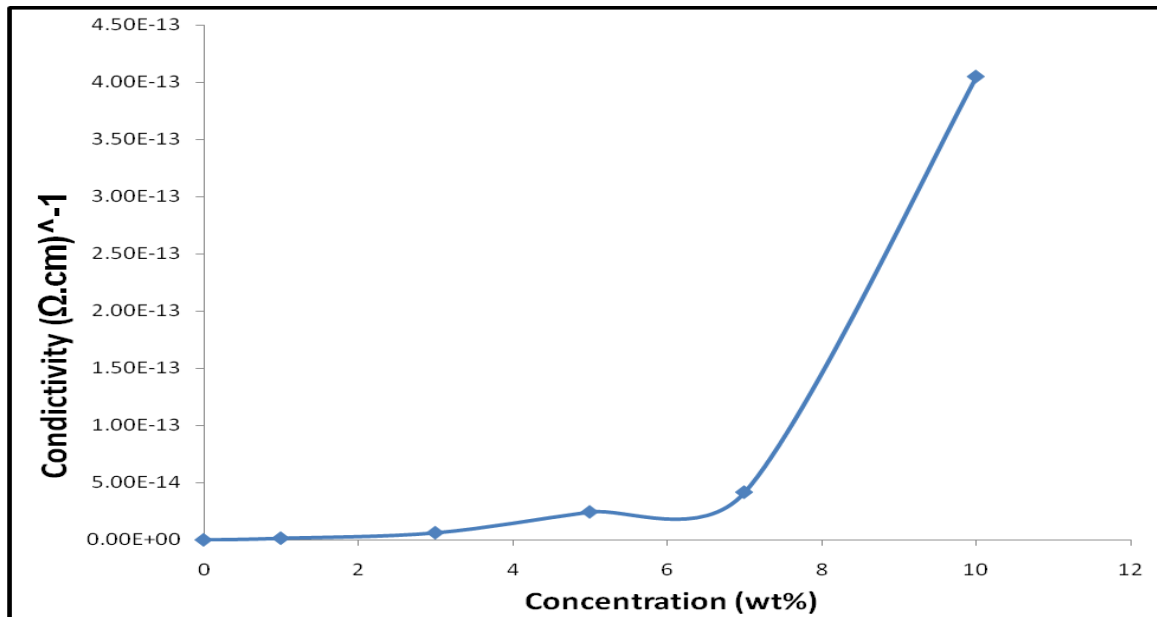


Figure (4-38) :The volume electrical conductivity  $\sigma_v$  ( $\Omega \cdot \text{cm}$ )<sup>-1</sup> for (PVA-CoCl<sub>2</sub>) films as a function of the concentration of (CoCl<sub>2</sub>) at Room temperature .

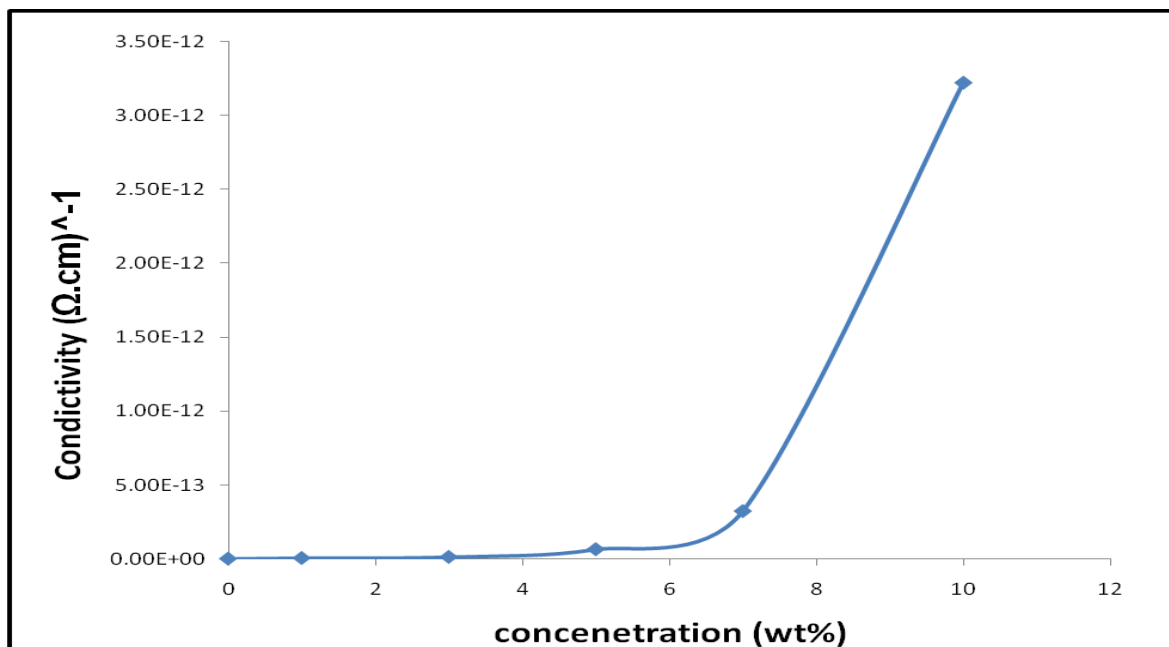
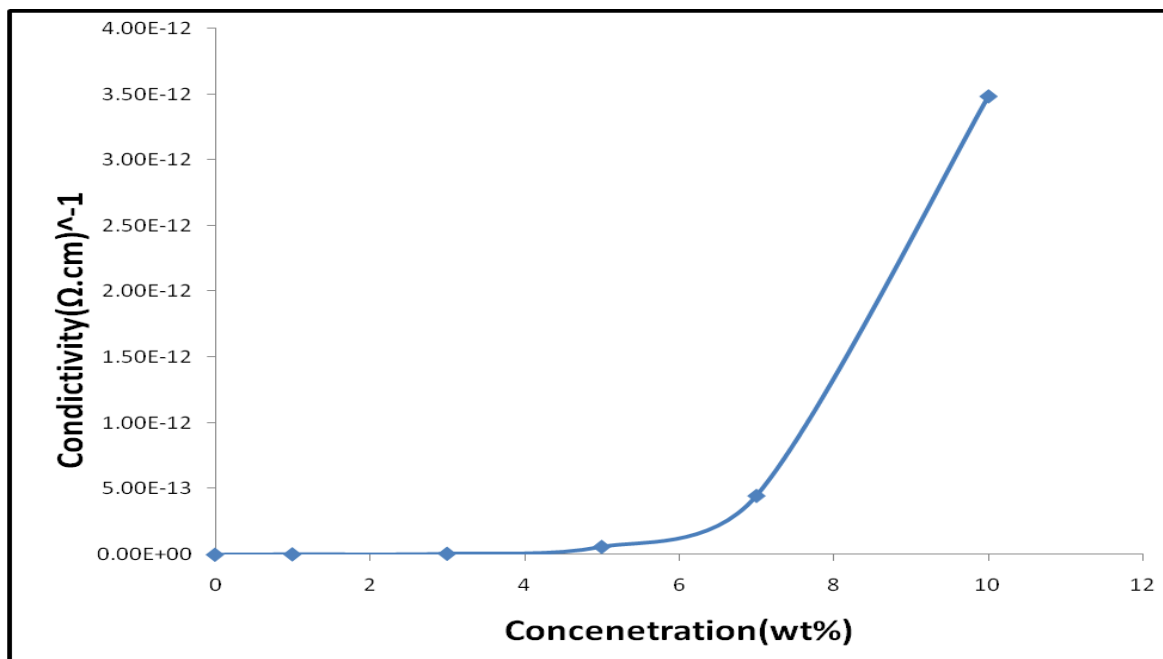


Figure (4-39) :The volume electrical conductivity  $\sigma_v$  ( $\Omega \cdot \text{cm}$ )<sup>-1</sup> for (PVA-CoNO<sub>3</sub>) films as a function of the concentration of (CoNO<sub>3</sub>) at Room temperature .



**Figure (4-40) :**The volume electrical conductivity  $\sigma_v (\Omega \cdot \text{cm})^{-1}$  for (PVA-CoCH<sub>3</sub>COOH) films as a function of the concentration of (CoCH<sub>3</sub>COOH) at Room temperature .

**Table (4-4)**  
Values of electrical conductivity with concentration of (CoCl<sub>2</sub> wt%) at (30°C)

(CoCl <sub>2</sub> ) wt%	$\sigma_v (\Omega \cdot \text{cm})^{-1}$
Pure (PVA)	1.47E-16
1	1.61E-15
3	6.41E-15
5	2.46E-14
7	2.47E-14
10	4.05E-13

**Table (4-5)**  
**Values of electrical conductivity with concentration of**  
**(CoNO<sub>3</sub>wt%) at (30°C)**

<b>(CoNO<sub>3</sub>) wt%</b>	<b><math>\sigma_v (\Omega. \text{cm})^{-1}</math></b>
<b>pure (PVA)</b>	<b>1.47E-16</b>
<b>1</b>	<b>4.90E-15</b>
<b>3</b>	<b>1.21E-14</b>
<b>5</b>	<b>6.40E-14</b>
<b>7</b>	<b>3.83E-13</b>
<b>10</b>	<b>3.22E-12</b>

**Table (4-6)**  
**Values of electrical conductivity with concentration of**  
**(CoCH<sub>3</sub>COOHwt%) at (30°C) .**

<b>(CoCH<sub>3</sub>COOH) wt%</b>	<b><math>\sigma_v (\Omega. \text{cm})^{-1}</math></b>
<b>Pure (PVA)</b>	<b>1.47E-16</b>
<b>1</b>	<b>2.90E-15</b>
<b>3</b>	<b>7.35E-15</b>
<b>5</b>	<b>5.97E-13</b>
<b>7</b>	<b>4.47E-13</b>
<b>10</b>	<b>3.48E-12</b>

### 4-3-1-2 The Effect of Temperature

Figures (4-(41-43)) show the relationship of volume electrical conductivity  $\sigma_v (\Omega.cm)^{-1}$  of (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films with different concentrations of (CoCl<sub>2</sub>,CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) salts with the temperature. We note that the electrical conductivity increases with increasing the temperature, the interpretation of this is that the polymeric chains and (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) could act as traps for the charge carriers which transited by hopping process. By increasing the temperature, segments of the polymer begins to move, releasing the trapped charges. The released of trapped charges is intimately associated with molecular motion. The increase of electrical conductivity with the temperature is attributed to two main parameters, charge carriers and mobility of these charges. The mobility depends on the structure and the temperature [10,66,67]. Tables (4-(7-9)) show the values of electrical conductivity in  $(\Omega.cm)^{-1}$  with the temperature in centigrade degree .

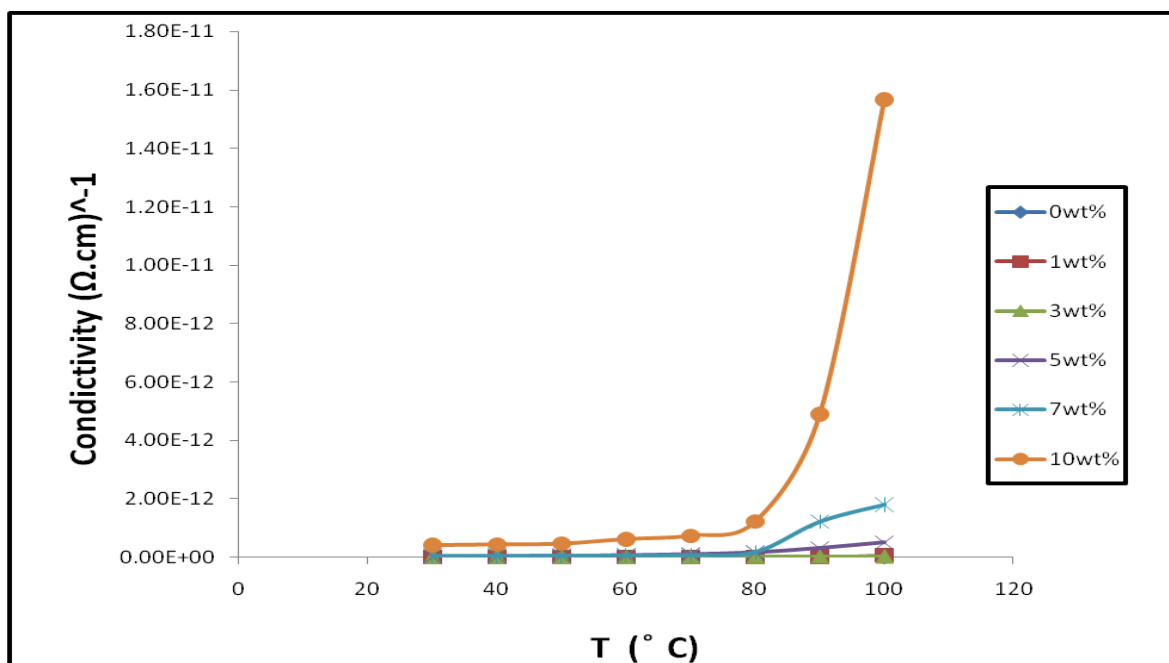


Figure (4-41) The relationship of volume electrical conductivity  $\sigma_v (\Omega.cm)^{-1}$  for (PVA-CoCl<sub>2</sub>) films with the temperature.



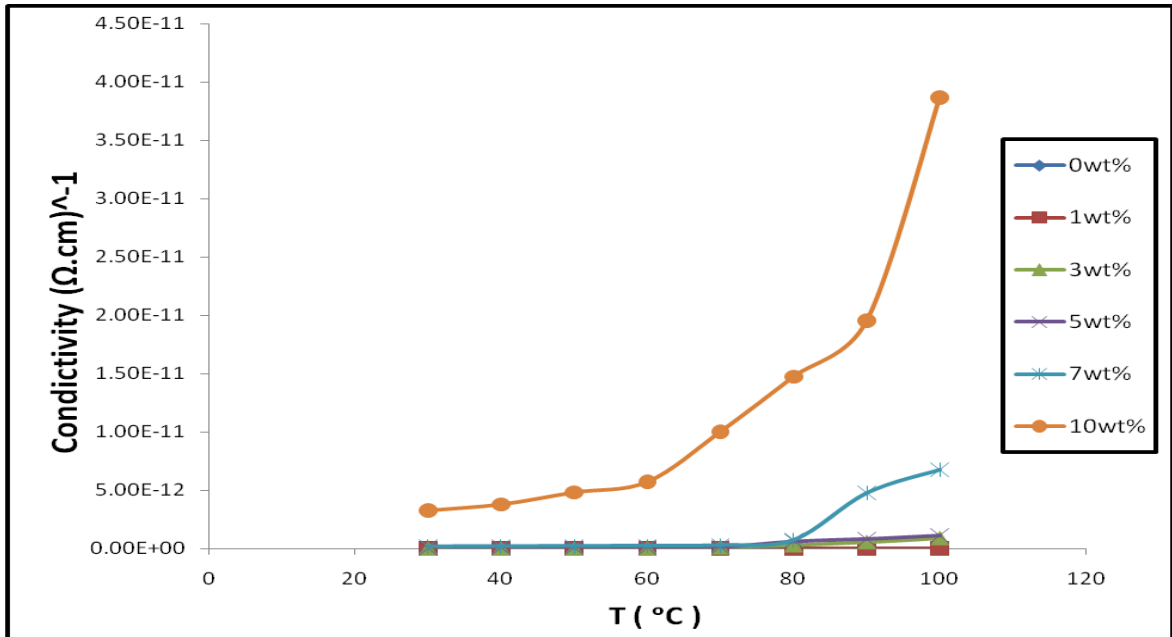


Figure (4-42) The relationship of volume electrical conductivity  $\sigma_v (\Omega.cm)^{-1}$  for (PVA-CoNO<sub>3</sub>) films with the temperature.

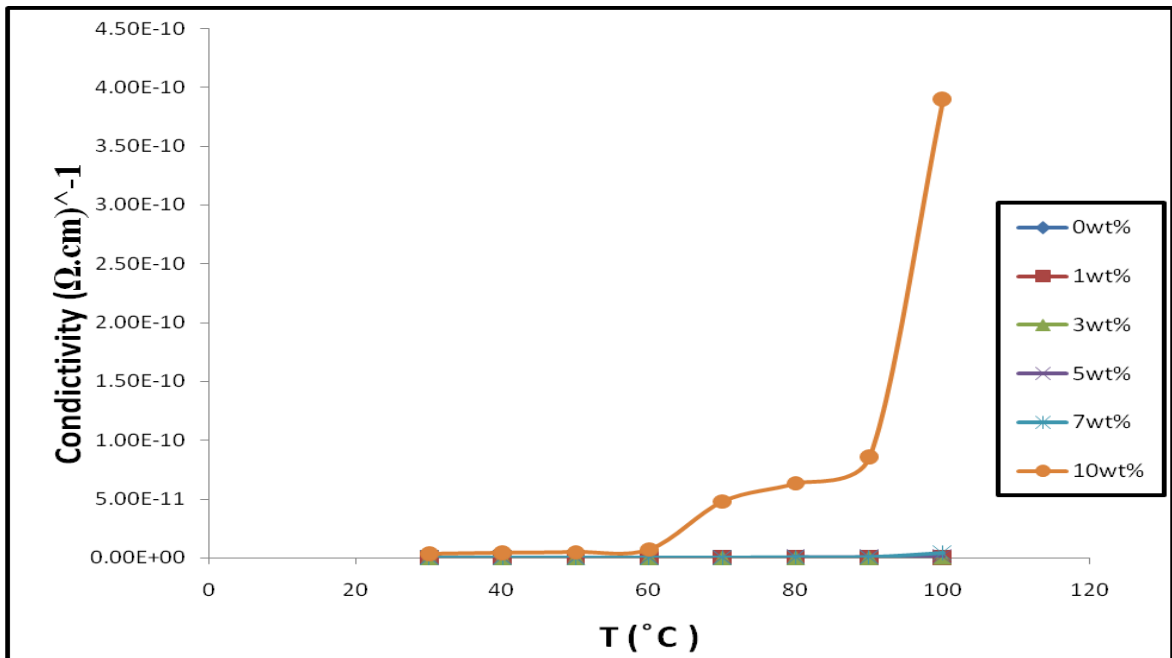


Figure (4-43) The relationship of volume electrical conductivity  $\sigma_v (\Omega.cm)^{-1}$  for (PVA-CoCH<sub>3</sub>COOH) films with the temperature.

**Table (4-7)**  
**Values of electrical conductivity  $\sigma_v$  ( $\Omega.cm$ )<sup>-1</sup> with the temperature for (PVA-CoCl<sub>2</sub>) films.**

T(°C)	$\sigma_v$ ( $\Omega.cm$ ) <sup>-1</sup> of (PVA- CoCl <sub>2</sub> )					
	Pure	1wt%	3wt%	5wt%	7wt%	10wt%
30	1.47E-16	1.61E-15	6.42E-15	2.46E-14	2.47E-14	4.05E-13
40	1.88E-16	1.92E-15	7.20E-15	3.44E-14	4.55E-14	4.31E-13
50	2.00E-16	2.70E-15	8.58E-15	4.52E-14	2.83E-13	4.58E-13
60	2.41E-16	3.28E-15	1.47E-14	7.13E-14	3.32E-13	5.30E-12
70	3.23E-16	3.64E-15	1.73E-14	4.37E-13	3.78E-13	9.26E-12
80	5.12E-16	4.51E-15	2.10E-14	4.81E-13	4.20E-13	3.73E-11
90	6.80E-16	5.28E-15	2.50E-14	5.54E-13	5.06E-13	3.90E-11
100	8.13E-16	7.77E-15	3.16E-14	5.05E-13	6.26E-13	4.37E-11

**Table (4-8)**  
**Values of electrical conductivity  $\sigma_v$  ( $\Omega.cm$ )<sup>-1</sup> with the temperature for (PVA-CoNO<sub>3</sub>)films.**

T(°C)	$\sigma_v$ ( $\Omega.cm$ ) <sup>-1</sup> of (PVA-CoNO <sub>3</sub> )					
	Pure	1wt%	3 wt%	5wt%	7wt%	10wt%
30	1.47E-16	4.90E-15	1.21E-14	6.40E-15	3.83E-14	3.22E-12
40	1.88E-16	5.18E-15	1.29E-14	5.29E-14	1.96E-13	3.75E-12
50	2.00E-16	5.69E-15	1.83E-14	5.96E-14	2.17E-13	4.78E-12
60	2.41E-16	7.96E-14	4.53E-14	3.58E-13	2.37E-13	5.69E-12
70	3.23E-16	1.10E-14	4.94E-14	5.47E-13	2.84E-13	1.00E-11
80	5.12E-16	1.58E-14	5.02E-14	6.17E-13	6.27E-13	1.47E-11
90	6.80E-16	1.80E-14	5.58E-14	8.21E-13	9.63E-13	2.00E-11
100	8.13E-16	4.05E-14	8.98E-14	9.89E-13	9.73E-13	3.87E-11

**Table (4-9)**  
**Values of electrical conductivity  $\sigma_v$  ( $\Omega.cm$ )<sup>-1</sup> with the temperature for (PVA-CoCH<sub>3</sub>COOH) films.**

T (°C)	$\sigma_v$ ( $\Omega.cm$ ) <sup>-1</sup> of (PVA-CoCH <sub>3</sub> COOH)					
	Pure	1wt%	3wt%	5wt%	7wt%	10wt%
30	1.47E-16	2.90E-15	4.35E-14	5.97E-14	4.47E-13	3.48E-12
40	1.88E-16	4.05E-15	4.95E-14	3.39E-13	2.60E-13	4.39E-12
50	2.00E-16	4.19E-15	6.23E-14	4.47E-13	2.67E-13	5.00E-12
60	2.41E-16	4.35E-15	7.67E-14	4.80E-13	2.91E-13	7.31E-12
70	3.23E-16	4.68E-15	8.05E-14	5.21E-13	3.36E-13	7.98E-12
80	5.12E-16	3.73E-14	1.42E-13	5.58E-13	6.27E-13	6.35E-11
90	6.80E-16	4.16E-14	7.44E-13	7.14E-13	4.22E-12	8.61E-11
100	8.13E-16	4.36E-14	4.73E-13	9.64E-13	4.58E-12	3.90E-10

#### 4-3-1-3 The Activation Energy

Figures (4-(44-46)) show the relation between ( $\ln\sigma_v$ ) and the inverse of absolute temperature for (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films with different concentrations of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) salts. The activation energy was calculated by using equation (2-24). It is clear from these figures that there are two transport mechanisms, giving rise to two activation energies ( $E_{a1}$ ) and ( $E_{a2}$ ). At higher temperatures range (343 – 373) K, the conduction mechanism is due to carrier excited into the extended states beyond the mobility edge and at lower temperatures range (303 – 333) K, the

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conduction mechanism is due to carrier excited into the localized states at the edge of the band [66] .

By adding low concentrations of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) the values of the activation energy are decreasing as a result of the impact of space charge. The addition of low concentrations creates local energy levels in the energy gap which could act as traps for charge carriers, which move by hopping among these levels.

By increasing the (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) concentrations, the activation energy decreases as a result of the increase of local centers, as shown in figures (4-(44-46)). Thus, the mechanism of conduction in the samples having low concentrations is the hopping .

The low values of the activation energy for (PVA- (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films are attributed to the formation of a continuous network of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) that contains paths inside the composites and allows the charge carriers to pass through and this leads to decrease the activation energy [10,68], as shown in the figures (4-(44-46)). Our results are nearly in agreement with [33]. Table (4-(10-12)) shows the values of activation energy in (eV) with concentration of (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH) wt% .

Table (4-10)

The values of activation energy in (eV) with concentration of (CoCl<sub>2</sub>) wt% .

Wt%	(303 – 333)K	(343 – 373)K
	E <sub>a1</sub> (eV)	E <sub>a2</sub> (eV)
Pure (PVA)	0.51	1.33
1	0.17	0.38
3	0.12	0.35
5	0.10	0.28
7	0.09	0.188
10	0.05	0.182

Table (4-11)

The values of activation energy in (eV) with concentration of (CoNO<sub>3</sub>) wt% .

Wt%	(303 – 333)K	(343 – 373)K
	E <sub>a1</sub> (eV)	E <sub>a2</sub> (eV)
Pure (PVA)	0.51	1.33
1	1.17	0.429
3	0.27	0.425
5	0.23	0.41
7	0.21	0.38
10	0.14	0.36

Table (4- 12)

The values of activation energy in (eV) with concentration of (CoCH<sub>3</sub>COOH) wt% .

Wt%	(303 – 333)K	(343 – 373)K
	E <sub>a1</sub> (eV)	E <sub>a2</sub> (eV)
Pure (PVA)	0.51	1.33
1	0.14	0.28
3	0.17	0.25
5	0.12	0.23
7	0.05	0.20
10	0.06	0.18

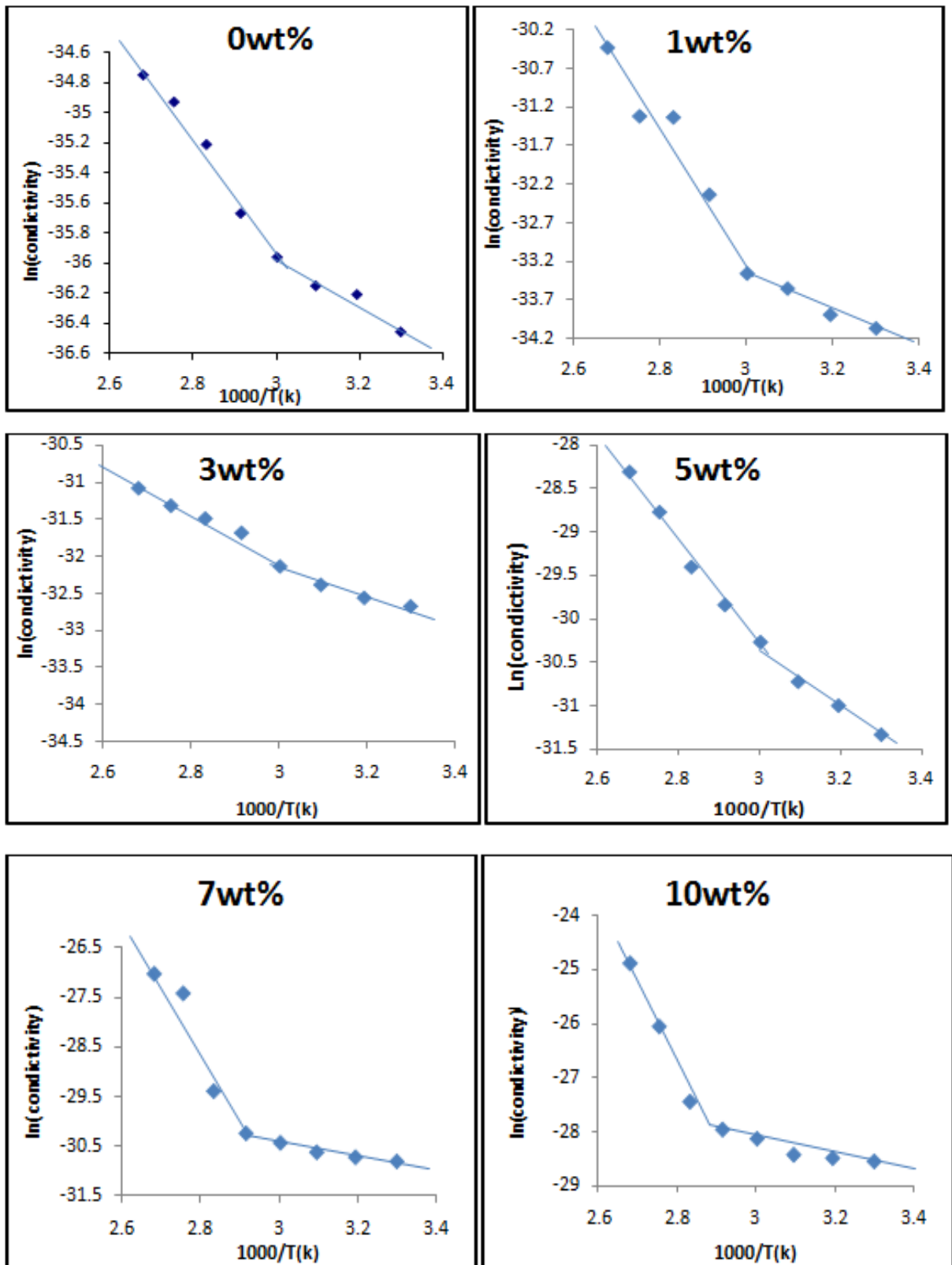


Figure (4-44) : The relation between  $\ln\sigma_v$  and the inverse absolute temperature for (PVA- $\text{CoCl}_2$ ) films.

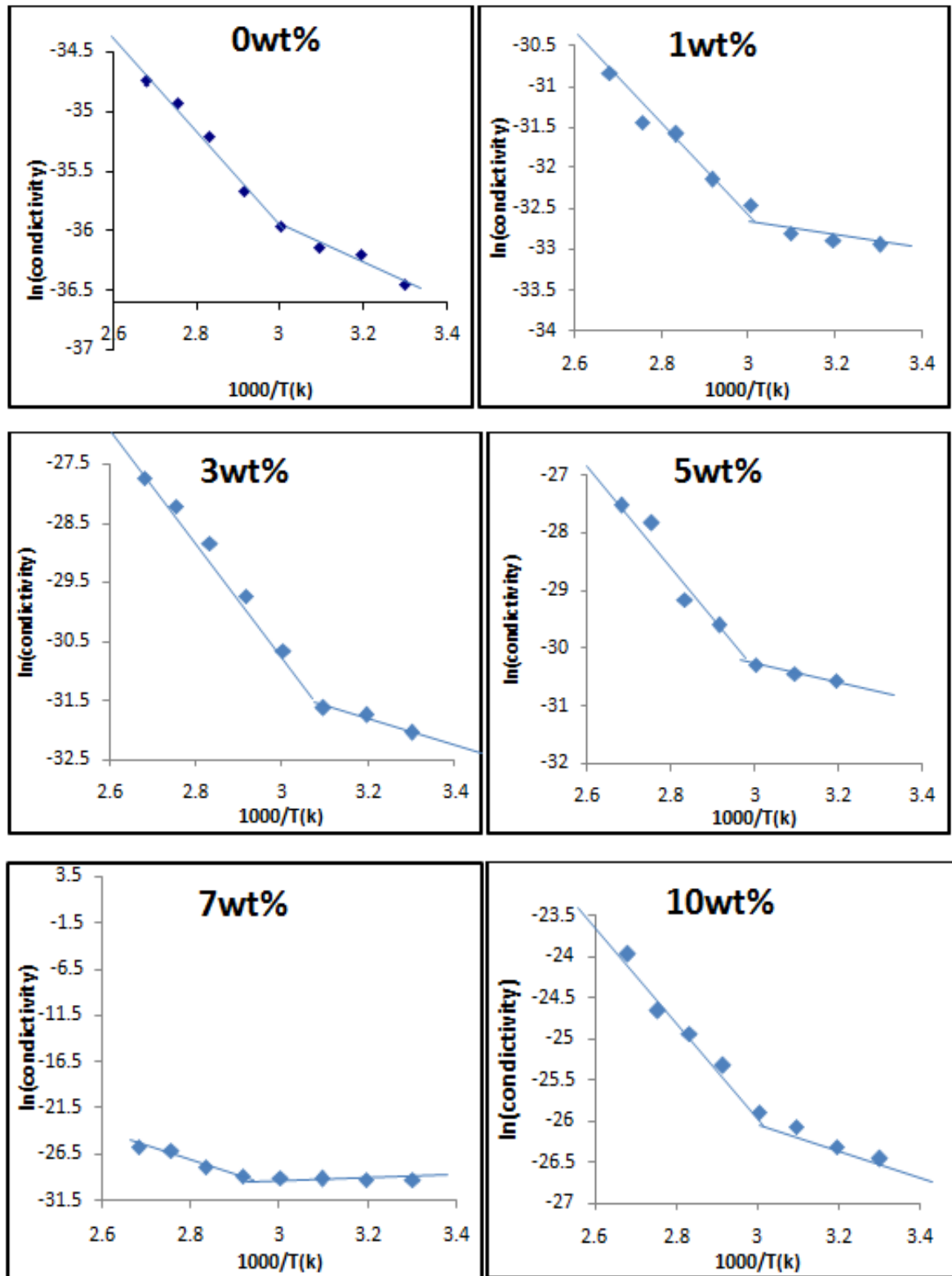


Figure (4-45) : The relation between  $\ln\sigma_v$  and the inverse absolute temperature for (PVA- $\text{CoNO}_3$ ) films.

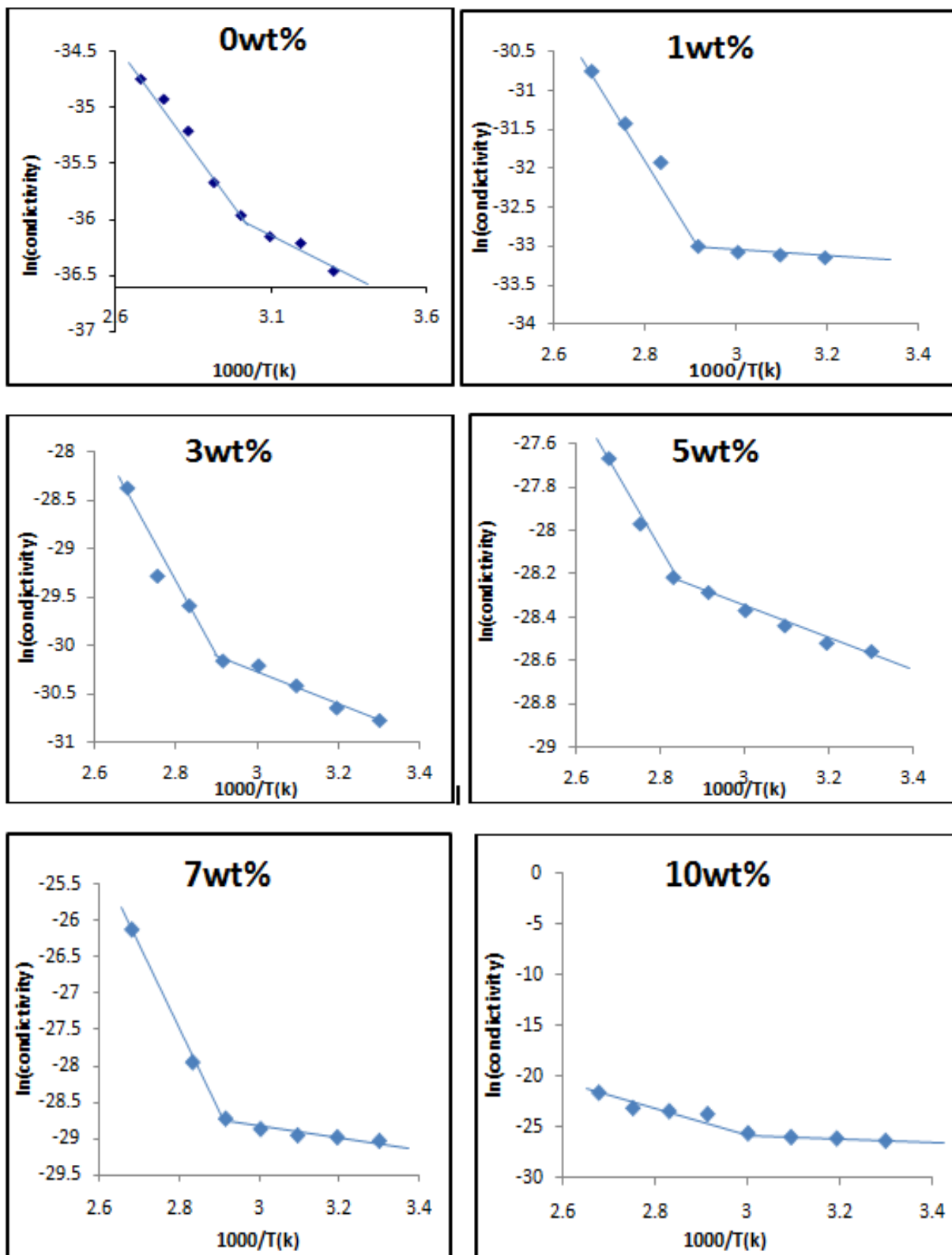


Figure (4-46) : The relation between  $\ln\sigma_v$  and the inverse absolute temperature for (PVA-CoCH<sub>3</sub>COOH) films.



## **4-4 Conclusions**

### **4-4-1 Optical Properties**

1-The absorbance and The absorption coefficient for (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films increases with increasing of the filler (wt%) content.

2- The absorption coefficient for (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films is less than ( $10^4$ ); This means that the electronic transition is indirect.

3-The energy gap of indirect transition for (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films decreases with increasing of filler (wt% ) content while Refractive index, Extinction coefficient, and real and imaginary parts of dielectric constant increases with increasing of filler (wt%) content.

### **4-4-2 Electrical Properties**

1-The D.C. electrical conductivity for (PVA- (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films increases with increasing of temperature and filler ( wt% ) content.

2-The activation energy for D.C. electrical conductivity for (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) decreases with increasing of the filler (wt%) content.

We found that the best salt of cobalt salts is (CoCH<sub>3</sub>COOH) because it has the less energy gap in most concentrations and has high absorbance, high Refractive index, high Extinction coefficient, and high real and imaginary parts of dielectric constant and less activation energy , then we can use this salt in more scientific applications .

#### **4-5 Future work**

**1-** Study of effect of irradiation Gamma and laser ray on some electrical and optical properties of (PVA- (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films.

**2-** Study of the thermal properties of (PVA-(CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films in high temperature range .

**3-**Study of the mechanical properties of (PVA- (CoCl<sub>2</sub>, CoNO<sub>3</sub> and CoCH<sub>3</sub>COOH)) films.

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