# *Preparation and Study of Some Physical Properties of (PVA-Copper Salts)Composite Films*

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# تحضير ودراسة بعض الخواص الفيزيائية لأغشية المتراكب (بولي فنايل الكحول-املاح النحاس )

رسالة مقدمة الى
مجلس كلية العلوم – جامعة ديالى وهي جزء من متطلبات نيل درجة
الماجستير في علوم الفيزياء

## من قبل

## مروه رشيد جوامير

بكالوريوس علوم فيزياء 2010 م

بإشرافه

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## 1-1  Introduction

Polymers have existed in natural form since the beginning of life such as DNA, RNA. Proteins and polysaccharides play crucial roles in plant and animal life. Early, man has exploited naturally-occurring polymers as materials requirements for providing clothes, decoration etc. However, the origin of today's polymer industry is commonly attributed to the nineteenth century when important discoveries were made in relation to the modification of certain natural polymers. In eighteenth century, Thomas Hancock gave an idea of modification of natural rubber through blending with ceatrain additives. Later on, Charles Good year improved the properties of natural rubber through vulcanization process with sulfur. The Bakelite was the first synthetic polymer produced in (1909) and was soon followed by the synthetic fiber and rayon, which was developed in (1911). The systematic study of polymer science has started only about a century back with the pioneering work of Herman Staudinger. Staudinger has given a new definition of polymer. In (1919), first published this concept that high molecular mass compounds were composed of long covalently bonded molecules [1].

Per last year composite materials attract the rapt attention both in industry applications and in science. In these materials there is the possibility to combine mechanical, electric and optical properties of constituent components in one sample. From optical point of view, several fascinating properties of these composites can be obtained [2].

The properties of polymer-mineral reinforced composites are determined by the component properties (particle shape, surface area, surface chemistry, polymer microstructure) as well as by the processing method and processing conditions. Among processing methods, injection

molding has strong influence on the internal microstructure of polymers and consequently on mechanical response of the material [3]. Now a days, thermoplastic polymers are widely used in various aspects of human society. They have several good properties such as good chemical resistance, better mechanical properties, cost effectiveness that make them the polymers of choice for numerous applications. Due to these superior properties of these materials, they have used both mixed with natural fillers and in manufactured composite forms. The use of thermoplastic polymer composites reinforced with natural fillers has been rapidly increasing in the automotive industry [4].

Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer. Due to the characteristics of easy preparation, we have good biodegradability, excellent chemical resistance and good mechanical properties: PVA has been used on many biomaterial applications [5]. Doping of polymers attracted the scientific and technological researchers, because of their wide applications. The dopant in polymer can change the molecular structure and hence the microstructure as well as macroscopic properties of the polymer [6].

## 1-2  Polymer Structure

Polymers form a very important class of materials without which life seems very difficult. They are all around us in everyday use; in rubber, in plastic, in resins, in adhesives and adhesives tapes. The word polymer is derived from greek words, poly= many and mers= parts or units of high molecular mass each molecule of which consists of a very large number of single structural units joined together in a regular manner. In other words, polymers are giant molecules of high molecular weight, called

macromolecules, which are built up by linking together a large number of small molecules, called monomers. The reaction by which the monomers combine to form polymer is known as polymerization. The polymerization is a chemical reaction in which two or more substances combine together with or without evolution of anything like water, heat or any other solvents to form a molecule of high molecular weight. The product is called polymer and the starting material is called monomer [1]. 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 amorphous [7].

## 1-3  Classification of Polymers

Polymer is a generic name given to a vast number of materials of high molecular weight. These materials exist in countless forms and numbers because of very large number and type of atoms present in their molecule. Polymer can have different chemical structure: physical properties, mechanical behavior, thermal characteristics, etc., and on the basis of these properties polymer can be classified in  different ways, which are summarized in table (1-1), whereas, important and broad classifications of polymers are described in the next section.

## Table (1-1): Classification of polymers

| Basis of Classification | Polymer Type |
|---|---|
| Origin | Natural, Semi synthetic, Synthetic |
| Thermal Response | Thermoplastic, Thermosetting |
| Mode of Formation | Addition, Condensation |
| Line Structure | Linear, Branched, Cross-Linked |
| Application and Physical Properties | Rubber, Plastic, Fibers |
| Tacticity | Isotactic, Syndiotactic, Atactic |
| Homogeneity | Homo Polymers,  Copolymers,  Composite Polymers |
| The Chains Lengths and Molecular Weights | Mono Disperse, Poly Disperse |

## 1-3-1 Origin

On the basis of their occurrence in nature, polymers have been classified in to three types [8]:-

**A- Natural Polymers:-** The polymers, which occur in nature are called natural polymers also known as biopolymers. Examples of such polymers are natural rubber, natural silk, cellulose, starch, proteins, etc..

**B- Semi synthetic Polymers:-** They are the chemically modified natural polymers such as hydrogenated, natural rubber, cellulosic, cellulose nitrate, methyl cellulose, etc.

**C- Synthetic Polymers:-** The polymers which have been synthesized in the laboratory are known as synthetic polymers. These are also known as manmade polymers. Examples of such polymers are polyvinyl alcohol, polyethylene, polystyrene, polysulfone, etc..

## 1-3-2 Thermal Response

On the basis of thermal response, polymers can be classified in to two groups [9]:-

**A- Thermoplastic Polymers:-** They can be softened or plasticized repeatedly on application of thermal energy, without much change in properties if treated with certain precautions. Example of such polymers are Polyolefins, nylons, linear polyesters and polyethers, PVC, sealing wax etc.

**B- Thermosetting Polymers:-** Some polymers undergo certain chemical changes on heating and convert themselves into an infusible mass. The curing or setting process involves chemical reaction leading to further growth and cross linking of the polymer chain molecules and producing giant molecules. For example, Phenolic resins, urea, epoxy resins, diene rubbers, etc.

## 1-3-3 Mode of Formation

On the basis of mode of formation, polymers can be classified as [8]:-

**A- Addition Polymers:-** They are formed from olefinic, diolefnic, vinyl and related monomers. They are formed from simple addition of

monomer molecules to each other in a quick succession by a chain mechanism. This process is called addition polymerization. Examples of such polymers are polyethylene, polypropylene, polystyrene.

**B- Condensation polymer:**- They are formed from intermolecular reactions between bifunctional or polyfunctional monomer molecules having reactive functional groups such as –OH, -COOH, -NH$_2$, -NCO, etc.

**1-3-4 Line Structure**

Polymers are classified depending on the structural composition in to [10]: -

**A**- **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). It is the same type of polymer used in the present study.

**B**- **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 shown in figure (1-1-b).

**C**- **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).
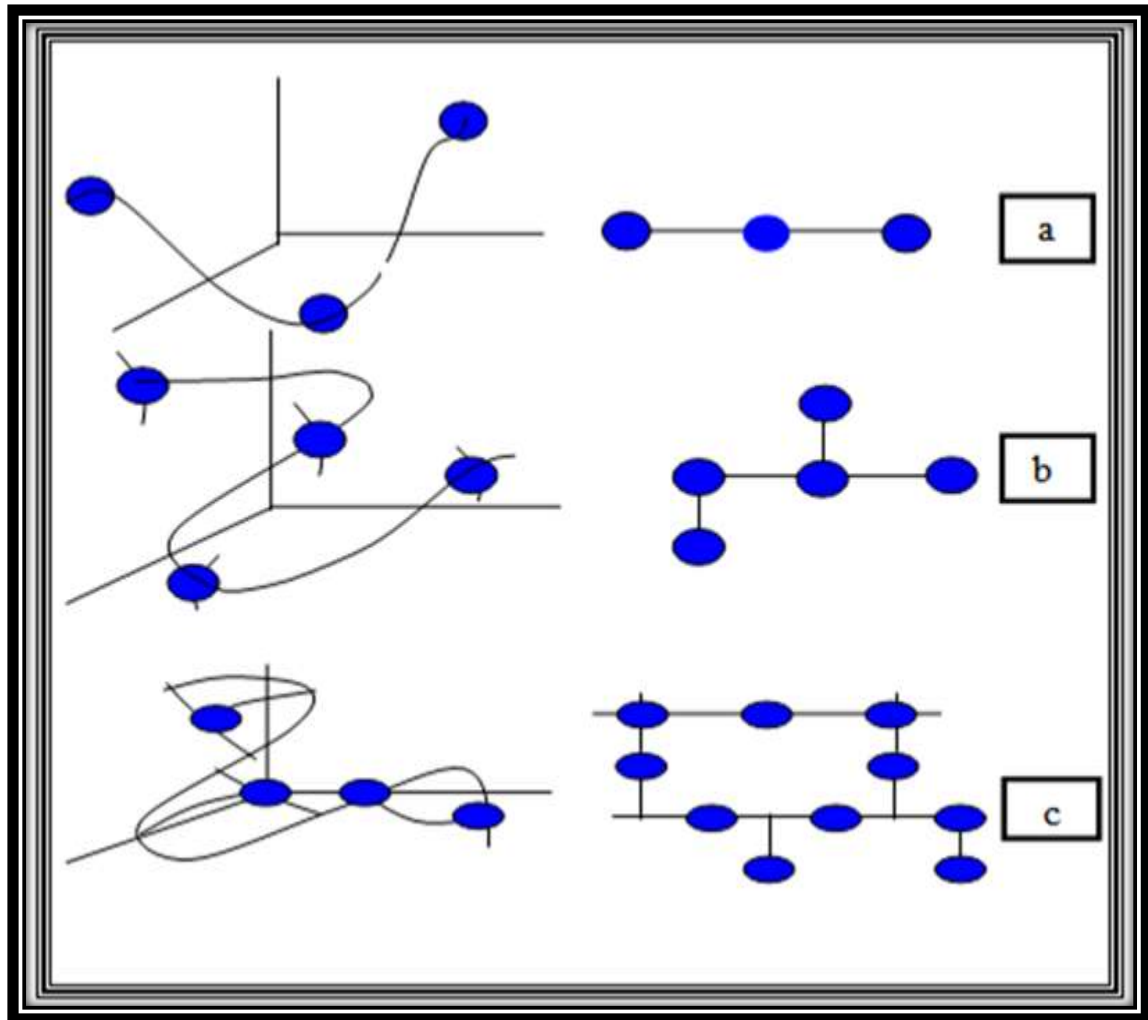


**Figure (1-1): The different types of polymeric chains [11]**

## 1-3-5  Application and Physical  Properties

Depending on its ultimate form and use a polymer can be classified  as [8]:-

**A- Rubber (Elastomers):-** Rubber is high molecular weight polymer with  long flexible chains and weak intermolecular forces.  They exhibit

tensile strength in the range of (300-3000) psi and elongation at break ranging between (300-1000)%. Examples are natural and synthetic rubber.

**B**- **Plastics**:- Plastics are relatively tough substances with high molecular weight that can be molded with (or without) the application of heat. These are usually much stronger than rubbers. They exhibit tensile strength ranging between (4000-15000) psi and elongation at break ranging usually from (20 to 200)% or even higher. The examples of plastics are, polyethylene, polypropylene, PVC, polystyrene, etc.

**C**- **Fibers**:- Fibers are long- chain polymers characterized by highly crystalline regions resulting mainly from secondary forces. They have a much lower elasticity than plastics and elastomers. They also have high tensile strength ranging between (20,000- 150,000) psi., are light weight and possess moisture absorption properties.

## 1-3-6  Tacticity:-

It can be defined as the geometric arrangement (orientation) of the characteristic group of monomer unit with respect to the main chain (backbone) of the polymers. On the basis of structure, polymer can be classified into three groups [8]:-

**A- Isotactic Polymer:-** It is the type of polymer in which the characteristic groups are arranged on the same side of the main chain, as in the figure (1-2-a).
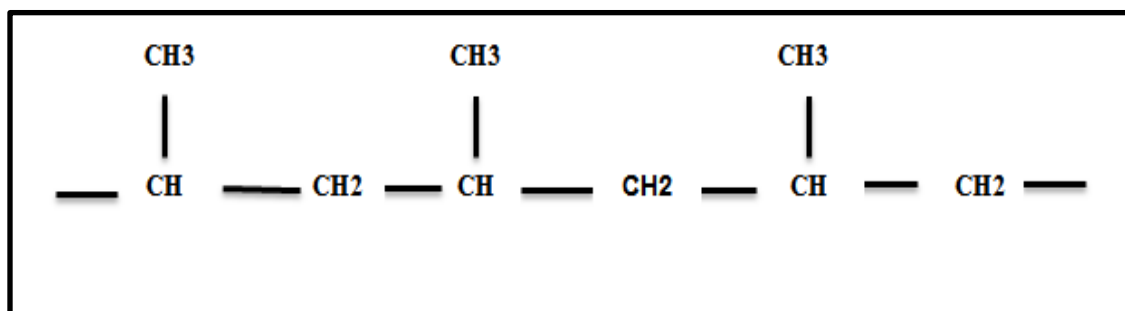
**Figure (1-2-a): Isotactic polypropene**

**B- Syndiotactic polymer:-** A polymer is said to be syndiotactic if the side group (characteristic group) arranged in an alternate fashion, as in the figure (1-2-b)
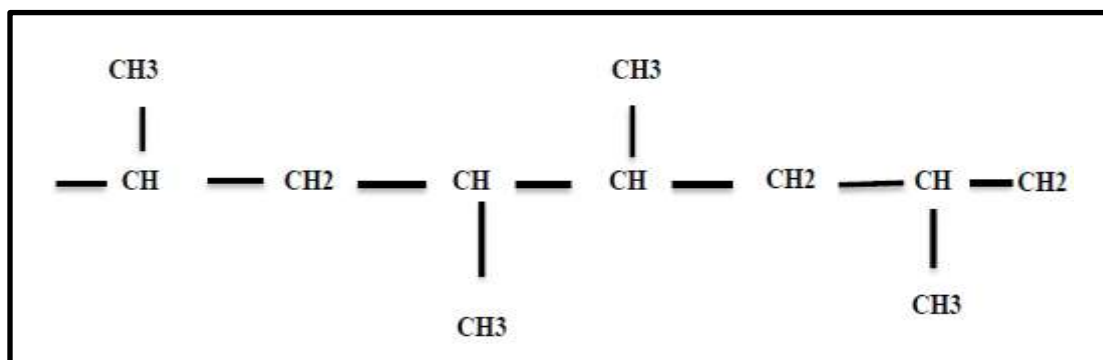


**Figure (1-2-b): Syndiotatic polypropene**

**C- Atactic polymer:-** A polymer is said to be atactic, if the characteristic groups (side group) are arranged in irregular fashion (randomness) around the main chain. It has proper strength and more elasticity, as in the figure (1-2-c).
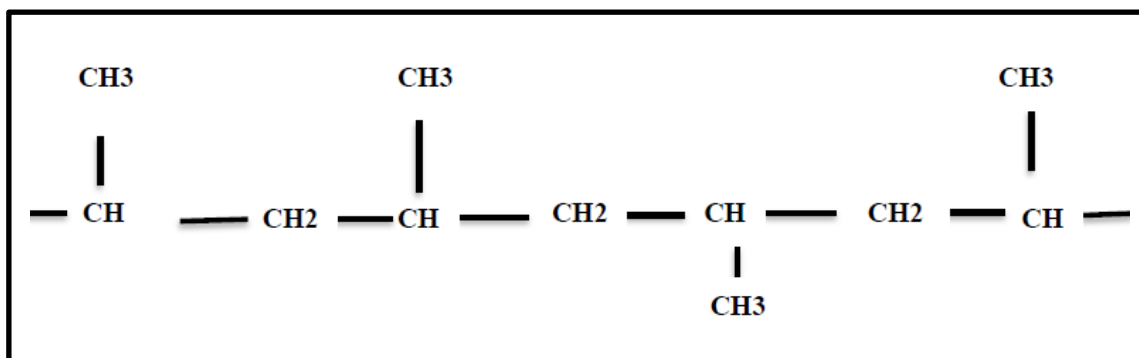
**Figure (1-2-c): Atactic polypropene**

## 1-3-7 Polymers Dependence on Homogeneity

Polymers are classified depending on the homogeneity of repeating units into [12,13]:

**A- Homo Polymers**

When the building blocks of a polymer are of one type, as in poly therphethals ethylene.

**B- Copolymers**

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

**C- 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.

# 1-3-8 Polymers Dependence on the Chains Lengths and Molecular Weights [14]:-

## A- Mono Disperse Polymers

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

## B- 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 shows the existence of a diverse distribution of the lengths of the chains and thus there is a multiplicity of molecular weights.

## 1-4 Polymer Composites

Composite materials are often classified by matrix type or reinforcement type. In the matrix classification, there are three main subsections: metal matrix composites (MMC), ceramic matrix composites (CMC) and polymer matrix composites (PMC). The high cost of production, difficulty of manufacture and higher density of MMC. CMC has limited most of these materials to special applications. Lower materials costs and relative ease of processing have allowed PMC composites to be integrated into many applications in everyday life. Composites are also classified according to the reinforcement type. Particulate composites are ones that use small particles, platelets, flakes or rods to reinforce the matrix, where the dimensions of the reinforcement are roughly similar [15]. The type of dispersed phase, its orientation (for the fibrous type), size, relative amount, and material properties will affect

the properties of the overall material. Examples of reinforcement include; Glass, Boron, Ceramic, Carbon, etc.

## 1-5 Factors Affecting Polymer Properties

Chemical and physical properties of polymers are determined by three major factors **:**

## 1-5-1 Chemical Bonds and Binding Forces

Chemical bonds and binding forces govern the physical properties of polymer. They can be divided into two groups. The basic chemical bonds include covalent, ionic, hydrogen and metallic which are responsible for binding atoms to form the polymer molecule. Most polymers, especially the organic ones have covalent bonds. The other group is the secondary forces that bind polymer molecules of the same chain or between different chains, resulting in crosslink and coherent polymers. Vander Waals force is an example of this group of secondary forces [16,17].

## 1-5-2 Polymers Structure and Status

The arrangement and binding of the repeating units of the polymer, the type of the substitution groups and chemical bonds offer the polymers a special structure and distinguished chemical and physical properties [18].

## 1-5-3 Average Molecular Weight

Polymers are distinguished from other materials that they have relatively large molecular weight. Most physical properties of polymers

depend on their molecular weights. Polymer properties such as strength, conductivity and solubility change with their molecular weight [19].

## 1-6 Mechanism of Polymerization

The linking of a large number of small molecules known as monomers, with each other to form a macromolecule or polymer molecule through chemical reactions is termed as polymerization. It can also be defined as the fundamental process by which low molecular weight compounds are converted into high molecular weight compounds. In addition to the structural and compositional differences between polymers, Flory stressed the very significantnt difference in the mechanism by which polymer molecules are built up. Although Flory continued to use the terms "addition polymerization" (polymerization by repeated addition processes) and "condensation polymerization" (polymerization by repeated condensation processes, i.e., with the elimination of small molecules) in his discussion of polymerization mechanism. The current terminology classifies polymerization into step growth polymerization and chain growth polymerization [13].

The degree of polymerization (Dp) is related to the molecular mass (M) of the polymer and is given by the equation (1-1) [13].

$$D_P = \frac{M}{m} \ldots\ldots\ldots\ldots(1\text{-}1)$$

Where (m) is the mass of the monomeric unit.

# 1-6-1 Condensation Polymerization or Step-growth Polymerization

Condensation Polymerization is a chemical reaction in which polymer is formed and a small molecule of by-product with a lower molecular weight is released. The by-product eliminated is called condensate. The reaction can take place between two similar or different monomers. It is also called step-growth polymerization [20,21].

# 1-6-2 Addition Polymerization or Chain Polymerization

In addition polymerization, two or more molecules of monomers attach together to form a polymer. In this polymerization, there is no elimination of any molecule. It is a chain reaction and no by product is released. It is obtained by linking together the monomer molecules by a chain reaction to give a polymer whose molecular weight is exactly an integral multiple of that of the monomer as in the case of polyethylene obtained by polymerization of ethylene. Only a single monomer is involved in addition to polymerization and hence the polymer is homopolymer. It contains the same monomer units. In addition polymerization reaction is usually induced by light, heat or a catalyst for opening the double bond of the monomer and creating the reactive sites [21].

# 1-7 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 higher degree of polymerization (ten thousands or more in some cases) are called high molecular weight polymers (molecular weight ranges from ($10^4$ – $10^6$ (g/mol)). Polymers with lower degree of polymerization (n ≈ 1-50) are called oligomers [16].

## 1-8 Preparation Methods of Polymer Films

There are some methods to prepare polymer films:-

## 1-8-1 Casting Method

To prepare thin film in the casting method, a certain amount of polymer material is dissolved in a suitable organic solvent such as Tetrahydrofuran (THF). To obtain a homogenous solution, the solvent evaporation rate must be reduced and the preparation time must be long [16].

## 1-8-2- Spin Casting Method

In this method, little amount of polymer solution is precipitated on the center of the rotating disc or nearby. The rotating is electrically operating in very 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 [16].

## 1-8-3 Dip Coating Method

In this method rotating disc is dipped in already prepared polymer solution. Then, the rotating 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 [16].

## 1-8-4 Sol-gel Method

This method is similar to 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 $SnO_2$ is prepared, the dipping speed and removal of the glass disc is about (1.5cm/min) [16]. After preparation, the film is dried at a temperature that depends on the type of used solvent in the preparation of the solution.

## 1-8-5 Languimer-Blodgett (LB) Method

This is one of the important methods of preparing homogenous thin films of very small 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 [16].

## 1-8-6 Electrochemical Method

Electrochemical polymerization 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 [22]. Figure (1-3) shows the main parts of an electrochemical cell:
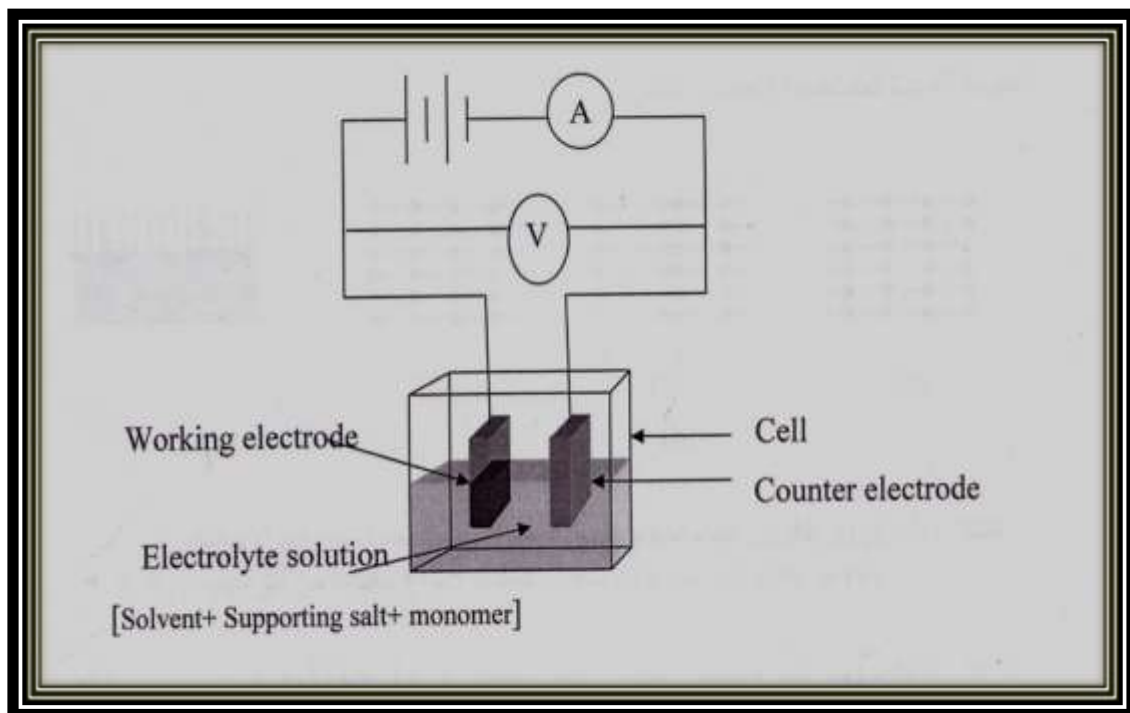
1- cell

2- Electrodes

3- Electrolyte solution

**Figure (1-3): The main parts of electrochemical cell [22]**

## 1-9  The Materials Used  in This Study

## 1-9-1  Polyvinyl Alcohol (PVA)

Polyvinyl 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 [23,24]. The first scientific reports on (PVA) were published in (1927) [25].

## 1-9-1-a  Physical Properties of (PVA)

The   physical   properties   of (PVA)   depend   on   the   method of preparation,  as  in  the  case  of  other  polymers. The  final  properties are affected  by  the  polymerization  conditions  of  parent  poly(vinyl acetate) used as well as the hydrolysis conditions, drying and  grinding. Table (1-2) shows the physical properties of (PVA).

## Table (1-2): Physical properties of polyvinyl alcohol (PVA) [26]

| Appearance | White –to-cream granule powder |
|---|---|
| Solution PH | (5.0-7.0) |
| Bulk Density, kg/m$^3$ | (400-432) |
| Specific Gravity | 1.30 |
| Resin Density, kg/m$^3$ | 1294 |
| Volume Specific, m$^3$/kg | 7.7 x 10$^{-4}$ |
| Specific Heat, J/kg· K | 1674 |
| Conductivity, Thermal W/(m.K) | 0.2 |
| Thermal Stability | Gradual discoloration about (100 $^o$C), Darkens rapidly above (150 $^o$C) ,Rapid decomposition above (200 $^o$C) |
| Melting Point (unplasticized) $^o$C | 230 for fully hydrolyzed grades ,(180-190) for partially hydrolyzed grades |
| Tg $^o$C (dry film ) | (75-85) |
| Storage Stability (solid) | Indefinite when protected from moisture |
| Flammability | Burns similarly to paper |
| Stability to Sunlight | Excellent |

## 1-9-1-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 increase in viscosity on standing and may even be gel [27]. The viscosity of solutions of partially hydrolyzed (PVA) grade is stable.

## 1-9-1-c   Crystallization 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 (PVA) have been reported, range is between (220°C) and (267°C) for fully hydrolyzed (PVA). Determination of the crystalline melting point using a normal differential thermal analysis technique (DTA) is different in melting point which may be due to decomposition [28,18].

## 1-9-1-d  Glass- Transition Temperature (Tg)

In the study of polymers and their applications, it is important to understand the concept of the glass transition temperature (Tg). The glass transition is a phenomenon observed in linear amorphous polymer. It occurs at fairly well defined temperature when the bulk material ceases to be brittle and glassy in character and becomes less rigid and more rubbery. The knowledge of (Tg) is essential in the selection of materials for various applications many physical properties change profoundly at the glass transition temperature, including mechanical properties and electrical properties. All of these are dependent on the relative degree of freedom for molecular motion within a given

polymeric material and each can be used to monitor the point at which the glass transition occurs [29,30].

The glass transition temperature of fully hydrolyzed (PVA) has been determined to be (85°C) for a high molecular weight material. The (Tg) for (87-89)% hydrolyzed (PVA) is (87°C). It is dependent on the degree of polymerization [12].

 (PVA) used in this study is (99%) hydrolyzed batch no. (6909/1) man date (9/2007) Gerhard Bachmann kG  Tuttlingen / Germann. Figure (1-4) shows the chemical starchier of (PVA).
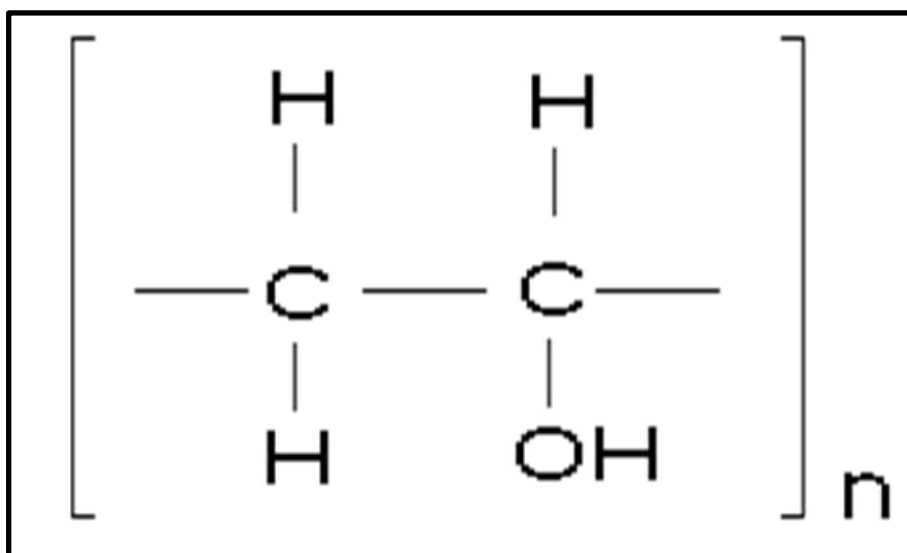


**Figure (1-4): Chemical Starchier of (PVA) [23]**

## 1-9-2 Copper Salts

Copper salts include: Copper Acetate, Copper Chloride and Copper Nitrate**.**

## 1-9-2-a Copper (II) Chloride

Copper (II) chloride is the chemical compound with the chemical formula $CuCl_2$. This is a light brown solid, which slowly absorbs

moisture to form a blue-green dehydrate. The copper (II) chlorides are some of the most common copper (II) compounds, after copper sulfate. Table (1-3) shows the physical and chemical properties of copper (II) chloride.

**Table (1-3): The physical and chemical properties of copper (II) chloride [31]**

| Chemical Name | Copper (II) chloride |
|---|---|
| **Molecular Formula** | $CuCl_2$ |
| **Molar Mass** | 134.45 g/mol (anhydrous) <br> 170.48 g/mol (dihydrate) |
| **Density** | 3.386 g/cm$^3$ (anhydrous) <br> 2.51 g/cm$^3$ (dihydrate) |
| **Melting Point** | 498 °C (928 °F; 771 K) <br> (anhydrous) <br> 100 °C (dehydration of dihydrate) |
| **Solubility in Water** | 70.6 g/100 mL (0 °C) <br> 75.7 g/100 mL (25 °C) <br> 107.9 g/100 mL (100 °C) |
| **Appearance** | Yellow-brown solid (anhydrous) <br> Blue-green solid (dihydrate) |

## 1-9-2-b Copper (II) Acetate

Copper acetate is a chemical compound with the formula $Cu(OAc)_2$ where OAc is acetate $CH_3CO_2$. The hydrated derivative, which contains one molecule of water for each Cu atom, is available commercially. Anhydrous $Cu(OAc)_2$ is a dark green crystalline solid, whereas $Cu_2(OAc)_4(H_2O)_2$ is more bluish-green. Since ancient times, copper acetates of some form have been used as fungicides and

green pigments. Today, copper acetates are used as reagents for the synthesis of various inorganic and organic compounds. Copper acetate, like all copper compounds, emits a blue-green glow in a flame. Table (1-4) shows the physical and chemical properties of copper acetate.

**Table (1-4): The physical and chemical properties of copper acetate [31]**

| Chemical Name | Copper acetate |
|---|---|
| **Molecular Formula** | $Cu(CH_3COO)_2$ |
| **Molar Mass** | 181.63 g/mol (anhydrous) 199.65 g/mol (monohydrate |
| **Density** | 1.882 g/cm$^3$ (monohydrate) |
| **Melting Point** | 115 °C (239 °F; 388 K) |
| **Solubility in Water** | 7.2 g/100 mL (cold water) 20 g/100 mL (hot water) |
| **Appearance** | Dark green crystalline solid |

## 1-9-2-c Copper (II) Nitrate

Copper nitrate is an inorganic compound with the chemical formula $Cu(NO_3)_2$, that forms a blue crystalline solid. Anhydrous copper nitrate forms deep blue-green crystals and sublimes in a vacuum at (150-200) $^o$C. Copper nitrate also occurs as five different hydrates, the most common ones being the trihydrate and hexahydrate. These materials are more commonly encountered in commerce than in the laboratory. Table (1-5) shows the physical and chemical properties of copper nitrate.

**Table (1-5): The physical and chemical properties of copper nitrate [31]**

| Chemical Name | Copper Nitrate |
|---|---|
| Molecular Formula | $Cu(NO_3)_2$ |
| Molar Mass | 187.5558 g/mol (anhydrous)<br>241.60 g/mol (trihydrate)<br>232.591 g/mol (hemipentahydrate) |
| Density | 3.05 g/cm$^3$ (anhydrous)<br>2.32 g/cm$^3$ (trihydrate)<br>2.07 g/cm$^3$ (hexahydrate) |
| Melting point | 256 °C (493 °F; 529 K) (anhydrous, decomposes)<br>114.5 °C (trihydrate)<br>26.4 °C (hexahydrate, decomposes) |
| Solubility in Water | 381 g/100 mL (40 °C)<br>666 g/100 mL (80 °C)<br>243.7 g/100 mL (80 °C) |
| Appearance | Blue crystals |

## 1-10 Literature Survey

Abd El-Kader and Orabi (2002) studied the effect of the molecular weights on the optical and mechanical properties of pure poly(vinyl acohol) (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, (ℎυ), was determined and

the band tails and energy gaps were calculated. It was found that the band tail increased, while the optical gaps decreased with increasing molecular weight, Young's modulus and the strength at the break for (PVA) films decreased as the molecular weight is increased [32].

Alwash (2010) studied the optical properties of poly(vinyl alcohol) films using aluminum sulphate as additive by measuring allowed direct transition energy gap. The results showed that the optical energy gap ($E_g$) for allowed direct transition decreases with increase the concentration of aluminum sulphate. The optical activation energy for allowed direct transition energy gap was evaluated using Urbach- edges method. It was found that ($\Delta E$) increases with increasing the concentration of $Al_2(SO_4)_3$ and decreases when temperature increases [33].

Chiad *et al.* (2010) studied the effect of $Cu(NO_3)_2$ doping on optical properties of polymer (PVA) films. The experimental results showed that the absorption edge was shifted towards long wavelength which identify a red shift. The doping effect on (PVA) polymer reduced the value of the energy gap. Form the transmission curve it seemed that the transmission remained approximately constant within the spectral region of (400-900) nm, this indicated the stability of these films within this spectral region [34].

Abass (2010) studied the optimization conditions for preparation of polyvinyl alcohol-alumina Gel composite and its properties. The results showed that the thermal conductivity of final gel composite product where a thermal conductivity coefficient (K) is decreased with increasing $Al_2O_3$ contents [35].

Nasar *et al.* (2010) studied structural, mechanical and thermal properties of polymer composites of polyvinyl alcohol with inorganic material. The results showed that the thermal conductivity of the polyvinyl alcohol/sodium sulphate and polyvinyl alcohol/lithium sulphate composite decreased with concentration of the salts increase in the polymer composite [36].

Abdelaziz (2011) studied the cerium (III) doping effects on optical and thermal properties of (PVA) films. The results indicated that the optical energy gab ($E_g$) increased with monotonic behavior as the cerium content increased. The dispersion of the refractive index was to discuss dinterms of the single-oscillator Wemple–DiDomernico mode (l) for obtaining the dispersion parameters. The obtained optical parameters were found to be strongly affected by $CeCl_3$ dopant [37].

Hamid (2011) studied the effect of $KMnO_4$ doping on optical properties of polymer (PVA) films. Transmission and absorption spectra were recorded in the wavelength range (300-900) nm. The study of the optical properties of the deposited films were done in order to identify the possible change that happens to the (PVA) films due to doping. The study of the optical parameters gave an indication that the doping affected all the studied parameters like absorbance, reflectance, refractive index and extinction coefficient [38].

Abdullah and Hussen (2011) studied the evolution of the optical properties of (PVA) films filled with sodium iodide. Transparent films of polyvinyl alcohol with different doping sodium iodide concentrations were prepared by using solution cast technique. The optical absorption measurements were carried out for all samples at room temperature

across the wavelength regions. The study was also extended to include the changes in the optical parameters including the band tail width and energy gap for the samples. It was found that the optical absorption was due to direct and indirect transitions, and the optical energy gap values shifted to lower energies with sodium iodide concentration for all transitions, also absorption spectra after annealing for three hours at temperature $(80°C)$ were being investigated. Moreover, the study of complex refractive index showed dependence on dopant concentrations [39].

Al-Taa'y *et al.* (2011) studied the optical properties of pure (PVA) and (PVA) doped with MR. They studied different percentages prepared with constant thickness using casting technique. They found that the optical properties of (PVA) were affected by increasing the impurity concentration [40].

Al-Rawi *et al.* (2011) studied the effect of additive poly(vinyl alcohol) polymer on properties of cement–silica. They found that the thermal  conductivity decreased with the increase in  (PVA) in solution [41].

Abdullah (2012) studied the optical absorption of polyvinyl Alcohol films doped with nickel chloride. The absorption spectral analysis showed that the optical energy gap was due to the direct and indirect allowed optical transitions. The optical energy gap of the  films decreased with increasing localized states in the optical band gap and also with increase of $NiCl_2$ contents. The reductions of optical energy band gap were observed for all samples after annealing at temperatures $(70°C)$ for three hours [42].

Rabee *et al.* (2012) prepared and studied the optical properties for (PVA-AlCl$_3$.6H$_2$O) composite. The results showed that the absorbance of composites increased with the increase in concentration of AlCl$_3$.6H$_2$O, refractive index real part of dielectric constant, Berwster angle and coefficient of finesses increased with increase in weight percentages of AlCl$_3$.6H$_2$O [43].

Chiad *et al.* (2012) studied the optical parameters of AgNO$_3$ dopped poly(vinyl alcohol) films. They found that refractive index, extinction coefficient, real and imaginary parts of dielectric constant and optical conductivity versus wavelength were plotted, and all these parameters were affected by increasing the AgNO$_3$ concentration [44].

Hashim *et al.* (2012) studied the optical properties of (PVA-CaO) composites. The results showed that the absorbance increased with the increase in weight percentage of calcium oxide. The absorption coefficient, extinction coefficient, refractive index and real and imaginary parts of dielectric constants increased with the increase in calcium oxide concentration [45].

Habubi *et al.* (2012) studied the optical properties of BaCl$_2$ doped polyvinyl alcohol films. They found that films had an indirect optical energy gap for indirect transition and decreased with increasing dopant concentration. Refractive index, extinction coefficient and Urbach tail were also investigated. It was found that all the above parameters were affected by doping [46].

Ahmed *et al.* (2013) prepared and studied the optical properties of (polymer-nickel nitrate) composite. They found that the optical energy

gap decreased with increasing $NiNO_3$ content. The refractive index (n), extinction coefficient (k) and static dielectric constant were calculated for the investigated films. The optical constants changed with increase in weight percentages of nickel nitrat [47].

Hashim *et al.* (2013) studied the optical properties of (PVA-$CrCl_2$) composites. The results showed that the absorbance increased with the increase in concentration of $CrCl_2$, absorption coefficient, extinction coefficient, refractive index and real and imaginary parts of dielectric constants were increasing with increase in $CrCl_2$ concentration [48].

Abdullah *et al.* (2013) studied the optical characterization of (polyvinyl alcohol–ammonium nitrate) polymer electrolytes films. They found that the energy gaps decreased upon the increase in salts concentration. The values of the width of the tails of localized states in the forbidden gap of the films obtained from Urbach plots varied from (0.64 eV) to (1.16 eV). The real and imaginary parts of dielectric constant of the polymer electrolyte films increased with the increase in $NH_4NO_3$ concentration. The dielectric constant showed decrease abruptly in the wavelength (235-260) nm, and finally become constant with increase in wavelength [49].

Rabee *et al.* (2013) prepared and studied the characterization of (PVA- $[Co(NH_3)_5Cl]Cl_2$]) composites. The experimental results showed that the absorption coefficient, energy gap of the indirect allowed and forbidden transition, extinction coefficient, real and imaginary parts of dielectric constant and refractive index changed with increase in $[Co(NH_3)_5Cl]Cl_2$ concentration [50].

Habeeb *et al.* (2013) studied the optical properties of (PVA-CoCl$_2$) composites. The experimental results showed that the absorption coefficient, optical energy gap, extinction coefficient, refractive index and real and imaginary parts of dielectric constant affected by addition different weight percentages from cobalt chloride [51].

Mahdy *et al.* (2013) studied the optical properties of (PVA-PEG-NiNO$_3$) composite. They found that the forbidden energy gap decreased with the increase in concentration of NiNO$_3$, while the absorption coefficient increased with the increase in filler (wt.%) content of NiNO$_3$ additive. The extinction coefficient, refractive index, real and imaginary parts of dielectric constant increased with the increase in concentration of NiNO$_3$ additive [52].

Abdul Hafidh *et al.* (2013) prepared and studied the characterization of (PVA-FeNO$_3$) composite. They found that the absorbance of (PVA-FeNO$_3$) composite increased with the increase in weight percentages of FeNO$_3$. The refractive index, real part of dielectric constant, Brewster angle and coefficient of finesses increase with the increase in weight percentages of FeNO$_3$ [53].

Abass (2013) studied the optical parameters of KMnO$_4$ doped (PVA). Films of pure (PVA) and (PVA) doped by KMnO$_4$ were prepared using casting method. KMnO$_4$ doping affected all the parameters, the energy gap (E$_g$) of (PVA) and KMnO$_4$ doped (PVA) were calculated and found that (E$_g$ = 4 eV) and (E$_g$ = 2.25 eV) respectively. He concluded that the skin depth of the doped polymer decreased in comparison with the undoped (PVA) [54].

Kadhim *et al.* (2013) studied the optical properties of (PVA-BaSO$_4$.5H$_2$O) composite. They  found that the absorption coefficient, extinction  coefficient, refractive  index and real and imaginary parts of dielectric  constants  increased  with  increasing  the  additional  of BaSO$_4$.5H$_2$O content [55].

Mustafa (2013) studied  the  optical  properties  of NaI doped polyvinyl alcohol films. The  results  showed  that the (E$_g$) of  the films decreased  with  increasing  NaI  contents.  The  absorbance,  absorption coefficient, extinction  coefficient, finesse  coefficient, refractive  index and  reflectance  of (PVA) doped  with NaI increase  with  increasing doping percentages. The  transmittance  decreased  with  increasing  the weight percentages. The real and imaginary parts of dielectric constant and  optical  conductivity increased   with   increasing  sodium  iodine concentration. The indirect optical energy gaps for these undoped and doped (PVA) films  were  estimated  to  be  about (5.05, 4.91, 4.79, 4.70 and 4.55) eV  for  indirect  allowed  transitions, where as  the  indirect forbidden energy gaps were  determined  as (4.91, 4.82, 4.75, 4.65 and 4.54) eV  with  increasing  sodium iodine contents [56].

Abid and  Habeb (2013) studied the effect of cobalt chloride CoCl$_2$ on the electrical and optical properties of (PVA-PVP-CoCl$_2$) films. The absorbance was recorded in the wavelength range (200-1100) nm, also the absorption coefficient, real and imaginary parts of dielectric constant, energy gap, extinction coefficient and refractive index were determined [57].

Abdullah *et al.* (2013) studied the optical properties of (PVA:CdCl$_2$.H$_2$O) polymer electrolytes. The optical transmittance

increased up to (98%) with increasing the wavelength for all films beyond ($\approx$240nm). The calculated energy band gap changed from (6.42 eV) (pure PVA) to (5.80 eV) (PVA-20%CdCl$_2$.H$_2$O). The real and imaginary parts of dielectric constant of the doped films increase with increasing CdCl$_2$.H$_2$O concentration, and it shows an abruptly decrease in the wavelength range (200-220) nm, and finally became constant with increase in photon energy [58].

Salman *et al.* (2013) studied the optical properties of polyvinyl alcohol (PVA) films doped with CoCH$_3$COOH salt. The results showed that the indirect allowed transitions, and the optical energy gap of the films decreased with increasing CoCH$_3$COOH content. Optical parameters such as absorption coefficient, refractive index, extinction coefficient and real and imaginary parts of dielectric constant of films were calculated as a function of doping [59].

Abdallh *et al.* (2013) studied the optical properties of poly(vinyl alcohol) films doped with copper chloride. They found that the optical energy gap (E$_g$) for allowed direct transition decreased with increasing the concentration of cupper chloride [60].

Khodair (2014) prepared and studied the optical properties of pure and yellow methyl – doped polyvinyl alcohol (PVA) films. He found that the films showed indirect allowed transitions that influenced by the doping. The optical energy gap decreased from about (5.732 eV) before doping to about (4.821 eV) and (3.819 eV) after doping. Optical constants like refractive index, extinction coefficient were calculated and correlated with doping [61].

Al-Dahash (2014) prepared and studied the characterization of ($PVA\text{-}SnCl_2$) composite. The forbidden energy gap decreased with increasing filler (wt.%) content, while the absorption coefficient, extinction coefficient and refractive index increased with increasing filler (wt.%) content [62].

Abbas *et al.* (2014) synthesized and studied the optical characterization of nickel doped poly vinyl alcohol films. The optical energy gap of the films decreased by the increase in doping (6-5.2) eV. Extinction coefficient and refractive index increased as the doping percentage increased [63].

Ganem *et al.* (2014) studied the effect of potassium bromide on optical properties of (PVA). They found that the absorption coefficient is smaller and more stable in the low photon energy region, and the absorption coefficient and more extinction coefficient increased with increase in potassium bromide concentrations. The absorption coefficient and extinction coefficient increased as a result of the scattering centers in the composites. The values of the refractive index (n) of the composites increase exponentially with increasing photon energy. The energy gap decreased with increase in the potassium bromide concentrations. The real and imaginary parts of dielectric constants showed the exponential increased with the increase in incident photon energy. It also increased with the increasing in potassium bromide concentrations [64].

Salman *et al.* (2015) prepared and studied some electrical and optical properties of ($PVA\text{-}NiCl_2$) composites. The experimental results for ($PVA\text{-}NiCl_2$) films showed that the transmittance decreased with increasing the filler content, while the absorption coefficient increased

with increasing the filler content. Moreover the results showed that allowed indirect transitions, and the energy gap ($E_g$) decreased with increasing the filler content [65].

Salman *et al.* (2015) prepared and studied of some optical properties of (PVA-Ni(CH$_3$COO)$_2$) composites. The experimental results for (PVA-Ni(CH$_3$COO)$_2$) films showed that the electronic transition allowed indirect transition, and the energy gap decreased with increasing the filler content. The absorption coefficient, refractive index, extinction coefficient and real and imaginary parts of dielectric constant were calculated. It was found that all these optical parameters increased with increasing the filler content [66].

Abdullah *et al.* (2015) studied the complexion formation of (PVA/PEO/CuCl$_2$) solid polymer electrolyte. The experimental results for (PVA – PEO – CuCl$_2$) films showed that the absorption edge for electrolyte samples shifted toward a lower energy region by increasing the salt concentration, leading to the band gap reduction. The band gap energy data showed that the incorporation of CuCl$_2$ into the polymeric system caused charge transfer complexes in the blend polymer. The (PVA/PEO/CuCl$_2$) solid polymer electrolyte films exhibited good (UV) shielding properties in the wavelength range from (190 to 400) nm [67].

Abid *et al.* (2015) studied the effect of CuO doped polyvinyl alcohol on the structural and optical properties of (PVA) films. The experimental results showed that the optical energy gap reduced as the doping percentage increased [68].

## 1-11  Aims of The Works

1-  Preparing the pure films of polymer (polyvinyl alcohol (PVA)), and doping them with copper salts (CuCl, $Cu(CH_3COO)_2$ and $Cu(NO_3)_2$) with different concentrations (0,2, 4, 6, 8 and 10) wt% .

2- Studying some optical and thermal properties for (PVA) and  (PVA-(copper salts) films.

3- Studying the effect of annealing on the optical properties for (PVA-the best salt of copper salts which have the best optical and thermal properties).