Republic of Iraq
Ministry of Higher Education
and Scientific Research
University of Diyala
College of Science
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Effect of Iron Salts on Some Physical Properties of Polymer (Polyvinyl Alcohol (PVA))

A Thesis

Submitted to the Council of the College of Science-University of Diyala in Partial Fulfillment of the Requirements for the Degree of Master of Sciences in Physics

by

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B. Sc. in Physics (2012)

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2016 AD ***1438 AH***

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة ديالى
كلية العلوم
قسم الفيزياء

تأثير املاح الحديد على بعض الخصائص الفيزيائية لبوليمر بولي فنايل الكحول (PVA)

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

من قبل

ميسم عبد الرحمن عيسى
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١٤٣٨ هـ ٢٠١٦ م

بسم الله الرحمن الرحيم

يا أيها الذين آمنوا إذا قيل لكم تفسحوا في المجالس فافسحوا يفسح

[illegible] وإذا قيل انشزوا فانشزوا يرفع الله الذين آمنوا

منكم والذين أوتوا العلم درجات والله بما تعملون خبير (11)

صدق الله العظيم

سورة المجادلة الآية (11)

Dedications

To my parents, who always picked me up on time and encouraged me to go on every adventure, especially this one

To my husband, for raising me to be believe that anything was possible and for making everything possible

To my supervisors, Prof. Dr. Sabah Anwer Salman and Prof. Asaad [illegible]

To my family, who support me with their kindness, patience and encouragement.

Allah bless you all

Maysam

Acknowledgements

Praise be to Almighty Allah, the most Merciful and Compassionate, For the ever gifts He has granted me without which this work would not have seen the light. Thanks are to His prophet Muhammad (May the Blessings and peace of Allah be upon him), the ever moral guidance for the humanity.

I would like to express my gratitude to my supervisors, ***Prof. Dr. Subah Anwer Salman*** *and* ***Prof. Asaad Ahmed Ka[illegible]*** *for their illuminating remarks and continuous support which encourage me agreat deal to complete this work.*

Special thanks are due to the Dean o[illegible] all the Staff of the Department of Physics for their assistance and especially for ***Marwa Rashed Jwameer.***

Finally, thanks are due to all who have helped me throughout this work, be they relatives or friends.

Abstract

The pure films of polymer (polyvinyl alcohol (PVA)) filled with iron salts ($FeCl_3$ and $Fe(NO_3)_3$) with different concentrations ((1, 3, 5, 7 and 9) wt%) have been prepared by using casting technique. The thermal and optical properties of pure and filled films with iron salts of polymer (polyvinyl alcohol (PVA)) were studied. The transmission and absorption spectra have been recorded [illegible]

[illegible]

The effect of iron salts concentration on the thermal properties of (PVA- iron salts) composites films have been investigated.

The experimental results of (PVA-iron salts) composites films show that the thermal conductivity decreases with increasing the filler content while the glass- transition temperature increases with increasing the filler content.

Also the effect of iron salts concentration on the optical parameters such as transmittance, absorbance, absorption coefficient, refractive index, extinction coefficient and real and imaginary parts of dielectric constant of (PVA-iron salts) composites films were studied.

The experimental results of (PVA-iron salts) composites films show that the transmittance decreases with increasing the filler content while the absorbance increases with increasing the filler content. The absorption coefficient, refractive index, extinction coefficient and real and imaginary parts of dielectric constant were found to increase with increasing the filler content. Moreover the results show that the electronic transitions are allowed indirect [illegible] and Urbach energy (E_u) decreases with increasing the filler content.

Also the effect of iron salts concentration on the bonds of pure (PVA) film were studied.

The experimental results show that the absorption bands of the bonds O-H, C-H, C=O, C=C, C-O, C-C and CH_2 of pure (PVA) film shift to higher wavenumbers with increasing the filler content in the doped (PVA) film with iron salts.

الخلاصة

حضرت الاغشية النقية للبوليمر (بولي فنايل الكحول (PVA)) والمشوبة باملاح الحديد ($Fe(NO_3)_3$ and $FeCl_3$ بتراكيز مختلفة ((1, 3, 5, 7 and 9) wt%) باستخدام تقنية الصب. لقد تمت دراسة الخصائص الحرارية والبصرية لأغشية البوليمر (بولي فنايل الكحول (PVA)) النقية والمشوبة بأملاح الحديد طيف النفاذية والامتصاصية سجلا في مدى [illegible]

[illegible] الطول الموجي (250-1100) nm [illegible]

[illegible] على الخصائص [illegible] (املاح الحديد-PVA).

أظهرت النتائج العملية لأغشية متراكبات (املاح الحديد-PVA) بأن التوصيلية الحرارية تقل مع زيادة نسبة التشويب لأملاح الحديد بينما درجة حرارة الانتقال الزجاجي تزداد بزيادة نسبة التشويب لأملاح الحديد.

كذلك تم دراسة تأثير تركيز أملاح الحديد على المعلمات البصرية (النفاذية، الامتصاصية، معامل الامتصاص، معامل الانكسار، معامل الخمود وثابت العزل بجزئيه الحقيقي والخيالي) لأغشية متراكبات (املاح الحديد-PVA).

أظهرت النتائج العملية لأغشية متراكبات (املاح الحديد-PVA) بأن النفاذية تقل مع زيادة نسبة التشويب لأملاح الحديد بينما الامتصاصية تزداد مع زيادة نسبة التشويب لأملاح الحديد. معامل الامتصاص، معامل الانكسار، معامل الخمود وثابت العزل بجزيئيه الحقيقي والخيالي يزدادون بزيادة نسبة التشويب لأملاح الحديد، وكذلك اظهرت النتائج بأن الانتقالات الالكترونية هي إنتقالات إلكترونية مسموحة غير مباشرة، ان فجوة الطاقة (E_g) وطاقة اورباخ (E_u) تقل بزيادة نسبة التشويب لأملاح الحديد.

كذلك تم دراسة تأثير تركيز املاح الحديد على الاواصر لغشاء (PVA) النقي.

أظهرت النتائج العملية بان حزم امتصاص الاواصر O-H, C-H, C=O, C=C, C-O, C-C and CH_2 لغشاء (PVA) النقي تنحرف نحو الاعداد الموجية الاعلى بزيادة نسبة التشويب بأملاح الحديد في غشاء (PVA).

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List of Symbols and Abbreviations

Symbol	Description	*Unit*
LED	Light Emitting Diode	**-**
FET	Filed Effect Transistor	**-**
PVA	Polyvinyl alcohol	**-**
FTIR	Fourier Transform Infrared	**cm^{-1}**
E_g	Energy gap	**eV**
A	Absorbance	**-**
$h\nu$	The photon energy	**eV**
UV	Ultra violet	[illegible]
VIS	Visible	**-**
x	Degree of polymerization	**-**
E_{ele}	The electronic energy	**eV**
E_{vib}	Vibration energy	**eV**
E_{rot}	Rotational energy	**eV**
E_{trans}	Translational energy	**eV**
B	Inversely proportional to amorphousity	**-**
α	The absorption coefficient	**cm^{-1}**
E_p	Energy of phonon	**eV**

I_o	The incident light intensity	**eV/m^2. s**
I	The penetrating light intensity	**eV/m^2. s**
t	The thickness of the matter	**µm**
Q	Heat flux	**W/m^2**
E_u	Urbach energy	**eV**
C	The light speed in vacuum	**m/s**
v	The light speed in matter	**m/s**
$k_\circ$	The extinction coefficient	-
λ	The wavelength	nm
ε	The complex dielectric constant	-
[illegible]	The real part of the dielectric constant	-
[illegible]	The imaginary part of the dielectric constant	[illegible]
DSC	Different Scanning Calorimeter	-
T_g	Glass-transition temperature	**˚C**
M	Molar mass	**gm mol^{-1}** **Kg mol^{-1}**
k	Thermal conductivity coefficient	**W/m. K**
$FeCl_3$	Iron Chloride	-
$Fe(NO_3)_3$	Iron Nitrate	-

1-1 Introduction

Polymers, as plastics and rubbers, pervade our lives and we come across them in many different forms. As such, their physical properties have great importance, and an understanding of them is vital for their uses in technology and engineering [1].

Polymers possess material properties which are distinctly different from those exhibited by metals, ceramics and glasses. Metals on heating can be transformed from hard solids to low viscosity liquids over a relatively small temperature range. Ceramics exhibit a hardness that does not very significantly with temperature up to the melting point and have poor impact properties and low elasticity. In contrast, polymers can be hard at low [illegible] comparable to metals [illegible] but on heating can be transformed into a rubbery state and exhibit a high degree of elasticity. Increasing the temperature further in certain cases allows [illegible] converted into [illegible] some polymers do not flow when heated and so cannot be reshaped [1].

Polymers are extremely long chained molecules that have repeating units [2,3]. In many polymers, very few interactions exist between the chains except Vander Waals forces. If Vander Waals forces were the only forces holding the chains together, little cohesion would exist between chains. The resulting material would likely be a liquid or a gel, which is not the case. Polymers are generally solids and this is due to entanglements of the long molecules. To have stable entanglements that restrict the flow of the polymer chains, polymers must have a critical molecular weight that is dependent on the flexibility of the backbone and the steric hindrance within the molecule [2].

The importance of the entanglements on the cohesion can be seen in cases when an assortment of different length strings are mixed into a ball, the short pieces of string could be easily removed. The intermediate length pieces of string could be removed only with some effort but it would take a substantial amount of effort to remove the longest strings. These entanglements influence the viscoelastic, melt viscosity and mechanical properties of the polymer [2].

Polymers are significantly less crystalline than other crystalline materials, such as metals or low-molecular-weight compo[illegible] and many are amorphous [2]. Figure (1-1) is a repres[illegible] of how polymer chains [illegible] non-crystalline [illegible] think of the amorphous polymer m[illegible] spaghetti. Some characteristics of amorphous polymers are that they have good mechanical properties and good dimensional stability. Amorphous polymer also shrink consistently during cooling, as well as being inherently transparent [4].

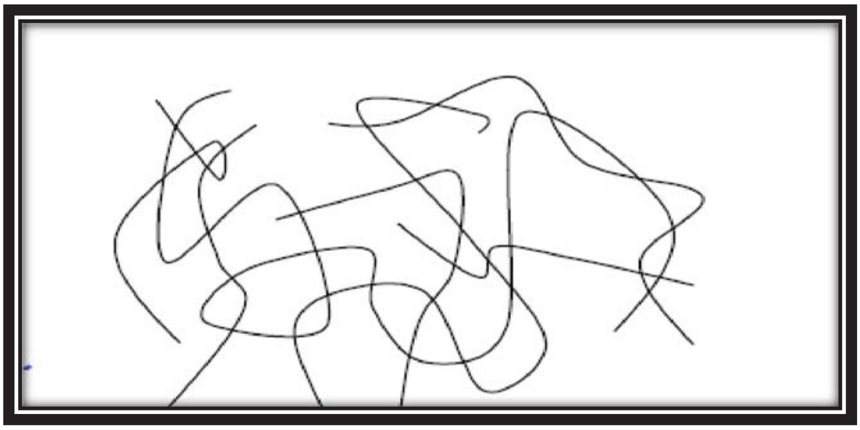

Figure (1-1): Representation of polymer chains in an amorphous polymer [2,4]

Semi-crystalline polymers generally orient themselves in a lamella structure [2]. An example of lamellar structure is the gills of a fish or mushroom. For a polymer to crystallize, the conditions during the cooling of a polymer melt have to allow the polymer chains to arrange themselves. The crystal sheets may be as thin as (100 to 200) A; between these crystalline sheets, there are amorphous regions [2]. It was found that as the lamellar structure thickness increased, the thermal conductivity of polyethylene did as well [5]. Figure (1-2) is an illustration of how polymer chains orient in a lamellae structure. This figure illustrates three possible ways the chains could orient in two dimensions, which can be expanded in to three dimensions. Semi-crystalline polymers have anisotropic shrinkage, very good electrical properties and are chemically resistant to some harsh environments [4].

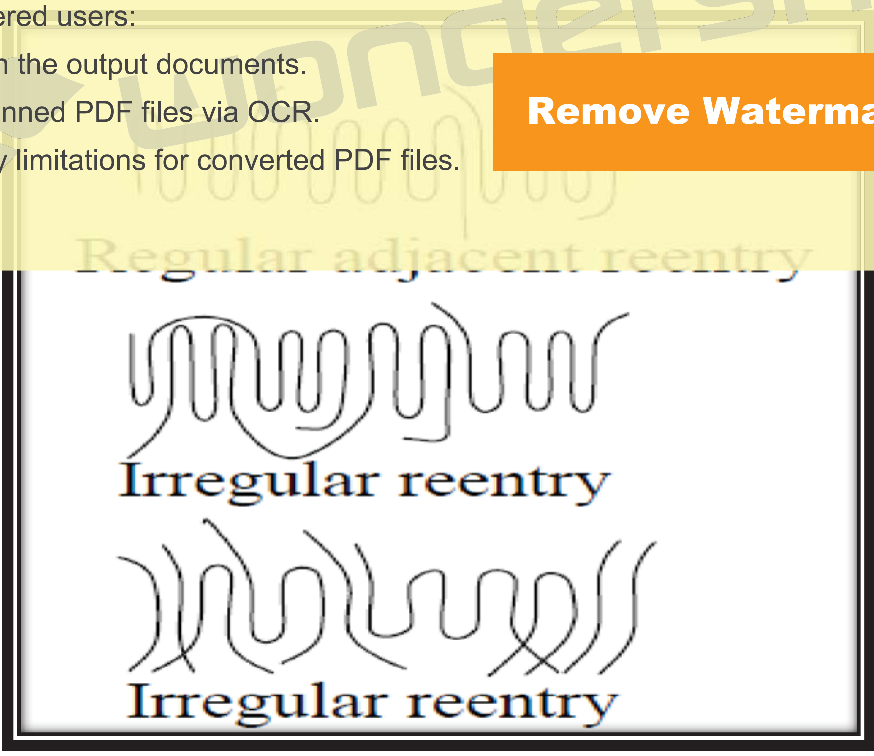

Figure (1-2): 2D representation of polymer chains in a semi-crystalline polymer [2,3]

1-2 Polymer Structure

In the teaching of physical polymer science, a natural progression of material begins with chain structure, proceeds through morphology and leads onto physical and mechanical behavior. Polymer chains have three basic properties:

1- The molecular weight and molecular weight distribution of the molecules.

2- The conformation of the chains in space. The term conformation refers to the different arrangements of atoms and substituents of the polymer chain brought about by rotations about single bonds. Examples of different polymer conformations include the fully extended planar zigzag, helical, folded chain and random coils.

3- The configuration of the chain. The term "configuration" refers to the organization of the atoms along the chain. Some scientists prefer the term "microstructure" rather than configuration. Configurational isomerism involves different arrangements of the [illegible] can be interconverted only by the breakage and reformation of primary chemical bonds [6].

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 (Vander Waals forces). When heated, these molecules can slide over each other as in polystyrene, polyethylene, polyvinyl alcohol and polyvinyl chloride [7].

2- Thermoset Polymers

These polymers are chemically changed when heated. Thermo sets 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, hard, non-conductive of heat and electricity because molecules of these polymers are connected by strong covalent chemical bonds. Phenol formaldehyde resin and urea-formaldehyde resin are examples of this [illegible]

1-3-2 Chemical Classification of Polymers

Polymers are classified depending on the structural composition to:

1- **Liner Polymers**

The essential structural units for these polymers are 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 (1-3-a).

It is the same type of polymer which is used in the present study.

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 (1-3-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 (1-3-c) [10].

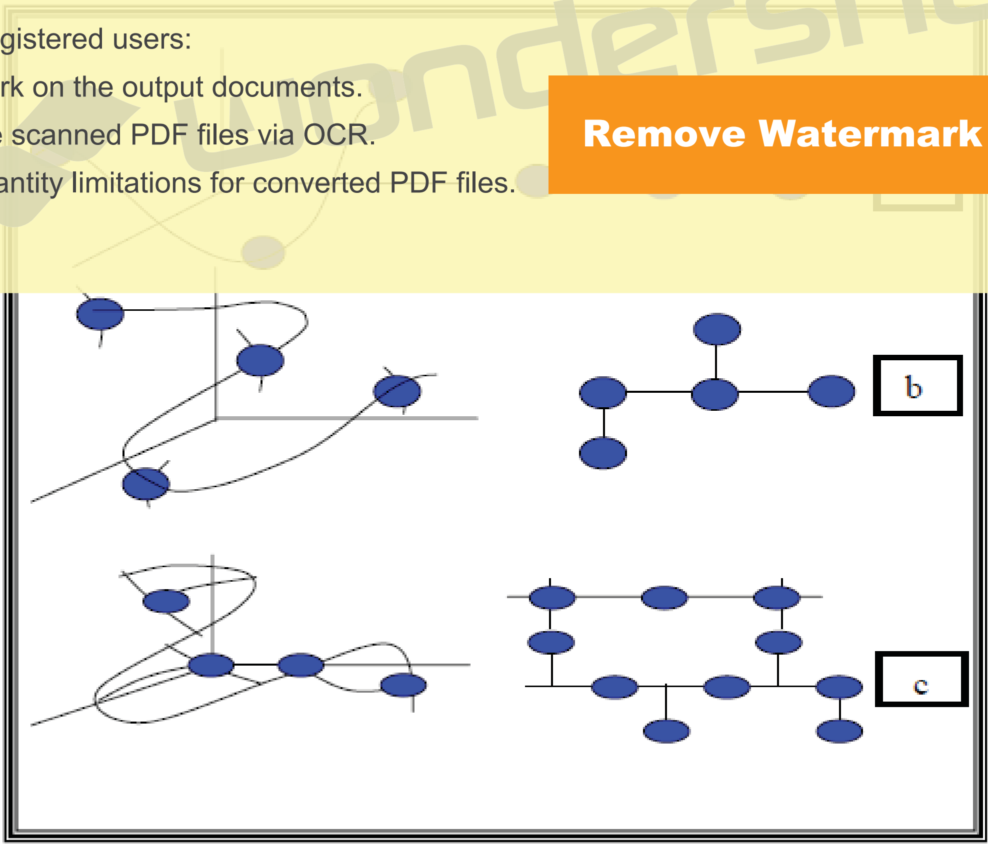

Figure (1-3): The different types of polymeric chains [11]

1-3-3 Polymers Dependence on Homogeneity

Polymers are classified depending on the homogeneity of repeating units in to:

1- Homopolymers

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

2- Copolymers

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

3- Composite Polymers

[illegible] some [illegible] homogeneous polymers [illegible] make change in some of its characteristics and the entering of new recipes on it [9,12].

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

Polymers are classified depending on the chain's lengths and molecular weights in to:

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 chains and thus there is a multiplicity of molecular weights [13].

1-4 Polymer 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 [illegible] and represent the most industrial [illegible] polymers [illegible] plastics, synthetic [illegible] and [illegible]

1-5 Characteristics of Polymers

1- Low density.
2- Low coefficient of friction.
3- Good corrosion resistance.
4- Good mould ability.
5- Excellent surface finish can be obtained.
6- Can be produced with close dimensional tolerances.
7- Economical.
8- Poor tensile strength.
9- Low mechanical properties.
10- Poor temperature resistance.
11- Can be produced transparent or in different color [15].

1-6 Polymer Composites

A composite is a material system composed of a combination of two or more materials that differ in form or material composition. The properties of a composite are different from those of its materials [16,9]; it is also cohesive in structure. The composite is comprised of two major components: the matrix which is the basic material and the additives. The matrix is the basic material, serving to enclose the composite and give it a 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 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 [13,17].

Composite materials are often classified by matrix type or reinforcement type. In the matrix classification, there a[illegible] 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 [13].

1-7 Molar Mass and Degree of Polymerization

Many properties of polymers show a strong dependence upon the size of polymer chains, so that it is essential to characterize their dimensions. This normally is done by measuring the molar mass (M) of a polymer which is simply the mass of (1 mole) of the polymer and usually is quoted in units of (g mol^{-1}) or (Kg mol^{-1}). The term ‘molecular weight is still often used instead of molar mass, but is not preferred because it can be somewhat misleading. It is really a dimensionless quantity, the relative molecular mass, rather than the weight of an individual molecule which is of course a very small quantity (e.g. ~10^{-19} – ~10^{-18} g for most polymers). By multiplying the numerical value of molecular weight by the specific units (g mol^{-1}) it can be converted into the equivalent value of molar mass. For network polymers the only meaningful molar mass is that of the polymer chains existing between junction point [illegible] molar mass of the network itself essent[illegible] of a homopolymer is related to the degree of polymerization (x), which is the number of repeat units in the polymer chain, by the simple relation:

$$M = xM_0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1\text{-}1)$$

Where M_0 is the molar mass of the repeat units. For copolymers the sum of the products (xM_0) for each type of repeat unit is required to define the molar mass [18].

1-8 Factors Affecting Polymer Properties

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

1-8-1 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 the group of secondary forces [19,20].

1-8-2 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 [21].

1-8-3 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 [22].

1-9 Preparation Methods of Polymer Films

1-9-1 Casting Method

To prepare 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 speed of solvent evaporation must be reduced and the preparation time must be long as menshined in chapter (3) [23].

1-9-2- 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 depend [illegible] rotation speed and spin time. To obtain a very thin film, the polymer solution must be diluted and rotation speed must be increased [20].

1-9-3 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 [20].

1-9-4 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 (PVA+ Barium nitrate) [20].

1-9-5 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 [20].

1-9-6 Electrochemical Method

Electrochemical polymerization in non-organic matter that 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 [24]. Figure (1-4) shows the main parts of an electrochemical cell:

1- cell
2- Electrodes
3- Electrolyte solution

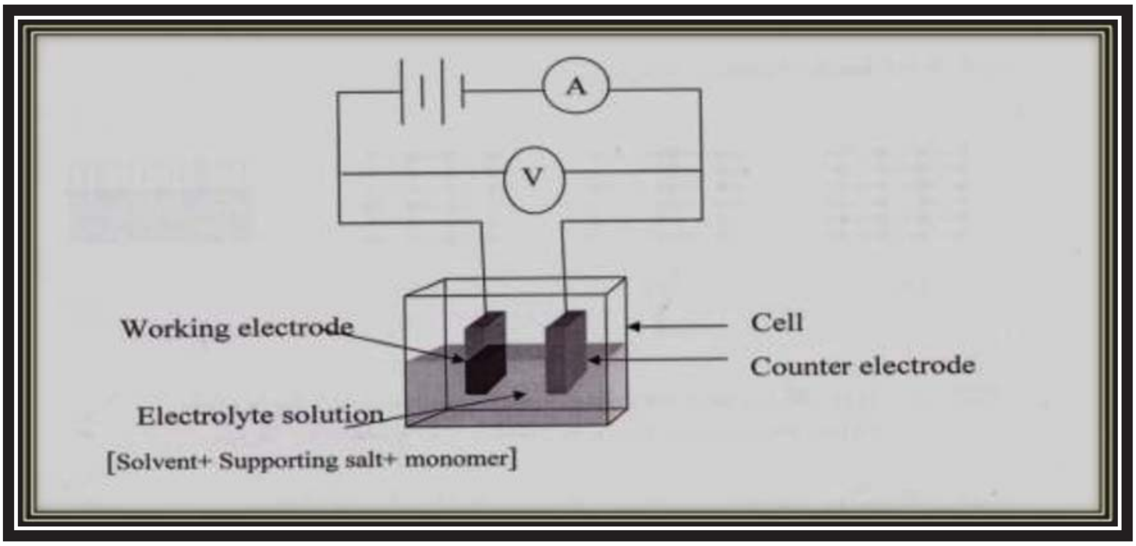

Figure (1-4): The main parts of electrochemical cell [24]

1-10 Application of composites

Polymeric materials are used in and on soil to improve aeration, provide mulch, promote plant growth and health [15].

1-10-1 Medicine

Biomaterials, especially heart valve replacements and blood vessels, are made of polymers like Dacron, Teflon and polyurethane. (PVA) used for eye drops and gliding contact lens solution [15].

1-10-2 Consumer Science

Plastic containers of all shapes and sizes are light weight and economically less expensive than the more traditional containers. Clothing, floor coverings, garbage disposal bags and packaging are other polymer applications [15].

1-10-3 Industry

Automobile parts, windshields for fighter planes, pipes, tanks, packing materials, insulation, wood substitutes, adhesives, matrix for composites and elastomers are all polymer applications used in the industrial market. (PVA) fiber used for strengthen concrete [15].

1-10-4 Sports

Playground equipment, various balls, golf clubs, swimming pools and protective helmets are often produced from polymers and (PVA) used in sport fishing [15].

1-11 Polyvinyl Alcohol (PVA)

Polyvinyl alcohol (PVA) is the largest synthetic water soluble polymer produced in the world [25]. [illegible] (PVA) [illegible] method of [illegible] partial hydrolysis process of polyvinyl acetate [26]. Table (1-1) shows the physical properties of polyvinyl alcohol (PVA).

Because of (PVA) is a polymer obtained by the hydrolysis process, the (PVA) has particularly notable properties than other thermoplastic. 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 [27]. 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 [28].

Table (1-1):

The physical properties of polyvinyl alcohol (PVA) [29]

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
Specific Volume , kg/ m^3	7.7 x 10^{-4}
Specific Heat, J/kg.K	1674
Thermal Conductivity, W/(m.K)	0.2
Th[illegible] Stabili[illegible]	Gr[illegible] °C [illegible] °C), Rapid decomposition above (200 °C)
Melting Point (unplasticized) °C	(230) for fully hydrolyzed grades ,(180-190) for partially hydrolyzed grades
T$_g$°C (dry film)	(75-85)
Storage Stability (solid)	Indefinite when protected from moisture
Flammability	Burns similarly to paper
Stability to Sunlight	Excellent

1-12 Iron (III) Chloride

Also called ferric chloride is a chemical compound with the formula $FeCl_3$ and with iron in the +3 oxidation state. The color of iron (III) chloride crystals depends on the viewing angle: by reflected light the crystals appear dark green, but by transmitted light they appear purple-red. Table (1-2) shows the chemical and physical properties of iron chloride.

Table (1-2): The chemical and physical properties of iron (III) chloride [30]

Chemical Name	Iron (II) chloride
Molecular Formula	$FeCl_3$
Molar Mass	162.2 g/mol (anhydrous) 270.3 g/mol (hexahydrate)
Density	[illegible] g/cm^3 (anhydrous)
Melting Point	[illegible] (anhydrous) 37 °C (99 °F; 310 K) (hexahydrate)
Boiling Point	315 °C (599 °F; 588 K) (anhydrous, decomposes) 289 °C (536 °F; 553 K) (hexahydrate, decomposes)
Appearance	Green-black by reflected light; purple-red by transmitted light

1-13 Iron (III) Nitrate

Or ferric nitrate, is the chemical compound with the formula $Fe(NO_3)_3$. Since it is deliquescent, it is commonly found in its nonahydrate form $Fe(NO_3)_3 \cdot 9H_2O$ in which it forms colorless to pale violet crystals. The chemical and physical properties of iron nitrate were shown in the table (1-3).

Table (1-3): The chemical and physical properties of iron (III) nitrate [30]

Chemical Name	Iron (III) nitrate
Molecular Formula	$Fe(NO_3)_3$
Molar Mass	241.86 g/mol (anhydrous) 403.999 g/mol (nonhydrate)
Density	1.6429 g/cm (nonhydrate)
Melting Point	47.2 °C (117.0 °F; 320.3 K) (nonhydrate)
Boiling Point	125 °C (257 °F; 320.3 K) (nonhydrate)
Appearance	Pale violet crystals

1-14 Literature Survey

Devi et al. (2002) studied the electrical and optical properties of pure and silver nitrate-doped polyvinyl alcohol films. The experimental results showed that the electrical conductivity increased with increasing dopant concentration up to (0.5 wt%) and then showed a decrease beyond this concentration. The optical energy gaps and band edge values shifted to lower energies on doping up to concentration of (0.5 wt%) but showed an increasing tendency for further increase in dopant concentration [31].

Tawansi et al. (2005) studied the physical properties of polymer (PVA) filled with $FeCl_3$. The experimental results showed that the filling level (FL) [illegible] physical parameter characterizing the other properties. The (XRD) scans revealed a semicrystalline feature of the virgin polymer and an existence of [illegible] of the [illegible] The dc electrical resistivity was measured in the temperature range of 300–400K. An intrachain one-dimensional interpolator hopping mechanism was assumed to interpret the electrical conduction. The (ESR) studies of (PVA) filled with various mass fractions of $FeCl_3$ revealed very complicated spectra due to hyperfine and fine structure [32].

Lee et al. (2008) studied the properties of nano-(ZnO/PVA/polyethylene oxide (PEO)) composite thin films, to explore the possibility of the mechanical and electronic properties of ZnO in the form of nanoparticles. Ultraviolet absorption and thermal behavior of thin films were determined as a function of nano-ZnO content up to (15 wt%).

The (UV-V) region is a transmission of films, nano-ZnO particles not only absorbs (UV) light, but also scatters visible light. Nano-ZnO (PVA) and (PEO) suspensions of (1%) ZnO have better transmission of visible light compared to higher ZnO concentrations [33].

El-Khodary (2009) studied the vibrational, thermal, optical and magnetic investigations of (PVA) films filled with $FeCl_3$ and $CoCl_2$. An assignment of the most notably infrared (IR) peaks was done. Significant vibrational deformations of certain (IR) peaks with filling were studied. The main characterizing temperatures were recorded, assigned and their (FL) dependence were studied using differential scanning calorimetric (DSC). The thermal analysis depicts better thermal properties of the filled polymer with increasing (X) and that represents the interesting industrial applications. The absorption peaks in the ultraviolet and visible regions were detected and assigned. Electron paramagnetic resonance (EPR) spectra are complicated and characterized by the hyperfine str[illegible] [illegible] of the reciprocal (dc) magneti[illegible] behavior characterized by localized magnetic moments. A correlation between vibrational, thermal, optical and magnetic properties was done [34].

Hema et al. (2009) studied the structural and thermal studies of ($PVA:NH_4I$). A new proton-conducting ($PVA:NH_4I$) polymer electrolyte has been prepared and characterized using (XRD), (FTIR) and (DSC). From the (FTIR) result, they have confirmed the interaction between the added salt and the host polymer matrix because of which there is variation in thermal constants (T_g and T_m), structural (crystallinity) and also the conductivity properties (σ_{dc}, E_a), etc. of the prepared polymer electrolytes [35].

El-Khodary (2010) studied the evolution of the optical, magnetic and morphological properties of (PVA) films filled with $CuSO_4$. The experimental results showed that the optical energy gap and the Urbach energy decreased with concentration of the salts increase in the polymer composite [36].

Nasar et al. (2010) studied the structural, mechanical and thermal properties of polymer composites of polyvinyl alcohol with inorganic material. They found 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 [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 (300-9[illegible] [illegible] given an indication that the doping affected all the studied parameters like absorbance, reflectance, refractive index and extinction coefficient [38].

Abdelaziz (2011) studied the cerium (lll) doping effects on optical and thermal properties of (PVA) films. The results showed that the thermal stability and the glass transition temperature of the doped films increased with the increase in concentration of the cerium. Both (XRD) and (FTIR) confirm the complex formation due to the presence of new peaks, broadening and shifting of the absorption bands [39].

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 the localized states in the optical band gap and also with increase of $NiCl_2$ content [40].

Ahmad et al. (2012) studied the electrical and optical properties of (PVA/LiI) polymer electrolyte films. They found that the optical energy gap from direct allowed transition decreases from (5.56 eV) of pure (PVA) to (4.95 eV) of (PVA+20%LiI) [41].

Hashim et al. ([illegible]) studied the optical properties of (PVA-[illegible]) composite. They found that the absorption coefficient, extinction coefficient, refractive index and real and imaginary parts of dielectric constant were increased with the incre[illegible] [illegible] increase [illegible]

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 content (wt%) of $NiNO_3$ additive. The extinction coefficient, refractive index and real and imaginary parts of dielectric constant increased with the increase in concentration of $NiNO_3$ additive [43].

Abdul Hafidh et al. (2013) prepared and studied the characterization of ($PVA-FeNO_3$) composite. They found that the refractive index, real part of dielectric constant, Berwster angle and coefficient of finesses of ($PVA-FeNO_3$) composite are increased with concentration of $FeNO_3$ [44].

Al-Taa'y (2014) studied the optical properties of polyvinyl alcohol (PVA) films doped with Fe citrate. In this work, the effect of Fe citrate impurity on the optical properties of (PVA) films has been studied. The results showed that the optical constant of the pure (PVA) films were increased after doping and with increasing impurity concentration. Moreover, the values of optical energy gap were decreased after doping and with increasing impurity concentration [45].

Abdullah et al. (2015) studied the complexion formation of ($PVA/PEO/CuCl_2$) solid polymer electrolyte. The experimental results of ($PVA - PEO - CuCl_2$) films showed that [illegible] shifted toward the lower energy [illegible] concentration, leading to the band gap reduction. The optical energy 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 - 400) nm [46].

Deshmukh et al. (2016) studied the Influence of K_2CrO_4 doping on the structural, optical and dielectric properties of polyvinyl alcohol/K_2CrO_4 composite films. Ultraviolet–visible spectroscopy, X-ray diffraction, thermogravimetric analysis, optical microscopy, scanning electron microscopy and dielectric devices are used in this research. Microscopic studies reveal that K_2CrO_4 was homogenously mixed with polyvinyl alcohol matrix due to interfacial interaction between polyvinyl alcohol and K_2CrO_4. The composite films showed very high dielectric constant and relatively low dielectric loss. Hence, such composite materials with improved dielectric properties could be useful for the fabrication of electrical charge storage device [47].

1-15 Aims of The Works

1- Preparing the thin films of polymer polyvinyl alcohol (PVA), and filled them with iron salts ($FeCl_3$ and $Fe(NO_3)_3.9H_2O$) with different concentrations ((0,1, 3, 5, 7 and 9) wt%).

2- Studying some optical and thermal properties of (PVA) film and (PVA-(iron salts) composites films.