جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة بابل – كلية التربية للعلوم الصرفة
قسم الفيزياء
الدراسات العليا – الدبلوم العالي

تصنيع ودراسة الخصائص التركيبية والبصرية لأغشية المتراكب النانوي (PVA/Co_3O_4)

بحث مقدم

إلى مجلس كلية التربية للعلوم الصرفة في جامعة بابل وهو جزء من متطلبات نيل درجة الدبلوم العالي تربية / فيزياء المواد وتطبيقاتها

من قبل الطالبة

رغدة كريم خضير زغير

بكالوريوس تربية فيزياء
جامعة بابل 2010 م

بإشراف

أ. د. فؤاد شاكر هاشم

1443 هـ

2021 م

Republic of Iraq
Ministry of Higher Education &
Scientific Research
University of Babylon
College of Education for Pure
Sciences
Department of Physics

Synthesis and investigation of the structural and optical properties of (PVA/Co_3O_4) nanocomposite

A research

Submitted to the Council of the College of Education for Pure Sciences of University of Babylon in Partial Fulfillment of the Requirements for the Degree of Higher Diploma Education/ Physics of Materials and its Applications.

By

Raghda Kareem Khudhair Zughair

B.Sc. in Physics

University of Babylon (2010)

Supervised by

Prof. Dr. Fouad Shakir Hashim

2021 م **1443 هـ**

آية الكرسي سورة البقرة آية ٢٥٥

Dedication

To…

My dear family; Father,

Mother,

Sister & brother

My dear husband Haedar,

And my sons; Laith & Taim

My close friends; Eman & Reem

To my teachers...

Who provide me with the keys to success

My beloved country Iraq…

The martyrs of Iraq…

with all the love and appreciation.

Acknowledgements

Thankfulness, praise be to Allah, the grace that befits his holy self, and peace and blessings be upon our Messenger, Muhammad Bin Abdullah, May Allah's prayers and peace be upon him and his family and companions

After completing this work, it is my pleasure to extend my sincere thanks and appreciation to the owner of the generous hands, who contributed with his abundance knowledge, his valuable time and his sincere help in helping me to traduce this research, **Professor Dr. Fouad Shakir Hashim**.

Thanks to the Deanery of the College of Education for the Pure Sciences/ University of Babylon and the Department of Physics for offering me the opportunity to complete my research. I also would like to express my thanks to all teachers, instructors and students of the Department of Physics for their assistance.

Many thanks go to those who support me and alleviate difficulties I have faced during my experimental work, special mention to assistant teacher Safa Ahmed and the respected friend Hanan Hussein and to everyone who helped me in a way or another during my preparation of this thesis. Apologize for whom I miss mentioning. I wish success to all.

Raghda ✍

Abstract

PVA polymer and its nanocomposite with different ratios of Co_3O_4 (2, 4, and 6) wt.% films were synthesized using solution casting method. The results were identified by Fourier transform infrared spectroscopy (FT-IR), optical microscope (OM) and UV-Visible spectroscopy.

FT-IR spectra confirmed of the produce the functional groups present in polymer nanocomposite systems. The optical microscope images indicate a good homogeneity and fine distribution of Co_3O_4 particles, as well as charge transfer and complex formation inside the blend polymer films.

UV-Visible spectroscopy showed that the optimum value of transmittance for polymer film is about 90% in the Vis and NIR regions. Reduced the transmittance of the nanocomposite films towards ultraviolet rays qualifies it to use as a packaging for storage drugs regardless of cost.

Indirect allowed and forbidden transition energy gaps were determined from the absorption spectrum, which their values decreased with increasing the Co_3O_4 NPs content, the value of allowed transition energy gap for PVA polymer and its nanocomposite with (2, 4 and 6) wt.% of Co_3O_4 NPs was: (E_g) =4.5 , 3.9 , 3.2 , 2.3 eV, and for forbidden transition energy gap: (E_g) =3.9 , 3.0 , 2.0 , 1.5 eV respectively.

It is markedly that indirect E_g^{opt} decrease with additives of Co_3O_4 NPs. The other optical properties such as refractive index, polarizability, extinction coefficient, real and imaginary parts of dielectric constant and dielectric loss angle was calculated.

Contents

List of Symbols

Symbol	Physical Meanings
A	Absorbance
I_A	Absorbed Light Intensity
α	Absorption Coefficient
ε	Complex dielectric constant
N	Complex refractive Index
δ	Dielectric loss angle
E	Energy
k_o	Extinction Coefficient
ν	Frequency
ε_i	Imaginary dielectric constant
I_o	Incident Intensity of Light
I	Intensity
E_g^{opt}	Optical energy gaps
E_{ph}	Phonon energy
h	Planck's constant
P	Polarizability
ε_r	Real dielectric constant
R	Reflectance
n	Refractive Index
t	Thickness
T	Transmittance
I	Transmittance Ray
K	Wave Vector
λ	Wavelength of Light

List of Abbreviations

Abbreviation	Physical Meanings
A.C	Alternating current
Co_3O_4	Cobalt Oxide
C.B	Conductive Band.
D.C	Direct current
FT-IR	Fourier-transform infrared spectroscopy
NP_s	Nanoparticles
OM	Optical Microscope
PVA	Poly vinyl alcohol
PNC_s	Polymer nanocomposites
RT	Room temperature
UV	Ultraviolet
V.B	Valence Band.

List of Figures

List of Tables

1.1 Introduction

In recent years, nanostructural materials have been actively studied due to both scientific interests and potential applications [1].

The application of nanosized materials and structures which by definition should fall in the range of 1–100 nm is an emerging area of nanoscience and nanotechnology. Nanotechnology is mainly concerned with synthesis of nanostructures of variable sizes, shapes, chemical compositions and controlled dispersity and their potential using for human benefits. The unique properties of nanomaterials are to quantum confinement or surface effect become operative on the nanoscale [2,3]. Both the synthesis and characterization of semiconductor nanostructures have been extensively investigated worldwide because they are building blocks for fabricating functional nanoscale systems with a wide range of technological applications, including nanoelectronics, data processing, biological and medical sensing. Among all semiconductor nanostructures, metal oxides nanostructures are the most studied because of their interesting properties and widely used as electronics, catalyst, non-linear optics, storage devices and so on [4].

Nanostructures of transition metal oxides have attracted significant attention in recent years because the mechanical, electrical, optical, or magnetic properties of Nano-structured materials often differ drastically from those of the corresponding bulk material and these properties can, in many cases, be tailored easily by controlling their structure, size, and environment. Among those transition metal oxides, cobalt oxide was found to have the largest figure of merit, that is, the ratio of the magnitude of the optical nonlinearity to the linear optical absorption. Cobalt oxide [$Co^{2+}(Co^{3+})_2O_4$], as the most stable phase in the Co-O system, is a mixed valence compound with a normal spinel

structure having Co^{2+} and Co^{3+} placed at tetrahedral and octahedral sites, respectively.

Materials containing Co_3O_4 have been widely used for electrode materials [5], heterogeneous catalysis [6], solid-state sensors [7], energy storage [6], and magnetic materials [8,9]. Due to the rapid progress of nanotechnology in recent years, Co_3O_4 nanoparticles have been synthesized by various methods such as chemical vapor deposition [10,11], spray pyrolysis [12], sputtering [13], hydrothermal [14], thermal decomposition [15], sol-gel [16], electrochemical deposition [17], wet chemicals [18], microwave assisted [19], and ionic liquid assisted [20].

Polymers resources consist of a large figure of structural units according to the relation of the same type [21]. Over the past few decades, polymers and plastics technology have a great speed developed [22]. Nearly 200 million tons per year of false resources were formed universally (~ 2% of the lumber used and ~5% of the oil harvested) to total the ever-growing requirements. As the developed world is using plastic tools at a rate of approximately almost 100 kg per person per year[23].

Polyvinyl alcohol (PVA) is one of the most ancient and widely used polymers. It has a wide range of physical properties that make it ideal for a variety of applications [25]. PVA, which is widely used in semi conductive applications, is thought to be valuable in industrial applications for polymer compounds made from PVA. One of the benefits of PVA is that it can be mixed in water, but it is resistant to solvent and oil effect and adherence to cellulose materials. As a result, it's widely used in papermaking, textiles, and filmmaking antioxygen [26].

Polyvinyl alcohol (PVA) is a semi-crystalline polymer, nontoxic, biocompatible and noncarcinogenic. Its hydrophilicity is an advantage for its

applications in the formation of composite films [26]. PVA possesses good dimensional stability and photo-stable upon UV–visible light irradiation. Also, it exhibits a low permeability to oxygen, which is attributed to the large inter-cohesive energy that results from the highly polar alcohol (−OH) group [27, 28].

The polymer-based nanocomposite is interesting field for research and engineering. That consists of a polymeric substance and a nanoscale material. Polymer-based nanocomposites exhibit substantial enhancements in different properties. The enhancement of the properties with the addition of nanoparticles can be achieved due to different factors, one of the most important factors is a respectable interfacial interaction of the polymer matrix with the nano-fillers. This also depends on homogeneous and fine dispersion of nanoparticles within the matrix[29,30].

1.2 Literature review:

Xiushan Zhu , *et al.* in (2012) [31] prepared thin films of PVA/Co_3O_4 nanocomposite by Spin coating method. The linear and nonlinear optical characteristics of thin films with thicknesses of hundreds of nanometers were investigated. The absorption spectra revealed two direct band gaps when the refractive index and absorption coefficient were evaluated (E_g = 1.38 eV and 2.0 eV).

Vikas Patil, *et al.* in (2012) [32] they prepared nanosized Co_3O_4 thin films on glass substrates by using sol-gel spin coating technique. The effect of annealing temperature (400˚C - 700˚C) on structural, morphological and optical properties of Co_3O_4 thin films and they were studied by UV visible Spectroscopy (UV-Vis). The optical band gap has been determined from the

absorption coefficient. They found that the optical band gap energy decreases from 2.58 eV to 2.07 eV with increasing annealing temperature between 400˚C - 700˚C. These mean that the optical quality of Co_3O_4 films is improved by annealing.

Chandrakala *et al*. in (2014) [33] showed that the dielectric constant and dielectric loss would increase with increasing of nanoparticles concentration, but decreases with increase of frequency. AC conductivity of PVA-ZnO-Ce_2O_3 nanocomposites was increased with increasing frequency. Optical properties show that the formation of charge transfer complexes between hydroxyl groups of PVA and NPs.

Çiğdem Bilkan, *et al.* in (2016) [34] prepared Cobalt oxide nanostructures by using a simple microwave-assisted method. The as-prepared sample has been investigated by UV–Vis spectroscopy, X-ray diffraction (XRD), On the other hand, frequency and voltage dependence of both the real and imaginary parts of dielectric constants (ε′, ε″) of Al/Co_3O_4-PVA/p-Si structures were studied at room temperature. The values of ε′, ε″ and tanδ were found to decrease with increasing frequency almost for each applied bias voltage, but the changes in these parameters become more effective in the depletion region at low frequencies due to the charges at surface states and their relaxation time and polarization effect.

Amit Kumar, *et al.* in (2018) [35] they have been synthesized a highly crystalline cobalt oxide (Co_3O_4) via calcination method. The crystallite size of the nanoparticles is 28.5 nm. Two direct band gap of Co_3O_4 is observed. The temperature dependent dielectric spectroscopy of PVA- Co_3O_4 composite film shows ferroelectric behavior. The dielectric constant of the composite film is almost 2.5 times compare to pure PVA at a 1kHz frequency and room temperature.

1.3 The Aim of the Work

This work is studying the morphological and optical properties of PVA polymer before and after adding different ratios of transition metal oxide Co_3O_4 NPs .

2.1 Introduction

The general overview of the theoretical part of this chapter focused on the description of polymers, physical concepts and laws used to describe the optical properties results.

2.2 Polymers

The word polymer is derived from Greek words, poly (many) and mers (parts) or units of the high molecular mass of each molecule which consist of a very large number of single structural units. In other words, polymers are giant molecules of high molecular weight, called macromolecules, which are build up by linking together of a large number of small molecules, called monomers. The reaction by monomers combine to form the polymer that is known as polymerization. The polymerization is a chemical reaction of two or more substances combine together with or without the evolution of anything like water, heat or any other solvents to form a molecule of high molecular weight[36].

2.3 Classification of polymers

2.3.1 Classification Based on the Structure of Polymers.

Based on the structure they classified into four types, as shown in figure (2.1)**:**

1. **Linear polymers**: Van der Waals bonding between chains. Examples: polyethylene and nylon.
2. **Branched polymers**: chain packing efficiency is reduced compared to linear polymers - lower density.

3. **Cross-linked polymers**: chain is connected by covalent bonds. Often, it is achieved by adding atoms or molecules that form covalent links between chains. Many rubbers have this structure.

4. **Network polymers**: 3D networks made from trifunctional mers. Examples: epoxies and phenol-formaldehyde [37].

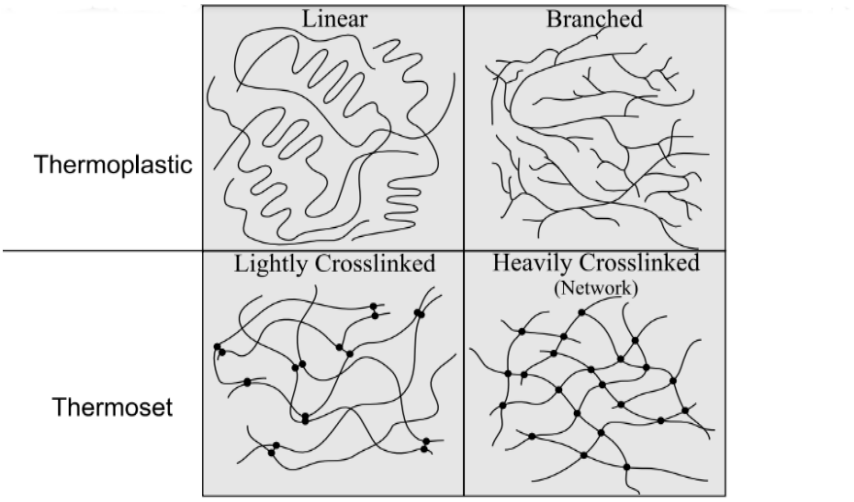


Figure (2.1): Polymer chains [37]

a) Linear polymers **b) Branched polymers**

c) Cross-linked **d) Network polymers**

2.3.2 Thermal Classification of Polymers:

Polymers are classified into two groups according to the temperature effect.

1. **Thermoplastic Polymers**: thermoplastic polymers may be either amorphous or crystalline that is rarely over 50 % crystalline. Crystalline polymers are often more dense than amorphous polymers due to closer packing of their long-chain molecule and, it used in general are to enhanced cracking and corrosion resistance [38]. The thermoplastic polymer properties are changed due to the influence of temperature, become they sticky flexible and with increasing of the temperature.

Meanwhile, it is returned to their original solid-state after decreasing the temperatures again. Such materials are usually produced by simultaneous heat and pressure application[39,40]. Polyethylene is an example of a commonly used crystalline thermoplastic polymer. Polymethyl methacrylate (PMMA) and polystyrene (PS) are amorphous thermoplastics (those without a normal molecular structure) [41,42]. Figure (2.2) illuminates the atomic configuration of thermoplastic polymers.

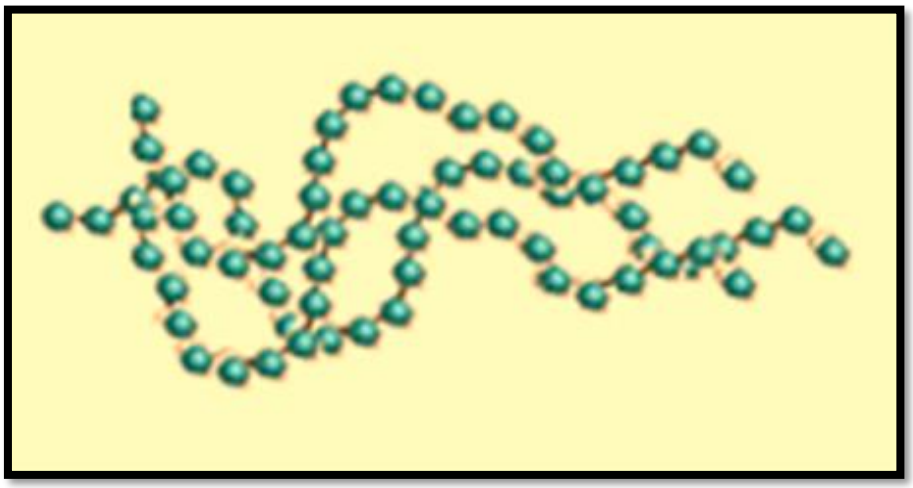


Figure (2.2). The atomic configuration of the thermoplastic polymer [43]

2. **Thermoset Polymers**: thermoplastics are most linear polymers and branched structure polymers with flexible chains that do not soften when heated due to strong covalent crosslinks. Thermoset polymers are generally harder and stronger than thermoplastics and have better dimensional stability. It usually uses as electrical and thermal insulation materials, adhesives, high-performance composites, and especially where high strength and modulus are required. Lightly cross-linking polymers are also called elastomers and have high flexibility [38]. These polymers when heated turn to hard, electricity, insoluble and non-

conductive of heat. This is because strong covalent chemical bonds are formed between the polymers molecules for instance phenol-formaldehyde and urea-formaldehyde resin [39,40]. They are utilized in many different applications such as dampers, seals, tires, and insulation. These are some examples of thermosetting polymers epoxides, amino, polyesters, rubbers and polyurethanes, etc.[41,42]. Figure 2.3 illuminates the configuration atomic of thermoset polymers.

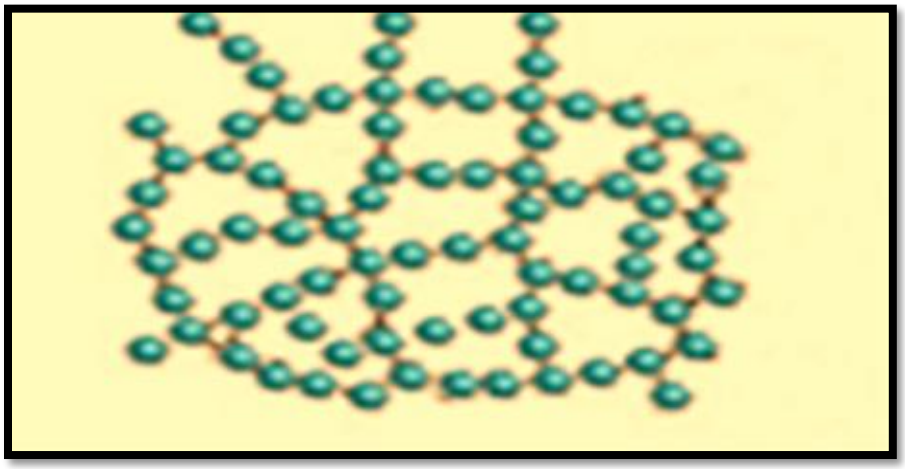


Figure (2.3): The configuration of atomic for thermoset polymers [46]**.**

2.4 Nanomaterials

According to the International Organization for Standardization (ISO), the prefix nano refers to a size ranging approximately from 1 to 100 nm [44]. As a comparison, the diameter of a carbon atom is about 0.25 nm, and the distance between carbon atoms is 0.15 nm. Nanomaterials are thus larger than single atoms or even small groups of atoms [45].

The definition for the nanomaterials were materials with any enteral or external structures on the nanoscale dimension [46].

The first scientist to raise attention on nanotechnologies, even if the word was not coined yet, was Richard Feynman. In a talk he gave in 1959 at the annual m2eeting of the American Physical Society entitled "There's plenty of room at the bottom, An invitation to enter a new field of physics," he challenged his fellow physicists to write the entire 24 volumes of the Encyclopedia Britannica on the head of a pin [47]. nanotechnology is based on the statement that it can change any property of any material with reducing at least one dimension of this material into the nanoscale [28].

2.5 Classification of Nanomaterials

2.5.1 Classification of nanomaterials according to origin

First, nanomaterials can be differentiated according to their origin: natural or anthropogenic. This last category can be divided into incidental and engineered nanomaterials, depending on whether their formation is intentional or not. Nanoparticles that have a natural and incidental origin are generally referred to as ultrafine particles. Natural sources of inorganic nanomaterials include, for example, erupting volcanoes and forest fires [49].

Manufactured nanomaterials are using a large diversity of chemical constituents, for example, metals, semiconductors, metal oxides, carbon, and polymers. They are designed for specific functionalities and can be surface treated or coated. They come in a large variety of forms: spheres, wires, fibers, needles, rods, tubes, shells, rings, plates, coatings, etc., as well as in more exotic flower like designs. Compared to natural and incidental nanomaterials, manufactured nanomaterials are characterized by their controlled dimension, shape, and composition [50].

2.5.2 Classification of nanomaterials according to dimensionality

A second categorization of nanomaterials is based on their dimensionality, as shown in figure (2.4) [51]. Nanomaterials with all external dimensions at the nanoscale, that is, between 1 and 100 nm, may be classified as zero-dimensional (0D). This includes quantum dots, which are semiconductor nanocrystals with dimensions < 10 nm that act as a potential well and are used in electronics to confine electrons and holes [52].

One-dimensional (1D) nanomaterials have two external dimensions at the nanoscale, the third one being usually at the microscale. This includes nanofibers, nanotubes, nanowires, and nanorods. With only one external dimension at the nanoscale, 2D nanomaterials comprise thin films, nanocoatings, and nanoplates. Thin films consist of ceramic or metal coatings that can be as thin as a few atomic layers [53].

The last dimensional category of nanomaterials, 3D nanomaterials, display internal nanoscale features but no external dimension at the nanoscale. This includes nanocomposites and nanostructured materials. Nanocomposites are multiphase solid materials with at least one of the phases with at least one nanoscale external dimension [54]. The term nanocomposite is generally used to describe nanofillers dispersed in a bulk matrix. These nanofillers can be selected among 0D, 1D, or 2D nanomaterials. Matrices may be polymers, ceramics, or metals. The final material can be 1D, 2D, or 3D, that is, a fiber, a film, or a volume [55].

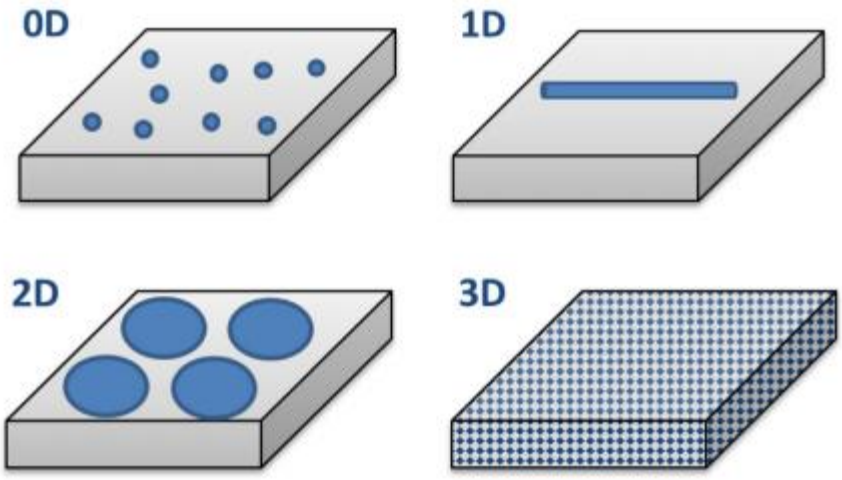


Figure (2.4): Dimensionality-based classification of nanomaterials.

2.6 Materials Used in This Work

2.6.1 Polyvinyl alcohol (PVA)

(PVA) is one of the earliest and best known polymers, with the molecular formula $(C_2H_4O)_n$, as shown in figure (2.5) [56]. Due to the importance of the OH group and hydrogen bonding, it was found to be useful in a variety of applications [57].

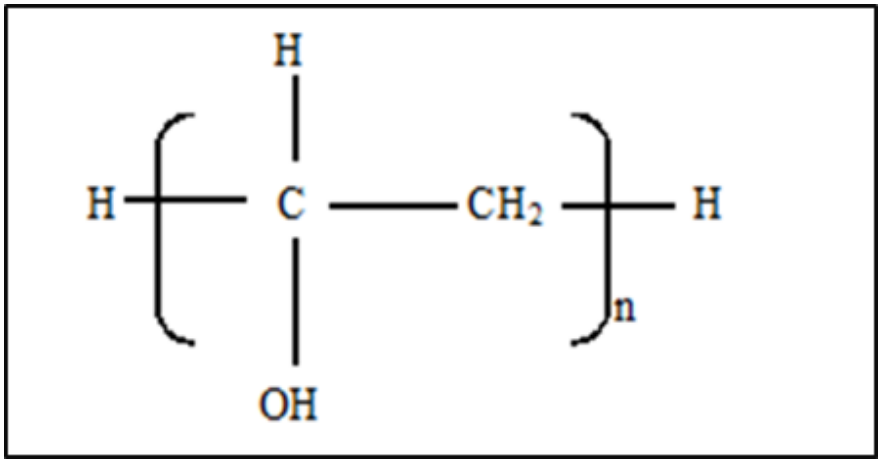


Figure (2.5): The chemical structure of PVA [58].

It is commercially produced by hydrolysis of poly (vinyl alcohol), as shown in Figure (2.6) [58].

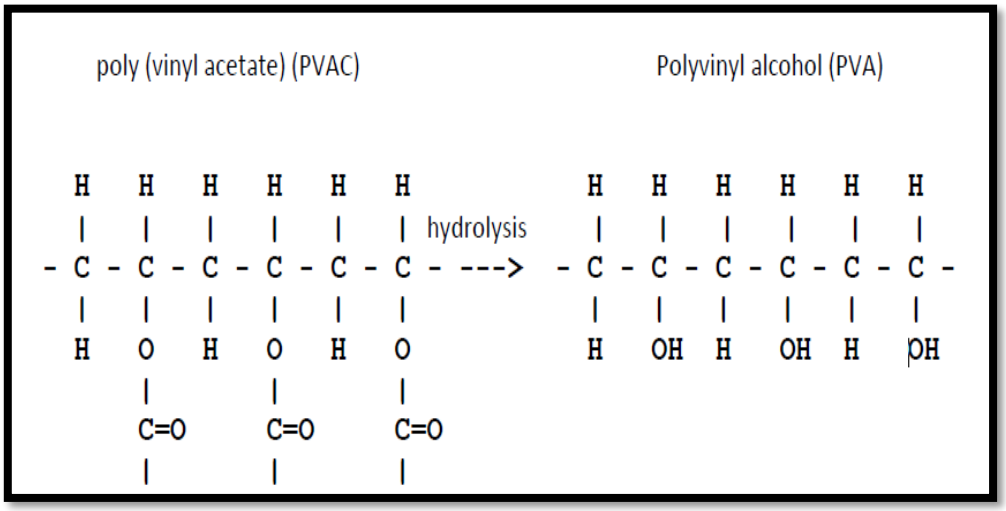


Figure (2.6): The preparation of PVA [58].

PVA is a water-soluble synthetic polymer that comes in the form of a granular powder that is odorless, translucent, tasteless, and white or cream in color. Since PVA is water-soluble, it can be used to make hydroxyl organic ingredients. PVA's biological degradation and biocompatibility are two of its most notable characteristics. PVA has a high tensile strength and longevity, as well as a high oxygen and scent buffer. Visual light transmission is excellent. It also has excellent shape, mixing, and adhesion characteristics [59]. In research applications the polymer composites of PVA are recognized for their utility [60]. PVA exhibits unique features, excellent chemical durability, environmentally friendly, optical and electrical characteristics. In polyvinyl alcohol, the presence of semi-cristalline regions – amorphous and crystalline regions that induce interfacial effects that increase physical properties – is critical [61].

The applications of PVA are adhesives, belts, binders, cementitious laminate, coatings, controlled drug delivery, electroconductive film, food, magnetic nanocomposite, membranes, paper (with pigments and optical brighteners), photographic papers, printing rolls, protective colloids, sanitary pads, seed tapes, sizing agents, toners, water-soluble laundry bags, warp sizing and wood glue [62]. Table (2.1) lists the key physical and chemical properties of PVA [63].

Table (2.1): Physical and chemical properties of (PVA) [62].

Property	**Description**
Appearance	clear, white to yellow granular powder
Molecular formula	$(C_2H_4O)_n$
Density at 20^o ($g.cm^{-3}$)	(1.19 - 1.31)
Bulk density at 20^o ($g.cm^{-3}$)	0.3-0.7
Solution PH	5- 6.5
Refractive index 20^o	1.49-1.51
Decomposition temperature °C	100 (color change); 150 (rapid darkening);200 (rapid decomposition)
Glass transition temperature (T_g) ^oC	Calc.= 84 ; exp.= 34-85
Melting temperature (T_m) ^oC	178; 230 (fully hydrolyzed), 180-190 (partially hydrolyzed)
Ignition temperature ^oC	79
Auto ignition temperature ^oC	450

2.6.2 Cobalt Oxide (Co_3O_4)

Cobalt Oxide (Co_3O_4) is a p-type semiconductor in which the Co^{3+} ions occupy the octahedral site and the Co^{2+} ions occupy the tetrahedral positions, forming a cubic close-packed configuration. Catalysts, solar selective absorbers, gas sensors, lithium ion batteries, supercapacitors, ink for glasses and ceramics, photocatalysis, magnetic materials, and chemical sensors are only a few of the uses for Co_3O_4. Precipitation, hydrothermal path, sol-gel technique, spray-pyrolysis, solvothermal, polymer assisted methods, electrochemical deposition, and other methods for synthesis of Co_3O_4 NPs have all been documented [64]. For Co_3O_4 at RT, there are a few simple physical parameters mentioned in Table (2.2).

Table (2.2): Different properties of Co_3O_4

Properties	
Chemical formula	Co_3O_4 -- $CoO.Co_2O_3$
Molar mass	240.80 g/mol
Appearance	black solid
Density	6.11 g/cm^3
Melting point	895 °C (1,643 °F; 1,168 K)
Boiling point	900 °C (1,650 °F; 1,170 K) (decomposes)
Solubility in water	Insoluble
Solubility	soluble in acids and alkalis
Magnetic susceptibility (χ)	$+7380 \cdot 10^{-6}$ cm^3/mol

2.7 The Interaction of light with matter

Matter can emit, absorb, transmit, and reflect (or scatter) light, usually, the effect of refraction is difficult to measure due to absorption and scattering. Interactions between light and matter determine the appearance of everything. light interacts with matter in ways such as emission and absorption. The photoelectric effect is an example of how matter absorbs light. What matter does with the energy from light depends on what kind of light it is and there is a whole spectrum of light called the electromagnetic spectrum. Despite the fact that light can travel through a vacuum, it cannot pass through all objects. Light can be transmitted, reflected, or absorbed when it strikes an object. The object is made up of molecules, and each molecule has electrons that can absorb energy and jump to higher energy levels. The electron will absorb this energy and re-emit it as heat if it corresponds to one of the electron energy levels [65,66].

2.8 Optical Parameters

It can determine many of the optical Parameters by observing the spectral shift in absorption and sample transmittance, those are:

2.8.1 Absorbance (A)

Absorbance can be defined as the ratio between absorbed light intensity (I_A) by material and the incident intensity of light (I_o) following equation: [67]

$$A = \frac{I_A}{I_\circ} \qquad (2.1)$$

2.8.2 Transmittance (T):

Dividing the intensity of the rays transmitting from the film (I_T) over the intensity of the incident rays on it (I_o) is called transmittance (T) and given by [68]:

$$T = \frac{I_T}{I_o} \qquad (2.2)$$

2.8.3 Absorption coefficient (α)

Absorption coefficient (**α**) can be defined as the energy decline ratio in the flow of the incident ray in the direction of the propagation of the wave in relation to the unit of distance. (**α**) depends on the incident of photon energy (hν), material properties, and prohibited band gap. The following equation [69] gives the energy of photons:

$$E = h\nu \qquad (2.3)$$

Where (h) Planck's constant and (ν) is the frequency, when the incident photon energy is less than the forbidden band gap, the photon will be transmitted, and transmittance gives from the following equation:

$$T = (1-R)^2 e^{-\alpha t} \qquad (2.4)$$

If the intensity of incident ray (Io) that incident on blend film material of thickness (t), the intensity of transmittance ray (I) gives by Beer Lambert law [70].

$$I = I_o \exp(-\alpha t) \qquad (2.5)$$

the absorption coefficient is measured by cm^{-1}.

$$\alpha t = 2.303 \log I/I_{\circ} \quad (2.6)$$

Where the amount of log (I/Io) represents the absorbance (A).

The absorption coefficient can be calculated using the following equation: [70,71]

$$\alpha = 2.303(A/t) \quad (2.7)$$

2.8.4 The electronic transitions:

The electronic transitions can be classified into two types:

2.8.4.1 Direct transition:

In semiconductors, this transformation occurs where the bottom of (C.B.) is precisely above the top of (V.B.), indicating that they have the same wave vector K i.e. $\Delta K=0$. The absorption appeared in this state when $h\upsilon \geq Eg$. This transition type required of the Law's conservation in energy and momentum, and has two types [72]:

a. Direct allowed transition:

This transition happens between the top points in the (V.B.) to the bottom point in the (C.B.), as shown in Figure (2.7 a).

b. Directly forbidden transitions:

This transition happens between near top points of (V.B.) and bottom points of (C.B.), as shown in figure (2.7 b). The optical band gap energies were determined using a Tauc plot, by the following equation [73]:

$$\alpha h\nu = B (h\nu - E_g{}^{opt})^r \quad (2.8)$$

where, B: is constant depending on the type of material, ν: is the frequency of the incident photon, the index r: identifies the type of electronic transition between the energy bands; the values t of 1/2 and 3/2 are associated with the allowed and forbidden direct transition.

2.8.4.2 Indirect transitions:

In indirect band gap materials, the bottom of (C.B) is not over the top of (V.B), in other words, the limit of the valence band (V.B) is located at various k-vectors than the minimum of the conduction band (C.B). , ($\Delta K \neq 0$), in this situation, and the absorption or emission of a phononon must be included in this transition form for the conservation of the energy and momentum law. There are two types of indirect transitions [74]:

a. Allowed indirect transitions:

These transitions happened between the top of (V.B.) and the bottom of (C.B.) which is found in a different region of (K-space) as shown in Figure (2.9.c).

b. Forbidden indirect transitions:

As shown in the figure, these transformations occurred between near points at the top of (V.B.) and near points at the bottom of (C.B.). Figure (2.7 d).

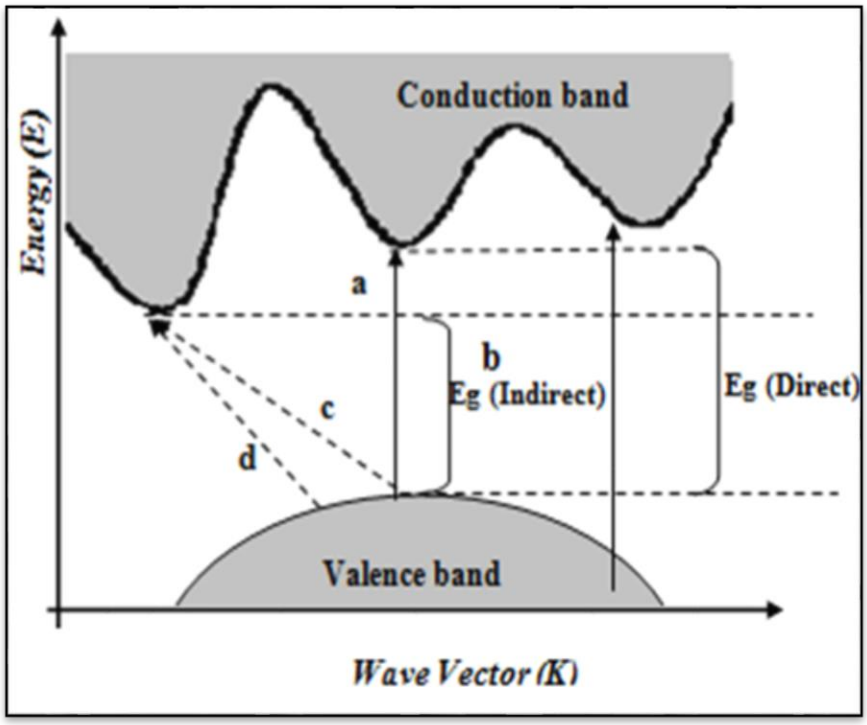


Figure (2.7): The electronic transitions types [75].

(a) Allowed Direct Transition **(c) Allowed Indirect Transition**

(b) Forbidden Direct Transition **(d) Forbidden Indirect Transition**

The transition absorption coefficient with a phonon absorption is given by [75]:

$$\alpha h\nu = B (h\nu - E_g^{opt} \pm E_{ph})^r \quad (2.9)$$

where E_{ph} means the energy of phonon, (-) means when phonon absorption and (+) means when phonon mission, r: means the exponential m transition, meanwhile r=3 for the forbidden indirect transition.

2.8.5 Refractive index (n):

The refractive index can be defined as a ratio between the velocities of light in a vacuum (c), to its velocity inside the material. The value of the refractive index (n) of the film is calculated from the equation [76]:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad (2.10)$$

The reflectance (R) of the material with transmittance (T) and absorbance (A) is given by the relation [76]:

$$R = 1 - A - T \quad (2.11)$$

Polarizability (P) can be calculated by a relationship [77], based on the refractive index:

$$P = \frac{3}{4\pi}\left(\frac{n^2-1)}{n^2+1)}\right. \quad (2.12)$$

2.8.6 Extinction coefficient (k_o):

As is seen in the following equation, the imaginary component of the complex refractive index N is called the extinction coefficient:

$$N = n - Ik_o \quad (2.13)$$

The extinction coefficient could be found using the relation [78]:

$$k_o = \alpha\lambda/4\pi \quad (2.14)$$

where (λ) is the wavelength of the incident ray.

2.8.7 Dielectric constant:

Dielectric constant workability of the material for polarization. The material 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. The real (ε_r) and imaginary (ε_i) parts of dielectric constant were determined from the complex dielectric ε [79]:

$\varepsilon = \varepsilon_r - i\varepsilon_i$ (2.15)

where ε_r represents the normal dielectric constant and ε_i is the the absorption associated with radiation by free carrier [80] .The relation between (ε) and (N) is expressed in the following equation:

$\varepsilon=N^2$ (2.16)

From the equation (2.26), the real and imaginary complex dielectric constant can be expressed by the following equation [81,82]:

$\varepsilon_r=n^2-k_o^2$ (2.17)

$\varepsilon_i=2nk_o$ (2.18)

2.8.8 Dielectric loss angle:

Dielectric loss is a loss of energy that goes into heating a dielectric material in a varying electric field whose expression is given by the following equation [83]

$\tan\delta = \varepsilon i/\varepsilon r$ (2.19)

and loss angle

$\delta = tan^{-1}(\varepsilon_i/\varepsilon_r)$ (2.20)

3.1 Introduction

This chapter covers the preparation and processing steps of the sample, as well as a description of the equipment and methods used in the preparation and measuring process, such as, Fourier Infrared Transform Spectrometer (FT-IR), Optical Microscope (OM) and Optical Spectrometer.

3.2 The Materials Used

The substances used in this research are:

3.2.1 Matrix material Poly (vinyl alcohol) (PVA)

PVA polymers (partially hydrolysis, molar Wt. = 60,000 g. mol^{-1}) could be supplied as granular form and water-soluble synthetic polymer from the Central Drug House, Ltd., Company, Indian, as shown in Figure (3.1).

Figure (3.1): Poly(vinyl alcohol) material

3.2.2 Additive material Cobalt oxide (Co_3O_4)

It is nanodots or nano powder are black spherical high surface area particles. poorly soluble. Nanoscale cobalt oxide particles are typically 10-30 nm with specific surface area (SSA) in the 130-150 m^2g^{-1} range. Cobalt oxide nanoparticles are also available in passivated and in Ultra high purity and high purity which has a melting

point of 895 °C (1,643 ° F; 1,168 K) a crystalline form. It has a molecular weight of 74.9326 g/mol a density of 6.11 g.cm^{-3}, as shown in figure (3.2).

Figure (3.2): Coblet oxide Co_3O_4 NPs

3.3 Synthesis of Polyvinyl alcohol film

The pure PVA films were primed by solution casting technique. It has excellent water solubility in PVA polymer. This is due to the forming (hydrophilic property) of strong H bonds between the polymer functional group and water molecules. In 50 ml of deionized water, 1 g of PVA was dissolved. The solution was stirred for 1hr with a magnetic stirred solution under the temperature of 75-80ºC awaiting the polymer became completely soluble, as shown in Figure (3.3). The resulting solution is cast onto very clean and dried (8 cm diameter) glass Petri dish cups of equal volume and held in the air for 240 hours at RT to dry until the solvent has evaporated entirely from the material. Then the drying film was peeled from the Petri dish and processed until used in the vacuum dryer. To obtain a nano composite that needs a wide area and equal thickness, this technique is necessary.

Figure (3.3) Stirred PVA solution under the temperature of 75-80ºC

3.4 Dissolving nanoparticles

Co_3O_4 NPs were mixed by solid state method, as shown in Figure (3.4 a), which include dissolving nanoparticles by ethanol solvent using crucible ceramic with pestle in which the materials grinded, then the dried powder become ready to be added to PVA solution, as shown in Figure (3.4 b).

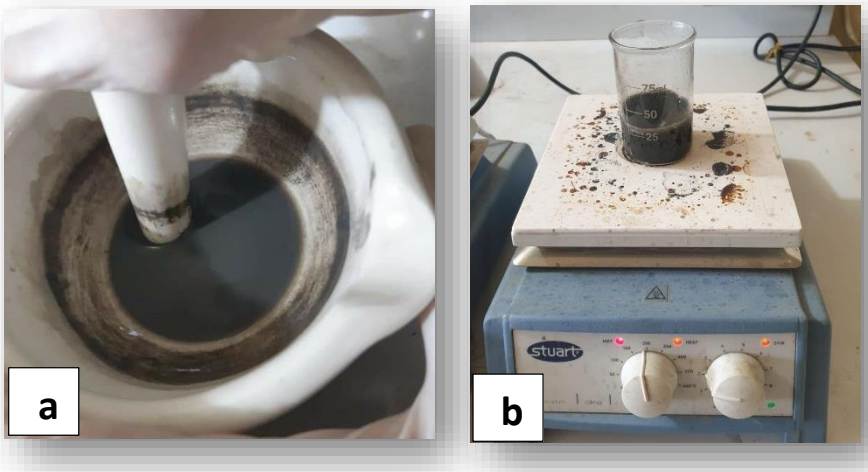


Figure (3.4) a: Solid state method
b: Mixed Co_3O_4 (dried powder) with PVA solution.

3.5 Purification of the nanocomposite

Film of PVA polymer and its nanocomposites with different ratios of (2, 4, and 6) wt.% Co_3O_4 as listed in Table (3.1), it was obtained according to the following: firstly, we used the solid state method which include dissolving it by ethanol solvent with continuous grinding in a crucible ceramic for 90 min. The grinded solution was dried at temperature 60˚C for 4 hr before adding it to the polymer solution. The polymer was continuing as in previous steps, even get a homogeneous solution. The casting method is used to get the nanocomposites cast on glasses petri dishes with an equal volume, then kept at RT under air for 240hr to dry as shown in Figure (3.5). The thickness of the produced films was between (100 ±4) μm which are measured by Digital Vernier Caliper.

Table (3.1): Summarized the under-study nanocomposite films contents

Sample	**PVA(g)**	**Co_3O_4 (g)**
PVA	1	0
PVA: 2wt.% Co_3O_4	0. 98	0.02
PVA: 4wt.% Co_3O_4	0.96	0.04
PVA: 6wt.% Co_3O_4	0.94	0.06

Figure (3.5): Cast technique

3.6 Measurements of Structural Properties

3.6.1 Spectral characterization for FTIR

FTIR spectra were recorded by FTIR Bruker company, German origin, type vertex -70. The spectrum of wave numbers considered is (500-4000) cm^{-1}, as shown in Figure (3.6). FTIR has been introduced at the University of Babylon / Education College for Pure Science / Physics.

Figure (3.6): FTIR spectroscopy

3.6.2 Optical Microscope

The sample of PVA polymer and (PVA:Co_3O_4) nanocomposite films are analyzed using the optical microscope, which was supplied from Olympus name (Top View) type (Nikon-73346), equipped with light intensity automatic controlled camera under magnification (40x), as shown in figure (3.7), it is implemented in the university of Babylon /college of education for pure sciences/ department of physics.

Figure (3.7): Optical Microscope

3.6.3 Optical properties measurements

The absorption spectra of (PVA) and its nanocomposite films were recorded in the wavelength range (200-1100) nm using the double-beam spectrophotometer (Shimadzu,UV-1800 A0, Japan), as shown in Figure (3.8). The absorption spectrum being recorded at RT to obtain the optical constants, absorbance, transmittance, absorption coefficient, indirect transition, extinction coefficient, refractive index, dielectric constant (real and imaginary parts). A computer program (UV Probe software) was used.

Figure (3.8): UV Photographic of spectrophotometer

4.1 Introduction

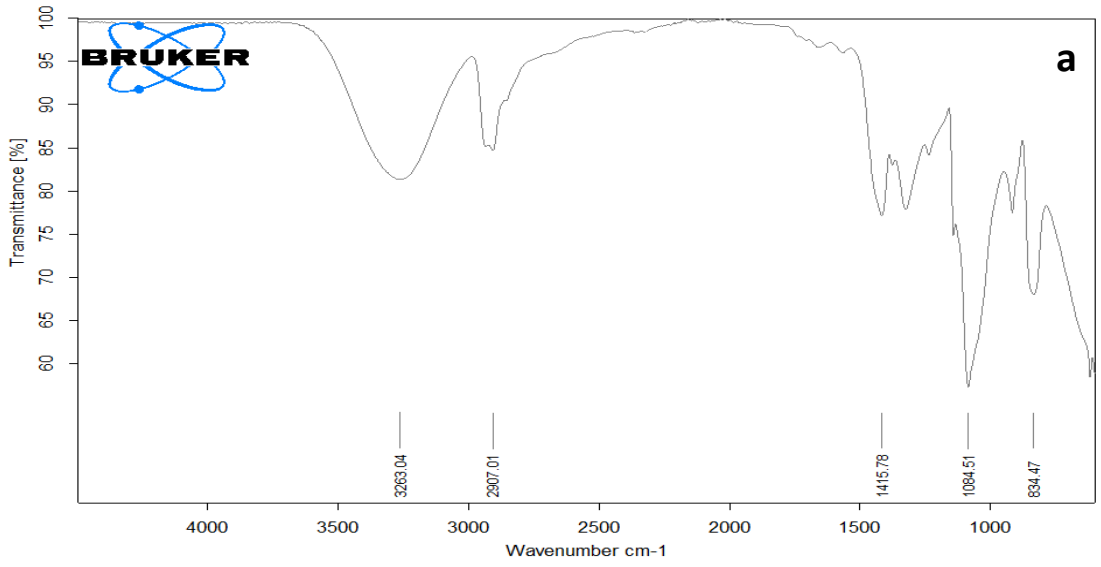
This chapter comprehensive evaluation the results obtained for the effect of Co_3O_4 NPs on the structural, and optical properties of PVA polymer and analysis of the results based on changes.

4.2 The Structural Properties of Polymer and its Nanocomposite Films.

4.2.1 Spectra in the Fourier Transform Infrared Radiation (FTIR) analysis result of the casting Films.

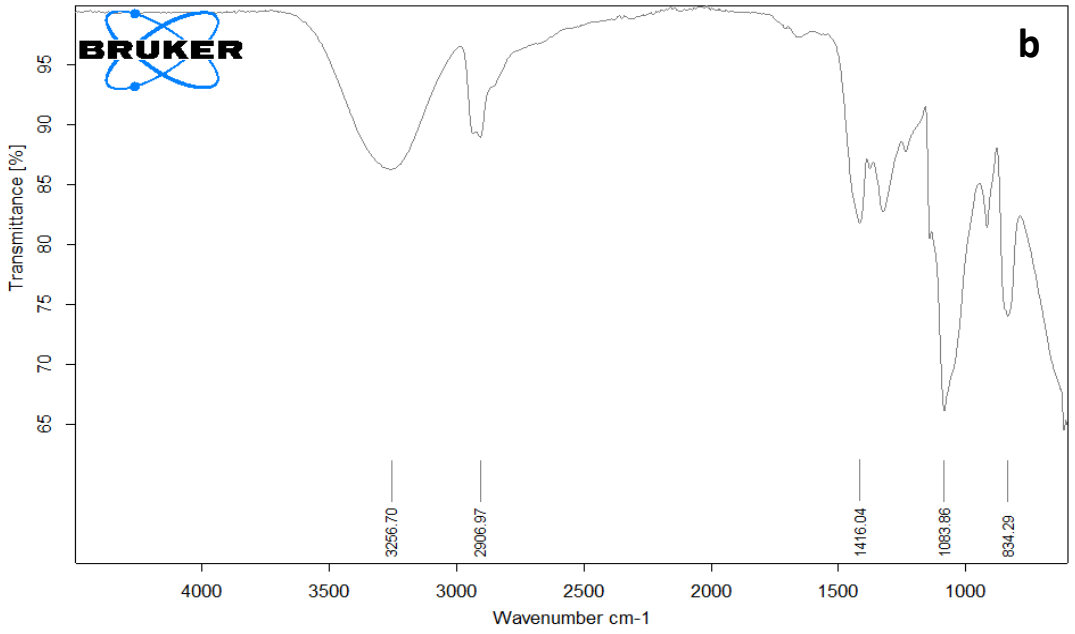
FTIR spectroscopy was used to analyze the interactions between atoms in the system. These interactions can cause changes in the vibrational patterns of the molecules in the polymer mixture. Figure (4.1) shows the FTIR spectra of pure PVA polymer and its nanocomposite films with different ratios of (2, 4, and 6) wt.% Co_3O_4 NPs under the investigated at RT in wavenumber (500-4000) cm^{-1} ranges.

The functional groups of PVA appeared at 3263, 2907, 1416, 1085, and 834 cm^{-1} corresponding to broad band to the stretching vibrations of hydroxyl groups O–H (PVA), Methyl C-H_3 asymmetric stretching band, Vinyl C-H in-plane bend, C-O stretching vibration (PVA), and peroxide C–O–O– stretching, respectively [85]. For ease of follow-up see Table 4.1.



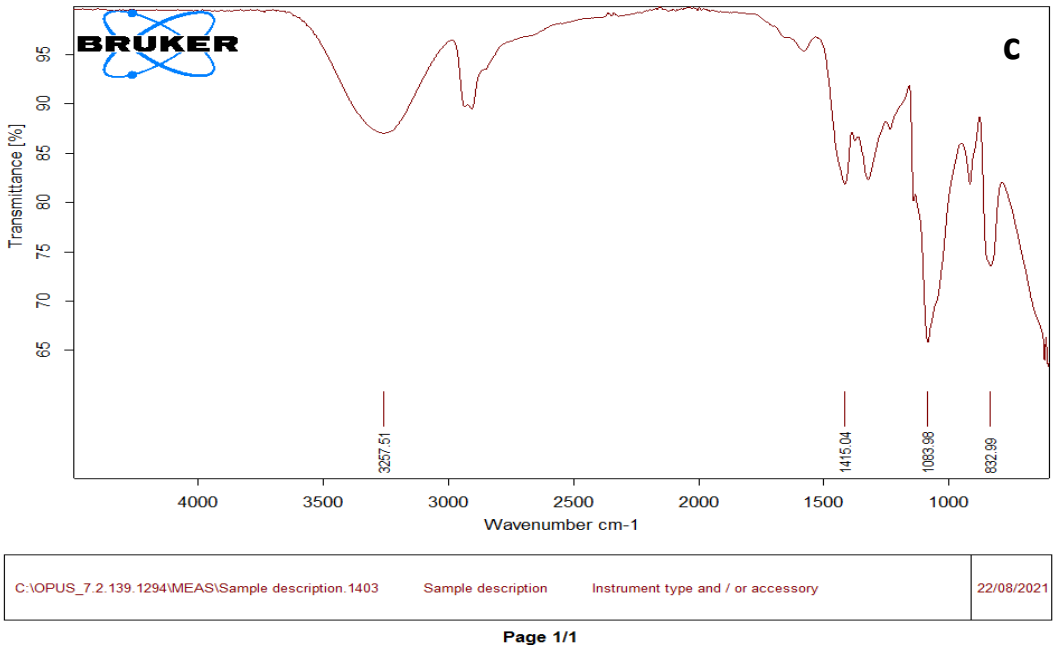
C:\OPUS_7.2.139.1294\MEAS\Sample description.1399	Sample description	Instrument type and / or accessory	22/08/2021

Page 1/1



C:\OPUS_7.2.139.1294\MEAS\Sample description.1401	Sample description	Instrument type and / or accessory	22/08/2021

Page 1/1



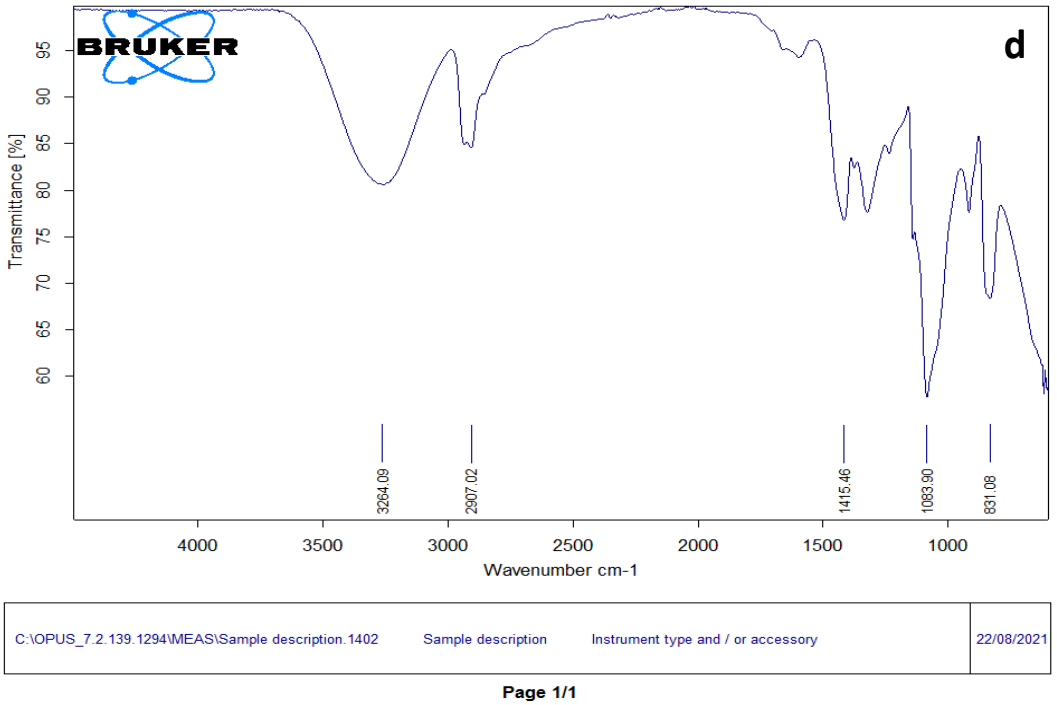


Figure (4.1): FTIR spectra of: a. PVA, b. 2wt.% Co_3O_4 NPs, c. 4wt.% Co_3O_4 NPs , and , d. 6wt.% Co_3O_4 NPs films.

Comparing these characteristic wavenumbers with those of pure PVA, it can be noticed that the characteristic peaks representing the PVA/Co_3O_4 nanocomposite was not apparent shifting as a result of the addition of Co_3O_4. From this analysis, it is understood that there are no new peaks of absorption, therefore no interactions between PVA polymer matrix and Co_3O_4 NPs.

Table 4.1. Functional group and its quantified frequencies.

Wavenumbers (cm^{-1})	**Assignments**
3263	O–H stretching vibrations
2907	Methyl C-H_3 asymmetric stretching band
1416	Vinyl C-H in-plane bend
1085	C-O stretching vibration
834	peroxide C–O–O– stretching

4.2.2 Optical microscope of the casting samples

Microscopy of nanocomposites is the nanoparticles diffusion test within the polymer mixture. The images of the surface of pure PVA polymer and its nanocomposite films with different ratios of (2, 4, and 6) wt.% Co_3O_4 NPs at magnification power (40X) were shown in Figure (4.2). The surface image of polymer film displayed in part (a) indicates a homogeneous phase without phase separation. From such Figure (part b, c, & d), it can be seen, that Co_3O_4 NPs are well dispersed on the surface of the polymer films. The Co_3O_4 NPs, formed clusters in the form of chains that extended along the surface of the films, attributed to the magnetic property possessed by Co_3O_4 nanoparticles, allowing the charge transfer inside the polymer films optimized with increasing the level of proportions.

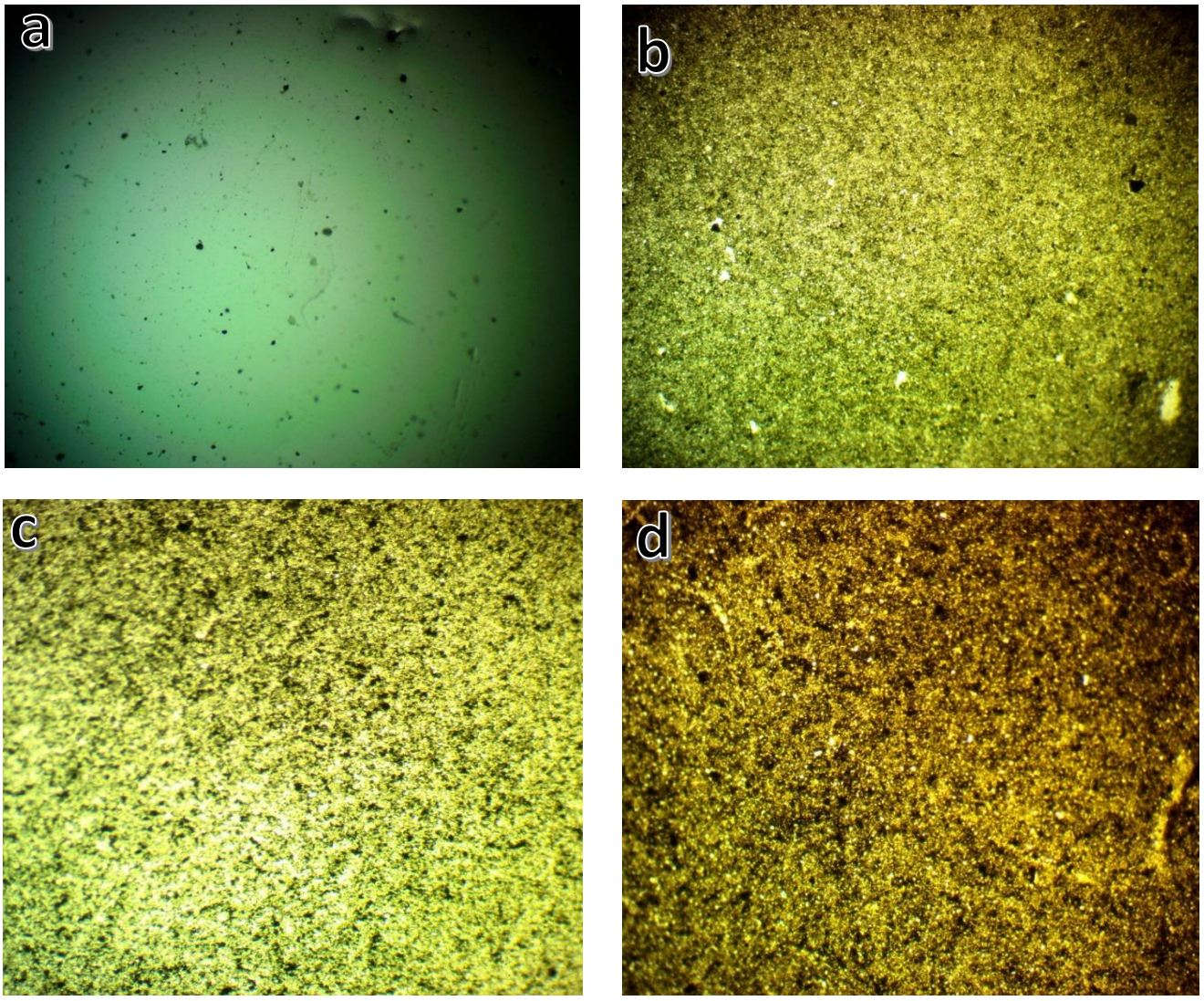


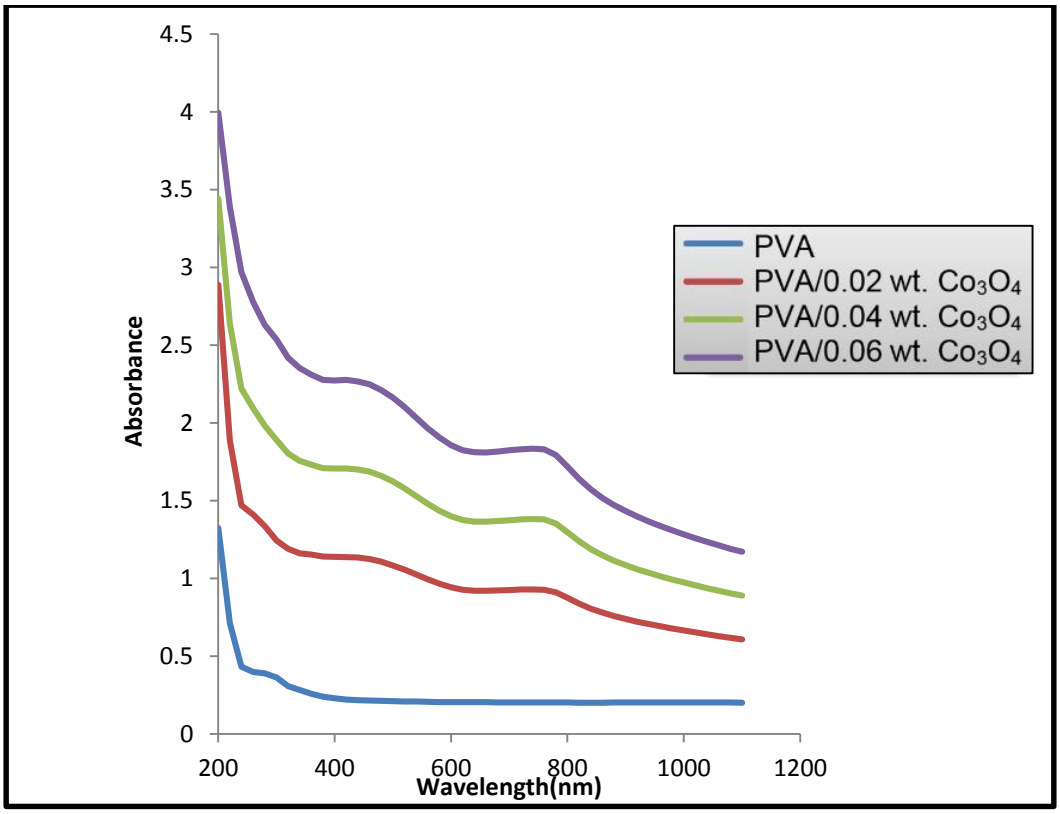
Figure (4.2) Photomicrographs (40X) for: a. PVA polymer b. PVA: 2wt.% Co_3O_4 NP c. PVA: 4wt.% Co_3O_4 NPs d. PVA: 6wt.% Co_3O_4 NPs.

4.3 The Optical Properties

The main purpose of studying the optical properties is to identify the effect of adding different ratios of (2, 4, and 6) wt.% Co_3O_4 NPs on the optical properties of PVA polymer. The research covers the recording of the spectra of absorbance for the films at RT, knowledge the types of electronic transitions, calculating energy gaps, and optical constants.

4.3.1 Absorbance (A)

Figure (4.3) presents the absorption spectra of PVA and its nanocomposites with different ratios of (2, 4, and 6) wt.% Co_3O_4 films in the range of UV-Vis-NIR, recorded at RT. The absorption edge for nanocomposite films was shifted toward longer wavelength side (red shift) with the addition of Co_3O_4 NPs, causing a decrease in the energy gap. Shift in absorption edge may attribute to the change in polymeric chain mobility during the blending process. The lowest absorption value obtained for the PVA is attributed to the free electrons that were bound to the atoms by covalent bonds, and the high absorption of nanocomposite films is attributed to the presence of electrons outside the orbits, which can absorb electromagnetic energy to interact with atoms and move to higher energy levels **[**86**]**. Improve the absorbance of UV waves for the nanocomposite films, making its suitable for different applications, for instance as a packaging for storage drugs regardless of cost.



Figure(4.3): UV-Vis absorbance spectra of PVA polymer and its nanocomposites with different ratios of Co_3O_4 NPs.

.

4.3.2 Transmittance (T)

Optical transmittance spectra of PVA and its nanocomposites with different ratios of (2, 4, and 6) wt.% Co_3O_4 films was calculated using equation (2-2) as in Figure (4.4). The transmittance decreases with the increase of the ratios of Co_3O_4 NPs, this is due to the agglomeration of NPs promoting an increase of the surface roughness leads to the increase of the surface scattering of the light with increasing concentrations. The optimum value of average optical transmittance for PVA film is about 90% of spectrum in the regions visible and near infrared, but it decreases drastically with an increase in the proportion of wt.% Co_3O_4. This property was due to the nature of the films surface and its absorption.

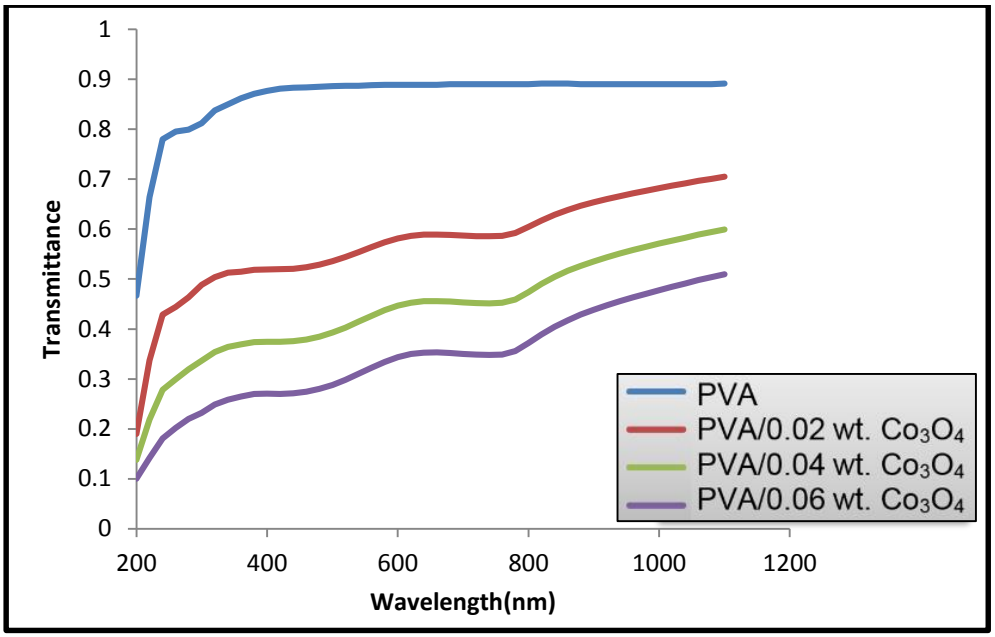


Figure (4.4): UV-Vis transmittance spectra of PVA polymer and its nanocomposites with different ratios of Co_3O_4 NPs.

4.3.3 Absorption coefficient (α)

Figure (4.5) illustrate the absorption coefficient of prepared nanocomposites increases with the increasing of the ratios of NPs, this is attributed to the increase of the number of charge carriers in nanocomposite films. The result of (α) for all prepared nanocomposites presented smallest at low energies, whereas increases with increasing energy of the incident photon, which is means that the energy of the incident photon is sufficient to interact atoms. This is in consonance with observations for similar studies of Co_3O_4 NPs [87]. Based on the (α) values of the prepared films (less than 10^4 cm^{-1}), indirect electronic transitions are extremely likely to occur. The films were calculated from the region of high absorption at the fundamental absorption edge using Lambert Beer's law (2.5).

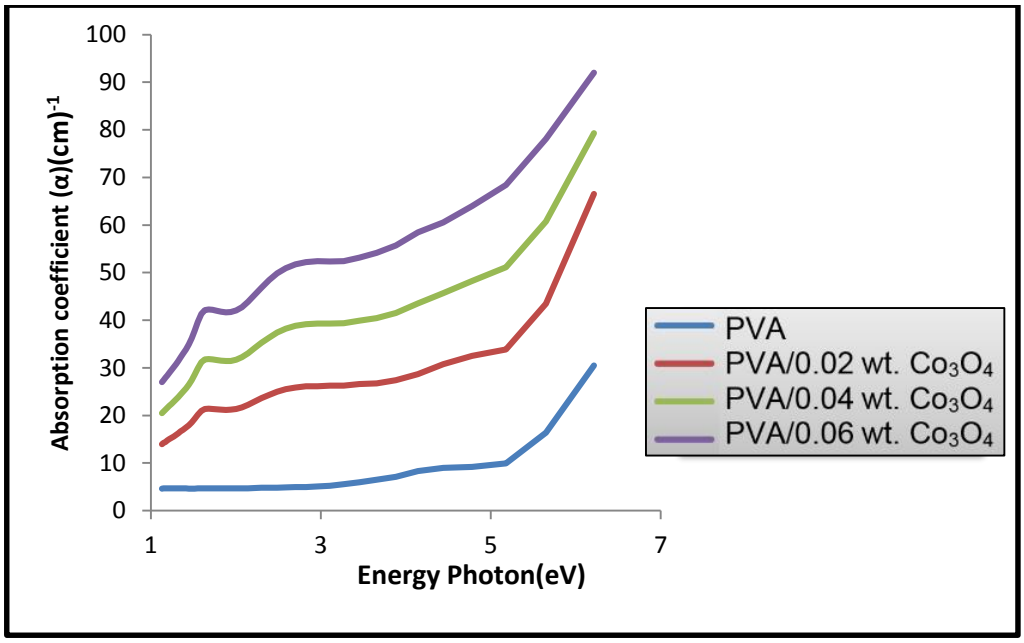


Figure (4.5): Absorption coefficient of PVA polymer and its nanocomposites with different ratios of Co_3O_4 NPs.

4.3.4 Optical energy gaps of the allowed and forbidden indirect transition

Depending on the absorption coefficient of the pure polymer and its nanocomposite films, the optical band gap energy can be determined from the plot of $(\alpha h\nu)^{1/r}$ (where r = 2 for allowed and 3 for forbidden indirect transition) versus photon energy ($h\nu$) shown in figures (4.6) and (4.7) using the Tauc relation (2.9). The both values allowed and forbidden indirect transitions and the difference between them are illustrated in Table (2).

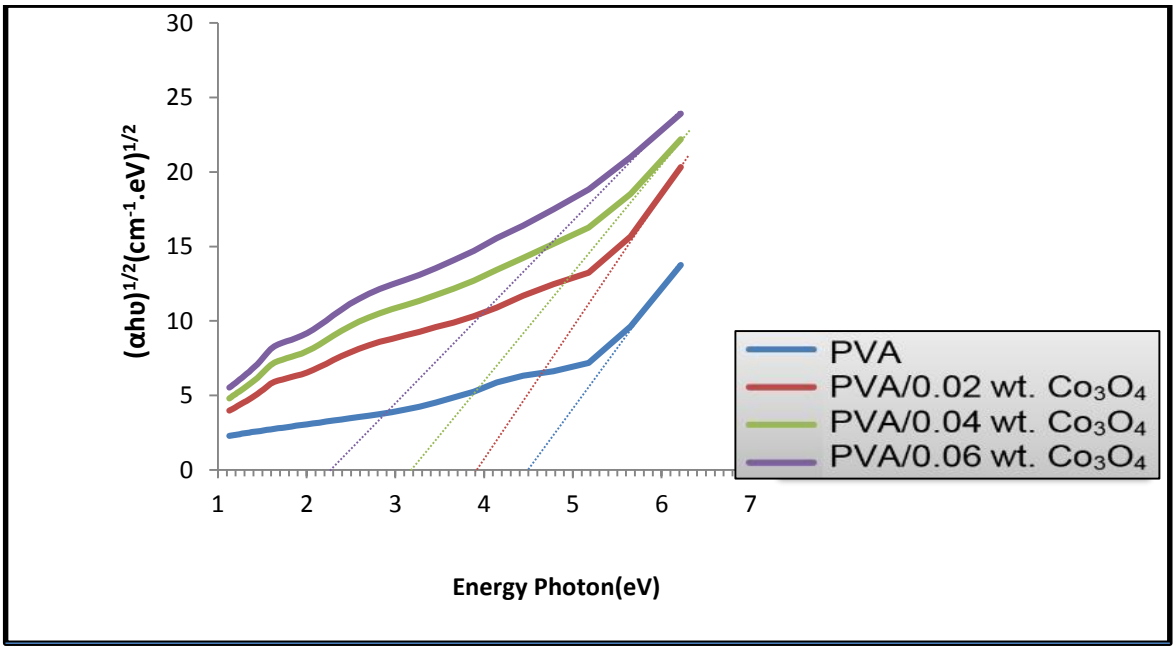


Figure (4.6): Relation between $(\alpha h\nu)^{½}$ versus $(h\nu)$ for PVA polymer and its nanocomposite films with different ratios of Co_3O_4 NPs.

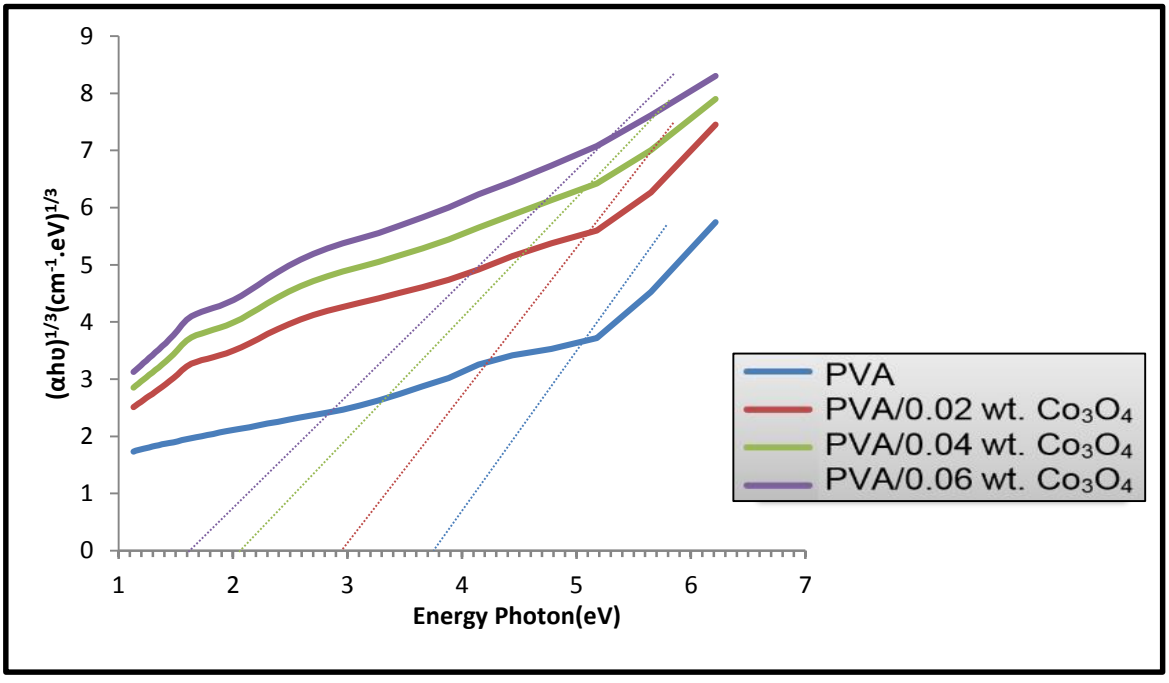


Figure (4.7): Relation between $(\alpha h\nu)^{⅓}$ versus $(h\nu)$ for PVA polymer and its nanocomposite films with different ratios of Co_3O_4 NPs.

Table (4.2): Optical energy gap E_g values for the allowed and forbidden indirect transition of PVA and its nanocomposites with different ratios of Co_3O_4 .

Sample	Allowed (eV)	Forbidden (eV)
PVA	4.5	3.9
PVA/ 2wt.% Co_3O_4	3.9	3.0
PVA/ 4wt.% Co_3O_4	3.2	2.0
PVA/6wt.% Co_3O_4	2.3	1.5

4.3.5 Refractive index (n), Polarizability (P) and Extinction coefficient (k_o)

The index of refractive (n), polarizability (P) and extinction coefficient (k_o) of PVA and its nanocomposite with different ratios of Co_3O_4 films were calculated from the relations (2.10, 2.12 and 2.13). From the Figure (4.8), it was found that the nanocomposite films are bigger than that of the PVA in the low energies region of the spectrum (Vis and NIR regions), due to the large index of Co_3O_4 [88]. The decrease in refractive index values at higher energies (UV region) correlates with the behavior of the polarizability as in figure (4.9).

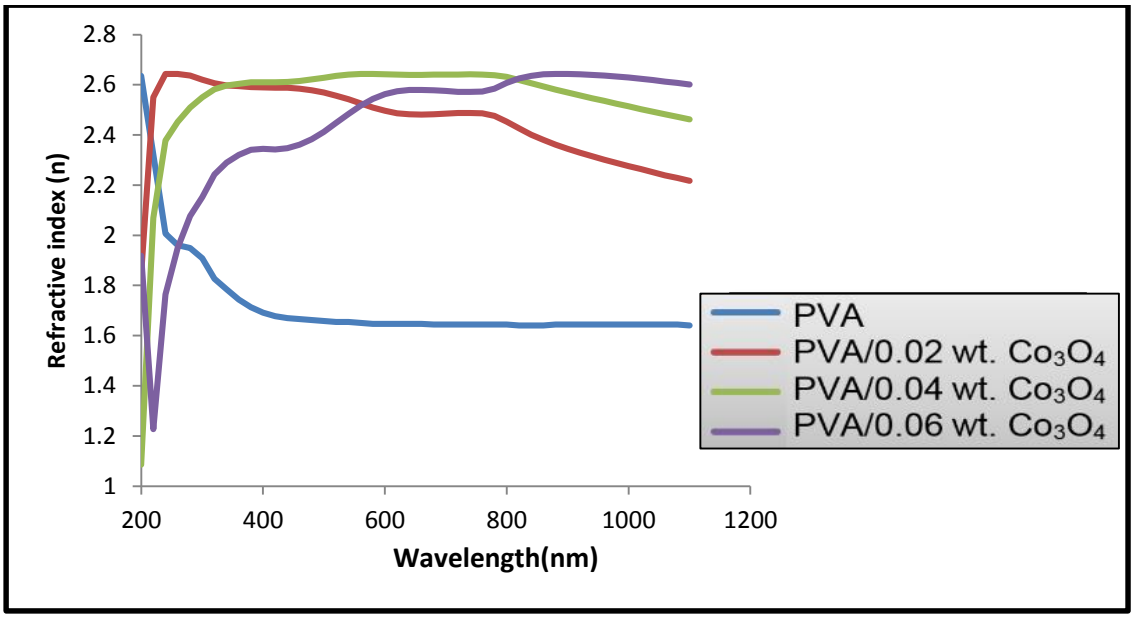


Figure (4.8): Refractive index of PVA and its nanocomposite films with different ratios of Co_3O_4 NPs .

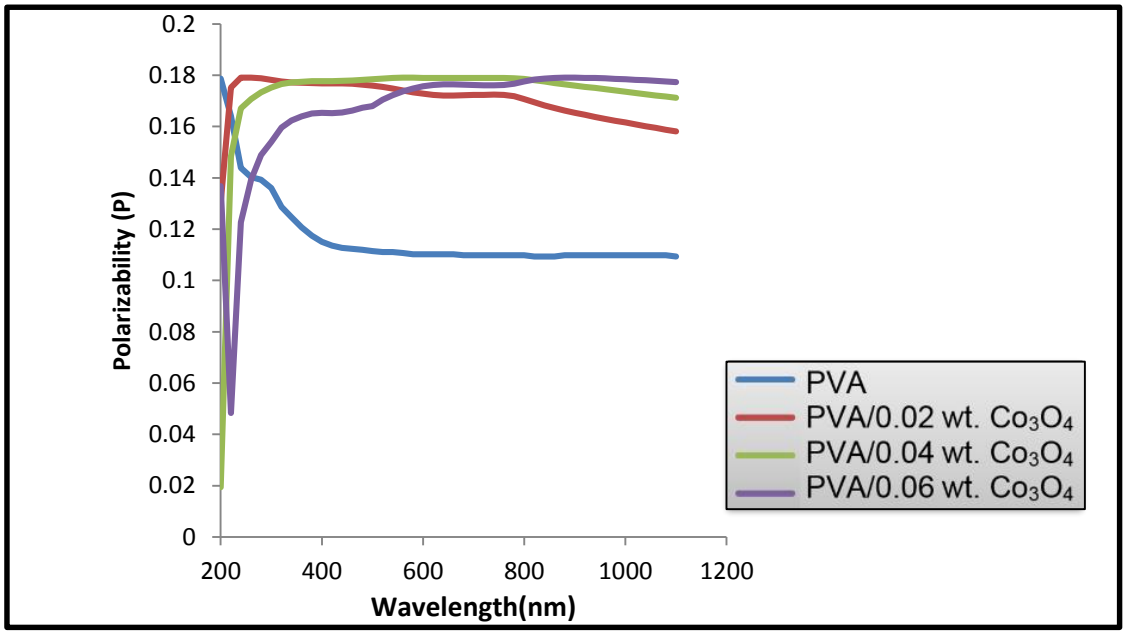


Figure (4.9): Polarizability of PVA and its nanocomposite films with different ratios of Co_3O_4 NPs.

From observation of the figure (4.9), it's worth noting that the behavior of the curves is similar to that of the refractive index, thus the higher the polarization, the higher the refractive index. The polarizability of the produced films rises when the optical energy gap decreases because electrons shift to higher levels, reducing the force of their binding to the nucleus. As a result, the polarizability rises. From observation of the Figure (4.10), it can be notice that the extinction coefficient of the nanocomposite films is much larger than that of the PVA in all regions. This results were directly depended on the absorption of light.

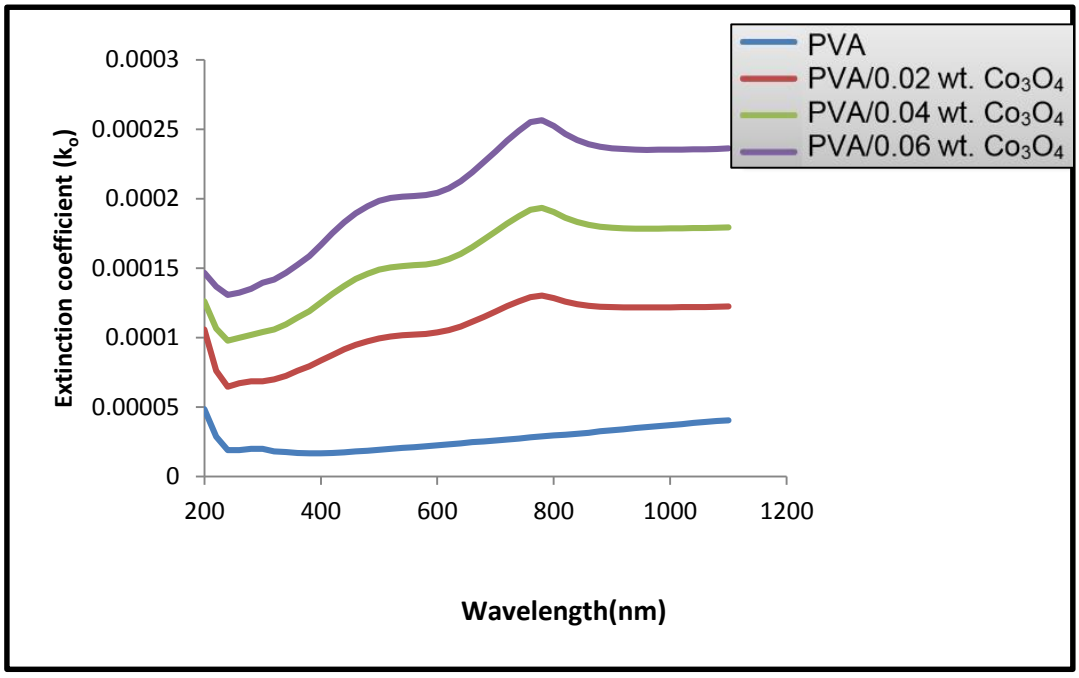


Figure (4.10): Extinction coefficient of PVA and its nanocomposite films with different ratios of Co_3O_4 NPs.

4.3.6 Real and imaginary parts of dielectric constant (ε_r, ε_i)

Real and imaginary dielectric constant (ε_r and ε_i) were calculated using equations (2-17 and 2-18). Figures (4.11) and (4.12) illustrated the variation of real ε_r and imaginary ε_i parts of the dielectric constant for pure polymer and its nanocomposite films with different ratios of Co_3O_4 NPs as a function of photon energy. it can be observed that there is an increase in the values of ε_r at low photonic energies for all nanocomposite films followed by a slow gradual decrease in the higher energies. The increase in the dielectric constant represents a fractional increase in charges within the polymers. The curve behaves of the imaginary dielectric constant before and after addition is seen similar to that of the real dielectric constant but its value is less.

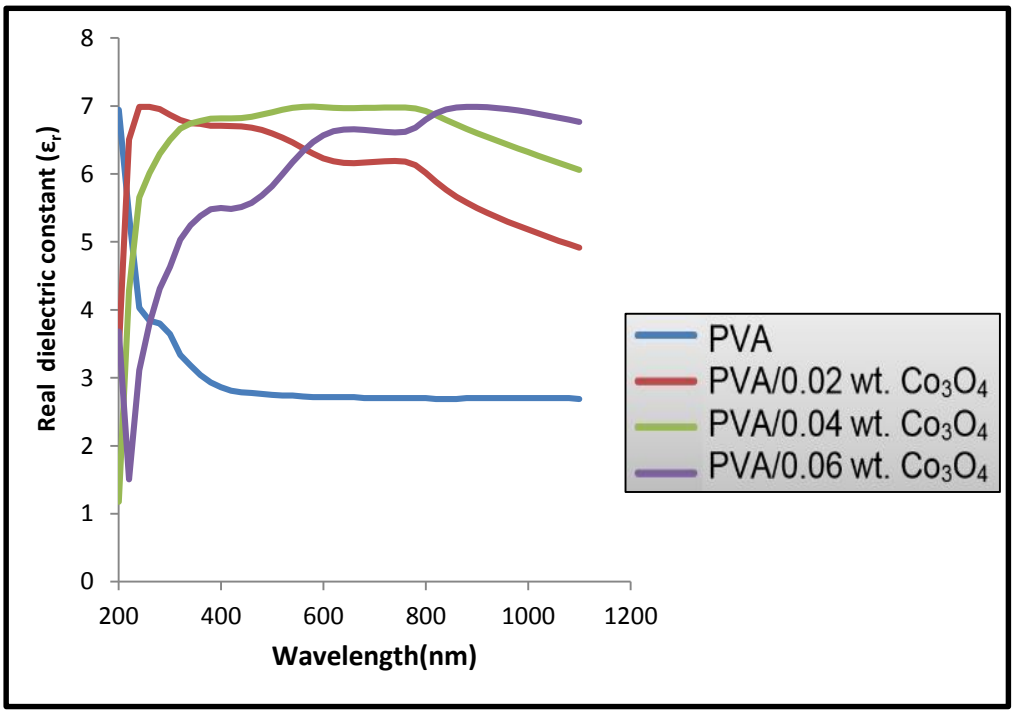


Figure (4.11): Real dielectric constant of PVA and its nanocomposite films with different ratios of Co_3O_4 NPs.

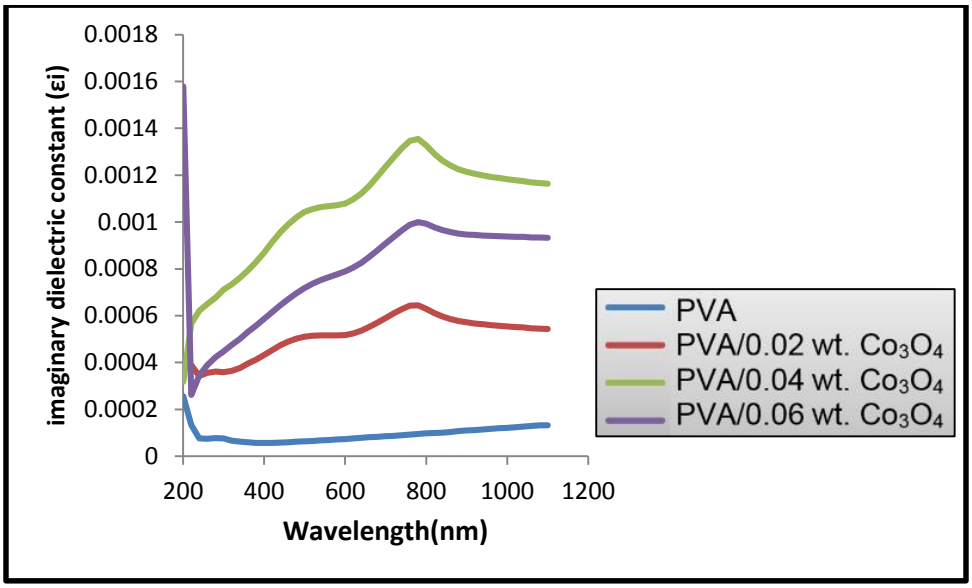


Figure (4.12): Imaginary dielectric constant of PVA and its nanocomposite films with different ratios of Co_3O_4 NPs.

4.3.7 Dielectric Loss angle

Dielectric loss is a loss of energy that goes for heating a dielectric material in a varying electric field. The dielectric loss angle is determined by the relation (2.19). The variations of dielectric loss for pure polymer and its nanocomposite films are represented in Figure (4.13). In general, there is an increase in the values of dielectric loss at low photonic energies, followed by a slight decrease and then it increases again within the energies close to the edge of fundamental absorption.

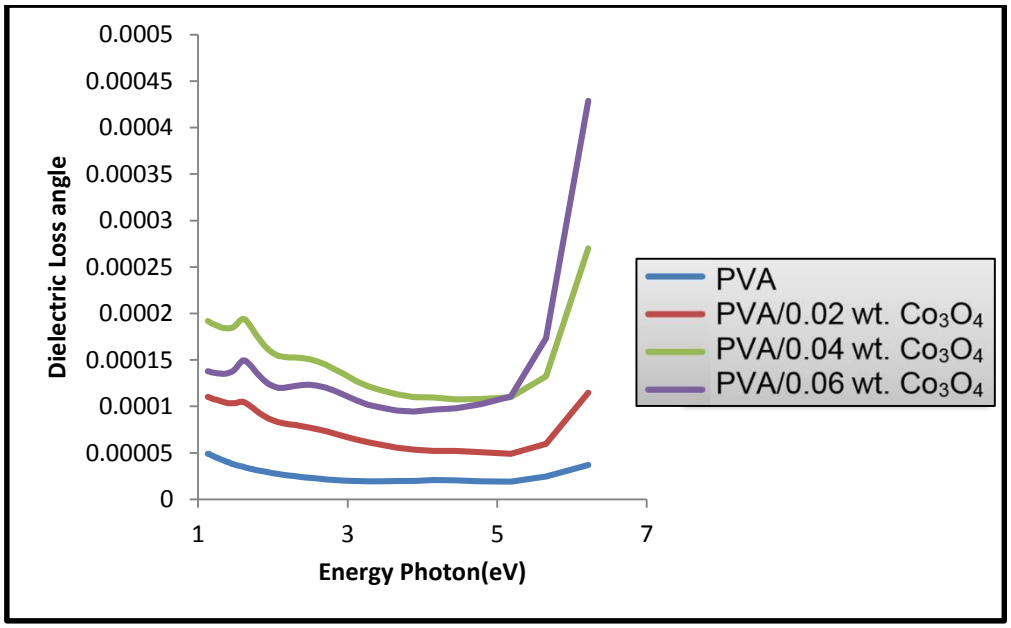


Figure (4.13): Dielectric loss plots of PVA and its nanocomposite films with different ratios of Co_3O_4 NPs.

4.4 Conclusions

1. FTIR indicates that no change in chemical structures between the polymer blend and the additives.
2. The Co_3O_4 NPs formed clusters in the form of chains that extended along the surface of the films, allowing the charge transfer inside the polymer films optimized with increasing the level of proportions.
3. Improving the absorbance of UV waves qualifies it to utilization as a packaging for storage drugs regardless of cost .
4. Optimum transmittance studies show high-transmittance value (about 90%) for polymer blend film in the regions VIS and NIR. indirect allowed and forbidden transition optical energy gaps values decreased with increasing the ratios of Co_3O_4 NPs.

4.5 Suggestions for Future work

1. Study the effect of humidity sensors on some physical properties of PVA: Co_3O_4 nanocomposite films.
2. Study of the mechanical and rheological properties of PVA with different wt.% of Co_3O_4 NPs.
3. PVA: black or green NiO and Co_3O_4 nanocomposite films fabricated by PLAL, characterized and applications.

References

[1] H. Guan, Ch. Shao, Sh. Wen, B. Chen, J. Gong and X. Yang, "A novel method for preparing Co_3O_4 nano fibers by using elecetrospun PVA/Cobalt acetate composite fibers as precursor", material chemistry and physics, vol.82, issue 3, 1002-1006 (2003).

[2] Y. Ma, M. Liu, A. Jaber, R.Y. Wang, Solution-phase synthesis and thermal conductivity of nanostructured CdSe, In_2Se_3 and composites thereof, J. Mater. Chem. A 3 13483–13491 (2015).

[3] P. Saha, T.P. Majumder, S.C. Debnath, Ultraviolet-visible and photoluminescence spectroscopy of newly synthesized CdSe nanostructures, Int. J. Eng. Sci. Innov. Technol. 3 (2) 86–91 (2014).

[4] G. Allaedini, A. Muhammad, Study of influential factors in synthesis and characterization of cobalt oxide nanoparticles, J. Nanostruct. Chem. 3 77, (2013).

[5] T. Maruyama and S. Arai, "Electrochromic properties of cobalt oxide thin films prepared by chemical vapor deposition," J. Electrochem. Soc. 143(4), 1383–1386 (1996).

[6] S. Tan, Y. Moro-Oka, and A. Ozaki, "Catalytic oxidation of olefin over oxide catalysts containing molybdenum. III. Oxidation of olefin to ketone over Co_3O_4-MoO_3 and SnO_2-MoO_3 catalysts," J. Catal. 17(2), 132–142 (1970).

[7] M. Ando, T. Kobayashi, S. Iijima, and M. Haruta, "Optical recognition of CO and H_2 by use of gas-sensitive $AuCo_3O_4$ composite films," J. Mater. Chem. 7(9), 1779–1783 (1997).

[8] M. G. Hutchins, P. J. Wright, and P. D. Grebenik, "Comparison of different forms of black cobalt selective solar absorber surfaces," Sol. Energy Mater. 16(1-3), 113–131 (1987).

[9] S. A. Makhlouf, "Magnatic properties of Co_3O_4 nanoparticles," J. Magn. Magn. Mater. 246(1-2), 184–190 (2002).

[10] L. M. Apatiga and V. M. Castano, "Magnetic behavior of cobalt oxide films prepared by pulsed liquid injection chemical vapor deposition from a metal-organic precursor," Thin Solid Films 496(2), 576–579 (2006).

[11] D. Barreca, C. Massignan, S. Daolio, M. Fabrizio, C. Piccirillo, L. Armelao, and E. Tondello, "Composition and microstructure of cobalt oxide thin films obtained from a novel cobalt (II) precursor by chemical vapor deposition," Chem. Mater. 13(2), 588–593 (2001).

[12] P. S. Patil, L. D. Kadam, and C. D. Lokhande, "Preparation and characterization of spray pyrolysed cobalt oxide thin films," Thin Solid Films 272(1), 29–32 (1996).

[13] J. G. Cook and M. P. Van Der Meer, "The optical properties of sputtered Co_3O_4 films," Thin Solid Films 144(2), 165–176 (1986).

[14] T. Mousavand, S. Takami, M. Umetsu, S. Ohara, and T. Adschiri, "Supercritical hydrothermal sythesis of organic-inorganic hybrid nanoparticles," J. Mater. Sci. 41(5), 1445–1448 (2006).

[15] L. M. Da Silva, J. F. C. Boodts, and L. A. D. Faria, "Oxygen evolution at $RuO_2(x)+Co_3O_4(1-x)$ electrodes from acid solution," Electrochim. Acta 46(9), 1369–1375 (2001).

[16] F. Svegl, B. Orel, I. G. Svegel, and C. V. Kaucic, "Characterization of spinel Co_3O_4 and Li-doped Co_3O_4 thin film electrocatalysts prepared by the sol-gel route," Electrochim. Acta 45(25-26), 4359–4371 (2000).

[17] C. Lin, J. A. Ritter, and B. N. Popov, "Characterization of sol-gel-derived cobalt oxide xerogels as electrochemical capacitors," J. Electrochem. Soc. 145(12), 4097–4103 (1998).

[18] I. G. Casella and M. Gatta, "Study of the electrochemical deposition and properties of cobalt oxide species in citrate alkaline solutions," J. Electroanal. Chem. 534(1), 31–38 (2002).

[19] I. G. Casella, "Electrodeposition of cobalt oxide films from carbonate solutions containing Co(II)-tartrate complexes," J. Electroanal. Chem. 520(1-2), 119–125 (2002).

[20] Z. G. Yu and B. C. Yang, "Morphotogical investigation on cobalt oxide powder prepared by wet chemical method," Mater. Lett. 62(2), 211–214 (2008).

[21] C. E. Carraher, "Polymer Chemistry," Sixth. U.S.A New York, (2003).

[22] L. H. Sperling, "Introduction to physical polymer science," Fourth. John Wiley and Sons, (2006).

[23] M . Rubinstein and R . H . Colby, “Polymer Physics,” USA, (2003).

[24] Oslanec, A. C Costa, and R. J. Composto," Effect of Block Copolymer Adsorption on Thin Film DE wetting Kinetics Macromolecules", Vol.33, No.15, PP. 5505-5512, (2000).

[25] A. Gautam and S. Ram, "Preparation and Thermomechanical Properties of Ag-PVA Nanocomposite Films", Mater. Chem. Phys., Vol.119, No.2, PP.266-271, (2010).

[26] Sheha E, Nasr M, El-Mansy MK "Characterization of poly (vinyl alcohol)/poly (3,4- ethylenedioxythiophene) poly(styrenesulfonate) polymer blend: structure, optical absorption, electrical and dielectric properties". Phys Scr 88:035701 (2013).

[27] Sinha S, Chatterjee SK, Ghosh J, Meikap AK "Dielectric relaxation and ac conductivity behavior of polyvinyl alcohol– HgSe quantum dot hybrid films". J Phys D Appl Phys 47:275301 (2014).

[28] Mahendia S, Tomar AK, Chahal RP, Goyal P, Kumar S "Optical and structural properties of poly(vinyl alcohol) films embedded with citrate-stabilized gold nanoparticles". J Phys D Appl Phys 44:205105 (2011)

[29] D. W. Callister, “Material Science and Engineering an Introduction,” Sixth. The University of Utah, John Wiley and Sons, Inc., USA., (2003).

[30] L. H. Dakhil and F. S. Hashim, “Study the Effect of Adding Iraqi Bentonite Kara Tepe on some Optical Properties of Poly (Methyl Methacrylate),” J. Eng. Applie Sd Sci., vol. 13, no. 18, pp. 7527–7532, (2018).

[31] X. Zhu, J. Wang, D. Nguyen, J. Thomas, R. A. Norwood, and N. Peyghambarian, “Linear and nonlinear optical properties of Co_3O_4 nanoparticle-doped polyvinyl-alcohol thin films,” Opt. Mater. Express, vol. 2, no. 1, p. 103, (2012).

[32] V. Patil1, P. Joshi1 , M. Chougule , Sh. Sen, "Synthesis and Characterization of Co3O4 Thin Film", 2, 1-7 (2012).

[33] H.N. Chandrakala, Shivakumaraiah, H. Somashekarappa, R. Somashekar, S. Chinmayee and Siddaramaiah, "Poly (Vinyl Alcohol)/Zincoxide-Ceriumoxide Nanocomposites: Electrical, Optical, Structural and Morphological Characteristics", Indian Journal of Advances in Chemical Science, Vol. 2, PP. 103-106,(2014).

[34] Ç. Bilkan a,n , Y. A. Kalandaragh b , Şemsettin Altındal c , Roya Shokrani-Havigh, " Frequency and voltage dependence dielectric properties, ac electrical conductivity and electric modulus profiles in Al/Co_3O_4-PVA/p-Si structures" , 154-160 (2016).

[35] Amit Kumar Das, Himadri Sekhar Tripathi, and Ajit Kumar Meikap, " Optical and dielectric properties of poly(vinyl-alcohol) - Cobalt oxide nanocomposite film", 1942, 110007 ,doi: 10.1063/1.5028990 (2018).

[36] T. Dalgleish, J. M. G. Williams, A. M. J. Golden, N. Perkins, L. F. Barrett, P. J. Barnard, C. Au Yeung, V. Murphy, R. Elward, and E. Watkins, "Polymers," J. Exp. Psychol. Gen, vol. 136, no. 1, pp. 23–42, (2007).

[37] L. Catherine, Brinson, Hal F., Brinson, "Polymer Engineering Science and Viscoelasticity: An Introducyion" , 10.1007/978-0-387-73861-1 (Chapter 4), 99–157. Springer (2008)

[38] H. F. Brinson and L. C. Brinson, "Polymer engineering science and viscoelasticity," An Introd., (2008).

[39] C. Maldonado-Codina and N. Efron, "Hydrogel lenses-materials and manufacture. A review," Optom. Pract., vol. 4, pp. 101–113, (2003).

[40] C. C. Okpala, "The benefits and applications of nanocomposites," Int. J. Adv. Eng. Tech, vol. 12, p. 18, (2014).

[41] M. S. Hasnain, S. A. Ahmad, and M. A. Minhaj, "Tahseen Jahan Ara , Amit Kumar Nayak Department of Pharmacy, Shri Venkateshwara University, Gajraula, India, Department of Pathology, King George's Medical University, Lucknow, India, Department of Pharmacology, Maulana Azad Medical College and Hospital, ," Appl. Nanocomposite Mater. Orthop., p. 127, (2018).

[42] R. Strumpler and J. Glatz-Reichenbach, "Conducting polymer composites," J. Electroceramics, vol. 3, no. 4, pp. 329–346, (1999).

[43] A. H. Mohaisen, "Study of electrical conductivity for amorphous and semi crystalline polymers filled with Lithium Fluoride Additive." M. Sc. Thesis, University of Mustansiriah, College of Science, (2009).

[44] ISO/TS 27687. Nanotechnologiesdterminology and definitions for nano-objectsdnanoparticle, nanofibre and nanoplate. International Organization for Standardization; (2008).

[45] Patricia I. Dolez, " Nanomaterials Definitions, Classifications, and Applications", ISBN 978-0-444-62747-6, (2015).

[46] Jeevanandam, J., Barhoum, A., Chan, Y. S., Dufresne, A., & Danquah, M. K. "Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations". Beilstein journal of nanotechnology, 9(1), 1050-1074,(2018).

[47] Feynman RP. There's plenty of room at the bottomdan invitation to enter a new field of physics. Caltech Eng Sci 1959;23:22e36. February 5, (1960).

[48] M. Krystek and M. Górski, "Nanomaterials in Structural Engineering," New Uses Micro Nanomater., (2018).

[49] Kumar CSSR. "Nanomaterials for the life sciences. Nanostructured oxides", vol. 2. Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA; (2009).

[50] Oberdorster G, Oberd € orster E, Oberd € orster J. Nanotoxicology: "an emerging discipline evolving from studies of ultrafine particles". Environ Health Perspect;113(7):823e39 (2005) .

[51] Monfort-Windels F, Lecomte J. Les "applications des nanotechnologies". Brussel (Belgium): Sirris e Driving Industry by Technology; 81 p. (2008).

[52] Smith AM, Nie S. Semiconductor nanocrystals: structure, properties, and band gap engineering. Acc Chem Res 16;43(2):190e200 (2010).

[53] Ohring M. "Materials science of thin films". Boston (MA): Academic Press; (2001).

[54] Camargo PHC, Satyanarayana KG, Wypych F. "Nanocomposites: synthesis, structure, properties and new application opportunities". Mater Res;12(1):1e39 (2009).

[55] Fricke J, Emmerling A. Aerogelsdpreparation, properties, applications. In: Reisfeld R, Jjørgensen CK, editors. Chemistry, spectroscopy and applications of solegel glasses, vol. 77. Springer Berlin Heidelberg; p. 37e87 (1992).

[56] A. H. Mohaisen, "Study of electrical conductivity for amorphous and semi crystalline polymers filled with Lithium Fluoride Additive", M.Sc. thesis, University of Mustansiriah, college of Science, 104 (2009).

[57] J. Pacansky, S. Schneider, "Electron beam chemistry in solid films of poly(vinyl alcohol): exposures under vacuum and under nitrogen at

atmospheric pressure; irradiation monitored using infrared spectroscopy", J. Phys. Chem. 94 ,pp.3166-3179, (1990).

[58] B. L. Lopez, A. I. Mejia and L. Sierra, "Biodegrade Ability of Poly-vinyl alcohol", Polym. Eng .and Sci, Vol.39, No.8, PP.1346-1352, (1999).

[59] C. Srikanth, C. Sr-idhar , B. M. Nagabhushana and R. D. Mathad, "Characterization and DC Conductivity of novel NiO doped Polyvinyl Alcohol (PVA) Nano-composite films", International Journal of Application or Innovation in Engineering & Management ,Vol. 3, pp, (2014).

[60] R. Oslanec, A. C Costa, and R. J. Composto," Effect of Block Copolymer Adsorption on Thin Film DE wetting Kinetics Macromolecules", Vol.33, No.15, PP. 5505-5512, (2000)

[61] J. E. Mark, " Polymer Data Hand Book", Oxford University Press, Vol.52, No.13, PP.1264-1266 (1998).

[62] Wypych, George. "Handbook of Polymers , PVAl poly(vinyl alcohol)", 610–614. doi:10.1016/B978-1-895198-92-8.50188-9, (2016)

[63] T. S. Gaaz, A. B. Sulong, M. N. Akhtar, A. H. Kadhum, A. Mohamad and A. A. Al-Amiery , " Properties and Applications of Polyvinyl Alcohol, Halloysite Nanotubes and Their Nanocomposites", Molecules, Vol.20, No.12, PP.22833-22847,(2015).

[64] Bhargava R, Khan S, Ahmad N, Ansari MMN. Investigation of structural, optical and electrical properties of Co_3O_4 nanoparticles. AIP Conf Proc. (2018).

[65] R. T. Kivaisi, "Optical properties of obliquely evaporated aluminum films," Thin Solid Films, Vol. 97, No. 2, pp. 153–163, (1982).

[66] A. Mohammed Akram, "plastics Chemistry", University of Mosul, (1993).

[67] M. A. Omer, "Elementary Solid State Physics," Addiso-We sly Publ, (1975).

[68] T.K. Hamad, " Refractive index dispersion and analysis of the optical parameters of (PMMA / PVA) thin film", Journal of AlNaharis University, Vol. 16, No. 3, pp .164-170, (2013).

[69] A. N. Donald, "Semiconductor Physics and Devices," (1992).

[70] A. N. Alias, Z. M. Zabid, A. M. M. Ali, M. K. Harun, and M. Z. A. Yahya, "Optical Characterization and Properties of Polymeric Materials for Optoelectronic and Photonic Applications", International Journal of Applied Science and Technology Vol. 3 No. 5; (2013).

[71] R. Naik, C. Kumar, R. Ganesan, and K. S. Sangunni, "Effect of Thickness on The Optical Properties Change in Bi / As_2S_3 Bilayer Thin Films", Chem. Mater. Res., vol. 6, no. 2, (2014).

[72] C.M Wolfe, N. Hoouyak, G. B. Still man, "Physical properties of Semiconductor", prentice Hall, New York, 108 (1989).

[73] J. Talc, A. Menth and D. Wood, "Optical and magnetic investigations of the localized states in semiconducting glasses", Phis, Rev. Lett, Vol.25, PP. 749-752, (1970).

[74] K.L. Chopra, P.D. Paulson, V. Dutta, "Thin-film solar cells: An overview, Progress in Photovoltaics" Research and Applications, Vol. 12, PP.69-92, (2004).

[75] D. Niemen, "Semiconductor Physics and Devices," University of New Mexico, (1992).

[76] V. N. Suryawanshi, A. S. Varpe, and M. D. Deshpande, "Band gap engineering in PbO nanostructured thin films by Mn doping," Elsevier, vol. 645, pp. 87–92, (2018).

[77] C. Kittle, "Introduction to Solid State Physics", 8th ed., John Wiley and Sons Inc. (2005).

[78] A. Loopy, "Microwaves in organic synthesis" 2nd end, Wiley -VCH Verilog GmbH and Co. K GA, Wenham, Germany, (2006).

[79] V. P. N. Nam poor and S. Thomas, "Ge 28 Se 60 Sb 12 / PVA Composite Films for Photonic Applications," Vol. 2, No. 4, pp. 167–174, (2010).

[80] M.Y. Nadeem, Waqas Ahmed. "Optical Properties of ZnS Thin Films", Turk J Phy,24 , 651, (2000).

[81] R. Naik, C. Kumar, R. Ganesan, and K. S. Sangunni, "Effect of Thickness on The Optical Properties Change in Bi / As_2S_3 Bilayer Thin Films," Chem. Mater. Res., Vol. 6, No. 2, pp. 1–2, (2014).

[82] O. Gh Abdullah, B. K. Aziz, and S. A. Hussen, "Optical Characterization of Polyvinyl alcohol -Ammonium Nitrate Polymer Electrolytes Films," Chem. Mater. Res., Vol. 3, No. 9, pp. 2225–0956, (2013).

[83] A. Hasnatand J. Plodder, "Dielectric properties of spray pyrolized of aluminum doped cadmium sulfide (Al-doped CdS) thin 109 films',„ International Journal of Physical Sciences, Vol. 7, No.47, pp.6158-6161, (2012).

[84] R. M. Silverstein,"Infrared spectroscopy" in (Spectrometric Identification of Organic Compounds (8^{th} Edition)), edited by David L. Bryce, (Wiley), 978-0- 470-61637-6, (2015).

[85] M. Dahshan,"Introduction to Material Science and engineering", 2^{nd}, McGraw Hill, New York, (2002).

[86] X. Zhu, J. Wang, D. Nguyen, J. Thomas, R. A. Norwood, and N. Peyghambarian, "Linear and nonlinear optical properties of Co_3O_4 nanoparticle-doped polyvinyl-alcohol thin films," Opt. Mater. Express, vol. 2, no. 1, p. 103, (2012).

[87] H. Yamamoto, S. Tanaka, and K. Hirao, "Nanostructure and optical nonlinearity of Cobalt oxide thin films," J. Ceram. Soc. Jpn. 112, S876–S880, (2004).

الخلاصة

تم تحضـيرأغشـية من بوليمر PVA ومتراكباته النانوية بنسـب مختلف (2 ، 4 ، 6 %) من أوكسيد الكوبلت Co_3O_4 باستخدام طريقة صب المحلول. تم الحصـول على النتائج عن طريق التحليل الطيفي للأشـعة تحت الحمراء لتحويل فوريه (FT-IR)، والمجهر البصـري (OM) والتحليل الطيفي للأشعة فوق البنفسجية UV.

أكدت أطيـاف FT-IR الى عـدم وجود تغيير في الأواصـــر الكيميـائيـة بين البوليمر والمواد المضـــافة. تشـــير صـــور المجهر الضـــوئي إلى تجانس جيد وتوزيع دقيق لجزيئات Co_3O_4 المضافة ، بالإضافة إلى نقل الشحنة والتكوين المعقد داخل أغشية البوليمر الممزوجة.

أظهر التحليل الطيفي للأشـــعة فوق البنفســـجية المرئية (UV) أن القيمة المثلى للنفاذية لغشـــاء البوليمر تبلغ حوالي 90 ٪ في منطقتي Vis و .NIR يؤهل انخفاض نفاذية أغشـــية المركبات النانوية تجاه الأشعة فوق البنفسجية لاستخدامها كغلاف لتخزين الأدوية بغض النظر عن التكلفة.

تم تحديد فجوات الطاقة الانتقالية غير المباشرة المسموح بها والممنوعة من طيف الامتصاص، والتي انخفضت قيمها مع زيادة محتوى Co_3O_4 NPs .

وكانت قيمة فجوة الطاقة الانتقالية المســـموح بها لبوليمر PVA ومركبته النانوية مع نســـب وزنية (2، 4 و6) % من Co_3O_4: 2.3 eV , 3.2 , 3.9 , 4.5= (E_g)

أما لفجوة الطاقة الانتقالية الممنوعة: 1.5 eV , 2.0 , 3.0 , 3.9= (E_g) على التوالي.

لوحظ أن E_g ^{opt} غير المباشرة تنخفض عند إضافة جسيمات Co_3O_4 النانوية.

الخصـائص البصـرية الأخرى كمعامل الإنكسـار، الإسـتقطابية، معامل الخمود، الأجزاء الحقيقية والخيالية لثابت العزل قد فحصت.