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Effect of Ferrite Nanoparticles on Optical Properties of Polymer Blend

A Research

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of Babylon in Partial Fulfillment of Requirements for the Degree of higher
diploma Education / Physics of material and its applications

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

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Dedication

To the Great Prophet of God, the Seal of Prophets "Mohammed"

To my sir Amir of the Faithful, "Imam Ali"

**To who gave me the endurance to complete my
road my father**

To the best woman in the universe my mother

To my supervisor

Dr. Ahmed Hashim

And

Everyone who has helped me

Qahtan ...

Acknowledgments

**In the Name of Allah, the Compassionate, the Merciful
First, thanks to Allah, the Lord of Earth and Heaven, for
completing my research.**

**Special thanks to the Deanery of the College of Education for
Pure Sciences/ University of Babylon and the Department of
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research.**

**Then I would like to express my thanks and appreciation to all
of.....**

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in supervising this study and for all the effort he made.
To my family, who helped me reach this stage of my studies.
the respected discussion committee.**

**And to everyone who helped me in my studies and
encouraged me even with a word.**

Abstract

In this study, the (PS-PMMA/Cobalt Ferrite) nanocomposites have been prepared using the casting method with variant content of Cobalt Ferrite nanoparticles (2.1, 4.2 and 6.3) wt.%. The optical properties of (PS-PMMA/Cobalt Ferrite) nanocomposites have been investigated. The absorbance, absorption coefficient, refractive index, extinction coefficient, dielectric constant (real, imaginary) and optical conductivity of (PS/PMMA/ Cobalt Ferrite) nanocomposites increased with the increasing of the concentrations of Cobalt Ferrite nanoparticles while the transmittance and the energy gap for indirect transition (allowed, forbidden) decreased with the increasing of the concentrations of Cobalt Ferrite nanoparticles. This result can be used for optoelectronic device.

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List of Abbreviations

Physical meaning	Symbol
Titanium Dioxide	TiO₂
Polyvinyl alcohol	PVA
X-ray-diffraction	XRD
Polymethylmethacrylate	PMMA
Poly styrene	PS
Cobalt Ferrite	CoFe₂O₄
Nanoparticle	NPs
Optical microscope	OM
Field Emission Scanning Electron Microscope	FESEM
Fourier Transformation Infrared Region	FTIR
Ultraviolet	UV
Conduction Band	C.B
Valence Band	V.B

List of Symbols

<i>Symbol</i>	<i>Physical Meanings</i>
n	<i>Refractive index</i>
k	<i>Extinction coefficient</i>
A	<i>Absorption</i>
I_o	<i>Incident intensity of light</i>
I_A	<i>Absorbed intensity of light</i>
T	<i>Transmittance</i>
I_T	<i>Intensity of transmitted</i>
k	<i>Wave vector</i>
α	<i>Absorption coefficient</i>
h	<i>Planck constant</i>
ν	<i>Photon frequency</i>
$E_g^{opt.}$	<i>Optical energy gap</i>
r	<i>Value determines the type of electronic transitions</i>
E_{ph}	<i>Energy phonon</i>
c	<i>Velocity of light</i>
λ	<i>Wavelength of light</i>
R	<i>Reflectance</i>
d	<i>Thickness</i>
N	<i>Complex refractive index</i>
ϵ'	<i>Dielectric constant</i>
ϵ	<i>Complex dielectric constant</i>
ϵ_1	<i>Real dielectric constant</i>

ϵ_2	<i>Imaginary dielectric constant</i>
σ_{op}	<i>Optical Conductivity</i>

Chapter one

Introduction and Literature

Review

1.1 Introduction

Nanotechnology is a new technology that can be used in many different fields. It has become very popular in a several of different fields over the last 10 years, including the mechanics, electronics, materials sciences, medicine, optics, airspace and oil. Its societal impact has been recognized as a significant factor. The prefix "nano" originates from the Greek word for "dwarf." "Nano" is a term that refers to extremely small objects. A nanometer (nm) is one billionth of a meter, or 10 angstroms. As example, a nanometer is ten thousand times less than the diameter of a human hair at 10^{-9} m. A human hair is around 50 microns in diameter [1].

Nanotechnology will enable the development of new materials providing the basis for the design and development of new properties and structures, which will result in increased performance, reduced cost of maintenance, and enhanced functionality [2]. Nanotechnology is a relatively new field of study that developed as a result of the observation that materials exhibit dramatically different characteristics at the nanoscale than at bigger particle sizes [3]. The researcher Feynman in 1959, pointed to the presence of something in the depths, there is plenty of room at the bottom. Norio Taniguchi coined the word "nanotechnology" in 1974 in Japan, as follows; Nanotechnology mainly consists of the processing of separation, consolidation and deformation of materials by one atom or one molecule [4].

Nanotechnology involves work from top-down, i.e. reducing the size of large structures to the minor design, such as photonic applications in nanoelectronics and nano engineering, or bottom-up, involving the transformation of individual atoms or molecules into the nanostructures and so more closely resembling biology [5]. Nanotechnologies are vital technologies for the twenty-first century, and significant research is being conducted on this subject. Soon, new applications can also become

accessible. Due to the fact that applications with nanoscale structural characteristics exhibit significantly different , chemical,biological and physical characteristics than their macroscopic equivalents, nanotechnology can be helpful on a variety of levels [6].

1.2 polymers structure

Polymers are composed of huge organic molecules (macro molecules) composed of repeated small structural (monomer units) that are joined together through a process known as polymerization. [7]. Molecules in polymers are made up of thousands of atoms that are linked together by covalent chemical bonds. The forces that hold the molecules together depend on the type of polymer they are made of. Due to the large, coupled molecules in polymers that are difficult to manage, there are only a few crystal connections in polymers at low temperatures. It is only in limited regions that a linear chain of molecules can arrange themselves in an organized form. In the solid state, polymers are comprised of crystalline and non-crystalline regions [8].

1.3 Chemical Classification of Polymers

Polymers can be classified according to their chemical structure:

1.3.1 Linear Polymers

The main structural unit of these polymers is a single molecular series for certain lengths that are linked together in a linear shape. It doesn't have any branches except for the twisted totals that are part of the monomer, as shown in figure (1.1.a).

Polyethylene, poly (vinyl chloride), polystyrene, poly (methyl methacrylate), nylon, and fluorocarbons are some of the more prevalent polymers that form linear shapes [9].

1.3.2 Branched Polymers

The reaction between poly-functional molecules results in structural units that can be connected in such a way as to form non-linear structures. In certain situations, the side growth of each polymer chain can be stopped before the chain has a chance to link up with another chain. The resulting polymer molecules are said to be branched. Branching can produce several physical properties in a polymer, such as a decrease in solvent solubility, a rise in the softening point and also a decrease in thermoplastic properties.

For instance, high density polyethylene (HDPE) is predominantly a linear polymer, while low density polyethylene (LDPE) has small chain branching [10], as shown in the figure (1.1.b)

1.3.3 Cross linked Polymers

There are a lot of chemical bonds that connect to each other in a complicated way in this type of thing. The format string is composed of three-dimensions polymer chains connected by a slew of than one site, or when monomers with effective totals are used rather than being contained two effective totals, as seen in the figure (1.1.c) [11,12].

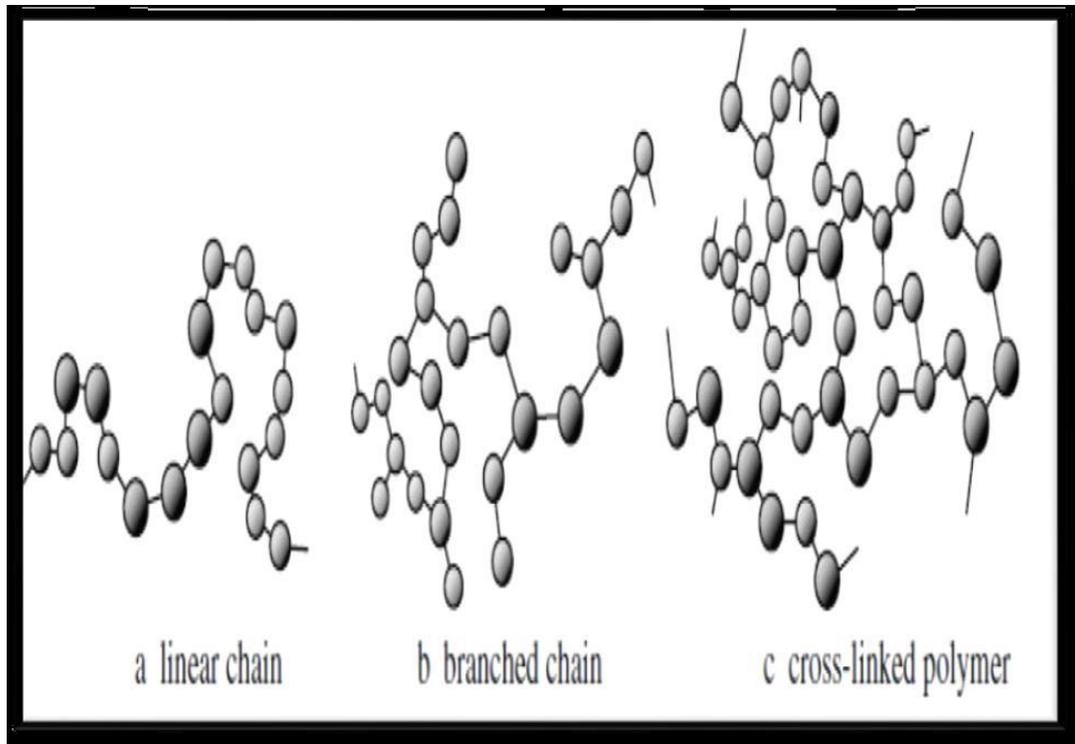


Figure (1.1): Constructivism for (a- Linear polymer, b- Branched polymer , c-Cross linked polymer) [12].

1.4 Thermal Classification of Polymers

Polymers are divided into groups based on how temperature affects them [13,14]:

1.4.1 Thermoplastic Polymers

The Temperature has an effect on these polymers' characteristics. The polymers degrade as the temperature increases. Possess a sticky and malleable nature; polymers revert to their solid state as the temperature decreases. Due to the fact that the molecules of the thermoplastic polymers are bound together via Intermolecular forces are weak (Van der Waals forces). When heated, these molecules slide over one another, which includes polyethylene, polystyrene, polyvinyl chloride, and polypropylene, as depicted in figure (1.2).

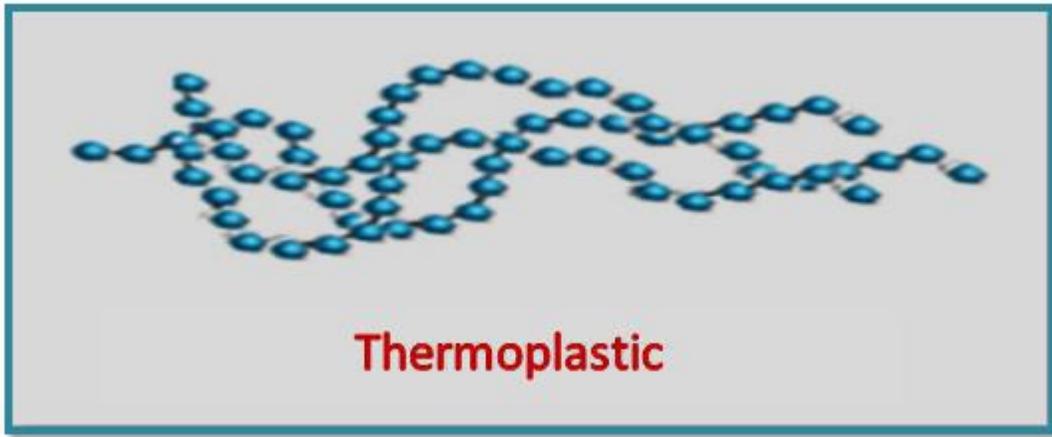


Figure (1.2) Thermoplastic polymer configuration [14]

1.4.2 Thermoset Polymers

Thermosets are typically three-dimensional networked polymers with a large degree of polymer chain crosslinking. When these polymers are heated, they change in a chemical way. These polymers become insoluble after being heated, do not conduct heat or electricity, and difficult since these polymers' molecules are connected via covalent solid chemical connections. This type of polymer includes urea-formaldehyde resin and phenol formaldehyde resin. The arrangement of thermoset polymers is illustrated in this figure (1.3)

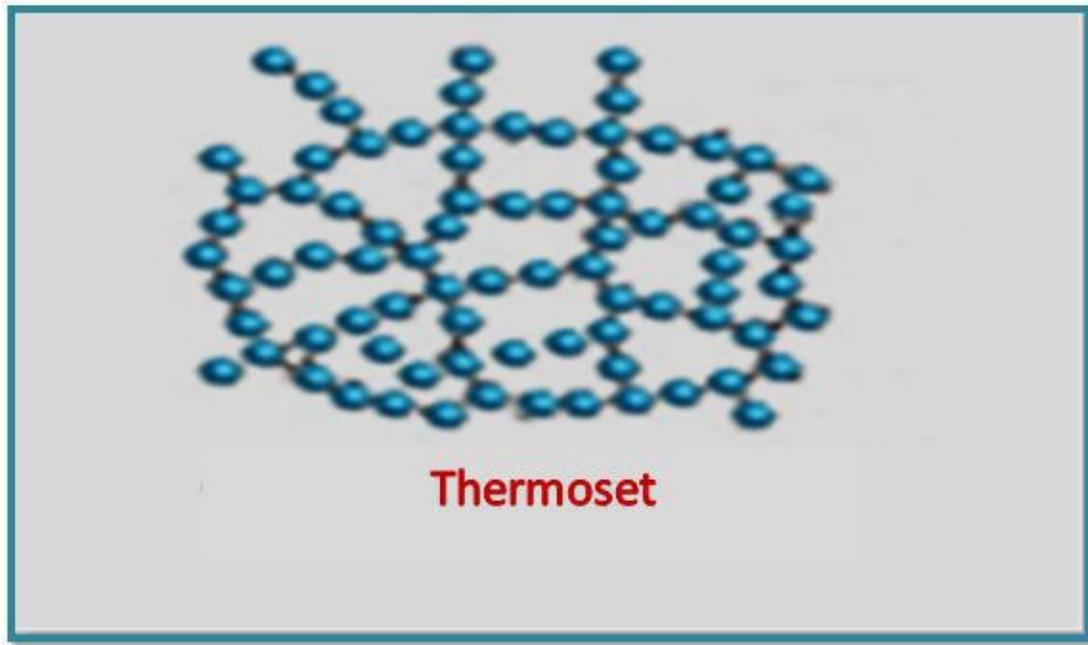


Figure (1.3) Thermoset polymer configuration [14]

1.4.3 Elastomers Polymers

Elastomers are a type of network polymer that is lightly cross-linked and may be reversibly stretched to extraordinary lengths. They have very tightly randomly coiled molecules when not stressed, but when they are stretched, they become a lot bigger and bend. This lowers the randomization of the chains, resulting in a decrease in the entropy of the material, which is caused by the retrospective force observed.

Cross-links prohibit molecules from moving past one another when a material is expanded. When the rubber cools (partially), it becomes crystal clear or glassy transparent. They do not flow when heated in the conventional sense due to cross-links. Neoprene and vulcanized rubber neoprene are as illustrated in figure (1.4).

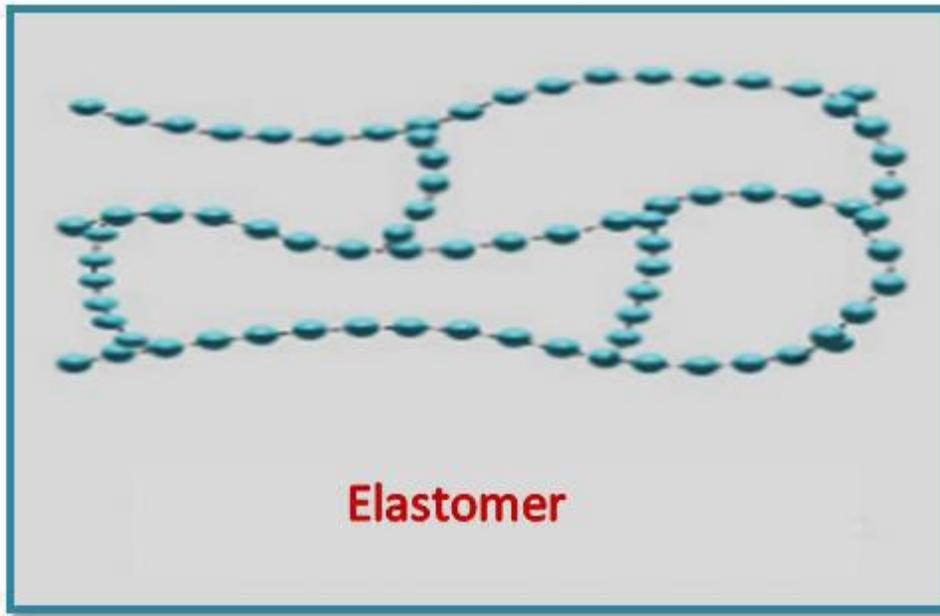


Figure (1.4): Elastomer polymer configuration [14]

1.5 Classification Based on Sources Polymers

Two major sources of polymers are as follows [15]:

1.5.1 Natural polymers

It is naturally occurring substance found in plants and animals, such as lumber, cotton, silk, natural rubber, and wool. Starch, protein, and cellulose are all natural foods that are composed of natural polymers.

1.5.2 Synthetic Polymers

The polymer is synthesized from simple chemical components and accounts for the great majority of industrially important polymers, including rubber, plastics, synthetic leather, and nylon textiles. Other qualities of synthetic polymers include physical and mechanical properties, as well as heat stability.

1.6 Classification of Polymers dependent on homogeneity

Polymers are divided according to the homogeneity for their repeating units into the following categories:

1.6.1 Homopolymers:

Homopolymers are materials composed entirely of one monomer [16].

1.6.2 Copolymers:

If their components have more than one monomer type, they are referred to as copolymers [16].

1.6.3 Composite Polymers:

It is the addition of materials to homogeneous polymers in order to modify certain of their properties and the incorporation of new recipes [17].

1.7 Nanomaterials

Nanomaterials studies is a discipline that approaches nanotechnology from a materials science perspective. A nanometer (nm) is a unit of measurement equal to one billionth of a meter. A single unit of a nanomaterial is between (1-100) nanometers in size.

These materials frequently exhibit exceptional qualities as a result of their shape, size, and chemical composition [18]. Two major causes contribute to nanoparticles' characteristics being notably different from those of ordinary materials: greater relative surface area and quantum effects [19].

1.8 Composite Materials

When two or more materials are combined in a way that is different in shape or material composition, the resulting composite has qualities that are distinct from the individual materials, this is referred to as a composite material system [20]. Additionally, it has a robust structure. The composite is composed of two primary components: the matrix (the fundamental material) and the additives. The matrix serves to encapsulate and bulk up the composite. It encircles and strengthens other components, forming a "compact system." Additives are substances that are added to polymers to give them specific properties and improve their basic properties. These substances can be added in granular form or as small particles. Additives can improve the overall conductivity, reduce porosity, improve friction, and some magnetic properties [21,22].

1.9 Nanocomposites

Nanocomposites consist of polymers that may be natural or synthetic, and they are nanomaterials, which refer to materials with nano-sized topography or composed of nano-sized building components. Although the terms nanomaterials and nanocomposite represent new and exciting areas in materials science, they have been used for centuries when they exist in nature. However, methods for characterizing and controlling the structure at the nanoscale have only stimulated much later [23]. A nanocomposite, is a conventional compound consisting of two parts, a filler and a matrix. In a conventional composite usually a fiber such as glass fiber or carbon fiber is used as a filler, in a nanocomposite, the filler is a nanomaterial. Examples of nanomaterials are carbon nanotubes, carbon fiber tubs, and nanoparticles such as gold, diamond, silver, silicon and copper [24].

The dispersion of inorganic nanocomposites into an organic polymer to form polymer nanocomposites has gained increasing attention in recent years. The fundamental and important role that nanostructure control composition and morphology play in their applications; The new properties of nanocomposites can be obtained through the successful transfer of the properties of the original components into a single material [25]. An important and significant challenge in developing nanocomposites is to find ways to create macroscopic components that take advantage of the unique physical and mechanical properties of the very small objects within them. On the other hand, the fracture toughness of such bio composites depends on the ultimate tensile strength(T) of the reinforcement. Crucially the use of nanomaterials allows the maximum theoretical strength of the material to be reached, because the mechanical properties become increasingly insensitive to defects at the nanoscale. Electrical, thermal and electronic properties and the electrochemical properties of nanocomposites can differ significantly from those of their constituent. The basic theory of nanocomposites is based on the principle that there is a very wide interface between the nano-sized building blocks and the polymer matrix that our study is based on this method or the nanocomposite [26].

1.10 Applications of Polymer Nanocomposites

The applications of polymer nanocomposites are based on: the matrix and the nanocomposites [27]. Among its many applications are:

- Cars (gasoline tanks, fenders, interior and exterior panels...etc).
- Construction (pull out the shape, panels).
- Electronics and electricity (printed circuits and electrical components).
- Food packaging (packaging, films).

- Cosmetics (controlled release of active ingredients).
- Dentistry (filling materials).
- Environment (biodegradable materials).
- Gas barrier (tennis balls, food and beverage packaging).
- Flame retardants, military, aerospace and commercial applications.

It can be noted that there are many industrial and medical applications of nanomaterials related to many fields, including engineering, biology, chemistry, computing, materials science, military applications, and communications, but their effects are difficult to enumerate benefits of nanotechnology include improved manufacturing methods, water purification systems, improved food production methods and energy networks, physical health promotion, nanomedicine. Products made with nanotechnology may require little labor earth, or maintenance, are high in productivity, low in cost, and have modest material and energy requirements [28].

1.11 Physical Properties of the Used Materials

1.11.1 Polystyrene (PS)

Polystyrene (PS) is a flexible plastic that is commonly used in several aspects of human life and industry due to its low cost, light weight, ease of fabrication, flexibility, thermal efficiency, durability, and moisture resistance. However, polystyrene is exceptionally stable and difficult to degrade in the surroundings after disposal [29]. It is produced by the polymerization of styrene and is the most widely used plastic. At room temperature, the thermoplastic polymer is a solid but when heated above 100 °C it flows. It becomes rigid again when it cools down. Polystyrene is insoluble in water. Polystyrene is compound that is non-biodegradable with a couple of exceptions. It is easily dissolved by many aromatic hydrocarbon solvents

and chlorinated solvents. It is widely used in the food-service industry as rigid trays, containers, disposable eating plates, bowls, etc [30]. Table (1-1) explain some physical properties of PS [21-32]

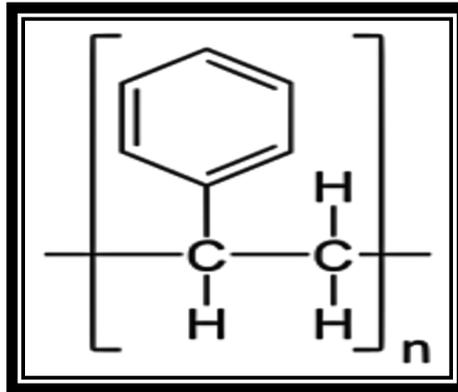


Figure (1.5): Molecular formula of PS

Table (1-1) Physical properties of PS [31-32]

Property	Description
Chemical formula	$(C_8H_8)_n$
Molecular Weight/ Molar Mass	104.1 g/mol
Density	1.04 g/cm ³
Solubility in water	Insoluble
Melting Point	240 °C
Boiling point	430 °C
Glass Transition Temperature (T _g)	100 °C

1.11.2 Poly methyl-methacrylate (PMMA)

Poly-methyl-methacrylate (PMMA) has been used for vertebra– plasty, the percutaneous augmentation of vertebral bodies, since the late 1980s (Galibert et al., 1987) and is today the most commonly used augmentation material [33]. The used matrix material is Poly methyl-methacrylate (PMMA) as a polymer waveguide that has attracted much attention for use as optical components and in optoelectronic devices due to its low cost and volume productivity. Poly-methyl-methacrylate is an important and interesting polymer because of its attractive physical and optical properties decisive about its broad application. This is a thermoplastic material with good tensile strength and hardness, high rigidity, transparency, good insulation properties and thermal stability dependent on tacticity. Poly-methyl-methacrylate has some disadvantages such as brittleness and low chemical resistance which can be eliminated by chemical or physical modification [34]. Poly-methyl methacrylate is one of the earliest and best-known polymers. Poly-methylmethacrylate was seen as a replacement for glass in a variety of applications and is currently used extensively in glazing applications. The material is one of the hardest polymers and is rigid, glass-clear with glossy finish and good weather resistance. Poly-methylmethacrylate is naturally transparent and colorless. The transmission visible light is very high. Polymeric composites of Poly-methylmethacrylate are known for their importance in technical applications [35]. Figure (1.6) explain the chemical structure of PMMA [35]. Table (1-1) shows some physical properties of PMMA [36].

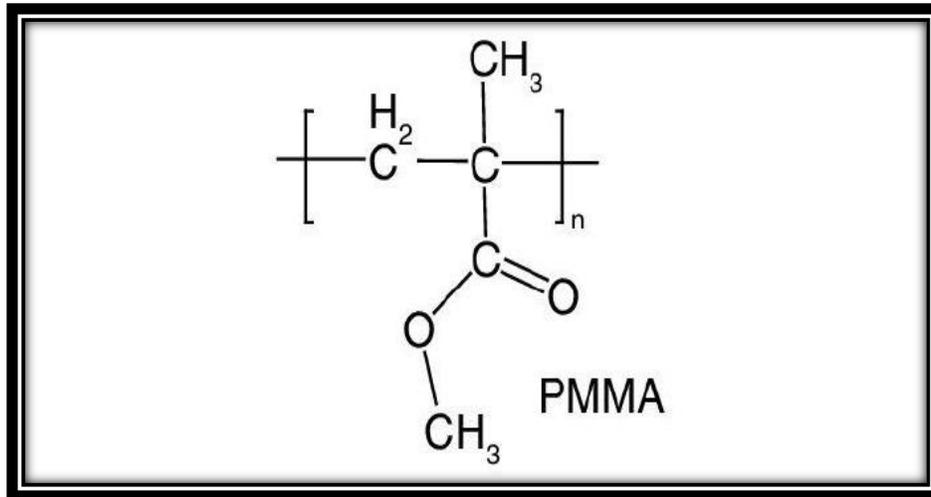


Figure (1.6): A chemical structure of the repeating unit of PMMA polymer [35].

Table (1-1): The most important physical properties of PMMA polymer [36].

Property	Description
Chemical formula	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}_3$
Density	1.2 g/cm ³
Melting point	140°C
Boiling point	200°C
Solubility in water	Insoluble
Solubility	Soluble in benzene, carbon disulfide, chloroform
Glass Transition Temperature Tg (K)	106 °C

1.12 Additive Material (Ferrite)

Ferrite is one of the magnetic oxide compounds, which comprise iron oxide as a major component [37]. Ferrites are usually ferrimagnetic ceramic compounds derived from iron oxides. Ferrites or ferrimagnetic oxides are dark brown or gray in appearance and very hard and brittle in physical character [38]. Ferrites show dielectric properties, that dielectric property means that even though electromagnetic waves can pass during ferrites, they do not easily conduct electricity [39]. This gives

them an advantage over iron, nickel and other transition metals that have magnetic properties in many applications because these metals conduct electricity [40].

Ferrite is chemical compounds (ferromagnetic materials) that are not conducive to electrically and that contain oxygen and at least two magnetic ions that contain the chemical formula (AB_2O_4) , (A) and (B) represent different metal cations consisting of different mixtures of iron oxides. Such as hematite (Fe_2O_3) or magnetite (Fe_3O_4) and other added mineral oxides such as CdO, ZnO, MnO, and AlO. Iron oxide (Fe_2O_3) is more probable than other oxides (manganese, cadmium, zinc, nickel, barium, lithium, etc.) . More than it, these low-cost materials are easy to assemble and offer more formability advantages than their metal and amorphous magnetic counterparts [41].

1.13 Types of Ferrites according to Magnetic Properties:

Ferrites can be divided according to its magnetization into two types hard and soft. This classification depends on the ability of ferrite to magnetize or demagnetize it. Soft ferrites are easily magnetized or demagnetized while hard ferrites are hard to magnetize or demagnetize [42].

1.13.1 Soft Ferrites

It is a type of ceramic that can be easily magnetized This indicates that magnetic materials have a low coercive field and high magnetization is required in many applications, and the hysteresis loop is long and narrow and therefore the energy loss is very low in these magnetic materials [43]. Soft ferrites have certain advantages over other electromagnetic materials including high electrical resistance, eddy current losses over a wide range and high and stable transmittance temperatures. Many examples of Spinel ferrites like manganese–zinc ferrite $(Mn,Zn,Fe)O_4$ system are commercially important soft magnets. In addition, lithium ferrite, nickel ferrite, and garnets are other examples of soft ferrites [44].

1.13.2 Hard Ferrites:

Hard ferrites of permanent ferrite magnets, which have a high coercivity and high remanence after magnetization, which has the high coercivity that means the materials are very resistant to becoming demagnetized, an essential property for a permanent magnet. They also have high magnetic permeability. These so-called ceramic magnets are cheap, and are widely used in house hold products such as refrigerator magnets. Iron oxide and barium or strontium carbonate are used in the manufacturing of hard ferrite magnets These are most common hard ferrites:

Strontium ferrite, $\text{SrFe}_{12}\text{O}_{19}$ ($\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$) used in small electric motors, microwave devices, recording media, magneto-optic media, electronic industry and telecommunication [45]

1.14 Literature Review

In (2015), Kadhim [46] studied the nanocomposite (PS/Ti) in a casting manner with the addition of different weight ratios of nano titanium. The effect of Ti addition on several optical characteristics of PS has been investigated at various wavelengths. With increasing Ti weight ratios, the extinction coefficient and absorption coefficient rise, while the energy gap of the indirect allowed and forbidden transition shrinks.

In (2016), Al-Ramadhan *et al.* [47] studied the optical and morphological properties of (PVA-PVP-Ag) nanocomposites, which prepared by casting method, UV-Vis spectroscopy at a wavelength of (200-900)nm was used to evaluate the optical characteristics, By increasing nanoparticle concentration and refractive index, the energy gap of indirect transition (allowed and forbidden) decreased from (4.8-3.9 allowed) to (4.7-3.8 forbidden) As the amount of Ag was increased, the AFM and OM data revealed a homogeneous distribution, a very smooth surface, and minimal roughness.

In(2017) Bhavsar, *et al* [48] simple solution casting method was utilized to synthesize aluminium oxide (Al_2O_3)doped polystyrene (PS) polymer nanocomposite films. As synthesized films were characterized using X-ray diffraction (XRD), Fourier transform infrared (FTIR)spectroscopy,ultra violet (UV)-visible spectroscopy, photoluminescence(PL) method and scanning electron microscopy (SEM).The crystalline nature of the films was found to decrease after incorporation of filler in the polymer matrix as revealed by XRD results. A new carbonyl group was appeared in the FTIR spectra and confirmed the charge transfer reaction between filler and polymer matrix. The decrease in the band gap was found with the filler concentration in the synthesized polymer nanocomposite films. Photoluminescence emission spectra of nanocomposites were observed at 411 nm, 435 nm and 462 nm, respectively in violet-blue region which indicates interaction between the dopant and the polymer matrix. The PL emission spectra of polymer nanocomposite films with 3 wt% of Al_2O_3 filler exhibited higher peak intensity. The Al_2O_3 filler dispersion is found to reduce band gap and promote luminescence property in polystyrene.SEM analysis indicates the agglomeration of Al_2O_3 nanoparticles into PS matrix at higher concentrations

In(2018) Demirbay and Uğur [49] studied the electrical and morphological properties of nanocomposite films made up of polystyrene (PS) latex which have different particle sizes and multi-walled carbon nanotubes (MWCNTs) were reported. Increment in PS latex size lead to the increase in the conductivity one order of magnitude from 10^{-5} S for 382 nm latex systems to 10^{-4} S for 560 nm latex system. The addition of MWCNTs as a nanofiller into PS latex enhanced the conductivity by 9 and 10 orders of magnitude, from 10^{-15} - 10^{-13} S for the pure PS polymers to 10^{-5} - 10^{-4} S at 20 wt% of MWCNTs. SEM images also showed the improved

MWCNT dispersion, with the increase in latex particle size in consistent with these experimental results

In(2019) Manhas, *et al* [50] studied the effect of the nanocomposite containing polypyrrole and polystyrene were synthesized by solution casting technique. The effect of different (especially small) concentrations of polypyrrole on structural and optical properties was studied. The results reveals that properties can be tuned significantly even with the inclusion of small filler concentration in the polymer matrix. A drastic decrease in the transmittance (up to 35%) has been observed even with small amount of filler concentration (i.e. 3%)

In (2020), Alsaad *et al.* [51] studied PMMA-PS/ZnO NPs solution was prepared by blending ZnO NPs with polymethylmethacrylate (PMMA)-Polystyrene (PS) with a molar ratio of 80% and 20% using solution mixing at concentrations of 2.5%, 5% and 10%. The dip-coating technique was used to get thin films of 300 nm thickness that are highly transparent and could be used for UV shielding. UV-Vis spectrophotometer measurements show that the transmittance for PMMA-PS/ZnO thin films has strong absorption in UV region ($\lambda \leq 300 \text{ nm}$) and high values of transmittance in the visible region. The transmittance of PMMA-PS lies in the range (60-68) % in the visible region. We found that the transmittance values increased gradually upon introducing the ZnO NPs in the films and exhibit a maximum value of 85% for PMMA-PS/10% NPs. As-prepared Transparent PMMA-PS/ZnO Polymeric Nanocomposite Films are of great quality and could be used for several important optical applications.

In(2021) Bag, *et al* [52] studied the addition of nanoparticles such as silver nanoparticles (AgNPs) into PS enhances its mechanical properties, gas barrier properties, thermal stability, and so forth. This study reports the development of

PS/Ag nanocomposite using green synthesized Ag NPs and waste thermocol, the green synthesized AgNPs were prepared in different concentrations and embedded accordingly into the PS matrix. The morphology of PS/Ag NCs was studied using Field Emission Transmission Scanning Microscopy (FE-SEM) and Fourier transform infrared spectroscopy (FTIR) was used to evaluate the prepared nanocomposites' surface chemical bonding and surface composition. The thermal property of the nanocomposites was investigated by Thermogravimetric analysis (TGA). The tensile strength of the composites was also estimated. These PS/Ag NCs showed an antibacterial effect against *Escherichia coli*, a disease-causing gram-negative bacterium commonly found in water. Among them, the PS/Ag NCs cup encapsulating 10% AgNPs showed optimum tensile strength and bacteria disinfection property. These nanocomposites have been utilized to prepare cups as a model of water tank for water storage having disinfection properties.

In(2022) Kumar *et al* [53] studied the effect europium-doped barium titanate particles were used as filler material and polystyrene was used as a matrix to fabricate PS/Ba $1-3x/2$ EuxTiO $_3$ /nanocomposites with $x = 0, 0.005, 0.015$ and 0.025 . A solid-state reaction was used to synthesize filler particles and the . The effects of ultrasonic treatment were also studied in the formation of nanocomposite materials. The quantitative and qualitative studies were conducted using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM), and ultraviolet-visible(UV-Vis) characterization techniques. The XRD data and FTIR data confirm the incorporation of filler particles in the polymer matrix. FE-SEM data confirms that the particles are in the nanophase. The optical band gap was directly affected by the filler particles and it started to reduce as concentration started to increase.

1.15 The Aim of Project

1. Preparation of (PS/PMMA/Cobalt Ferrite) nanocomposites
2. Studying the optical properties of (PS/PMMA/Cobalt Ferrite) nanocomposites.

Chapter two

Theoretical Part

2.1 Introduction

This chapter includes a general description of theoretical part of the studies, as well as physical concepts, scientific clarifications, relationships, and rules utilized to understand the findings.

2.2 The Optical Properties

Optical properties can be defined as the interaction between electromagnetic radiation or light with matter that includes absorption, reflection in addition to polarization, etc.[54]. The study of the optical properties of films is of great importance in finding the optical constants through which it is possible Identifying the value of the optical energy gap, as well as we can know the other constants of absorption and transmittance and their coefficients, as well as the damping coefficient and the real and imaginary dielectric coefficients[55].

2.2.1 Absorbance (A) and Transmittance (T)

a. Absorbance(A): the absorbance defines as the ratio between the intensity of the absorbed radiation by the membrane (I_A) to the original intensity of the radiation incident on it (I_o) and the absorbance is a unit-free quantity. It is given by the following relationship[56]:

$$A = I_A / I_o \quad (2.1)$$

b. Transmittance(T): it is defined as the ratio between the intensity of the radiation passing through the membrane (I_T) and the original intensity of the radiation incident on it (I_o) , which is also a quantity devoid of units, and is given by the following relationship[57]:

$$T = I_T / I_o \quad (2.2)$$

The value of the reflectivity can be found from the knowledge of the spectral absorption and permeability by adopting the law of energy conservation, In the following relationship[58]:

$$A+ R+T=1 \quad (2.3)$$

2.2.2 The electronic transitions

Electronic transmission are divided into two types[54,59]:

1. Direct Transition

This transition occurs in semiconductors when the bottom of the conduction band (C.B.) is exactly over the top of the valence band (V.B.), that meaning they have the same wave vector value ($\Delta\mathbf{k}=\mathbf{0}$). The conservation of energy and momentum was needed for this transition form. There are two types forms of direct transitions[54]:

a. Direct Allowed Transition

As shown in Figure (2.1,a), this transition occurs between the top points in the (V.B.) and the bottom points in the (C.B.).

b. Direct Forbidden Transition

This transition happens between near top points of (V.B.) and near points in the bottom of (C.B.), as shown in Figure (2.1, b).

2. Indirect Transition

In these transition types the bottom of conduction band is not over the top of valence band. The electron transits from (V.B.) to (C.B.) not perpendicularly, they in different regions of (\mathbf{K}) space ($\Delta\mathbf{K} \neq \mathbf{0}$). This type of transition occurs with the

help of a particle known as a "Phonon". there are two types of indirect transitions [54,55]:

a. Allowed Indirect Transition

As shown from figure (2.1) these transitions happen between the top of (V.B.) and the bottom of (C.B.) in a different region of (**K-space**).

b. Forbidden Indirect Transition

As shown from figure (2.1) in (d), these transitions occurred between near points in the top of (V.B.) and near points in the bottom of (C.B.). The (Taos's equation) is used to calculate the optical energy gap value of the allowed and forbidden indirect transition [54,55].

$$\alpha h\nu = B_0 (h\nu - E_g \pm E_{\text{Phonon}})^r \quad (2.4)$$

Where E_{Phonon} means the energy of phonon, (-) when phonon absorption and (+) means when phonon emission, E_g means energy gap, h means blank constant, r means the exponential constant; its value depends on the type of transition, $r=2$ for the allowed indirect transition, meanwhile $r=3$ for the forbidden indirect transition.

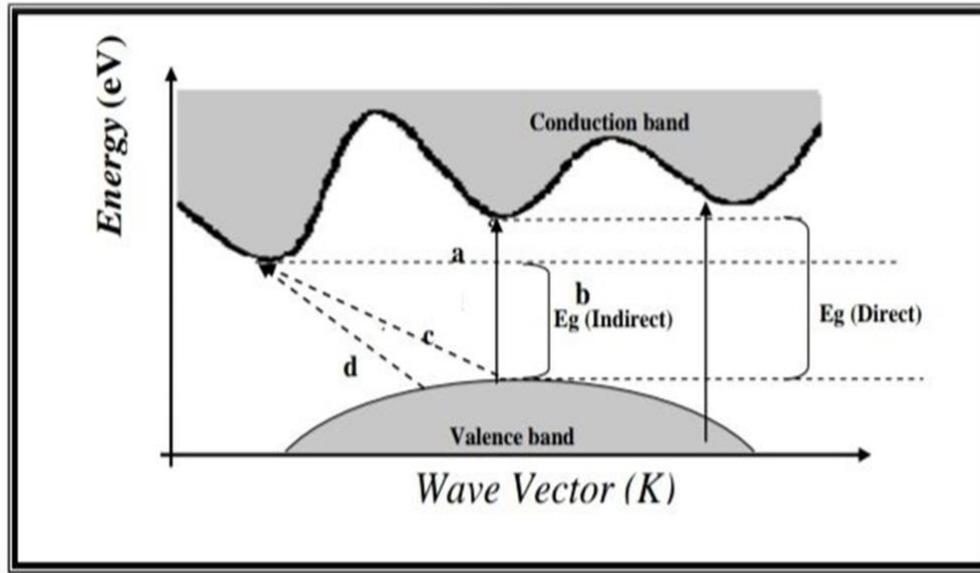


Figure (2.1): Types of electronic transfers [54,55]

- | | |
|---------------------------------|----------------------------------|
| (a) Allowed direct transition | (b) Forbidden direct transfers |
| (c) Allowed indirect transition | (d) Forbidden indirect transfers |

2.2.3 Optical Constants

1. Optical absorption coefficient (α)

It is the decrease in the radiation energy incident on the material and it depends on the energy of the incident rays and the nature of material that falls on it; and it is measured in cm^{-1} unit. If the energy of the photons ($h\nu$) is equal to the energy gap (E_g), then the photons are absorbed to generate a pair (electron-gap) as shown in (a) from Figure (2.2). But if the energy of the photons ($h\nu$) is greater than the energy gap (E_g), then it can be a transition process occurs in the semiconductor and produces an excitation of the electron from the valence band to the conduction band [56]. While the extra energy is dissipated to be in the form of heat, as shown in (b) from Figure (2.2). Both (a) and (b) are referred to as self-transition, or packet to packet transition, But if the energy of the photons ($h\nu$) is less than the energy gap

(E_g), the absorption will only take place in the presence of localized energy levels in the blocked gap that are caused by chemical impurities and physical defects, as shown in (c) from figure (2.2). This process is called non-self-transfer [60,61].

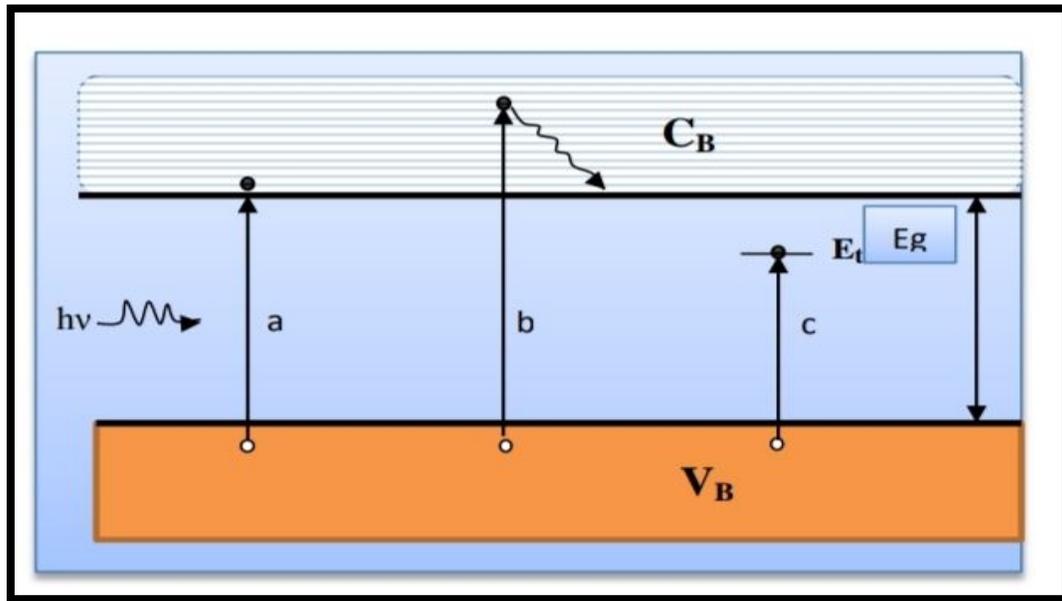


Figure (2.2): Self and non-self-transitions of semiconductors [60,61]

The absorption coefficient can calculate of the relationship called (Per-Lamberts relationship)[62]:

$$I = I_0 e^{-\alpha t} \quad (2.5)$$

Where (I_0) and (I) are the intensity incident ray before and after it passes through the material respectively, (α) is the absorption coefficient, and (t) thickness of film. After reworking the equation (2.6) above we get[63]:

$$\alpha = 2.303 A/t \quad (2.6)$$

where A: absorbance and t : thickness

2. Extinction coefficient (k)

It is defined as the amount of attenuation in the intensity of electromagnetic radiation as a result of the interaction of electromagnetic rays and particles of the thin film material, the damping coefficient can be calculated through the following equation, which is related with the absorption coefficient[64]:

$$k = \alpha\lambda / 4\pi \quad (2.7)$$

Where λ (cm) is the wavelength of the incident radiation and α (cm^{-1}) absorption coefficient.

3. Refractive index (n)

The index of refraction of a material is the ratio of the velocity of the light in vacuum to that of the specimen [65]:

$$n = c / v \quad (2.8)$$

where (n) refractive index, (c) the velocity of light in a vacuum, and (v) the velocity of light in any material medium. Refractive index can be expressed by the following equation [66]:

$$n = (1 + R^{\frac{1}{2}})/(1 - R^{\frac{1}{2}}) \quad (2.9)$$

Where (n) the refractive index, (R) the reflection, and (k) extinction coefficient.

4. Dielectric constant (\mathcal{E})

Represents the ability of a substance to be polarized, when the interaction between light and the charges of the medium occurs the resulting polarization of the charges of this medium is described by the nodal dielectric constant (ϵ) that defined by the following equation[66]:

$$\mathcal{E} = \mathcal{E}_1 - i\mathcal{E}_2 \quad (2.10)$$

Where \mathcal{E} : complex dielectric constant, \mathcal{E}_1 :the real part of the dielectric constant, and \mathcal{E}_2 : the imaginary part of the dielectric determined constant. The real and imaginary part of dielectric constant can be by using equations[66]:

$$\mathcal{E}_1 = n^2 - k^2 \quad (2.11)$$

$$\mathcal{E}_2 = 2nk \quad (2.12)$$

2.2.4 Optical conductivity

Is the phenomenon of an increase in the number of charge carriers (electrons or holes) as a result of a light beam incident on a semiconductor. The optical conductivity can be calculated from the equation[66]:

$$\sigma_{op} = \alpha \frac{nc}{4\pi} \quad (2.13)$$

Where (σ_{op}) the optical conductivity, (α) is the absorption coefficient, (n) the refractive index, (c) the speed of light.

Chapter Three

Experimental Part

3.1 Introduction

In any experimental work, there are a specific mechanism for manner of working, devices to examine the samples and an exact theorem to explain the results. In this chapter we will illustrate in details the materials used and the preparation process with devices that used in this work to find out the optical properties.

3.2 Materials

The used materials in this study are:

3.2.1 Matrix Material

1. Polystyrene (PS):

The polymer is used as granular form and could be obtained from local markets, white colors and high purity (99.99%). Polystyrene (PS) is a polymer characterized by its amorphous structure and the presence of numerous side groups. At ambient temperatures, the substance in question exhibits properties of hardness rigidity and transparency.

2. Poly (methyl methacrylate) PMMA

Poly (methyl methacrylate), also known as acrylic, is a transparent thermoplastic. It has a melting point of about (140) C° and a density (1.2) g/cm³.

3.2.3 Additive Nanomaterial

1. (Cobalt Ferrite): It was obtained as powder from (Nano shell USA) company with grain size (20nm) and high purity (99.9%).

3.3 The Preparation of (PS/PMMA/Cobalt Ferrite) Nanocomposites

Polystyrene (PS)/ Poly (methyl methacrylate) PMMA doped with Cobalt Ferrite nanoparticle has been prepared by casting method. The pure polymer blend film was prepared by dissolving of 0.5 gm in chloroform (50 ml) and the solution was thoroughly mixed with a magnetic stirrer and then added 0.5 gm from PMMA with continuous magnetic stirrer until the solvent is homogenous. The fabricated of nanocomposite by adding of the Cobalt Ferrite NPs to solution PS/PMMA with content 2.1, 4.2 and 6.3 wt. % are shown in table (3-1) and then casting on glass betri dish. Finally, the samples are ready for the study the optical properties.

Table (3-1): Weight percentages for nanocomposites (PS/PMMA/Cobalt Ferrite)

PS wt. %	PMMA wt. %	Cobalt Ferrite wt. %
0.5	0.5	0
0.489	0.489	2.1
0.479	0.479	4.2
0.468	0.468	6.3

3.4 Optical Properties Measurements

At the University of Babylon, Department of Physics, College of Education for Pure Sciences, the absorption spectrum of (PS/PMMA/Cobalt Ferrite) Nano composites films were measured with a double beam spectrophotometer (Shimadzu model UV-1800 Ao (JAPAN) in the wavelength range (190-1100) nm. As shown in figure (3.1). It found at room temperature; the absorption spectrum was recorded. The optical constants, absorption coefficient, extinction coefficient, refractive index, and energy gaps are all examples of parameters were calculated using a computer program.



Figure (3.1): Image of UV spectrophotometer (photometer).

Chapter Four

Results and Discussion

4.1 Introduction

This chapter included the results and its discussion of the optical measurements for (PS/PMMA/Cobalt Ferrite) nanocomposites.

4.2 Optical Properties

The main purpose of studying the optical properties of the (PS/PMMA/Cobalt Ferrite) nanocomposites is to identify the effect of adding (Cobalt Ferrite) nanoparticles on the optical properties of (PS/PMMA) films. The research covers the recording of the spectrum of absorbance for the (PS/PMMA/Cobalt Ferrite) films at room temperature and calculating the absorption coefficient, extinction coefficient, and other optical constants, as well as identifying the types of electronic transitions and calculating energy gaps.

4.2.1 The Absorbance

Figure (4.1) demonstrates the influence of Cobalt Ferrite NPs on the absorbance of a PS/PMMA film throughout a wavelength range of 280-880 nm. Since free electrons absorb incident light, the absorbance of PS/PMMA/Cobalt Ferrite nanocomposite rises as the Cobalt Ferrite ratio rises. Also, it notes that the absorbance has higher value at UV regions which attributed to the to the increased charge carriers and the occurrence of some bonds breaking. This result is agreed with researchers [67].

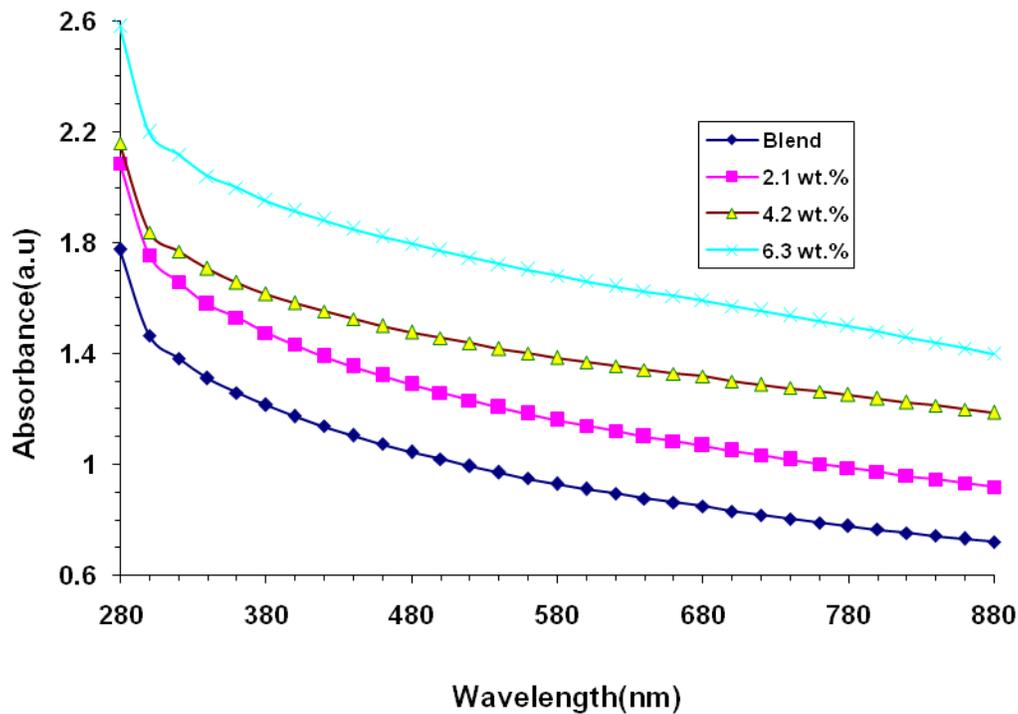


Figure (4.1): Absorbance of the PS/PMMA/Cobalt Ferrite nanocomposites with wavelength.

4.2.2 The Transmittance

Figure (4.2) illustrates the optical transmittance of PS/PMMA/Cobalt Ferrite nanocomposites versus wavelength. From this figure, it can be obtained that the transmittance decreased with increasing concentration of Cobalt Ferrite NPs, which attributed to an increase in absorbance. This result is agreed with researchers [67].

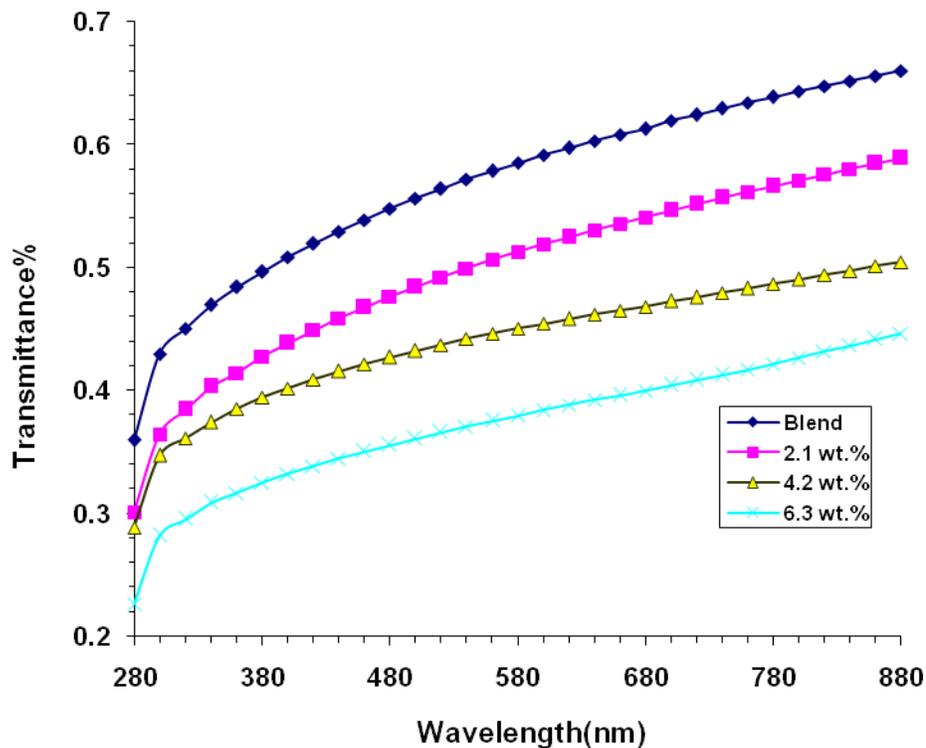


Figure (4.2): Optical transmittance of PS/PMMA/Cobalt Ferrite nanocomposites.

4.2.3 The absorption coefficient

The absorption coefficient was calculated from equation (2.6). Figure (4.3) displays the absorption coefficient of the (PS/PMMA/Cobalt Ferrite) nanocomposites with the photon energy. The absorption coefficient might help you figure out what kind of electron transition you're dealing with. It is assumed that direct electron transitions occur when the material's absorption coefficient is large 10^4 cm^{-1} . When the absorption coefficient is low 10^4 cm^{-1} , an indirect transition of electrons is assumed. The values of the absorption coefficient of (PS/PMMA/Cobalt Ferrite) nanocomposite is less than 10^4 cm^{-1} and the transition of electron is indirect. From these figures, the absorption coefficient of nanocomposites rises with the rises of the content of Cobalt Ferrite NPs, this is due to the rise of various charge carriers

and therefore rising the absorption and absorption coefficient for (PS/PMMA/Cobalt Ferrite) nanocomposites. This result agrees with [68].

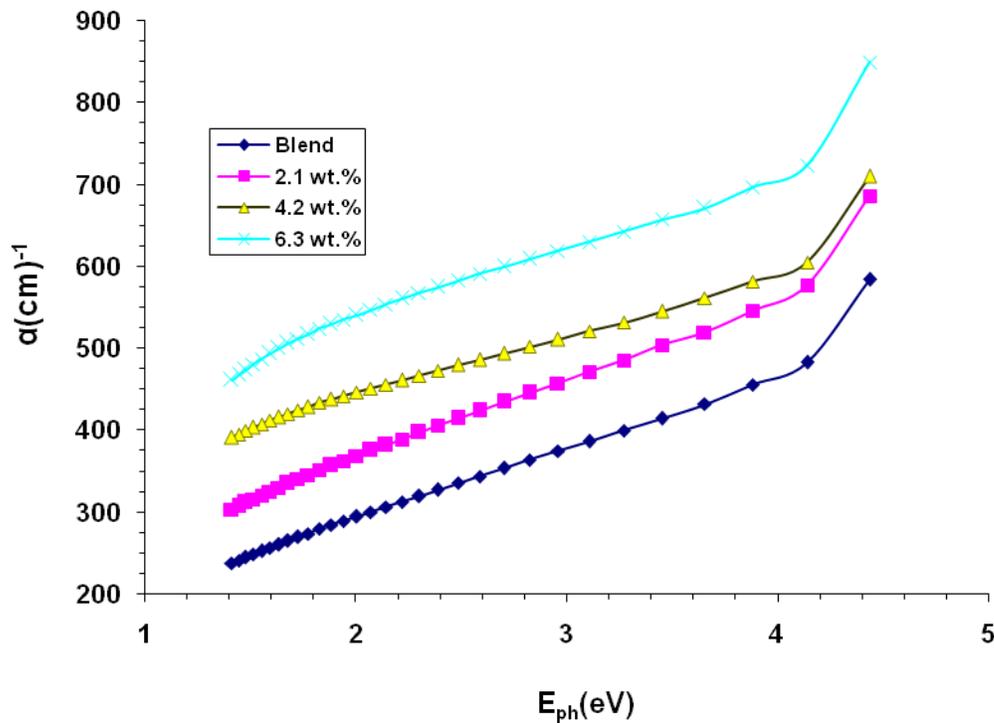


Figure (4.3): The variation absorption coefficient of (PS/PMMA/Cobalt Ferrite) nanocomposite with the photon energies.

4.2.4 The indirect energy gap

The gap of energy was calculated from relation (2-4). The energy gap for allowed and forbidden indirect transitions of PS/PMMA/Cobalt Ferrite nanocomposites are explained in figures (4.4) and (4.5) may find the energy gap for the indirect transition by plotting the data or tang cut from the top of the curve to the (x axis) at (hv). From these figures, the energy gap is decreased with the increasing concentration of the PS/PMMA/Cobalt Ferrite NPs. This action is due to the formation of levels in the energy gap and therefore, these local levels decrease the energy gap with the increase of the PS/PMMA/Cobalt Ferrite nanocomposite. Table (4-1) obtained the values of allowed and forbidden energy gap. This result agrees with researchers [67,69].

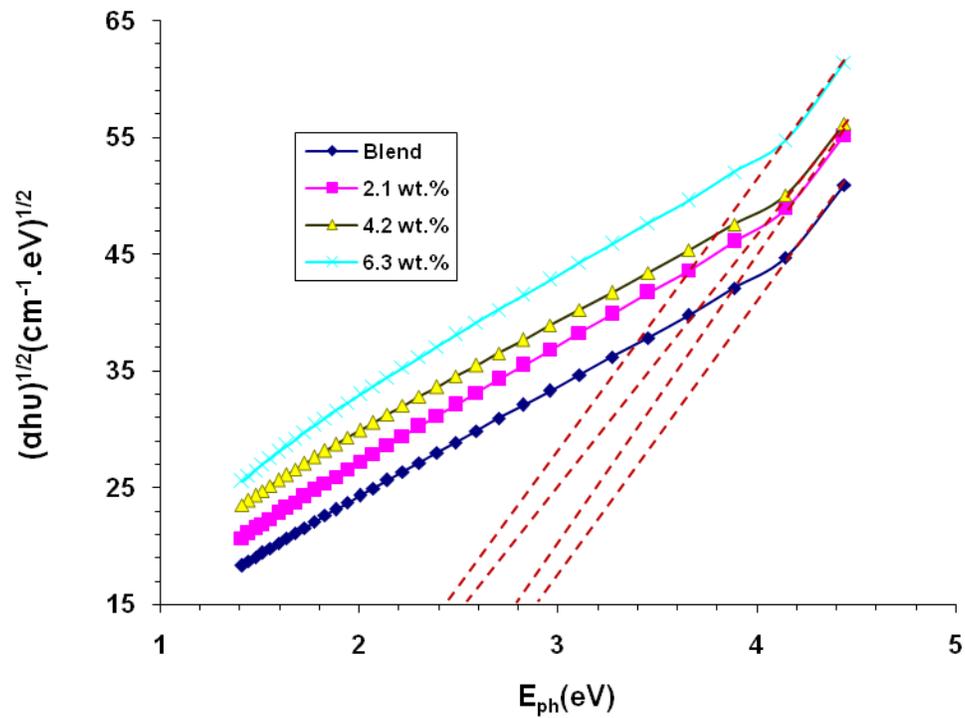


Figure (4.4): The E_g for the allowed indirect transition $(\alpha h\nu)^{1/2} (\text{cm}^{-1}.\text{eV})^{1/2}$ of (PS/PMMA/Cobalt Ferrite) nanocomposite.

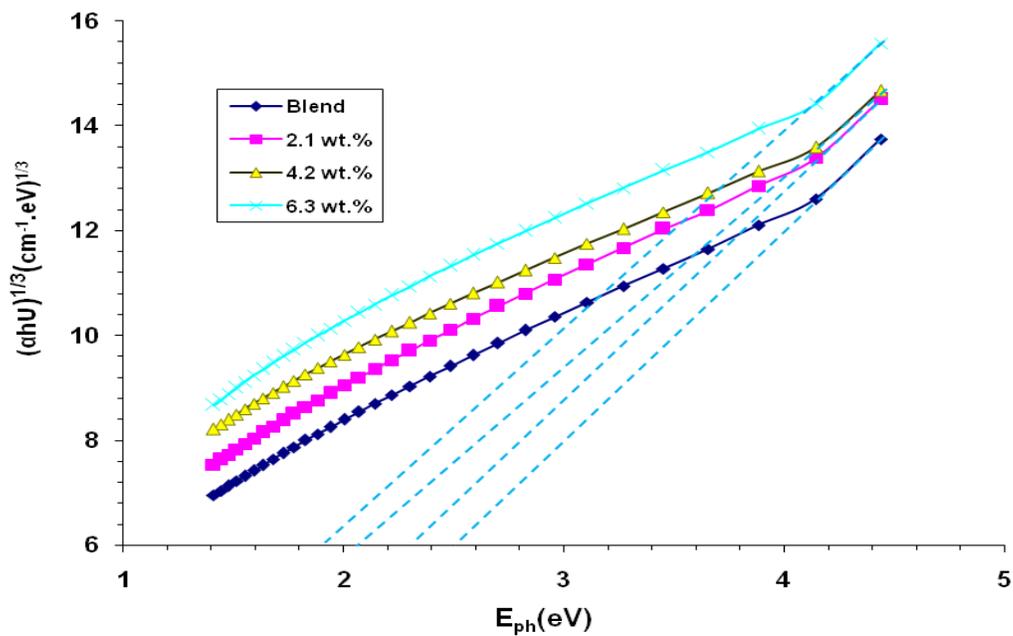


Figure (4.5): The E_g for the forbidden indirect transition $(\alpha h\nu)^{1/3} (\text{cm}^{-1}.\text{eV})^{1/3}$ of (PS/PMMA/Cobalt Ferrite) nanocomposite.

Table (4-1) The values of energy gap of (PS/PMMA/Cobalt Ferrite) nanocomposites

Cobalt Ferrite NPs wt% content	Allowed of indirect energy gap (eV)	Forbidden of indirect energy gap (eV)
0	2.9	2.57
2.1	2.8	2.27
4.2	2.57	2.1
6.3	2.41	1.9

4.2.5 The Extinction coefficient

The extinction coefficient (K) was calculated (2-7). Figure (4.6) displays the extinction coefficient for (PS/PMMA/Cobalt Ferrite) nanocomposites with wavelength. It is important to note that the extinction coefficient increased when Cobalt Ferrite NPs concentration increased. This explanation relates to the increased absorption coefficient with increasing Cobalt Ferrite NPs. The results agreed with [70]

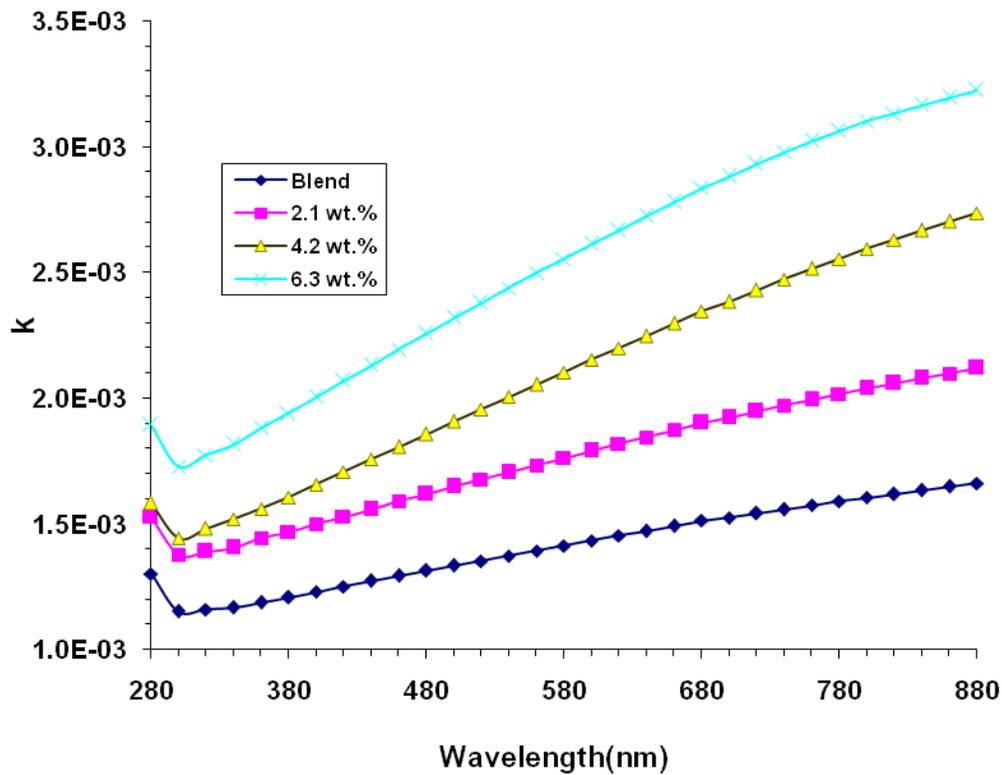


Figure (4.6). Extinction coefficient for (PS/PMMA/Cobalt Ferrite) nanocomposites.

4.2.6 The refractive index (n)

The refractive index (n) of (PS/PMMA/Cobalt Ferrite) nanocomposites was calculated from the equation (2-9). The refractive index of (PS/PMMA/Cobalt Ferrite) nanocomposites with wavelength as shown in figure (4.7). From these figure, the refractive index inclines to increase as the increasing concentration of Cobalt Ferrite NPs. The cause for this is that as the rise of Cobalt Ferrite content, the density of the nanocomposites rises as well. This result are agree with researchers [71].

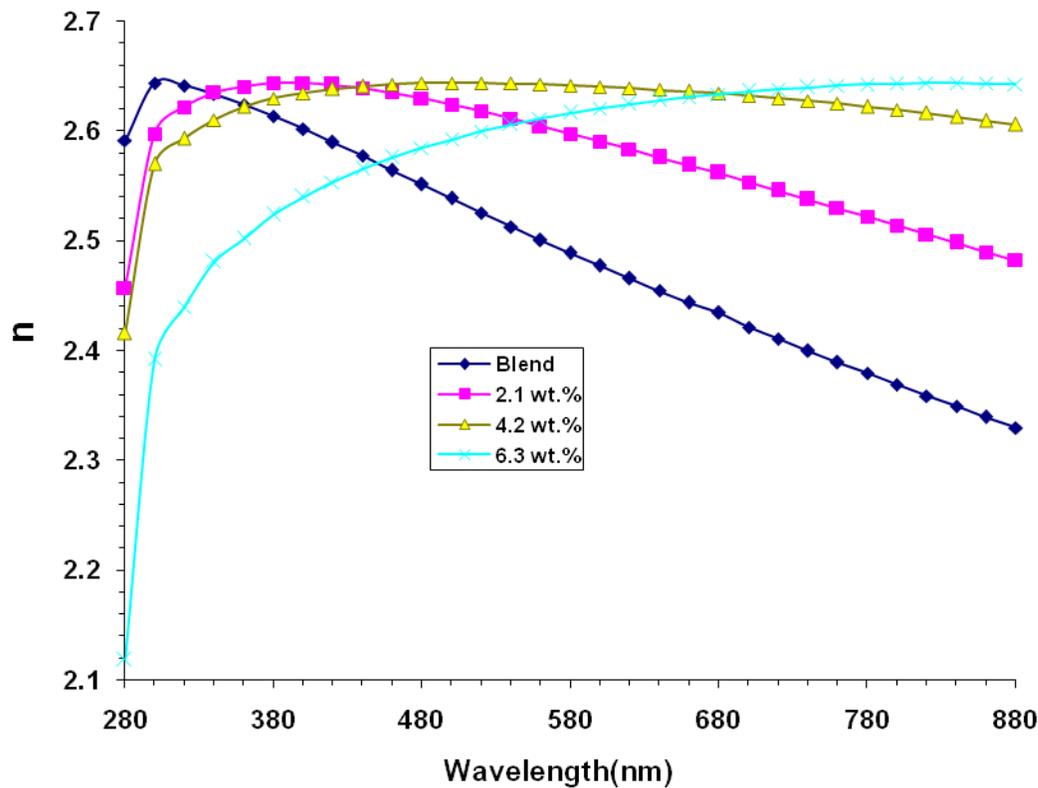


Figure (4.7) Refraction index of (PS/PMMA/Cobalt Ferrite) nanocomposites versus wavelength.

4.2.7 The real and imaginary dielectric constant (ϵ_1 and ϵ_2)

The real and imaginary (ϵ_1 and ϵ_2) components of the dielectric constant were calculated from the equations (2-11) (2-12). The variation of ϵ_1 and ϵ_2 of (PS/PMMA/Cobalt Ferrite) nanocomposites with wavelength are explained in figures (4.8) and (4.9). From these figures, the real and imaginary of the dielectric constant of the (PS/PMMA/Cobalt Ferrite) nanocomposite are increased with the increasing of Cobalt Ferrite NPs content. The increase in electrical polarization related to the influence of nanoparticles content in the sample caused this finding [72]. The real and imaginary of the dielectric constant of nanocomposite change with wavelength. This is due to the ϵ_1 depending on refractive index since the outcome of

extinction coefficient is minor, whereas the ϵ_2 depends on the extinction coefficient. This result agrees with researchers [73].

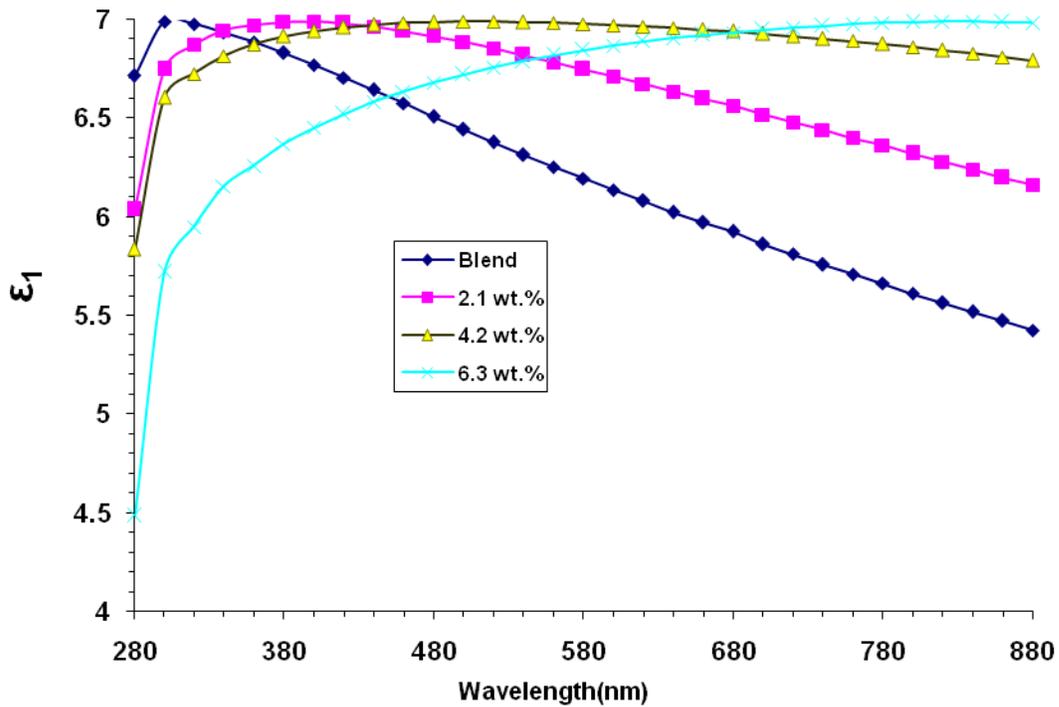


Figure (4.8) Variation of (ϵ_1) for PS/PMMA/Cobalt Ferrite nanocomposite versus wavelength.

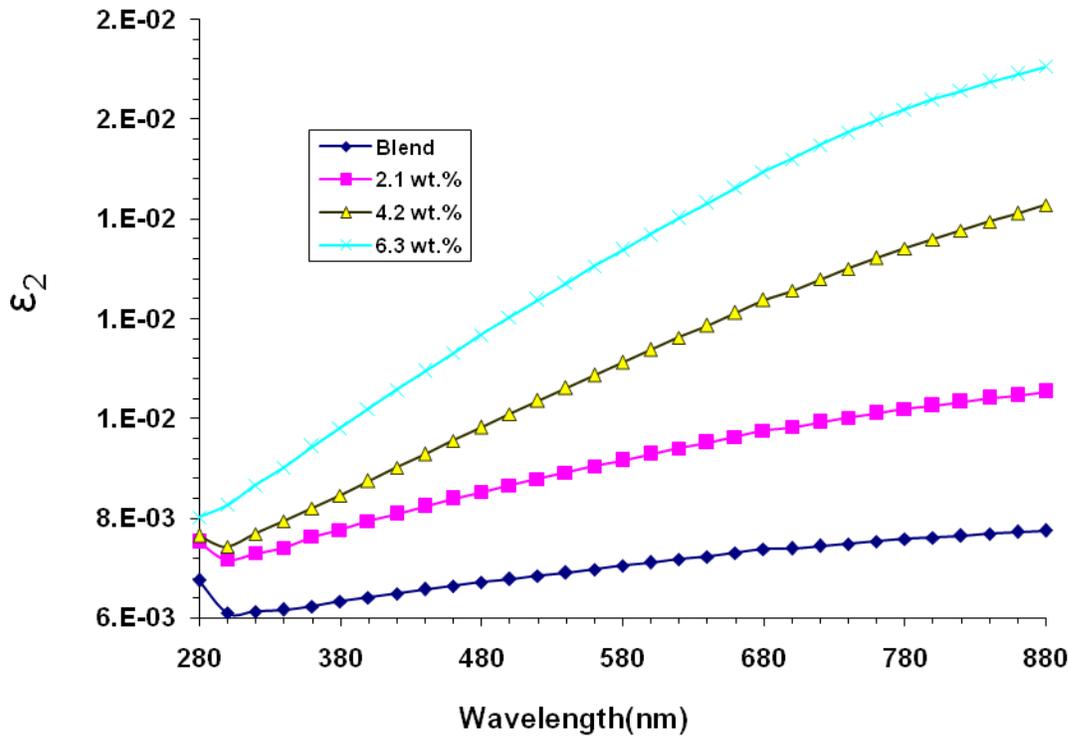


Figure (4.9) Variation of (ϵ_2) for PS/PMMA/Cobalt Ferrite nanocomposite versus wavelength.

4.2.8 The optical conductivity ($\sigma_{op.}$)

The optical conductivity ($\sigma_{op.}$) was determined by the relation (2-13). Figure (4.10) shows the optical conductivity of PS/PMMA/Cobalt Ferrite nanocomposites with wavelength. The optical conductivity of the PS/PMMA/Cobalt Ferrite nanocomposite increases as the Cobalt Ferrite content increases, which is related to the formation of local states in the energy gap, rising nanoparticle content induced a rise in the density of local phases in the band structure therefore, a rise in the absorption coefficient suggests an increase in σ_{op} of the nanocomposites. The results are agreed with [74].

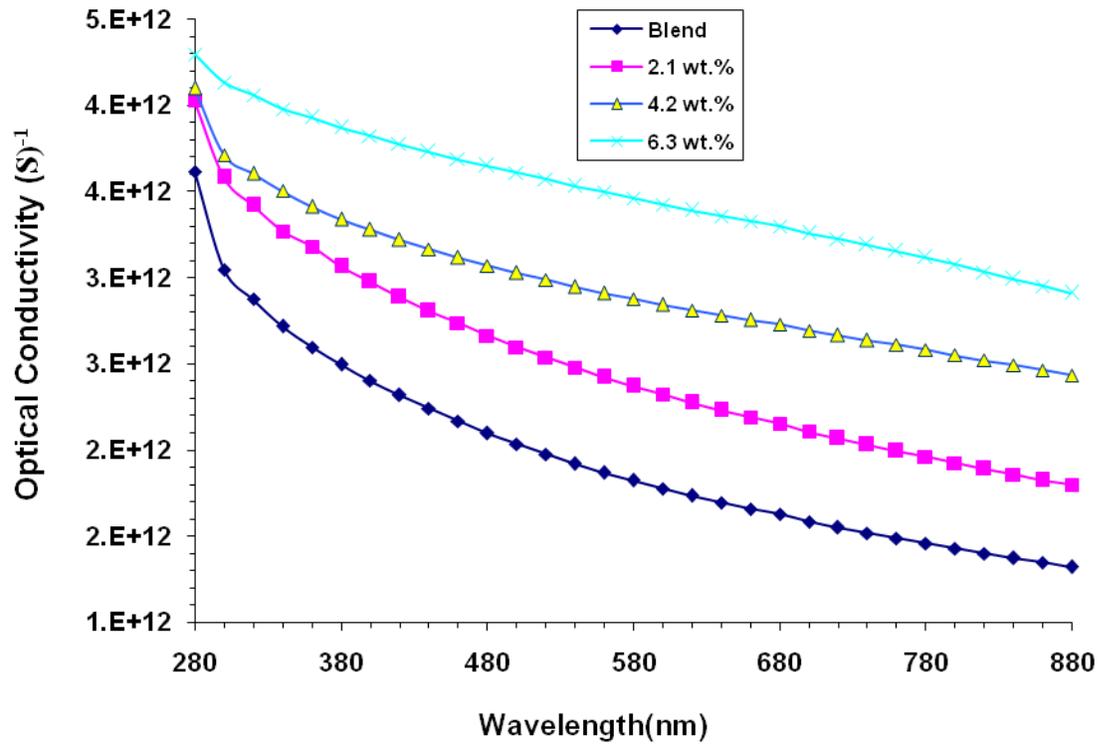


Figure (4.10) Variation of optical conductivity of PS/PMMA/Cobalt Ferrite nanocomposite versus wavelength.

4.3 Conclusions

From the obtained optical results and discussions can be concluded:

The absorbance, absorption coefficient, refractive index, extinction coefficient, dielectric constant (real, imaginary) and optical conductivity of (PS/PMMA/Cobalt Ferrite) nanocomposites increased with the increasing of the concentrations of Cobalt Ferrite nanoparticles while the transmittance and the energy gap for indirect transition (allowed, forbidden) decreased with the increasing of the concentrations of Cobalt Ferrite nanoparticles. This result can be used for optoelectronic device.

4.4 Future Work

- 1- Studying the structural and electrical properties of (PS/PMMA/Cobalt Ferrite) nanocomposites.
- 2- Apply of (PS/PMMA/Cobalt Ferrite) nanocomposites as photodetector and gas sensor.

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الخلاصة

في هذه الدراسة، تم تحضير المتراكب النانوي (PS/PMMA/Cobalt Ferrite) باستخدام طريقة الصب مع نسب وزنية مختلفة من جسيمات النانوية Cobalt Ferrite (2.1, 4.2, و 6.3 wt%). تم تشخيص الخصائص البصرية للمتراكب النانوي (PS/PMMA/Cobalt Ferrite). الامتصاصية، معامل الامتصاص، معامل الانكسار، معامل الخمود، ثابت العزل الحقيقي والخيالي، التوصيلية البصرية تزداد مع زيادة تركيز جسيمات النانوية Cobalt Ferrite بينما النفاذية وفجوة الطاقة للانتقال غير مباشر المسموح والممنوع تقل مع زيادة تركيز جسيمات النانوية Cobalt Ferrite. هذه نتائج يمكن استخدامها كتطبيق في الاجهزة البصرية الالكترونية.



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قسم الفيزياء

تأثير جسيمات فرايت نانوية على الخصائص البصرية لخليط بوليمري.

بحث مقدم

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

من قبل الطالب

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