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University of Babylon, College of Education
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# Optical Properties of Polymers Blend (PMMA – PS) with Copper Nanowires

## A research

Submitted to the council of College of Education for Pure Science, Babylon University as Partial Fulfillment of the Requirement of the Degree Higher Diploma Education / Physics of Materials and Applications

## By

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**2021 A.D.** **1442 A.H**

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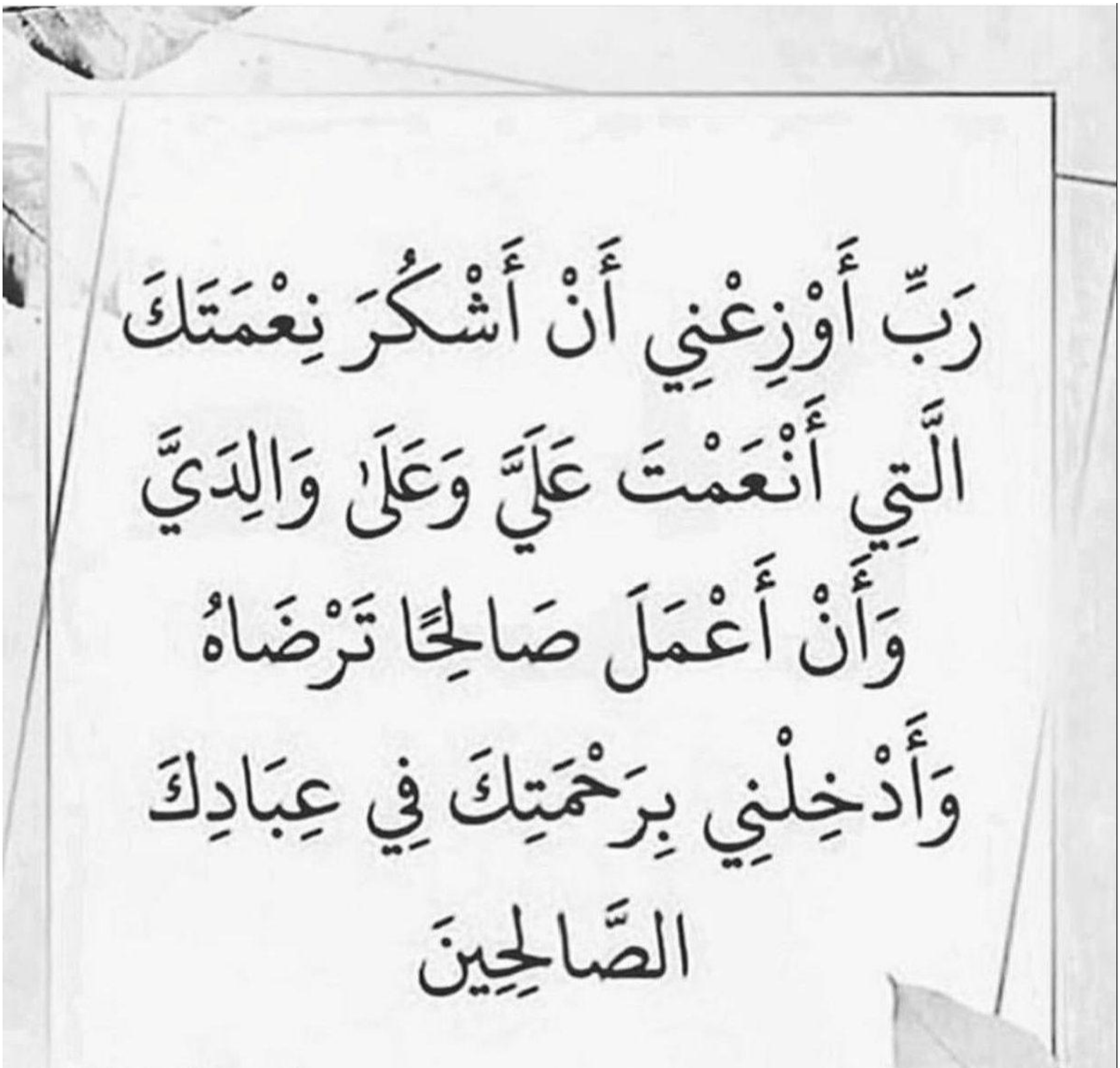
# بِسْمِ اللَّـهِ الرَّحْمَـٰنِ الرَّحِيمِ




**صَدَقَ اللهُ العَلِيُّ العَظِيم**

# Dedication

**I dedicate this humble work**

» To my father and mother who gave me care and politeness...

» To my brothers and sisters who gave me strength and patience...

» To my wife and children (Ali & Fatima) who have given me love and mercy...

» To the soul of my grandfather and grandmother, may God have mercy on them

» To my friends who gave me encouragement and advice

» To my teachers who gave me respect and appreciation

To everyone who made every effort to help me, even with advice, and strive to educate me, even with a letter in my academic life

**Researcher**

Ameer

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**First:** Praise be to God for inspiring us with knowledge, and blessings and peace be upon the Prophet Muhammad and his family.

I would also like to express my deep appreciation and sincere thanks to my esteemed supervisor, **Prof. Dr. Bahaa H. Rabie**, for his support, guidance and encouragement throughout the duration of the project. I also extend my sincere thanks to the Dean of the College of Education for Pure Sciences, and the Physics Department staff for their generous assistance in using the department's laboratories.

**Finally,** I thank my colleagues for their assistance and cooperation throughout the preparation of this letter.

**Researcher**

Ameer

# Abstract

In this research, the effect of adding different concentrations of copper nanowires **Cu NW** on the optical properties of the polymer mixture **PMMA − PS** was studied. The **Cu NW** were added with different weight ratios [(**0**, **0.19**, **0.39** & **0.59**) **wt**%] to the polymer mixture **PMMA − PS**.

By casting method before and after addition, the films of the nanocomposite were prepared. The optical absorption was recorded in the wavelength range (**200 − 1100 nm**).

The optical constants, absorption coefficient, extinction coefficient and the allowed and forbidden indirect energy gap for electronic transitions were determined. In addition, the real and imaginary dielectric constant were determined.

Through practical measurements of the optical properties of the as−prepared nanocomposite samples, it was observed that the **energy gap and transmittance** **decrease** by increasing the addition of the weight ratios of **Cu NW**. Whereas each of **absorption, absorption coefficient, extinction coefficient, refractive index and real and imaginary parts of the dielectric constant** **increases** with increasing concentrations of copper nanowires.

# Contents

# List of Symbols

| Symbol | Physical Meanings | Unites |
|---|---|---|
| $\Delta G_{mix}$ | Change in Free Energy | $(\mathbf{J})$ |
| $\Delta H_{mix}$ | Change in Enthalpy | $(\mathbf{J})$ |
| $\Delta S_{mix}$ | Change in Entropy | $(\mathbf{J \cdot K^{-1}})$ |
| $T$ | Absolute Temperature | $(\mathbf{K})$ |
| $A$ | Absorbance | (%) |
| $I_A$ | The intensity of radiation absorbed | $(\mathbf{eV/m^2.s})$ |
| $I_\circ$ | Original Intensity of Light | (Lumen) |
| $I_T$ | The intensity of radiation transmitted from the membrane | $(\mathbf{eV/m^2.s})$ |
| $R$ | The Reflectance | (%) |
| $I_R$ | The intensity of the radiation reflected from the membrane | $(\mathbf{eV/m^2.s})$ |
| $t$ | Thickness of thin | $(\mathbf{Cm})$ |
| $\alpha$ | Absorption Coefficient | $(\mathbf{nm^{-1}})$ |
| $B$ | Constant depends on the nature of the substance | … |
| $h$ | Planck's Constant | $(\mathbf{J.s})$ |
| $E_g^{opt}$ | Energy Band Gap | (eV) |
| $n$ | Real of Refractive Index | … |
| $c$ | Speed of Light in a Vacuum | $(\frac{\mathbf{m}}{\mathbf{s}})$ |
| $v$ | Speed of Light in the Sample | $(\frac{\mathbf{m}}{\mathbf{s}})$ |
| $k$ | Extinction Index | $(\mathbf{m^2/mol})$ |
| $n^*$ | Complex Refractive Index | … |

| | | |
|---|---|---|
| $i$ | Imaginary Number | … |
| $\lambda$ | Wave Length | (Nm) |
| $\pi$ | Fixed Ratio | … |
| $\sigma_{opt}$ | Optical Conductivity | $(\mathbf{s^{-1}})$ |
| $\varepsilon$ | Dielectric Constant | … |
| $\varepsilon_1$ | The real part of the dielectric constant | … |
| $\varepsilon_2$ | The imaginary part of the dielectric constant | … |

## List of Abbreviations

| **Abbreviations** | **Physical Meanings** |
|---|---|
| *PMMA* | Polymethylmethacrylate |
| *PS* | Polystyrene |
| *Cu NW* | Copper Nanowires |
| *UV* | Ultra Violet |
| $T_g$ | Glass Transition Temperature |
| *AC* | Alternating Current |
| *DC* | Continuous Current |
| *V.B* | Valence Band |
| *C.B* | Conduction Band |
| *PMNC* | Polymer Matrix nanocomposites |
| *MMNC* | Metal Matrix nanocomposites |
| *CMNC* | Ceramic Matrix nanocomposites |

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# CHAPTER ONE

# INTRODUCTION AND LITERATURE REVIEW

## 1.1 Introduction

The characteristic properties of metal nanoparticles and nanocomposites have been the subject of study for a long time because of their unique optical [1], thermal, mechanical, electronic and electrical properties [2]. It is used in many applications such as solar cells, optical sensors, & etc [3]. as well as optical properties [4]. noble metal nanoparticles stimulate great interest for implementation in photonics [5]. If the properties of polymer can also be tuned in correct direction with enhanced optical properties of metals, these materials could be best candidates for space application. The size dependent structural, optical, thermal and electronic properties can be tailored to be suitable for device applications by varying the particle size. Small changes of the configuration of the composite concerning the metal fraction as well as the size and shape of the nanoparticles can lead to dramatic changes in the electrical and optical properties. In the last few decades, the study of optical properties of nanocomposites has been stimulated by promising applications. The Significant changes in thermal [6]. Functions, and superior mechanical performance (e.g. stiffness and tensile strength) compared with any other known form of the material. These outstanding properties make the polymer nanofibers to be optimal candidates for many important applications. A number of processing techniques such as drawing template synthesis phase separation self-assembly electrospinning etc. have been used to prepare polymer nanofibers in recent years[7]. Can be observed in properties of such materials even for very small fraction of the nanoparticles. However, of being such nanocomposites may be, the process of blending or dispersing nanoparticles in a polymer matrix has provide to be problematic. Once well dispersed in a matrix, the intrinsic properties of a nanostructured material are determined by its size, shape, composition, crystallinity and structure[8].

## 1.2 Polymer Structure

It is a compound with a large molecular weight and is often organic. It is formed from small repeating units called monomers by a process called polymerization [9]. Of each molecule the polyethylene structure "**figure (1-1)**" [10]. Contains thousands of atoms covalently linked and attracted to each other by forces depending on the type of polymer, Polymers are composed of large and interlocking molecules among themselves. It is difficult to control and therefore we note Crystal bonding in the polymer in certain and limited places with a decrease in its temperature, and thus the polymer consists of crystalline and non-crystalline regions and the highly crystalline polymer contains approximately (90%) of the crystalline regions, while the rest of the area is completely amorphous [11].

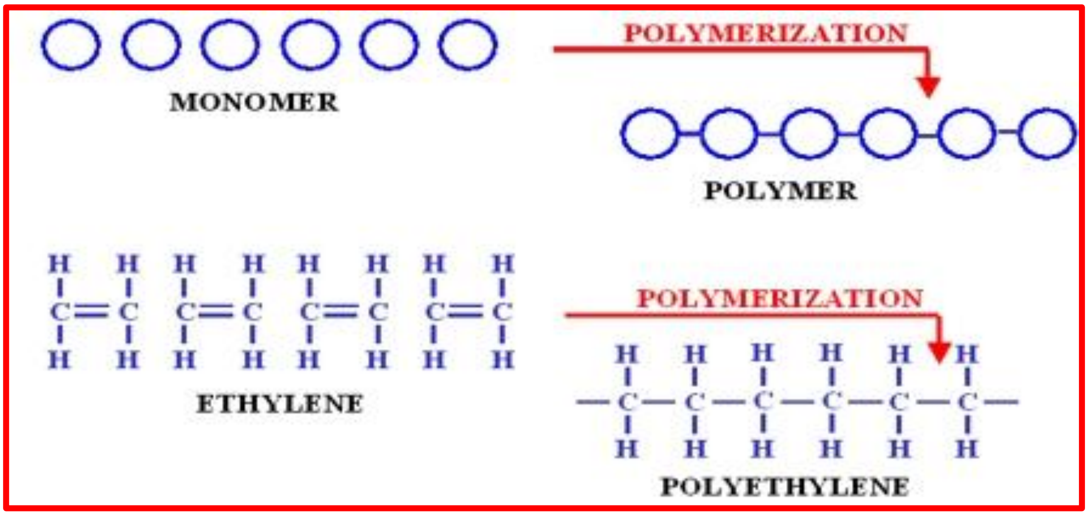



**Figure (1-1): Polyethylene Structure[10]**

## 1.3 Classification of polymers

Polymers can be classified according to several specifications, including:

### 1.3.1 According to its effect on temperature

### 1. thermoplastic polymers

They are polymers that are solid in normal temperatures and when the temperature increases, they soften and increase their flexibility so that they turn into viscous fuses, and the reason for this is the forces of attraction between the molecules of this type and are caused either by the polarity or the weak Van der Waals forces, where when heated, the molecules slide over each other. The other is as in polystyrene, polyethylene, polypropylene and others [12].

### 2. thermoset polymers

This type of polymers does not fuse with heating, but suffers from chemical changes when heated, where the polymeric chains intertwine and become poor conductors of heat and electricity as a result of chemical bonding with strong bonds [13] where an atom or group of atoms covalently participate forming a three-dimensional block, and these polymers include phenol-formaldehyde resins and resin Urea-formaldehyde and others [14], and as shown in **Figure (1-2).**

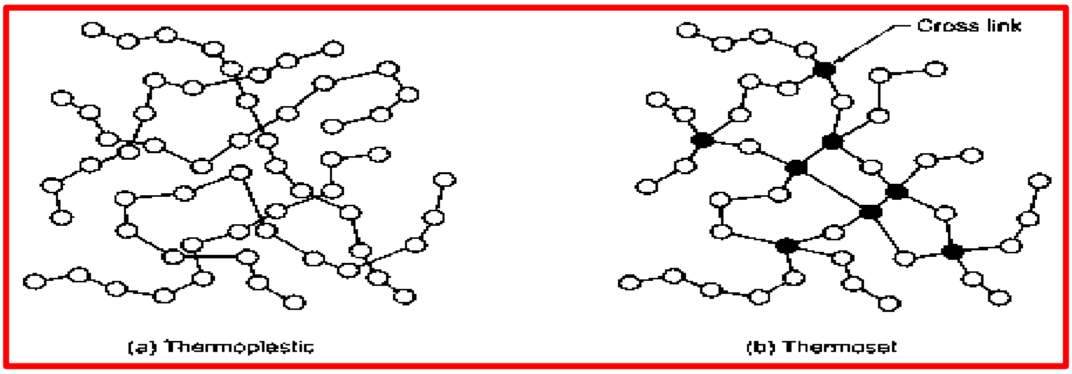



**Figure (1-2): Difference between thermoplastic and thermosetting polymers [15].**

## 1.3.2 Chemical classification of polymers

Polymers can be classified according to the structural synthesis of the chains that make up the polymers into linear polymers and branched polymers in addition to cross-linked polymers, and these types can be represented The three are as shown in the **figure (1-3)**:

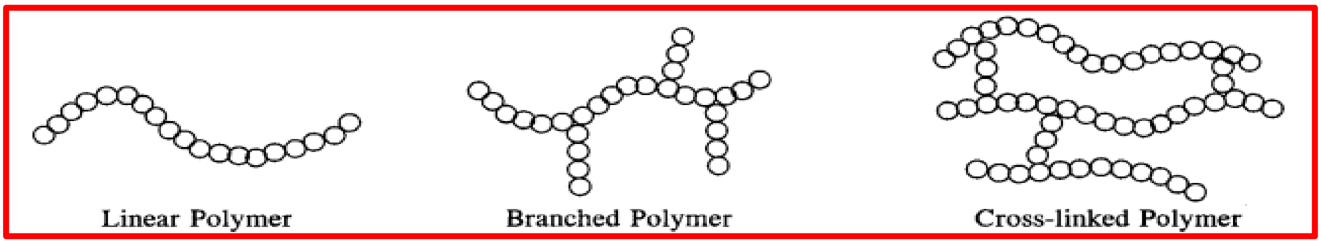



**Figure (1-3): Types of Polymers according to their structre (a) linear (b) branched (c) crosslinked polymers [16]**

## 1. Linear polymers

The basic structural unit of these polymers is represented by one molecule in a specific long chain linked to each other in a linear manner, meaning that it does not contain branches [17], and as in the **figure (1-3).**

## 2. Branched polymers

This type of polymer is characterized by having a long and branched chain, and its branches are characterized as having a peaceful structure, a comb structure or a cruciform structure, and these branches are characterized by having different lengths [18], and as shown in the **figure (1-3).**

## 3. Cross linked polymers

The bonds of this type of polymers are intertwined with each other and in complex manner, where the shape of the polymeric chain is in three dimensions formed by the linking of these chains with each other in multiple locations[19], and as shown in the **figure (1-3).**

## 1.4 The polymers used

Two types of polymers were used, one of them is **polymethylmethacrylate (PMMA)** and the other is **polystyrene (PS)**.

### 1.4.1 Polymethylmethacrylate (PMMA)

**Polymethylmethacrylate (PMMA)** is an inexpensive syntheticthermoplastic polymer that has excellent chemical, physicaland mechanical properties[20]. Like other polymeric materials, Where it is one of the most transparent types of polymers, with hardness, durability and high flexibility, and at the molecular level, it is amorphous due to the presence of rather large side ramifications, as shown in **Figure (1-4)**:

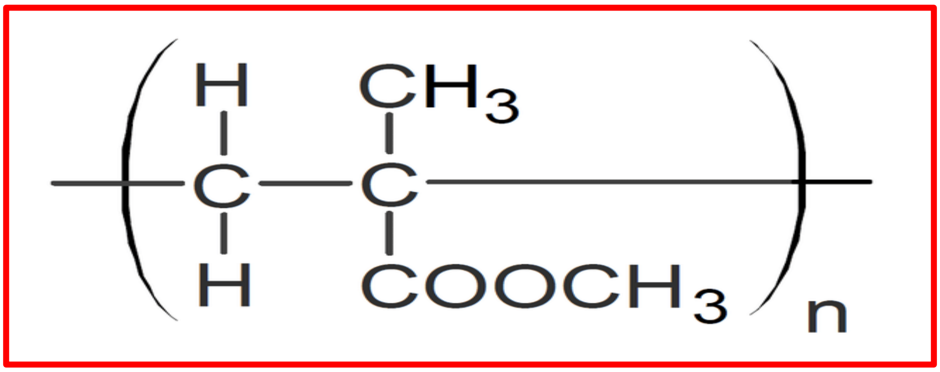



**Figure (1-4): Chemical Structure of Polymethacrylate (PMMA) [21]**

It is characterized by its resistance to acids and diluted alkaline chemicals, but it dissolves in organic solvents such as chlorofoam, benzene and caesarol[22]. As a result of its high transparency and great resistance to atmospheric influences, it is used as an alternative to glass as transparent protective panels as in aircraft, factories, greenhouses and optical equipment such as lenses, prisms and many others[23]. It is also used in the manufacture of geometric shapes, decorations and furniture for its easy formation, light weight and cheap price[24]. Therefore, it is called by several trade names, including toughened glass, Plexiglas, and Lucite glass used for construction purposes, which is known as organic glass[25]. The **table (1-1)** shows some physical properties of polymethacrylate.

**Table (1-1):** The most important physical properties of PolyMethyl Methacrylate (**PMMA**) **[26]**

| Punctuation | Properties | Poly(methyl methacrylate |
|---|---|---|
| 1 | Tensile strength ($Mpa$) | 72.4 |
| 2 | Modulus of elasticity ($Gpa$) | 3 |
| 3 | shock energy (J) | 1.9 |
| 4 | Density ($^{g}/_{cm^3}$) | 1.19 |
| 5 | electrical resistance ($\Omega.cm$) | $10^{16}$ |
| 6 | Dielectric strength ($^{MV}/_{m}$) | 19.7 |
| 7 | Melting point ($^{\circ}C$) | 180 |
| 8 | degree of glass transition ($^{\circ}C$) | 105 |
| 9 | The type of intermolecular force acting between its polymeric chains | Forces of induction and diffusion |
| 10 | molecular Weight of Repeat unit ($g\ mol^{-1}$) | 100.12 |

## 1.4.2 Polystyrene (PS)

**Polystyrene (PS)** plastic is a naturally transparent thermoplastic that is available as both a typical solid plastic as well in the form of a rigid foam material and It has good mechanical and electrical properties[27]. It is characterized by its resistance to acids, bases or alcohol, but it dissolves in aromatic hydrocarbons, benzene and esters[28]. Its can be made from a monomer known as styrene and The **figure (1-5)** shows the structure of polystyrene.

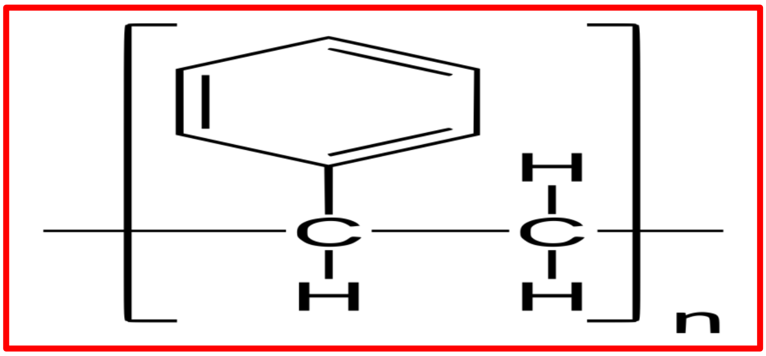



**Figure (1-5): polystyrene structure (PS) [29]**

As a result of its mechanical properties, where it does not expand or contract, and its electrical properties, as it is an electrical insulator, so it is used in the manufacture of panels, rulers and electrical connection cables[30]. The **table (1-2)** shows some physical properties of Polystyrene (PS) [ 31].

**Table (1-2):** The most important physical properties of Polystyrene **(PS)[ 31]**

| Punctuation | Properties | Poly(styrene) |
|---|---|---|
| 1 | Tensile strength ( $^{kg}/_{m}$) | $(35 - 84)^{10}$ |
| 2 | Elongation(%) | 1.0-2.5 |
| 3 | Density ( $^{g}/_{cm^3}$) | 1.09-1.04 |
| 4 | refractive index | 1.59-1.60 |
| 5 | dielectric constant | 2.4-2.65 |
| 6 | crystal melting point $T_m$ ( $^{\circ}C$) | 240 |
| 7 | degree of glass transition $T_g$ ( $^{\circ}C$) | 100 |
| 8 | Molecular Weight of Repeat unit ($g\ mol^{-1}$) | 104.15 |

## 1.5 Polymer Blends

Recently, there has been a clear interest by scientific researchers in polymer blends because of their good properties such as elasticity, strength and others[32].

Polymer blends are known as. Mix. Homogeneous mixture of two or more different polymers[33]. It can be homogeneous (mixed) or heterogeneous (polyphasic)[34]. This includes both crystalline and amorphous polymers[35]. But if two polymers are chemically dissimilar, they can be miscible [35]. The miscibility of two polymers depends mainly on the specific interactions between the polymer chains[36]. This depends on the second law of thermodynamics, which is explained by the entropy factor and is given by the following equation:

$$\Delta G_{mix} = \Delta H_{mix} - T\,\Delta S_{mix} \dots\dots\dots\dots\dots\dots\dots\dots\dots \mathbf{1} \quad [37]$$

Where, $\Delta G$ is the change in free energy, $\Delta H$ is the change in enthalpy, $\Delta S$ is the change in entropy, and $T$ is the absolute temperature.

For a homogeneous miscible blend the Gibbs free energy of mixing requires a negative value. For high molecular weight polymer blends, the gain in entropy is negligible. Hence, the free energy of mixing can only be negative if the heat of mixing is negative. This means that the mixing must be exothermic, which usually requires specific interactions between the blend components. These interactions may range from strongly ionic to weak and non-bonding, including hydrogen bonding, ion-dipole[38][39].

three types of blends can be distinguished: (*i*) completely miscible blends, (*ii*) partially miscible blends, and (*iii*) fully immiscible blends. Completely miscible blends consist of one homogeneous phase. This type of blend exhibits only one glass transition temperature ($T_g$), which is between the ($T_g$) of both blend components with a close relation to the blend composition. Partially miscible blends, in which a part of one blend component is dissolved in the other, exhibits normally good compatibility and fine phase morphologies. However, fully immiscible blends exhibit a coarse phase morphology having a sharp interface and a poor adhesion between both blend phases. This is the reason for often observed poor properties of immiscible blends[40].

## 1.6 Nanocomposites

Nanocomposites are **composite materials** whose components contain nanoparticles additives[41]. Whereas:

A composites materials is defined as a substance that arises from the union of two or more substances, where each of them has different properties from the other, which combine to form a new substance whose properties differ from the properties of each of the common substances in its composition and with a coherent structure resulting from the homogeneity of two different substances in terms of composition[42]. The composites consists of two basic components, the material of the **materix** and the **additive** materials.

The **base material** is the most quantitative material that surrounds the other components and works to cohesive their elements and link the parts together to form a compact system[43].

As for **additives**, they are substances that are added to polymeric materials with the aim of giving them pre-determined characteristics and improving some other properties such as improving electrical conductivity, reducing porosity, raising the polymer's resistance to shocks and friction and many more[44]. These materials are added in the form of **granules**[45]. And when these **additives** have one of their dimensions at the Nano level $\mathbf{(1-100)}\ nm$, then the compound will be called **(nano – composite**) [46].

According to the matrix material, they can be classified into polymer matrix nanocomposites (PMNC), metal matrix nanocomposites (MMNC), and ceramic matrix nanocomposites (CMNC) [47].

As these additions will give it new and distinct properties and may be in some respects unique to the properties of both components such as light weight and good strength in addition to lots of unique features[48], which makes it a multifunctional material with wide applications. As a result, the interest and efforts of scientific researchers in these materials have been remarkably devoted, especially the additive and the way it interacts with the host material, for its wonderful improvements compared to With pure polymers. And therefore , The development of nanoscience and technology through the creation of new Nano-sized materials promises us unique optical, electrical and mechanical properties that are quite different from those properties when these same materials are in a large state [49].

## 1.7 Copper nanowires (Cu NW)

Copper is a chemical element, a type of metal and the second most important mineral in terms of multiple benefits after iron, and its chemical formula is **Cu** [50]. It was discovered by man thousands of years ago. Copper is available in nature and exists in several forms, for example in the form of red pieces mixed with rocks. It is found in nature in several forms, either singly or in combination, for example, oxides, [51]. It can be prepared (obtaining its pure fraction) by electrolysis. Since copper is an important source in itself for nature and for humanity, its uses and uses varied, as it is used in the manufacture of electrical wires and alloys and is used as a means of heat transfer because it is characterized by high heat quality. It is included in human food and many other uses [52]. In view of the properties and applications of copper, scientists and researchers have focused on and studied it intensively. When using nanotechnology and producing nano-copper in the form of wires[53], Wherein, copper nanowires are rectangular nanostructures with an average diameter of ($\mathbf{40-100}$ nm) and a length of up to ($\mathbf{50}\ \mu m$)[54], experiments have proven that its electrical conductivity is extremely high and with good flexibility. Thus, they have achieved many applications where it cannot be limited, for example, its entry into the manufacture of solar cells and devices, smartphones, touch screens and many more[55].

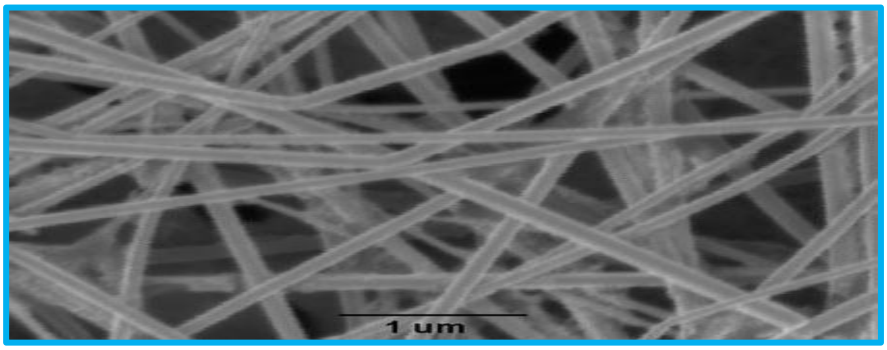



Figure (1-6) : Copper nanowires with **Diameter**: ~100nm & Length: ~50-200µm[56]

**Table (1-3):** physical properties of Copper (**Cu**) **[57]**

| Punctuation | Properties | Copper |
|---|---|---|
| 1 | Phase at STP | solid |
| 2 | Melting point | 1357.77 ($K$) |
| 3 | Boiling point | 2835 ($K$) |
| 4 | Density (near r.t.) | 8.96 ($\frac{g}{cm^3}$) |
| 5 | when liquid (at m.p.) | 8.02 ($\frac{g}{cm^3}$) |
| 6 | Heat of fusion | 13.26 (kJ/$mol$) |
| 7 | Heat of vaporization | 300.4 (kJ/$mol$) |
| 8 | Molar heat capacity | 24.440 [$J/(mol \cdot K)$] |

## 1.8 Literature Survey

### 1. M.F.H. Kadhemy et al in 2017

There has been a great deal of work on the optical characteristics of nanocomposites. The impact of $\mathbf{CuO_2}$ doping % on (PMMA/PS) polymer blends films of the optical characteristics was examined $\mathbf{CuO_2}$ concluded that the structure of the host polymer blends had changed. The index n and the coefficient k of extinction have also increased with an increase in $\mathbf{CuO_2}$ concentration[58].

### 2. Alsaad, A. M., et al in 2020

investigated the optical characteristics of thin **Polystyrene (PS)** films with various **ZnO** nanoparticle concentrations. The study also includes modifications to the optical parameters, including the tail width of the strip and band gap energy for the samples[59].

### 3. A.Raheem., et al In 2010

Where theystudied the optical properties of **PS polystyrene** upon addition of ($\mathbf{Al_2O_3}$), where the absorption and transmittance spectra of the wavelength range (300-900) $nm$ were recorded and the absorption coefficient and energy gap of the allowed and forbidden indirect transmission were calculated and found that the absorption coefficient It increases with the increase in the percentage of additives, and the experimental results prove that the optical absorption coefficient is less than ($\mathbf{10^4}$) $\boldsymbol{cm^{-1}}$ and that the energy gap of the forbidden indirect transmission will decrease with the increase in the weight ratios of the additives, and that the inertia coefficient increases with the increase in the weight ratios of the additives[60].

### 4. Agarwal, S., et al in 2016

presented a method for computation of **poly para xylylene–silver** nanocomposite optical properties. The resulting data was used to build multilayer polymeric interference filters[61].

## 5. H.Hakim in 2015

Where he prepared the nanocomposite (**$PMMA - Y_2O_3$**) and studied its optical properties and found that the absorption of this compound increases with increasing concentrations of yttrium nanoparticles. The optical constants (absorption coefficient, extinction coefficient, refractive index and real and imaginary dielectric constants) for this nanocomposite increase with increasing concentrations of yttrium oxide nanoparticles. While the energy gap is decreasing[62].

## 6. Patil, M. T., et al in 2016

Where he studied the effect of copper oxide nanoparticles on the optical and electrical properties of methyl methacrylate polymer, and he concluded that the absorbance, absorption coefficient and other optical properties of the nanocomposite (**PMMA-CuO**) increase with increasing concentration of nano-oxide nanoparticles added to the polymer[63].

## 7. Lopes, A. C., et al in 2014

In **2014**, the researcher **Lopes, A. C. and others** studied the electrical and optical properties of the composite **(PS- $NH_3$)** at room temperature, and it was noticed that the optical constants increased with the increase in the concentration of the additive (**$NH_3$**) to the matrix material **(PS)**[64].

## 8. Guo, L., et al in 2016

In the year **2016**, **Guo, L. and others** studied the dielectric properties of the composite **(PS-ALN),** and the experimental results showed that these properties are a function of the concentration of the **(aluminum- nitride)** additive, temperature, frequency, and the dependence of the inter polarization of the composite on the particle size of the additive **(ALN)**[65]**.**

## 1.9 The Aims of Project

Extracting a composite from a polymeric mixture consisting of (**PMMA** – **PS**) and adding copper nanowires (**Cu NW**) to test the optical properties in that composite.

# CHAPTER TWO

# THEORETICAL PART

## 2.1 Introduction

In general, this chapter includes the study of the physical laws and relationships used in calculating the results related to the optical properties represented by absorbance, transmittance, energy gap, optical constants and other properties.

## 2.2 The Optical Properties

In recent years, the research on studying the optical properties of polymers has increased, and through our study of these properties, we can know and the possibility of using these polymers in many practical applications such as, Optical data transmission and storage And many other applications. These properties include absorption, permeability, reflectivity, and others. Also, the study of these properties provides us with knowledge of the components of the polymeric material and the elements involved in its chemical structure[66].

### 2.2.1 The Absorbance (A)

**The absorbance ($A$)** is defined as the ratio between the intensity of radiation absorbed by the membrane ( $I_A$) to the original intensity ($I_\circ$), and it is devoid of units and is given by the following relationship[67]:

$$\mathbf{A = \frac{I_A}{I_\circ}} \dots\dots\dots\dots\dots\dots\dots\dots\dots (\mathbf{2-1}) \quad [67\ P8]$$

### 2.2.2 Transmittance (T)

**The transmittance ($T$)** is defined as the ratio between the intensity of radiation transmitted from the membrane ($I_T$) to the intensity of the incident radiation ($I_\circ$) and as well as being devoid of units and is given by the following relationship:

$$\mathbf{T = \frac{I_T}{I_\circ}} \dots\dots\dots\dots\dots\dots\dots\dots\dots (\mathbf{2-2}) \quad [68]$$

**The absorbance and transmittance are related to the following relationship:**

$$\mathbf{A = \log\frac{1}{T}} \dots\dots\dots\dots\dots\dots\dots\dots\dots (\mathbf{2-3}) \quad [69]$$

**The permeability values can be extracted from the following relationship:**

$$\mathbf{T = e^{-\alpha}} \dots\dots\dots\dots\dots\dots\dots\dots\dots (\mathbf{2-4}) \quad [69]$$

## 2.2.3 Reflectance (R)

**The Reflectance (R)** is defined as the ratio between the intensity of the radiation reflected from the membrane ($I_R$) to the intensity of the incident radiation ($I_∘$), which is devoid of units and is given by the following relationship:

$$\mathbf{R = \frac{I_R}{I_\circ}} \dots\dots\dots\dots\dots\dots\dots\dots\dots (\mathbf{2-5}) \ [70]$$

The Reflectance depends on the wavelength of the incident light, the angle of incidence and the nature of the surface[71].

It is worth noting that the sum of the absorbance, transmittance and reflectivity is equal to a constant:

$$\mathbf{R + T + A = 1} \dots\dots\dots\dots\dots\dots\dots\dots\dots (\mathbf{2-6}) \ [72]$$

## 2.3 The Optical constants

### 2.3.1 The absorption coefficient (α)

The absorption coefficient ($\alpha$) is defined as the rate of decrease in the energy of the incident electromagnetic rays to the rate of a unit distance in the direction of propagation of the wave within the medium. And it can be calculated in terms of the optical absorption spectrum, given by the following relationship:

$$\boldsymbol{\alpha = 2.303\frac{A}{t}} \dots\dots\dots\dots\dots\dots\dots\dots\dots (\mathbf{2-7}) \ [73]$$

where (A) is absorbance and (t) is thickness of thin film.

**The absorption coefficient (α)** depends on the properties of the material and **the energy of the incident photon ($\boldsymbol{\nu h}$)** in terms of the energy gap and the type of electronic transitions, as shown by the following relationship:

$$\boldsymbol{\alpha h\nu = B\,(h\nu - E_g^{opt})^n} \dots\dots\dots\dots\dots\dots\dots\dots\dots (\mathbf{2-8}) \ [74]$$

Where, $\boldsymbol{\nu}$ is the frequency, $\boldsymbol{B}$ is a constant that depends on the nature of the substance, $\boldsymbol{h}$ is Planck's constant, $\boldsymbol{E_g^{opt}}$ is the energy band gap between the valence band (V.B) and the conduction band (C.B) and $\boldsymbol{n}$ is a constant that depends on the nature of the electronic transitions, Where:

n=**1/2** for **direct** allowed transition

n= 2 for indirect allowed transition

n=3 for direct forbidden transition

n=**3/2 direct** forbidden transition.

As shown in the figure (2-1):

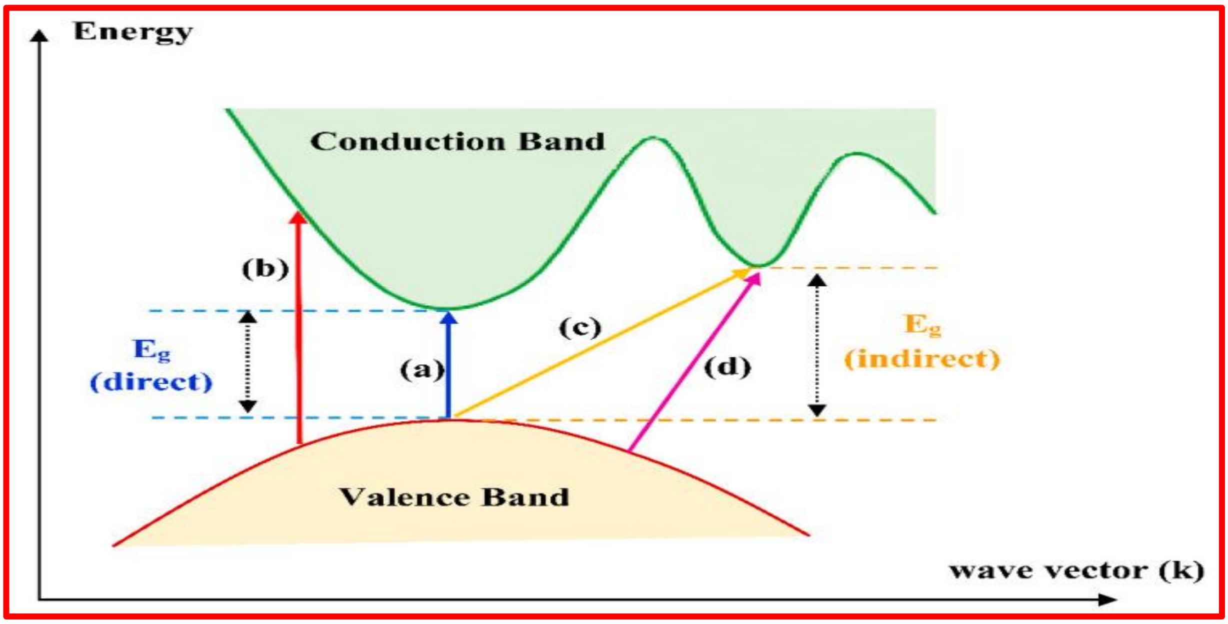



**Figure (2-1): The transition process [75]:**

(a) refers to allowed direct transition, **(b)** refers to forbidden direct transition, **(c)** refers to the allowed indirect transition, and **(d)** refers to the forbidden indirect transition.

## 2.3.2 The regions of absorption edge

Absorption edge can be defined as the rapid increase obtained in absorption, provided that the energy of the absorbed radiation is equal to the energy of the band gap. Where the absorption edge represents the least energy difference between the lowest point in the conduction band and the highest point in the valence band [76].

**Absorption regions can be classified into three regions [77]:**

**A. High absorption region:**

the absorption coefficient (α) is **high**, it is about $(\alpha \geq 10^{4} cm^{-1})$ **.**

**B. Exponential region:**

The value of the absorption coefficient $(\alpha)$ is **between**

$(1\, cm^{-1} < \alpha < 10^4\, cm^{-1})$.

**C. Low absorption region:**

the absorption coefficient $(\alpha)$ is **very small**, it is about $(\alpha < 1cm^{-1})$.

And as shown in **figure (2-2)**:

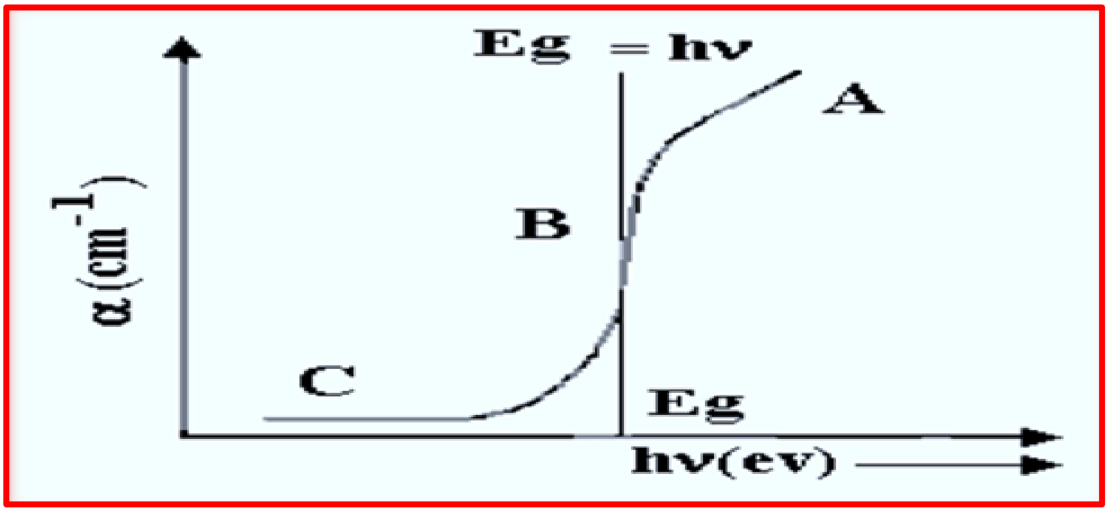



Figure (2-2) **Regions of absorption edge:**

**A-** High absorption region. **B-** Exponential region. **C-** Low absorption region[77].

## 2.3.3 Refractive index ($n$)

**The refractive index ($n$)** is defined as the ratio between the speed of light ($c$) in a vacuum to its speed in the sample (**v**), and which is a quantity without units and is given by the following equation:

$$n = \frac{c}{v} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2-9) \quad [78]$$

**The refractive index depends** on the density of the medium, and which is directly proportional to it, as well as on the temperature.

**In the case of polymers**, the matter is different, as the refractive index depends mainly on the length of the polymeric chain, the molecular structure of the polymer, and the wavelength of the light falling on the sample[79][80].

The refractive index can be deduced in terms of **Reflectance** ($R$) according to the following relationship:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2-10) \quad [81]$$

## 2.3.4 Extinction Coefficient ($K_\circ$)

The damping coefficient is defined as the relative energy loss experienced by the electromagnetic wave as it passes through the sample (the attenuation of the wave inside the sample)[82].

There is a relationship between the refractive index ($n$) and the Extinction index ($K_\circ$), which is:

$$n = n^* - iK_\circ \dots\dots\dots\dots\dots\dots\dots\dots\dots (2-11) \quad [83]$$

Whereas, the imaginary part of the **complex refractive index** ($n^*$) represents the Extinction index.

**The Extinction coefficient** ($K_\circ$) can be **calculated** from the following relationship:

$$K_\circ = \frac{\alpha\lambda}{4\pi} \dots\dots\dots\dots\dots\dots\dots\dots\dots (2-12) \quad [84]$$

## 2.3.5 The Dielectric Constant ($\varepsilon$)

**The dielectric constant ($\varepsilon$)** is defined as a measure of the dielectric of a material and can be calculated from the following relationship:

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 \dots\dots\dots\dots\dots\dots\dots\dots\dots (2-14) \quad [86]$$

Where $\varepsilon_1$ Represents **the real part of the dielectric constant and $\varepsilon_2$** Represents **the imaginary part of the dielectric constant.**

**The real part $\varepsilon_1$** and **the imaginary part $\varepsilon_2$** of the dielectric constant were calculated from the following relationships:

$$\varepsilon_1 = (n^2 - K_\circ^2) \dots\dots\dots\dots\dots\dots\dots\dots\dots (2-15) \quad [87]$$

$$\varepsilon_2 = (2nK_\circ) \dots\dots\dots\dots\dots\dots\dots\dots\dots (2-16) \quad [87]$$

Where **the real part of the dielectric constant ($\varepsilon_1$)** shows how slow the speed of light is in the sample, and **the imaginary part of the dielectric constant** ($\varepsilon_2$) shows how the dielectric absorbs energy from an electric field due to the movement of dipole electrons, and the electronic polarization is dominant at the optical frequencies represented by light waves[88].

# CHAPTER THREE

# EXPERIMENTAL PART

## 3.1 Introduction

This chapter includes the stages of preparing samples of Nanocomposites **(PMMA-PS-Cu NW),** and preparing them for examination, by making measurements by ultraviolet visible spectroscopy, in order to know the effect of adding nanowires on some optical properties, with a general description of the devices used. In the preparation and measurement stages.

## 3.2 The Used Materials

### 3.2.1 Polymers

Two polymers were used in this work:

1- **polymethylmethacrylate** (PMMA)**:** It was manufactured by the German company **(Tuttlingen)** in the form of granules with a purity of (99%)
2- **Polystyrene** (PS)**:** It was manufactured by the German company **(Dentaurum)** in the form of granules with a degree of purity (99%) and can be obtained from the local markets.

### 3.2.2 Nanomaterials

**copper nanowires** (**Cu** NW) were used as an additive and it was obtained as a **powder** from (US Research nanomaterials) **company** with **diameter** (100 nm), **length** (10 µm) and a high degree of **purity** (99.5%).

## 3.3 Preparation of (PMMA − PS − Cu NW) nanocomposite

**1-** The nanocomposite was prepared by dissolving (**0.6** wt.%) of **PMMA** and (**0.4** wt.%) of **PS** in **40** $mm^3$ of **pure benzene** under a **temperature** of (**60**°C) and mixing it using a **Magnetic Stirrer** for (**40**) **minutes** to obtain a homogeneous solution.

**2-** Then the nanomaterial (**Cu** NW) was added to the solution consisting of **(PMMA-PS)** with different weight percentages (**0, 0.19, 0.39** & **0.59**) Wt.%, As shown in the table (3-1) and mix it for (**20**) **minutes** to get homogeneous solution.

**Table (3-1):** Weight percentage for (**PMMA − PS − Cu NW**) nanocomposites.

| **N.** | $PMMA_{Wt}$ | $PS_{Wt}$ | $Cu\ NW_{Wt}$ |
|---|---|---|---|
| 1 | 0.6 | 0.4 | 0 |
| 2 | 0.704 | 0.296 | 0.19 |
| 3 | 0.708 | 0.292 | 0.39 |
| 4 | 0.712 | 0.288 | 0.59 |

**3-** Using the method of pouring into the glass mold (petri dish has diameter **10** $cm$) and leaving it for **72 hours** to dry. Using a micrometer to measure the thickness of the membrane, the thickness of these samples was taken with a range **(150** $\mu m$**)**.

## 3.4. Optical property measuring device

It was completed recording the absorption spectrum of the prepared nanocomposite samples by **device (UV-Spectrophotometer model-1800)**, manufactured by **(Shimadzu) company**, at room temperature and for the wavelength range **(200-1100)** $\boldsymbol{nm}$, as shown in the **figure (3-1)** and through the results of the absorption spectrum, It was completed Calculation of other optical properties such as absorption coefficient, refractive index, extinction coefficient, energy band gap, dielectric constants (real and imaginary) and optical conductivity.

**Figure 3-1 UV-Visible Spectrophotometer (Shimadzu -1800)**

# CHAPTER FOUR

# RESULTS AND DISCUSSION AND CONCLUSIONS

## 4.1 Introduction

This chapter includes the results of examining the structure of the nanocomposite **(PMMA-PS-Cu NW)** and its **optical properties** of absorbance and transmittance, absorption coefficient, energy bandgap, extinction coefficient, refractive index, real and imaginary parts of the dielectric constant, and photoconductivity. where it was done Discussing the effect of adding concentrations of **(Cu NW)** Nanowires on the optical properties of the polymeric mixture **(PMMA-PS)** in this chapter.

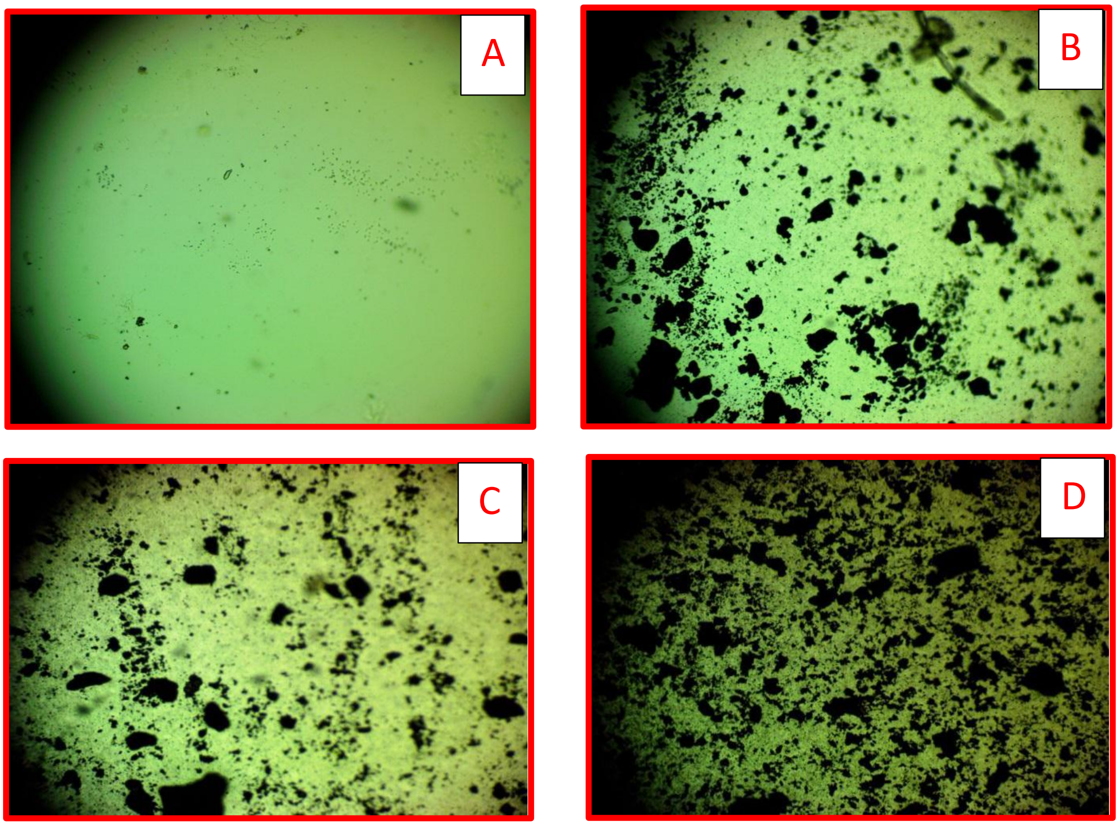
## 4.2 Optical microscope

It was completed examination of the prepared nanocomposite samples using a optical microscope, which was **manufactured by (Olympus) company. Type (Nikon-73346)**, as shown in **Figure (3-2)**, **under** the power of magnification (**10x**) to photograph the fine details of these samples, as it is equipped with an automatic light control camera.

**Figure 4-1: Optical Microscope**

## 4.3 Optical microscopy examinations

**Figure (4-2)** several images of samples of different concentrations at the magnification power **(10x)** of the films of the nanocomposite **(PMMA-PS-Cu NW)**. Where we notice from the figure shown below that when increasing the concentrations of copper nanowires **(Cu NW)** of the polymeric mixture **(PMMA-PS)** down to **(0.59) Wt%** will be formed Copper nanowires are a continuous network inside the polymeric mixture and this network containing paths that allow charge carriage to pass through them.




**Figure(4.2): Photomicrographs $(x^{10})$ for PMM − PS − Cu NW nano composites**
**(A) PMMA − PS blend, (B) 0.19 wt% Cu NW (C) 0.39 wt% Cu NW (D) 0.59 wt% Cu NW**

## 4.4 The optical properties of (PMMA-PS-Cu NW) Nanocomposite

### 4.4.1 The Absorbance (A) and Transmittance (T)

**Figure (4-3) shows** the absorbance variance of the nanocomposite **PMMA-PS-Cu NW** as a function of the wavelength of the incident light. **Notice:**

Increasing the absorbance of all nanocomposite samples in the **UV** region. As a result of the high energy of the photons of these incident rays, which is estimated to be greater than **(3 eV**), which is sufficient to interact with atoms and the occurrence of electronic transitions from a low energy level to a higher one, i.e. from the valence band to the conduction band by absorbing a photon of known energy for each electron. By knowing the changes in the absorbed and emitted radiation, we can determine the types of possible electronic transitions [89].

And low absorbance values for all nanocomposite samples in the visible spectrum region. As a result of the low energy of the photons of these incident rays, which is not enough to interact with atoms and the occurrence of electronic transitions.

Thus, photons are transmit, and the transmittance for all nanocomposites increases with the increase in the wavelength of the light falling on the samples and its approach to the visible spectrum region[90].

**As shown in the figure (4-4)** which shows a discrepancy the transmittance of the nanocomposite **(PMMA-PS-Cu NW)** as a function of the wavelength of the incident photon.

In addition, through the **figures (4-3) and (4-4)**, we notice clearly, an increase in the absorption and a decrease in permeability with the increase in the concentration of **Cu NW**.

This behavior is due to the fact that the nanowires are characterized by a very high absorption rate as a result of their high diffusion through the mixture **(PMMA-PS)**, whereby the increase in the percentage of added concentrations increases the agglomeration of the nanowires and thus increases the number of charge carriers (free electrons). This behavior is consistent with the researcher findings [91].

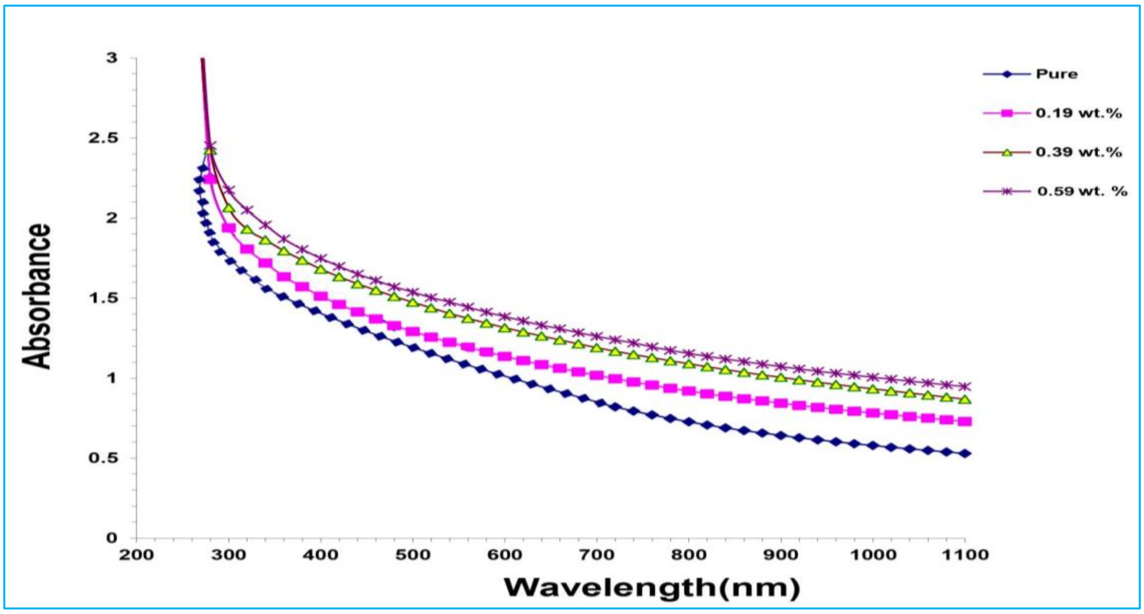



**Figure (4-3):** Variation of absorbance spectrum of nanocomposite samples (PMMA – PS – Cu NW) with different weight ratios of (Cu NW) concentrations as a function of wavelength

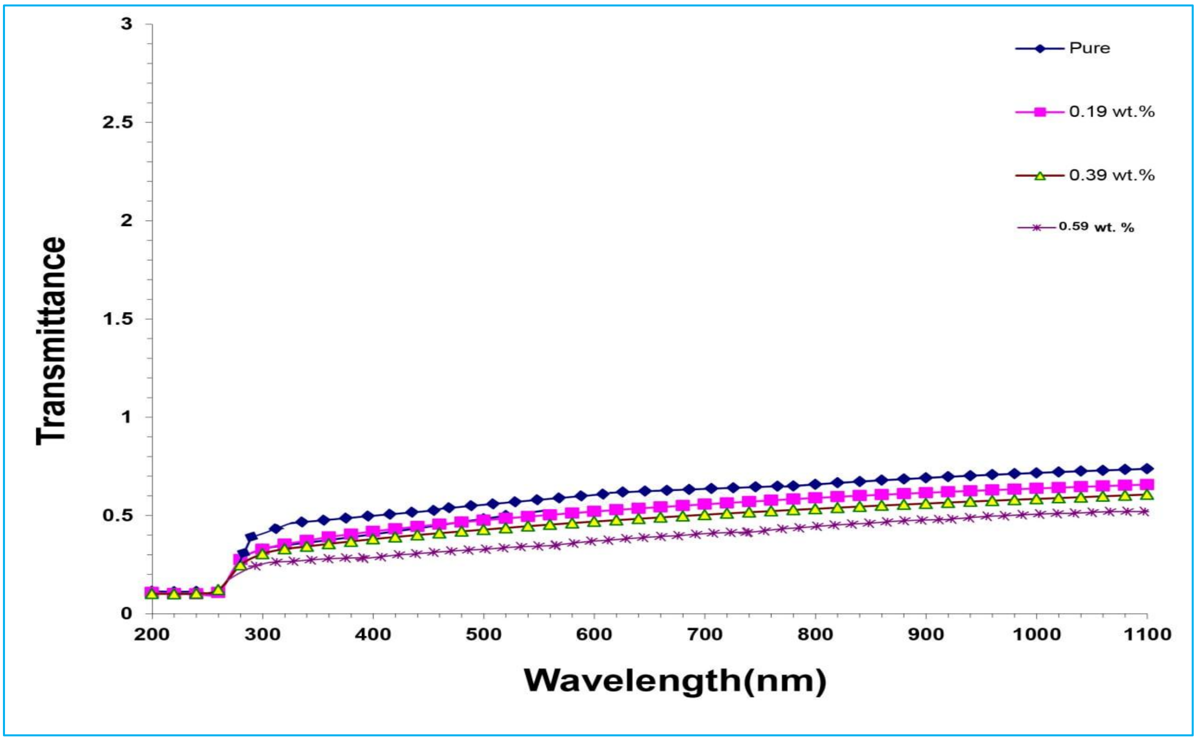



**Figure (4-4):** Variation of the transmittance spectrum of nanocomposite samples (PMMA – PS – Cu NW) with different weight ratios of (Cu NW) concentrations as a function of wavelength

## 4.4.2 The Absorption Coefficient ($\alpha$)

**The figure (4-4)** shows the variation of the absorption coefficient for the nanocomposite samples **(PMMA-PS-Cu NW)** as a function of the energy of the incident photon.

The absorption coefficient is **directly proportional** to the photon energy, and it was calculated using **equation (2-8)**.

Determining the amount of the absorption coefficient enables us to know the nature of electronic transitions[92]. When the values of the absorption coefficient of (**PMMA-PS-Cu NW)** nanocomposite are high $(\alpha > 10^4)cm^{-1}$, it is expected that direct transition of electron. While, when the values of the absorption coefficient of **(PMMA-PS-Cu NW)** nanocomposite are low $(\alpha < 10^4)\ cm^{-1}$, it is expected that indirect transition of electron. And through the figure we notice that, whereas:

The lowest value of the absorption coefficient is at the lowest energy of a photon, and here the possibility of electrons transferring is small because the energy of the incident photon is not enough to transfer from the valence band to the conduction band **($E_g > \upsilon$h)**.

In addition, we note that:

The amount of the absorption coefficient increases with the increase in the concentrations of the additive material, as a result of the increase in the number of energy-absorbing molecules and thus the increase in the values of the absorption coefficient [93].

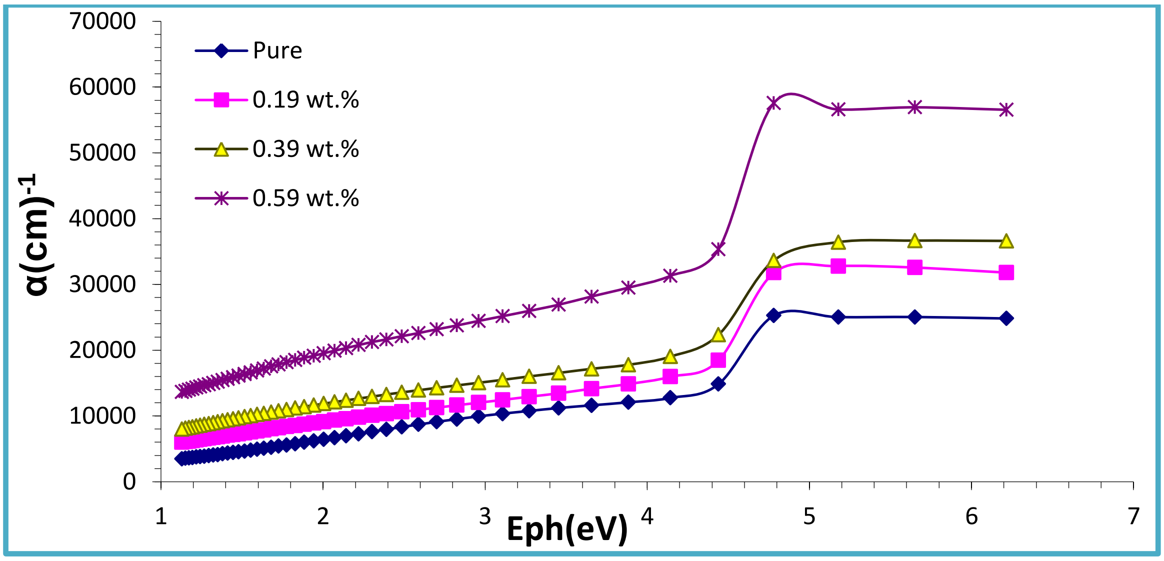



**figure (4-5): variation of the absorption coefficient for the nanocomposite samples (PMMA − PS − Cu NW) as a function of the energy of the incident photon.**

### 4.4.3 The energy gap of the indirect transitions

**The figure (4-5)** shows the variation of absorption edge $(\alpha h\upsilon)^{\frac{1}{2}}$ for the nanocomposite samples **(PMMA-PS-Cu NW)** as a function of the energy of the incident photon.

The optical energy gap (**allowed and forbidden**) for indirect transitions was calculated using **equation (2-8),** and the results were fixed as shown in **Table (4-1).** Where at (**n = 2**), the allowed optical energy gap for indirect transitions will appear, as shown in **Figure (4-6).**

By taking a straight line tangent from the top of the curve in the direction of the $(x)$ axis at $[(\alpha h\upsilon) = 0]$, we will get the optical energy gap that is prohibited for indirect transmission. Through this, we note that the energy gap values decrease with increasing concentration of (**Cu NW**). This behavior is due to the generation of localized levels in the energy gap, so the transition in this case is in two stages:

**First:** the transition from the equivalence beam to the local levels.

**The second:** the transition from the local levels to the conduction package as a result of increasing the concentrations of copper **(Cu NW)**

This leads us to the fact that the nanocomposites are of a heterogeneous type and the electronic conduction through them depends on the concentration of the nanowires. In other words, increasing the concentration of nanowires leads to providing paths for electrons within the polymeric mixture (**PMMA-PS**) that facilitate the passage of the electron from the valence band to the conduction band, and this explains the decrease in the energy gap by increasing the added concentrations, and this is consistent with the results of the researcher [62].

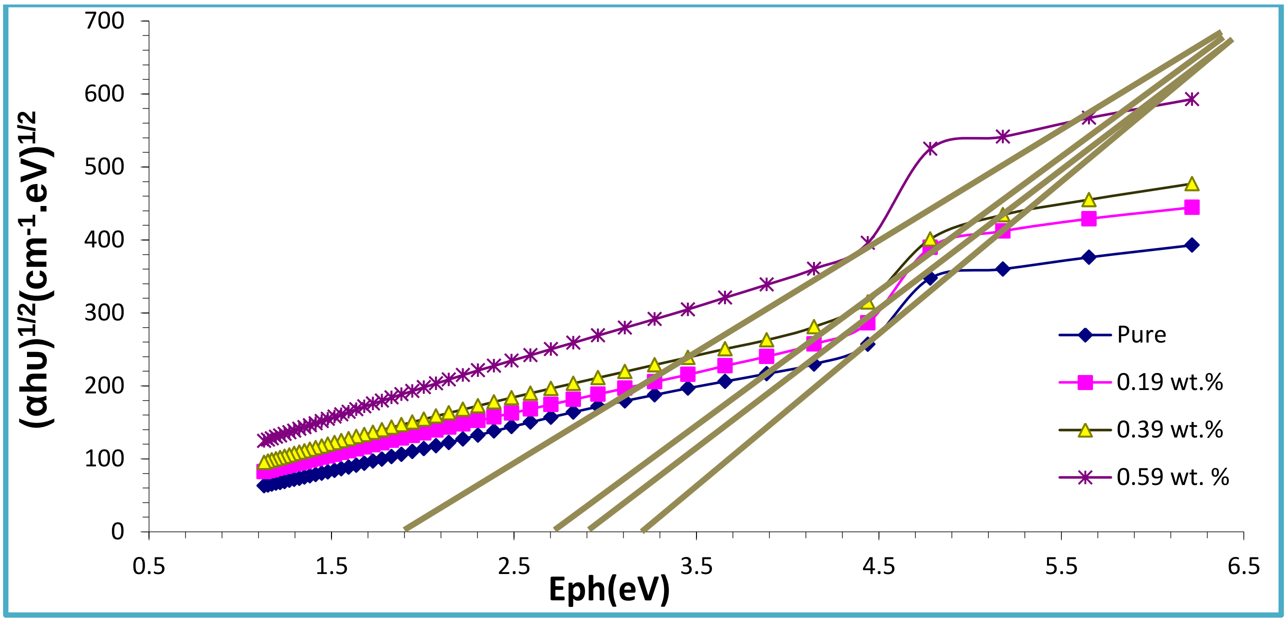



**Figure 4-6: variation of absorption edge $(\alpha h\upsilon)^{\frac{1}{2}}$ for the nanocomposite samples (PMMA − PS − Cu NW) as a function of the energy of the incident photon.**

And can calculation of the optical energy gap that is forbidden for the **indirect transitions** when the value of **n=3** of the nanocomposite **(PMMA-PS-Cu NW) in the same way** calculation of the optical energy gap allowed for the indirect transitions. And as shown in **Figure (4-7)**.

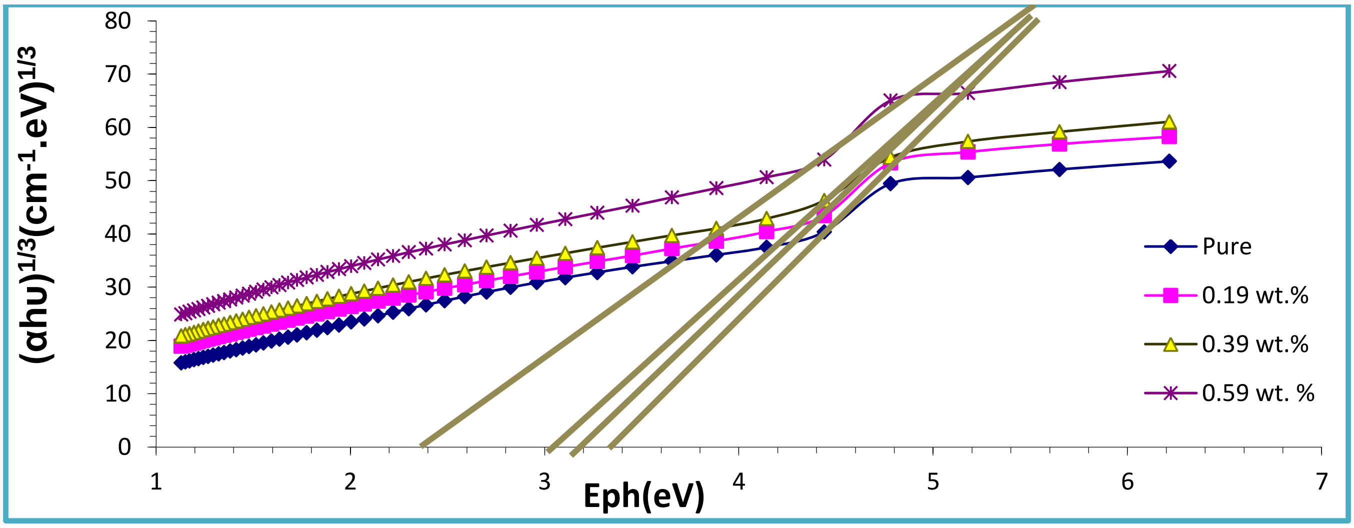



**Figure 4-7: variation of absorption edge $(\alpha h\upsilon)^{\frac{1}{3}}$ for the nanocomposite samples (PMMA − PS − Cu NW) as a function of the energy of the incident photon.**

The table (4-1) shows values of energy band gap for the **allowed and forbidden indirect transition for** (**PMMA − PS − Cu NW**) nanocomposite:

| **Concentration Cu NW** | $E_g(eV)$ | |
|---|---|---|
| | **allowed** | **forbidden** |
| **0** | 3.2 | 3.38 |
| **0.19** | 2.9 | 3.2 |
| **0.39** | 2.7 | 3.05 |
| **0.59** | 1.9 | 2.39 |

## 4.4.4 The Refractive index (n)

**The figure (4-7)** shows the variation of **the refractive index (*n*)** for the nanocomposite samples **(PMMA-PS-Cu NW)** as a function of the emitted wavelength. The refractive index is calculated using **equation (2-9)**. And through the figure we notice that, **whereas** the refractive index **(*n*)** of the nanocomposite increases with the increase in the concentration of **(Cu NW)**.

This behavior is due to the increased density of the Nanocomposite in the ultraviolet region. And less transmittance in this region.

It decreases with increasing wavelength i.e. near infrared rays due to the high transmittance in this region and this agrees with the results of the researcher [60]. In addition, we note that the values of the refractive index increase with the increase in the energy of the photon, this indicates that the light passes through those samples in the ultraviolet and visible spectrum at a slower speed, but at a higher speed in the visible and near infrared region.

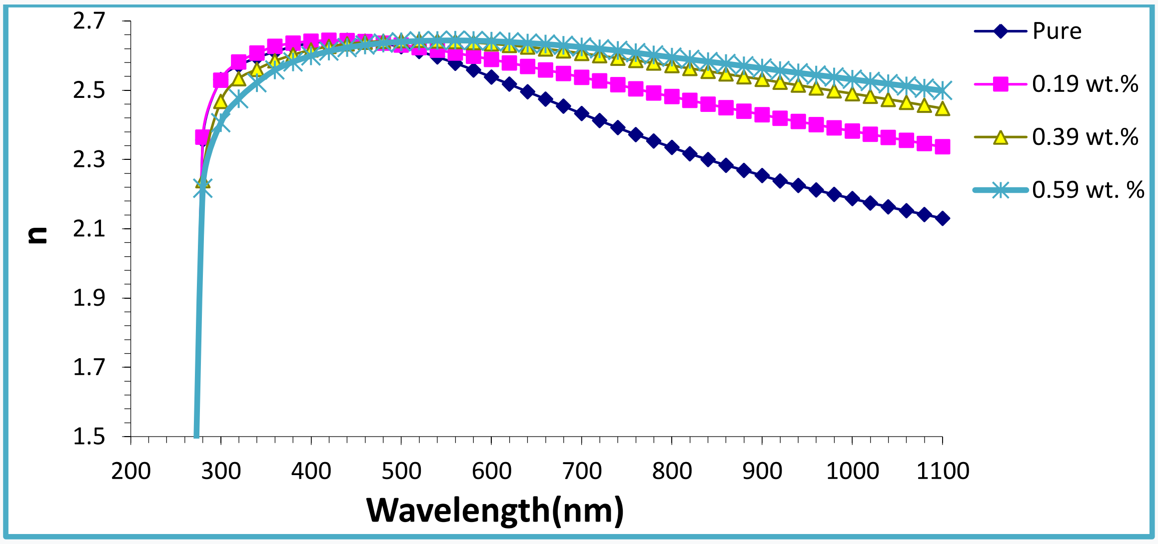



Figure (4-8): **variation of the refractive index ($n$) for the nanocomposite samples ($PMMA - PS - Cu\ NW$) as a function of the emitted wavelength.**

## 4.4.5 The Extinction Coefficient ($K_\circ$)

**The figure (4-9)** shows the variation of The Extinction Coefficient **($K_\circ$)** for the nanocomposite samples **(PMMA-PS-Cu NW)** as a function of the wavelength.

The refractive index is calculated using **equation (2-11)**. And through the figure we notice that, **whereas** the extinction coefficient of the nanocomposite increases with the increase in the concentration of copper nanowires **(Cu NW)**.

This behavior is due to the increased optical absorption coefficient and photon scattering within the polymeric matrix material (**PMMA-PS**) [94]. In addition, the increase of the extinction coefficient **($K_\circ$)** at the high photon energy in the ultraviolet region as a result of the high absorbance in this region of the nanocomposite samples.

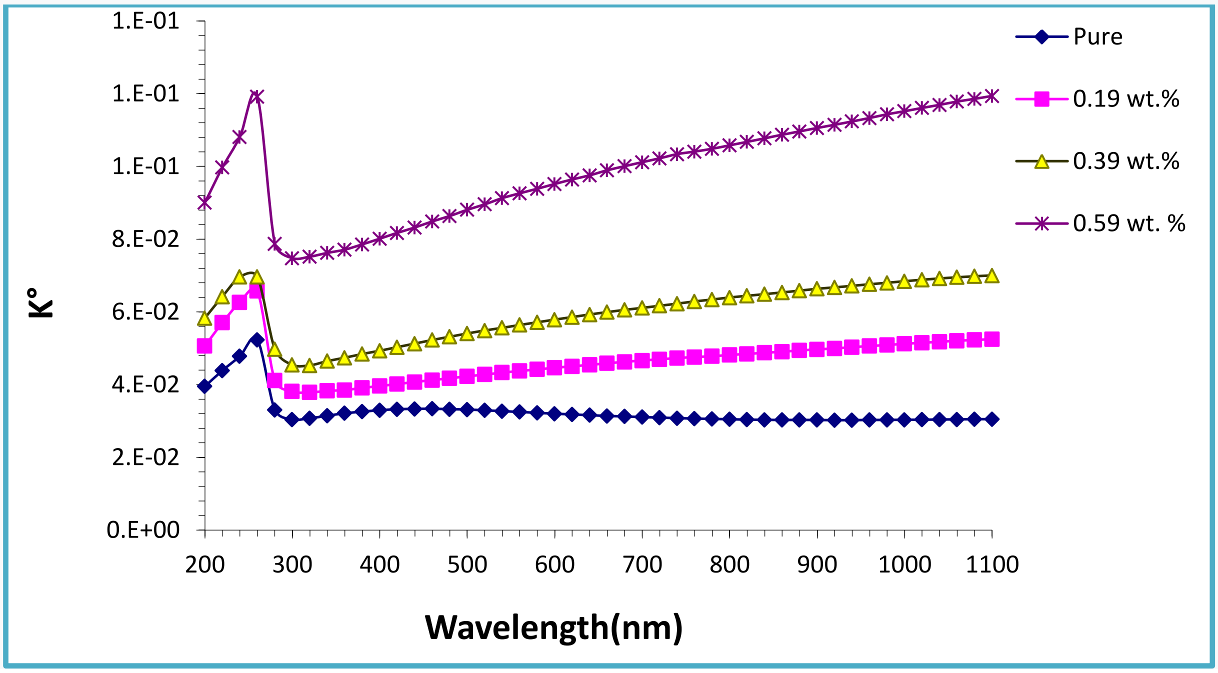



**Figure (4-9): variation of The Extinction Coefficient (K∘) for the nanocomposite samples (PMMA − PS − Cu NW) as a function of the wavelength**

## 4.4.6 The Real and Imaginary Parts of Dielectric Constant

The two figures **(4-10)** and **(4-11)** show the variation of the **real and imaginary** dielectric constant of the nanocomposite **(PMMA-PS-Cu NW )** as a function of wavelength, **respectively**. And through the figure we notice that**,** whereas The dielectric constants (real and imaginary) increase with increasing concentration of the nanomaterial **(Cu NW).**

This behavior is due to the increase in the electric polarization due to the increase in the concentration of nanowires in the sample, and the effect is clear in the region of high energy photons. The increase in the dielectric constants of the polymer mixture (**PMMA-PS**) represents a partial increase in the number of charges inside it [95].

The difference between the real and imaginary parts of the dielectric constant of a mixture (**PMMA-PS**) with wavelength is that the real part of the dielectric constant depends on the refractive index because the effect of the extinction coefficient is very small. and the imaginary part of the dielectric constant depends on the extinction coefficient. especially in the infrared and visible regions, where the refractive index is almost constant, while the extinction coefficient increases with increasing wavelength [96].

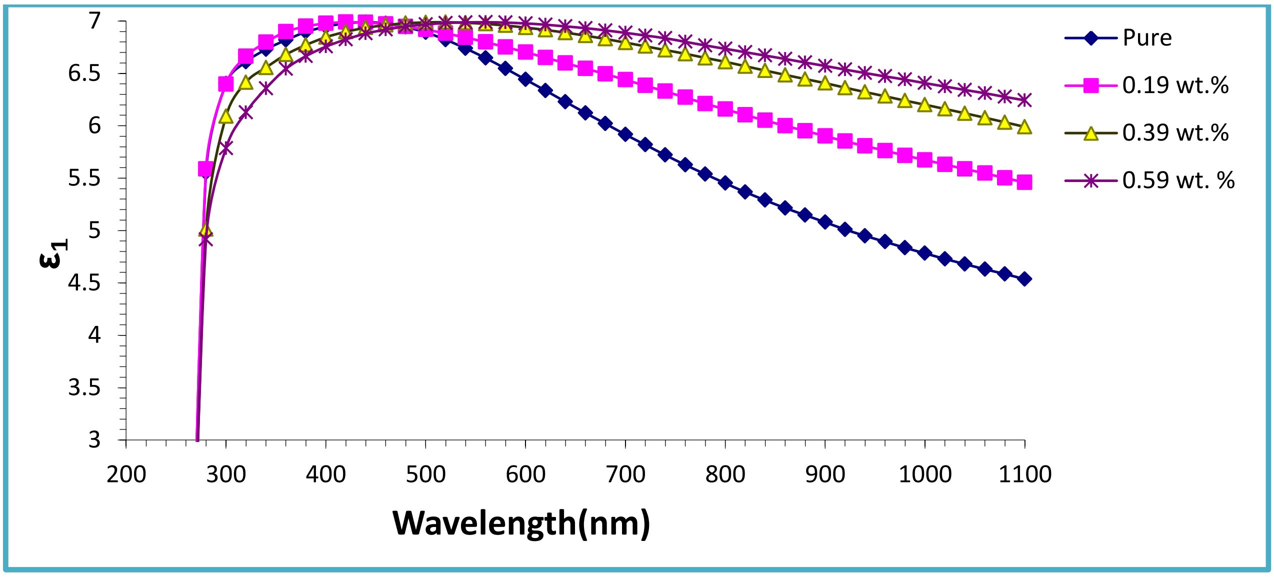



**Figure (4-10): The relationship between the real part of dielectric constant for (PMMA – PS – Cu NW) nanocomposite with wavelength**

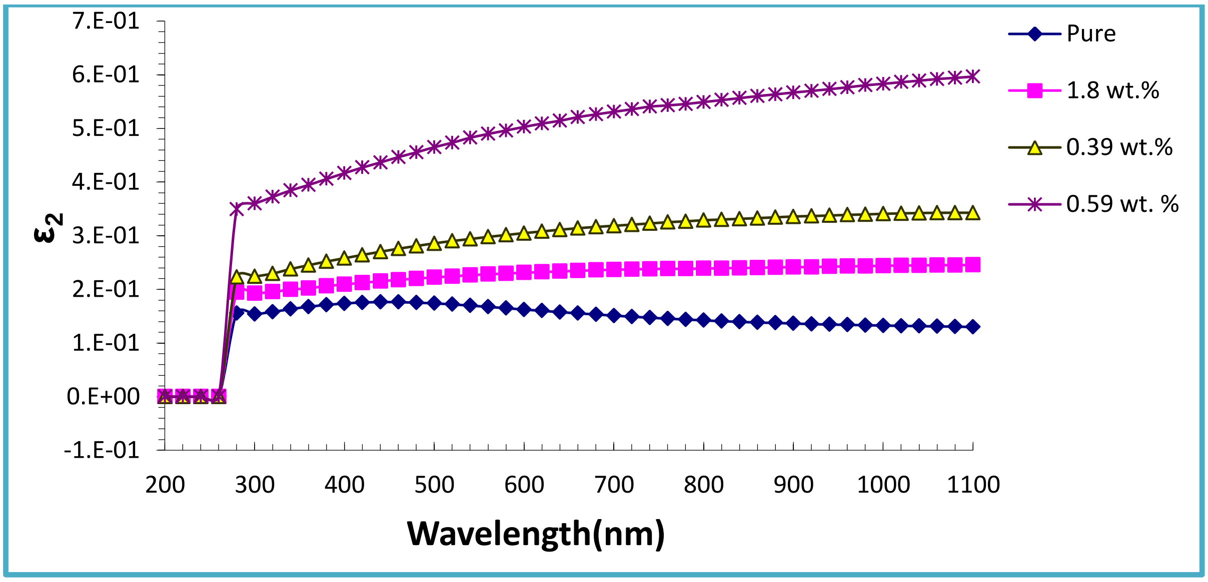



**Figure (4-11): The relationship between the imaginary part of dielectric constant for (PMMA – PS – Cu NW) nanocomposite with wavelength**

## 4.5 Conclusions

**1.** The absorbance, absorption coefficient, Extinction coefficient, refractive index and dielectric constant (**real** and **imaginary**) of the nanocomposite (**PMMA – PS – Cu NW**) increase with increasing concentration of copper nanowires.

**2.** The energy gap and transmittance **decrease** with increasing concentration of **Cu NW**.

**3.** The nanocomposites can be semiconductor and thus can be used in many industrial applications such as biological sensors in diagnostic laboratories, sensors and elements of optical devices and others.

## 4.6 Future Work

**1.** Irradiation of the polymer used by research with gamma rays.

**2.** Research about electrical properties (**DC** & **AC**).

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# الخلاصة

في هذا البحث تمت دراسة تأثير إضافة تراكيز مختلفة من أسلاك النحاس النانوية (**Cu NW**) على الخواص البصرية لـخليط البوليمر (**PMMA − PS**). حيث تمت إضافة أسلاك نانوية من النحاس بـنسب وزنية مختلفة [ ( 0,0.19,0.39, & 0.59 )Wt% ] إلى خليط البوليمر (**PMMA − PS**).

ومن خلال طريقة الصب قبل وبعد الإضافة ، تم تحضير أغشية المتراكب النانوي (**PMMA − PS** − **Cu NW**) بـالنسب المذكورة أعلاه. تم تسجيل الامتصاص البصري في مدى الطول الموجي (**200** − **1100 nm**).

وتم تحديد الثوابت الضوئية كمعامل الامتصاص ومعامل الانقراض وفجوة الطاقة غير المباشرة المسموح بها والممنوعة للتحولات الإلكترونية. بالإضافة إلى ذلك ، تم تحديد ثابت العزل الكهربائي الحقيقي والخيالي.

من خلال القياسات العملية للخصائص البصرية لـعينات المتراكب النانوي المحضر ، لوحظ أن (فجوة الطاقة والنفاذية) تقل بزيادة اضافة النسب الوزنية لأسلاك النحاس النانوية. بينما كل من (الامتصاصية ، معامل الامتصاص ، معامل الانقراض ، معامل الانكسار والأجزاء الحقيقية والخيالية من ثابت العزل) تزداد بزيادة تراكيز أسلاك النحاس النانوية.

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة بابل / كلية التربية للعلوم الصرفة – قسم الفيزياء


# الخصائص البصرية لـخلائط بوليمرية (PMMA – PS) مع الأسلاك النانوية لـلنحاس

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**بحث مقدم الى**

**مجلس كلية التربية للعلوم الصرفة – جامعة بابل**

**وهي جزء من متطلبات نيل درجة الدبلوم العالي تربية / فيزياء المواد وتطبيقاتها**


**من قبل**

**أمير حسين عيسى كاظم**

**بـكالوريوس تربية في الفيزياء**

**إشراف**

**أ.د. بهاء حسين ربيع**



**1442 هـ** **2021 م**