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The Influence of Manganese Oxide Addition on Optical Properties of Polymer Blend

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

By

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بِسْمِ ٱللَّهِ ٱلرَّحْمَٰنِ ٱلرَّحِيمِ

اقْرَأْ بِاسْمِ رَبِّكَ الَّذِي خَلَقَ * خَلَقَ
الإِنْسَانَ مِنْ عَلَقٍ * اقْرَأْ وَرَبُّكَ الأَكْرَمُ
* الَّذِي عَلَّمَ بِالْقَلَمِ * عَلَّمَ الإِنْسَانَ مَا لَمْ
يَعْلَمْ

صَدَقَ اللهُ العليُ العظيمْ

(سورة العلق: ١-٥).

Dedication

To my father and my mother

To my brothers

To my close friends

To all martyrs

To my wife

And

My children

Musa & Rugia

Yousif

Acknowledgment

First, praise is to Allah for inspiring us to acquire knowledge, and peace be upon the Messenger Mohammed and his family.

I would also like to express my profound appreciation and sincere thanks to my respected supervisor Prof. Dr. Ahmed Hashim Mohaisen Al-Yasari for his support, guidance, and encouragement throughout the duration of the project.

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Finally, I thank my colleagues for their help and cooperation throughout the thesis stages.

Yousif

Supervisor Certification

I certify that this thesis titled "**The Influence of Manganese Oxide Addition on Optical Properties of Polymer Blend**," was prepared by (**Yousif Yousif Mijbil Radhy**), under my supervision at Department of Physics, College of Education for Pure Sciences, University of Babylon, as a partial fulfillment of the requirements for the degree of Higher Diploma Education / Physics of Materials and its Application

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We, the examining committee, certify that we have read the thesis, "**The Influence of Manganese Oxide Addition on Optical Properties of Polymer Blend,**" and examined the student **"Yousif Yousif Mijbil Radhy"** in its contents. We found that it is adequate with (   ) as the thesis meets the standards for the degree of Higher Diploma Education / Physics of Materials and its Application

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List of Symbols

Symbol	Description
A_0	Absorbance
I_A	Absorbed light intensity
A	Absorption coefficient
E_a	Activation energy
W	Angular frequency
A	Area
K_B	Boltzmann constant
ΔH	Change in enthalpy
ΔS	Change in entropy
ΔG	Change in free energy
n^*	Complex refractive index
ʹE	Dielectric constant
K	Extinction coefficient
υ	Frequency

T_g	Glass transition
ε_2	Imaginary dielectric constant
I_o	Incident intensity of light
L	Length
C	Light speed in vacuum
T_m	Melting temperature
σ	Optical conductivity
E_g^{opt}	Optical energy gap
E_{ph}	Photon energy
PEG	Polyethylene glycol
PVA	Polyvinyl alcohol
ε_1	Real dielectric constant
R_0	Reflectance
N	Refraction index
T	Temperature
T	Thickness of the sample

T_0	Transmittance
I_T	Transmitted intensity beam
UV	Ultraviolet spectrum
$\varepsilon_{\circ}$	Vacuum permittivity
λ	Wavelength of photon

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Abstract

This study scrutinizes the susceptibility of the optical properties of polyvinyl alcohol (PVA)-Polyethylene glycol (PEG) blend to the addition of manganese dioxide (MnO_2) nanoparticles with 0, 1.8, 3.6, and 5.4 wt. %. Then, the casting method was applied to produce the final nanocomposite films that subjected to a wavelength range from 200 nm to 800 nm to record the absorption spectrum. Hence, we have measured the absorption coefficient, extinction coefficient, allowed indirect energy gap, forbidden transition, real dielectric constant, and imaginary dielectric constant. The main outcome is that there is an increase in the optical constants with the increasing weight ratio of MnO_2 nanoparticles. However, the calculated energy gap was observed it decrease with the increasing of the percentage weight of MnO_2 nanoparticle.

CHAPTER ONE: INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

The properties of metal oxide nanoparticles have been the subject of study for a long time because of their unique optical [1], thermal, mechanical, electronic and electrical properties [2]. Plasmon resonance allows for the enhancement and manipulation of local electromagnetic fields at nanoparticle surface due to surface effects. As a result of these singular optical features, noble metal oxide nanoparticles stimulate great interest for implementation in photonics [3], biotechnology and space applications. Owing to interesting optical properties of nanocomposites which are different from the ones of individual metals, these materials have drawn much attention. Combining metal oxide nanoparticles and polymer together enhances the optical properties of nanocomposites and also alter the mechanical behavior of the polymer. The former is of prime importance due to its possible application in polarizers [4], light stable color filters [5], solar cells and optical sensors [6]. If the properties of polymer can also be tuned in correct direction with enhanced optical properties of metal oxide nanoparticles, 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 nanocomposites 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. Significant changes in thermal [7] as well as optical properties can be observed in properties of such materials even for very small fraction of the nanoparticles[8]. However, as attractive such nanocomposites may be, the process of blending or dispersing nanoparticles in a polymer matrix has proven 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.

1.2 Polymer Blends

The synthesis of polymer blends depends on the compatibility and/or miscibility of their components. Most experimental studies have been carried out by casting from solution, though most commercial polymer blends are prepared by melt mixing by twin-screw extruders. The miscibility of two polymers is depending on the specific interactions between polymer chains. This can be explained by the factor of entropy in the following equation, which represents the second law of thermodynamics [8].

$$\Delta G_{mix} = \Delta H_{mix} - T\,\Delta S_{mix} \tag{1-1}$$

Where, ΔG is the change in free energy, ΔH is the change in enthalpy, ΔS 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, dipole-dipole, and donor-acceptor interactions. Based on the miscibility, 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, which strongly depend on the size and distribution of the phases [9].

Forming polymer blends is a traditional method for making new materials with enhanced properties. Unfortunately, because of the large unfavorable enthalpy, most polymer blends tend to phase separate, which results in poor mechanical properties. Therefore, controlling the phase behavior and morphology becomes a key factor in determining the performance of polymer blends, which mainly rely on the interface between polymer components. Traditionally, block and graft copolymers are used to strengthen the interface and stabilize the morphology. However, they are system specific, relatively expensive to engineer, and very difficult to produce for systems with more than two components [10].

1.3 Nanocomposites

Nanocomposites are as multiphase materials, where one of the components has nanoscale additives. According to matrix materials, nanocomposites can be classified as polymer matrix nanocomposites (PMNC), metal matrix nanocomposites (MMNC), and ceramic matrix nanocomposites (CMNC) [11, 12]. Polymers have been used as insulators in early works because of their dielectric properties and high resistivity. Polymer-based insulators are used in electrical devices to separate conductors without passing current through themselves. The insulator applications of polymers include corrosion protective electronic devices, printed circuit boards and cable sheathing materials. Polymers have several advantages, such as low cost, easy processing, flexibility, good mechanical properties and high strength. In the microelectronic fabrication industry, it is used in the photolithography process [13-15].

Polymeric nanocomposites consisting of inorganic nanoparticles and organic polymers represent a class of materials that have motivated considerable interest in recent years [16].The nanocomposites applications are quite promising in the fields of microelectronic packaging, medicine, automobiles, optical integrated circuits, drug delivery, injection molded products, sensors, membranes, aerospace, packaging materials, coatings, fire-retardants, adhesives, consumer goods [17].

1.4 Polyvinyl Alcohol (PVA)

Polyvinyl alcohol (PVA) is a vinyl polymer joined by only carbon–carbon linkages. The linkage is the same as those of typical plastics such as polyethylene, polypropylene, and polystyrene, and of water-soluble polymers such as polyacrylamide and polyacrylic acid [18]. Due to its interesting optical properties, PVA is considered as one of the most significant commercial polymers. The instability of the vinyl alcohol monomer with respect to acetaldehyde is the reason PVA is prepared by first polymerizing vinyl acetate followed by converting the produced polyvinyl acetate to PVA. Because of its high refractive index, excellent elasticity, lack of color and low cost, PVA has been utilized as a nonlinear optical element, a polymer waveguide and for the replacement of glass in its uses in industrial applications. In addition, the development of PVA based complexes can be achieved effectively due to the existence of hydroxyl groups on the carbon chain backbone of PVA which provides a source for hydrogen bonding that facilitates this process [19].

1.5 Polyethylene glycol (PEG)

Polyethylene glycol (PEG) is an organic polymer composed of carbon, oxygen, and hydrogen. It consists of pairs of methylene (CH_2) units separated by ether linkages (O–C–O) [20]. Its degree of crosslinking and molecular weight dictates whether it will have the form of a hard solid, elastomer, or liquid[21]. Polyethylene glycol is usually a low molecular weight polymer ($< 1000\ g/mol$), while polyethylene oxide is a higher molecular weight polymer with the same repeat unit ($> 10\,000\ g/mol$) [22]. PEG is soluble in water, methanol, ethanol, acetonitrile, and dichloromethane. It is an important component of many nonionic surfactants. PEG has a low glass transition temperature [23], low toxicity, and tunable viscosity [24], all of which make it a good candidate as a lubricant in aqueous and non-aqueous environments [25]. The uses and applications of PEG are extremely widespread [26].

1.6 Nano Manganese dioxide

In recent days, manganese dioxide nanoparticles (MnO_2 NPs) have intrigued material science researches extensively due to its wide range of applications. They are widely used in energy storage devices (lithium-ion batteries, capacitors), catalysts, adsorbent, sensors and imaging, therapeutic activity. Since they hold a lot of distinguished potentials, a robust protocol for cheap, stable and eco-friendly MnO_2 NPs is necessary. They can be categorized into different phases like α, β, δ and others. Thus, owing to their peculiar character, they could be utilized for various purposes depending on the mode of action and applications [27]. Among various metal oxide nanoparticles manganese dioxide is an important transition metal oxide of p-type semiconducting materials with a band gap of 3.3 eV and 3.8 eV [28].

1.7 Literature Survey

Majeed Ali Habeeb and Waleed Khalid Kadhim, 2014, studied the optical properties of (PVA-PVAC-Ti) nanocomposites. They showed that the optical constants increase with the increasing of titanium nanoparticles concentration; while the energy gap decreased with increasing the weight percentages [29].

A. Hashim, M. Kaiser and H. Hakim, 2015, The Effect of $NiNO_3$ on Optical Properties for (PVA- PEG) Composites Polymers by [30] Their experimental results showed that the absorption coefficient less than $10cm^{-1}$ this is indicates to forbidden and allowed indirect electronic transitions, the forbidden energy gap decreases with the increasing of the concentration of NINO, the extinction coefficient is increases with the increasing of the concentration of NINO, additive the refractive index increases with the increasing of the concentration of NINO, additive. The real and imaginary parts of dielectric constant increases with the increasing of the concentration.

Optical Properties of (PVA-PAA-Ag) Nanocomposites by A. Abass, R. Naife, F. Lafta and A. Hashim in 2015[31]. The experimental results showed that the absorbance (A) of polymers mixture, absorption coefficient (α), extinction coefficient (k), refractive index (n) and real and imaginary dielectric constants (ε_1 and ε_2) increase with the increasing of the weight percentages of silver nanoparticles. The energy gap (E_g) of polymers is decreased with the increase of the silver nanoparticles concentrations.

Structural, optical and thermal characterization of $MnCl_2$ composites doped in PEG/PVA blends Films studied by M. Hammed, A. Mohammed, and M. Suhail, in 2017 [32]. Their results showed that the absorbance of composite (PVA:PEG/$MnCl_2$) increased with the increasing of composite (PVA:PEG/$MnCl_2$) concentrations also the optical energy gap for electrons transitions both are direct and indirect allowed.

Preparation of (PVA-PEG-PVP-MgO,CoO) nanocomposites and their optical properties were study by I. R. Agool and A. Hashim in 2018[33]. The results showed that the absorbance (A) of nanocomposites increased with the increasing of the concentrations of magnesium oxide and cobalt oxide nanoparticles. The optical constants (absorption coefficient (α), extinction coefficient (k), refractive index (n), real and imaginary dielectric constants ($\varepsilon_1$and ε_2)) of nanocomposites increase with the increasing of the weight percentages of magnesium oxide and cobalt oxide nanoparticles. The energy gap (E_g) of (PVA-PEG-PVP) decreases with the increase of the weight percentages of magnesium oxide and cobalt oxide nanoparticles.

Optical characterization of Ag nanoparticles doped in polyvinyl alcohol (PVA) and Polyethylene glycol(PEG-4000) blend Films studied by Fouad Z Razooqi in 2020[34]. Their results showed that the optical constants increase with the increasing of silver nanoparticles concentration and the energy gap decrease with the increasing the weight percentages of silver nanoparticle.

Effect of nano CuO doping on structural, thermal and optical properties of PVA/PEG Blend by Ali A. Alhazime in 2020 [35]. The experimental results showed that the energy gap values for polymer blends decreased from 5.3 to 4.7 eV with the addition of CuO nanoparticles. The absorption spectra revealed an apparent change with doping concentration. Different optical parameters were discussed in detail and proved to be directly affected by nanoparticles doping concentrations.

Synthesis and optical properties of PVA/PANI/Ag nanocomposite films by M. Abdelhamied, A. Atta, A. Abdel Reheem, A. Farag, and M. Okr in 2020 [36]. The optical bandgap of PVA/PANI blends and PVA/PANI/Ag nanocomposites was determined by the ultraviolet (UV) absorbance, which showed a decreasing compared with a pristine PVA film.

Doaa E. Al-Kateb and Ali R. Abdulridha in 2021 [37], studied the effect of Sr_2NO_3- nanoparticles doped in (PVA/PVP) on the structural and optical properties of (PVA/PVP) films. in this study, the absorbance increased by increasing of Sr_2NO_3 nanoparticles concentrations, the energy-gap (allowed and forbidden) transitions decreased by increasing of the nanoparticles concentration.

1.8 The Aims of the Project

1. Preparing new type of (PVA-PEG-MnO_2) nanocomposites to be used in a wide variety of industrial applications.
2. Study the optical properties of (PVA-PEG- MnO_2) nanocomposite using the double beam spectrophotometer (shimadzu, UV-18000A) in wavelength (200-800)nm.

CHAPTER TWO: THEORETICAL PART

2.1 Introduction

This chapter includes a theoretical part which focuses on the theories of optical properties. There is increasing research in nanocomposites owing to improvements in optical properties. In particular, nanoparticles represent advanced technological materials because of their high refractive index. Nanocomposites of organic and inorganic materials can possess advantages of both organic polymers (dielectric, ductility, flexibility) and inorganic materials (high thermal stability, rigidity, strength, high refractive index, hardness), thus they would have many applications [38].

2.2 The Optical Properties

In recent years, the search for optical properties has increased because of their applications in integrated optics such as optical information, optical modulation, and optical data storage. The study of optical absorption is useful for the elucidation of the electronic structure and determine direct and indirect transitions [39]. The addition of nanoparticles into polymers improves the electrical, optical and mechanical properties of the materials. Metal oxides nanoparticles with polymers were investigated as alternatives for optical applications such as micro optical elements and planar waveguide devices. The developments of polymer nanocomposite structures due to their ease of processing and production, good adhesion with reinforcing elements, light weight, resistance to corrosive environment and in some cases ductile mechanical performance [40, 41].

2.2.1The Absorbance (A_0) and Transmittance (T_0)

Study of optical properties for polymers have widely applications in optical devices and electronic devices and like fuel cells, solar cells, solid state batteries. And medical technological applications [42]. The valuable information such as the electronic band structure and the optical energy band gap are obtained by absorption coefficient. The absorption coefficient $\alpha(\nu)$ can be determined from the optical absorption spectrum by the following equation [18, 19]:

$$\alpha = 2.303\ \frac{A_0}{t} \tag{2-1}$$

Where, t is the sample thickness and A_0 is defined by log (I_0/I_T) where I_0 and I_T are the incident intensity and transmitted intensity beams, respectively. The direct and indirect transitions can be defined in view of the models proposed by[43]:

$$\alpha h\nu = B_0\left(h\nu - E_g^{opt}\right)^r \tag{2-2}$$

Where, ν is the frequency, B_0 is a constant, h is Planck's constant, E_g^{opt} is the energy band gap between the valence band and the conduction band and r can take the values 0.5, 1.5, 2, and 3 for transitions designated as indirect allowed, indirect forbidden, direct allowed and direct forbidden, respectively as shown in figure (2-1). The calculation of values of optical energy band gap includes the plotting of $(\alpha h\nu)^{\frac{1}{r}}$ against $h\nu$ [44].

The reflectance (R_0) has been determined from values of transmission (T_0), and absorbance (A_0), using the relationship [45]:

$$A_0 + R_0 + T_0 = 1 \tag{2-3}$$

Where R_0 is the reflectance, T_0 is the transmission and A_0 is the absorbance

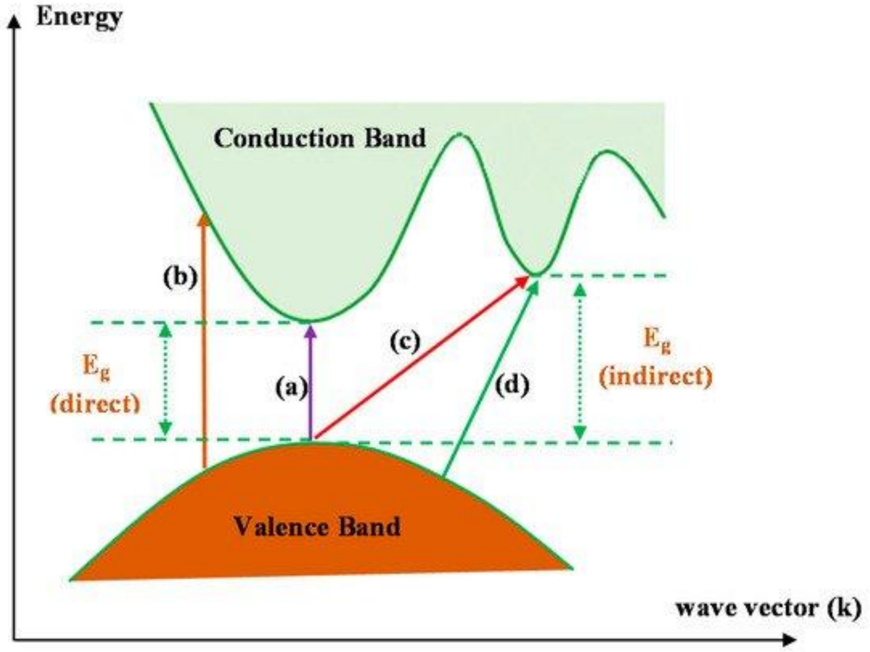


Figure (2-1). The transition process [46]. Where (a) refers to allowed direct transition, (b) refers to forbidden direct transition, (c) refers to the allowed indirect transition, and (d) refers to the forbidden indirect transition.

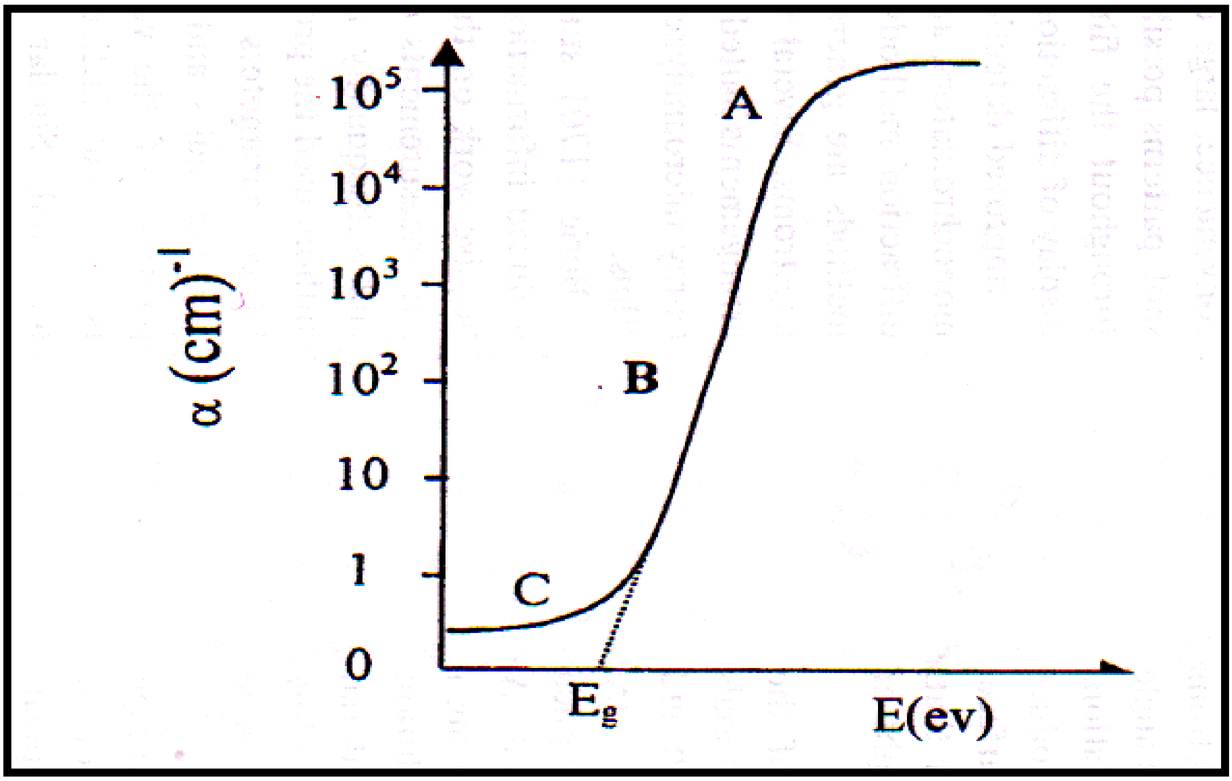
2.2.2 The Absorption Regions

The absorption regions can be classified into three regions [47]:

A. High absorption region: the magnitude of absorption coefficient (α) is larger or equal to $(10^4\ cm^{-1})$.

B. Exponential region: the value of absorption coefficient (α) is equal to $(1\ cm^{-1} < \ \alpha \ < 10^4\ \ cm^{-1})$.

C. Low absorption region: the absorption coefficient (α) is very small, it is about $(\alpha < 1cm^{-1})$ as shown in Figure (2-2) which shows the absorption regions



Figure(2-2). The absorption regions [49].

2.2.3 The Refractive Index and Extinction Coefficient

The index of refraction of a material is the ratio of the velocity of the light in vacuum to that of the specimen [48]:

$$n = \frac{c}{v} \tag{2-4}$$

$$n^* = n - ik \tag{2-5}$$

$$k = \frac{\alpha\lambda}{4\pi} \tag{2-6}$$

Where (c) is the velocity of the light in vacuum and (v) is the velocity of the light in specimen, n^* is complex refractive index, n is real part of refractive index, k is imaginary part of refractive index (extinction coefficient), and λ represents the wavelength of photon. The energy loss of electromagnetic radiation through that medium is measured by the extinction coefficient of a particular substance.

The real part of refractive index (n) can be determined by [49]:

$$n = \frac{1+\sqrt{R_0}}{1-\sqrt{R_0}} \tag{2-7}$$

Where R_0 is reflectance.

2.2.4 The Dielectric Constant and Optical Conductivity

The real part of the dielectric constant shows how much it will slow down the speed of light in the sample and the imaginary part of the dielectric constant shows how a dielectric absorbs energy from an electric field due to dipole motion. The real part and imaginary part of the dielectric constant have been determined by [50]

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 \tag{2-8}$$

$$\varepsilon_1 = (n^2 - k^2) \tag{2-9}$$

$$\varepsilon_2 = (2nk) \tag{2-10}$$

Where ε is the dielectric constant, ε_1 is the real part of the dielectric and constant ε_2 is the imaginary part of the dielectric constant. The optical conductivity was calculated using the following relation [51]:

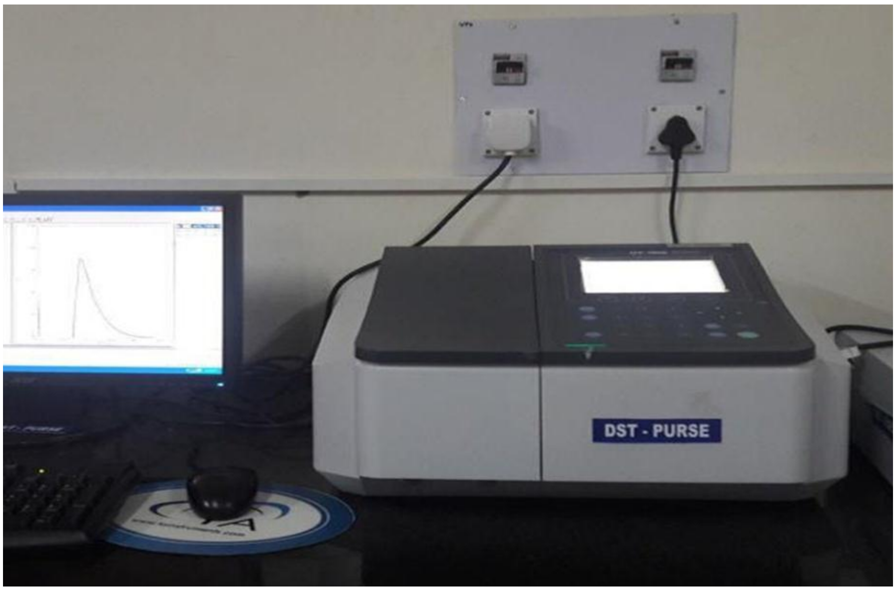
$$\sigma = \frac{\alpha n c}{4\pi} \tag{2-11}$$

Where (σ) is the optical conductivity, (α) is the absorption coefficient, (n) is real part of refractive index and (c) is the velocity of the light in vacuum

CHAPTER THREE: EXPERIMENTAL PART

3.1 Introduction

This chapter includes the stages of sample preparation of (PVA-PEG-MnO_2) nanocomposites, samples tests and measurements by ultraviolet–visible spectroscopy as shown in Figure (3-1).



Figure(3-1). UV–Visible Spectrophotometer (Shimadzu -1800).

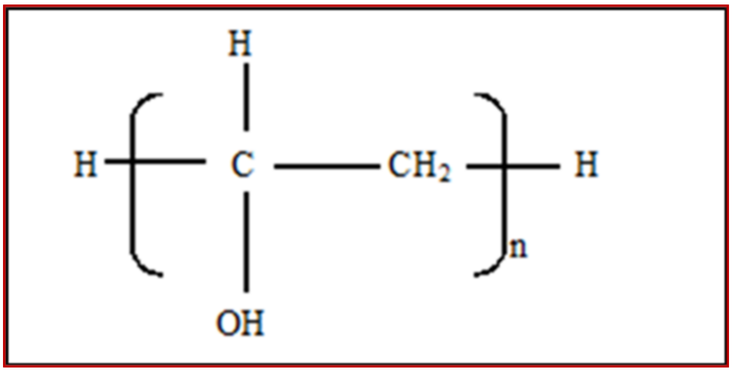
3.2 The Materials Used in This Work

3.2.1 Polymers

Two polymers were used in this work:

A) Polyvinyl alcohol (PVA)

used as powder form and could be obtained from local markets with high purity (99.8%). PVA is one of the earliest and best known polymers, with the formula $(C2H4O)_n$, as shown in Figure (3-2). It was seen to use in a variety of applications and is currently used extensively in semiconductors applications [52].



Figure(3-2). Chemical Structure of PVA [52].

Poly (vinyl alcohol) is a water-soluble synthetic polymer and is an odorless, translucent, tasteless, white or cream colored granular powder, because with the existence of many hydroxyls, PVA is easily soluble in water and soluble in hydroxyl-contained organic compounds. The prominent properties of poly (vinyl alcohol) are its biodegradability in the milieu and biocompatibility. Poly (vinyl alcohol) has high tensile strength and flexibility, high oxygen and aroma barrier property. It also has admirable film forming, blending and adhesive properties [53].The transmission for visible light is very high. Polymeric composites of PVA are known for their importance in technical applications [54]. PVA has unique properties, good chemical stability, eco-friendly, optical and electrical properties. The significant feature of polyvinyl alcohol its semi crystalline nature which is the presence of both amorphous and crystalline regions causing interfacial effects which increases the physical properties [55].

Table (3-1) : Physical and chemical properties of polyvinyl alcohol (PVA)[56].

Property	Description
Appearance	White to ivory white granular powder
Molecular formula	$(C_2H_4O)n$
Density	1.3 g/cm^3
Solution PH	5- 6.5
Refractive index	1.55
Glass transition temperature (T_g)	85 ^oC
Melting temperature (T_m)	230 °C

B) Polyethylene glycol (PEG)

It was obtained as powder form and could be obtained from local markets with high purity (99.8%). The chemical formula is [H (OCH2CH2)n OH]. Chemical name is [a hydro-o-hydroxypoly (oxy-1,2-ethanediyl)].

Solubility in all grades of polyethylene glycol are soluble in water and miscible in all proportions with other polyethylene glycols (after melting, if necessary). Aqueous solutions of higher molecular-weight grades may form gels. Liquid polyethylene glycols are soluble in acetone, alcohols, benzene, glycerin, and glycols. Solid polyethylene glycols are soluble in acetone, dichloromethane, ethanol (95%), and methanol; they are slightly soluble in aliphatic hydrocarbons and ether, but insoluble in fats, fixed oils, and mineral oil. PEG is used to make emulsifying agents and detergents, and as plasticizers, humectants, and water-soluble textile lubricants. The wide range of chain lengths provides identical physical and chemical properties. Figure (3-3) shows the chemical structure of Polyethylene glycol[57].

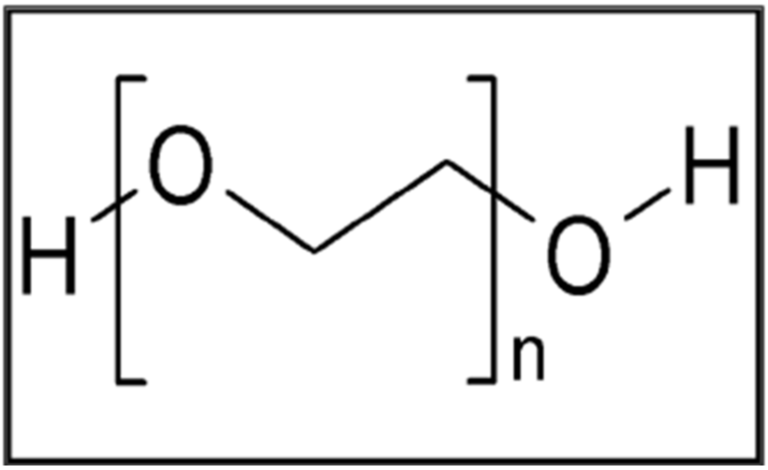


Figure (3-3) The Chemical Structure of PEG [57].

It is widely used in a variety of pharmaceutical formulations including parenteral, topical, ophthalmic, oral and rectal preparations. Polyethylene glycol has been used experimentally in biodegradable polymeric matrices used in controlled-release systems.

PEG or polyethylene glycols are used in great variety of applications because of their chemical structure, their low toxicity, their solubility in water and their lubricating properties.

They provide flexibility in choosing properties to meet the requirements of many different applications. In the rubber industry, they serve as heat transfer agents, mold release agents, rubber compounders, lubricants, and pigment carriers [58]. Table (3-2) shows the physical properties of PEG.

Table (3-2): Physical Properties of (PEG) [58].

Physical properties	Units	Result
Molecular weight	g/mol	4000
Solution PH	-------	4.5-7.5
Viscosity at 99 °C	mm^2/s	110-158
Viscosity at 25 °C	mm^2/s	Solid at specified temp.
Melting point	°C	50-58
Density	gm/cm^3	1.09
Refractive Index at 25 °C		1.456
Solubility in Water % by weight	-------	50
Surface Tension at 25 °C	N/m	Solid at specified temp.
Glass transition temperature T_g	°C	53-55
Liquid specific heat at 30-60 °C	$KJ/(kg.K)$	2.25
Coefficient of thermal expansion at 20 °C	$°C^{-1}$	Solid at specified temp.
Thermal conductivity at 26 °C	$W/m.K$	Solid at specified temp.

3.2.2 Metal Oxide Nanoparticles

Manganese dioxide nanoparticles (MnO_2)

It was obtained as powder from Nano Shel USA company with size ($30nm$) and high purity (99.9%). Manganese oxide nanoparticles have been also widely used for dye removal due to the effect of the chemical and physical interactions which occur between the organic (polymer) and inorganic (manganese dioxide nanoparticles) components. Manganese dioxide nanoparticles material is not only nontoxic but also has highly active and strong oxidations because the oxidation number of Mn is +4. In addition, manganese oxide nanoparticles have been used as adsorbents and catalytic materials . Hence, most research focus on investigating the ability of Fenton catalytic oxidation of manganese oxide, especially manganese dioxide (MnO_2), for degradation of dye molecules[59].

3.3 Preparation of (PVA-PEG-MnO_2) Nanocomposite

The nanocomposite of (PVA-PEG-MnO_2) is prepared by dissolving 0.5 gm. of polymers in 15 ml of distilled water with different concentrations, which are 80 wt.% PVA, 20 wt.% PEG by using magnetic stirrer to mix the polymers for 1 hour to obtain more homogeneous solution. The MnO_2 nanoparticles are added to polymers mixture with different concentrations are (0, 1.8, 3.6 and 5.4) wt. % as shown in table (3-3). The casting method is used to prepare the samples of (PVA-PEG-MnO_2) nanocomposite in the template (petri dish has diameter10 cm). The sample was prepared with thickness range (130) µm.

Table (3-3) : Illustrate samples no. and (PVA-PEG- MnO_2) nanocomposites

Sample No.	PVA (gm.)	PEG (gm.)	MnO_2 (gm.)
0	0.4	0.1	0
1	0.3928	0.0982	0.009
2	0.3856	0.0964	0.018
3	0.3784	0.0946	0.02

3.4 The Optical Properties of(PVA-PEG-MnO_2)Nanocomposite

The optical properties of (PVA-PEG-MnO_2) Nanocomposite include: the absorbance, transmittance, absorption coefficient, energy band gap, extinction coefficient, reflection index, dielectric constants, and optical conductivity. The optical properties of (PVA-PEG- MnO_2) nanocomposite are measured by using the double beam spectrophotometer (shimadzu, UV-18000A) in wavelength (200-800) nm.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Introduction

This chapter includes the results and discussion of the structural, optical measurements for (PVA-PEG-MnO_2) nanocomposite. The effect of addition the MnO_2 nanoparticles on optical properties of (PVA-PEG) blend well be discussed in this chapter. The absorbance and transmittance; the absorption coefficient and energy band gap; the extinction coefficient and refractive index; the real and imaginary parts of dielectric constant; and the optical conductivity for (PVA-PEG-MnO_2) nanocomposite were also investigated.

4.2 The Absorbance and Transmittance of (PVA-PEG-MnO_2) Nanocomposite

Figure (4-1) shows the variation of absorbance for (PVA-PEG-MnO_2) nanocomposite with wavelength of the incident light.

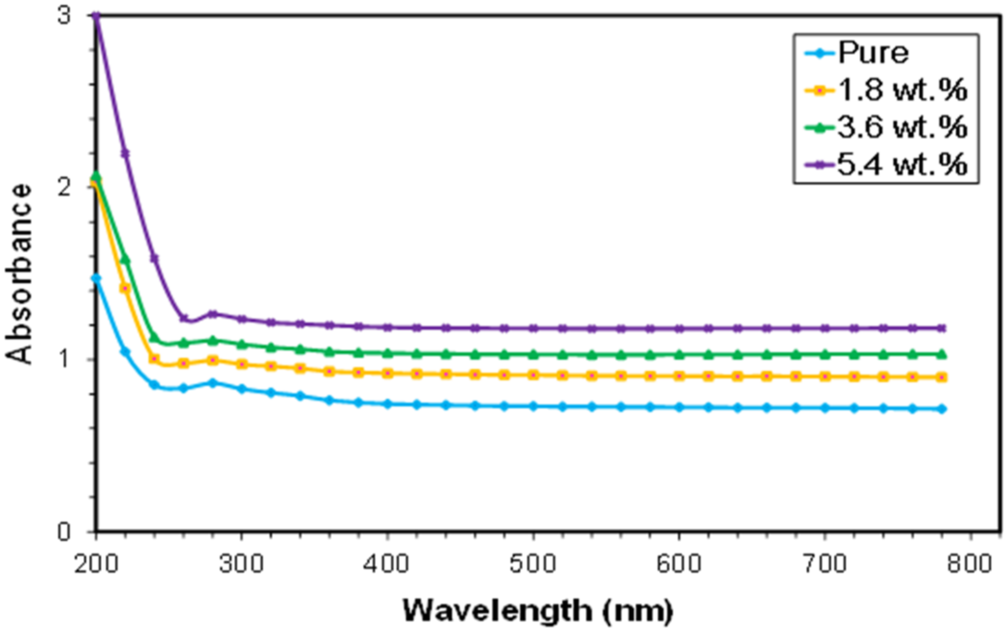


Figure (4-1) Variation of absorbance for (PVA-PEG-MnO_2) nanocomposite with wavelength.

The figure shows that there was an increasing in the absorption for all samples of nanocomposite at UV region; this is due to the excitations of donor level electrons to the conduction band at these energies. The high absorbance of the sample for nanocomposite at UV region attributed to the energy of photon enough to interact with atoms; the electron excites from a lower to higher energy level by absorbing a photon of known energy. The changes in the absorbed and transmitted radiation can refer to the types of possible electron transitions. Fundamental absorption of absorbance spectra refers to band to band or excitation transition [60]. At visible and near infrared regions, the absorbance of all samples for nanocomposites has low values, this behavior attributed to the energy of incident photons doesn't enough energy to interact with atoms, thus the photons will be transmitted when the wavelength increases [61], Hence the transmittance increases for all nanocomposites as shown in Figure (4-2) which show that the variation of the transmittance for (PVA-PEG-MnO_2) nanocomposite with wavelength of the incident light.

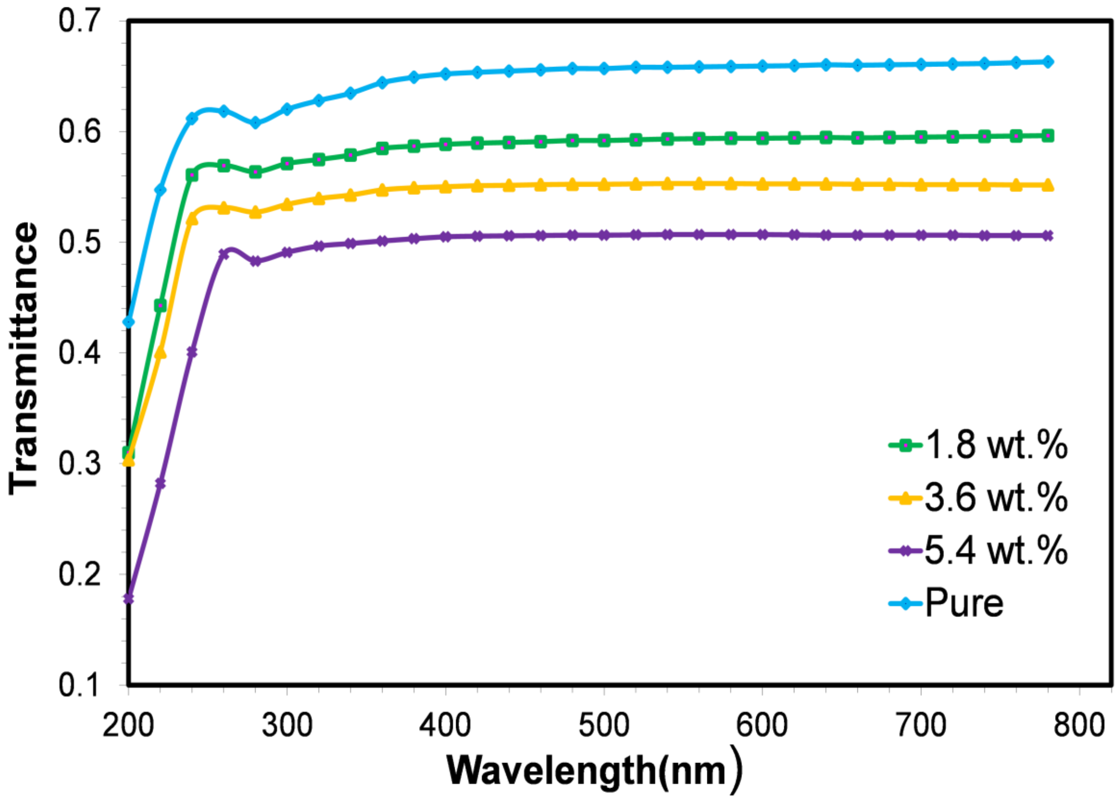


Figure (4-2) Variation of transmittance for (PVA-PEG-MnO_2) nanocomposite with wavelength.

As shown in figures, the absorbance increases and the transmittance decreases with the increasing of the concentrations for MnO_2 nanoparticles, this is due to the agglomeration of nanoparticles with increasing concentration and increase of the number of charge carriers [62]. The ($PVA-PEG-MnO_2$) nanoparticles have highest absorbance which attributed to the high diffusivity of Manganese dioxide nanoparticles in (PVA-PEG) blend. This behavior consistent with the results of researcher.

4.3 The Absorption Coefficient and Energy Band Gap of ($PVA-PEG-MnO_2$) Nanocomposite

The absorption coefficient of nanocomposite is calculated by using Equation (2-1). Figures (4-3)-(4-5) show the variation of absorption coefficient for ($PVA-PEG-MnO_2$) nanocomposite as a function of photon energy of the incident light.

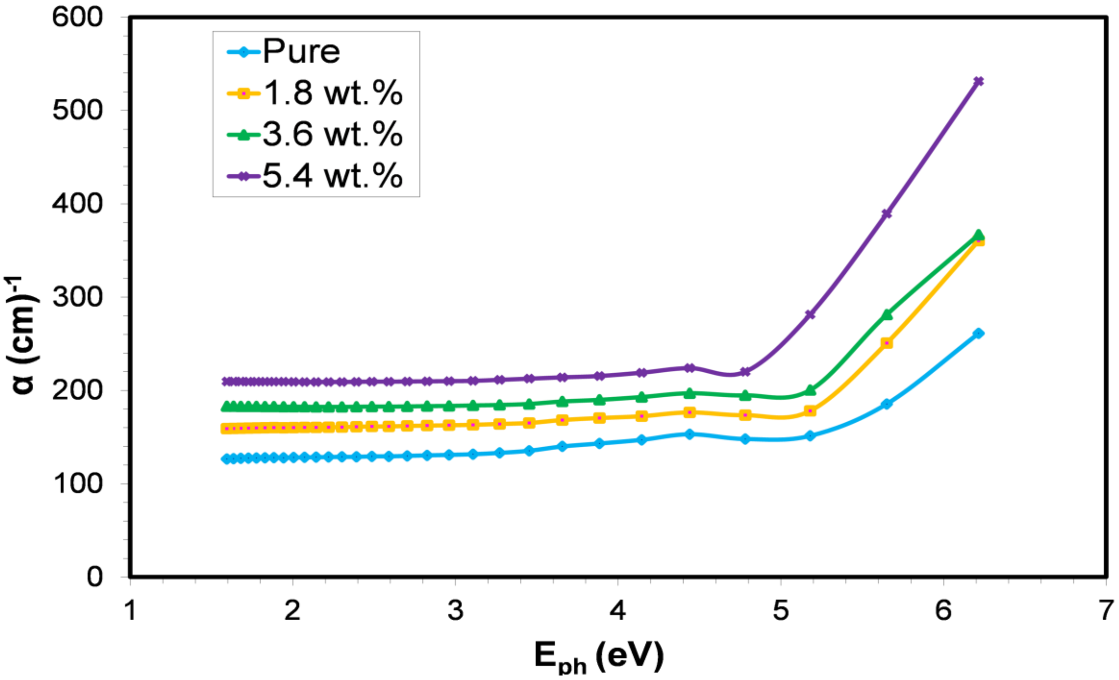


Figure (4-3) Variation of absorption coefficient (α) for ($PVA-PEG-MnO_2$) nanocomposite with photon energy.

As shown in the figures, the absorption coefficient of the samples for nanocomposite is high at high energy. This means that the electron transition has high possibility. In other words, the energy of incident photon is enough to transit the electron from the valence band to the conduction band which due to the energy of the incident photon is greater than the energy band gap. The absorption coefficient assists to know the nature of electron transition. When the values of the absorption coefficient of material are high $(\alpha > 10^4) cm^{-1}$, it is expected that direct transition of electron. While, when the values of the absorption coefficient of material are low $(\alpha < 10^4) cm^{-1}$, it is expected that indirect transition of electron. The value of absorption coefficient of (PVA-PEG-MnO_2) nanocomposite is low $(\alpha < 10^4) cm^{-1}$; the transition of electron is indirect. The absorption coefficient of nanocomposites increases with the increasing of the concentration of nanoparticles; this is attributed to the increasing of number of charge carriers, hence, increase the absorbance and absorption coefficient for (PVA-PEG-MnO_2) nanocomposite[63]. The energy band gap of nanocomposite is calculated by using Equation (2-2). The energy gap for allowed indirect transitions of (PVA-PEG-MnO_2) nanocomposite is shown in the Figure (4-4).

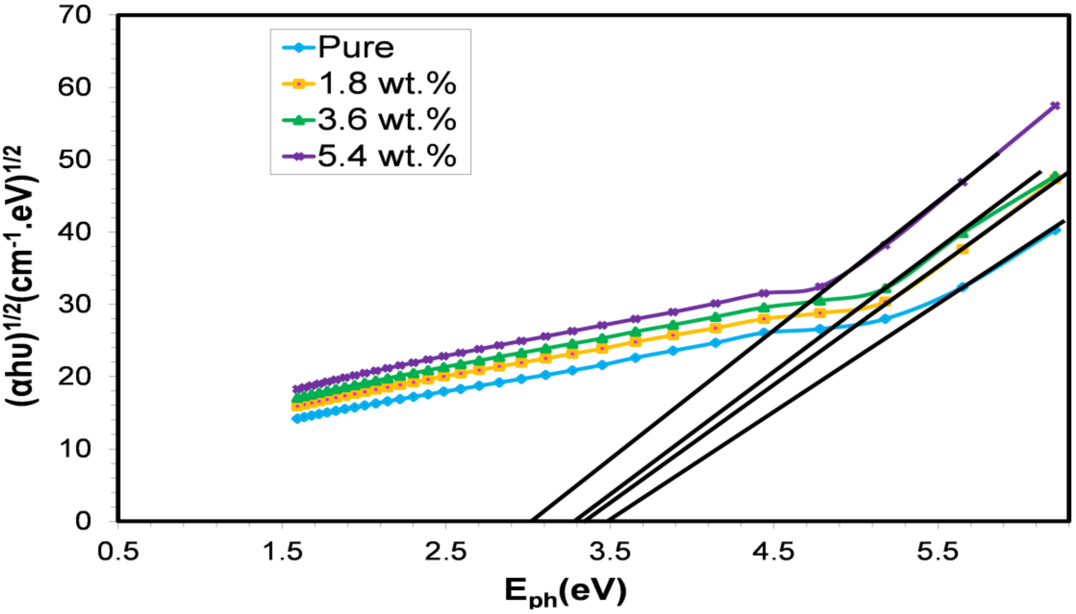


Figure (4-4) Variation of $(\alpha hv)^{\frac{1}{2}}$ for (PVA-PEG-MnO_2) nanocomposite with photon energy.

The energy gap for forbidden indirect transitions of (PVA-PEG-MnO_2) nanocomposite is shown in Figure (4-5).

As is shown in the figures, the energy gap for allowed and forbidden indirect transitions of nanocomposite is decreased with the increasing of the MnO_2 nanoparticles concentration, this behavior is due to the creation of levels in the energy gap; the transition of electron in this case is conducted in two stages that involve the transition from the valence band to the local levels in energy gap and to the conduction band as a result of increasing the MnO_2 nanoparticles concentration; the electronic conduction depends on nanoparticles concentration [64, 65].

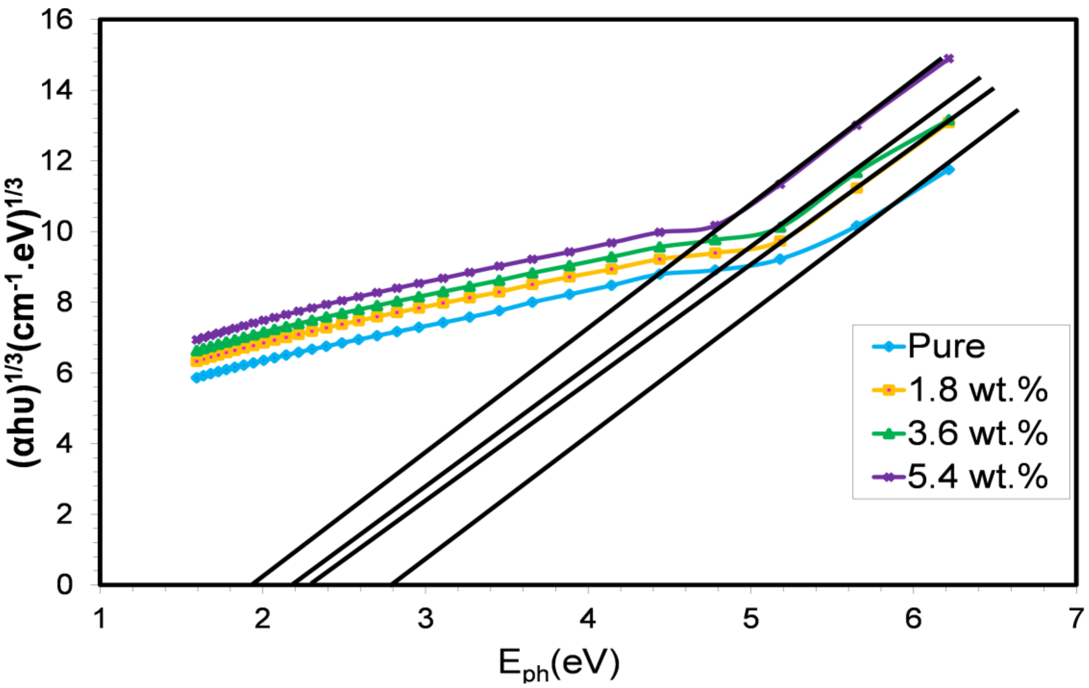


Figure (4-5) Variation of $(\alpha h\nu)^{\frac{1}{3}}$ for (PVA-PEG-MnO_2) nanocomposite with photon energy.

4.4 The Extinction Coefficient and Refractive Index of ($PVA-PEG-MnO_2$) Nanocomposites

The extinction coefficient is calculated by using Equation (2-6). Figures (4-6) shows the variation of extinction coefficient for ($PVA-PEG-MnO_2$) nanocomposite as a function of wavelength. The figure shows that the extinction coefficient of nanocomposite increases with the increasing of the MnO_2 nanoparticles concentration; this is due to the increase in optical absorption and photons dispersion in the (PVA-PEG) polymer matrix [66]. The extinction coefficient of nanocomposite has high value at UV region, this behavior attributed to high absorbance of the sample of nanocomposite. Also, extinction coefficient of nanocomposite increases with the increasing of the wavelength at visible and near infrared regions which attributed to the absorption coefficient of nanocomposite is approximately constant at visible and near infrared region, hence, the extinction coefficient increases with the increasing of the wavelength according to Equation (2-6) [67].

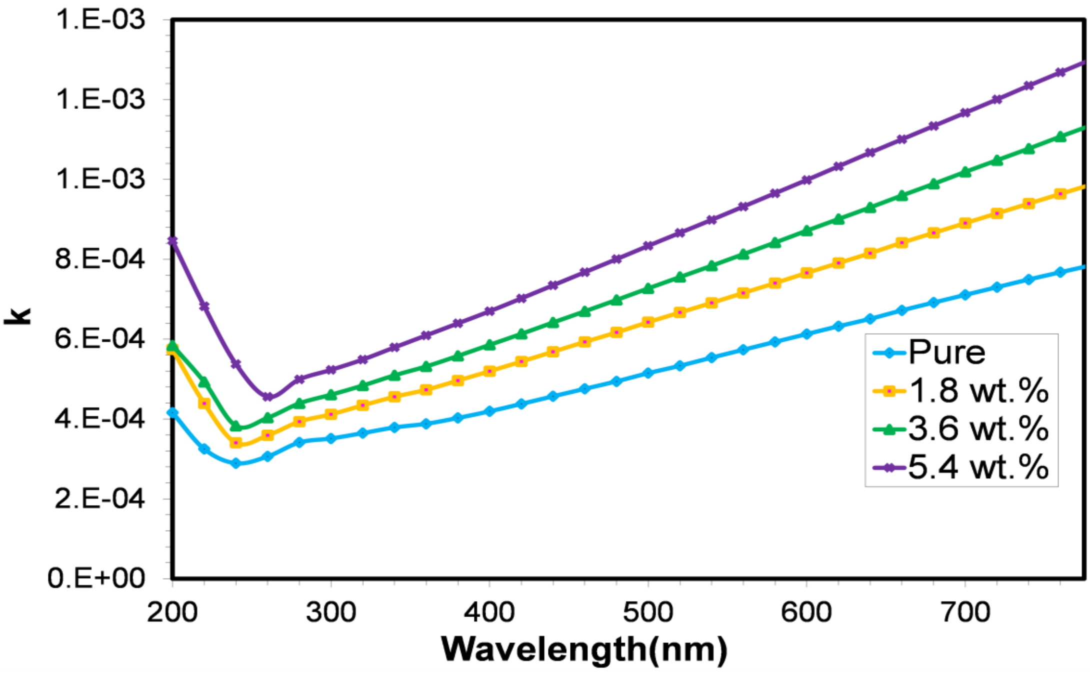


Figure (4-6) Variation of extinction coefficient for ($PVA-PEG-MnO_2$) nanocomposite with wavelength.

The refractive index is calculated by using Equation (2-7). The refractive index of (PVA- PEG-MnO_2) nanocomposite as a function of wavelength is shown in Figure (4-7). As shown in the figure, the refractive index of nanocomposite increases with the increasing of the MnO_2 nanoparticles concentration; it is decreased with the increase of the wavelength. This behavior attributed to the increase of the density of nanocomposite. When the incident light interacts with a sample has high refractivity at UV region, hence, the values of refractive index will be increased [68,69].

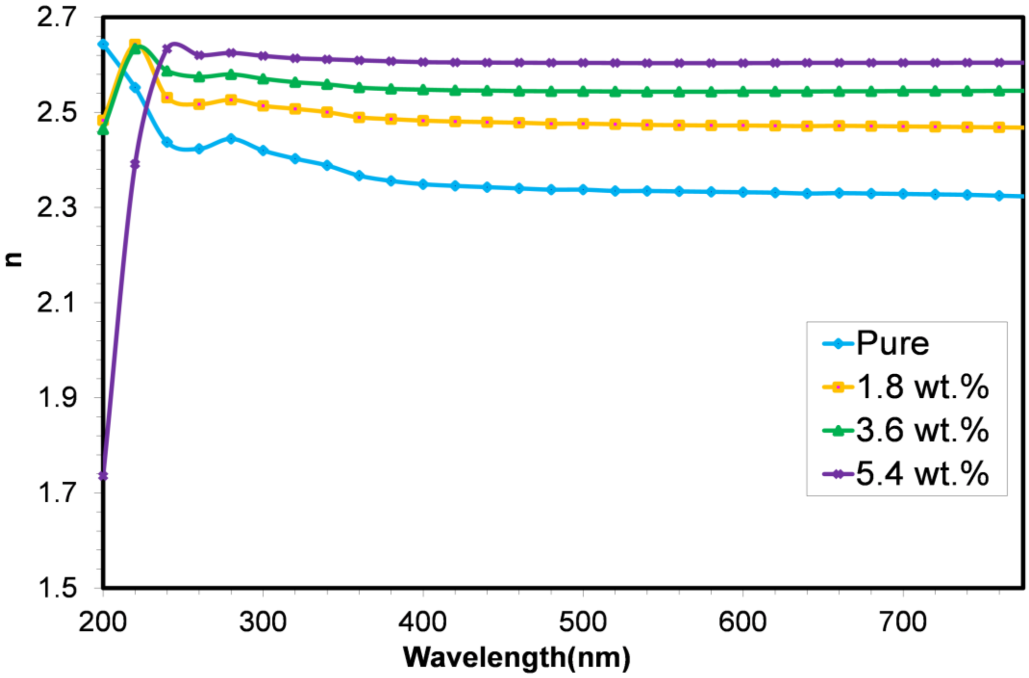


Figure (4-7) Variation of refractive index for (PVA-PEG-MnO_2) nanocomposite with wavelength.

4.5 The Real and Imaginary Parts of Dielectric Constant of (PVA-PEG-MnO_2) Nanocomposite

The real and imaginary parts of dielectric constant are calculated by using Equations (2-9) and (2-10) respectively. Figure (4-8) shows the variation of the real dielectric constant with the wavelength for (PVA- PEG-MnO_2) nanocomposite as a function of wavelength. The effect of MnO_2

nanoparticles on the imaginary part of dielectric constant is shown in Figure (4-9) for (PVA-PEG-MnO_2) nanocomposite. The figure show that the real and imaginary parts of dielectric constant of (PVA-PEG) blend are increased with the increasing of MnO_2 nanoparticles concentration, this behavior attributed to the increase of electrical polarization due to contribution of nanoparticles concentration in the sample i.e., the increase in the dielectric constant of (PVA-PEG) blend represents a fractional increase in charges within the polymers [70]. As shown in the figure, the real and imaginary parts of dielectric constant of (PVA-PEG) blend are changed with the wavelength, this is due to the real part of dielectric constant depends on refractive index because the effect of extinction coefficient is very small and the imaginary part of dielectric constant depends on extinction coefficient especially in the visible and near infrared regions of wavelength where the refractive index is approximately constant while extinction coefficient increases with the increase of the wavelength [71].

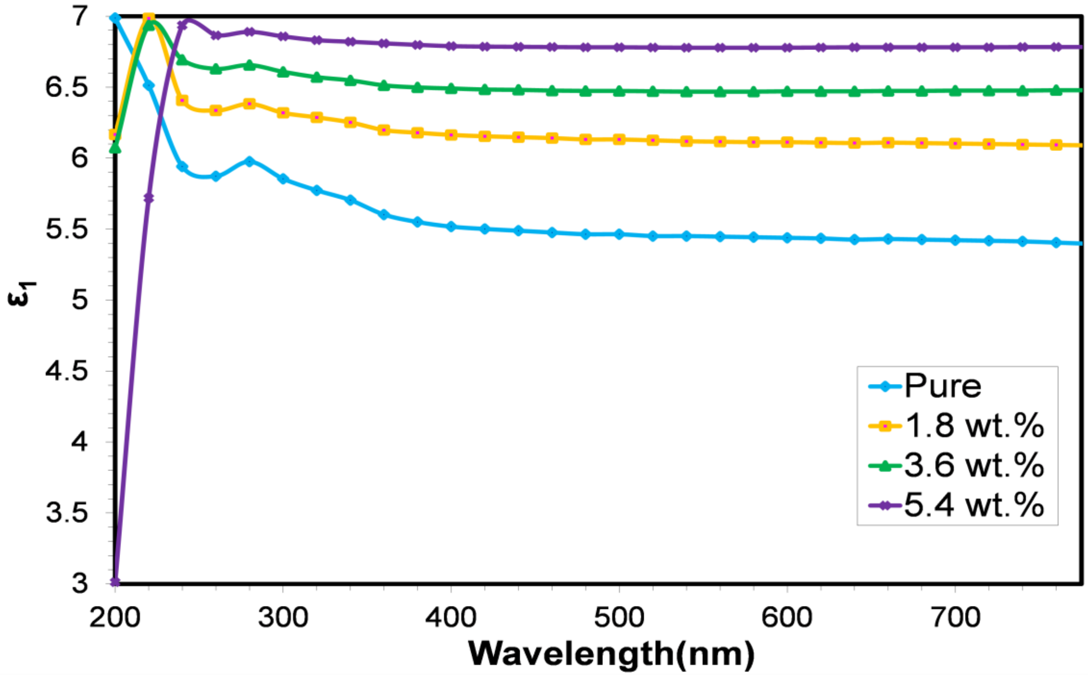


Figure (4-8) Variation of real part of dielectric constant for (PVA-PEG-MnO_2) nanocomposite with wavelength.

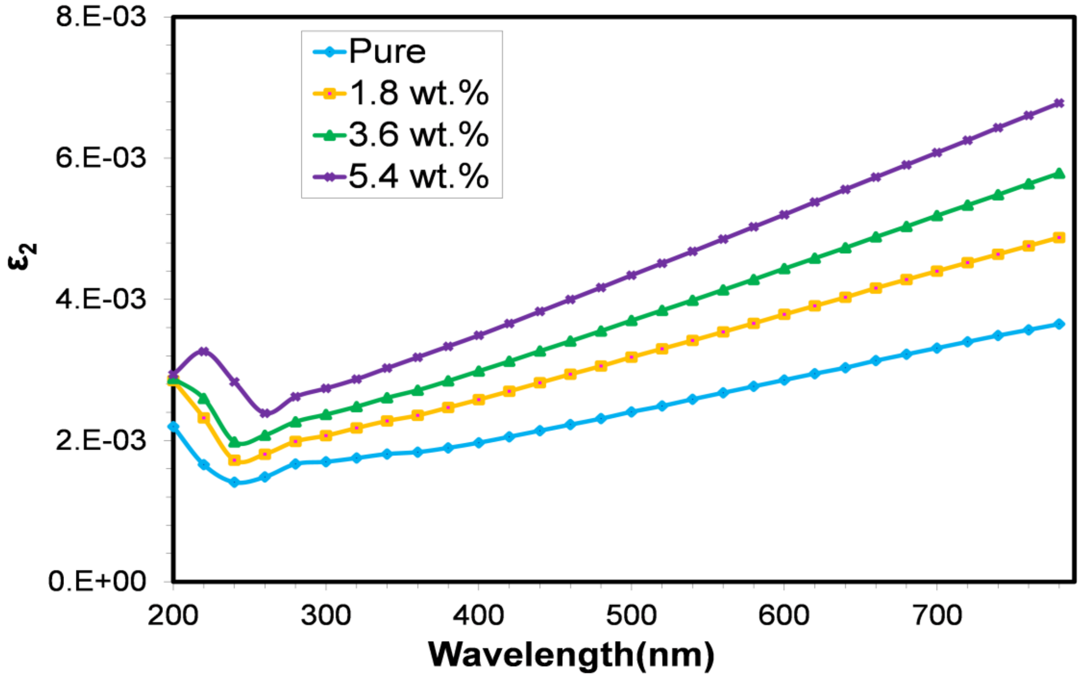


Figure (4-9) Variation of imaginary part of dielectric constant for (PVA-PEG-MnO_2) nanocomposite with wavelength.

4.6 The Optical Conductivity of (PVA-PEG-MnO_2) Nanocomposite

A Figure (4-10) shows the variation of optical conductivity with the wavelength for (PVA- PEG-MnO_2) nanocomposites that calculated by using Equations (2-11). The figure show that the optical conductivity of the sample of nanocomposite are decreased with the increasing of the wavelength, this behavior attributed to the optical conductivity depends strongly on the wavelength of the radiation incident on the sample of nanocomposite; the increase of optical conductivity at low wavelength of photon is due to high absorbance of all samples of nanocomposites in that region, hence, increase of the charge transfer excitations. The optical conductivity spectra indicated that the samples are transmittance within the visible and near infrared regions [72]. Also, the optical conductivity of nanocomposite is increased with the increase MnO_2 nanoparticle concentration, this behavior related to the creation of localized levels in the energy gap; the increase of MnO_2 nanoparticle concentration increasing the density of localized stages in the band structure, hence, increase of the absorption coefficient consequently increasing the optical conductivity of (PVA- PEG-MnO_2) nanocomposite [73].

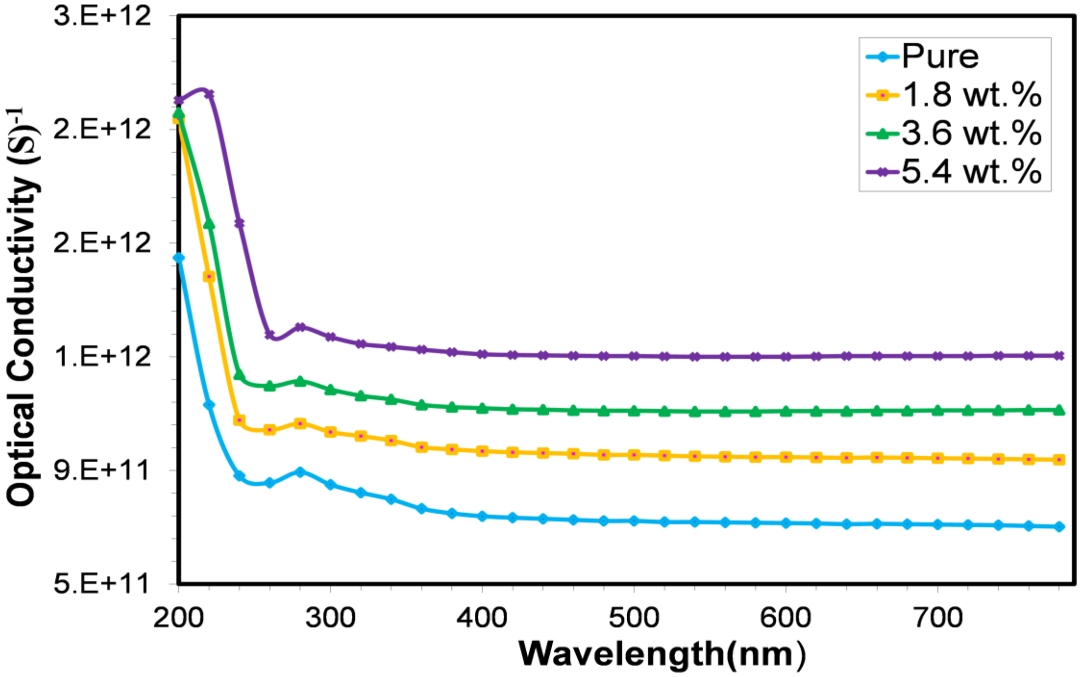


Figure (4-10). Variation of optical conductivity for (PVA-PEG-MnO_2) nanocomposite with wavelength.

CHAPTER FIVE: CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

1. The absorbance, absorption coefficient, extinction coefficient, refractive index, real and imaginary dielectric constants of (PVA-PEG) blend are increase with increasing the MnO_2 nanoparticle concentrations which make it can be used in different photonics and electronics applications
2. The transmittance and energy band gap are decreased with increasing the MnO_2 nanoparticle concentration.
3. The (PVA-PEG-MnO_2) nanocomposites have high absorbance in the UV region.

5.2 Future work

1. Studying the effect of MnO_2 nanoparticles on the thermal conductivity of (PVA-PEG) blend.
2. Study of mechanical properties of (PVA-PEG- MnO_2) nanocomposite.
3. Studying the effect of gamma irradiation on the optical and electrical properties of (PVA-PEG- MnO_2) nanocomposite.
4. Studying the effect of temperature on the dielectric properties of (PVA-PEG- MnO_2) nanocomposite.
5. Effect of MnO_2 nanoparticles on the glass transition temperature of (PVA-PEG) blend.

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الخلاصة

تتضمن هذه الدراسة تأثير إضافة جزيئات ثنائي اوكسيد المنغنيز النانوية على الخواص البصرية لخليط بولي فينيل الكحول (PVA) و بولي إيثيلين جلايكول(PEG) حيث حضرت عينات المتراكب النانوي بإضافة نسب من جسيمات ثنائي أوكسيد المنغنيز النانوية (MnO_2) بنسب وزنية مقدارها (٠ ، ١.٨ ، ٣.٦ ، ٥.٤) إلى خليط (PVA-PEG) وان أغشية المتراكب النانوي قد تم تحضيرها بطريقة الصب و تم تسجيل طيف الامتصاص في نطاق طول موجي (٢٠٠ - ٨٠٠) نانومتر بعد ذلك تم تحديد الثوابت البصرية (معامل الامتصاص ، معامل الخمود) فجوة الطاقة للانتقال غير المباشر المسموح به والممنوع ، وثوابت العزل الحقيقية والخيالية فوجد ان الثوابت البصرية تزداد بزيادة تركيز الجسيمات النانوية (MnO_2) وان فجوة الطاقة تقلصت مع زيادة النسب المئوية لوزن جسيمات MnO_2 النانوية.

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وزارة التعليم العالي والبحث العلمي
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تاثير اضافة اوكسيد المنغنيز على الخصائص البصرية لخليط بوليميري

بحث مقدم الى كلية التربية للعلوم الصرفة بجامعة بابل
كجزء من متطلبات درجة الدبلوم العالي تربية/ فيزياء المواد وتطبيقاتها

من قبل

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