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The Effect of $BaTiO_3$ Nanoparticles on Some Physical Properties of PEG for Antibacterial Application

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بسم الله الرحمن الرحيم

وَمَآ أُوتِيتُم مِّنَ ٱلۡعِلۡمِ إِلَّا قَلِيلا

صدق الله العلي العظيم

سورة الاسراء : الآية٨٥

Supervisor certification

I certify that this thesis is titled (**The Effect of $BaTiO_3$ Nanoparticles on Some Physical Properties of PEG for Antibacterial Application**) was prepared by (**Walaa Sabah Abd-alsada Minse**) under my Supervision at Department of physics, College of Science, University of Babylon as a partial fulfillment of the requirements for practical degree of physics Master thesis in (Solid State Physics).

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DEDICATION

Everything I am, or ever will be, I owe it to my mother.

To my biggest supporter, who keeps saying "I am proud of you" in my failures before my successes. To my father.

To the flower of my life, my husband and daughter, as soon as I see them, my determination to achieve my dream increases so that they can be proud of me.

To my sisters and brother.

To my friends.

Dedication this humble effort.

Walaa

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Summary

In this study, solutions of (PEG-$BaTiO_3$) were prepared as: 2g amount of PEG was dissolved in distilled water (50) ml as a solvent with stirring about (3) min at room temperature until a homogenous viscous liquid solution was formed. The nanoparticle material ($BaTiO_3$) added to the blend solution with weight percent of (0, 2, 4, 6) % and leave it on the stirring for a period of 5 minutes at a room temperature The resulting homogeneous solutions (PEG-$BaTiO_3$) were casted onto a clean glass plate and then transfer it with placed on a flat surface at room temperature for 48 hours to dry.

Structural properties of the thin- film have been studied by Scanning Electron Microscope (SEM), Optical Microscope OM and Fourier Transform Infrared Spectroscopy (FTIR).images of the SEM and OM depict the surface morphology of nanocomposite before and after addition $BaTiO_3$, the pure polymer (PEG) has a good homogeneity for their $BaTiO_3$ and the diffusion of nanoparticles clearly appear in the SEM and OM images, that is mean the nanoparticle clearly diffused in the film. Experimental results for structural properties show that images of (FT-IR) spectra to physical mixture seemed to be only summation PEG spectra and their additions. The results shown that there was no interaction between the PEG and nanoparticle ($BaTiO_3$).

The optical properties of the prepared films and liquid were investigated by obtaining the transmittance spectrums in the UV regions as a function of wavelength from 200 nm to 1100 nm. The values of absorbance, absorption coefficient, extinction coefficient, refractive index, for the liquid and films increasing with the increase of $BaTiO_3$ nanoparticles concentration. While the

transmittance and energy gap decreases with the increase of the $BaTiO_3$ nanoparticles concentration.

Electrical properties including D.C conductivity measurement of the films and molar conductivity of liquid were studied. The results showed that electrical conductivity increases with the increase of the $BaTiO_3$ nanoparticles concentrations, and that the molar conductivity decreasing with the increase of $BaTiO_3$ nanoparticles concentrations.

The results of applications for prepared nanocomposites showed the antibacterial properties of the (PEG -$BaTiO_3$) nanocomposites were tested against gram positive (S. aureus) and gram negative (E. coli). The results showed the inhibition zone was increased with increase the $BaTiO_3$ nanoparticles concentration .

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List of Symbols

Symbol	***Physical meaning***
A	Absorbance
T_r	Transmittance
α	Absorption Coefficient
N	Refractive index
D	Average Crystallite Size
C	Speed of light in vacuum 2.998×10^8m/s
T	Thickness of the film
V	Speed of light in medium
E_g	Energy Gap
K_n	Extinction coefficient
R	Reflectance

I_A	Incident intensity of light
I	Incident intensity of light
k_o	Extinction Coefficient
K	Wave Vector
k_B	Boltzmann’s Constant
λ	Wavelength
M	Molar Concentration
m^*	Effective Mass
M_{wt}	Molecular Weight
η_{red}	Reduced viscosity
η_{sp}	Specific viscosity
η_{rel}	Relative viscosity
η_s	Shear viscosity
η_0	Viscosity of the solvent
C	Concentration
C_m	Molar concentration
R	Reflectance
R_e	Resistance of the Film
T	Absolute Temperature
t_o	Initial Time
t_1	Final Time
T_{sub}	Substrate Temperature
υ	Frequency
Λ	Molar conductivity
H	Planck constant
μ	Mobility

μ_p	Hole Mobility
μ_n	Electron Mobility
σ	Electrical Conductivity
σ_{op}	Optical Conductivity
$\sigma_{d.c}$	D.C. Conductivity
ρ	Electrical resistivity

List of Abbreviations

Symbol	*Physical meaning*
OM	Optical Microscope
FT-IR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscope
PEG	Polyethylene glycol
$BaTiO_3$	Barium titanate
UV	Ultra Violet Spectrum
VIS	Visible Spectrum
V.B	Valence Band
C.B	Conduction Band

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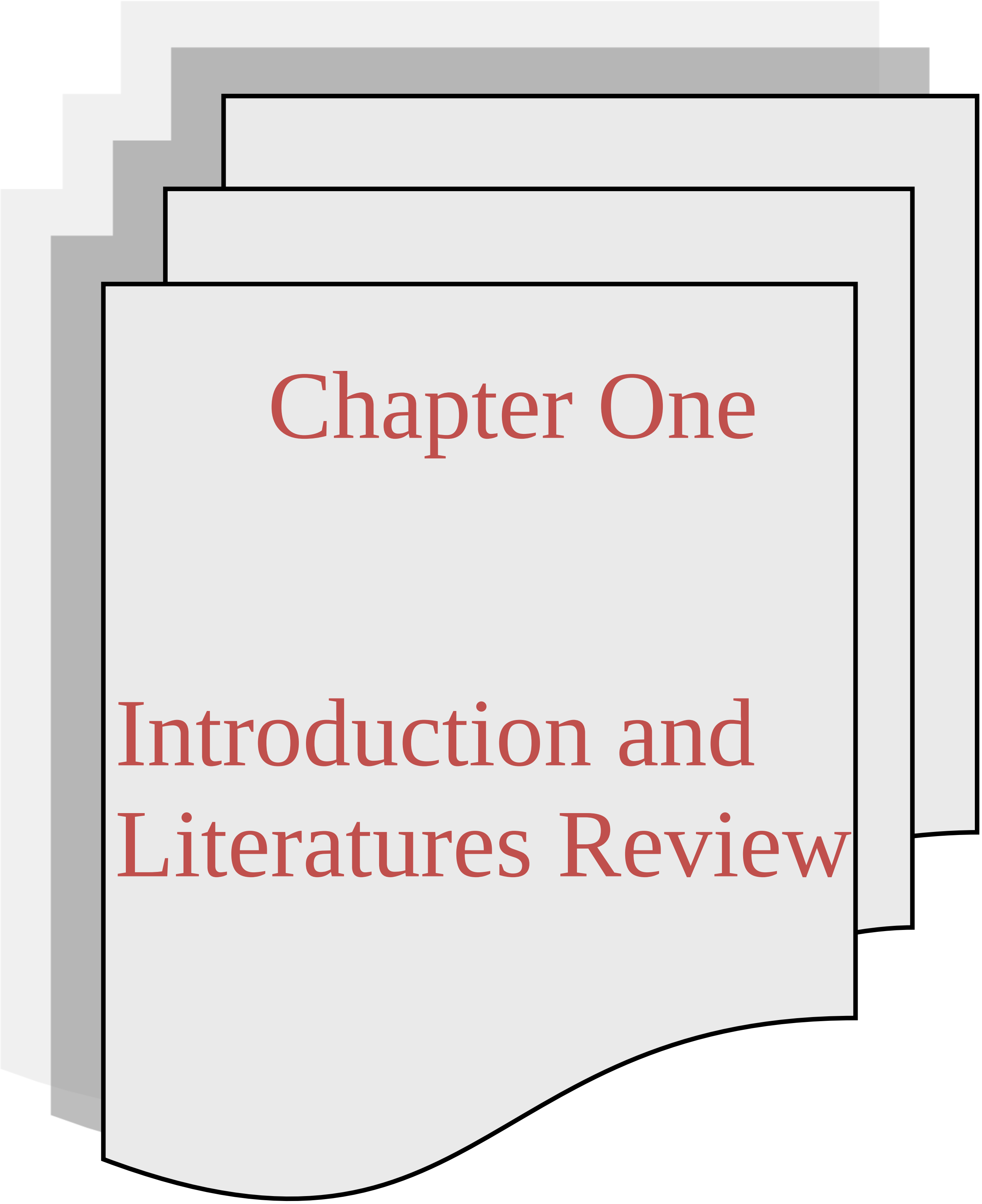


Chapter One

Introduction and Literatures Review

1.1 Introduction

Polymer science was born in the great industrial laboratories of the world of the need to make and understand new kinds of plastics, rubber, adhesives, fibers and coatings. Only much later did polymer science come to academic life. Perhaps because of its origins, polymer science tends to be more interdisciplinary than most sciences, combining chemistry, chemical engineering, materials and other fields as well [1].

Materials classified as (polymers) are a long chain molecules with a repetition of structural units. The structural units are called (monomer), which are connected to each other by covalent bonds. A polymer consists of large organic molecules (macromolecules) of repeating small structural units monomers connected together in a process called polymerization. Each molecule is composed of thousands of atoms connected by covalent chemical bonds. Molecules in a polymer attract each other by forces that depend on the type of the polymer [2, 3].

Polymers are widely used in electrical and electronic applications. In early works, polymers have been used as insulators because of their high resistivity and dielectric properties. Polymer-based insulators are used in electrical equipment to separate electrical conductors without passing current through themselves. The insulator applications of polymers include printed circuit boards, wire encapsulates, corrosion protective electronic devices, and cable sheathing materials. [4, 5].

Polymers possess many characteristics such as low cost, easy configuration, high resistance, flexibility, in addition to the mechanical properties of things, so it is used in electronic devices industry [6].

Nanomaterials can be defined as materials possessing, at minimum, one external dimension measuring 1-100nm and can be classified according to dimensions into; three dimensions as nanoparticles and nanoshells, two dimensions as nanotube nanofibers, and nanowire, as well as one dimensions as thin films and layers [7].

The definition given by the European Commission states that the particle size of at least half of the particles in the number size distribution must measure 100nm or below [8,9].

1.2 Nanocomposites

Nanocomposites are multiphase materials, where one of the components has nanoscale additives [10]. The addition of inorganic nanoparticles into a polymer matrix will change both properties from inorganic nanoparticles and polymer to be enhanced and hence advanced new functions can be generated to the nanocomposites [11,12].Composite Materials means the group of engineering materials produced by adding certain weight or volume ratios of one or more materials.

Reinforcement Materials for Base Material (Matrix Material) So that the supporting materials are well combined and mixed with the mold material which ensures a homogeneous overlap in which the particles of the supporting materials are ideally distributed. The purpose of producing overlapping materials is to add certain properties to the mold material or to add traits that were not inherent to it[13].

The nanocomposites applications are quite promising in the fields of microelectronic packaging, medicine, optical integrated circuits, drug delivery, sensors, packaging materials, coatings and adhesive [14].These advanced nanocomposites have many advantages such as low cost production and the possibility of device fabrication on large scale and flexible substrates[15].

1.3 Classification of Polymers

The Polymers is classified into several different ways based on some special considerations like structure, origin, polymerization, etc. Showed in Figure 1.1 [16].

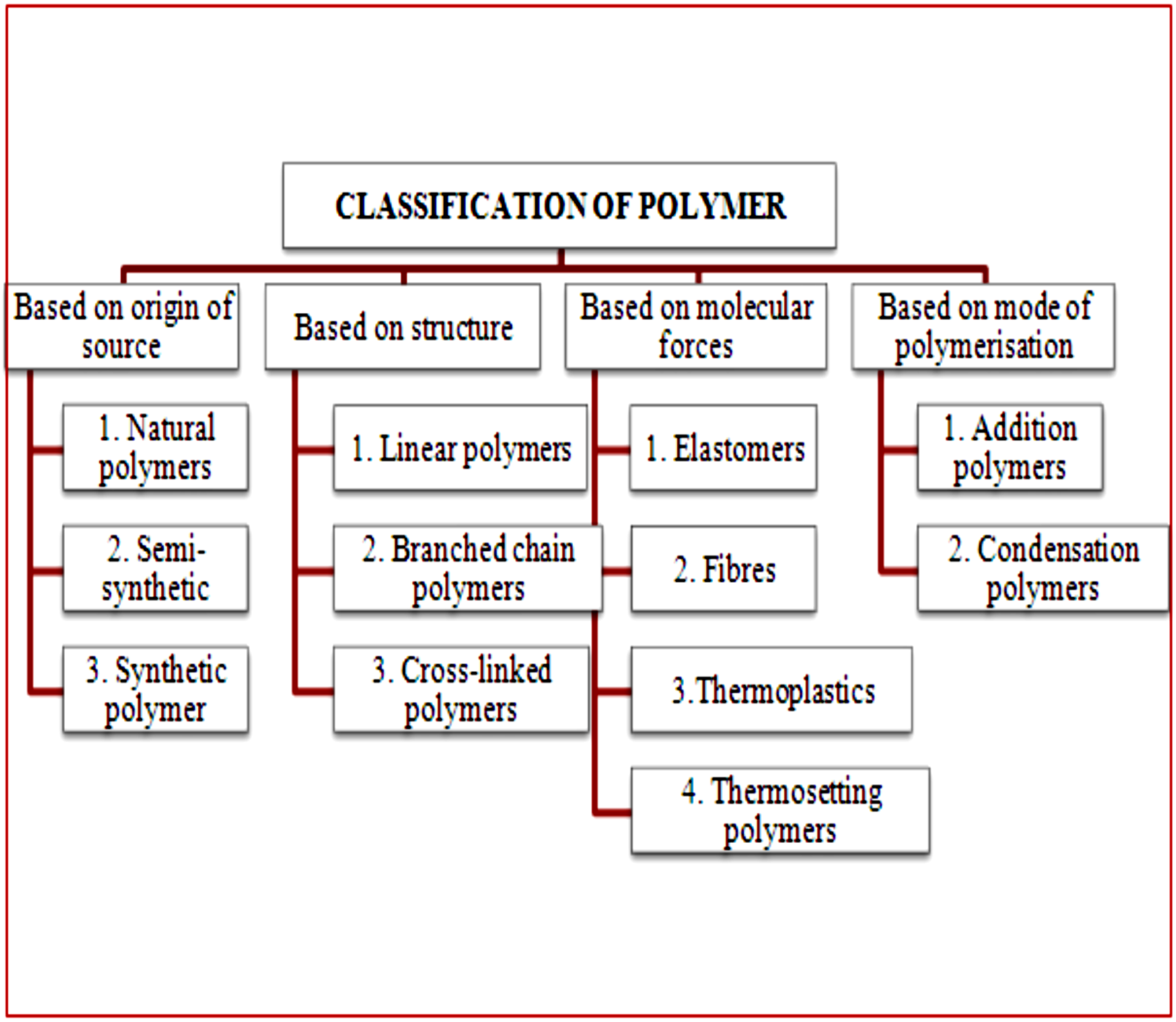


Figure 1.1 diagram of Polymers Classification.

1.3.1 Classification Based on Source

Based on sources of polymers they classified into three types [17].

a - Natural Polymers:

The polymers, which occur in nature are called natural polymer also known as biopolymers. Examples of such polymers are natural rubber, natural silk, cellulose, proteins.

b – Semi synthetic Polymers

They are the chemically modified natural polymers such as hydrogenated natural rubber, cellulosic, cellulose nitrate, methyl cellulose, etc.

c – Synthetic polymer

The polymer which has been synthesized in the laboratory is known as synthetic polymer. These are also known as manmade polymers. Examples of such polymers are polyvinyl alcohol, polyethylene, polystyrene, polysulfone, etc.

1.3.2 Classification Based on the Structure to Polymers:

The Polymers classified depending on the structural composition to [18].

a- Linear Polymers

In these polymers, monomers are linked with each other and form a long straight chain, these chains has not any side chains . For linear polymers, there may be extensive Van der Waals and hydrogen bonding between the chains such as PEG and CMC, their molecules are closely packed and have high density, tensile strength.

b- Branched Polymers

They have a straight long chain with different side chains, Their molecules are irregularly packed hence they have low density, tensile strength and melting point, ex. polypropylene , amylopectin and glycogen.

C- Cross Linked Polymers or (Network polymers)

Those polymers in which two linear chains are joined together by covalent bonds and it have three dimensional, Degree of crosslinking is a number of junction point per unit volume, Polymers crosslinking are hard, rigid .and brittle due to their network structure, Polymers Crosslinked do not dissolve in solvents because all the polymer chains are covalently tied together, but they can absorb solvents, Ex. Bakelite, melamine, formaldehyde resins, vulcanized rubber etc.

1.3.3 Classification Based on Polymerization Process

In this basis have classified in to two types [19].

a - Addition Polymerization

The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds, The polymers formed by the addition of monomers repeatedly without removal of by products are called addition polymers,

b- Condensation Polymerization

The polymers which are formed by the combination of two monomers with the elimination of small molecules such as water, alcohol, hydrogen chlorid etc., are known as condensation polymers.

1.4.4 Classification Based on Molecular Forces

Mechanical properties of polymers such as toughness, tensile strength and Elasticity depended on intermolecular forces like as Van-Der Waals forces and Hydrogen bonding. On the basis of these forces, they are classified into [20, 21].

a – The Elastomers

Also known as rubbers, these are polymers which can undergo large elongations under load, at room temperature, and return to their original shape when the load is released. There are number of man-made elastomers in addition to natural rubber. These consist of coil like polymer chains those can reversibly stretch by applying a force .Examples of Elastomers are Butadiene, silicones and Thiokol.

b –The Fibers

These are solids which can form thread like structures and have high tensile strength. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature used in textile industry. Examples are polyamides, polyesters, Polyurethanes, Protein derivatives, etc

c –The Thermoplastic Polymers

These plastics soften when heated and harden when cooled – processes that are totally reversible and may be repeated. These materials are normally fabricated by the simultaneous application of heat and pressure. They are linear polymers without any cross-linking in structure where long molecular chains are bonded to each other by secondary bonds or inter-wined. They have the property of increases plasticity with increasing temperature which breaks the secondary bonds between individual chains. Common thermoplasts are: acrylics, PVC, nylons, polypropylene, and polystyrene.

d - Thermosetting Polymers

These Polymers require heat and pressure to mold them into shape. They are formed into a permanent shape and cured or 'set' by chemical reactions such as extensive cross-linking. They cannot be re-melted or reformed into another shape but decompose upon being heated to too high a temperature. Thus thermosets cannot be recycled, whereas thermoplasts can be recycled. The term thermoset implies that heat is required to permanently set the plastic. Example Epoxies, vulcanized rubbers and phenolic.

1.4 Polyethylene Glycol (PEG)

The production of polyethylene glycol was first reported in 1859. Both A. V. Lourenço and Charles Adolphe Wurtz independently isolated products that were polyethylene glycols [22].PEG is a polyether compound with many applications, from industrial manufacturing to medicine. PEG is also known as polyethylene oxide (PEO) or polyoxyethylene (POE), depending on its weight. Figure (1.2) explain the structure of PEG is commonly expressed as $H-(O-CH_2-CH_2)_n-OH$) [23].

PEG 6000 is a water-soluble and waxy solid that is used extensively in the several industries such as rubber, textile, paper, metal, wood, pharmaceutical, cosmetics and coating. PEG recognizes by many characteristic such as, highly compatible to various kinds of organic compounds, high boiling point, easy control of the degree of condensation, controllable hygroscopic property, less toxicity and less skin irritation [24].

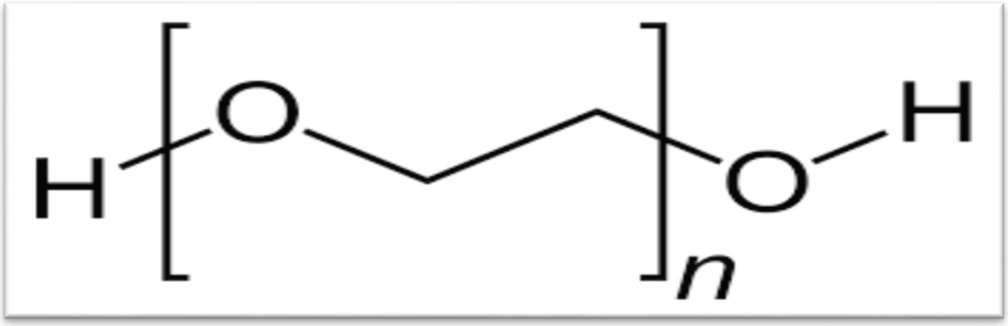


Figure 1.2structure of PEG.

The properties of Polyethylene Glycol can be expressed in the table (1) below:

Table (1) Properties of Polyethylene Glycol [23].

Molecular formula	**PEG**
Chemical formula	HO(C2H4O)7Nh
Density	1.21g/cm^3
Molecular weight	5000-70000 g/mol
Collar	white
Metaling point	58-60°C
Boiling point	250°C
Solubility	in water

1.5 Barium titanate ($BaTiO_3$) Nanoparticles

Barium titanate with different additives and dopants is one of the most useful ferroelectric materials suitable for wide fields of application such as multilayer capacitors, thermistors, varistors and energy converting systems [25]. BaTiO3 powder is usually mixed with various types of additives in order to obtain the better performances and a good control over a grain size and electrical characteristics of ceramics. It has been found that the dielectric properties of polycrystalline $BaTiO_3$ depend in a great extent on the grain growth during sintering and on additive type and concentration [26]. Figure (1.3) show Structure of cubic $BaTiO_3$ where the red spheres are oxide centers, blue are Ti^{4+}cations, and the green spheres are Ba^{2+}[27].

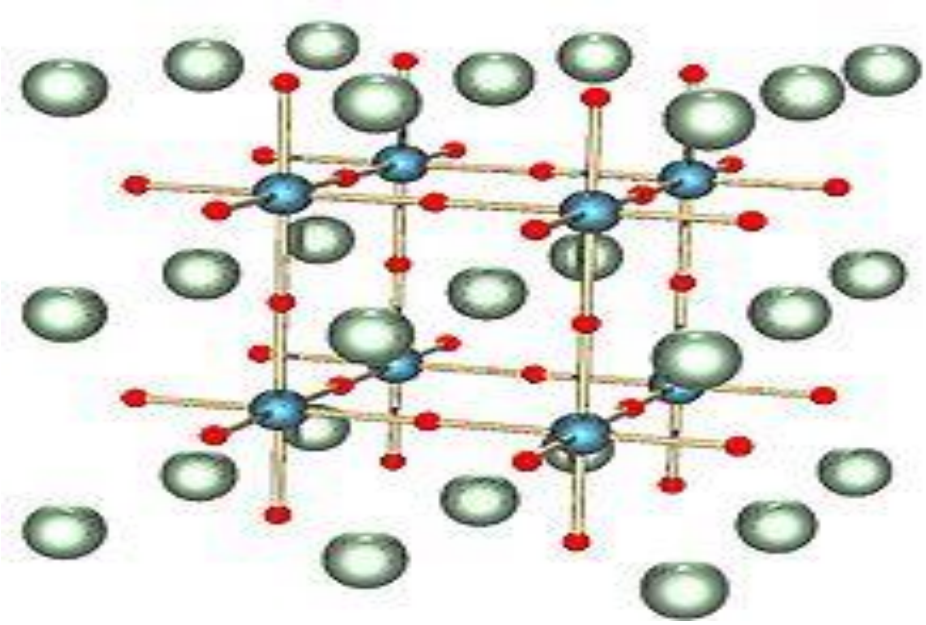


Figure 1.3 Structure of $BaTiO_3$.

The properties of Barium titanate ($BaTiO_3$) can be summarized in the table (1-2) below

Table (1-2) Barium titanate ($BaTiO_3$) properties [26, 27].

Molecular formula	**$BaTiO_3$**
Chemical formula	$BaTiO_3$
Molar mass	233.192 g
Density	6.02 g/cm^3
Band gap	3.2 Ev
Crystal structure	Tetragonal
Appearance	white crystal
Metaling point	1.625°C
Solubility in water	insolubility

1.5 Literature Review

- **In (2015) K. AbdAli and A.O.M Al-Ogail. [28]** Studied some physical properties of polyethylene glycol type (PEG 6000) polymer before and after adding some cellulose derivative polymers:Optical properties such as absorbance transmittance, reflectance, absorption coefficient and refractive index have been measured. Where the values of absorbance increase when concentration increase because the addition led to increase the values of concentration in same volume, then increase the number of particles that absorb the energy of incident light and Rheological properties for solution samples such as density which shows that increases the density values with increasing concentration of PEG and this is because the increased the mass of the solution and viscosity have been measured it also Increasing with the concentration .

- **In (2016) A.O.M. Al-Ogaili, K. Abdali and E.Y.Khudair. [29]** studied the optical properties for (PEG-TiO2) nanocomposites. For this purpose, solutions were prepared with different percentage (0.5 and 1) wt. % of (TiO2) nanoparticles. Experimental results for optical properties show that the electronic transitions were indirect, the values of the energy gap has been found, it decreases with the increase of the concentration of the additive. The optical constants absorption coefficient, refractive index, extinction coefficient, have all been measured and it was found out that all these constants increase with the increase of the concentration of (TiO2) nanoparticles.
- **In (2017) A, Mohammed ,M.H. Suhail and M. Ghazi1.[30]** .studied Polymer films of PEG and PVA and their blend with different concentrations of MnCl2 (0, 2, 4, 6 and 10 wt. % .) were study using casting technique. The optical properties of (PVA:PEG/MnCl2) contain the recording of absorbance (A) and explain that the absorption coefficient (α), refractive index (n), extinction coefficient (k_o) increase with increasing the concentration of Composite (PVA:PEG/MnCl2). The optical energy gap for electrons transitions both are decreases and indirect allowed.
- **In (2018) A.K.R.Sunaja, D.D.Pinheiro and S.L.Narayana [31]**. Studied the morphological structures of the prepared nanoparticles for polyethylene glycol (PEG) capped ZnO and tungsten doped PEG capped ZnO nanoparticles by SEM that show higher c1rystallite size and large particle size as compared to PZn nanoparticles.FourierTransformInfraredSpectroscopy (FTIR),Ultraviolet Diffus e Reflection Spectroscopy (UV) been studied. The optical energy gap for electrons transitions are decreases with increases the concentration of ZnO

nanoparticles. The prepared nanoparticles exhibit significant antibacterial properties against gram-positive Bacillus cereus and gram-negative Escherichia coli bacterial strains by agar well diffusion method.

- **In (2018) C.Swaroop and M.Shukla [32].** This study aimed at the development of flexible films based on polylactic acid (PLA) incorporated with polyethylene glycol (PEG) and reinforced with MgO nanoparticles using the solvent casting method. The key mechanical, antibacterial and optical properties of the prepared films. Optical properties of PLA films changed significantly with incorporation of PEG and MgO nanoparticles. Furthermore, a remarkable improvement in antibacterial efficacy was demonstrated by the addition of PEG and MgO nanoparticles. FTIR of prepared films suggested successful preparation of PLA/PEG/MgO nanocomposite films while surface morphology studied by SEM techniques revealed fine dispersion of MgO nanoparticles in them.

- **In (2019) S. Zhu, Ji, T., B. Yang and Z. Yang [33].** Studied A new shape-stabilized PCM *i.e.*, PEG/KH-LDHs was successfully prepared using solution impregnation method, showed from scanning electron microscope. The pristine LDHs particles have sizes of approximately 200 nm with typically plate-like shapes, and smooth surface. In addition, the agglomerate state of the LDHs particles can also be clearly observed. The total absorption strength of PEG in the ultraviolet region is weak and a weak absorption peak is observed at a wavelength of approximately 250 nm in the PEG absorption curve, for the 55PEG/KH-LDHs, a strong absorption peak appears at a wavelength of 300 nm indicating a higher absorptive ability to UV than that of pure PEG.

- **In (2020) E. T. Abd-AL Hussein, and A. M. Hameed [34].** Studied some optical properties of polyethylene glycol (PEG) by adding different weight percentages of aluminium nanoparticles 0, 2, 4, 6 and 8 % and for achieving a new composite material with improved characteristics. Nano-composite thin films were prepared by solution casting method with different weight percentages of Al nanoparticles. The optical properties measurement by using (UV–VIS) spectrophotometer at wavelength range 220 – 1100 nm were determined. Results show that the absorbance spectrum increased with increase the weight percentages of Al- nanoparticles and the values of absorption coefficient have increased as well as refractive index values increased with the addition of aluminium nanoparticle. The optical microscopy results after the addition of Al-nanoparticles explain the morphology of PEG composite indicating to the good adhesion and interference (strong bonding) between PEG with Al- nanoparticles dispersed within its structure.

- **In (2021) T.S.Soliman M.F.Zaki M.M.Hessien and S.I.Elkalashy [35]** studied barium titanate ($BaTiO_3$) nanocrystalline particles and to fabricate polyvinyl alcohol (PVA) films hosting $BaTiO_3$ in order to enhance structural and optical properties. By means of cast solution, the PVA – $BaTiO_3$ nanocomposite films are prepared. The polymer films are described by Fourier-Transform Infrared (FTIR) and UV–vis spectroscopy. The study of FTIR indicates that complexity is established between $BaTiO_3$ nanoparticles and PVA matrix. It is noticed that as the $BaTiO_3$ nanoparticles concentration increases in the PVA matrix, the optical band gap decreases. The extinction coefficient, refractive index, optical conductivity and dielectric constants of the polymer films are also increases.

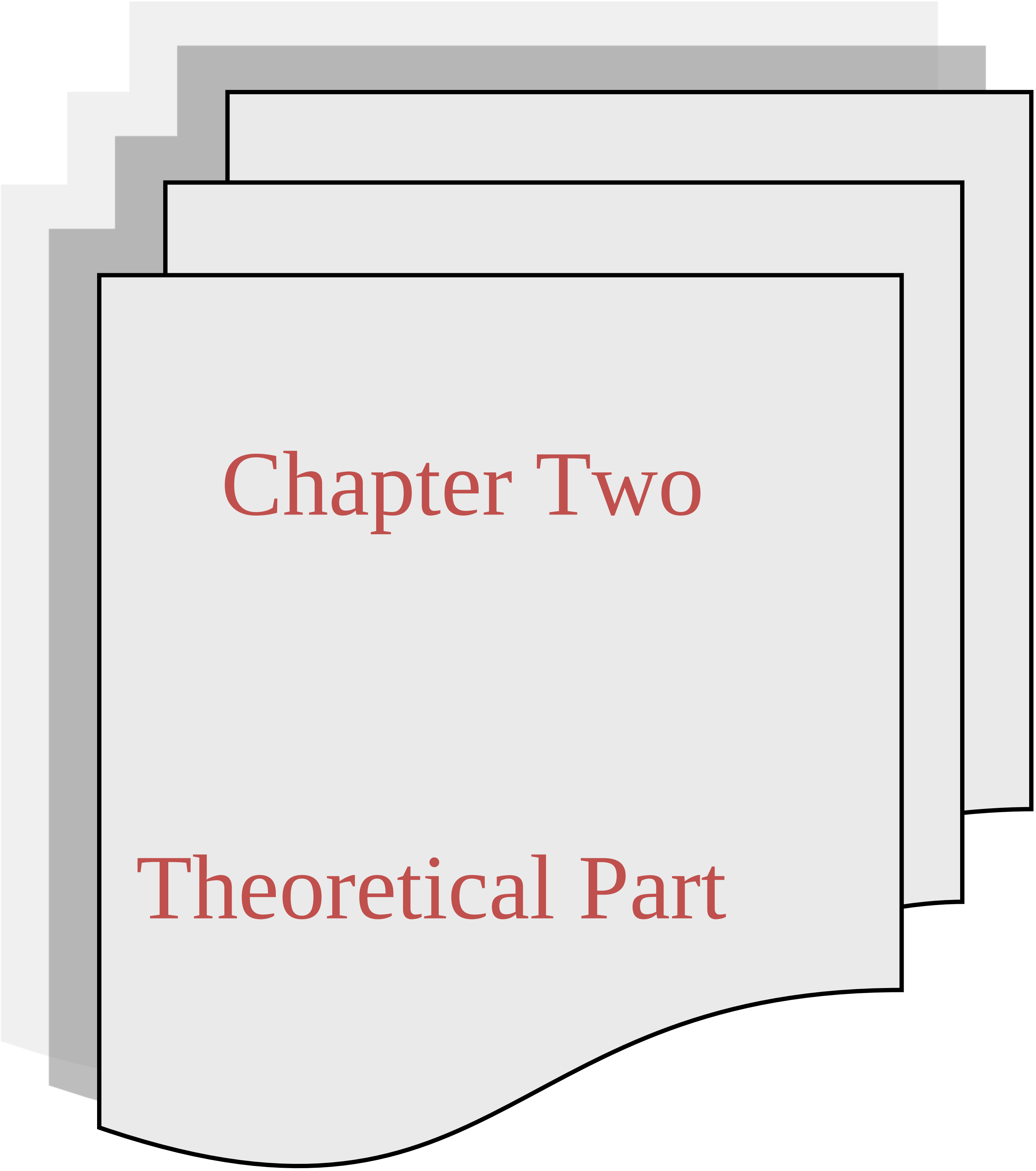
1.7 Amis of the Research

The aims of research listed as:

1-Preparation of PEG- $BaTiO_3$ Nano-composite by using solution method

2-Studeing the structural, optical and electrical properties of PEG-$BaTiO_3$ Nano-composite.

3- Application of PEG- $BaTiO_3$ Nano-composite for antibacterial activity .



Chapter Two

Theoretical Part

2.1 Introduction

This chapter describes the theoretical part, the mathematical relations used and the physical concepts, and the laws used to interpret the obtained results.

2.2 Structural Properties

This property is an important tool for studying crystal structural of thin film.

2.2.1-Fourier Transform Infrared (FTIR)

The (FTIR) is a technique that is used to obtain an infrared spectrum of emission, photoconductivity, absorption or Raman scattering of the solid, the liquid or the gas. The (FTIR) spectrometer simultaneously collects spectral data in a wide range of spectral range. Spectra were recorded with a scanning range of (500-4000) cm^{-1} and resolve ($1cm^{-1}$) [36].

2.2.2 Scanning Electron Microscope (SEM)

Scanning electron microscope with energy dispersive X-ray spectroscopy (SEM is the best known and most widely-used of the surface analytical techniques. High resolution images of surface topography, with excellent depth of field, are produced using a highly-focused, scanning (primary) electron beam. The primary electrons enter a surface with an energy of 0.5 – 30 kV and generate many low energy secondary electrons. The intensity of these secondary electrons is largely governed by the surface topography of the sample [37]. The scheme of SEM operation is illustrated in Figure (2-1), which consists of electron gun as electron source, two condenser lenses, scanning coils, which facilitates the deflection of electron beam in x and y directions, objective lens, and detectors for backscattered and secondary electrons. SEM operates inside vacuum chamber with high-energy electron source (2-25kV). Condenser lenses focus the electron beam into a nanometer size. The reflected electron from the sample, backscattered or secondary electrons, are collected by the detector to provide an image of the sample. In many cases, the backscattered electrons reflected from the sample are used in analytical SEM due to the relation of intensity and atomic number of materials [38].

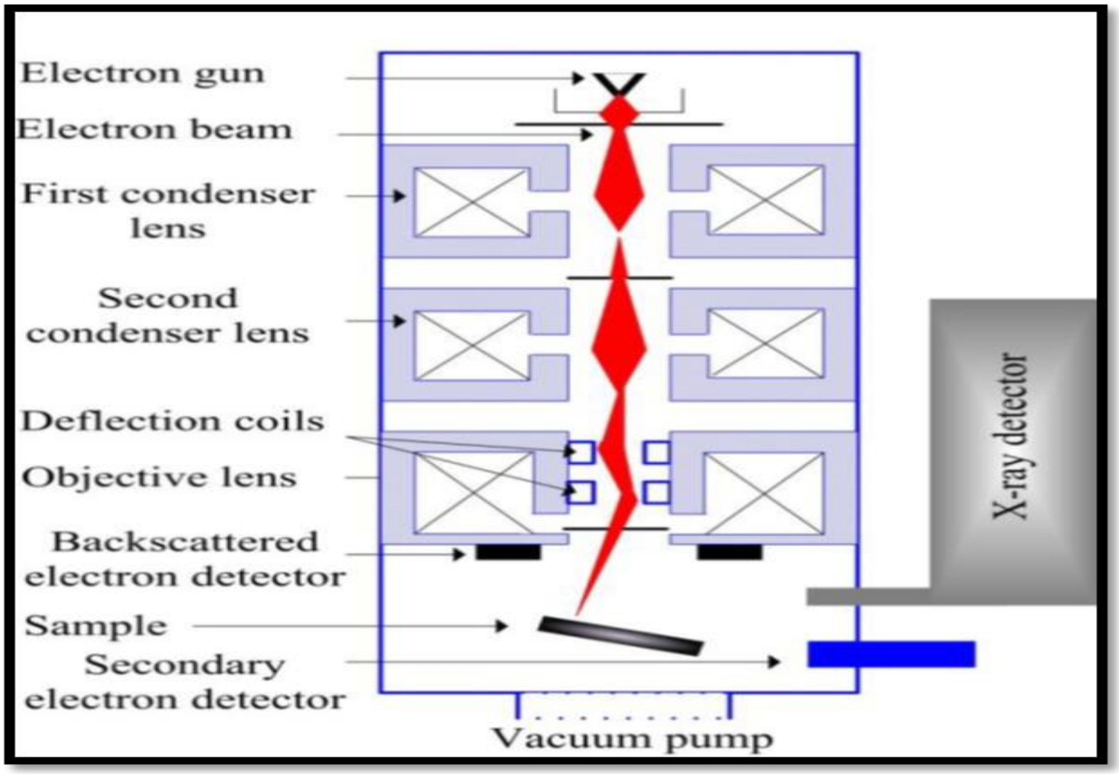


Figure 2.1 Schematic illustration of the operation of SEM.

Two imaging modes are available in SEM; Secondary Electron Imaging (SEI) or Backscattered Electron Imaging (BEI). In the former, low energy secondary electrons (typically < 50 eV) emitted from the interaction between the incident beam of high energy electrons with the atoms of the sample via inelastic collisions are detected and used to build an image of the surface topography of the sample. Due to the relatively low energies of these secondary electrons, only those from the surface (a very thin layer of tens of nanometers) are able to emerge from the sample. In the| case of BEI, the image is derived from scattered or reflected electrons from elastic collisions of the high energy electron beam with the nuclei of the atoms at high angles approaching 180°c Figure. (2-2).

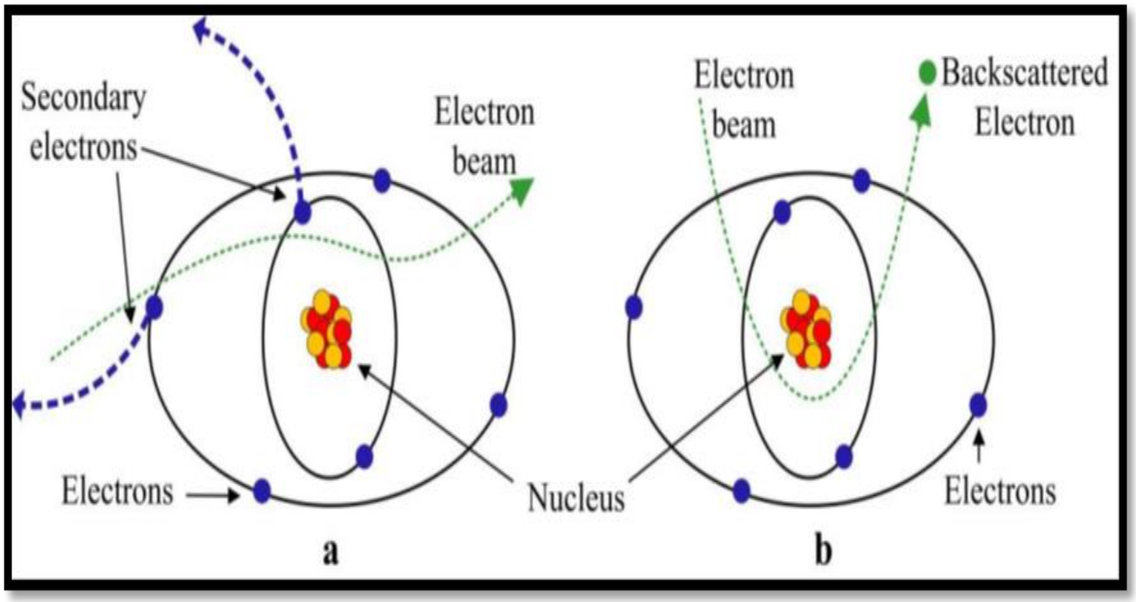


Figure 2.2 Interaction between electrons beam and sample producing (a) secondary electrons and (b) backscattered electrons .

The yield of backscattered electrons is a function of atomic number. Heavier elements, i.e. those with higher atomic number, reflect a greater proportion of electrons and so appear brighter, and lighter elements with a low atomic number reflect a lower proportion of electrons and appear darker. The contrast indicates the average atomic number of the elements present within the microstructure and is indicative of the varying elemental compositions [39].

2.3 Optical Properties

The spectrums of absorption, transmittance of a polymer assist in identifying many optical properties in different ranges of wavelengths. Conducting examination at the ultraviolet spectrum range enables us to know the type of the bonds, orbital and energy beams. The study at the visible spectrum range provides sufficient information about the behavior of a matter to solar applications. The study at the infrared range is very important in knowing the general structure of a polymer and the elements consisting its chemical structure [40].

2. 3.1 The Absorbance (A) and the Transmittance (T)

Absorbance defined as the ratio between absorbed light intensity (I_A) by material and the incident intensity of light (I_o) [33].

$$A = \frac{IA}{Io} \qquad (2\text{-}1)$$

The optical absorbance coefficient (α_{op}) of solution and film is given by the equation [41].

$$\alpha_{op} = 2.303\frac{A}{d} \qquad (2\text{-}2)$$

Where (d) represent a thickness of sample.

Transmittance (Tr) can be expressed as the ratio between **(I/I_o)**, so (I) the intensity of the transmitting rays through the film and (I_o) the intensity of the incident ray , and it relates to absorption through relation [42].

$$T_r = e^{-2.303A} \qquad (2\text{-}3)$$

2.3.2 Reflectance (R)

The Reflectance be expressed for the law of conservation of energy from absorption and transmission spectrum by the relation [43].

$$R + T + A = 1 \qquad (2\text{-}4)$$

2.3.3 Optical Constants

The optical properties of homogenous matters (absorbance, transmittance and reflectance) are described by three parameters:

1. Refractive Index (n)

The refractive index can be defined as a ratio between the speed of light in a vacuum (c), to the speed of light in a medium (v) and given by the equation given by the relation [44]:

$$n = \frac{c}{v} \qquad (2\text{-}5)$$

Value of refractive index can be calculated by using equation depending on the reflectance and extinction coefficient (K) by relation [44,45].

$$R = \frac{(n-1)^2+k^2}{(n+1)^2+k^2} \qquad (2\text{-}6)$$

When k equal zero (k=0) equation (6) become

$$R= \frac{(n-1)^2+0}{(n+1)^2+0} \qquad (2\text{-}7)$$

Then refractive index will become

$$n=\frac{1+\sqrt{R}}{1-\sqrt{R}} \qquad (2\text{-}8)$$

2. Extinction Coefficient (K)

The imaginary part of complex refractive index it represents by(n*) and the amount of attenuation of an electromagnetic wave that is traveling in a material, where it values depend on the density of free electrons in the material and also on the structure nature represents the extinction coefficient [46].

$$n^* = n - i K \qquad (2\text{-}9)$$

Where:

(n) Represent the real part of refractive index.

(n*) represent complex refractive index that depends on the material type, crystal

Structure (particle size), stress in the crystal and crystal defects, so (K) extinction Coefficient is given by equation [47]:

$$K = \alpha_{op}\,\lambda / 4\pi \qquad (2\text{-}10)$$

Where:

(λ) Represent the wavelength of incident photon.

3-Absorption Coefficient (α)

Absorption coefficient according to beer lambert low can be defined as the relative rate of decrease in the light intensity (I) along the propagation path [48].

$$\alpha = \frac{1}{I}\frac{d[I]}{dt} \qquad (2\text{-}11)$$

Where:

I The intensity of light in (W/cm^2) and t The thickness of thin film (cm)

we can give by [49].

$$\alpha = \frac{2.303.A}{t} \qquad (2\text{-}12)$$

In semiconductor (α) is strong function of the wavelength or photon energy where the photon energy is given by [48]

$$E = h\nu \qquad (2\text{-}13)$$

Where ν the frequency in (HZ) and h plank constant ($1.6 \times 10^{-34} J.s$)

2.3.4The Fundamental Absorption Edge

The fundamental absorption refers to band-to-band or to excitation transitions (i.e. the excitation of an electron from the valence band to the conduction band), it manifests itself by a rapid rise in absorption, which can be used to determine the energy gap of the semiconductor. Absorption regions can be classified into three regions [50].

a) High Absorption Region:

This region is shown in Figure 2.3. In part (A), the magnitude of absorption coefficient (α) is larger or equal to (10^4 cm^{-1}). From this region the magnitude of forbidden optical energy gap (E_g $^{opt.}$) can be introduced.

b) Exponential Region:

This region is shown as in Figure 2.3. In part (B) the value of absorption coefficient (α) is equal to (1 cm<α< 10^4 cm^{-1}). It refers to the transition between the extended levels from the (V.B) to the local levels in the (C.B) and from local levels in (V.B) to extend the levels in (C.B).

c) Low Absorption Region

The absorption coefficient (α) in this region is very small. It is about (α < 1 cm^{-1}). The transition happens in this region because of density of state in mobility gap resulted from faults structural, as in Figure 2.3, the part (C).

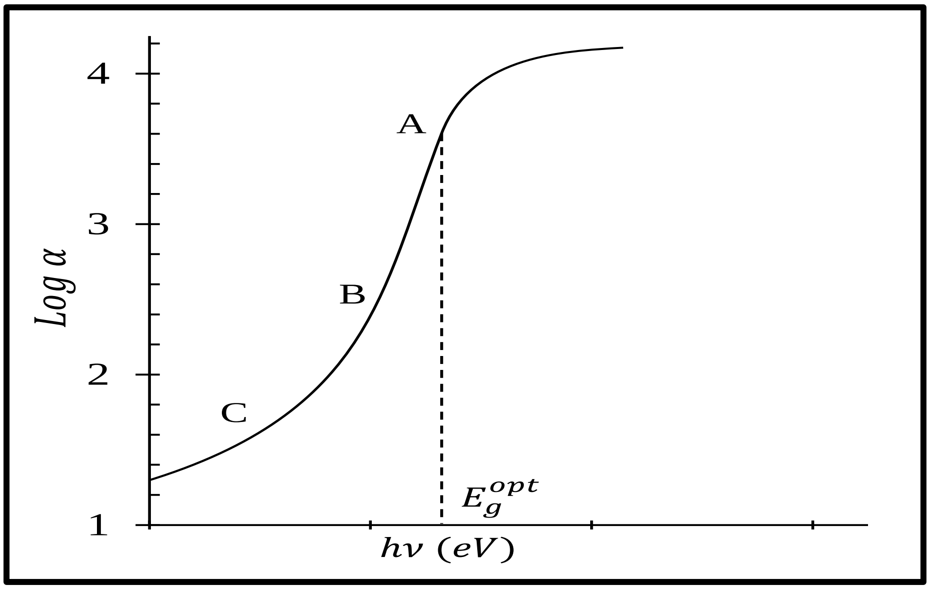


Figure 2.3 the variation of absorption edge with absorption regions.

2.3.5 Electronics Transition

The absorption of radiation, which leads to electronic transition between the valence and conduction bands, is split into direct and indirect transition as shown in Figure 2.4 [51].

The direct transition happens in semiconductors when the bottom of (C.B) is exactly over the top of (V.B). This means that they have the same value of wave vector, i.e. ($\Delta K=0$) in this state the absorption appears when ($h\nu = E_g{}^{opt}$). This transition type required for the Law's of conservation of energy and momentum. These direct transitions have two types [52].

a) Direct Allowed Transitions

The transition happens from the top points in the (V.B) and the bottom point in the (C.B), as shown in Figure 2.4.a.

b) Direct Forbidden Transitions

This transition happens from near top points of (V.B) and the bottom moints of (C.B) [44]. As shown in Figure 2.4.b. The absorption coefficient for this transition type is given as relation:

$$(\alpha h\nu) = B\,(h\nu - E_g{}^{opt})^r \qquad (2.14)$$

Where:

$E_g{}^{opt}$: energy gap between direct transitions.

B: constant depended on type of material.

r. exponeat constant, its value depended on type of transition:

r=1/2 for the allowed direct transition.

r=3/2 for the forbidden direct transition.

For the indirect transition in this case the bottom of (C.B) is not over the top of (V.B), in curve (E-K). The electron transits from (V.B) to (C.B) is not perpendicularly where the value of the wave vector of electron before and after the transition is not equal ($\Delta K \neq 0$). This transition type happens with helpful of particle called "Phonon", for conservation of the energy and momentum law. There are two types of indirect transitions, they are [53].

c) Allowed Indirect Transitions

These transitions happen between the top of (V.B) and the bottom of (C.B) which is found in the difference region of (K-space) as in Figure 2.4.c.

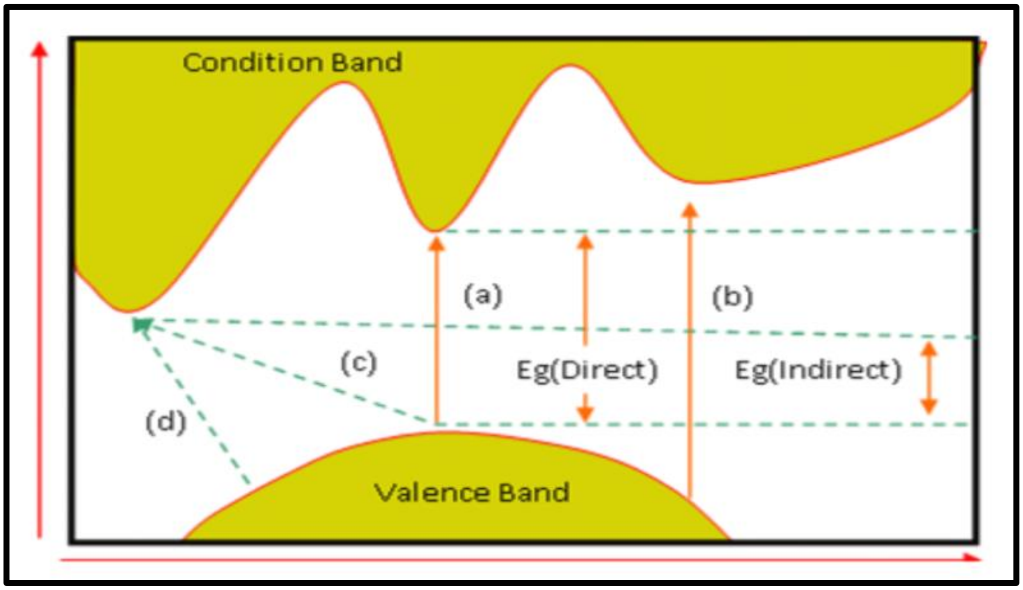


Figure 2.4 the transition types.

(a) Allowed direct transition. **(c) Allowed indirect transition.**

(b) Forbidden direct transition. **(d) Forbidden indirect transition.**

d) Forbidden Indirect Transitions

These transitions happen between the nearest points on the top of (V.B) and near points in the bottom of (C.B) [45], as shown in Figure 2.4.d. The absorption coefficient for transition with a photon absorption is given by:

$$(\alpha\, h\nu) = B\,(h\nu - E_g^{\,opt} \pm E_{ph})^r \qquad (2.15)$$

Where:

E_{ph} energy of the phonon, is (-) when phonon absorption, and (+) when photon emission.

r =2 for the allowed indirect transition

r = 3 for the forbidden indirect transition

2.4 Rheological Properties

The viscosity is very important phenomena of materials in general and especially in polymer materials, the viscosity of polymer solution is known as a measure of molecular weight, since the initial work to Staudinger in (1930), as the viscosity of the solution is mainly to gauge the size or stretch the molecules of polymer in the space of the solution. The polymer solutions are characterized as unique solutions for other materials being more viscous [54]

The ratio of the viscosity of the polymer solution to the viscosity of the solvent, can be approximated by measuring the time required for a given volume of the two solutions to pass through a capillary. Viscosity (η_{rel}) is expressed in the following relation [55].

$$\eta_{rel} = \frac{\eta_s}{\eta_o} \qquad (2\text{-}16)$$

Where (η_o) is the viscosity of solvent.

2.5 Electrical Properties

The electrical properties of semiconductors depend on the nature of semiconductors they being pure or doped, crystalline or amorphous. The electrical properties of materials are determined not only by chemical composition, but also by the arrangement of atoms in the solid, and the existence of defects when gives rise to the electron states in the energy gap which effected the electrical properties of material, this defect can be reduced by many processes such as the annealing process. Transport properties such as D.C electrical conductivity (D.C) important electrical properties [56,57].

The conductivity for solution of a water is be highly depends on the concentration of sometimes chemical species and dissolvesalts which tend to ionize in the solution. The electrical conductivity of a water samples is used as an indicator of how impurity-free, ion-free or salt-free or the sample is the purer the water and the higher the resistivity (the lower the conductivity)[58].

2.5.1 D.C. Electrical Conductivity

The electrical conductivity of polymers depends on the free ions which are not chemically connected to the large molecules. The volumetric electrical resistance (R_v) can be calculated for a regular body with a section having a constant area (A) along the length (L), using the relation [59].

$$R_v = \rho_v \frac{L}{A} \qquad (2.17)$$

Where (ρ_v) is the volume resistivety that is different according to the substance it equals the inverse of the bulk conductivity. This means that volume conductivity is [59].

$$\sigma_V = \frac{1}{\rho_V} = \frac{L}{R_V\, A} \qquad (2.18)$$

2.5.2Molar Conductivity (Λ)

It's defined as the ratio between the electrical conductivity of solutions and the molar concentration of the same solution and given by the following equation [60]:

$$\Lambda = \frac{\sigma}{C_m} \qquad (2\text{-}19)$$

Where (C_m) is the molarity, in mole per volume.

2.6Application of (PEG-$BaTiO_3$) Nanocomposites for Antibacterial Activity

The emergence of infectious diseases in general poses a serious threat to public health worldwide, especially with the emergence of antibiotic-resistant bacterial strains. Therefore, there is incentive to develop new bactericidal. Generally, both gram-positive and gram-negative bacterial strains are thought to present a major public health problem. Over the years, antibiotics have been used to control infections resulting from both community and hospital environments [61, 62].

Current advances in the field of Nano biotechnology, particularly the ability to prepare metal oxide nanomaterials of specific size and shape, are likely to lead to the development of new antibacterial agents. The functional activities of nanoparticles are influenced largely by the particle size. Therefore, nanoparticles have received great attention due to their unique physical, chemical, and effective biological properties in various fields, including medicine [63, 64].

The antibiotics wide scale use in the prevention and treatment of bacterial infections has led to the spread of resistant microorganisms requiring the development of new active molecules against bacteria. Nanoparticles are similar in size to biological micromolecules and smaller than human cells. The development of nanotreatment strategies represents a opportunity to enhance medical treatments [65,67].

Chapter three

Experimental part

3.1 Introduction

This chapter contains explanation of the materials used in the research and an explanation of the method of preparing the nanocomposite (PEG-$BaTiO_3$) in the form liquid and films using the solution casting method, in addition to a brief explanation of the devices used and the method of work and measurement.

3.2 The Materials Used in the Work

Basic materials used were polyethylene glycol (PEG) of molecular weight 6000) and purity is 99 % and the secondly or additive material that is bare nanomaterial ($BaTiO_3$) purity is 99.999 %.As shown in the figure (3-1).

Figure 3.1 (a) polyethylene glycol (PEG) (b) Barium titanate $BaTiO_3$.

3.3 Diagram the Steps of Procedure

The steps of the work can be represented by the following diagram .

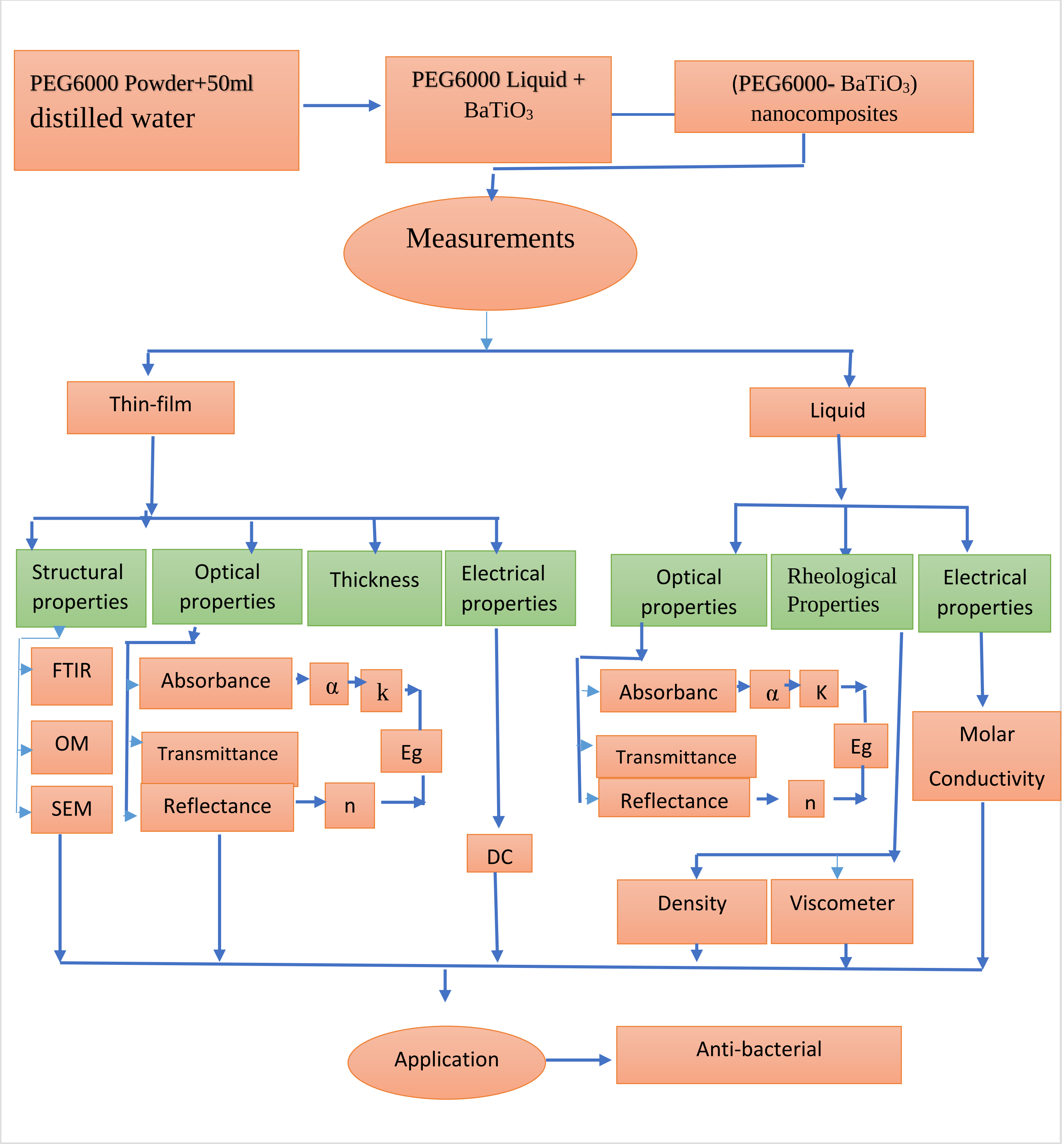


Figure 3-2 Diagram showing the steps of procedure.

3.4 Samples Preparation

3.4.1 Solutions Preparation

Solution of PEG-$BaTiO_3$ were prepared by using the solution casting method as: 2g amount of PEG was dissolved in distilled water (50)ml as a solvent with stirring about 3 minutes at room temperature [68]. Until a homogenous viscous liquid solution was formed. The nanoparticle material ($BaTiO_3$) added to the blend solution with weight percent's of (0, 2, 4 , 6) % and leave it on the stirring for a period of (5) min at room temperature The resulting homogeneous solutions (PEG-$BaTiO_3$).The concentrations of these solutions have been calculated by the relation below

$$\text{Concentration} = \frac{(\text{Mass of solute})}{(\text{Volume of solution})} \text{ x } 100\ \% \qquad (3.1)$$

$$\text{Molar Concentration} = \frac{(\text{Mass of solute})}{(\text{Volume of solution})} \times \frac{1}{\text{Molecular weight}} \qquad (3.2)$$

Table (3-1) Ratios of materials used to prepare a liquid and thin film PEG-$BaTiO_3$.

PEG g	$BaTiO_3$ g	Distillated water (mol)
2	0	50
1.98	0.02	50
1.96	0.04	50
1.94	0.06	50

3.4.2 Substrates Preparation

The cleaning of substrates is very important process because the influences like oil or dust effect on the properties of thin films, clean substrate is also essential to achieve good film adhesion.

3.4.2.1 Glass Substrate

PEG and $BaTiO_3$ thin films deposited on glass substrate, made in China, have dimension (2.5×2.5) cm^2 area using a steel-cut machine. This process can be summarized in the following steps:

1. Washing the glass substrate with water and cleaning powder to remove any oil or dust that might be on the substrate of the surface, then putting them under tap water for (2) min.

2. Drying the substrates and with soft paper (lines paper) and kept to be used in time. Now the slides are ready to deposit the thin films on them.

3. Cast homogeneous solutions (PEG-$BaTiO_3$) onto the clean glass plate and, and then transfer it and place it on a flat surface at room temperature for 48 hours to dry.

3.5 Measurement

3.5.1 Thickness Measurement

There are many ways in which the thickness of films is measured, such as weight method, optical method, electrical and other methods. In this process, we are using of Lambda (LIMF- 10) device, the device measurement is easy to set up and used. It is suitable for both the manufacturing line and desktop measure with the ability to connect to your microscope to reduce the spot size or to dismantle for sole spectroscopic use. It is found that the thickness of the films prepared is (79.1, 80.3, 81.3, 81.31) nm respectively. This system is in Basic Education College of Science – University of Babylon..

3.5.2 Structural Properties for Nanocomposites

The Structural measurements include :

3.5.2.1 The Fourier Transform Infrared Spectroscopy (FT- IR)

FT-IR is a technique used to obtain an infrared spectrum of the absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. The (FT-IR) spectrometer simultaneously collects spectral data in a wide spectral range. The (FTIR) spectra were obtained by (Broker), a (Vertex 70) spectrometer, manufactured by Japan. The scanning range is from (500-4000) cm^{-1} and the resolution of (1 cm^{-1}). The device that found in College of Education for Pure Science-Babylon University.

3.5.2.2 Optical Microscope

The (PEG – $BaTiO_3$) nanocomposites samples are examined by using the optical microscope (supplied from Olympus name (Toup View) type (Nikon - 73346)) in University of Babylon - College of Education for Pure Sciences with magnification (40x) .

3.5.2.3 Scanning Electron Microscope

The surface morphology of (PEG–$BaTiO_3$) nanocomposites for concentration (0, 0.02, 0.04 and 0.06 g) of $BaTiO_3$, was tested by using scanning electron microscope Scanning electron microscopy (SEM) .This analysis was carried out in Iran.

3.5.3 Optical Measurements for Nanocomposites

A double beam UV-vis 1800 Shimadzu spectrophotometer is used to measure the absorption of PEG and $BaTiO_3$ thin films in the range (200-1100) nm. The background correction is taken for each scan. The transmittance and reflectance data can be used to calculate absorption coefficients of the films at different wavelength which have been used to determine the energy gap E_g .This device is present in the laboratory of Polymer at Physics Department- College of Science - University of Babylon.

3.5.4 Rheological Properties for Nanocomposites

Rheological measurements for polymer solutions as follow

a) The density of the (PEG) solutions has been measured for all concentrations by using a density bottle method with a volume of (25mL) and electronic balance industrialized by a company (Mettler Switzerland) with accuracy (10^{-4}) before and after adding ($BaTiO_3$) for all concentrations.

b) The viscosity has been measured before and after adding ($BaTiO_3$) for all concentrations by using Ostwald–tube viscometer device. This device is found in Babylon University/College of Science/Department of chemistry. Then have been calculated before and after adding ($BaTiO_3$) for all concentrations by the equations listed in chapter two.

3.5.5 Electrical Properties for Nanocomposites

Electrical measurement include

3.5.5.1 D.C Electrical Properties for Nanocomposites.

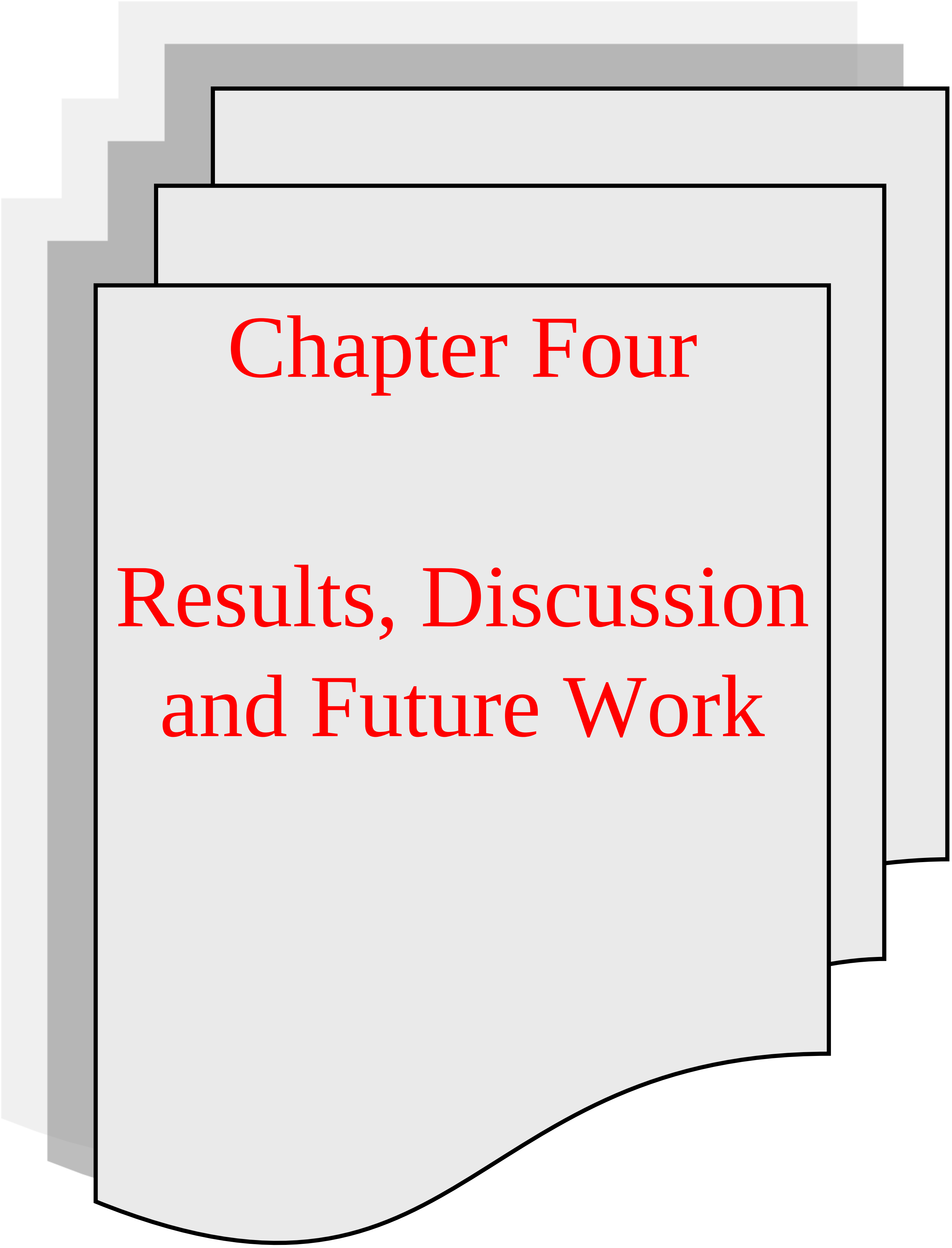
The D.C electrical conductivity of (PEG-$BaTiO_3$) nanocomposites are measured by measuring the D.C electrical resistance at room temperature by using the Kiteley electrometer type 2400 source mater that found in College of Education for Pure Science-Babylon University.

3.5.5.2 Electrical Conductivity Meter

The electrical conductivity has been measured using (DDS-307 microprocessor conductivity meter-England) at room temperature, the calibration was made and the correction factor taken account in measuring the samples, all conductivities values have been measured for PEG concentration before after adding ($BaTiO_3$). This device is found in found in Babylon University/College of Science/Department of Physics.

3.6Application of(PEG-$BaTiO_3$) Nanocomposites for Antibacterial Activity

Antimicrobial activity of the (PEG-$BaTiO_3$) nanocomposites tested samples were determined using a disc diffusion method. The antibacterial activity was done by using gram positive organism (Staphylococcus aureus) and gram negative organism (Escherichia coli). Bacteria (Staphylococcus aureus and Escherichia coli) were cultured in Muller-Hinton Medium. The solution of the (PEG-$BaTiO_3$) nanocomposites were placed in the holes and incubated at 37 Cº for 24 hours. The inhibition zone diameter was measured.



Chapter Four

Results, Discussion and Future Work

4.1 Introduction

This chapter includes the results of the structural, optical, Rheological and electrical measurements for (PEG-$BaTiO_3$) nanocomposites. We discuss the effect of Weight ratios additive ($BaTiO_3$) nanoparticles on the optical, electrical and structural properties of liquid and thin films. Effect of antibacterial activity applications of (PEG-$BaTiO_3$) nanocomposites are also discussed.

4.2 Measurement of Thin Film

4.2.1 The Structural Properties of (PEG, $BaTiO_3$) Nanocomposites

The structural properties of nanocomposites studied using three techniques. Scanning Electron Microscope, Fourier Transform Infrared Radiation, Optical Microscope.

4.2.1.1 The Fourier Transform Infrared Radiation of (PEG-$BaTiO_3$)

The (FT-IR) spectrum of PEG and PEG-$BaTiO_3$ Nano companies are shown in Figure (4.1). It notice, the beak at 2920 cm^{-1}formed as a result of stretching the group of CH_2 groups. The beak at 1339 cm^{-1} was attributed to CH_2-O and show peak at 2882cm^{-1}revert to a CH_2 group(stretching) in polymer .tow strong band observed at around 1340 cm^{-1} and 1279cm^{-1} are attributed to the bending and stretching mode of C-H group respectively .It also notice the appearance of peaks at 1102 cm^{-1}repressive the presence of CH_2-O groups. The peak in 958 cm^{-1} attributed to CH_2 group.

Consequently, (FT-IR) spectra to physical mixture seemed to be only summation PEG spectra and their additions. The results shown that there was no interaction between the PEG and nanoparticle ($BaTiO_3$) and this is the same behavior of reference [69].

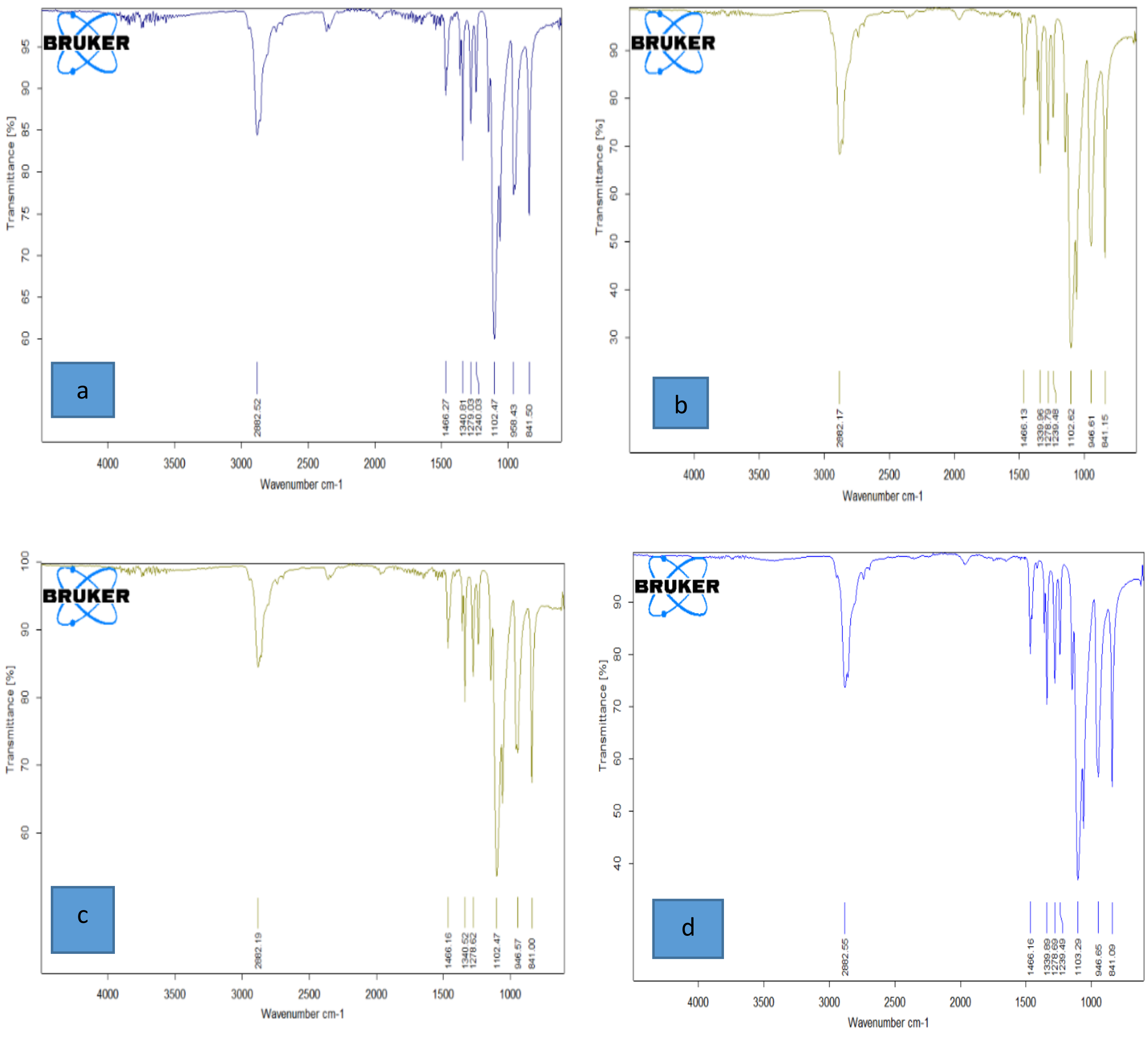


Figure 4.1 FTIR spectra for (PEG-$BaTiO_3$) nanocomposites (a) pure (b) for 0.02 $BaTiO_3$nanoparticle (c) for 0.04 $BaTiO_3$ nanoparticle (d) for 0.06 $BaTiO_3$ nanoparticle.

4.2.1.2 The Optical Microscope (OM)

It be used to investigate from the diffusion of nanoparticle inside the polymer figure (4.2) show the of Optical Microscope images of PEG-$BaTiO_3$ nanoparticles at magnification power (40x). After added Barium titanate $BaTiO_3$ nanoparticles the diffusion of nanoparticles clearly appear in (b, c ,d)

Whereas at high percentages the presence of nanoparticles which is uniformly distributed inside the (PEG-$BaTiO_3$) composite where charge carriers are allowed to pass through the paths, this is agree with the results of Ramesh and Vijaya [70].

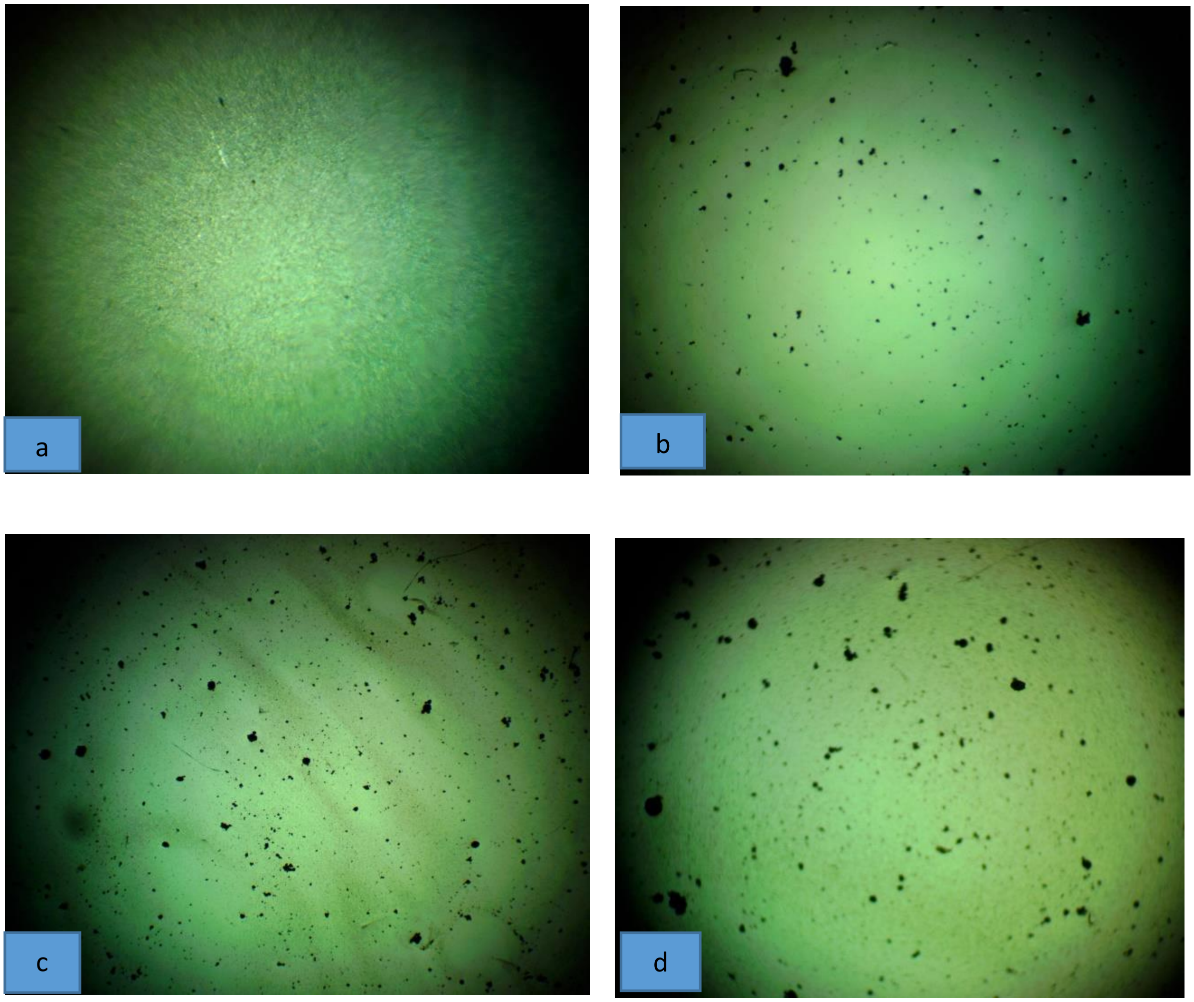
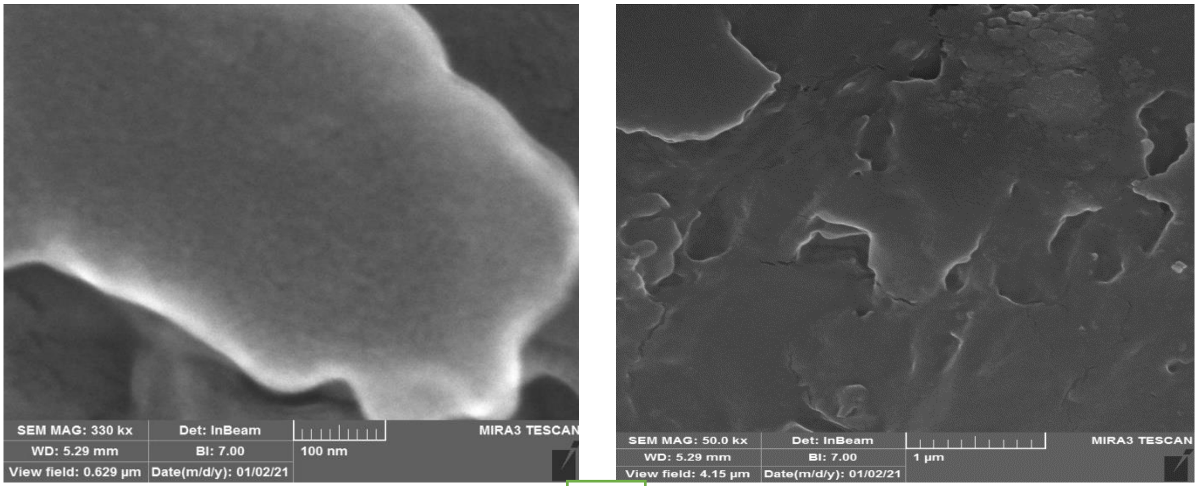


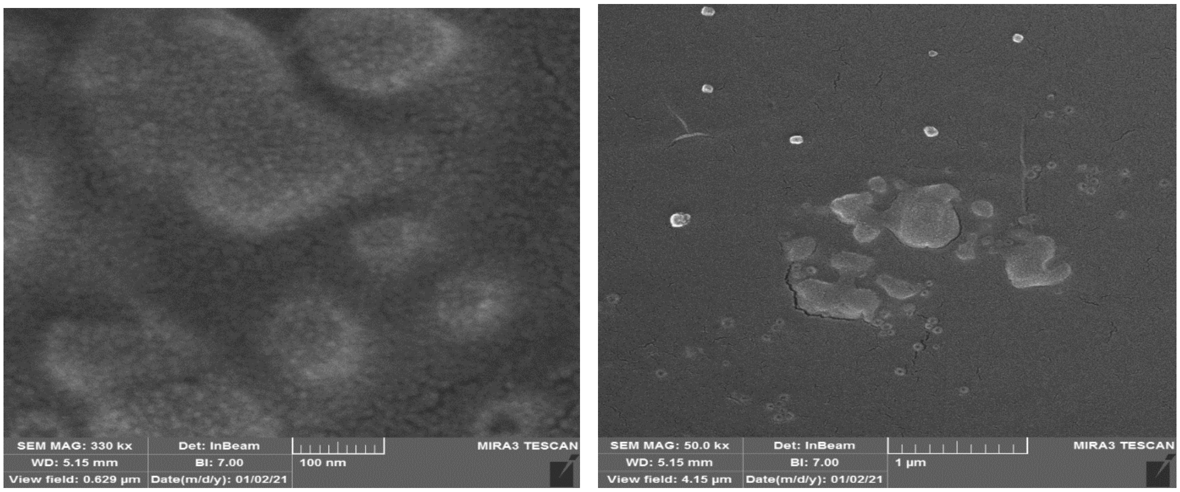
Figure 4.2The Optical microscope (OM) (a) pure (b) for 0.02gm $BaTiO_3$ nanoparticle (c) for 0.04gm $BaTiO_3$ nanoparticle (d) for 0.06gm $BaTiO_3$ nanoparticle.

4.2.1.3 Scanning Electron Microscope (SEM) Measurements

The surface structure of (PEG- $BaTiO_3$) nanocomposites thin film can be imaged through SEM with high clarity. Figure (3.4) shows the typical SEM images of the (PEG-$BaTiO_3$) nanocomposites without and with different concentrations of ($BaTiO_3$) nanoparticles content. Image (a) in figure (4.3) for polymers is found to be softer, homogenous and coherent. It is apparent that the addition of ($BaTiO_3$) nanoparticles in (PEG-$BaTiO_3$) nanocomposites exhibits changes in the surface morphology of such system images(b, c). The surface morphology of nanocomposites shows many aggregates or chunks randomly distributed on the top surface [71]. Image (d) shows an increase in the number of black dots on the surface with increasing concentration of ($BaTiO_3$) nanoparticles. This results agree with the results of the previous researcher [72].



a



b

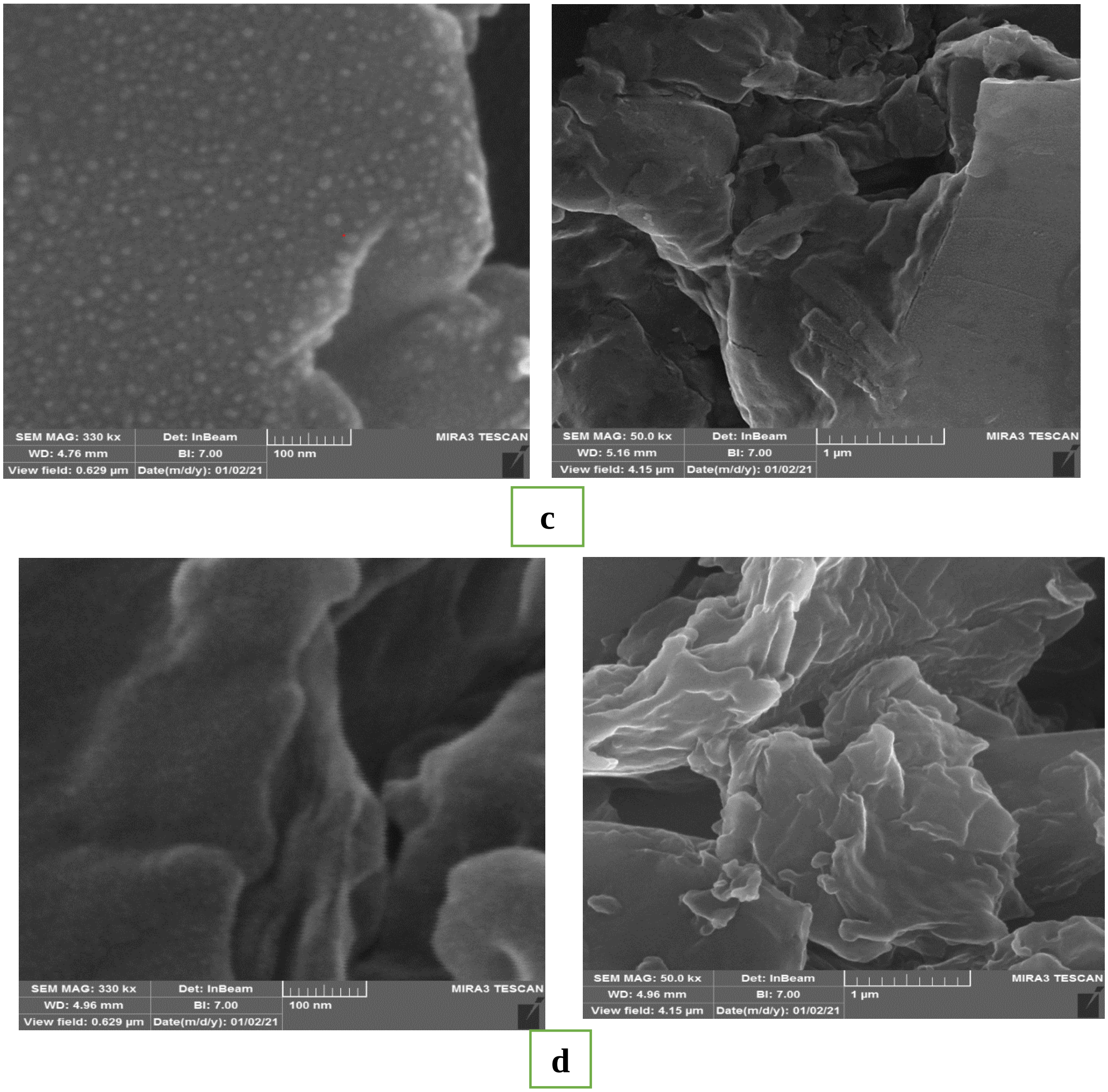


Figure 4.3 The (SEM) image of (PEG-$BaTiO_3$) (a) pure (b) for 0.02 $BaTiO_3$ nanoparticle (c) for 0.04 $BaTiO_3$ nanoparticle (d) for 0.06 $BaTiO_3$ nanoparticle.

4.2.2 The Optical Properties of (PEG, $BaTiO_3$) Nanocomposites

Main purpose of studying the optical properties of the (PEG-$BaTiO_3$) nanocomposites are to identify the effect of adding the ($BaTiO_3$) nanoparticles on the optical properties of thin films and liquid. Was measured include:

absorbance, transmittance, absorption coefficient, energy band gap, extinction coefficient and refractive index.

4.2.2.1 The absorption (A)

The absorption spectra of PEG-BaTiO$_3$ shows in the figure (4.4) with various wavelength in the range around (200 – 1100) nm at room temperature .It can be observed from the figure that the absorbance for all films have A peak at wavelength in the neighborhood of the fundamental absorption edge (296 nm). This behavior can be explained as follows: at high wavelength the incident photons do not have enough energy to interact with atoms, the photon will be transmitted. When the wavelength decreases at ultraviolet region, the interaction between incident photon and material will occur, and then the absorbance will increasing [73]. In other meaning, the incident light is absorbed by the free electrons. Consequently, by the increases of the weight percentages of nanoparticle, absorbance is increasing. These results are in agreement with researcrhes [74, 75].

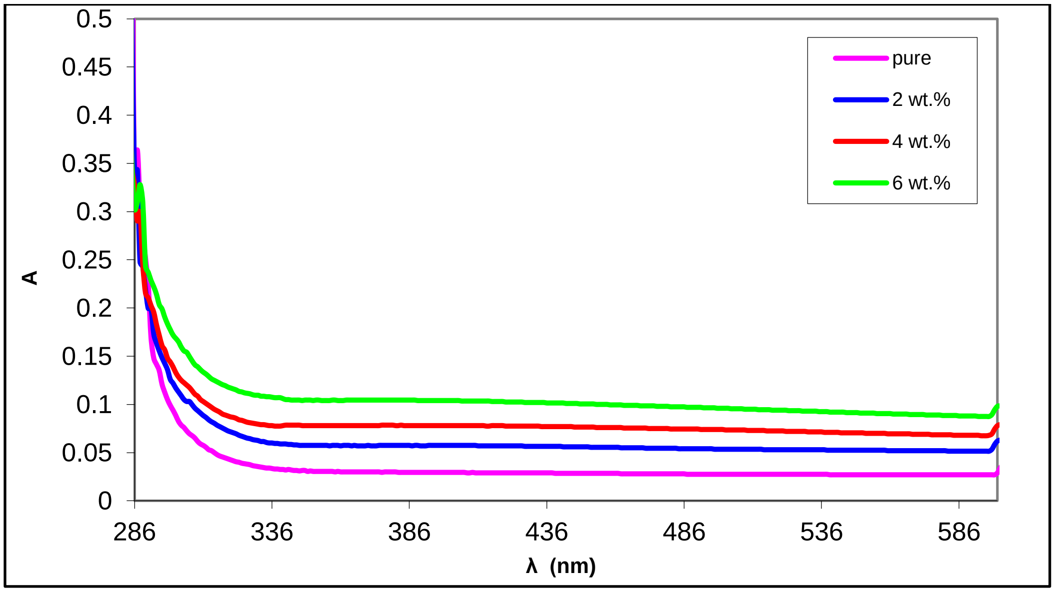


Figure 4.4 The absorbance as function of wavelength (nm) for (PEG - BaTiO$_3$).

4.2.2.2Transmittance (T)

The optical transmittance spectrum as a function of wavelength of incident light on (PEG-$BaTiO_3$) films by adding different concentration of ($BaTiO_3$) is shown in the figure (4.5) shows that transmittance decreases with the increasing of the concentration ,this is caused by the added $BaTiO_3$ contains electrons in it is outer orbits can be absorb the electromagnetic energy of the incident light and travel to higher energy levels, this process is not accompanied by emission of radiation because the traveled electron to higher levels have occupied vacant positions of energy bands ,thus part of the incident light is absorbed by the substance and does not penetrate through it ,on the other hand, the presence of surface defects and the roughness of the surface and fabricating honeycomb structures this leads to increased dispersion of the falling radiation .Then decrease in the Transmittance of the polymer films [76].

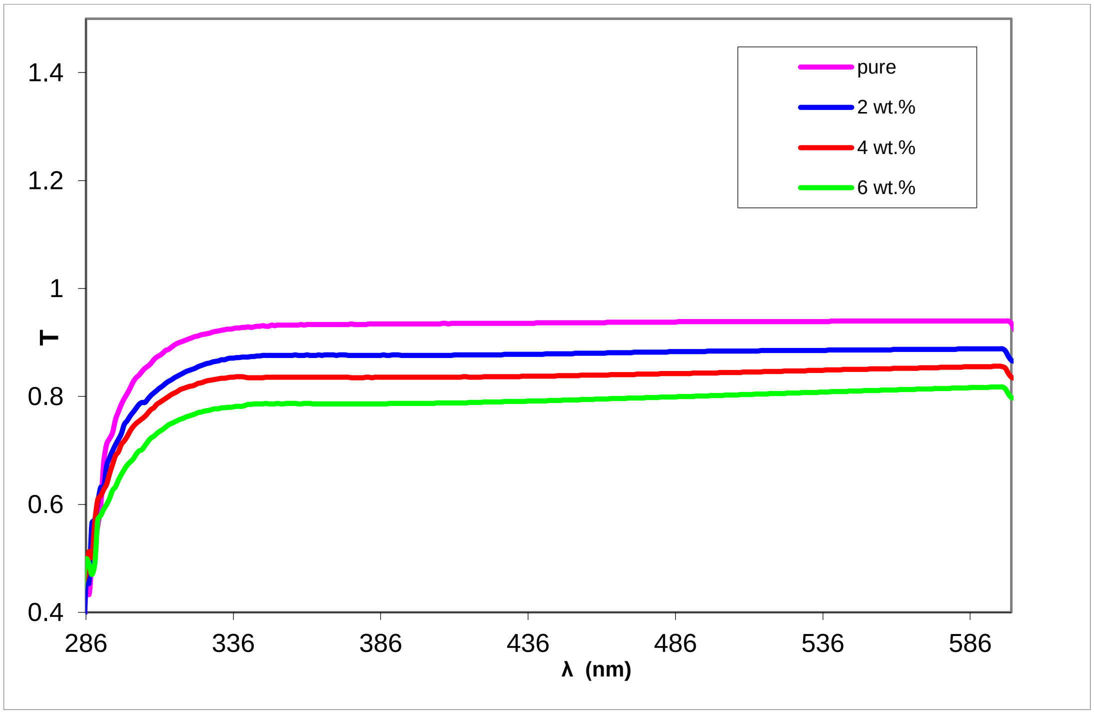


Figure 4.5 The Transmittance as function of wavelength (nm) for (PEG-$BaTiO_3$).

4.2.2.3 The Reflectance (R)

The relation between the reflectance and the wavelength of the incident light for the (PEG- $BaTiO_3$) nanocomposites with various concentration contents is shown in Figure (4.6). It is clear that there is no change in the position of the peak for all amounts of adding the concentration to the PEG polymer, on the other hand observed that the reflectance decreased with increased the ($BaTiO_3$).

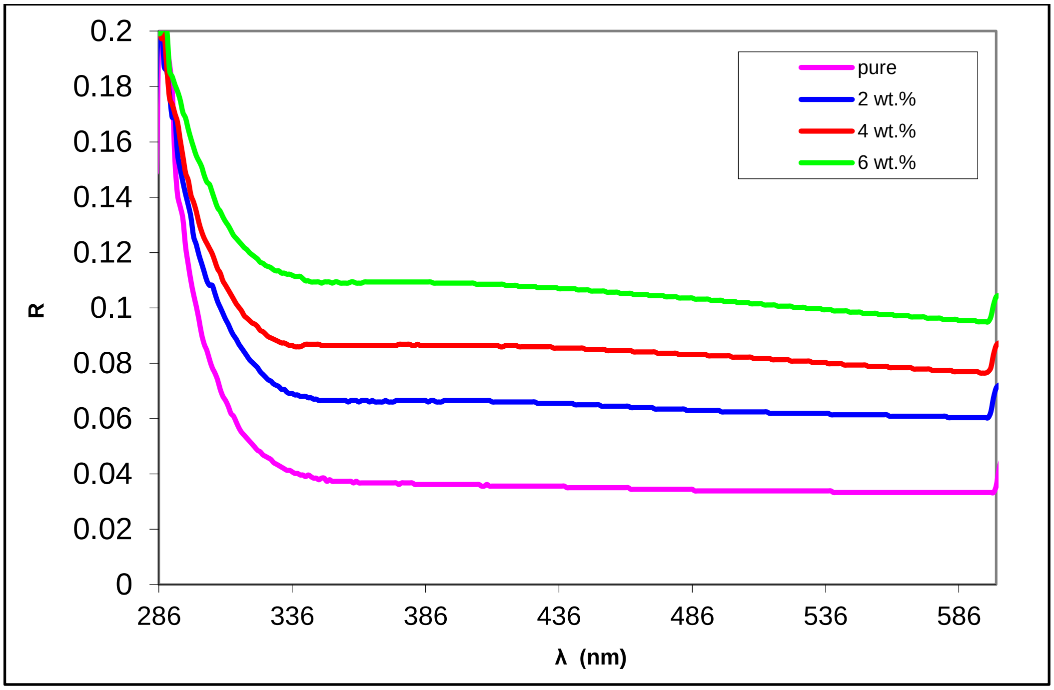


Figure 4.6 The Reflectance as function of wavelength (nm) for (PEG-$BaTiO_3$).

4.2.2.4 Absorption Coefficient (α)

Figure 4.7 shows the absorption coefficient α $(cm)^{-1}$ as a function of wavelength for (PEG-$BaTiO_3$) nanocomposite. It can be seen that the absorption coefficients smallest at high wavelength and low energy, this means that the possibility of electron transition is little because the energy of the incident photon is not sufficient to move the electron from the valence band to the conduction band $(h\upsilon < E_g)$.

At high energies, absorption is bigger, this means that there is a great possibility for electron transitions. Consequently, the energy of incident photon is enough to move the electron from the valence band to the conduction band, the energy of the incident photon is greater than the forbidden energy gap, it is expected that indirect transition of electron occurs, and the electronic momentum is maintained with the assistance of the phonon [77]. Among other results is that the coefficient of absorption for the (PEG-$BaTiO_3$) nanocomposites is less than $10^4 cm^{-1}$at low concentrations. These results are in agreement with researcrhes [78].

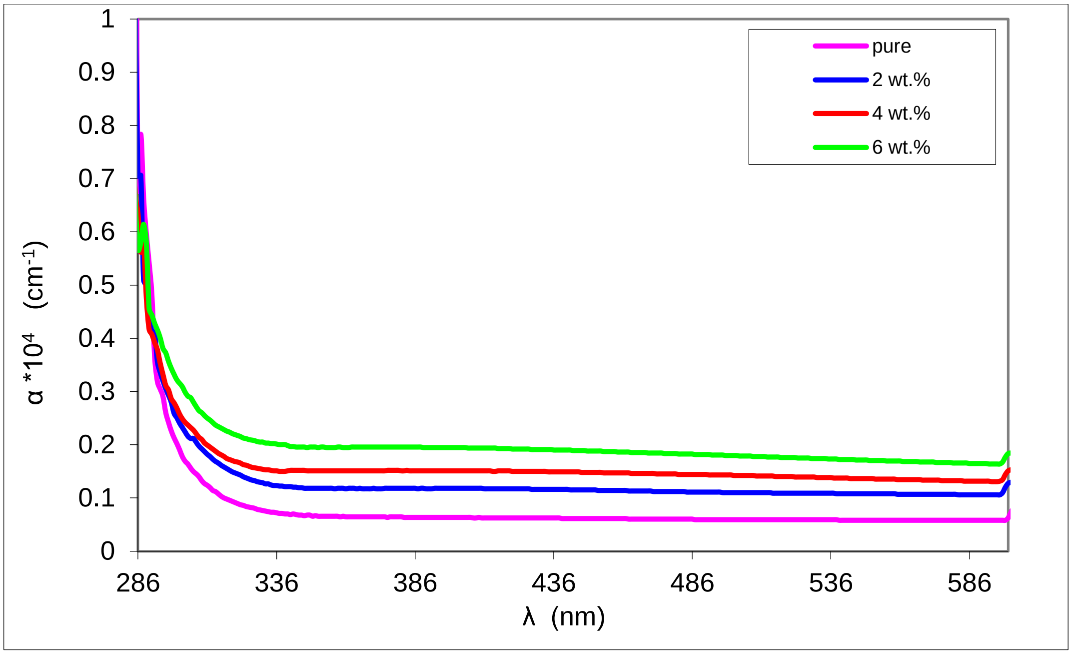


Figure 4.7 The absorption coefficient α $(cm)^{-1}$ as a function of wavelength (nm) For (PEG-$BaTiO_3$).

4.2.2.5 Extinction Coefficient (k)

The extinction coefficient inertness obtained by the electromagnetic wave inside the matter the amount of what the electrons absorb the material from the energy of the falling photons, and on this basis its value is determined by the interactions of the electromagnetic wave with the medium and the inactivity factor is calculated through the absorption factor calculated from the absorbance spectrum from the absorption spectrum .Figure (4.8) shows the variation of extinction coefficient for (PEG-$BaTiO_3$)nanocomposites withphoton wavelength . from figuer (4.5) noticed the extinction coefficient depends on the absorption coefficient, if the extinguishing factor increases with the increase of photon energy and also increases with the increase of the deformation rate.These results are in agreement with of Ghanipour and Dorranian [80].

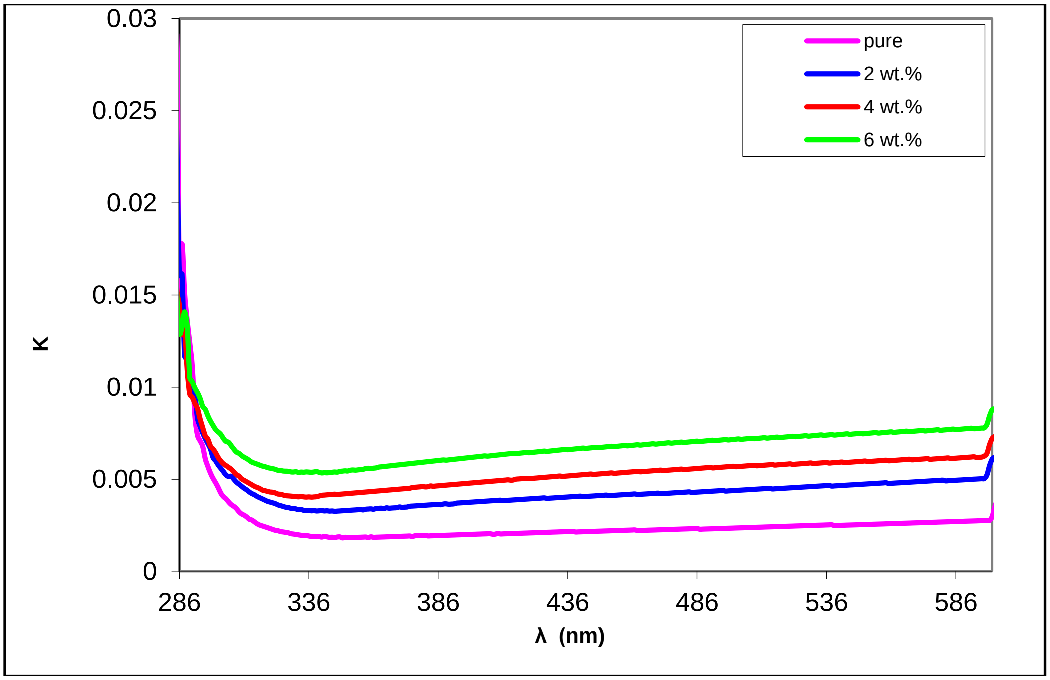


Figure 4.8 The Extinction Coefficient as a Function of Wavelength for (PEG -$BaTiO_3$) liquid.

4.2.2.6 The Refractive Index (n)

The refractive index is defined as the ratio of the velocity of light in space to the velocity of light in the medium. The figure(4.9) shows that the refractive index values of pure(PEG) and (PEG-$BaTiO_3$) are increasing linearly with the increase of the concentrations of $BaTiO_3$ ratio, This behavior attributed to the increase of the density of nanocomposites, it is decreased with the increase of the wavelength, this is agree to the result[81].

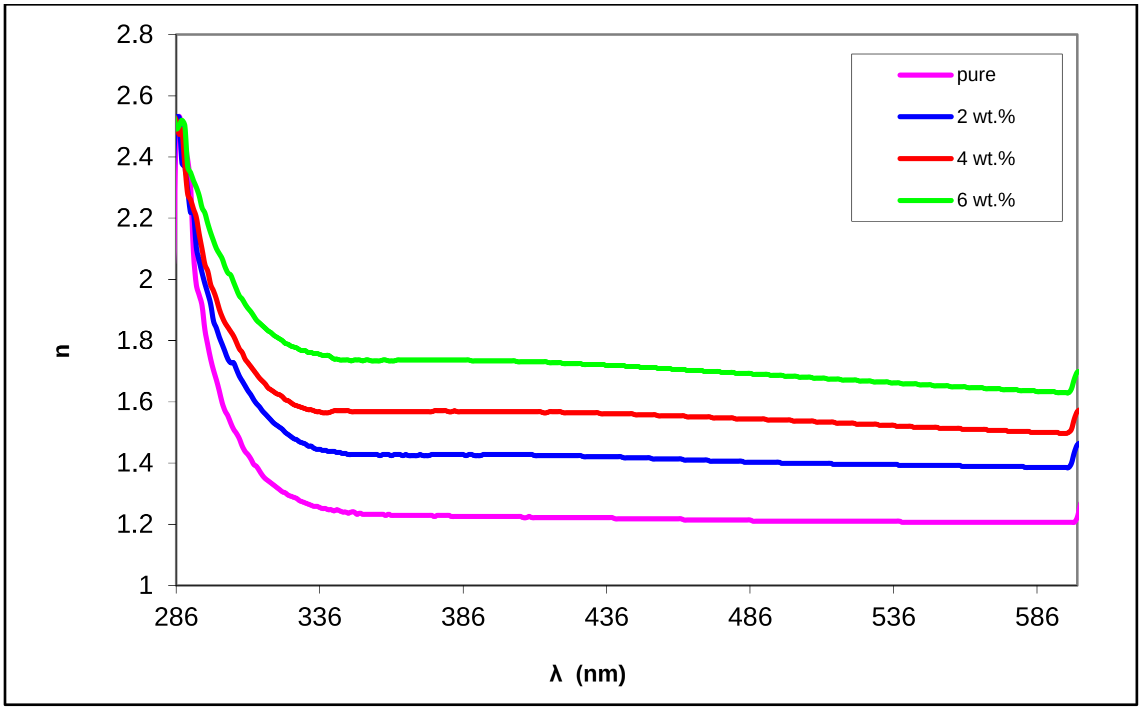


Figure (4.9) The refractive index for (PEG-BaTiO$_3$) nanocomposites.

4.2.2.5 Optical Energy Gaps of the (allowed) Indirect Transition

The values of $(\alpha h\nu)^2$ plotted against (hv) of (PEG) and (PEG-BaTiO$_3$) blend films. Are shown in the figure (4-10) shows that the optical energy gap values of pure PEG and PEG –BaTiO$_3$ are decreasing with the increasing of the weight percentages . Where the energy gap for pure BaTiO$_3$ films was (3.96 eV) and this value decreasing with the increase of the doping ratio to (3.46 eV) , this decrease can be explained by The emergence of electrons with more electrons in the conduction package as a result of adding impurities does not correspond to the appearance of gaps in the valence beam as it is in the semiconductor pure, but rather moved from a level of energy located under the conduction called the donor level where the electrons are the primary vectors and the gaps of the secondary vectors .The obtained values are shown in tables (4.2) we can see that the values of optical energy gap decrease with the increasing of the weight percentages. These results are in agreement with[79].

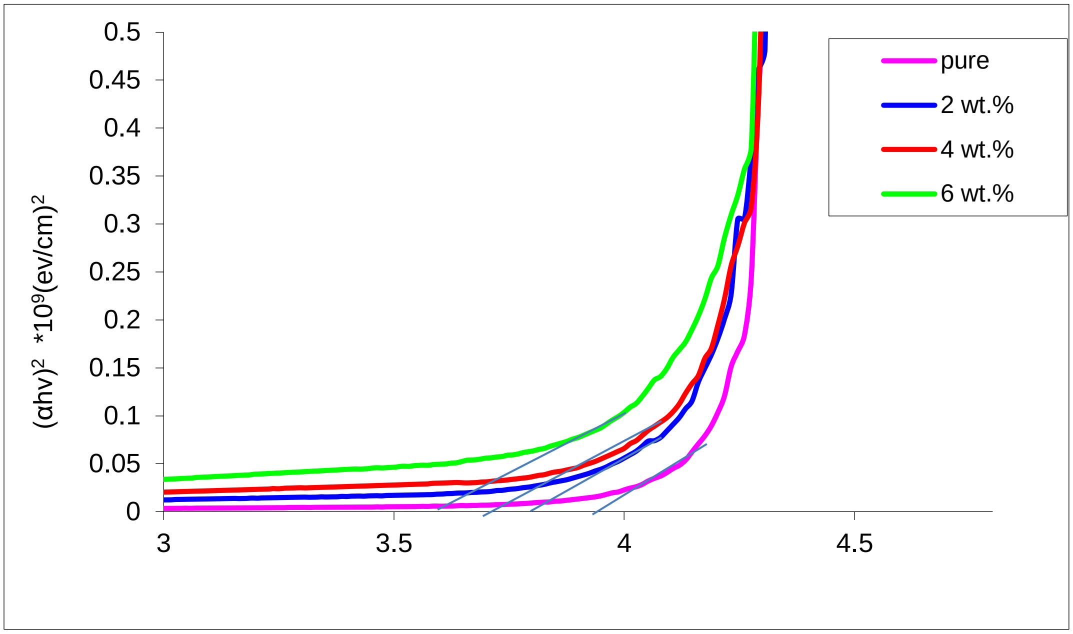


Figure 4.10a Relation between $(\alpha h\nu)^2$ versus photon energy.

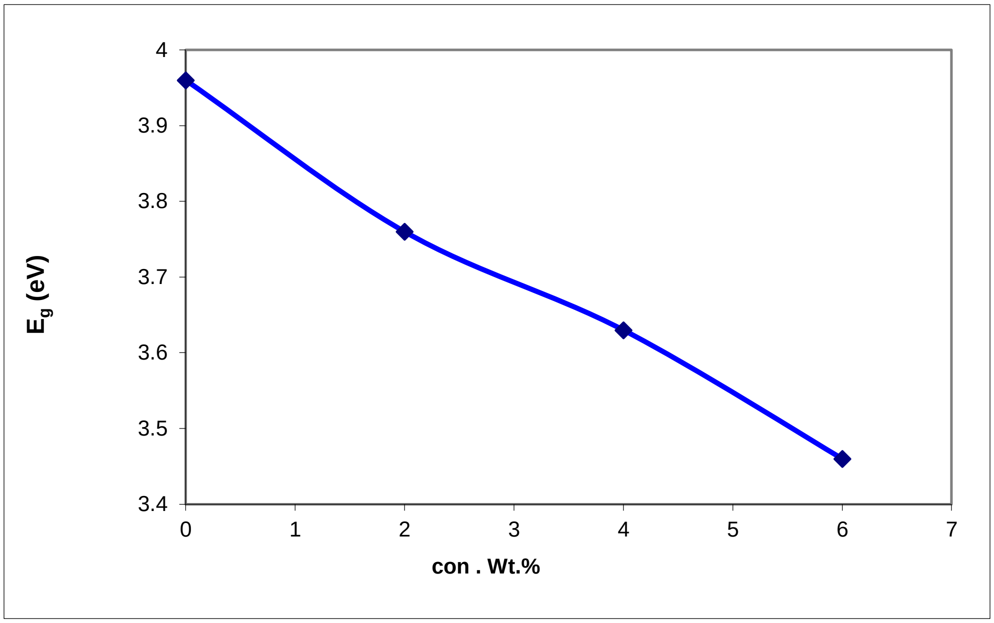


Figure 4.10b Relation between E_g and doping ratio for thin film

Table (4.2) The values of optical energy gap for with doping ration for (PEG-BaTiO3) thin films.

$BaTiO_3$ wt.%	E_g(eV)
0	3.96
2	3.76
4	3.63
6	3.46

4.2.3 The Electric Properties of (PEG, $BaTiO_3$) Nanocomposites

4.2.3.1 The Electrical Conductivity (D.C)

Figure (4.11) show the varation of D.C electrical condectivity of (PEG-$BaTiO_3$)nanocomposite with $BaTiO_3$ concentrations .electrical conductivity ($\sigma_{D.C}$) was measured for all weight ratios of the (PEG-$BaTiO_3$) nanocomposite recorded at room temperature .from figure (4.11) it has been observed that the electrical conductivity values of the nanocomposite are increases by increasing the weight ratio of the $BaTiO_3$ concentration. The increases in the weight ratio leads to an increasing in the number of ions and free electrons on a regular basis, which increases the interaction between the mixture particles, which in turn leads to disturbance within the mixture, This explanation agrees with researchers [82] The electrical conductivity of (PEG-$BaTiO_3$) nanocomposites could be increased as a result of increasing of free charge carriers, this is similar with the result of Srikanth et al [83].

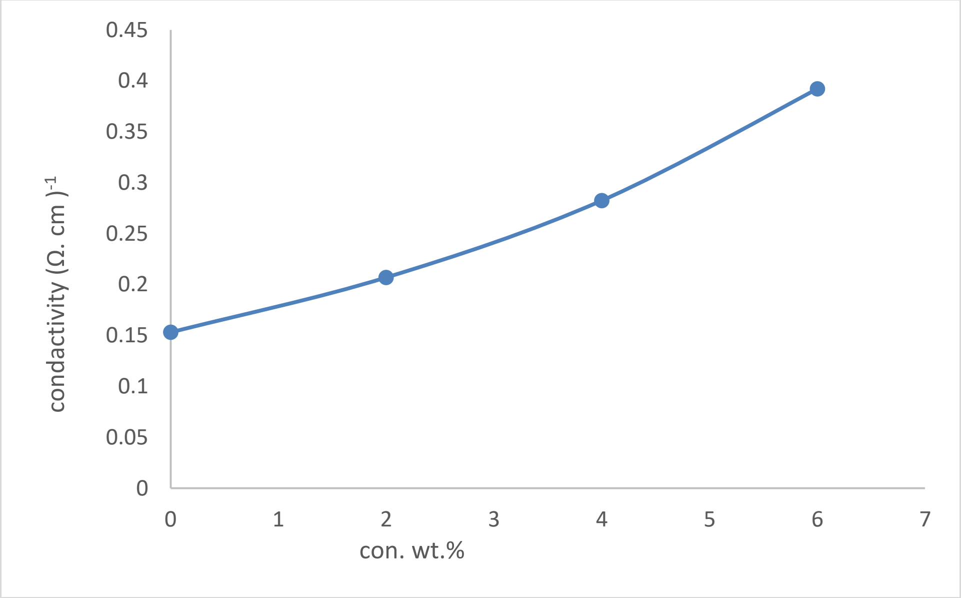


Figure 4.11 The variation of D.C electrical conductivity of (PEG-BaTiO3) nanocomposites as function of $BaTiO_3$ nanoparticles concentrations.

4.3 Measurement of Liquid

4.3.1 The Optical Properties of (PEG- $BaTiO_3$) Nanocomposites

4.3.1.1 The Absorbance (A)

Absorbance measurements of PEG before and after adding ($BaTiO_3$) nanoparticles were plotted against different wavelengths in the range between (200-1100) nm as shown in Figure (4.12). It can be observed from the figure that the absorbance for all liquid sample have A peak at wavelength in the neighborhood of the fundamental absorption edge (280 nm). The relation between the absorbance with wavelengths for pure and doped for different ratio of doping, the absorbance of pure PEG and its additives are increasing with the increase of the Weight ratios of ($BaTiO_3$). Because the absorbance is directly proportional with Weight ratios according to the Lambert-Beer law (2-6) this is because the u0069addition led to increase the values of Weight ratios in same volume, then increase the number of particles that absorb the energy of incident light.

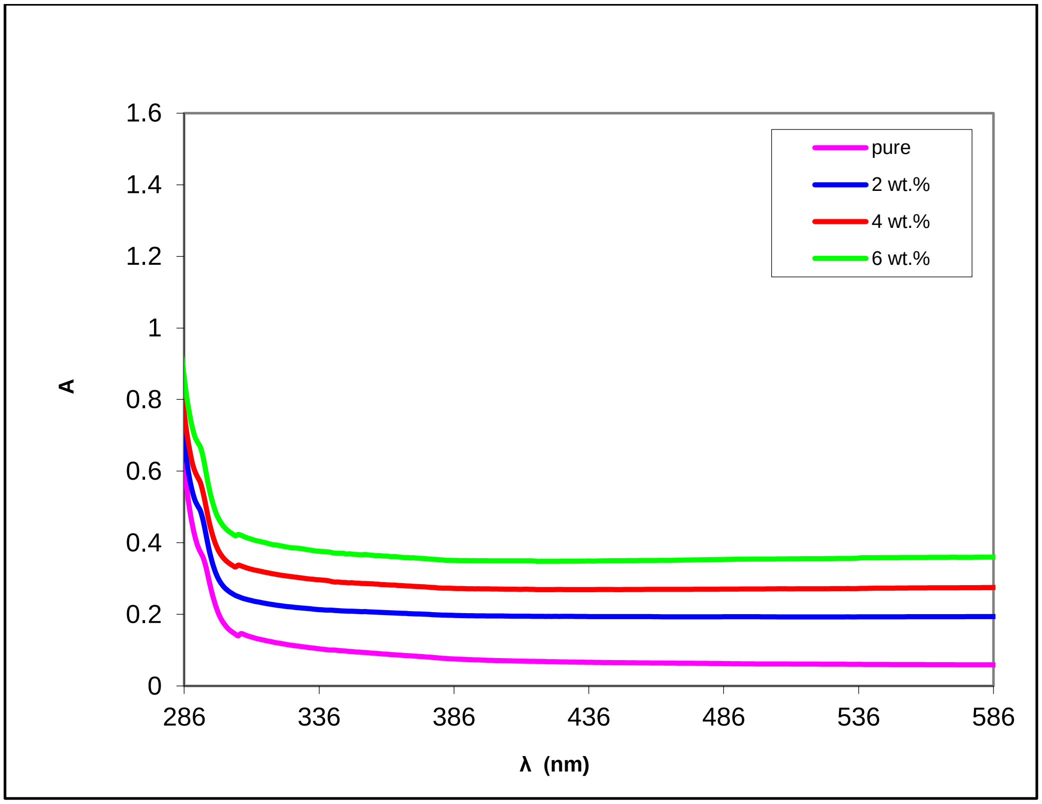


Figure 4.12 The absorbance vs wavelength for PEG and (PEG-$BaTiO_3$) liquid.

4.3.1.2 The Transmittance (T)

The Transmittance can be calculated using the equation (2-3). Figure (4.13) shows that transmittance of the solution has low values at the wavelength that lies in (280) nm, where there is a dcreases in the transmittance with increses in the $BaTiO_3$ nanoparticles or increasing of wavelength so that absorbance value decreases, where the transmittance is inversely proportional with absorbance .as a result increases clusters of nanoparticle and increases the percentage of Weight of the number of charge carriers This basically confirms that the absorption and the transmittance depends on the energy of the incident photon .

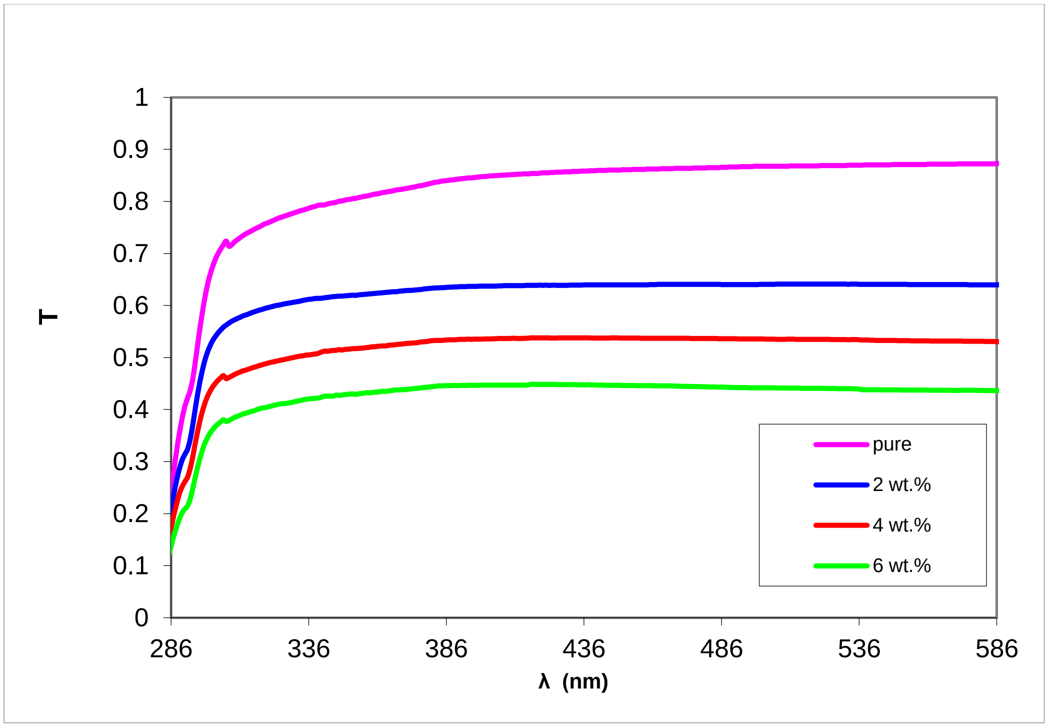


Figure 4.13 The Transmittance vs Wavelength for PEG and (PEG- $BaTiO_3$) liquid.

4.3.1.3 The Reflectance(R)

The Reflectance can be calculated using the equation (2-4).Figure (4.14) shows that the reflectance increasing with the decreases of wavelength. The addition of $BaTiO_3$ nanoparticles led to increase the reflectivity because the increased of nanocomposite density. Reflectivity is high at a certain point on the ultraviolet spectrum.

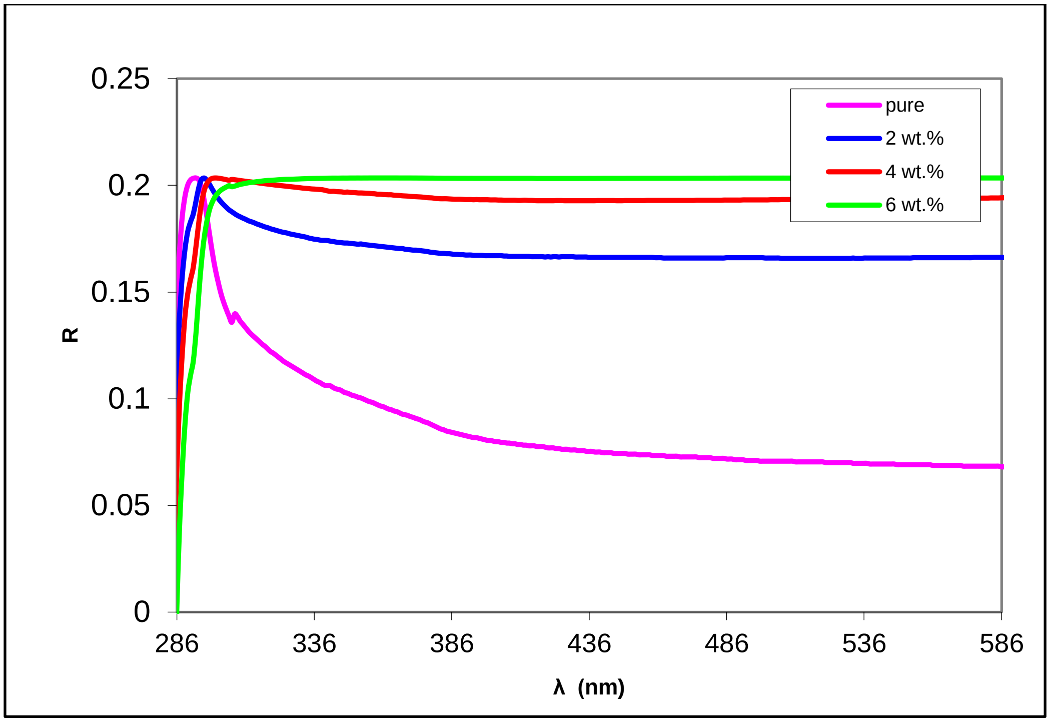


Figure 4.14 The Reflectance vs wavelength for PEG and (PEG- $BaTiO_3$) liquid.

4.3.1.4Absorption Coefficient (α)

The main objective of studying the absorption coefficient is to identify the amount of energy through the absorbent medium and depends on the thickness and type of the medium .The values of (α) for all thin films are found to be smaller than 10^4 cm^{-1} in the visible region , which means that the liquid have indirect optical energy gap. The absorption coefficient α $(cm)^{-1}$ as a function of wavelength for (PEG-$BaTiO_3$) nanocomposite as shows in Figure (4.15).

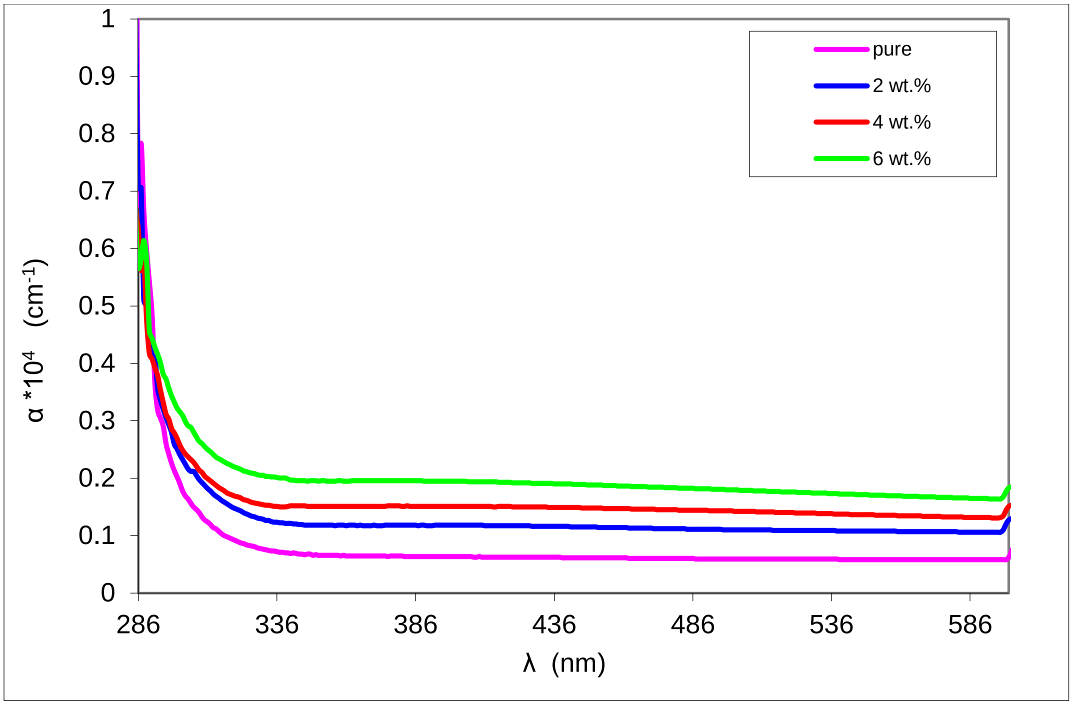


Figure 4.15 The absorption coefficient α $(cm)^{-1}$ as a function of wavelength (nm) For (PEG-$BaTiO_3$) liquid

4.3.1.5 Extinction coefficient (K)

The variation of the extinction coefficient for (PEG-$BaTiO_3$) nanocomposites as a function of wavelength shown in figure (4.16). The figure shows that extinction coefficient increases with increasing the concentration of ($BaTiO_3$) nanoparticle, this is due to the increase in optical absorption and photons dispersion in the (PEG-$BaTiO_3$) nanocomposite . The extinction coefficient of nanocomposites has high values at UV region, this behavior attributed to high absorbance of all samples of nanocomposites.

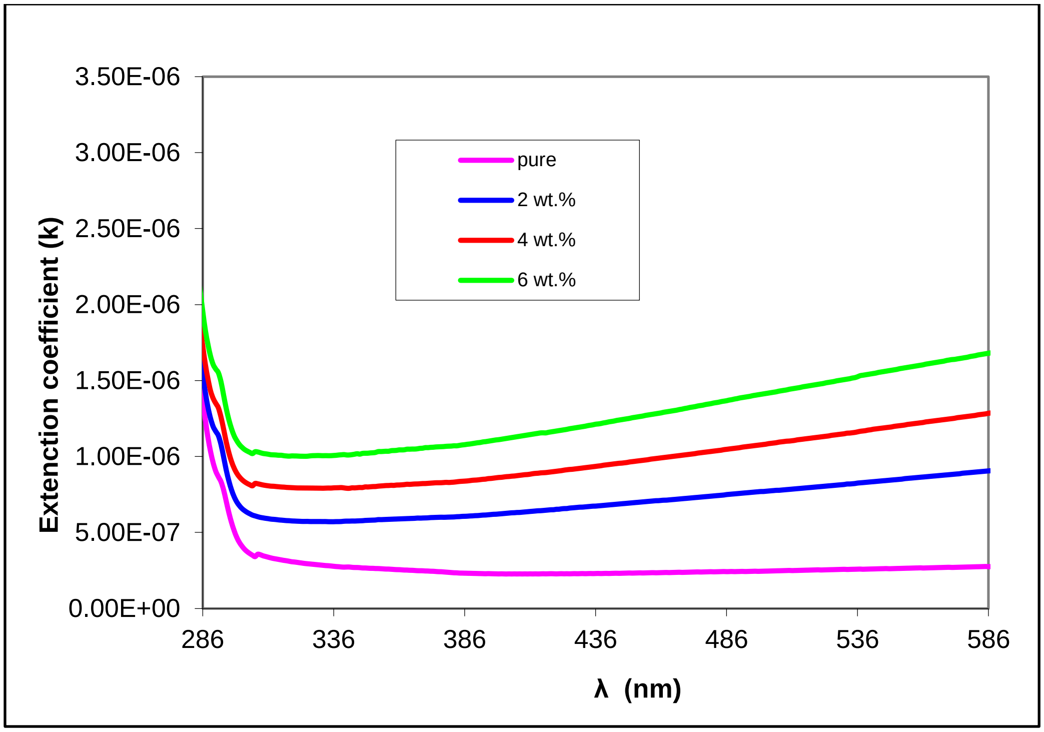


Figure 4.16 The Extinction Coefficient as a Function of Wavelength for (PEG -BaTiO3) liquid

4.3.1.6 Refractive Index (n)

The refractive index is defined as the ratio of the velocity of light in space to the velocity of light in the medium. The figure(4.17) shows that the refractive index values of pure (PEG) and (PEG-$BaTiO_3$) are increasing linearly with the increase of the concentrations of $BaTiO_3$ .This behavior attributed to the increase of the density of nanocomposites, it is decreased with the increase of the wavelength, this is similar to the result.

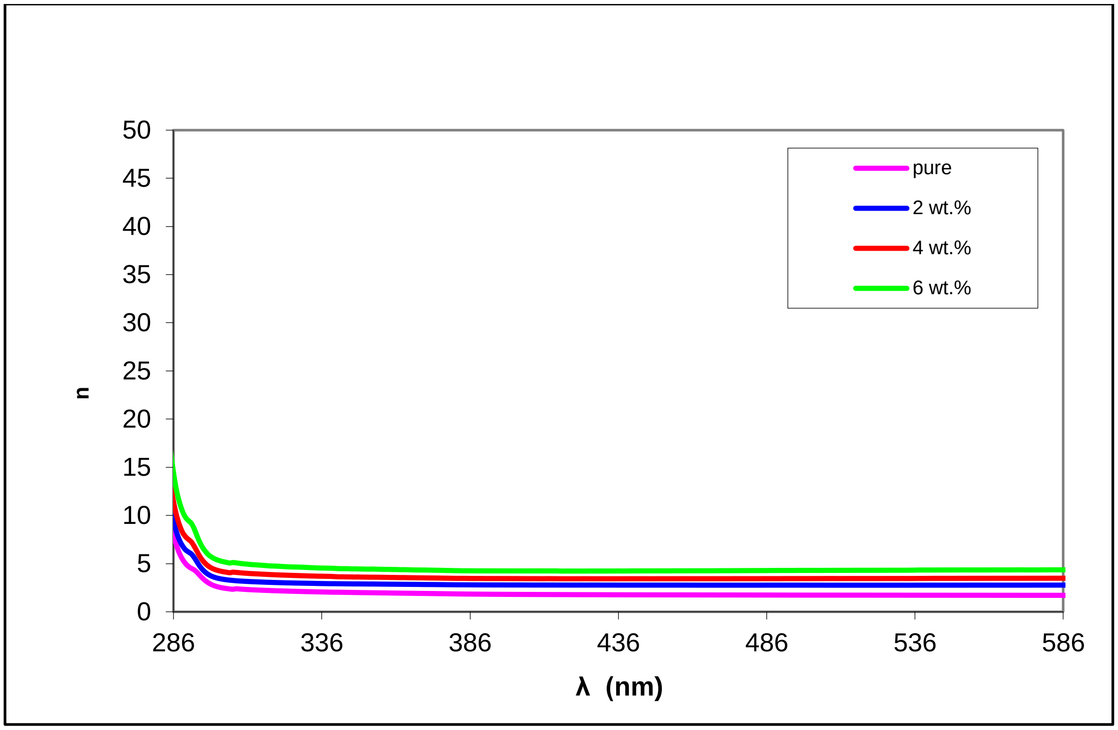


Figure 4.17 the refractive index for PEG-BaTiO3) nanocomposites as a function of incident Wavelength (nm).

4.3.1.7 Optical Energy Gaps of the (allowed) Indirect Transition

The values of $(\alpha h\nu)^2$ plotted against (hv) of (PEG) and (PEG-$BaTiO_3$) liquid as shown in Figure (4.18). Extrapolating the straight line of the plot $(\alpha h\nu)^2$ versus (hv) for zero absorption coefficient values ($\alpha = 0$) give the energy band gap value for the allowed indirect transition. It appears from Figure the values of optical energy gap decrease with the increasing of the weight percentage of the $BaTiO_3$ added. The energy gap for pure PEG liquid equal to (3.46 eV) , the value after adding (0.02g) from $BaTiO_3$ equal to (3.35 eV), the value for (0.04g) from $BaTiO_3$ equal to (3.25eV) and for (0.06g) from $BaTiO_3$ become (3 eV).

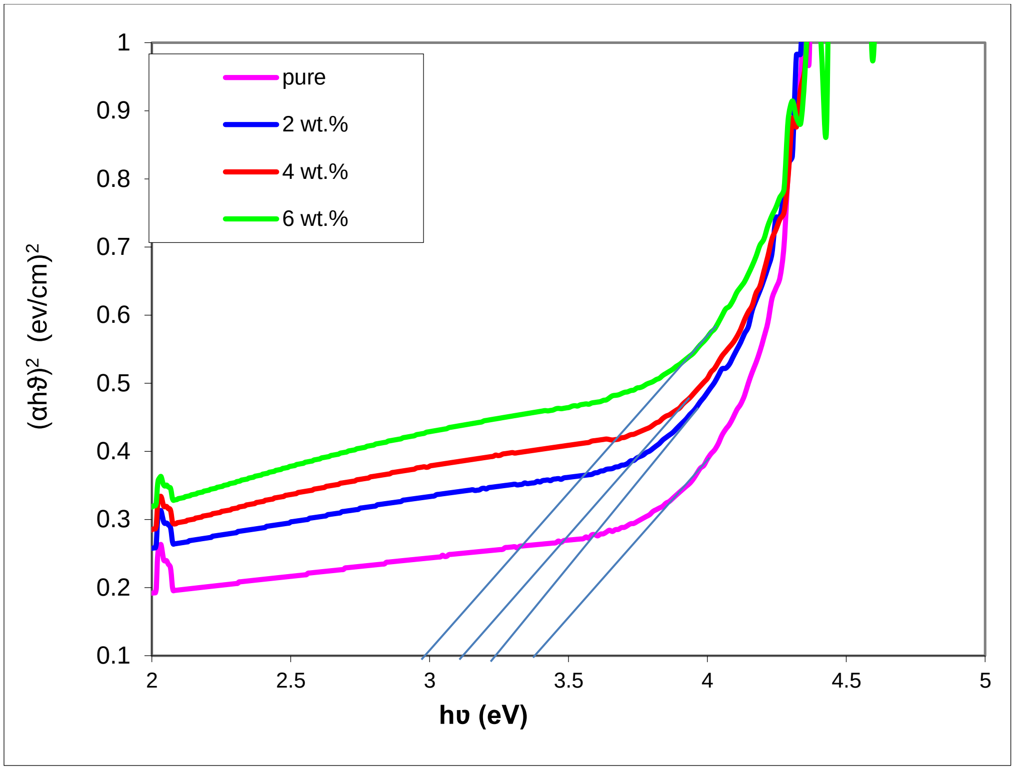


Figure 4.18a Relation between $(\alpha h\nu)^2$ versus photon energy.

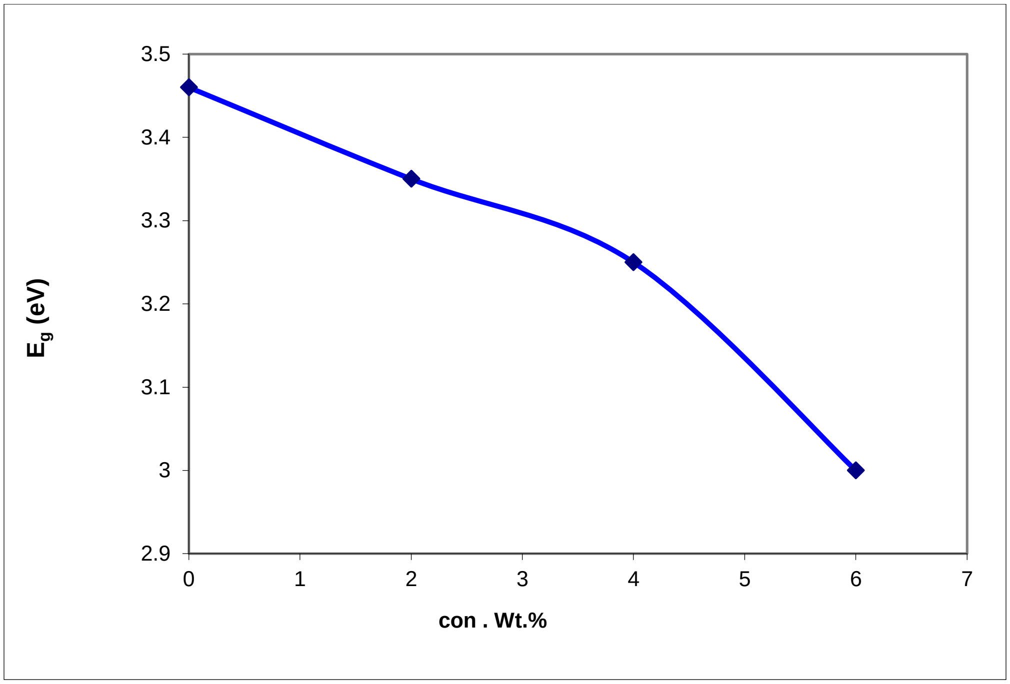


Figure. 4.18b Relation between E_g and doping ratio for (PEG-$BaTiO_3$) liquid.

Table (4.3) the values of optical energy gap for with doping ration for ($PEG-BaTiO_3$) liquid.

$BaTiO_3$ wt.%	E_g(eV)
0	3.46
2	3.35
4	3.25
6	3

4.3.2 Rheological Properties of ($PEG, BaTiO_3$) Nanocomposites

This properties include the polymer density and the polymer viscosity.

4.3.2.1 - The Density

Density was measured for all solutions of PEG polymer before and after adding different weights from $BaTiO_3$. The value of density increases with increasing concentration of $BaTiO_3$, which may because to the increased mass of the solution and swell happening in polymer particles as a result of soluble in distilled water and especially polymers of higher molecular weight figure (4.19) shows the variation of density with concentration . From figure (4.19) it can be notice that the density increases after the addition of $BaTiO_3$, since the density defined as mass per unit volume and addition different weight of $BaTiO_3$ to a fixed volume of solvent, causes a linear increment for density.These results in behavior are similar to those of the researchers [84].

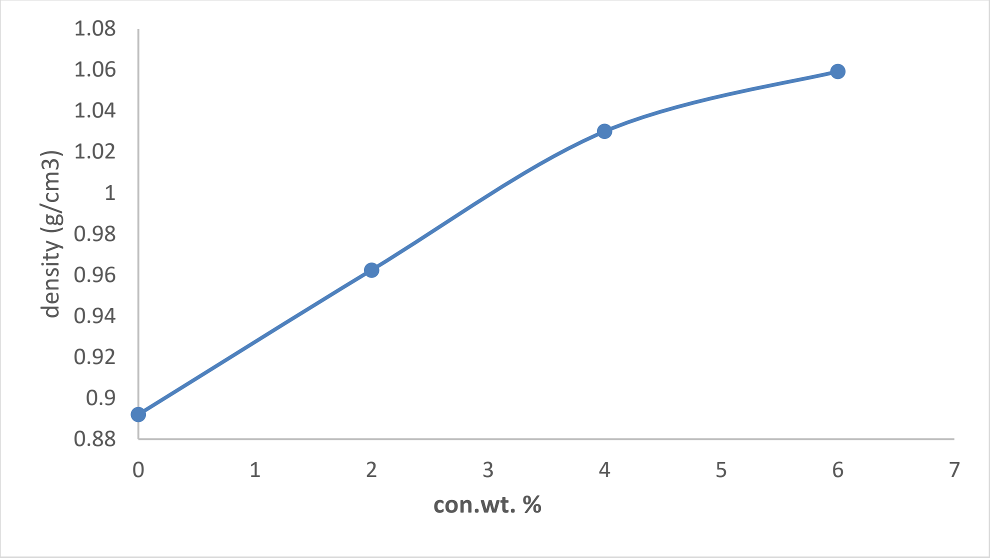


Figure 4.19 Density vs concentrations of PEG solutions before and after addition of $BaTiO_3$

4.3.2.2The viscometer

The values of viscosity have been measured for PEG polymer solution before and after adding different weight of $BaTiO_3$.The results are illustrated in Figure (4.20). The increasing of viscosity with concentration of PEG polymer attributed to the mechanism that hydrogen bonding of water attached to oxygen sites, which leads to solvation sheaths and increase in the size of the molecules also the viscosity, furthermore water act as plasticizer that reduce tensile strength and increase its chains. Adding $BaTiO_3$ made enhancement for these viscosities because the viscosity describes a fluids internal resistance between molecules so when we added $BaTiO_3$ there will be more viscous.

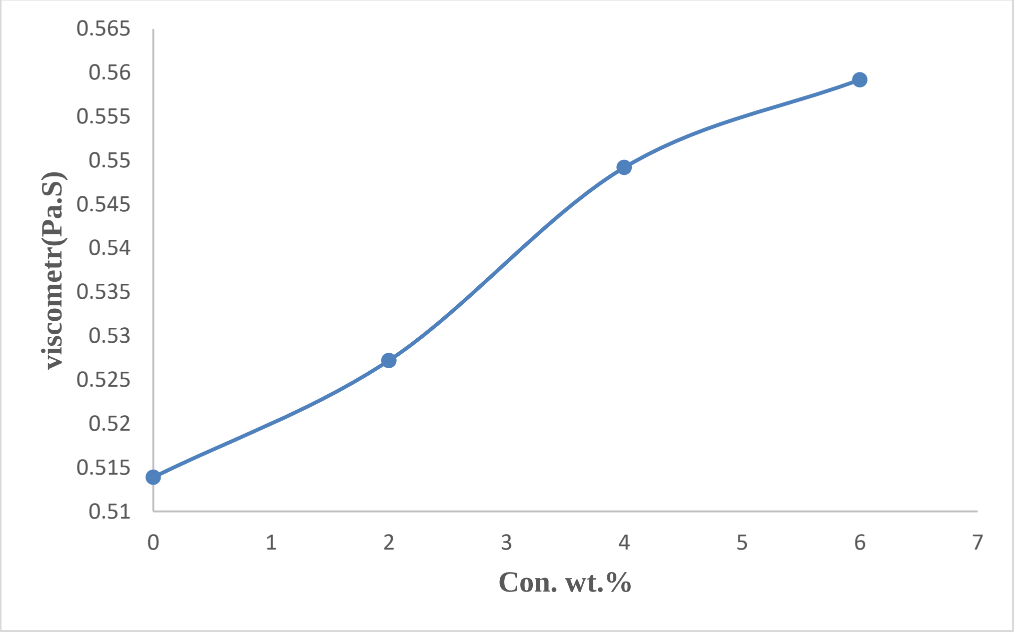


Figure. 4.20 Relative viscosity versus concentration for polymeric solutions.

4.4 The Electric Properties of (PEG, $BaTiO_3$) Nanocomposites

4.4.1Molar Conductivity

Figure (4.21) shows that the molar conductivity values decrease with increasing the concentration of $BaTiO_3$ this is due to the diluted solutions that does not happen any interaction among molecules and the electrostatic repulsion between particles that generated leads to a decrease in bonding molecular between polymer molecules and the solvent, which lead to increase the dimensions of the polymer and consequently to slow down the movement of ions and this does not happen in high concentrations [85]. Figure(4.21) shows that the molar conductivity values decreased after the addition of $BaTiO_3$ due to the formation of electrodes temporarily on molecules due to the addition $BaTiO_3$ and that the polymer molecules being large, they have the ability to inductively polarization which in turn leads to increased molar connectivity [86].

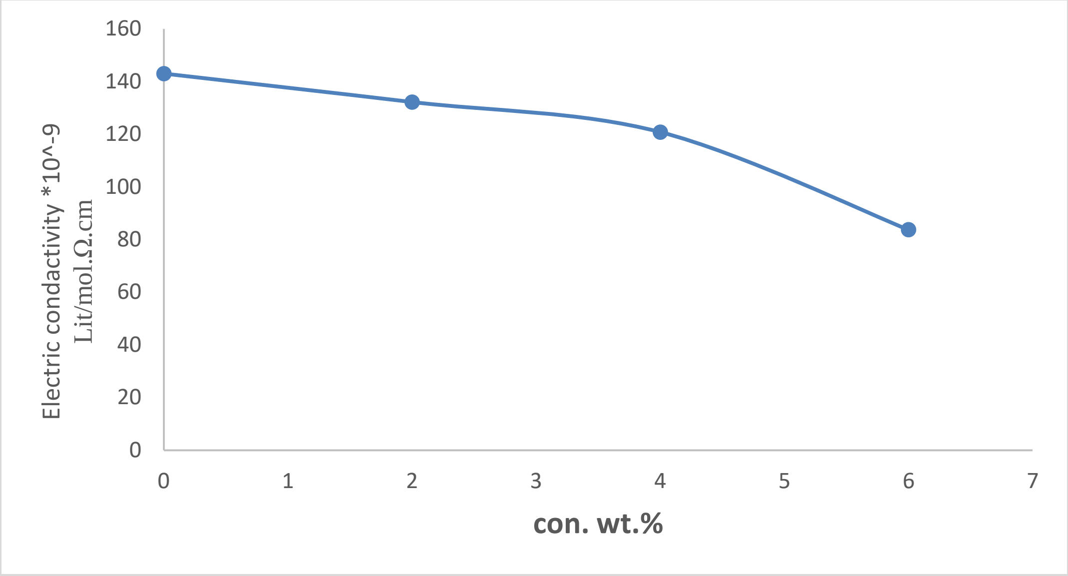


Figure 4.21 Molar conductivity versus square root of concentration for composite.

4.5 Application of (PEG-$BaTiO_3$) nanocomposites for antibacterial activity

The antibacterial activity of the (PEG-$BaTiO_3$) samples tested against gram negative (Escherichia coli) and gram positive (Staphylococcus aureus) as shown in Figure (4.22). From the figure, the inhibition zone increases with increase in $BaTiO_3$ nanoparticles concentrations. The reason for the antibacterial activity of (PEG-$BaTiO_3$) nanocomposites may be due to the presence of reactive oxygen species (ROS) generated with different concentration of $BaTiO_3$ nanoparticles. Chemical interaction between hydrogen peroxide and membrane proteins could be the reason for the antibacterial activity of nanocomposites. The hydrogen peroxide produced enters the cell membrane of bacteria and inhibition them. The other possible mechanism of action is that the $BaTiO_3$ nanoparticles in nanocomposites are carrying the positive charges and the microbes are having the negative charges which create the electromagnetic attraction between the nanoparticles and the microbes. When the attraction is made, the microbes get oxidized and inhibition instantly. The results indicated that (PEG-$BaTiO_3$) films possessed a strong antibacterial activity with the increase in the weight percentages of $BaTiO_3$nanoparticles, this is similar with the results of Prabhu *et al.* [87], kumar and krishnan [88] and Khandanlou *et al.* [89].

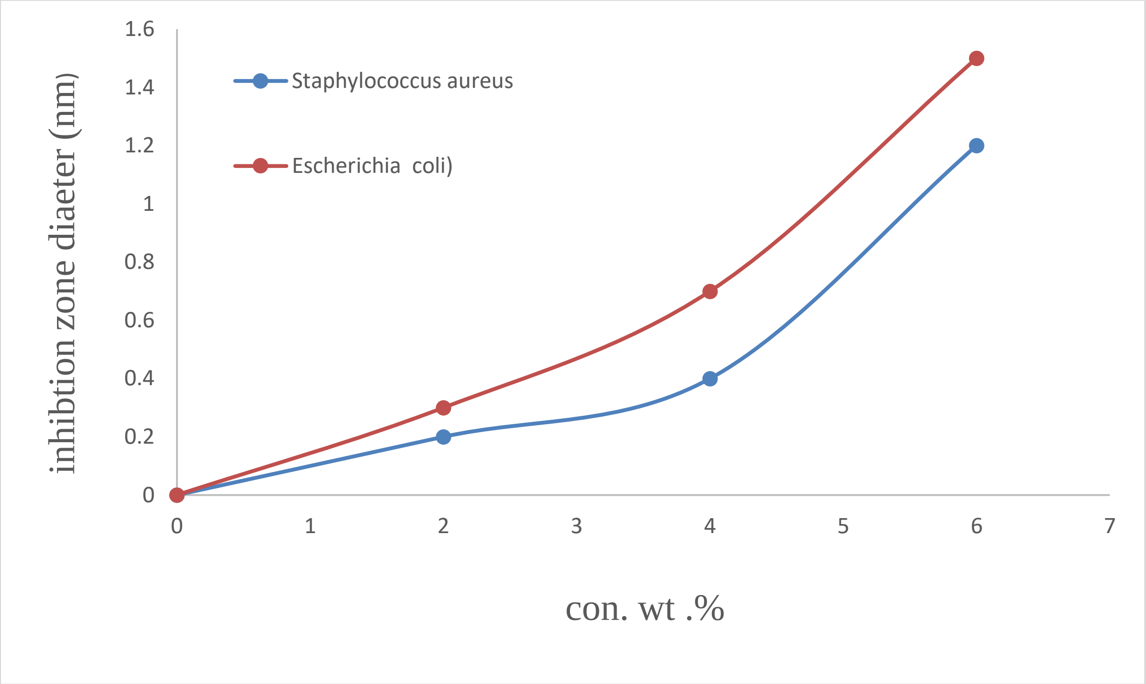


Figure 4.22 antibacterial effect of (PEG-$BaTiO_3$) nanocomposite as a function of $BaTiO_3$ nanoparticles concentrations on S. aureus and E. coli .

4.6 Conclusions

From properties pure PEG and (PEG-$BaTiO_3$) we conclusions:

1. PEG polymers show a continuous change in their physical properties as a result of adding ($BaTiO_3$) led to the improvement of all properties.
2. The high absorption in (UV) region makes the films good material for screening of (UV) portion of the electromagnetic spectrum which is dangerous to human and animal health. Also adding ($BaTiO_3$) to PEG lead to increase reflectivity in (UV) region, therefore it can be used as a coating for different types of glass to protect it against of the solar radiation puls reduce it intensity .
3. The transmittance and energy band gap of (PEG-$BaTiO_3$) decrease with increasing the $BaTiO_3$ nanoparticles concentrations exactly at 6 wt. % consecration.
4. Adding $BTiO_3$ to PEG leads to increase the conductivity, therefore conductivity it be high when consecration (6 wt. %).
5. The inhibition zone of (PEG-$BaTiO_3$) nanocomposites against S. aureus and E. coli increases with increasing the concentrations of $BaTiO_3$ nanoparticles, which mean the (PEG-$BaTiO_3$) nanocomposites may be used for coating materials or shielding for antibacterial activity application with high activity.

4-7 Future Works

1. -Study of temperature effects, the electro-optical properties andthe mechanical properties of (PEG-$BaTiO_3$) nanocomposites.

2. Study the effect of gamma rays on the physical properties of the solutions and (PEG-BTiO$_3$) thin films and find out the possibility of hardness thin films as a result of radiation and change their mechanical properties.
3. Preparation of thin film of this polymer after doping via another technique with other elements and study the optical and electrical properties.
4. Take different molecular weights of PEG such as 8000-20000 and mixed it with Ba-compounds to synthesized nano-composites films .

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الخلاصة

في هذه الدراسة ، تم تحضير محاليل (PEG-$BaTiO_3$) ، على النحو التالي: كنسبة 2g من البولي اثلين كلايكول PEG مذابة في الماء المقطر (50)ml كمذيب مع التحريك لمدة 3min عند درجة حرارة الغرفة حتى يتم تكوين محلول سائل لزج متجانس. تمت إضافة مادة الجسيمات النانوية ($BaTiO_3$) إلى محلول المزيج بنسب %(0,2,4,6) وتركها عند التحريك لمدة 5min عند درجة حرارة الغرفة. المحاليل المتجانسة الناتجة (PEG-$BaTiO_3$) تم صبها على لوح زجاجي نظيف ثم نقلها ووضعه اعلى سطح مستو عند درجة حرارة الغرفة لمدة 48 h حتى تجف .

تم دراسة الخصائص التركيبية للاغشية عن طريق المجهر الماسح الإلكتروني SEMوالمجهر الضوئي OMومطياف الاشعه تحت الحمراء FTIR . توضح صورSEM و OM التشكل السطحي للمركب النانوي قبل وبعد إضافة $BaTiO_3$ وإن البوليمر النقي (PEG) لديه تجانس جيد مع $BaTiO_3$ ويظهر انتشار الجسيمات النانوية بوضوح في صور SEM و OM ، وهذا يعني أن الجسيمات النانوية منتشرة بوضوح في الغشاء الرقيق .وتظهر النتائج التجريبية للخصائص التركيبية لم يكن هناك تفاعل بين PEG والجسيمات النانوية($BaTiO_3$).

تمت دراسة الخواص البصرية للأغشية والسائل المحضرين من خلال الحصول على أطياف النفاذية في مناطق الأشعة فوق البنفسجية كدالة للطول الموجي من nm(200-1100). تزداد قيم الامتصاصية ومعامل الانكسار معامل الامتصاص، معامل الخمود للسائل وللأغشية النقية والمشوبه . اماالنفاذيه و فجوه الطاقه تقل بزيادة نسبة تركيز الماده النانويه $BaTiO_3$.

تمت دراسة الخواص الكهربائيه بما في ذلك قياس التوصيليه الكهربائيه المستمره للأغشية والتوصيل المولي للسائل. أظهرت النتائج أن الموصلية الكهربائية تزداد مع زيادة نسبة التشويب لتركيز الماده النانوية $BaTiO_3$ ، وأن الموصلية المولية تتناقص مع زيادة نسبة تركيز الماده النانوية $BaTiO_3$.

اختبرت المتراكبات النانوية (PEG-$BaTiO_3$) كمضادات لبكتريا موجبة غرام (المكورات العنقودية الذهبية) وسالبة غرام (الاشريشيا القولونية). بينت النتائج أن منطقة التثبيط ازدادت بزيادة تراكيز الجسيمات النانوية$BaTiO_3$.

وزارة التعليم العالي والبحث العلمي
جامعة بابل- كلية العلوم
قسم الفيزياء

تأثير الجسيمات النانوية $BaTiO_3$ على بعض الخصائص الفيزيائية لPEG لتطبيق المضاد للبكتريا

رسالة مقدمة الى
مجلس كلية العلوم – جامعة بابل
وهي جزء من متطلبات نيل شهادة الماجستيرفي العلوم /الفيزياء

قدمتها
ولاء صباح عبد الساده منسي

بكالوريوس في الفيزياء/٢٠١٨

اشراف

الاستاذ الدكتور

رحيم كعيد كاظم حسين

١٤٤٣هـ ٢٠٢١م