Republic of Iraq
Ministry of Higher Education
and Scientific Research
AL–Nahrain University
College of Science
Department of Physics

Physical Properties of PMMA/ZnO Composite Material

A Thesis

Submitted to the College of Sciences /Al-Nahrain University in Partial
Fulfillment of the Requirements for the Degree of Master of Science
in Physics.

By

Zaman Sahhib Obaid

B.Sc Physics 2009/ College of Science/ Al-Nahrain University

Supervised by

Dr. Thamir Abdul Jabbar Jumah

(Assist. Prof.)

May, 2017 Shaaban, 1438

Supervisor Certification

I certify that this thesis entitle **“Physical Properties of PMMA\ZnO Composite Material”** was prepared under my supervision at the College of Science/ Al-Nahrain University as a partial requirement of the degree of Master in Physics.

Signature:
Name: Dr. Thamir Abdul Jabbar Jumah
Scientific Degree: Assist. Professor
Date: / 5/ 2017

In view of the available recommendation, I forward this thesis for debate by the examining committee.

Signature:
Name: Dr. Saad Naji Abood
Scientific Degree: Professor
Title: Head of Physics Department

Data: / 5 / 2017

Committee Certification

We, the examining committee certify that we have read this thesis entitled **"Physical properties of PMMA/ZnO composite material"** and examined the student **"Zaman Sahhib Obaid"** in its contents and that in our opinion, it is accepted for the Degree of Master of Science in **Physics.**

Signature:
Name: **Dr. Emad K. Al-Shakarchi**
Scientific Degree: **Professor**
Address: Dep. of Physics, College of Science/
Al-Nahrain University
Date: / 10/ 2017
(Chairman)

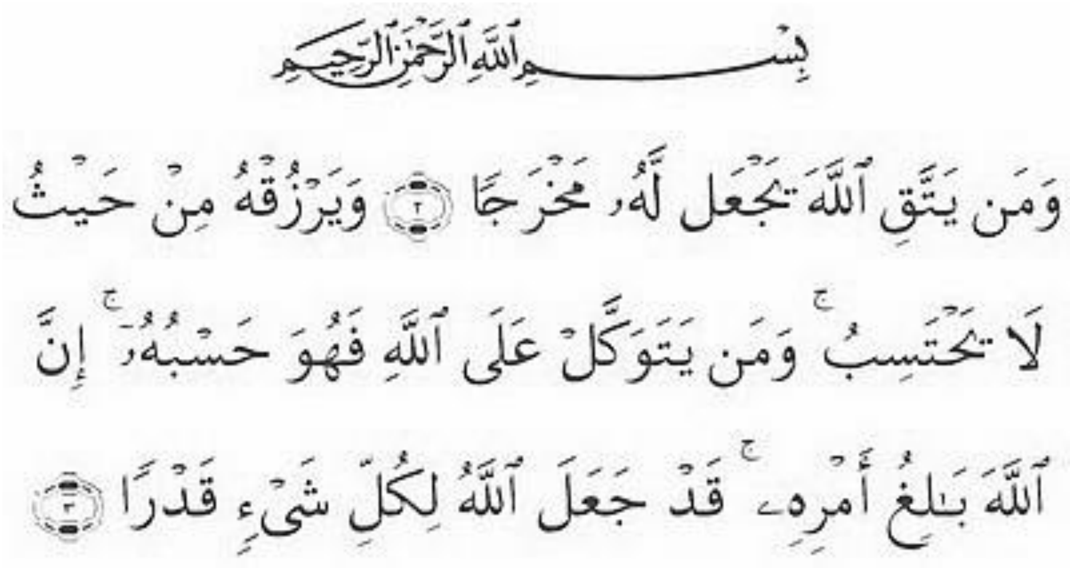
Signature:
Name: **Dr. Abbas F. Essa**
Scientific Degree: **Professor**
Address: Dep. of Physics, College of Science/ University of Wassit
Date: / 10/ 2017
(Member)

Signature:
Name: **Dr. Akram R. Jabur**
Scientific Degree: **Assist. Professor**
Address: Dep. of Material Engineering / University of Technology
Date: / 10/ 2017
(Member)

Signature:
Name: **Dr. Thamir Abdul Jabbar**
Scientific Degree: **Assis. Professor**
Address: Dep. of Physics, College of Science/
Al-Nahrain University
Date: / 10/ 2017
(Member & **Supervisor**)

I hereby certify upon the decision of examining committee

Signature:
Name: **Dr. Hadi M. A. Abood**
Scientific Degree: **Professor**
Title: Dean of College of Science
Date: / 10/ 2017



بِسْمِ ٱللَّهِ ٱلرَّحْمَٰنِ ٱلرَّحِيمِ

وَمَن يَتَّقِ ٱللَّهَ يَجْعَل لَّهُۥ مَخْرَجًا ﴿٢﴾ وَيَرْزُقْهُ مِنْ حَيْثُ
لَا يَحْتَسِبُ ۚ وَمَن يَتَوَكَّلْ عَلَى ٱللَّهِ فَهُوَ حَسْبُهُۥٓ ۚ إِنَّ
ٱللَّهَ بَٰلِغُ أَمْرِهِۦ ۚ قَدْ جَعَلَ ٱللَّهُ لِكُلِّ شَىْءٍ قَدْرًا ﴿٣﴾

صدق الله العظيم

سورة الطلاق:[2-3]

Dedication

To the memory of

Prof. Dr. Sabah M. Jumah

And

Assist. Prof. Dr. Mazin Fadheel

Zaman

Acknowledgement

I would like to express my deep gratitude and appreciation to my supervisor, Assist. Prof. Dr. Thamir Abdul Jabbar for his guidance, suggestions, and encouragement throughout the research work.

I also wish to thank Dr. Hassan N. Hashim/ SEM Lab. /Physics Dep. / Al-Nahrain University and Prof. Dr. Emad K. Al-Shakarchi / XRD Lab. /Physics Dept. / Al-Nahrain University for their Lab. assistances to accomplish this task .

Finally, I wish to acknowledge the staff of Physics Dep. / College of Science / Al-Nahrain University.

Zaman

Summary

This project involves the studying of both optical and electrical properties for the poly methyl methacrylate/zinc oxide composite. These materials were selected because they have an industrial applications and available in local market.

Zinc oxide powder with different concentration (4, 8, 10 and 12) % from the total weight was mixed carefully with PMMA. Manual mixing and molding processes were used to prepare the circular shape composites with the same diameter and thickness at the ambient temperature by using ultra sonic water bath.

The structural composites are studied via X-ray diffraction technique, where the results showed absent any chemical reaction between the matrix and enhancement zinc oxide when they compared with the reference charts.

Basic chemical groups were diagnosis via Fourier transfer infrared technique. The absorption peaks as a function of wavelength number found at the same wave number for PMMA and the PMMA/ZnO composite with different concentration.

UV-visible technique was used to investigate the optical properties, the result pointed that the refractive index and energy gap values suffered reduction due to zinc oxide particles increasing, the absorption and extinction coefficients increased when the zinc oxide particles increased.

High frequency LCR meter was used to study the dielectric properties; it was found that dielectric constant and dielectric loss suffered decreasing with the increasing of zinc oxide particles in the PMMA

Content

Chapter Three (Experimental part)

Chapter Four (Result and Discussion)

Chapter Five (Conclusion and Future Work)

List of Tables

List of Figures

List of Symbols and Abbreviations

Symbol	Description	Units
I	Transmittance intensity of the electromagnetic wave	**W/m^2**
I_o	Incident intensity of the electromagnetic wave	**W/m^2**
α	Absorption coefficient	**cm^{-1}**
A	Absorbance	
E_g	Forbidden energy gap	**eV**
h	Plank constant	
n^*	Complex refractive index	
PMMA	Poly methyl methacrylat	
ZnO	Zinc Oxide	
k_o	Extinction coefficient	
XRD	X-ray diffraction	
SEM	Scanning Electron Microscope	
FTIR	Fourier Transfer Infrared Spectroscopy	
λ	Wave length	**Nm**
f	Frequency	**Hz**
n	Refractive index	
R	Reflectance	
t	Thickness of the sample	**Mm**
T	Transmittance	
UV	Ultraviolet spectrum	
tanδ	Dielectric loss tangent	
C	Capacitance	**F**
C_o	Capacitance vacuum	**F**
C_D	Capacitor containing an insulator material	**F**
ε_o	Permittivity of vacuum	**F/cm**
ε_r	Relative (Complex) permittivity	
έ	Dielectric constant	

ἒ	Dielectric loss	
E	Electrical field	**N/C**
i	Imaginary number	

Chapter One

Introduction and Literature Review

Chapter One
Introduction and Literature Review

1.1 Introduction

The field of materials science and technology considered the most enormous and challenging areas of science in both branch of old and new advance science. Materials science is a field cover the oldest history and even named it such (Bronze Age, Iron Age, etc …) and represent the steps approach to break through developments in the whole life [1].New materials emerge due to requirement to improve the efficiency of structure and its performance, and new materials in turn give new area to develop updated structures and technology. The process in development of materials, structures, and technology is associated with composite materials considered one of the best manifestations of the new materials [2].

Solid materials can be classified into many groups depending on their chemical bonds which found between the atoms and molecules in addition they depending on these atomic structures so the researchers classified materials into three main groups metal, ceramic and polymers.

Composite material considered an intermediate classification of solid state material which consists of two or more combined materials [3].

1.2 Polymer

Polymer is a compound with high molecular weight, this component consisting of a large number of structural units connected to each other by chemical bonding; these units may be of the same type or of two different types. The unit builds up named monomer, is also used to identify the chemical repeat unit to give the big chain named polymer [4].

1.3 Polymers Categorization

Polymers are categorized by the researchers in several ways. More details about polymers categorization mentioned as following:

1.3.1 Categorization based on source

There are three types mentioned in literatures as follows:

1-Naturalness: it is exist in nature. Nucleus proteins, enzymes and natural rubber are an example for this type.

2-Semi-manufactured: it is naturalness but have been slightly modified using a simple chemical reaction to change its physical properties such as cellulosic and cellulose esters.

3-Manufactured: it is polymerized by simple chemical molecules, such as PVC, PMMA and nylon [5].

1.3.2 Structural Categorization

1-Linear, Branch and Cross Linked:

The functionality is the term which represents the vacancies available for molecules to bind with each other in any polymerization process, so the structural units can be classified depending on this functional into monofunctional, biofunctional and polyfunctional.

Linear polymer obtained from a sequence linear of biofunctional linkages, the branched polymer may be produced from the linking of polyfunctional units but with side growth terminated.

The crosslinked polymer obtained from growing the polyfuncthional and the biofunctional in a chemical reaction to linked them to each other [6].

2- Amorphous and Crystalline:

Due to the large polymer molecules, they do not have regular and stable crystal structures. The crystalline state of polymers is found in the polymeric material in a region known as crystalline regions, which are regular structures that arise as a result of a regular arrangement of parts of polymer chains. These areas form a percentage; this percentage is called the degree of crystallization which depends on several factors, including the nature of the active groups in the polymer chain, its size and range, in addition the polarity, branching type and the regularity of this chain. When the branching type is reduced and the chains became more homogeneous and regular the ability of crystallization increased and vice versa due to the increasing of intermolecular forces [6].

3- Homogenous and Common polymers:

In general researchers classified polymers into homogenous polymers and a common polymers based on the structural unites. Homo polymer consists of one type of structural units, but copolymer consists of two or more types of the structural unites [4, 6].

1.3.3 Categorization Based on Thermal Behavior (Thermoplastics and Thermosets)

Thermoplastic and thermo sets are the major groups based on their thermal processing behavior at chemical processing. Thermoplastics polymers can be heat softened in order to process into a desired shape. In same time the wastes thermoplastics can be recovered and refabricated by undergo heat and pressure, for example of this type the commercial thermoplastic are polystyrene, polyolefins, polypropylene and poly (vinyl chloride). While the other types of polymers called thermosets are polymers whose individual chains have been reacted by linked covalent bonds during polymerization process or by subsequent chemical or thermal treatment during fabrication into a desired shape. Thermoset polymers are once formed (i.e one can carry out just one chemical process). The cross linked reaction networks resist heat softening, mechanical deformation, such scratched and chemical solvent attack, but at a time thermosets cannot be thermally processed. Due to these properties thermosets are suitable materials for composites, coatings, and adhesive [7].

1.4 Bonding in Polymers

There are two mainly types of bonding in polymers known as primary which are called the chemical bonds such ionic bond, covalent bond and metallic bond. The second type of bonds known physical bonds such Vander Waals bond and hydrogen bond. More details about each kind of bonds are explained in the following:

1.4.1 Chemical Bonds

1-Ionic Bond: These bonds exist in inorganic compounds. The structure of these compounds may be obtained because of two atoms that are different in the ability to acquire or loss electrons so Coulomb force will arise between these positive and negative ions producing ionic bonds. Ionic bonds may exist in polymers when adding some ions to obtain a cross linked polymer.

2-Covalent Bond: it is obtained by the contribution of one or more of the electrons between the atoms, producing side tension that works to hold the resulting molecule. Atoms tend to contribute or share their electrons in a way that makes their electronic shell full. This bond is the main bond in macro molecular substance.

3-Metallic Bond: it is a type of chemical bonding that arises from the electrostatic attractive force between conduction electrons (in the form of an electron cloud of delocalized electrons) and positively charged metal ions. It may be described as the sharing of free electrons among a lattice of positively charged ions [8].

1.4.2 Secondary Bond Forces

1-Van der Waals bond: it is instantaneous dipole effect, and induced dipole interaction, is an intermolecular force or inter atomic force that causes an attraction between temporarily induced dipoles in nonpolar molecules and atoms because of asymmetrical distribution of electrons due to their movement. Van der Waals bonding is much weaker than both ionic and covalent bonding, and usually weaker than hydrogen bonds. The energy produced by van der Waals force varies with the inverse sixth power of the intermolecular distance. There is repulsion arises when the atoms get more closely than an equilibrium distance of 3 to 5 A^0, it is the same with primary acting force. The energy of standard intermolecular attractive forces is (8-40) kJ/mole.

2-The Hydrogen Bond: it is occurred between molecules that contain a polar covalent bond that requires the presence of a high electronegative atom such as fluorine, oxygen or nitrogen which bound to hydrogen atom. Due to the small size of the hydrogen atom, the dual electron will be attracted to the positive proton of the hydrogen atom. Hydrogen bond strength lie between 5-30 kg / mol. [8].

1.5 Poly Methyl Methacrylate

The trade names of poly methyl methacrylate are PMMA, Plexiglas, Lucite; the family class is vinylidene polymers (acrylics). The chemical formala of PMMA structure is:

$$-[CH_2-C(CH_3)(COOCH_3)]-$$

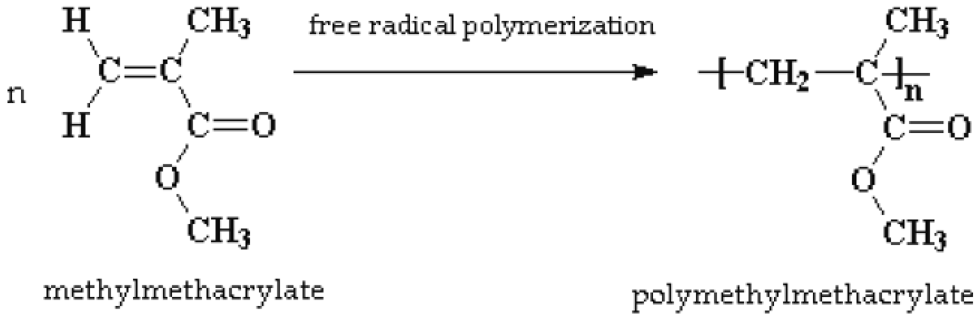
This type of polymers has a special optically properties, where its transparent about 92% transmission, theoretical limit for the incident visible region and has very little ultraviolet absorption up to 260 nm and high weather ability with high sensitivity to electron radiation, table (1-1) state other physical properties of PMMA.

PMMA used in several applications, it can used instead of glass as well as can be used in component deep UV and as a resistance fo electron beam or ion-beam resists in microelectronics chips manufacturing [9].

Table (1-1) Some physical properties of PMMA [10]

Properties	Values
Water Absorption	0.3- 2 %
Tensile Strength, Ultimate	47- 79 MPa
Electrical Resistivity	10^{14} - 10^{15} Ω.cm
Loss factor, 20°C, 1000 Hz, 60% humidity	0.04
Dielectric Constant	2.8- 4
Dielectric Constant, Low Frequency	3- 4
Transmission, Visible	80- 93 %
Refractive Index	1.49- 1.498
Melting Point	130°C
Glass Temperature	100 - 105 °C

Poly methyl methacrylate is produced by free radical polymerization of methyl methacrylate in mass or suspension polymerization according to the following chemical equation [11]:



The PMMA considered an amorphous material because of the methyl ester pendant groups which block the crystallization by preventing molecules to form crystalline bonds with each other [12].

1.6 Composite Materials

Composite materials are materials made from two or more constituent materials, the first with big ratio material known as matrix and the others small ratio materials called additives or reinforced materials, these materials have different physical properties which remain separate and distinct on a macroscopic level within the final structure. Composites are a new substance used to making some useful thing or artifact [13].

The composite materials can be categorized as the following flow chart:

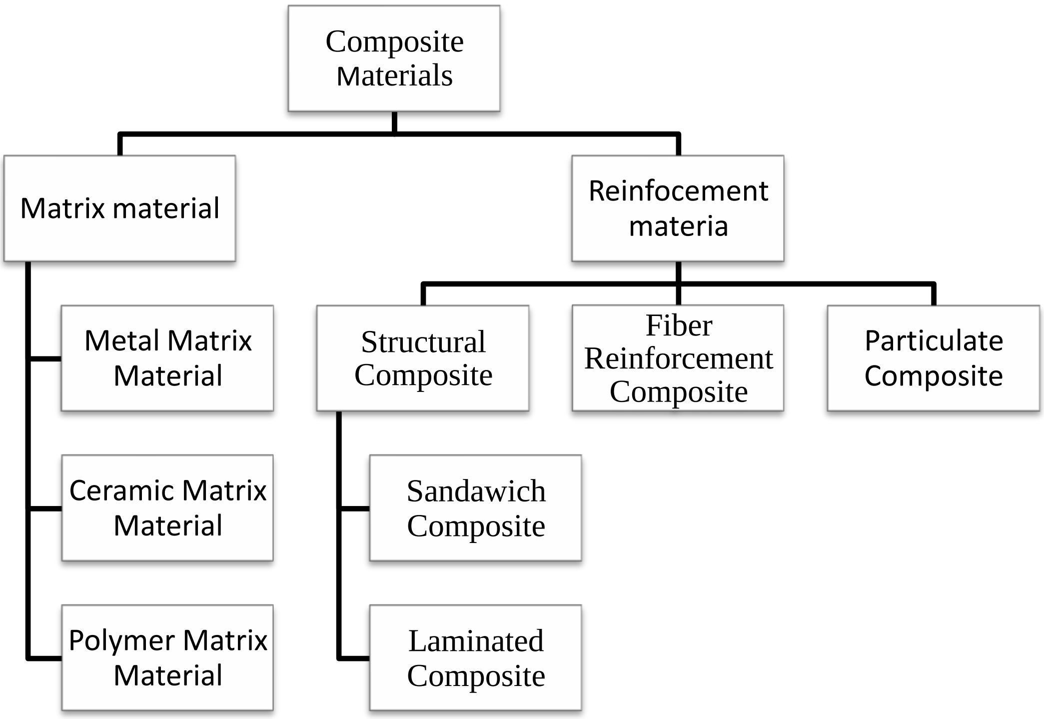


Fig (1-1) Flow chart for composite categorization [14].

1.7 Zinc Oxide Compound

Zinc Oxide represents semiconductor it is a metallic compound with energy gap about 3.4 eV in the near UV and crystallizes preferentially in the hexagonal wurtzite type structure shows in figure (1-2) [15].

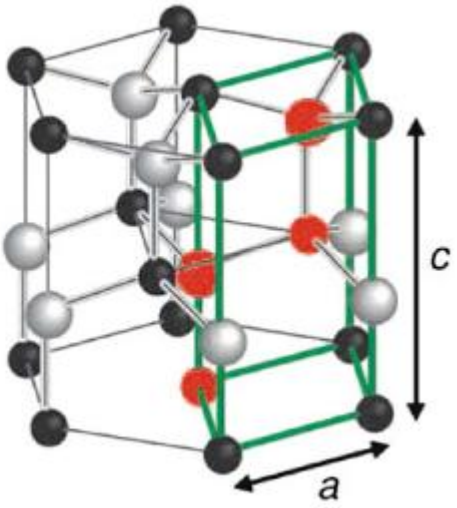


Fig (1-2) Wurtize lattice [16].

Zinc oxide is an unrivaled material that shows semiconducting and piezoelectric dual properties. The privation of a centre of symmetry with large electromechanical make compound in strong piezoelectric and pyro electric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensors.

Because of the wide band gap the ZnO compound semiconductor is suitable for short wavelength optical and electronic applications. Zinc oxide compound has a high exciton binding energy around 60 meV.

Because the transparent to visible light, the ZnO can be made highly conductive by doping [17]. More physical properties shows in table (1-2).

Table (1-2) Some physical properties of ZnO [18]

Property	Value
Lattice Lattice constant	Hexagonal, Wutzite a=0.324 nm, c=0.519 nm $\alpha=\beta\neq\gamma=90^0$
Molecular weight	81.38 g/mol
Density	5.87 g/cm^3
Dielectric constant	8.54
Refractive index	2.008
Energy band gap	3.2 eV
Specific heat	9.66 cal/ (mol. K)
Melting point	Vaporizes at 1700^0 C at normal atmosphere, melting at 1975^{0}C under pressure.
Solubility in H_2O	1.6*10^{-6} per gram of H_2O at 25^{0}C

1.8 Literature review

These literatures summarize the latest researches that have been written and published in the last 12 years:

In 2005 Hong Wen Wang et al. [19] prepared by in situ intercalative polymerization Poly (methyl methacrylate) (PMMA) with clay nano composite (PCN) material. They used XRD, FTIR and TEM to characterize the structure of the PCN; they studied the dielectric properties under frequency lie in between (100-10^6) Hz. They observed by TEM that MMT clay was intercalated and non homogenous distributed in the PCN material. They also found that the dielectric constant and loss was decreased when the concentration of the clay increasing in the PCN material.

In 2005 Erjun Tang et al. [20] synthesized a nano composite of PMMA/Zinc oxide by a polymerization process to study the optical properties for this composite for using it in UV shielding application. They found that the absorption spectrum was increased with the increasing of ZnO nano particles inside the matrix material.

In 2006 Mustafa M. Demir et al. [21] prepared ZnO/PMMA nano composites by in situ bulk polymerization. They improved the free radical bulk polymerization process by dispersing surface modified zinc oxide nano particles (ZnO) in methyl methacrylate (MMA) as well as the thermal stability of the formed polymer. They found that the vinylidene end groups and head to head links restricted the formation of chains , which shifts the onset of thermal decomposition to the system where decomposition occurs by random chain splitting.

In 2006 R. Y. Hong et al. [22] synthesized PMMA/ ZnO nano composite by grafting poly methyl methacrylate (PMMA) onto the ZnO particles. They found by using FTIR spectroscopy and thermo gravimatry TG that the desired polymer chains have been covalently bonded to the surface of zinc oxide nano particles. They also found that increasing the concentration of monomer could increase the grafting percentage and therefore enhance the dispersibility.

In 2007 Ahmad A. H et al. [23] studied the dopping effect on optical constants of Poly methyl methacrylate, the dopped blue methylene (mb) and red methyl (mr) used to dope the (PMMA) with different thickness lay between (0.1-0.2) mm, the wavelength range was between (200-900) nm. They found that refractive index and extinction coefficient showed irregular changes with the increasing of metylene blue dopant concentrations, while refractive index and extinction coefficient of PMMA doped with methylene red proclaimed a systematic increase with increasing dopant concentration. Also they found that when increasing (mr) concentration the value of the refractive index of PMMA doped with (mr) are lower than the values of samples doped with (mb) in the wavelength range between (400-550) nm.

In 2008 Zainab A. [24] studied the effect of nickel salt on electrical properties of poly methyl methacrylate. She prepared PMMA films with nickel salt additive with different concentration (1,2,3,4)% from the total weight and with fixed thickness (130±5) micrometer. She found that the DC electrical conductivity is increased by several orders of magnitude with increasing salt content and applied temperature ranged from (30-100) C. She found too that the activation energy was decreased with increasing salt concentrations.

In 2008 Moriyuki Sato et al. [25] prepared Zinc oxide/PMMA nano composite by using radical polymerization process to study the optical properties of this composite. They found that the absorption was increased in the UV region and there are photo luminescent in blue range when the ZnO nano particles distributed homogenously inside the polymathyle metha crylate.

In 2010 Bahaa H. et al. [26] studied some electrical properties of TiO_2 /PMMA composites. They found that when the concentration of additional TiO_2 and the temperature increased the D.C. electrical conductivity and the activation energy changed.

In 2010 Muhammad H. et al. [27] studied the effect of iron chromate on the optical properties of PMMA Films. They found that the absorption edge affected as a red shift in its values which indicate that when the doping concentration increased there was an increase in the energy gap (Eg).

In 2010 R. Sreega et al. [28] studied optical properties for ZnO/PMMA nanocomposite which prepared by wet chemical synthesis . They found that the spectra of the ZnO colloids show strong UV emission attributed to exciton emission and the strong green and blue emissions attributed to the defect emission in the ZnO, they found too the efficiency of the nonlinear absorption is found to increased with the band gap increasing and the value of nonlinear absorption coefficient as well as refractive index is found to be increasing with increase in particle size.

In 2010 B. Kulyk et al. [29] studied the optical properties of ZnO/PMMA nano composite films; these films were prepared by embedding of ZnO nano particles into PMMA polymeric matrix. They found that these films show high optical transmittance in near UV-VIS region and presence of the near band excitonic peak. Also they found that the intensity of UV exciton related band enhance in respect to the intensity of the green band when the ZnO structure changes from single crystal to the nanostructures and then to the nano composite film.

In 2011 Gaurang Patel et al. [30] studied the optical properties of the poly methyl methacrylate-TiO_2 composite, this composite prepared by using the casting method to prepare the composites with different concentrations of TiO_2, the transmission and absorption spectra recorded by using the UV-VIS spectroscopy to find the other optical properties and constants. They found direct and indirect band gap, the absorbance edge and refractive index was nonlinearly proportion with the concentration of TiO_2. They also found that the optical dielectric constant (ε_r) was increased with increasing the concentration of TiO_2 in composites.

In 2012 P.P Jeeju et al. [31] prepared films of ZnO/PS/PMMA nano composit by using spin coating technique to enhance the optical properties of theses nano composite. They found that the ZnO/PS/PMMA nano composite films with 10 wt.% ZnO content exhibit as a shielding in the UV region and, high transparency in the visible region. They found these results indicated optical limiting type nonlinearity in the films due to two photon absorption. They also found that the minimum transmittance of around 0.25 has been observed in the ZnO/PS/PMMA nano composite films which is much lower compared to that in ZnO/PMMA and ZnO/PS nano composite films.

In 2013 Yewei Zhan et al. [32] fabricated transparent and UV-shielding ZnO/PMMA nano composite by incorporating suitable UV absorbing ZnO quantum dots into a transparent PMMA matrix. They prepared nano particles ZnO of about 5 nm by using a sol gel route and then the 3 (trimethoxysilyl) propyl methacrylate (TPM) as a coupling agent was bound to the surface of ZnO quantum dots to controlling the agglomeration of quantum dots and reinforcing the compatibility between ZnO quantum dots and PMMA matrix. They found that the transparent ZnO/PMMA nano composite films showed notable UV absorbing capability and the high optical transparency in the visible wavelength region.

In 2013 khalid et al. [33] studied the optical properties of $CrCl_2$/PMMA composites, the samples was prepared with different concentration of $CrCl_2$ and with different thickness. They found that the optical constants were increased and the forbidden energy gap was decreased when the particles of $CrCl_2$ increased inside the polymer.

In 2013 Basavaraja Sannakki and Anita [34] studied the dielectric properties of ZrO_2/PMMA composites, they prepared polymer with different thickness and composites with different weight percentage of ZrO_2 but with the same thickness. They found that dielectric permittivity of the PMMA films behaved nonlinearly as frequency increases over the range 50-300 Hz, where as above 300 Hz the values of dielectric constant remains constant. But it is observed that the dielectric constant and impedance of PMMA increased as thickness of the film increases and the A. C. conductivity of PMMA films remains constant up to frequency of 1MHz and above. Also they found that dielectric permittivity of the ZrO_2/PMMA composite films decreased gradually up to frequency of around 1 KHz and at higher frequencies it remains constant for all the weight percentages of ZrO_2.

In 2014 Farooq Momtaz [35] studied the electrical properties of (PMMA/Ti) and (PMMA/Ag) nano composites. He prepared nano composites by using casting method with different concentration of (Ag) and (Ti). He found that the D.C electrical resistance for (PMMA/Ag) and (PMMA/Ti) nano composites has negative thermal coefficient, it was decreased with the increasing of the temperature, also found that the D.C electrical conductivity for the nano composites increases with the increasing of the additives concentration but the temperature and the activation energy decreased for all samples nano composites with increasing the additives concentration. In the A.C electrical properties he found that the dielectric constant and dielectric loss of the nano composites decreased with increasing of the frequency of applied electrical field and they increased with the increasing of the concentration of the additives.

In 2014 Nahida and Marwa [36] studied the optical and electrical properties of Ag/PMMA composite, they prepared the samples as films with different concentration by using cast method they found that there was nonlinear proportional between the optical constants and the concentration ratio, which was attributed to their incompatibility. Also they found that an increasing in the absorption spectra with increasing of the silver concentration in Ag/PMMA composites, they refer it to the increasing in localized states. They also found the best conductivity was at 9%Ag ratio, and the lowest receptivity.

In 2014 Shahad Hussain [37] studied the optical properties of TiO_2/PMMA nano composites; she prepared nano composites with different concentration of TiO_2. She found that the absorbance of the nano composites increased by increasing the concentration of the titanium dioxide nano particles. Also she found the absorbance in the UV region was high but was low in the visible and infrared regions, the electronic transitions in these two kinds are indirect (allowed and forbidden) at low concentrations, the indirect energy gaps decreased with increasing of the TiO_2 nano particles concentration, the refractive index, extinction coefficient and the dielectric constant (real part and imaginary) increased with increasing the concentration of the titanium dioxide nanoparticles.

In 2015 Bahaa and Bariq [38] studied the optical properties of CuO/PMMA nano composites by using casting method for preparing these nano composites with different concentrations of CuO, they found that the absorption coefficient, extinction coefficient, refractive index and real and imaginary dielectric constants of (PMMA/CuO) nano composites increased with the increasing of the copper oxide nano particles concentrations and the energy band gap of (PMMA/CuO) nano composites was decreased with the increase of the copper oxide nanoparticles concentrations.

In 2016 P. Maji et al. [39] studied the structural, dielectric, optical and A. C. conductivity properties PMMA–ZrO_2 polymeric nano composite films. They prepared these films by sol casting technique. They found by using XRD that the polymeric PMMA–ZrO_2 nano composite films appeared the crystalline nature, by the UV–VIS spectroscopy they found that the nano composite films had highly visible with light transparency and high UV shielding efficiency and the dielectric permittivity and dissipation factor decreased with frequency and increased with temperature. In addition the values for dielectric constant found relatively high at low frequency (100 Hz) they attributed it to the existence of interfacial polarization.

In 2016 Rodrig Balen et al. [40] synthesized films and fibers of zinc oxid/poly mythel methacrylate nano composite to study the structural and optical properties for these composites. They found that near 370 nm the absorption was intense and broad that mean optical properties of PMMA improved due to inclusion of ZnO nano particles inside the composite.

The different between these literatures and this research the way of preparation and the value of the optical constant but they have the same behavior in increasing and decreasing.

1.9 Aim of work

PMMA and its composite have important application and feature in which enables to use in many fields, therefore several aims can estimated and summarized as following:

1-Preparation PMMA and composite material by cold mixing process regarding all the parameters in which affected on the specimens quality.

2- Studying the structure of PMMA and PMMA/ZnO composite by non destructive tests.

3- Studying the optical and electrical behavior of PMMA and PMMA/ZnO composite.

Chapter Two

Theoretical part

Chapter Two
Theoretical Part

2.1 Introduction

Studying theoretical and practical physical properties are important matter, their importance in the manufacturing process of polymers where can introduce a lot of improvements. The properties that had been studied in this research include both optical and electrical properties which explain as following:

2.2 Optical Properties

Optical properties of materials are very important because it can obtain information about the internal structure ,the nature of the bonds and their employment by knowing the amount of absorbance ,reflectance and transmittance of these materials. In the ultraviolet range (200-350) nm the energy gap and kind of bonds can be determined, the visible spectrum (350-750) nm gives an idea about the use of these materials in solar applications and over 750 nm in the infrared range gives an information about the composition of polymers and materials enter in this composition [41].

2.3 Optical Constants

2.3.1 Absorption Coefficient

Absorption coefficient can be defined; it is the ratio of decrease in radiation energy flux to the unit of distance towards the wave propagation in the material which depends on the type of absorbent material and wavelength of the incident wave [42].

The absorption coefficient can be calculated by using Lamberts law which states that absorbance of a material sample is directly proportional to its thickness (path length) (t) ,and it can be written as the following:

$$\frac{I}{I_\circ} = e^{-\alpha t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (2\text{-}1)$$

Where $\frac{I}{I_\circ}$ the ratio of the transmittance intensity of the incident wave to the incident intensity of the same wave which represent the transmittance of the electromagnetic wave (T) and because the absorbance (A) written as:

A= Log $(\frac{I}{I_\circ})$, then by doing some mathematical steps the absorption coefficient can be written as [43]:

$$\alpha = \frac{2.303}{t} A \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (2\text{-}2)$$

Where: α is the absorption coefficient.

2.3.2 Refractive Index and Extinction Coefficient

Refractive index represents the ratio of the electromagnetic wave speed in vacuum to the electromagnetic wave speed inside the material. Equation (2-3) gives the law which used to calculate the refractive index [44]:

$$n = \sqrt{\frac{4R - k_0{}^2}{(R-1)^2} - \frac{(R+1)}{(R-1)}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (2\text{-}3)$$

Where (R) is the reflectance which can be calculated in terms of the absorption and the transmission from the energy conservation law [45]:

$R = 1-A-T$ …………………. (2-4)

Complex refractive index can be written as following

$n^{*}=n-ik_{0}$ ………………………(2-5)

Where n it is the real part of refractive index.

k_0 it is the extinction coefficient represents the imaginary part.

n^* it is a complex number represent the complex refractive index that depends on several characteristic factors such as crystal defect and crystal structure.

The extinction coefficient represents the amount of attenuation of an electromagnetic wave that is traveling in a material, where it values depends on the density of free electrons in the material and also on the structure nature, this coefficient can be calculated by using the following equation [46]:

$k_{0}=\frac{\alpha\lambda}{4\pi}$ ……………….(2-6)

2.4 Absorption Edges

The absorption edge of solid materials begins with the optical transitions between the top of valence band and the bottom of conduction band and it is represent less difference in energy between the lowest point in the conduction band and the highest point in the valance band [47]. The absorption edge can be recognized by three main regions (high, exponential and low) absorption regions as show in figure (2-1), the regions are explained more as following [48]:

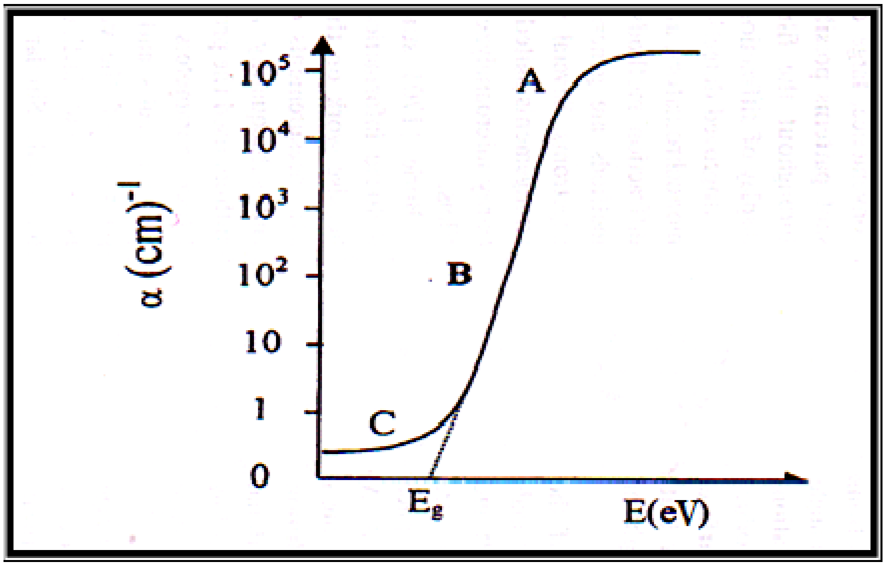


Fig (2-1): Absorption regions [49].

1- High (A)

It is the region where absorption coefficient records its highest values which equal or greater than (10^4 cm^{-1}). Forbidden energy gap (E_g) can be calculated from this region.

2-Exponential (B)

It is the region where the absorption coefficient (α) is lie between (1-10^4) cm^{-1}. This region is produced by electron transition from the extended levels of the valance band to the local level of the conduction band and electron transition from the local level of valance to the extended level of the conduction band.

3- Low (C)

The absorption coefficient (α) in this region is very small, it is less than $1cm^{1}$. The transition happens in the tails of forbidden energy gap[48].

2.5 Optical Transition

There are two types of optical transition that can occur at the fundamental edge of crystalline materials, direct and indirect as show in figure (2.2). Both transitios involve the interaction of an electromagnetic wave with an electron in the valence band, which is raised across the fundamental gap to the conduction band [50].

Direct and indirect transition occurred when electrons transited from top of the valance band to bottom of the conduction band. These transitions depend upon the wave vector k. If the transitions have the same values of wave vector, it is a direct transition so the momentum and energy are conserved and the energy which acquired by the electron is the same energy of the photon that interacts with it which is equal to or greater than the forbidden energy gap.

In indirect transitions, the value of the wave vector is different from one transition to another. These transitions are accompanied by the emission of phonons to maintain the momentum conserved [51].

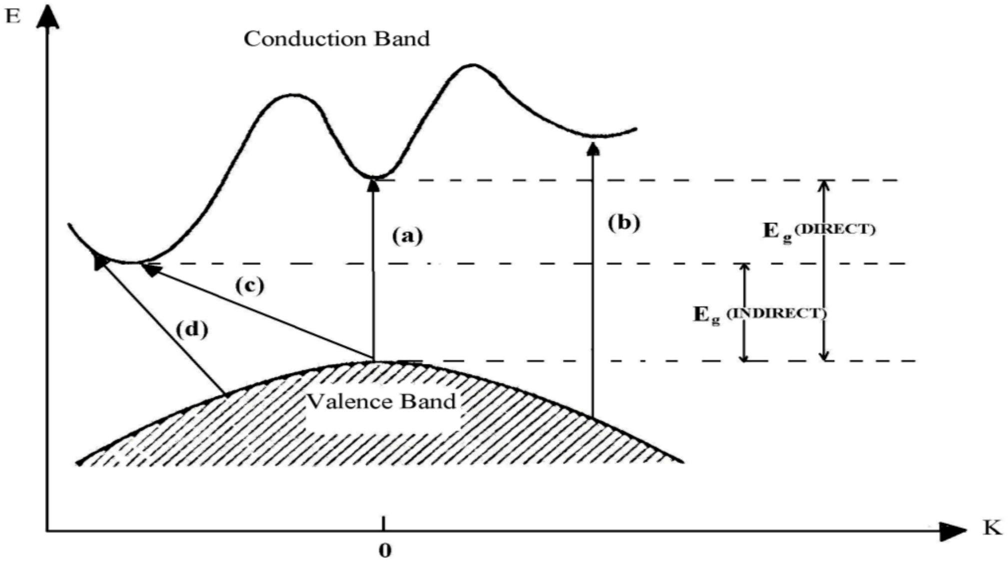


Fig (2-2) Types of electronic transition ((a) Allowed, (b) Forbidden) direct, ((c) Allowed, (d) Forbidden) indirect [52].

The equation which associates the absorption coefficient with energy gap is:

$$(\alpha\, hf) = B_x\,(hf - E_g)^{r} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2\text{-}7)$$

Where

E_g : the energy gap.

B_x : constant depending on the nature of the material.

hf: the energy of the incident photon.

For direct transition $r=\frac{1}{2}$ or $\frac{3}{2}$ depending on whether the transition is allowed or forbidden in the quantum mechanical sense and for allowed indirect transition r=2 or for forbidden indirect transition r= 3 [50, 53].

2.6 Dielectric Properties

The good electrical insulating properties and mechanical toughness and flexibility in organic polymer play an essential role in the integrated circuits industry as photo resists that define the microscopic patterns required, also polymers can be made to be photoconductive, piezoelectric, and pyroelectric, which makes them well adapted to xerography and sensor applications [54].

2.7 Electrical Polarization

Electric polarization refers to the phenomenon in which the centers of positive and negative charges do not coincide. It commonly occurs in a dielectric material when it is exposed to an electric field [55]

2.8 Types of Polarization

Three main polarization mechanisms can occur within a dielectric material, they are electronic polarization, ionic polarization and dipolar polarization. Electronic polarization happened because of the displacement of the electron shell relative to a nucleus. Ionic polarization rises from the displacement of a charged ion with respect to other ions. Dipolar polarization comes from molecules with a permanent electric dipole moment that can change orientation in an applied electric field [56].

The space charge is another type of polarization which it is the aggregation of mobile charges at structural surfaces due to the grain boundaries or the interfaces between the material and the electrodes [57].

2.9 Relative Permittivity

The relative permittivity or electric dielectric is a characteristic for the insulator materials. It is represent the capability of materials to polarized and it is the ratio between the capacitance of capacitor with material presence C_D to the capacitance of capacitor with air presence $C_\circ$,

$$\varepsilon_r = \frac{C_D}{C_\circ} \quad \ldots\ldots\ldots\ldots\ldots \text{(2-8)}$$

$$C_\circ = \varepsilon_\circ \frac{A}{t} \quad \ldots\ldots\ldots\ldots\ldots \text{(2-9)}$$

$$\varepsilon_r = \frac{C_D\ t}{\varepsilon_\circ\ A} \quad \ldots\ldots\ldots\ldots\text{.. (2-10)}$$

Where: ε_r is the dielectric constant.

$\varepsilon_\circ$: it is vacuum permittivity .

t: it is the distance between the capacitance plates (thickness of sample).

A: it is the area of one of the capacitance plate (the surface area of the sample) [58].

If an alternating field applied to dielectric material the isolation cannot follow the field due to effect of dipoles orientation so the dielectric constant treated as a complex quantity. Debye equations give the variation of real and imaginary parts of the complex dielectric constant with frequency (f) [59]:

$\varepsilon_r = \dot{\varepsilon} - i\ddot{\varepsilon}$ ……………... (2-11)

The loss is expressed in terms of the phase angle **δ** as

Tan **δ**= $\frac{\ddot{\varepsilon}}{\dot{\varepsilon}}$ …………… (2-12)

The variation of dielectric constant with frequency shown in figure (2-3).

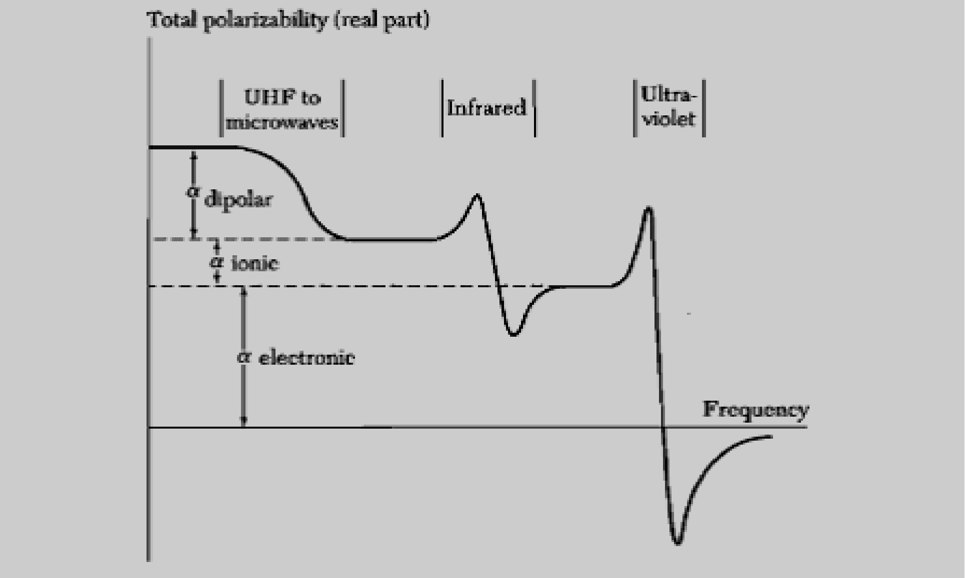


Fig (2-3) Dielectric constant against frequency [56].

Chapter Three

Experimental Part

Chapter Three
Experimental part

3.1 Introduction

This chapter includes the material to be used, the method of samples preparation and their testing stages in addition to description of the practical equipment and tools used in the preparation and testing devices.

3.2 Selection of Materials:

The materials were selected in this project was explained in some details as following:

3.2.1 Matrix Material:

Poly methyl methacrylate (PMMA) resin prepared by using acrylic powder with methyl methacrylate liquid monomer, they were from marlic medical industries Co., Iran, shows in figure (3-1).

Fig (3-1) Cold cure acrylic powder and liquid

These powder and liquid contain some additives specified in table (3-1), they are used by dentists to fabricate the teeth molds and they commercially called cold cure acrylic.

Table (3-1) Components of the powder and liquid used in matrix material [60]

Powder	**Liquid**
Acrylic polymer beads	Monomer
Initiator	Inhibitor
Pigments	Accelerator
Dyes	Plasticizer
Opacifier	Cross linking agent
Plasticizer	
Dyed organic fibers	
Inorganic Particles	

3.2.2 Reinforced Material

Zinc oxide (ZnO) powder of particles with average particle size equal to (315 nm) and it was provided from Fulka Co. , honeywell Inc. ,US. It was used as reinforced material to the PMMA matrix for preparing a PMMA/ZnO composite material.

3.3 Specimen Preparation:

In order to prepare the specimens corresponding to the proper technique, Poly methyl methacrylate resins had been prepared manually by mixing acrylic powder and the liquid monomer according to the following procedure points:

1-Each type of polymer was weighted carefully in different percentage rates (40:60, 50:50, 60:40, 65:35) % powder to liquid respectively, for this accurate method sensitive balance, four digits, BL210S model was from Sartorius company, Germany, had been used to achieve this purpose.

2- Mixing process was performed manually for four minutes until the mixture became more viscose and casted in aluminum mold with diameter 33 mm and a depth of 10 mm.

3- For curing process an ultrasonic water bath JP-020S model from Skymen cleaning equipment Shenzhen Co., China was used for 30 minutes until the mixture became solid state polymer in form of PMMA by the chemical reaction as following:

Polymer+ peroxide initiator+ monomer+ inhibitor+ amine accelatore→ PMMA+ heat

4- Decontamination process should be achieve for molds and tools which were used, distilled water and Ethanol alcohol are the main solution used in this purpose. Finally an oven model UT 5050 E from heraeus, US, was used for heat cleaning and drying at a temperature of 100^0 C for five minutes.

5- Composite polymer consist of PMMA/ZnO had been prepared as a form of circular shape of diameter 33mm with nearly 0.515mm thickness, PMMA with (50:50) % powder to liquid was used. Zinc oxide (ZnO) was added with different concentration (4, 8, 10, 12) % from the total weight as stated in table (3-2), the total weight of prepared specimen was 1.4g. The preparation of composite material was initially done by mixing acrylic powder with zinc oxide powder and to ensure homogeneity a magnetic stirrer from stuart scientific, UK was used for 45 minutes to obtain a good homogeneity and then the liquid was added, all them mixed manually for 5 to 7 minutes depending on the amount of additive, the samples was left for curing at atmosphere condition for 48 hours.

Table (3-2) The concentration of the matrix materials and the additive

Materials Samples	Powder (g)	Liquid (ml)	ZnO (g)
PMMA	0.7	0.75	0
PZ1	0.672	0.71	0.056
PZ2	0.644	0.685	0.112
PZ3	0.63	0.67	0.14
PZ4	0.616	0.655	0.168

3.4 Materials Characterization Methods

3.4.1 Structure Analysis by X-Ray Diffraction

One of the most important non destructive devices is the X-ray diffraction technique. It can provide unique information about materials such as phases, structure, orientation, phase concentration, etc, when X ray photon interacts with matter the constructive interference obtained if the path difference between diffracted photons from two adjacent planes is an integer number of wavelength. The spacing between the planes can be determined by Bragg's law. The position of the peaks in the diffraction pattern depends on the structure, lattice parameters, then these information give qualitative of materials. The intensity of the peaks are determined by the scattering power of the atoms, this parameters give information about the concentration of each phases in the material which be test, i.e. gives the quantitative information.

The XRD system used was X'Pert^3 Powder from PANalytic, Netherlands, found in Al Nahrain university, collage of science, with target of Cu Kα radiation, wavelength $1.54A^0$ and 2theta lays between 20-80 degree From the International Union for Crystallography (IUCr) by using (COD# 210-7059) for ZnO [61] and by using the crystal diffract software one can analyze the obtained data which is pointed to the characterization of material subjected to test.

3.4.2 Fourier Transform Infrared Spectroscopy

This device is an analytical technique used to identify organic (sometimes inorganic) materials. This technique measures the absorption of infrared radiation by the sample material versus wavelength. The infrared absorbed by the bonds identify the molecular components and the structure of this material. One can investigate these bonds by comparing the patterns of the samples with SDBS# 02036(Japanese structure organic database) for the matrix material [62]. The device was used from Shimadzu, IR-pristage21 model, Japan located at Ibn Sina state company.

3.4.3 Scanning Electron Microscope (SEM)

Scanning electronic microscope is a type of electron microscope that images the surface of sample with high energy electron beam, by interacting the electrons with the atoms, those electrons can produce signals which contains information about surface so morphology, topography, particle size and particles distribution can be investigate. FEI inspect S50 model from Thermo Fisher Scientific, Netherland was used, and it was located in Al Nahrain University, collage of science.

3.5 Optical Analysis

To evaluate the PMMA and the composite optically one can use the UV-VIS spectroscopy. The available UV-VIS spectroscopy was determined by the wavelength in between (200-800) nm.

UV-Visible spectrometer device double beam was UV-1601PC made by shimadzu, Japan found in Al Nahrain University, collage of science, this device was used to investigate the optical properties by recording the absorption versus wavelength.

3.6 Dielectric measurement

Capacitance (C) and loss angel tangent (D) as a function of frequency were measured by using HF LCR, from 6500P series made by Wayne Kerr Electronics, UK, with frequency range (10^3-10^8) Hz. The samples were coated on both sides by graphite, and copper wires used as electrodes.

Chapter Four
Results and Discussion

Chapter Four
Result and Discussion

4.1 Introduction

This chapter is dealing with discussion of results concerned the structural, optical and electrical properties of the PMMA and PMMA/ZnO composite, involve the comparison with other literatures studied before. The sake of comparison is to the better understanding of all conditions surrounded the subject.

4.2 Structural Analysis

4.2.1 X-Ray Diffraction Analyzing

The pattern in figure (4-1) represents the XRD pattern of the ZnO which used as additive to the PMMA, more details about this pattern mentioned in table (4-1). The figure (4-1) was matching with the CIF file which taken from the X-ray diffraction database of crystallography open database. The major lattice planes showed at the (011) and (010) where the intensities pointed to the concentration of the phases in the bulk material.

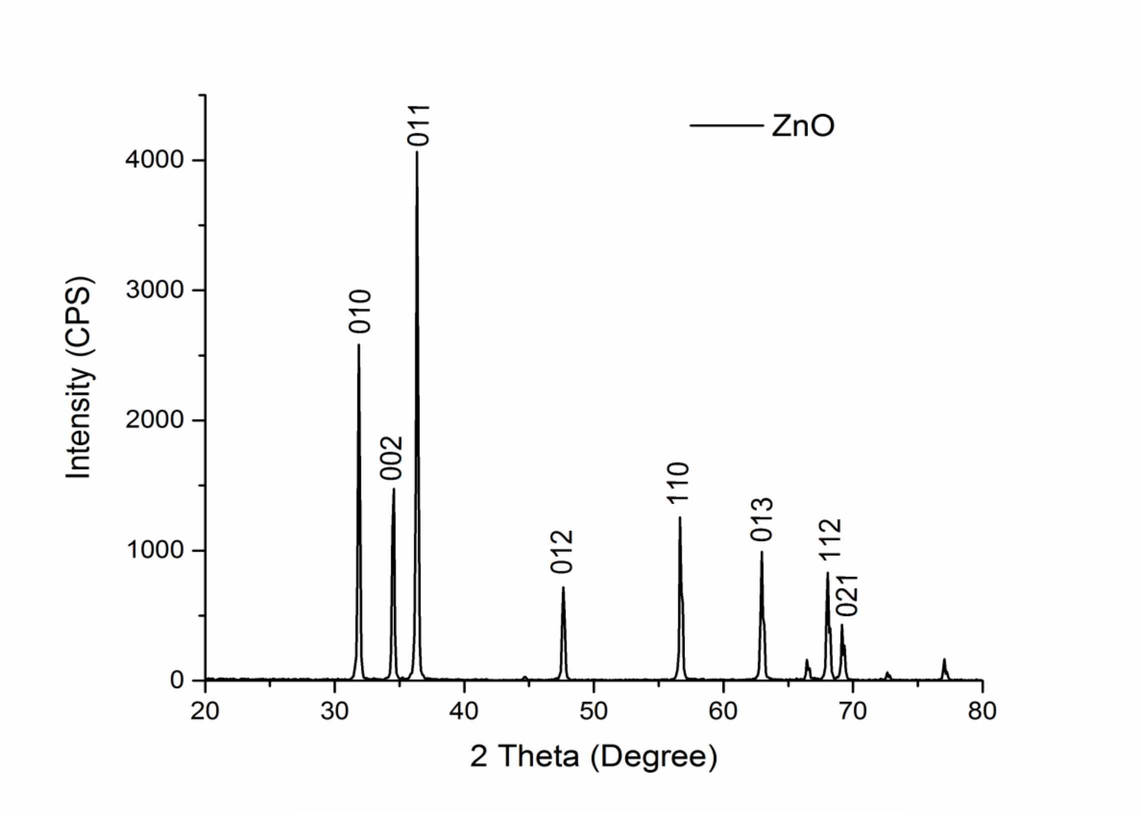


Fig (4-1) XRD pattern for ZnO

Table (4-1) Structure data for ZnO

hkl	(010)	(002)	(011)	(012)	(110)	(013)	(112)	(021)
2 theta	31.8^0	34.4^0	28.7^0	47.4^0	56.6^0	62.9^0	68^0	69.1^0
d (A^0)	2.813	2.598	2.473	1.908	1.624	1475	1.377	1.358
a= b=3.2478Å, C=5.1958Å , unit cell = 47.5Å^3								

The PMMA/ZnO composites patterns are represented on the figures (4-2 to 4-5) respectively according to the concentration of ZnO in polymer and more details about these patterns are mentioned in table (4-2).

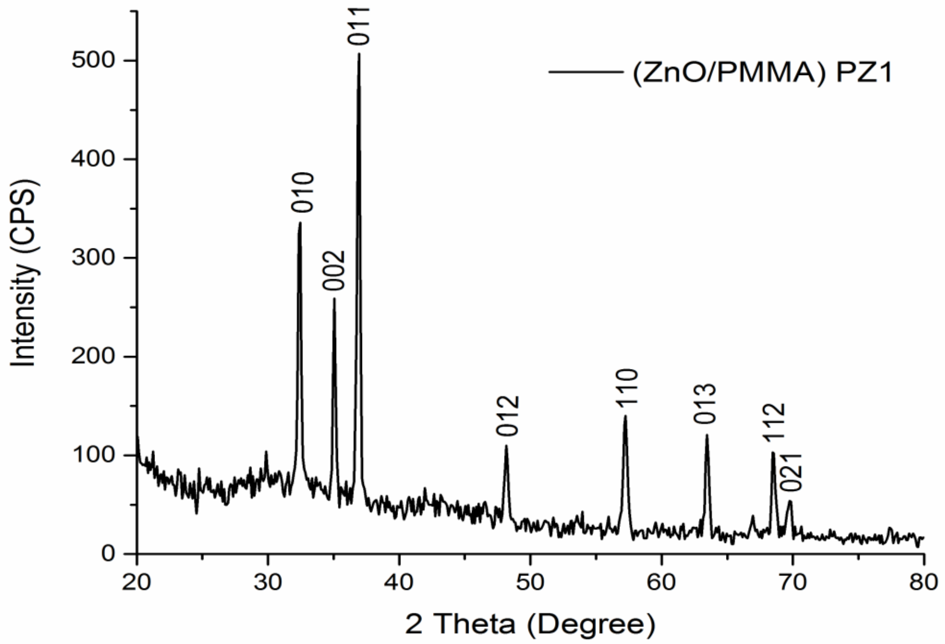


Fig (4-2) XRD pattern for PZ1

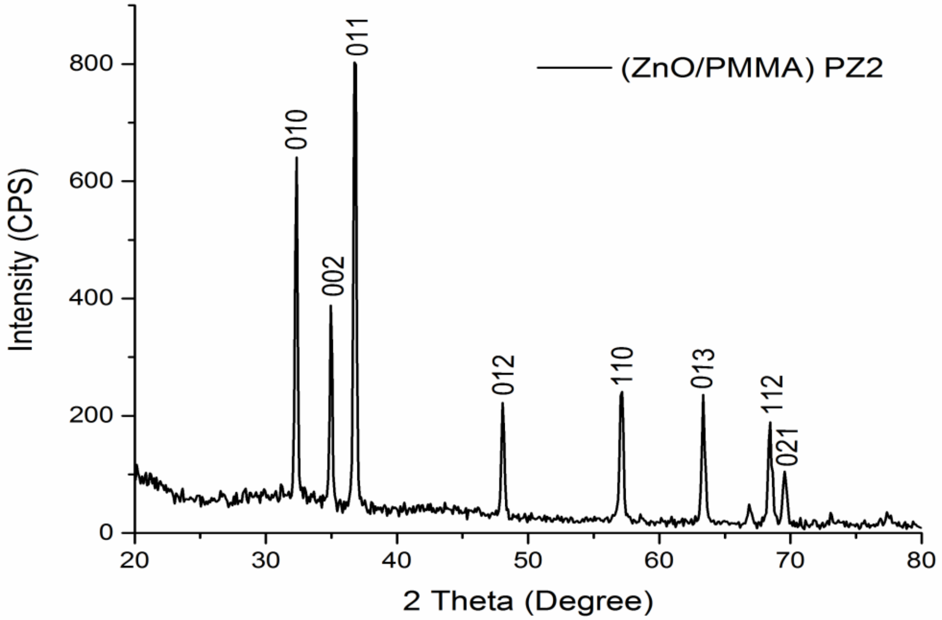


Fig (4-3) XRD pattern for PZ2

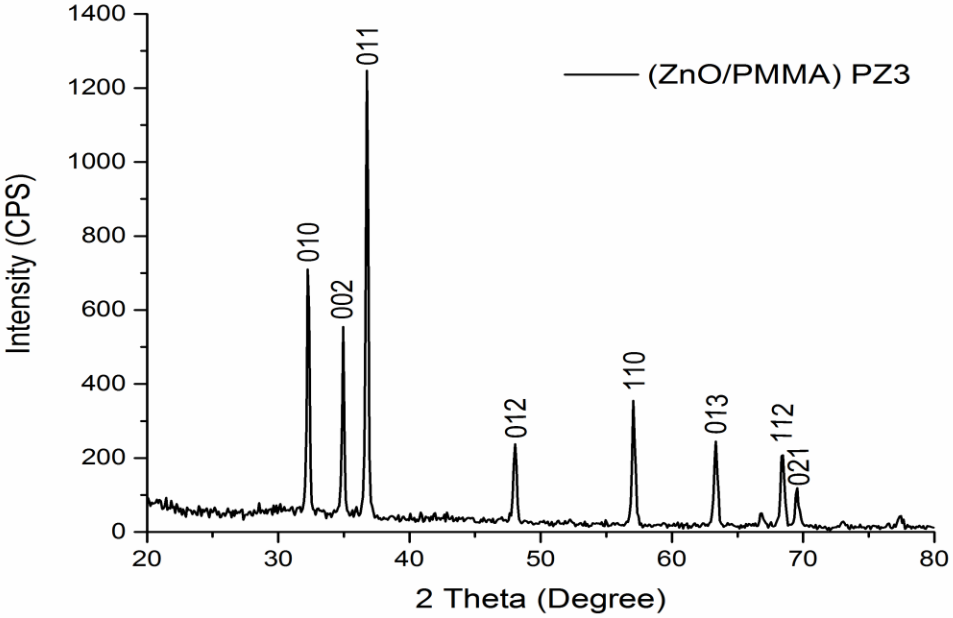


Fig (4-4) XRD pattern for PZ3

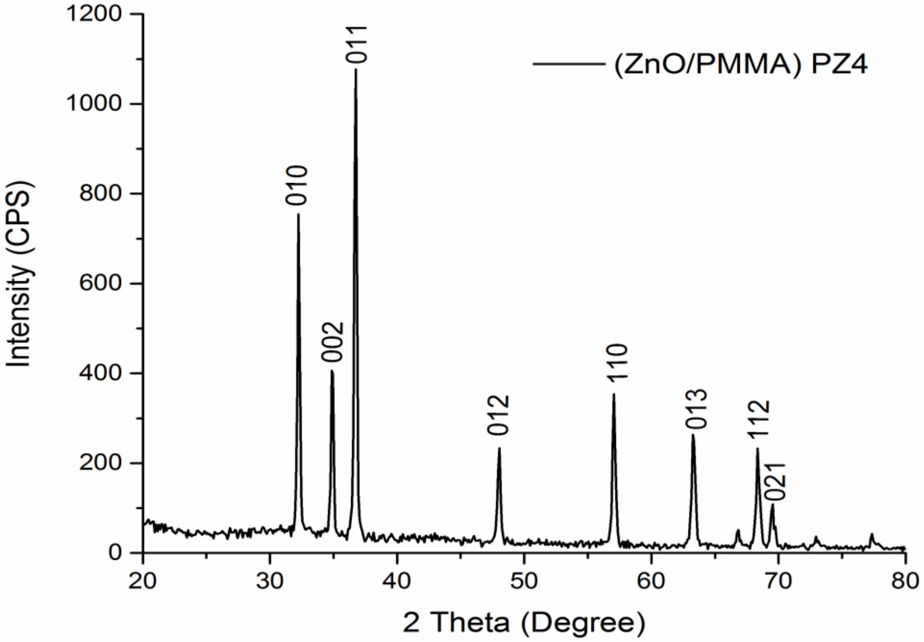


Fig (4-5) XRD pattern for PZ4

Table (4-2) Structure data for the PMMA/ZnO composite with different concentration

PZ1	hkl	(010)	(002)	(011)	(012)	(110)	(013)	(112)	(021)
	2 theta	32.3^0	35^0	36.8^0	48.1^0	57.1^0	63.3^0	68.4^0	69.6^0
	d (A^0)	2.768	2.560	2.437	1.892	1.611	1.467	1.370	1.349
	a= b=3.2278Å, C=5.1659Å , unit cell = 46.6Å^3								
PZ2	hkl	(010)	(002)	(011)	(012)	(110)	(013)	(112)	(021)
	2 theta	32.3^0	34.9^0	36.7^0	48.1^0	57^0	63.4^0	68.4^0	69.6^0
	d (A^0)	2.768	2.567	2.433	1.891	1.613	1.465	1.369	1.349
	a= b=3.2278Å, C=5.1659Å , unit cell = 46.6Å^3								
PZ3	hkl	(010)	(002)	(011)	(012)	(110)	(013)	(112)	(021)
	2 theta	32.2^0	34.9^0	36.7^0	47.9^0	57^0	63.3^0	68.4^0	69.5^0
	d (A^0)	2.776	2.567	2.443	1.895	1.613	1.467	1.369	1.351
	a= b=3.2378Å, C=5.1659Å , unit cell = 46.9Å^3								
PZ4	hkl	(010)	(002)	(011)	(012)	(110)	(013)	(112)	(021)
	2 theta	32.2^0	34.8^0	36.6^0	47.9^0	57^0	63.3^0	68.3^0	69.5^0
	d (A^0)	2.776	2.574	2.449	1.895	1.613	1.467	1.371	1.351
	a= b=3.2478Å, C=5.1859Å , unit cell = 47.4Å^3								

Some remarkable points were noticed in these patters as following:

1- The reflected X-rays at the same angle pointed on figure (4-1) and the peak intensity was increased with ZnO increasing inside the matrix material.

2- According to the previously point the ZnO particles could not be reacted with PMMA and there is no chemical bond with the PMMA but may be a secondary bonds are found.

3- According to these previous points the ZnO particles were dispersed into PMMA and act as a reinforcement metal oxide, thus the new material is a composite.

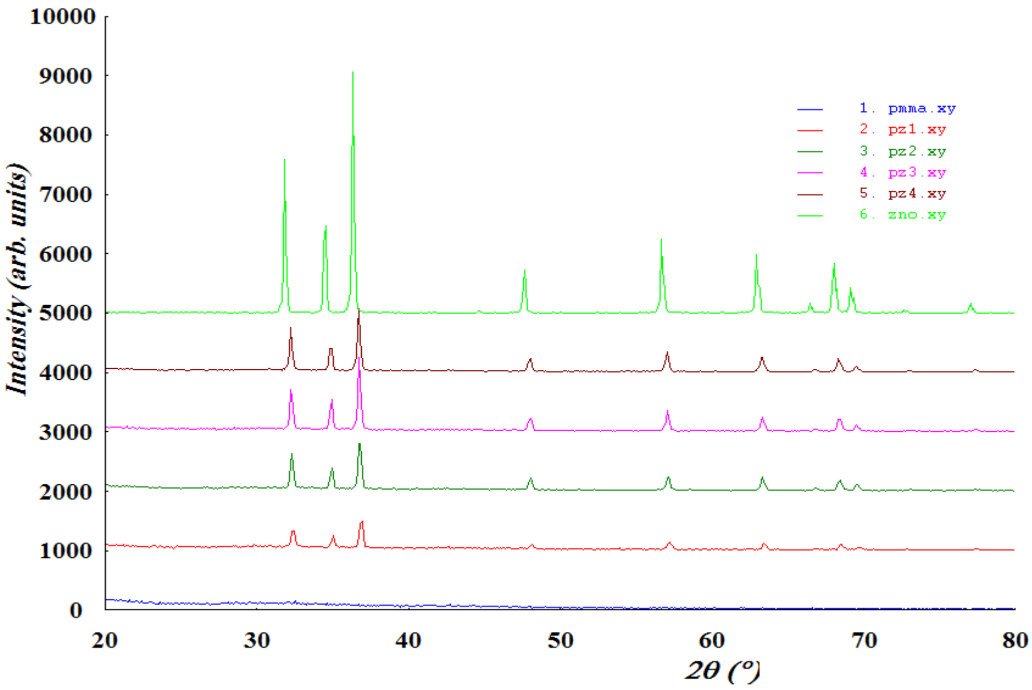


Fig (4-6) Combination of XRD patterns for PMMA, ZnO and the composite with different concentration

Figure (4-6) shows the direct proportion between the intensity of beaks and the concentration of the additive.

4.2.2 FTIR Analyzing

The absorption IR by PMMA molecules is characterized the molecular structure by identifying the joined bonds which show in the transmission spectrum of FTIR. The FTIR spectra of the PMMA illustrated in figure (4-7).

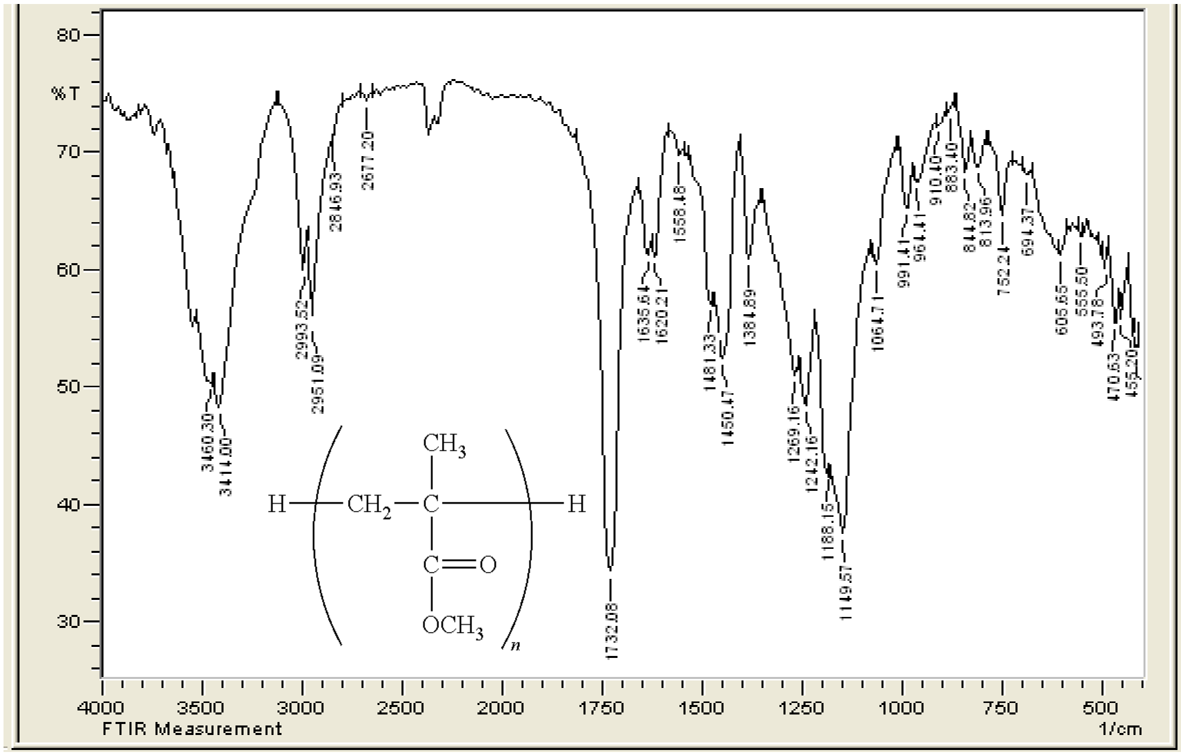


Fig (4-7) FTIR spectrum for PMMA

Two main regions are noticed, the left region lie between (1500-4000)cm^{-1} is called diagnostic region and the second region lie between (400-1500)cm^{-1} it is called fingerprint region pointed to functional group region, the left region specially close to 4000 cm^{-1} it is for the high energy bonds. The peak at 3414 cm^{-1} represent O-H stretching vibration, the absorption band at 1732.08 cm^{-1} is characteristic of C=O stretching vibration from PMMA. The absorption band at 1149.57 cm^{-1} represents C-O stretching vibration in PMMA. In the region 2951.09 cm^{-1} the absorption band corresponds to C-H stretching and the absorption band at 1242.16 cm^{-1} represents C-C also from PMMA. The peak in the region 1450.47 cm^{-1} is characteristic of carbon double bond corresponds to an organic amine found as an additive to accelerate the self cure [60].

When adding ZnO into PMMA matrix one can notice the same behavior of the charts as shown in figures (4-8_4-12).

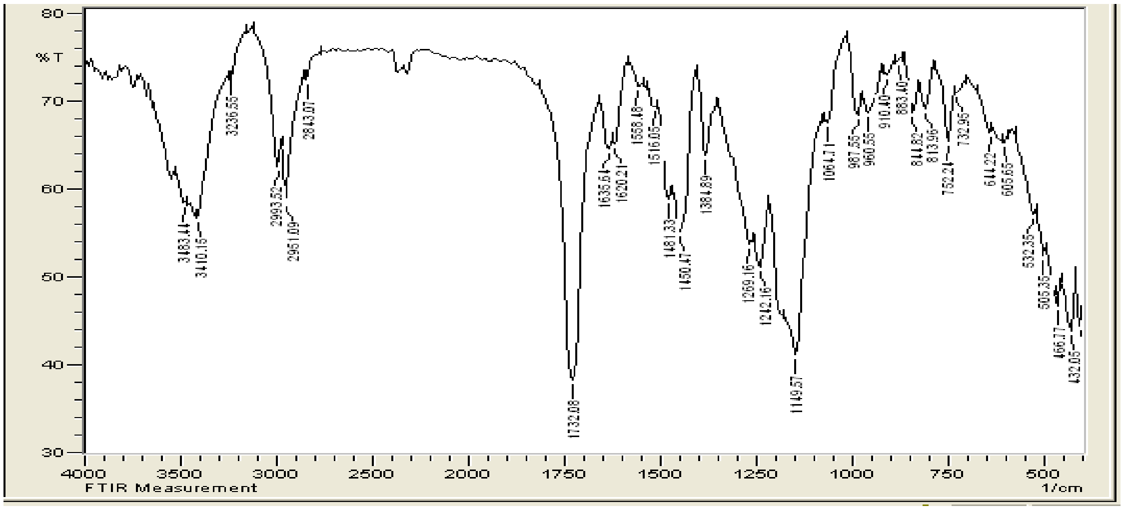


Fig (4-8) FTIR spectrum for PZ1

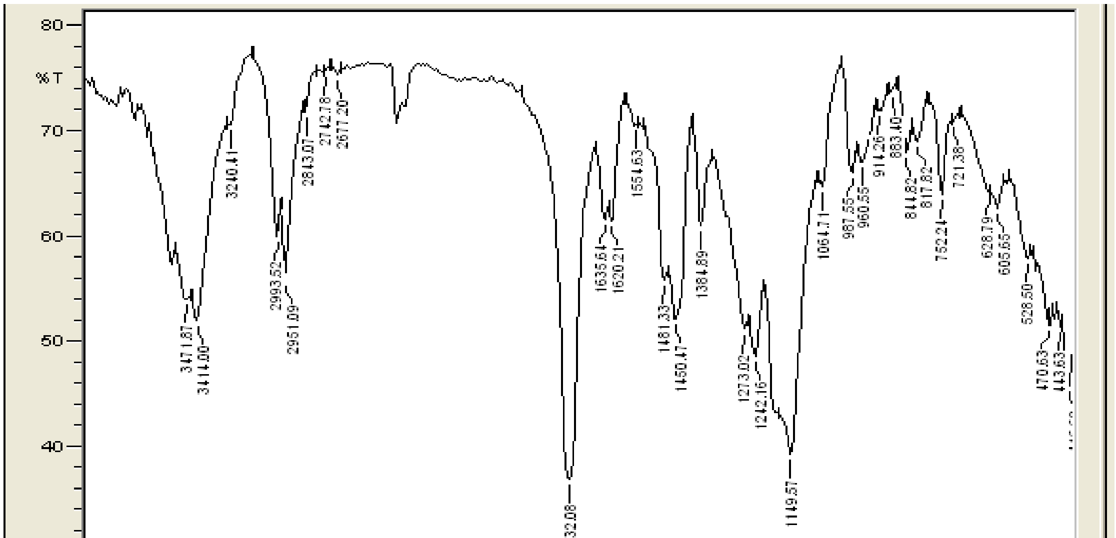


Fig (4-9) FTIR spectrum for PZ2

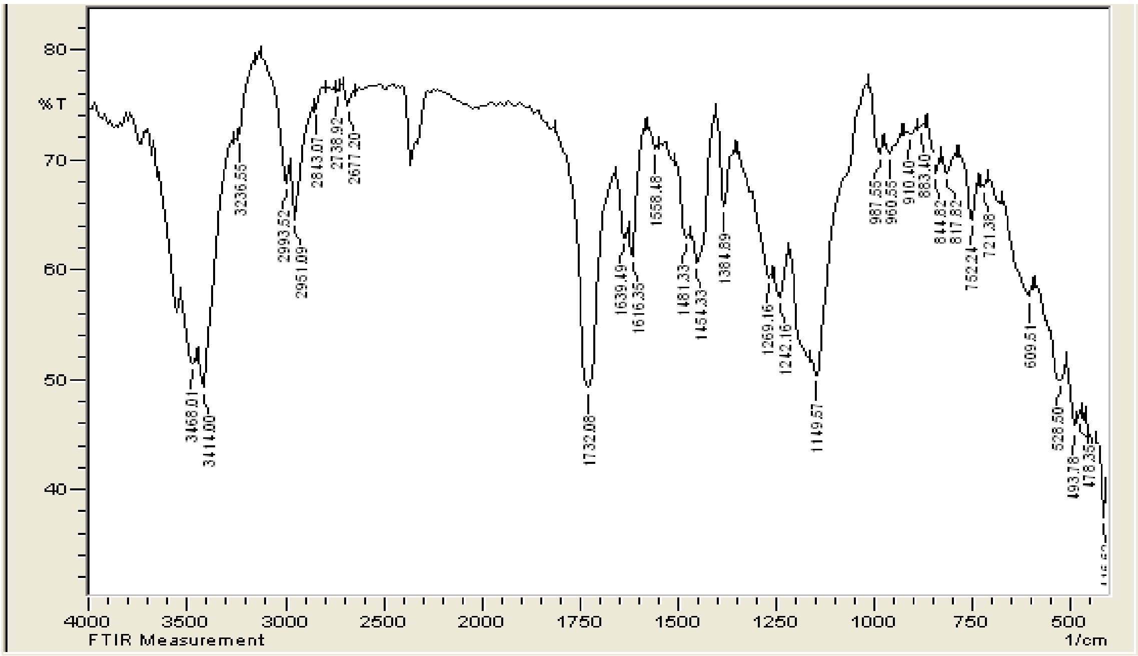


Fig (4-10) FTIR spectrum for PZ3

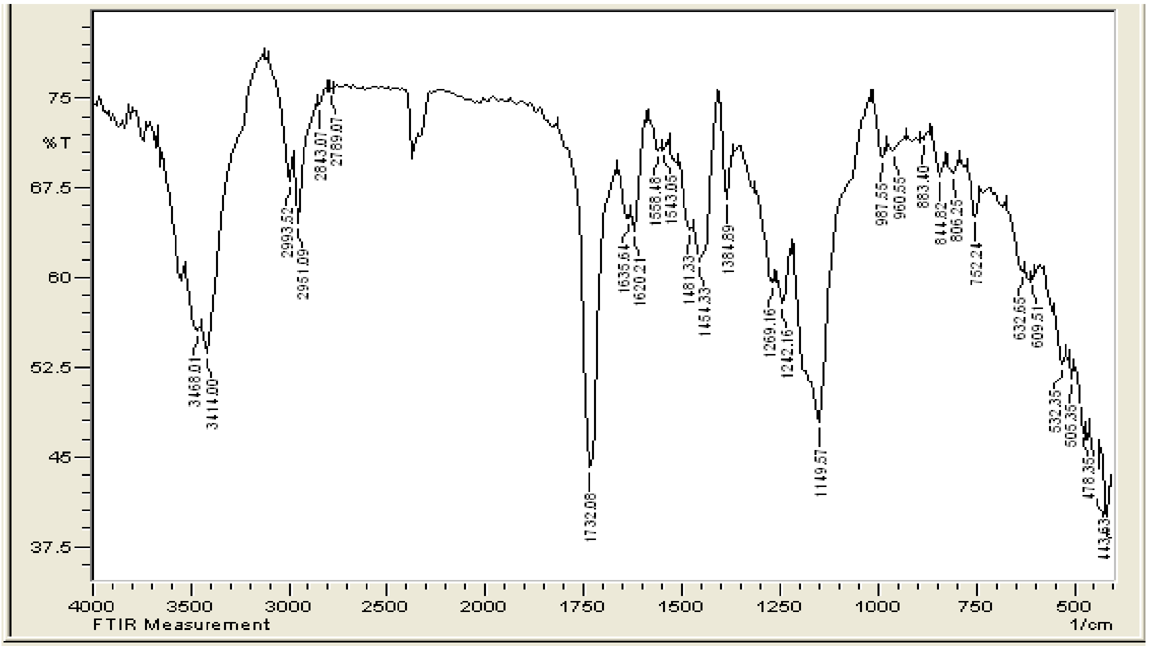


Fig (4-11) FTIR spectrum for PZ4

The bonds are oscillating at the same regions of wave number except some change in the intensities of some absorption waves; it may be due to the wagging oscillating in the covalent bonds of the functional groups of PMMA as shown in figure (4-13).

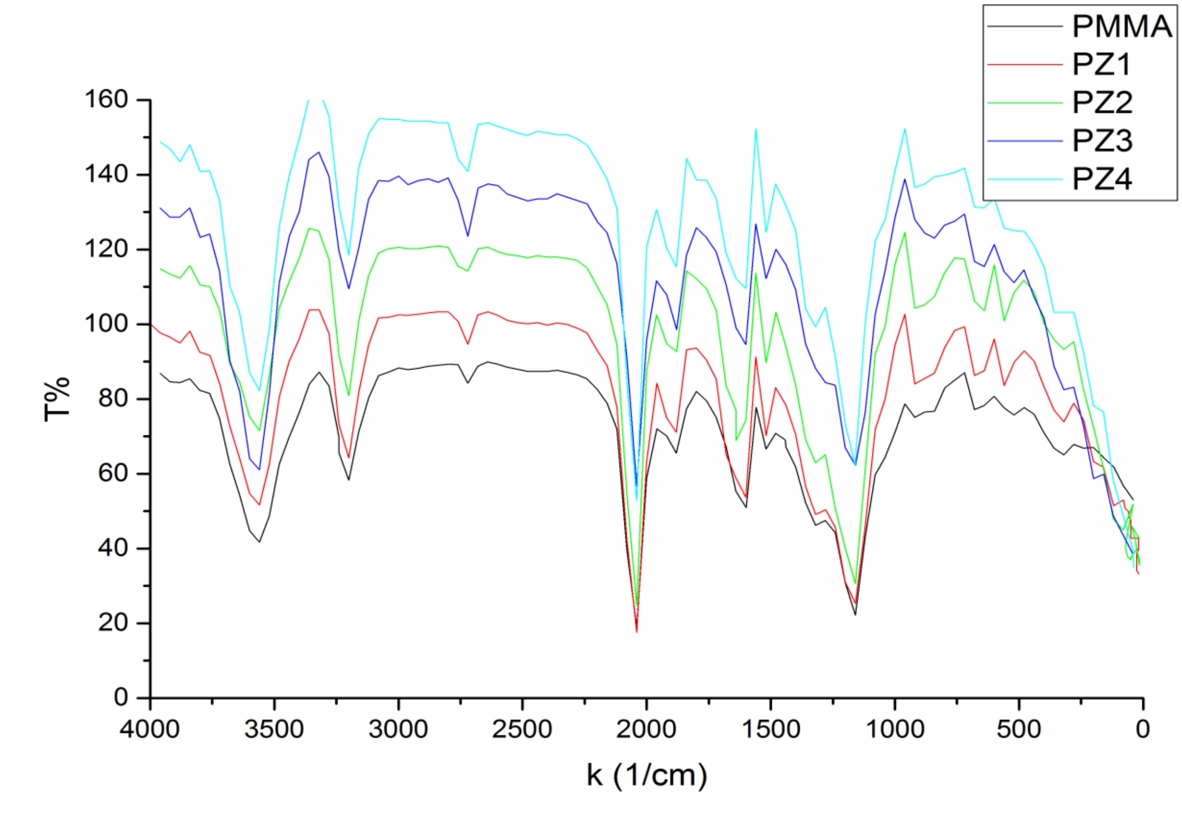


Fig (4-12) Combination of FTIR spectrum for PMMA, ZnO and the composite with different concentration

This is evidence that no chemical reaction was happened between the PMMA and ZnO hence the resulting material is a composite where the PMMA considered matrix and the ZnO considered a reinforcement additives.

4.2.3 SEM Examining

Top and side view for the composite show in figures (4-13) and (4-14) respectively.

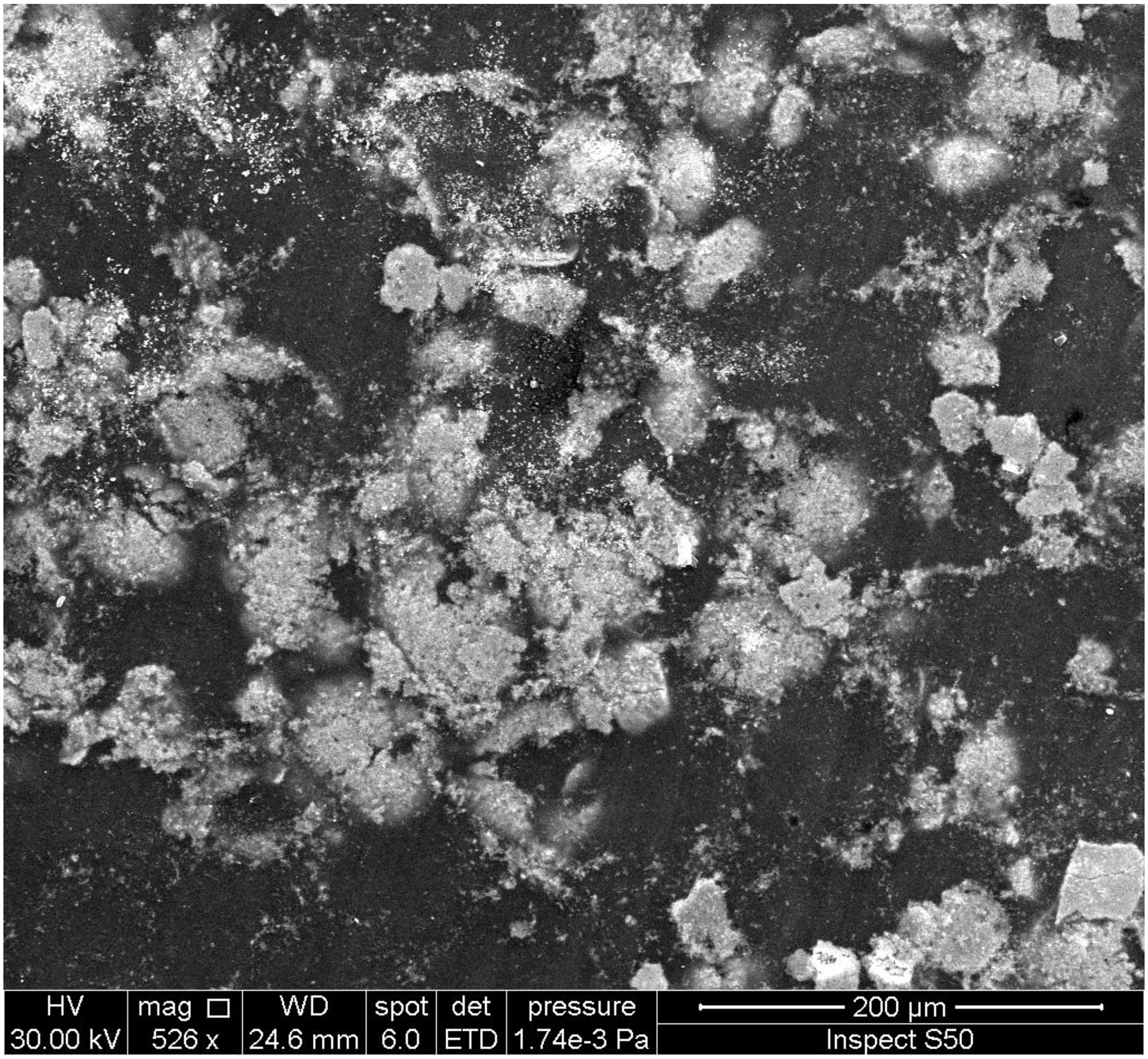


Fig (4-13) Top view by SEM for PMMA/ZnO composite

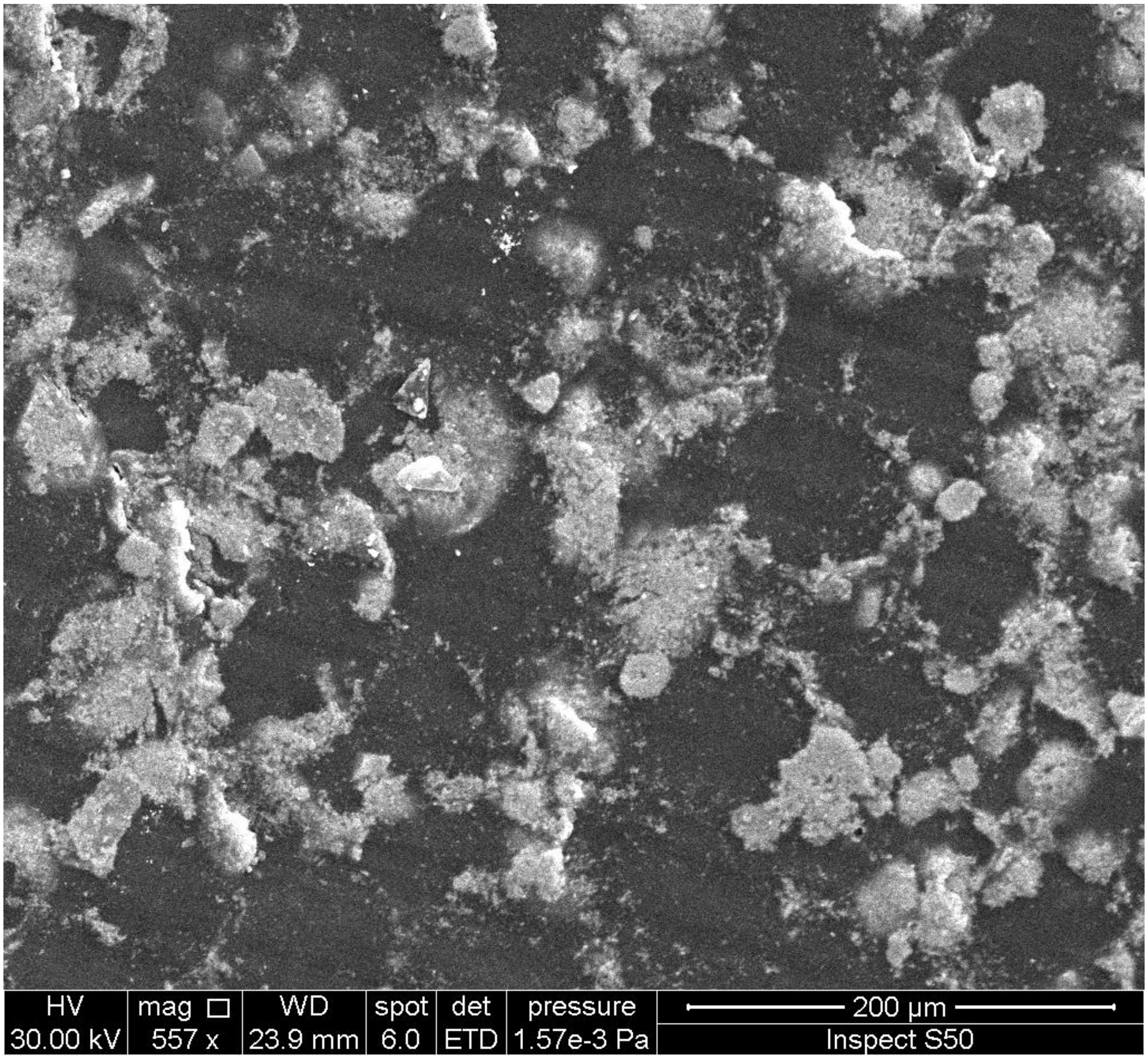


Fig (4-14) Side view by SEM for the PMMA/ZnO composite

ZnO particles showed irregular distribution in PMMA matrix because of the mixing was carried out by hand layout and the viscosity of the PMMA was too much.

These reasons made the ZnO particles aggregate to form different shapes in some regions which take place in a whole matrix and occupy the spaces among the molecules.

4.3 Optical Properties of PMMA and PMMA/ZnO Composite

According to the energy conservative law and by referring to the quantum confinement one can conclude what will be happen if the incident wave length reacted with the outer shell electron. Hence the electrons either absorb the photon or reflect the photon depending upon two parameters, frequency of the incident photon and the energy gap of the subjected material. Some variables will be discussed in the followings sections; they are related to the optical properties of PMMA and PMMA/ZnO.

4.3.1 Absorbance (A) and Transmittance (T)

The absorbance (A) versus wave length shown in figure (4-15) for the PMMA and the PMMA/ZnO composite with different concentration, one can notice that the absorbance was took high value near the absorption edge 340 nm for PMMA and then decreases in the visible and near infrared regions, the same behavior occurs with composites except the absorption edge which increased respectively with the additive increased.

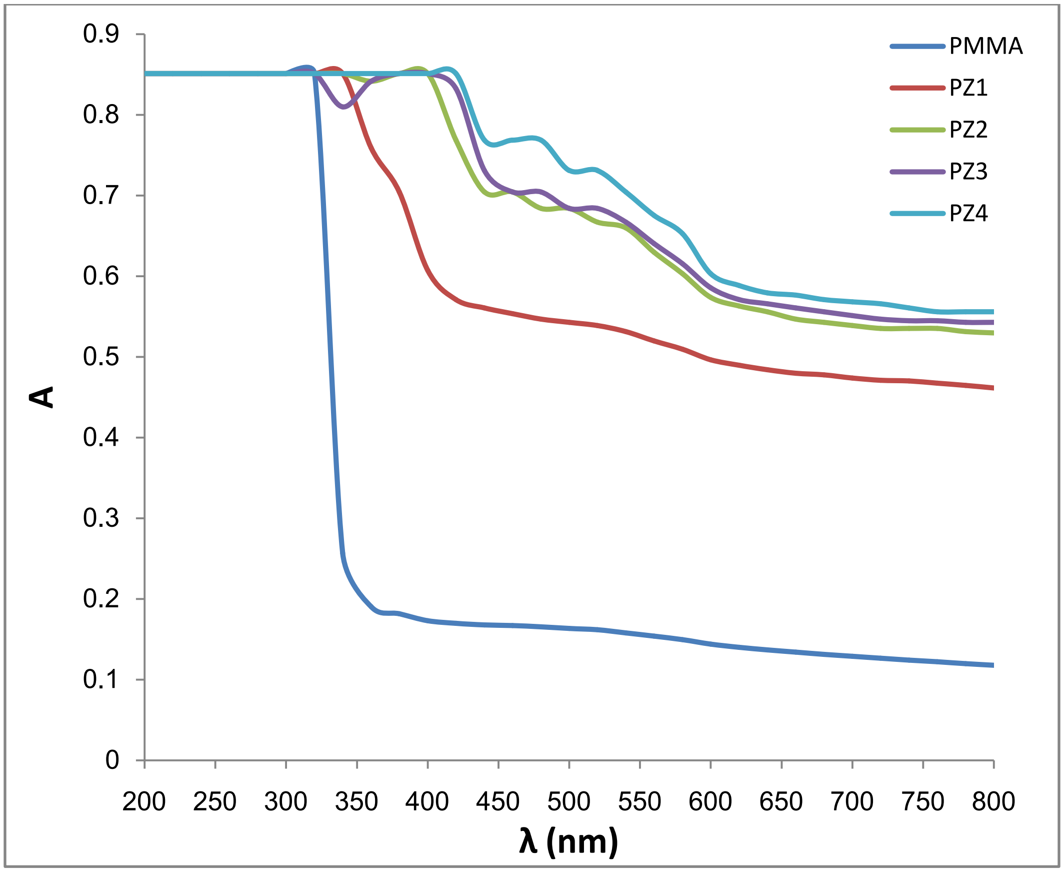


Fig (4-15) Absorbance spectrum for PMMA and its composite

This behavior occur because it is at high wavelength the photon has no enough energy to interact with matter so the photons transmit and the transmittance increased in this region in both PMMA and the PMMA/ZnO composite. Figure (4-16) shows the transmittance spectrum as a function of wavelength. In the UV and near the visible regions the photon has enough energy to interact with the matter so the absorption increased and the transmittance decreased; these results are consistent with other researchers [20] and [37].

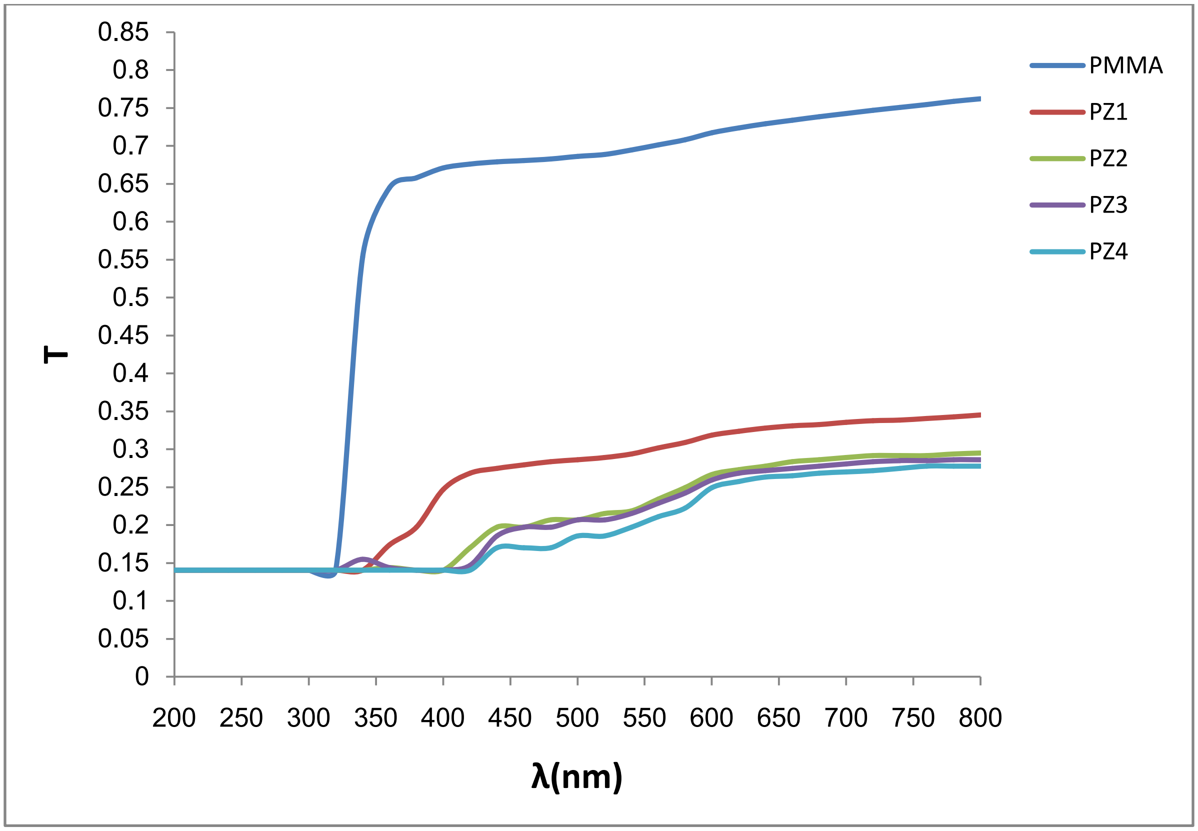


Fig (4-16) Transmittance spectrum for PMMA and its composite

4.3.2 Absorption coefficient

Figure (4-17) shows absorption coefficient (α) as a function to wavelength for PMMA and PMMA/ZnO composite, α was calculated by using equation (2-2), from the figure one can notice that for both the PMMA and the PMMA/ZnO composite the absorption coefficient decreases at high wavelength region because the low energy of the incident photon (hf < E_g) which not enough to make the electron transits from the valance band to conduction band, but in low wavelength region close to absorption edge the absorption coefficient increases because of the high energy of incident photon (hf > E_g) it was enough to transit the electron from the valance band to conduction band. Other result showed the value of the absorption coefficient was less than 10^4 cm^{-1} and it was increased with ZnO concentration increasing, these results are agree with [38].

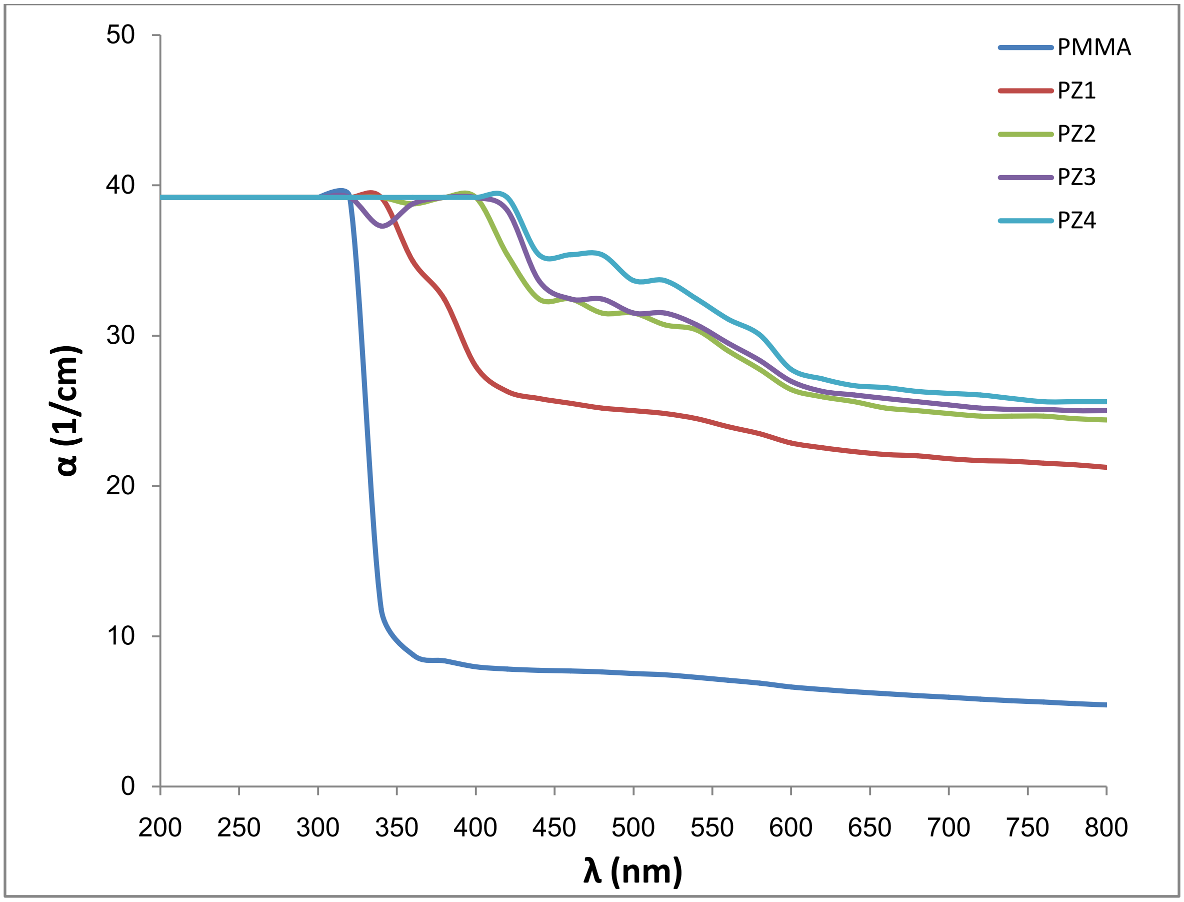


Fig (4-17) Absorption coefficient for PMMA and its composite

4.3.3 Refractive Index and Extinction Coefficient

Refractive index (n) calculated from equation (2-3), it well known the refractive index depending on the density of the material so when an additive increases in material then the refractive index increases but in figure (4-18) one can notice that the refractive index of the PMMA/ZnO composite decreased when the ZnO particles increased.

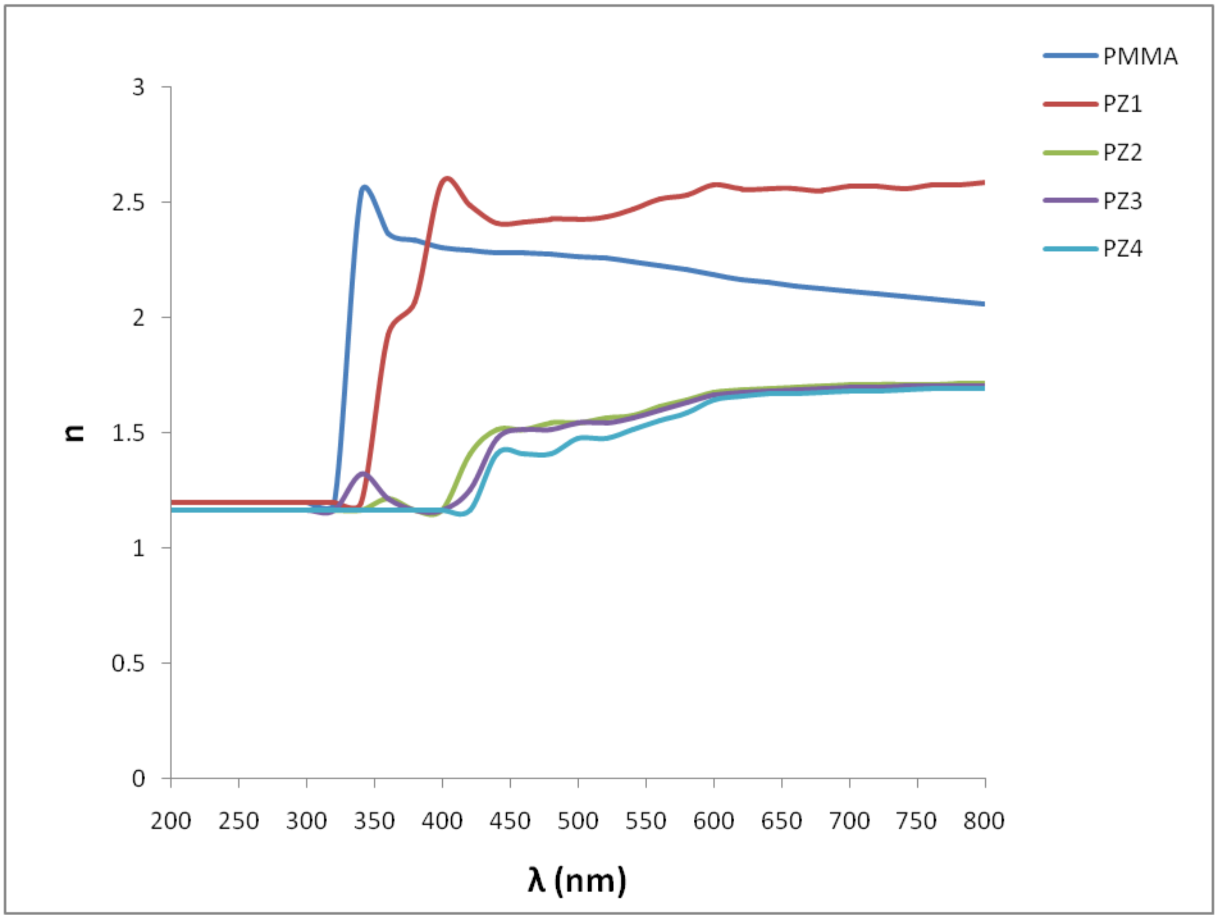


Fig (4-18) Refractive index for PMMA and the composite with different concentration

The explanation of this behavior depend on the Ewald-Oseen extinction theorem [63], when an electromagnetic wave incident on the material, the atoms and electrons excited, so they will oscillate and emit an electromagnetic waves in the same frequency of the original electromagnetic wave but with different phase which interface with the original wave, because of that the phase velocity of the new electromagnetic will change, there are some probabilities for how the phase velocity change in material but the two important probabilities relate to this behavior are: either the phase difference between the emitted wave and the original is 270^0 so the phase velocity become greater so the refractive index decreased and become negative, or the phase difference is 180^0 then the destructive interference happened between the emitted wave and the original so the refractive index become imaginary [64]. From these probabilities one can conclude the phase difference in this case was close to 180 degree or between (180 and 270) degree so the refractive index decreased, this result agree with the irregular and nonlinear results which found by researchers [23] and [30].

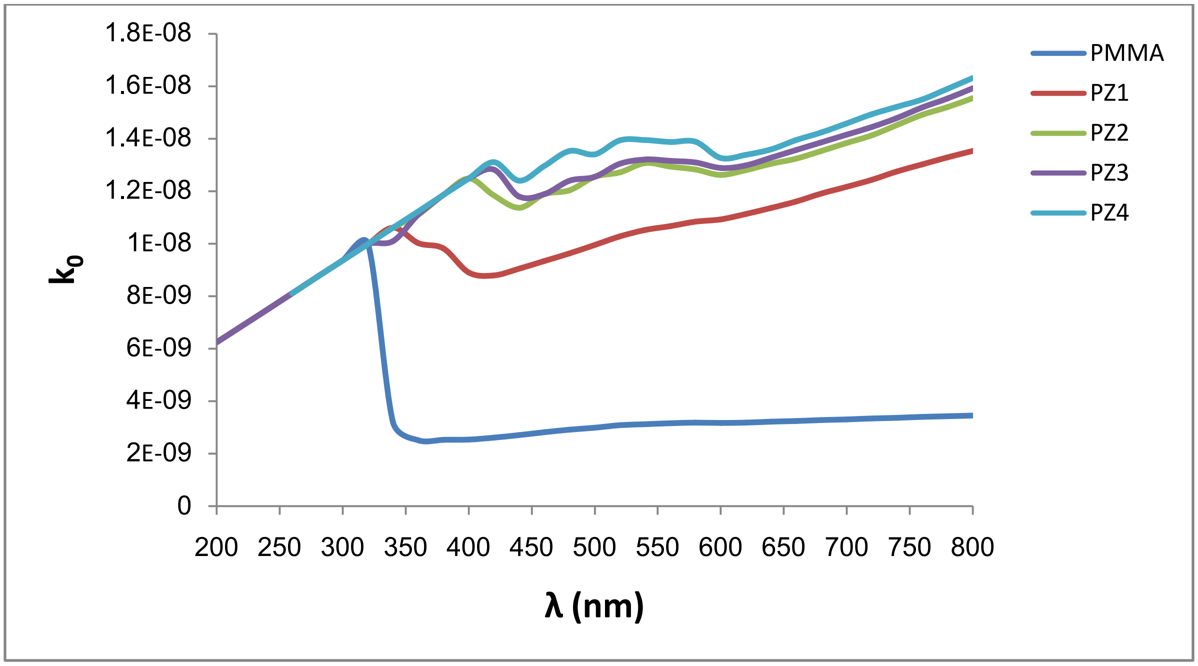
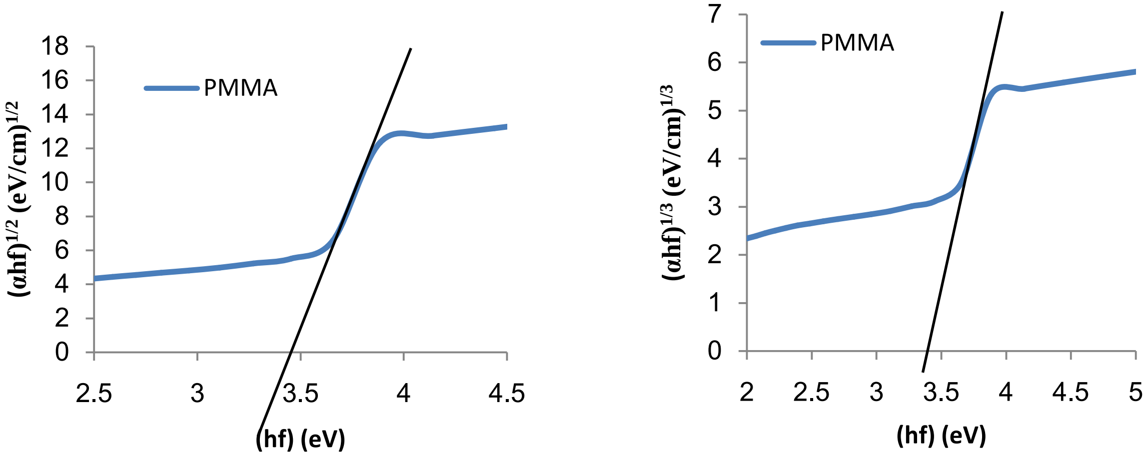


Fig (4-19) Extinction coefficient for PMMA and its composite

Extinction coefficient was calculated by using equation (2-6), figure (4-19) shows the extinction coefficient versus wavelength for the polymers and the composites, the increasing of k_0 with the increasing of the additive concentration can be notice, this increasing because of the density increasing of the samples and due to the slight difference in the thickness of the sample leading to attenuate the electromagnetic wave. This result agrees with [33].

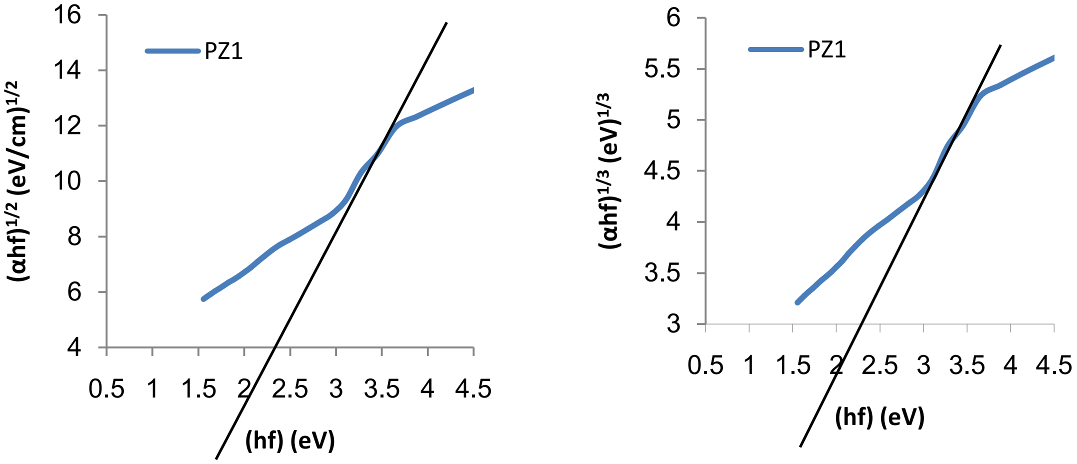
4.4.3 Optical Transition

The figures (4-20) to (4-24) show how the energy gap for allowed and forbidden indirect transition calculated by using equation (2-7). Only indirect transition occurs when $\alpha < 10^4$ cm^{-1}.



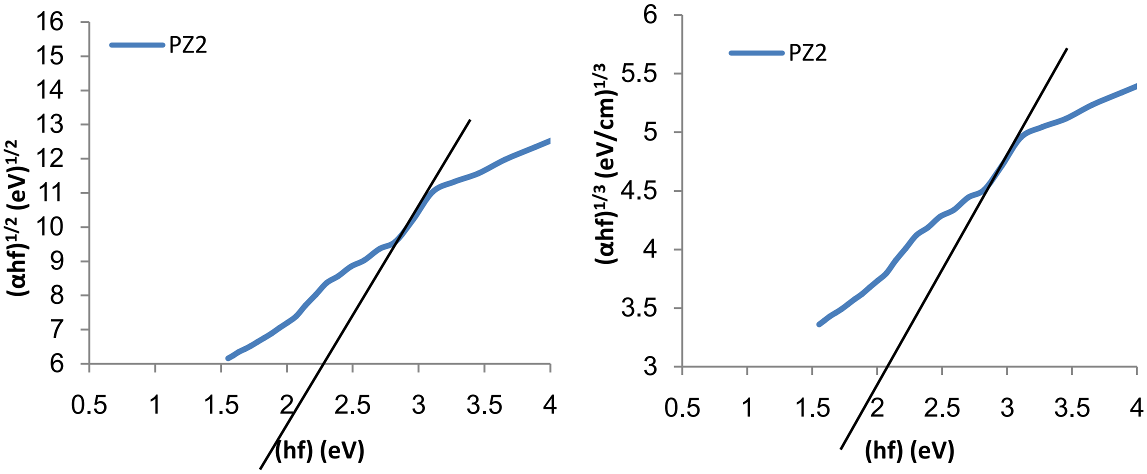
(a) Allowed **(b) Forbidden**

Figure (4-20) Allowed and forbidden energy gap for PMMA



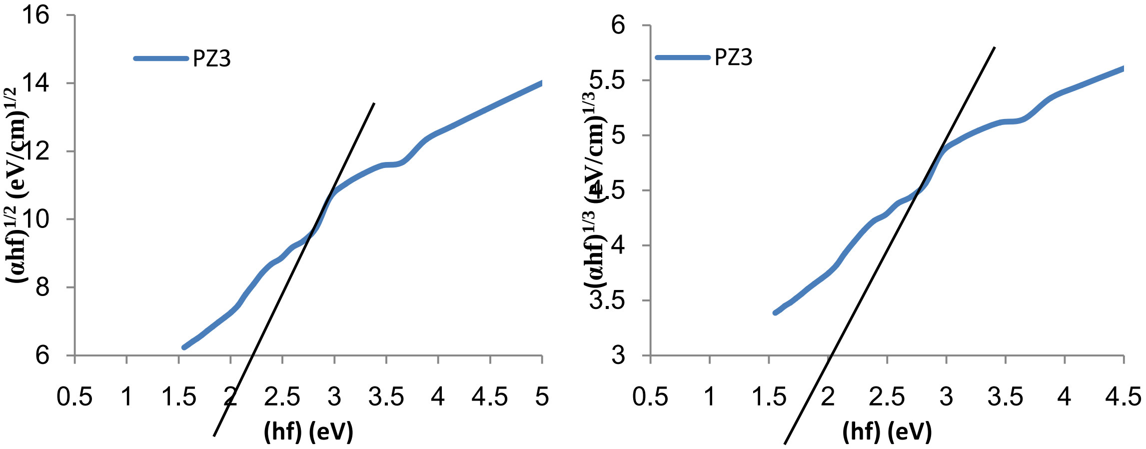
(a) Allowed **(b) Forbidden**

Fig (4-21) Allowed and Forbidden energy gap for PZ1



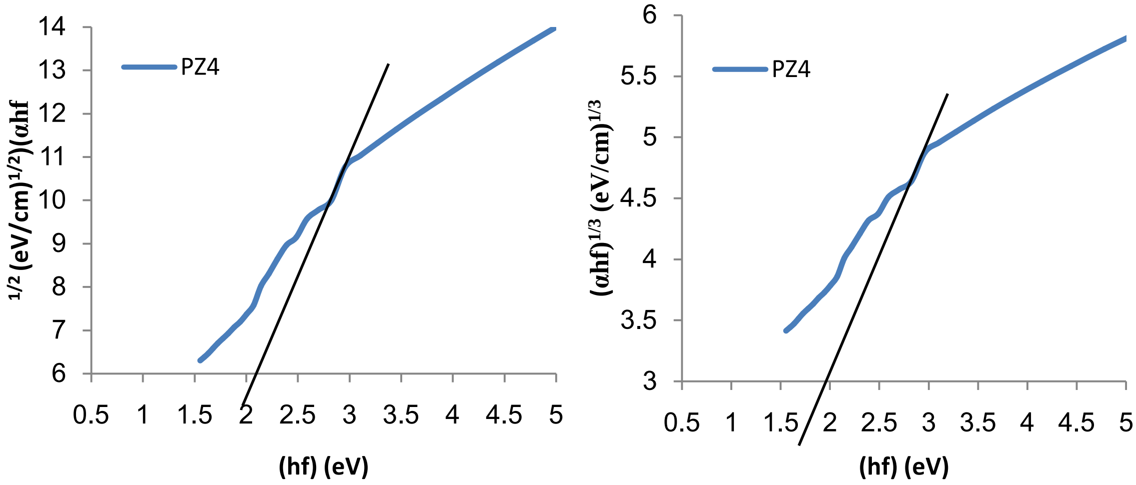
(a) Allowed **(b) Forbidden**

Fig (4-22) Allowed and Forbidden energy gap for PZ2



(a) Allowed **(b) Forbidden**

Figure (4-23) Allowed and Forbidden energy gap for PZ3



(a) Allowed **(b) Forbidden**

Fig (4-24) Allowed and Forbidden energy gap for PZ4

The data listed in table (4-3) which estimated from the previous figures, one can note that the forbidden energy gap decreases with the increasing of ZnO particles because of the localized levels which configured between the valance band and the conduction band, these levels made Fermi level shifted near the conduction band of the composites materials. This is the reason for the increasing of interaction between the electromagnetic wave with the material and hence the ZnO/PMMA composite become more absorber than pure PMMA when subjected the material under the test the UV-VIS range, and thus increases the amount of electrons moving from the valance band to the conduction band. These results agree with researchers [33] and [37].

Table (4-3) Forbidden energy gaps indirect transition.

Sample code	E_g(eV)	
	Allowed	Forbidden
PMMA	3.45	3.4
PZ1	2.35	2.30
PZ2	2.30	2.10
PZ3	2.20	2.05
PZ4	2.10	2.00

4-5 Dielectric Properties

The dielectric constant was calculated by using equation (2-10), figure (4-25) shows the dielectric constant versus frequency logarithm, the dielectric constant decreased with increasing of the ZnO concentration in zone of log (f) lie between (3 to 5) , this decreasing because of the non homogenous distribution of the ZnO inside the matrix material that was clear in the SEM pictures, this non homogenous distribution block the orientation of the dipoles inside the material, and as it is known the polymer is a macromolecule with folds, so the ZnO particles get in these folds then they block the dipoles orientation.

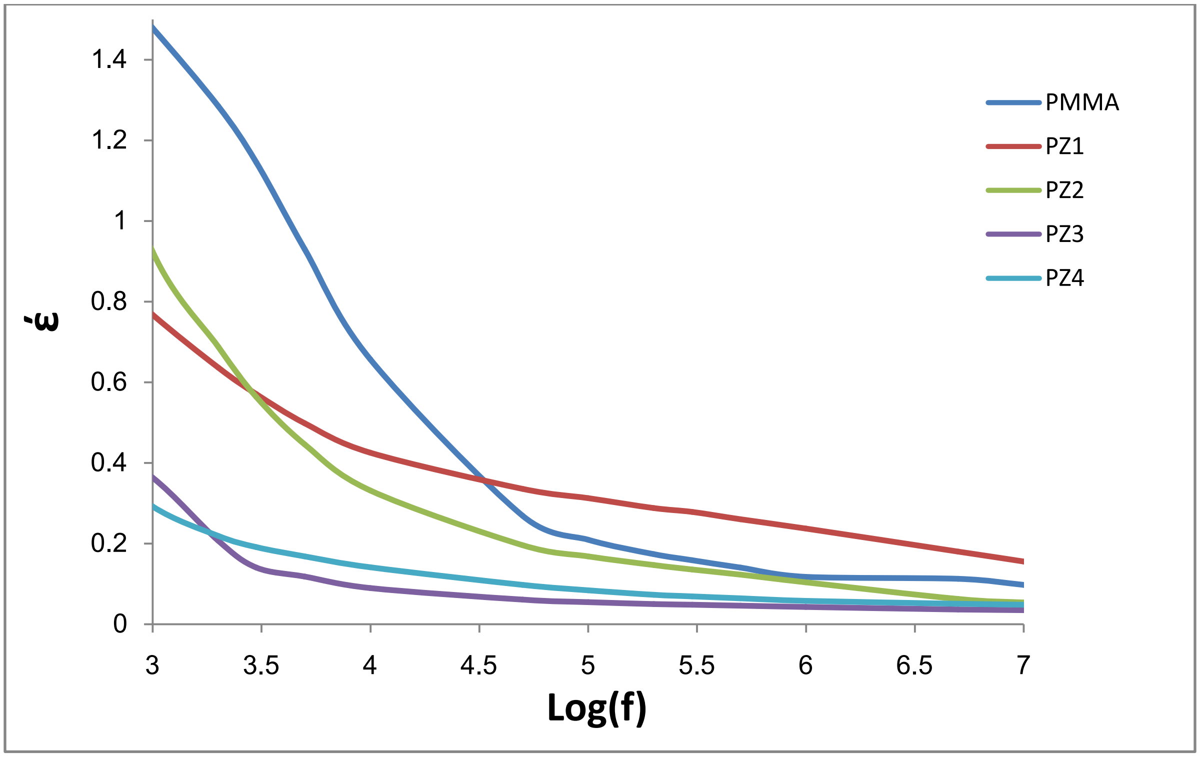


Fig (4-25) Dielectric constant for PMMA and the composite with different concentration

In the range between (5-7) for log(f) one can notice that the dielectric constant of the PMMA and the composites have been close to each other that because of the fast alternative of the electric field so the relaxation time increases which leads other polarization types appear in subsequent frequencies. The response of ionic polarization to the alternative electric field is small compared to the electronic polarization because the mass of the ions is greater than the mass of the electrons. Electronic polarization is the only one at high frequencies which makes the dielectric constant almost constant for all samples at high frequencies.

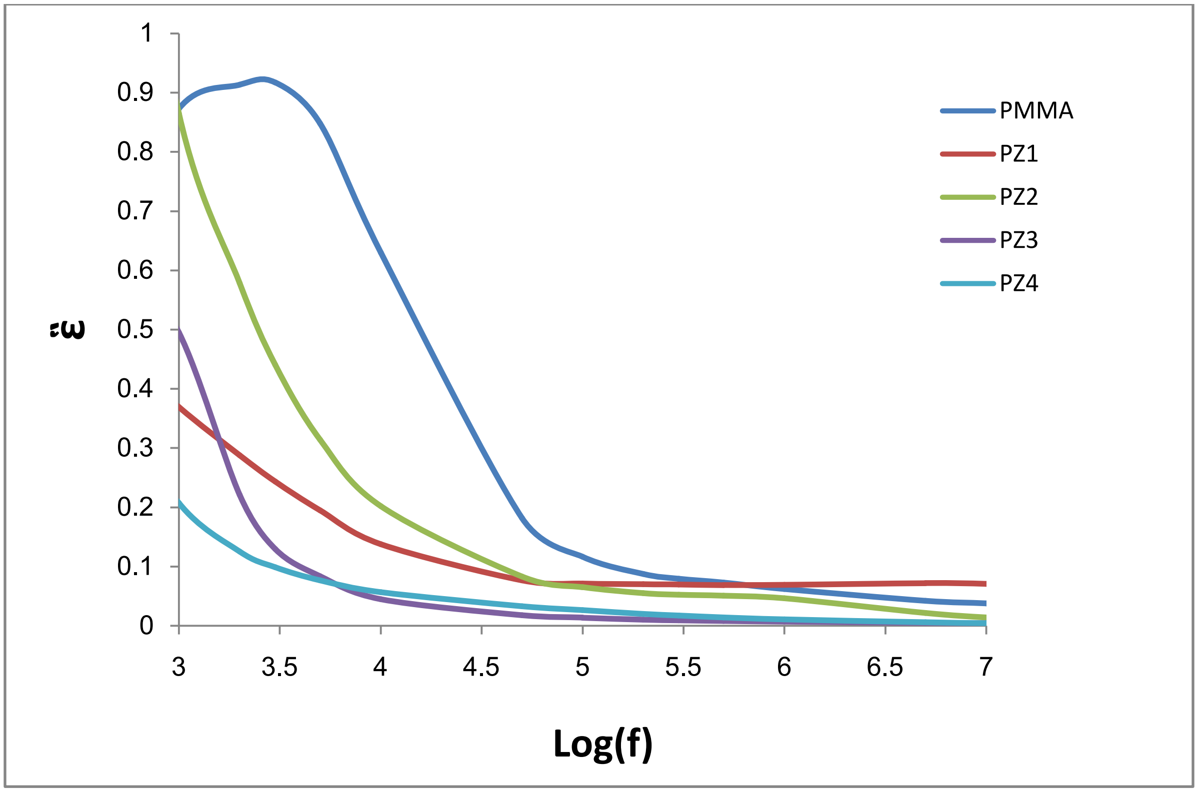


Fig (4-26) Dielectric loss for PMMA and the composite with different concentration

The dielectric loss also decreased with the increasing of the ZnO concentration. As it is known the dipoles inside the dielectric materials change their direction with the varying of the electric field so because of these orientation and vibration heat will produce through dielectric loss, so if the orientation decreases the dielectric loss will decrease. These results of dielectric constant and loss agree with the results which it found by the researchers [19] and [34].

Chapter Five
Conclusions and Future Work

Chapter Five

Conclusion and Future work

5.1 Conclusion

1- The XRD and FTIR analysis proved that the prepared material of PMMA with ZnO as additive was composite and no new chemical compound found.

2- As the ZnO particles increased the absorption of wavelength increase especially in UV region, this mean the PMMA/ZnO composite will be improve the weather ability of polymer so it can be used as a protection layer in the solar cells application.

3- As the ZnO particles increase in PMMA matrix then the energy gap suffered decreased in its value and the composite become less insulating and approach towards the semiconductor.

4- Increasing ZnO particles in the PMMA matrix made a reduction in both values of dielectric constant and dielectric loss, especially at high frequency.

5.2 Future Work

Due to the experimental results in the present work and for a complementary identification of PMMA and its composite we can suggest these future work:

1- Study the thermal and mechanical behavior of PMMA and its composites.
2- Study the electrical properties of PMMA and its composites under applying alternative voltage.
3- Study the electrical and optical properties of PMMA with other metal oxides.
4- Investigate the electrical properties of polymer enhanced with nano silver approach to make conductive polymer.

References

[1] Sybrand van der Zwaag, “Self Healing Materials”, Springer, Netherland, 2007.

[2] Evgeny V. Morozov, Valery Vasiliev, “Advanced Mechanics of Composite Materials and Structural”, Elsevier, 2013.

[3] William D. Callister, Jr. , David G. Rethwisch, “Fundamentals of Materials Science and Engineering”, John Willy and sons**,** 2008.

[4] David I. Bower, “An Introduction to Polymer Physics”, Cambridge University press, 2002.

[5] Prof. Premamoy Ghosh, “Fundamentals of Polymer Science”, Polymer Study center, 2006

[6] Robert O. Ebewele, “Polymers Science and Technology”, CRC Press, 2000.

[7] Joel R. Fried, “Polymer Science and Technology”, Prentice Hall, 2014.

[8] Fred W. Billmeyer, “Text Book of Polymer Science”, John Willy & sons ,1984.

[9] Shaw Ling Hsu, “Polymer Data Handbook”, Oxford university press, 1999.

[10] D.W. Van Krevelen, “Properties of Polymers”, Elsever, 2009

[11] Stevens, Malcolm P., “Polymer Chemistry: An Introduction”, Oxford university press, 1998

[12] John Brydson, “Plastic Materials”, Butterworth-Heinemann press, 7th Edition, 1999.

[13] Kumar DA, Abdul Kalam SD, Design, “Analysis and Comparison between the Conventional Materials with Composite Material of the Leaf Springs”, Fluid Mech Open Acc 3:127, Vol 3, 2476-2296, 2016.

[14] P. K. Mallick, “Composite Engineering Handbook”, Marcel Dekker, 1997.

[15] C. Klingshirn, ZnO Material, “Physics and Application” ChemPhys Chem, 8, 782 – 803, 2007.

[16]Claus F. Klingshirn, Andreas Waag, Axel Hoffmann, Jean Geurts, “Zinc Oxide: From Fundamental Properties Towards Novel Applications”, Springer, 2010.

[17] Zhong Lin Wang, “Zinc oxide Nanostructures: Growth, Properties and Applications”, J. Phys.: Condens. Matter, 16**,** R829–R858, 2004.

[18] Xiaoge Gregory Zhang, “Corrosion and Electrochemistry of Zinc”, Plenum Press, 1996

[19] Hong-Wen Wang, Chain-Fang Shieh, Kung-Chin Chang, Hsuan Chih Chu, “Synthesis and Dielectric Properties of Poly(methyl methacrylate) Clay Nanocomposite”, Vol. 97, 2175–2181, 2005.

[20] E. Tang, Guoxiang Cheng, Xiaolu Ma, “Preparation of Nano ZnO /PMMA Composite Particles via Grafting of the Copolymer onto the Surface of Zinc Oxide Nanoparticles” , Powder Technology, 161, 209–214, 2006.

[21] Mustafa M. Demir, Mine Memesa, Patrice Castignolles, Gerhard Wegner, “PMMA/Zinc Oxide Nanocomposites Prepared by In-Situ Bulk Polymerization”, Macromol. Rapid Commun., 27, 763–770, 2006.

[22] R.Y. Hong, J.Z. Qian, J.X. Cao, “Synthesis and Characterization of PMMA Grafted ZnO Nanoparticles”, Powder Technology ,163, 160–168, 2006.

[23] Ahmad A.H., Awatif A.M. and Zeid Abdul-Majied N., “Dopping Effect On Optical Constants of Poly methyl methacrylate (PMMA)” , Eng. & Technology, Vol.25, No.4, 2007.

[24] Zainab A., “Effect of Nickel Salt on Electrical Properties of Poly Methyl Methacrylate”, Journal of College of Education, 3, 321-327, 2008.

[25] Moriyuki Sato, Akihito Kawata, Shigekazu Morito, Yuzuru Sato, Isao Yamaguchi, “Preparation and Properties of Polymer/Zinc Oxide Nanocomposites using Functionalized Zinc Oxide Quantum Dots”, European Polymer Journal 44, 3430–3438, 2008.

[26] Bahaa Hussain, Marwa Abdul-Muhsien, Ahmad Hashim, “Study of Some Electrical Properties for PMMA-TiO2 Composites”, atti della Fondazione Giorgio Ronchi Anno LXVI No.1, 2010.

[27] Muhammad Hameed Abdul-Allah, Sami Salman Chiad, Nadir Fadhil Habubi, “The Effect of Iron Chromate on the Optical Properties of PMMA Films”, Diyala journal for pure science, VOL.6, No.2, 2010.

[28] R. Sreeja, Jobina John, P.M. Aneesh, M.K. Jayaraj, “Linear and Nonlinear Optical Properties of Luminescent ZnO Nanoparticles Embedded in PMMA Matrix”, Optics Communications, 283, 2908–2913, 2010.

[29] B. Kulyka, V. Kapustianyka, V. Tsybulskyya, O. Krupkab, B. Sahraouic, “Optical Properties of ZnO/PMMA Nanocomposite Films”, Journal of Alloys and Compounds, 502, 24–27, 2010.

[30] Gaurang Patel, M.B.Sureshkumar, Purvi Patel, “Effect of TiO2 on Optical Properties of PMMA: An Optical Characterization, Advanced Materials Research”, Vols. 383-390, pp. 3249-3256, 2012.

[31] P.P. Jeeju a, S. Jayalekshmi, K. Chandrasekharan, P. Sudheesh , “Enhanced Linear and Nonlinear Optical Properties of Thermally Stable ZnO/PolyStyrene/PolyMethyl Methacrylate Nanocomposite” , Thin Solid Films, 531, 378–384, 2013.

[32] Yewei Zhang, Shendong Zhuang, Xiaoyong Xu, Jingguo Hu, “Transparent and UV-Shielding ZnO/PMMA Nanocomposite Films”, Optical Materials, 36, 169–172, 2013.

[33] Khalid Al-Ammar, Ahmed Hashim, Maithem Husaien, “Synthesis and Study of Optical Properties of (PMMA-CrCl2) Composites”, Chemical and Materials Engineering, 1(3), 85-87, 2013.

[34] Basavaraja Sannakki and Anita, **“**Dielectric Properties of PMMA and its composites with ZrO_2”, Physics Procedia, 49, 15 – 26, 2013.

[35] Farooq Momtaz Abd Omran, “Study of the Electrical Properties of (PMMA-Ag) and (PMMA-Ti) nanocomposites”, M.Sc Thesis, Babylon University, College of Education for Pure Sciences, 2014.

[36] Nahida G.Hamed and Maraw Rahem, **“**To Study the Silver Concentration Effect on the Optical and Electrical Properties of the Ag/PMMA Composites”, Eng. &Tech.Journal, Vol. 32, Part (B), No.1, 2014.

[37] Shahad Hussein, “Study the Optical and Mechanical Properties of (PMMA-TiO_2)Nanocomposite”, M.Sc. Thesis, Babylon University, Collage of science, 2014.

[38] Bahaa H. Rabee, Bairaq Abd Al-Kareem, “Study of Optical Properties of (PMMA-CuO) Nanocomposites”, International Journal of Science and Research, Vol.5, Issue4, 2014.

[39] P. Maji, R.B. Choudhary, M. Majhi,Department, “Structural, Optical and Dielectric Properties of ZrO_2 Reinforced Polymeric Nanocomposite Films of Polymethyl Methacrylate (PMMA)”, Optik, 127, 4848–4853, 2016.

[40] Rodrigo Balena, Wilian Vidotto da Costaa, Jéssica de Lara Andradea, Juliana Francis Piai, Edvani Curti Muniza, Mychelle Vianna Companhonid, Tânia Ueda Nakamurad, Sandro Marcio Limae, Luis Humberto da Cunha Andradee, Paulo Rodrigo Stival Bittencourtf, Ana Adelina Winkler Hechenleitnera, Edgardo Alfonso Gómez Pinedaa, Daniela Martins Fernandesa, “Structural, Thermal, Optical Properties and Cytotoxicity of PMMA/ZnO Fibers and Films: Potential

Application in Tissue Engineering", Applied Surface Science, 385, 257–267, 2016.

[41] Rebek, J.F, "Experimental Methods in Polymer Chemistry", John Wiley and Sons, New York, (1980).

[42] D. Greenaway and G. Harbeke, "Optical Properties and Ban Structure of Semiconductors", Pergamon press, New York, (1966).

[43] W. Klopffer, "Introduction to Polymer Spectroscopy", Springer, 1984.

[44] H. A. Macleod, Thin Film Optical Filter, Mc Graw Hill NewYork (2001).

[45] A. Ahmed, A. Awatif and A. Zeid, "Dopping Effect on Optical Constants of (PMMA)", J.Eng and Technology, V.25, PP.137-139, N.4, 2007.

[46] Abdul J.Kareem, Majeed H.Ali, Karrar AbdO .Ali, "Effect of Adding (PEG-Cellulose Derivatives) on Optical Properties of Cosmetics Face Powders", RRPL, 6(2), PP. 071-082, 2015.

[47] S.M.Sze, Kwok K.Ng, "Physics of Semiconductor Devices", Wiley, 3rd Ed., 2006.

[48] J. I. Pankove**, "**Optical Process in Semiconductors", Dover Publishing, New York, 1971.

[49] Y. N. Al-Jamal, "Solid State Physics", Al-Mosel University, 2nd Ed., Arabic Version, 2000.

[50] N. F. Mott, E. A. Davis, "Electronic Processes in Non-Crystalline Materials", Oxford University Press, 2nd Ed., 1979.

[51] Takahiro Numai, "Fundamentals of Semiconductor Lasers", Springer, 2015.

[52] S. M. Sze, "Physics of Semiconductor Devices", John Wiley and Sons, 1981.

[53] A. Madau, M. P. Show, "The physics and Application of Amorphous Semiconductors", Academic press,1986.

[54] National Research Council, "Polymers" National Academy press,1995.

[55] S. Wen and D.D.L. Chung, "Electric polarization in Carbon Fiber Reinforced Cement", Cem .Concr Res .3,1, (1), 141- 147, 2001.

[56] C. kittle, "Introduction to Solid State Physics" ,John Willy & sons , 8th edition, 2005.

[57] Kwan Chi Kaw, "Dielectric Phenomena in Solids", Elesvier, 2004.

[58] Von Hipple, A.R., "Dielectric Materials and Applications", MIT Press, 4th Edition, 1966.

[59] D.B. Sirdeshmukh , L. Sirdeshmukh, K.G. Subhadra, "Macro and Micro Properties of Solid Material", Springer, 2006.

[60] Ronald L. Sakaguchi, John M. Powers, "Craig's Restorative Dental Materials", Elsevier, 13th edition, 2012.

[61] Abrahams S. C., Kvick A., "Atomic Displacement, Anharmonic Thermal Vibration, Expansivity and Pyroelectric Ceafficient Thermal Dependences in ZnO", Acta Crystallographica B (39,1983), 45, 34-40, 1989. www.crystallography.net

[62] Spectral Database for Organic Compounds SDBS , National Institute of Advanced Industrial Science and Technology (AIST), Japan. http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng

[63] Masud Mansuripur , "Classical Optics and its Applications", Cambridge press, 2002.

[64] Richard P. Feyman, Robert B. Leighton, Matthew Sands, "The Feyman Lecture on Physic", Addison Wesley publishing, 1977.

ألخلاصة

تضمن مشروع البحث دراسة الخواص البصرية والكهربائية لمتراكب متعدد مثيل ميثاكريلايت/ اوكسيد الزنك. تم اختيار تلك المواد لأهميتها الصناعية ووفرتها في ألأسواق المحلية.

استخدمت طريقة الخلط اليدوي والقولبة اليدوية في تحضير نماذج متراكبات دائرية الشكل ذات قطر وسمك ثابتين عند درجة حرارة المحيط وبأستخدام حمام مائي ذي موجات فوق الصوتية.

درست البنية التركيبية لعينات المتراكبات بواسطة تقنية حيود ألأشعة السينية وأظهرت النتائج عدم حصول اي تفاعل كيميائي بين مادة المصفوفة والمادة المضافة عند مقارنتها بالمخططات المرجعية.

شخصت المجاميع الكيمائية ألأساسية بأستخدام تقنية تحويلات فورير في المنطقة تحت الحمراء وقد وجد ان قمم الأمتصاص كدالة للطول الموجي لم تتغير للبوليمر وللمتراكب بأختلاف تراكيز المضاف.

استخدمت منظومة مطياف ألأشعة فوق البنفسجية-ألأشعة المرئية في دراسة الخصائص البصرية اذ بينت النتائج انخفاض في فجوة الطاقة وفي مقدار معامل ألأنكسار بزيادة جسيمات المادة المضافة, وزيادة معاملي ألأمتصاص والخمود بزيادة جسيمات المادة المضافة.

أستخدمت منظومة (ملف-متسعة-مقاومة) بالترددات العالية لدراسة الخصائص العزلية ,وجد ان ثابت العزل والخسارة العزلية يتناقصان بزيادة تركيز المادة المضافة.

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة النهرين
كلية العلوم
قسم الفيزياء

الخصائص الفيزيائية لمادة ألمتراكب PMMA/ZnO

رسالة
مقدمه الى مجلس كلية العلوم/ جامعة النهرين
كجزء من متطلبات نيل شهادة الماجستيرفي علوم الفيزياء

من قبل
زمن صاحب عبيد
بكلوريوس علوم الفيزياء 2009

بأشراف
ألأستاذ المساعد الدكتور
ثامر عبد الجبار جمعة

شعبان
1438هـ

أيار
2017 م