CHAPTER ONE

BASIC CONCEPTS

1-1 Introduction:-

Polymeric materials are of interest in scientific and technological research, because they can be tailored to meet specific requirement for a variety of applications, this is mainly due to lightweight, good mechanical strength, and optical properties(Jabbar et al., 2010).

Poly vinyl alcohol (PVA) is one of the most important polymeric materials, and one of the earliest and best known polymers which was seen to be used in a variety of applications and is currently used extensively in semiconductors applications, and it also has many applications in industry and is of relatively low cost in manufacture(Jabbar et al., 2010).

Polymeric composites of PVA areknown for their importance in technical applicationswhich has been widely used in adhesives, emulsificants, in the textile and paper industry applications(S.Chiad et al., 2014).Few years ago, PVA has been used in pharmaceutical and biomedical applications for controlled drug release tests due to its degradable and non-toxic properties.(Reis et al., 2006).

Metal/polymer composites have attracted considerable interest in recent years because of the advantageous properties of metals and polymers built into them. Studies of doping transition metal halides into PVA are important for determining and controlling the operational characteristic of the different PVA composites. Since $AgNO_3$ is a fast conducting ion in a number of crystalline and amorphous materials, its incorporation within a polymeric system may be expected to enhance its electrical and optical properties(Chiad et al., 2012), and to study the optical properties of matter through spectroscopy.

Spectroscopy is now accepted as a common method to investigate matter by measuring the light absorbed or emitted, that is, studying the interaction of light and matter (Ionita, 2014). More recently, the definition has been expanded to include the study of the interactions between particles such as electrons, protons, and ions, as well as their interaction with other particles as a function of their collision energy. Historically, spectroscopy referred to the use of visible light dispersed according to its wavelength, e.g. by a prism. Later, the concept was expanded greatly to comprise any measurement of a quantity as function of either wavelength or frequency. Spectroscopic data is often represented by a spectrum, a plot of the response of interest as a function of wavelength or frequency and this data are useful in the optical characterization of any matter.

Optical characterization techniques are usually non-destructive, fast, and of simple implementation, most requiring very little sample preparation. These techniques explore the change on intensity, energy, phase, direction, or polarization of the light wave after interaction with the object being studied. Many of them can be performed at room temperature and atmosphere, dispensing. The optical properties of a material depend on its structural, morphological, electronic and physical properties, which make them very powerful characterization techniques. Optical properties of materials have played a major role in the advancement of science and our current understanding of the universe(Soares, 2014).

Recently, doped polymers have been a subject of considerable interest because their physical and chemical properties make them useful for specific applications(Jabbar et al., 2010).

The recent studies on the electrical and optical properties of polymers have attracted much attention in view of their application in electronic and optical devices. Electrical conduction in polymers has been studied with the aim to understand the nature of the charge transport prevalent in these materials while the optical properties were intensity investigated in order to achieve better reflection, antireflection, interference and polarization properties(Ahmad et al., 2012).

1-2 Study Objectives:-

The objectives of this study are:-

- To determine the optical properties of pure PVA.
- To study the effect of doping silver nitrate, on the optical properties of the pure PVA.

1-3 Thesis Structure:-

This thesis composed of three chapters; chapter one presents the basic concepts related to light nature, laser characteristics, light matter interaction, measuring of intensity, transmission and reflection, the applications of bulk materials, and finally a literature review about the subject of this work.

Chapter two covers the experimental part of this work, the materials used and their specifications, the fabricated as disks with different thicknesses, in addition to the set up used and the procedure followed to determine the absorption coefficient and then the calculation of other optical properties of each disk.

Chapter three presents the results, discussion, followed by conclusions and recommendations.

1-4 Laser properties:-

The word laser has its origin in an acronym of the words light amplification by stimulated emission of radiation. The principle of operation, which is based on the use of stimulated emission of electromagnetic radiation in a medium of molecules or atoms, with more particles in the upper (excited) state than in the lower state (i.e., with an inverted population).

A laser generally requires three components for its operation: the active medium, the pumping system and the optical resonator. The active medium is a collection of atoms or molecules that can be excited to a state of inverted population; where more atoms or molecules are in an excited state than in some lower energy state. The active medium can be a gas, a liquid, a solid material, or a junction between two slabs of semiconductor materials. The pump is an external energy source that produces a population inversion in the laser gain medium, pumps can be optical, electrical, chemical, or thermal in nature. The optical resonator has the task to store a coherent electromagnetic field and to enable the field to interact with the active medium(Renk, 2012). Laser light differs in a number of respects from the light emitted by, for example, domestic light bulb or a gas discharge tube.

1-4-1 Coherence :-

Coherence is one of the unique and interesting properties of laser light. It refers to the degree of correlation between the phases at two different points on beam of light. This property states that all photons emitted from the laser are exactly in the same phase. It is grouped into two categories: temporal coherence and spatial coherence. Temporal coherence refers to correlation in phase at a given point in a space over a length of time or it can be defined as the measure of the correlation between the phases of a light wave at different points along the direction of propagation. Spatial coherence is a measure of the correlation between the phases of a light wave at different point's transverse to the direction of propagation. Coherence is the basis of applications in holography and measurement.

1-4-2 Directionality:-

The propagation and directionality of radiation is described by diffraction theory. Maximum intensity of radiation is limited by the angle of divergence. The laser medium will be amplified only radiation propagated on direction of optical cavity axis. Construction of optical cavity leads to a low beam divergence which means a high directionality (Herman and Boboescu).

1-4-3 Monochromaticity:-

It is the ability of laser to produce a well-defined color or wavelength. The frequency emitted by the laser is given by the difference in energy between the energy levels for which there is radiation emission. The two energy levels between which are laser radiation emission occurs are stable. Thus, a single frequency is emitted and amplified in the optical cavity. This means that laser radiation has a single wavelength. This means that the radiation emitted by the laser is monochromatic (Herman and Boboescu).

1-4-4 Brightness:-

Brightness or intensity of the laser light is defined as the power density per unit solid angle and it is extremely high compared with that of a conventional source.

1-5 Transparent and opaque materials:-

When light enters matter, its electromagnetic field reacts with the near fields of its atoms. In dense matter, light is quickly absorbed within the first few atomic layers and, because it does not emerge from it, that matter is termed nonoptically transparent. In contrast to this, some types of matter do not completely absorb light. Such matter, termed optically transparent matter, allows light to propagate through it and emerge from it. Examples of optically transparent matter include water and clear glass. Some passes a portion of light energy through it and absorbs the remainder it is called Semitransparent. Such matter attenuates the optical power of visible light, and it may be used to make an optical device known as optical attenuator, for example most transparent matter, semitransparent mirrors.

An optical filter allows selected frequencies to be propagated through it. For example red, green, yellow, or blue glass (each allows a selected range of frequencies to be propagated through it).Some matter in the ionized state absorbs selected frequencies and passes all others. For example the sun's ionized surface (Interaction of light with matter, n.d).

1-6Isotropy and anisotropy:

Most materials are category to isotropic and anisotropic materials. Anisotropic materials are materials whose properties are directionally dependent. Common examples of anisotropic materials are wood and composites. All metallic crystals are inherently anisotropic due to the directional differences in inter-atomic stiffness in the crystal structure, which a light ray may travel with different speeds for different directions of vibration and in which the angle between the vibration directions and ray path may not always be 90° (Lane, 2013). The index of refraction of such crystals varies according to the vibration direction of the light; the optical indicatrix is no longer a sphere but an ellipsoid (Weber,M.J, 2003). Unlike isotropic materials that have material properties identical in all directions, and the vibration direction of a light ray is always perpendicular to the ray path. Whereas amorphous materials such as glasses and plastics are isotropic, only those crystals with cubic symmetry are isotropic (Weber,M.J, 2003, Lane, 2013).

1-7Light matter interaction:-

When light travels through a medium, it can be scattered (elastically or in elastically), absorbed, or transmitted. The important interactions are absorption and scattering. Scattering means that a photon is absorbed and immediately emitted again, the absorbed energy equals the emitted energy and, as a result, it does not change the wavelength of the light and only the direction will be changed while the absorption of a photon results in the transition of an atom or molecule to a state of higher energy(Flammer et al., 2013). This interaction depends on physical, chemical, and structural properties of the matter, as well as intensity and energy of the photons. Depending on the energy of the photons, different excitations are generated in the matter. Photons on the UV and visible region of the spectrum, for example, are more likely to interact with the electrons of the outer shells, while infrared photons interact with lattice and molecular vibrations and rotations, creating phonons, see Fig 1-1(Soares, 2014). The basic process of the interaction of light with matter can be described more precisely by means of quantum theory: the electron of an atom, a molecule, or an atomic lattice can absorb a photon and use its energy to jump into an energetically higher state. Conversely, an electron can fall into a state of lower energy, with the energy difference being sent out as a photon. Actually, it is usually not just a single electron but, rather, the whole shell of an atom or molecule that experiences a change of state in these processes. (Flammer et al., 2013).

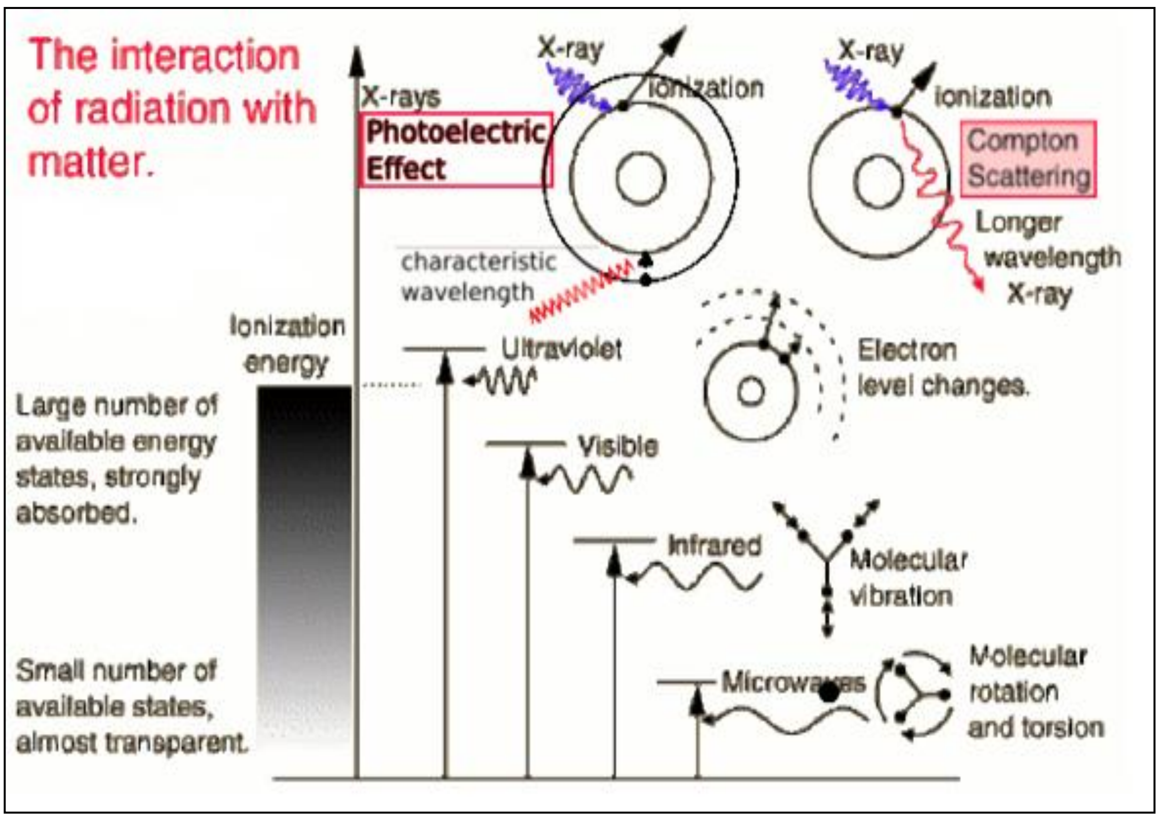


Figure (1-1):Interaction between light and matter(Abd Alraheim, 2015).

1-7-1 Absorption:-

The absorption of light is one of the most important techniques for optical measurements in solids and it is the property of the material of transferring energy from the photons to its atoms and molecules. The ratio of the energy transferred to the matter from the incident light to the total incident energy is called Absorptance (A).Absorption is described by the absorption coefficient (α) which is a measure of the rate of decrease in the light intensity as it passes through a given substance(Mollazade et al., 2012). In other words it gives the probability of absorption per unit length and its unit (m^{-1}) (Svensson, J. 2007).

1-7-1-1 Beer-Lambert Law:-

The Beer–Lambert law states that there is a logarithmic relation among the absorption coefficient, distance the light travels through the material (L), and light intensity before (I_o), and after (I) it passes through the material(Mollazade et al., 2012)**.**A beam of light passing through a matter of absorbing molecules transfers energy to the molecules as it proceeds, and thus decreases progressively in intensity. The decrease in the intensity or irradiance (I), over the course of a small volume element is proportional to the irradiance of the light entering the element, the concentration of absorbers (C), and the length of the path through the element (dx):

$$\frac{dI}{dx} = -\varepsilon_o C \quad (1.1)$$

The proportionality constant (ε_o) depends on the wavelength of the light and on the absorber's structure, orientation and environment. Integrating Eq.

(1.1) shows that if light with irradiance I_0 is incident on a cell of thickness t, the irradiance of the transmitted light will be:

$$I = I_o e^{(-\varepsilon_o \mathrm{Ct})} = I_o 10^{(-\varepsilon \mathrm{Ct})} = I_o 10^{-A} \quad (1.2)$$

Here A is the absorbance or optical density of the sample (A= εCt) and ε is called the molar extinction coefficient or molar absorption coefficient:

$$\varepsilon = \frac{\varepsilon_o}{ln(10)} = \frac{\varepsilon_o}{2.303} \quad (1.3)$$

The absorbance is a dimensionless quantity, so if C is given in units of molarity (1 M=1 mol/dm^3) and t in cm, ε must have dimensions of M^{-1} cm^{-1}. Eq (1.1) and (1.2) are statements of Beer's law, or more accurately, the Beer-Lambert law(Parson, 2007).

1-7-2 Reflection:-

Reflection occurs when a wave hits the interface between two dissimilar media, so that all of or at least part of the wave front returns into the medium from which it originated. Reflection of light may be specular or diffuse. The first occurs on a smooth surface. The second occurs on a rougher surface. Reflectance is the ratio of reflected power to incident power, in other words, reflectance (R)relates the intensity reflected (I_R)to the incident intensity (I_0), generally expressed in decibels or percent(Pedrotti and Pedrotti, 1993).

1-7-3 Dispersion:

The refractive index is related to the dielectric coefficient of the material and to the characteristic resonance frequencies of its dipoles. The dipoles of the material, therefore, interact more strongly with (and absorb more) optical frequencies that are closer to their resonance frequencies. Consequently, the refractive index $n(\omega_o)$ is optical frequency dependent. The dependency of the refractive index of the material on the optical frequency is termed material dispersion. The dispersion can be formally defined as $dn/d\lambda$, which is the slope of the curve of refractive index n, against wavelength λ. Although the dispersion of many materials is rather small, it is important to include it when calculating the optical properties of optical components. Silica, a key ingredient of optical fiber cable, has a refractive index that varies with optical frequency as it shows in figure (1-2). Therefore, dispersion plays a significant role in fiber optic communications(Tilley, 2004).

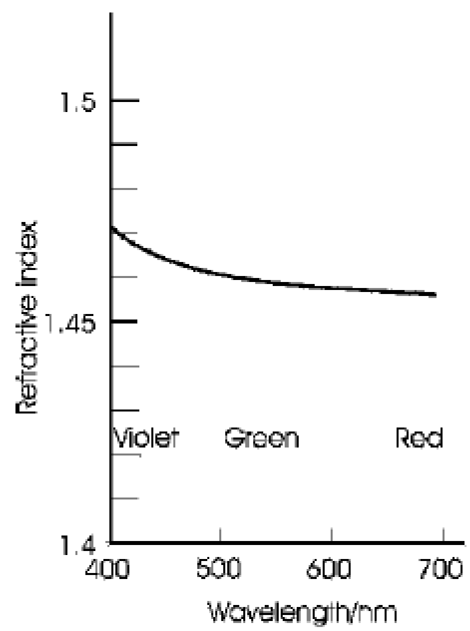


Figure (1-2): The dispersion of fused silica glass(Tilley, 2004).

1-7-4 Scattering:

Scattering is the redirection of light caused by the light's interaction with matter. The scattered electromagnetic radiation may have the same or longer wavelength (lower energy) as the incident radiation, and it may have a different polarization. The scattered light is generated by absorb the incident light and quickly reemit the light in a different direction. If the reemitted light has the same wavelength as the incident light, the process is called Rayleigh scattering(Vandergriff, 2008). If the reemitted light has a longer or shorter wavelength, the process is called Raman scattering or Brillouin scattering when acoustic modes are responsible for the scattering(Soares, 2014, Vandergriff, 2008).

1-8Refractive index and extinction coefficient:

The absorption and refraction of a medium can be described by a single quantity called the complex refractive index. This is usually given the symbol ń and is defined through the equation:

ń= n + i k. (1.4)

The real part of ń, namely n, is the same as the normal refractive index defined in Eq(1.4). The imaginary part of ń, namely k, is called the extinction coefficient.

As we will see below, k is directly related to the absorption coefficient aof the medium.

The relationship between α and k can be derived by considering the propagationof plane electromagnetic waves through a medium with a complex refractive index. If the wave is propagating in the z direction, the spatial and time dependence of the electric field is given by

E (z, t) = $E_0 e^{\mathrm{i}(ßz-\omega t)}$(1.5)

where ß is the wave vector of the light and ω is the angular frequency. $E_0$is the amplitude at z = 0. In a non-absorbing medium of refractive index n, the wavelength of the light is reduced by a factor n compared to the free space wavelength λ. ß and ω are therefore related to each other through:

$$ß = \frac{2\pi}{(\lambda/n)} = \frac{n\omega}{c} (1.6)$$

This can be generalized to the case of an absorbing medium by allowing the refractive index to be complex:

$$ß = ń\frac{\omega}{c} = (n + ik)\frac{\omega}{c} (1.7)$$

On substituting Eq (1.7) into Eq(1.5), we obtain:

$$E\ (z, t) = E_0 e^{i(ń\omega z/c - \omega t)}$$

$$E\ (z, t) = E_0 e^{-k\omega z/c} e^{i(n\omega z/c - \omega t)}\ (1.8)$$

This shows that a non-zero extinction coefficient leads to an exponential decay of the wave in the medium.

The optical intensity of a light wave is proportional to the square of the electric field, namely I ∝E E* (where E* is a conjugate of E). We can therefore deduce from Eq (1.8) that the intensity falls off exponentially in the medium with a decay constant equal to 2 x (kω/ c). On comparing this to Beer's law given in Eq (1.2)we conclude that:

$$\alpha = \frac{2k\omega}{c} = \frac{4\pi k}{\lambda} (1.9)$$

whereλ is the free space wavelength of the light. This shows us that k isdirectly proportional to the absorption coefficient(Fox, 2002).

1-9 Relationship between Transmittance, Reflectance, and Absorptance:

Radiant flux incident upon a surface or medium undergoes transmission, reflection, and absorption. Application of conservation of energy leads to the statement that the sum of the transmission, reflection, and absorption of the incident flux is equal to unity, or

$$\alpha + \rho + \tau = 1 \qquad (1.10)$$

In the absence of nonlinear effects (i.e., Raman Effect, etc.)(Abd Alraheim, 2015).

$$\alpha(\lambda) + \rho(\lambda) + \tau(\lambda) = 1 \qquad (1.11)$$

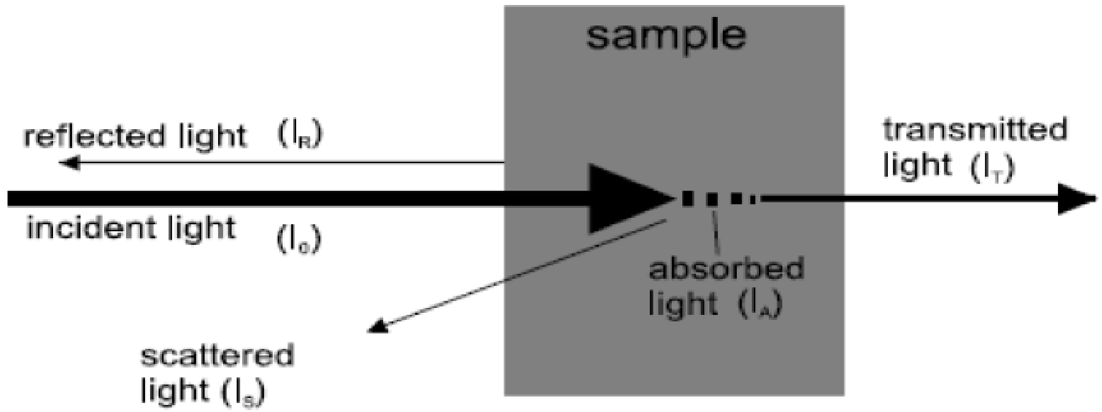
1-10Intensity measurement:-

An intensity measurement is obtained by converting the intensity into voltage through a shunt resistance. The voltmeters then measures the voltage to the resistance limits. The important parameter to consider in estimating the quality of the measurement is the voltage drops to the limits of the shunt resistance (Abd Alraheim, 2015).

When EM waves with intensity I_0 interact with matter of finite thickness, some fraction of intensity I_R is reflected, a fraction I_S is scattered, a fraction I_A is absorbed as the radiation passes through, and a fraction I_T is transmitted. This is shown in figure (1-2) and it should be obvious that(Northrop, 2005).

$$I_R + I_S + I_A + I_T = I_0 \quad (1.12)$$

The light intensities I_0 , I_T , I_R and I_s can easily be measured by placing a detector at the corresponding position. All the information about the sample goes into I_A, but this value cannot be measured directly. I_A can only be accessed by evaluating Eq(1.12)(Abd Alraheim, 2015).



Figure(1-3): Energy balance of incident light upon interaction with asample(Abd Alraheim, 2015).

1-11 Transmission measurement:-

Transmission spectroscopy is the most widely used measurement technique. It is simple and can be applied to characterize gases, liquids and solids. Quantitative evaluations are based on the Beer Lambert law as described above. Polished windows must not be touched or even scratched. Fingerprints in the light path cause light scattering, hence reducing the accuracy of the measurement. Normal incidence of the incoming light is required in order to minimize reflection(Abd Alraheim, 2015).

1-12 Composite materials:-

Composites are solids made up of more than one material at the macro scale to obtain a useful structural material, designed to have enhanced properties compared with the separate materials themselves.

Composites are widely used in nature. For example, wood is composed of strong flexible cellulose plus stiff lignin, and bone consists of strong soft collagen (a protein) plus apatite (a brittle hard ceramic).The two normal constituents of a composite material are the Fiber and the Matrix. Depending upon how they are bound together, different types of composite materials can be obtained. Composites are also widely used for advanced engineering applications, and from use in aircraft(Tilley, 2004).

Polymer-matrix composites are the most common due to the low cost of fabrication. Polymer-matrix composites are used for lightweight structures (aircraft, sporting goods, wheelchairs, etc.). In addition to vibration damping, electronic enclosures, asphalt (composite with pitch, a polymer, as the matrix), and solder replacement(Chung, 2001).

The recent application of composite PVA/$AgNO_3$ film could be used successfully and optimally in measurement of radiation dose in radiation therapy relative to TLD method as well as the absorbed dose simulation in 3D and dose chart, in addition to specific advantage such as chemical change assessment by Raman spectroscopy (Omer et al., 2015).

1-13 The applications of bulk materials:-

Electronic applications include electrical, optical, and magnetic applications, as the electrical, optical, and magnetic properties of materials are largely governed by electrons. There is overlap among these three areas of application.

Optical applications have to do with lasers, light sources, optical fibers (materials of low optical absorptivity for communication and sensing), absorbers, reflectors and transmitters of electromagnetic radiation of various wavelengths (for optical filters, low-observable or Stealth aircraft, radomes, transparencies, optical lenses, etc.), photography, photocopying, optical data storage, holography, and color control.

All classes of materials are used for electronic applications. Semiconductors are at the heart of electronic and optoelectronic devices. Metals are used for electrical interconnections, EMI shielding, cables, connectors, electrical contacts, and electrical power transmission. Polymers are used for dielectrics and cable jackets. Ceramics are used for capacitors, thermoelectric devices, piezoelectric devices, dielectrics, and optical fibers.

Electronic materials are in the following forms: bulk (single crystalline, polycrystalline, or, less commonly, amorphous), thick film (typically over 10 μm thick, obtained by applying a paste on a substrate by screen printing such that the paste contains the relevant material in particle form, together with a binder and a vehicle), or thin film (typically less than 1500 Å thick, obtained by vacuum evaporation, sputtering, chemical vapor deposition, molecular beam epitaxy, or other techniques). Semiconductors are typically in bulk single-crystalline form (cut into slices called “wafers,” each of which may be subdivided into “chips”), although bulk polycrystalline and amorphous forms are emerging for solar cells due to the importance of low cost. Conductor lines in microelectronics are mostly in thick-film and thin-film forms (Chung, 2001).

1-13-1 Optical components:-

1-13-1-1 Attenuators:-

Attenuators are used in a wide variety of applications and can satisfy almost any requirement where a reduction in power is needed. Attenuators are used to extent the dynamic range of devices such as power meters and amplifiers, reduce signal levels to detectors, and are used daily in lab applications to aid in product design. Also many medical applications, communications, tissue interactions needed to control the incident power via attenuator (Al-hai and Mirgani, 2005).

1-13-1-2 Optical filters:-

Optical filters are devices that selectively transmit light of different wavelengths, usually implemented as plane glass or plastic devices in the optical path which are either dyed in the bulk or have interference coatings. The optical properties of filters are completely described by their frequency response, which specifies how the magnitude and phase of each frequency component of an incoming signal is modified by the filter.

The optical filters can be classified into two broad categories as diffraction or interference filters. The important class of optical filters is tunable optical filters, which are able to dynamically change the operating frequency to the desired wavelength channel (Djordjevic et al., 2010).

Filters of different kinds are employed to select a certain spectral region. Relatively narrow spectral regions can be isolated using an interference filter. Such a filter for a wavelength λ is in its simplest form, Fabry-Perot interference with mirror separation of $\lambda/2$. Filters for the short wavelength region $\lambda<240$nm, are frequently made in this way with partially reflecting metal layer on each side of a $\lambda/2$ dielectric layer.

If narrow region of transmission typical for an interference filter is not required, simpler and much cheaper absorption filter can frequently be used. Absorption filters, in contrast to interference filters, can be used at any angle of incidence and can thus be used in strongly converging or diverging beams.

A filter is characterized by its transmittance (T), or optical density (D). D and T are related according to (Al-hai and Mirgani, 2005)

$$D = \log \frac{I}{T} \quad (1.)$$

Optical filters are commonly used in photography, in many optical instruments, In astronomy, and in fluorescence applications such as fluorescence microscopy and fluorescence spectroscopy.

1-13-1-3 Polarizes:-

Polarizer is an optical filter that lets light waves of a specific polarization pass and blocks light waves of other polarizations. It can convert a beam of light of undefined or mixed polarization into a beam of well-defined polarization that is polarized light.

Polarized light can be obtained or analyzed using certain prisms or polarizing films. Reflection at a non-normal angle of incidence at the flat surface of an optical material also results in a certain degree of polarization according to the Frensel formula (Al-hai and Mirgani, 2005).

1-14Literature review:-

Ghanipour and Dorranianin 2013 studied the effect of silver nanoparticles doped in PVA on the structural and optical properties of composite films. Structural properties are studied using X-ray diffraction and FTIR spectrum. Results showed that by doping silver nanoparticles in PVA number of Bragg's planes in the structure of polymer and its crystallinity are increased noticeably. Ag-O bonds are formed in the films and the band gap energy of samples are decreased.

Ahmad et al., in 2012 studied the electrical and optical properties of PVA/LiI polymer electrolyte films. At low frequency, the variation of dielectric constant and dielectric loss with frequency showed the presence of material electrode inter-face polarization processes. The exponent factor found was between 0.98 and 0.442 and obeys the universal power law. The absorption of pure and doped films was studied in the visible and ultra-violet wavelength regions. It was observed that the new absorption peaks at 290 and 375 nm are due to the formation of charge transfer complex. From direct allowed transition the optical energy gap decreases from 5.56 eV (for pure PVA) to 4.95 eV (for PVA+20%LiI).

Jabbar et al.,in 2010 studied the optical characterization of silver doped polyvinyl alcohol films using UV/VIS spectroscopy. It was found that these thin films have an indirect optical band gap (2.4-1.3) eV as the doping percentage increases. Extinction coefficient and refractive index increase as the doping percentage increases, while in general the optical dispersion parameters show an opposite behavior with doping.

Chiad et al., in 2012 studied the characterization of Silver/ Polyvinyl alcohol (Ag/PVA) films prepared by casting technique. Results showed that the optical conductivity increased with increasing dopant concentration up to 5wt% of the content. The increase in conductivity for dopant concentration is attributed to the formation of charge transfer complexes. Optical absorption studies in the wavelength range (300–900) nm showed peak in the wavelength region 430 nm for differently doped films, in addition to the peak for undoped PVA. The band edge values shifted to lower energies on doping up to a dopant concentration of 5wt%.

Mustafa, F. A in 2013 studied the optical characteristics of polyvinyl alcohol (PVA) doped with different concentrations of NaI nanocrystalline powders.

The optical properties of samples were investigated by measuring optical absorption spectra in the wavelength range from 190 to 850nm using UV-VIS spectroscopy. The results showed that Eg_{opt} of films decreases with increasing NaI contents. The absorbance, absorption coefficient, extinction coefficient, finesse coefficient, refraction index and reflectance of PVA doped with NaI increased with increasing the doping percentages except the transmittance. The real and imaginary parts of the dielectric constant and optical conductivity increased with the increase in sodium iodine concentration.

Guyotand Voué in 2015 studied the Optical properties of Ag-doped polyvinyl alcohol nanocomposites which made of polymer films embedding silver nanoparticles were prepared by thermal annealing of polyvinyl alcohol films containing $AgNO_3$. Low (2.5 % w:w) and high (25 % w:w) doping concentration of silver nitrate were considered as well as their effect on the optical properties of thin (30 nm) and thick (300 nm and more) films. The topography and the optical properties (refractive index n and extinction coefficient k) of such films were studied by atomic force microscopy and spectroscopic ellipsometry. For a given doping level, the parameters of the surface plasmon-polariton resonance (amplitude, position and width) were shown to be thickness-dependent. Multivariate statistical analysis techniques (principal component analysis and support vector machines) were used to explain the differences in the optical behavior of the thick and thin films.

Abdul Nabi et al., in 2014 studied the optical properties of pure and doped polyvinyl chloride (PVC) films, prepared by using casting technique, with different nanosize zinc oxide (ZnO) concentrations (1–20) wt% have been studied. The optical properties were studied by using the absorbance and transmittance measurement from computerized UV-visible spectrophotometer in the spectral range 200–800 nm. This study reveals that the optical properties of PVC are affected by the doping of ZnO where the absorption increases and transmission decreases as ZnO concentration increases. The extinction coefficient, refractive index, real and imaginary parts, infinitely high frequency dielectric constant and average refractive index values were found to increase with increasing impurity percentage.

CHAPTER TWO

THE EXPERIMENTAL PART

2-1 Introduction:-

This chapter presents the experimental setup and the function of each component in addition to study the fabricated samples that were used in this work and finally the experimental procedure. The experimental work was done in the following steps:

2-2 The experimental setup:-

A sketch diagram of the experimental setup is shown in figure (2-1). It is composed of the followings:

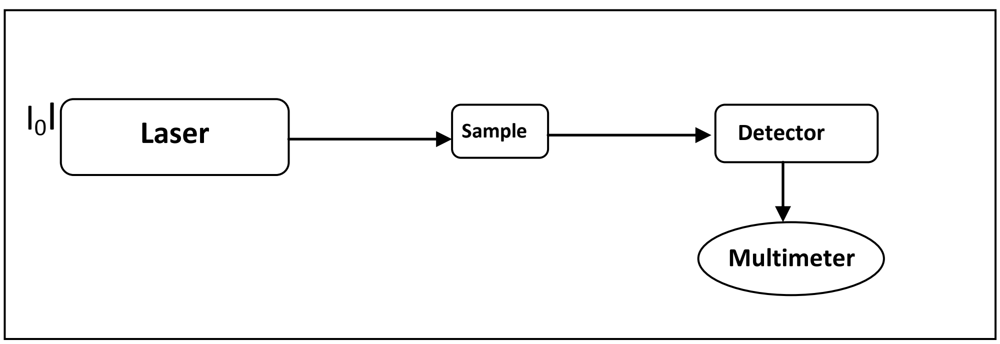


Figure (2-1):A sketch diagram of the experimental setup

2-2-1 The Lasers and light sources:-

Different lasers and monochromatic light sources were used to determine the optical properties of the samples

2-2-1-1Helium – Neon (He-Ne) laser:-

The He-Ne laser is certainly the most important of the noble gas lasers. Laser action is obtained from transitions of the neon atom, while helium is added to the gas mixture to greatly facilitate the pumping process .The laser oscillates on many wavelengths; by far the most popular is λ= 632.8 nm (red). Other wavelengths include green (543 nm) and infrared, at λ = 1.15μm (Svelto and Hanna, 1998).

Laser transitions are 5s→ 3p result in generation of laser radiation of a wavelength of 632.8 nm. The helium–neon laser is a three-level laser type(Bertolotti, 2015).

The He-Ne laser used in this work was supplied from PHYWE SYSTEM GmbH Company, Germany. Its specifications are listed in table (2-1)

Table 2-1: He-Ne laser basic specifications

Wavelength	632.8 nm
Power	1 mW
Type	CW
Beam diameter	0.5- 1.7 m rad
Divergence & Efficiency	< 0.1%
Classification	Class I

2-2-1-2Diode lasers (omega laser XP):-

Omega laser used in this work is Class 3B Gallium Aluminium Arsenide Lasers, known as GaAlAs manufactured by Omega Company-England. Omega Laser system includes a choice of control unit plus a range of interchangeable probes like 675nm, 820nm, and 915nm. Each probe is produced to emit laser light at a specific wavelength. Its specifications are listed in table 2-2.

Table 2-2: Omega laser XP basic specifications

Specifications of the visible red (675 nm) probe:	
Wavelength	675 nm
Power	30 mW
Power Density	0.24 W/cm^2
Classification	Class III-B
Specifications of the infrared probe 820 nm:	
Wavelength	820 nm
Power	200 mW
Power Density	1.60 W/cm^2
Classification	Class III-B
Specifications of the infrared probe 915 nm:	
Wavelength	915 nm
Power	200 mW
Power Density	1.60 W/cm^2
Classification	Class III-B

2-2-1-3 Green diode laser (532nm):-

Diode lasers represent one of the most important class of lasers in use today, not only because of the large variety of direct applications in which they are involved, but also because they have found a widespread use as pumps for solid-state lasers.

The area of semiconductor lasers is a rapidly evolving field that can be classified into high-power diode lasers, external cavity lasers, and miniature lasers. Semiconductor lasers work via direct electrical excitation, are compact, offer wavelength tunability, and can be very stable (Duarte,F.J.,2015)

Green Diode laser is used in pumping solid state laser, because of its compact size, long lifetime, low cost, and easy operatability, in addition it was widely used in scientific experiments, measurements, optical sensors, communication, spectrum analysis, medical treatment, etc. The green diode laser used in this work was supplied from Roithner lasertechnik,Austria company. Table 2-4 lists the specifications of this laser.

Table 2-4: Green diode laser basic specifications

Wavelength	532 nm
Output power	1000 m W
Beam size type $1/e^2$	1.2 mm
Beam circularity	≤ 1.3:1
Beam divergence	≤ 2.0 m rad
Mode	TEM_{00}
Operating voltage	4-6 V DC
Operating Current (25 ^oC)	< 300 mA

2-2-1-4 Red diode laser (671nm):-

Red diode laser is a solid state single longitudinal mode. It has been widely used in DNA sequencing, flow cytometry, cell sorting, optical instrument, spectrum analysis, interference, measurement, holography, laser printing, chip inspection, physics experiment, etc. The red diode laser used in this work was manufactured by Riothner lasertechnik company, Austria. The specifications are listed in table 2-5 below

Table 2-5: Basic specifications of red diode laser

Wavelength	671nm
Output Power	100 mW
Transverse Mode	TEM00
Operating Mode	CW
Operating Temperature (°C)	15~35

2-2-1-5 Monochromatic UV light (365nm):-

The monochromatic UV LED emitter provides superior radiometric power in the wavelength 365 nm with a high efficacy and surface mount ceramic package with integrated glass lens. The UV light has wide use in applications like curing, sterilization, currency verification, and various medical applications. The monochromatic UV light used in this work was supplied from Riothner lasertechnik company, Austria. The specifications are listed below in table 2-6.

Table2-6: The specifications of monochromatic UV light

Wavelength	365 nm
Output Power	1000 m W
Operating Temperature (°C)	25 °C

2-3 The samples:-

In this work, the powder of PVA and KCl was used to fabricate consistent diskswith different thicknesses using micrometer to determine the thickness, and then these disks were doped with silver nitrate.

2-3-1 PVA:

Polyvinyl alcohol (PVA) has the idealized formula [$CH_2CH(OH)$]n , which is an artificial polymer essentially made from polyvinyl acetate through hydrolysis as in figure (2-2). It has been applied in the industrial, commercial, medical, and food sectors and has been used to produce many end products, such as lacquers, resins, surgical threads, and food packaging materials that are often in contact with food(Gaaz et al., 2015).

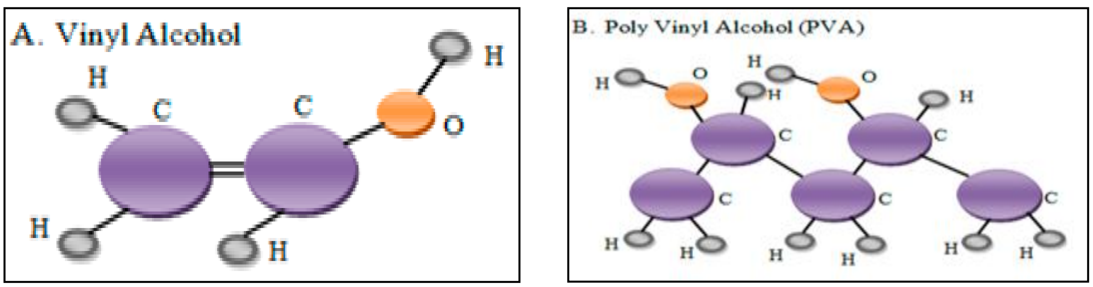


Figure (2-2): (a) The structure of vinyl alcohol;
(b) PVA is synthesized by the hydrolysis of polyvinyl acetate(Gaaz et al., 2015).

2-3-1-1 Structure and properties of PVA:

The basic properties of PVA are dependent on the degree of polymerization or on the degree of hydrolysis, specifically whether it is full or partial as in figure (2-4), which in turn dictates its categorization into two groups, namely, (a) partially hydrolyzed and (b) fully hydrolyzed

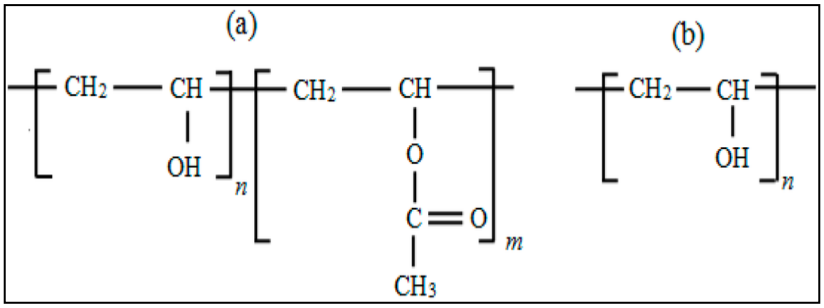


Figure (2-3):Structural formula for PVA: (a) partially hydrolyzed; (b) Fully hydrolyzed(Hassan and Peppas, 2000).

The molecular weight distribution is an important characteristic of PVA because it affects many of its properties including crystallizability, adhesion, mechanical strength, and diffusivity(Hassan and Peppas, 2000). And also the molecular weights obtained for PVA products may vary (20,000–400,000), depending on the length of the initial vinyl acetate polymer, the level of hydrolysis to eliminate the acetate groups and whether it occurs under alkaline or acidic conditions.(Gaaz et al., 2015)

The chemical and physical properties of PVA may vary based on the percentage of hydrolysis, which determines the PVA grade and its molecular weight. PVA itself has substantial tensile strength, more flexibility, and hardness characteristics. PVA is a water-soluble polymer. The physical properties of PVA, including film form, are highly affected by the degree of hydrolysis, molecular weight, and its crystal precipitation(Gaaz et al., 2015).

2-3-2 Silver Nitrate:-

Silver nitrate is an inorganic compound with chemical formula $AgNO_3$ shown in Figure (2-4). This silver nitrate is sensitive to light ingredient in photographic film and is a corrosive compound. Silver nitrate is used in many ways in organic synthesis, e.g. for deprotection and oxidations. Silver nitrate had been used in this work as addition material to PVA which can cause a remarkable change in their properties. The silver nitrate has a molecular weight of 169.87, boiling point 444 ^{o}C, melting point 212 ^{o}C. It crystallized in rhombic structure, decomposed by heat to give Ag^{+}, NO_2 and O_2(Suliman, 2015).

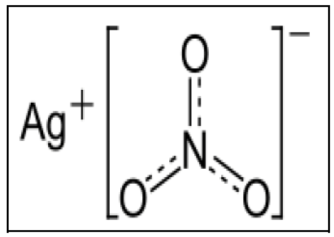


Figure (2-4): The chemical structure of the silver nitrate compound(Suliman, 2015)**.**

2-4The photodetector:-

The photodetector converts the optical signal into an electrical signal in order to be processed and displayed (Ionita,I., 2015). In other words, a photodetector is a device that measures optical power by absorbing energy from an optical beam. All photodetectors are square-law detectors that respond to the intensity, rather than the field amplitude, of an optical signal. Commonly used photodetectors are based on either thermal effects or electric effects (Degiorgio,V.and Cristiani,I.,2014).

PIN photodiode was used in this work which is a semiconductor device that consists of an intrinsic (lightly doped) region that is sandwiched between a p-type and an n-type layer. When this device is reverse-biased, it exhibits an almost infinite internal impedance (I.e., like an open circuit), with an output current that is proportional to the input optical power.

2-5 Multimeter:-

The Fluke 83III used in this work was manufactured by Industrial Electrician Combo Kit. Fluke 83III has a unique function for accurate voltage and frequency measurements on adjustable speed motor drives and other electrically noisy equipment. it is widely used in our life for Multi-use with AC/DC voltage and resistance measurement(farnell.com).

2-6 Arrangement of the setup:-

The setup was arranged as shown in figure (2-5) where the samples were placed between the monochromatic light source and the detector in order to be exposed to the light from the source, while detector was connected to the multimeter. The second setup was arranged as shown in figure (2-6) where the monochromatic light source and the detector were located at angle of 45^0 with the samples, the detector connected to the multimeter

Figure (2-5): photo of setup arrangement

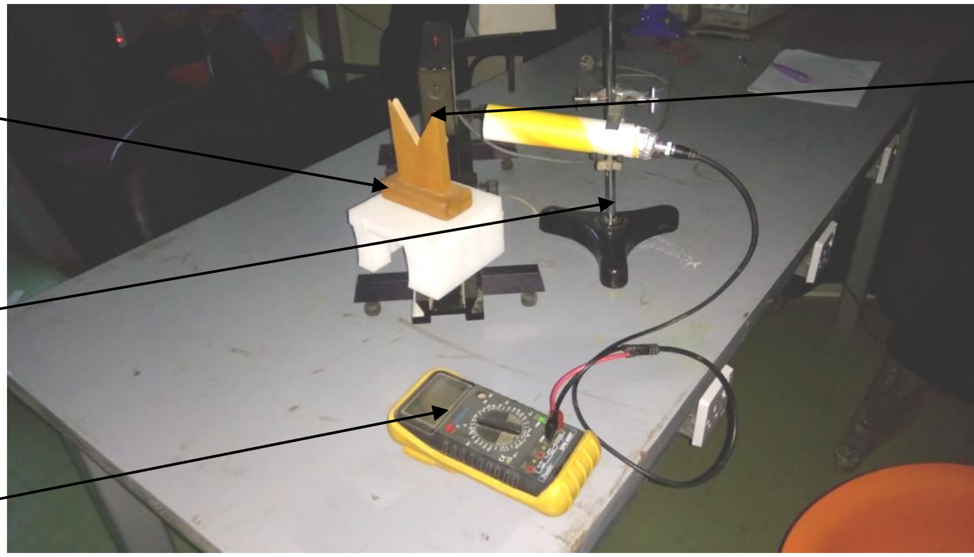


Figure (2-6): photo of the second setup arrangement

2-7 The experimental procedure:-

The experimental procedure was done as follows:-

1- Disks with different thickness of pure PVA were fabricated adding KCl In order to make consistent disks using compressor. The thickness of the produced disks was measured using micrometer.

2- Then, The experimental setup was arranged as shown in figure (2-5) where the light sources (He-Ne laser, different Diode lasers, and UV LED) were used, separately.

3- The intensity of each light source was measured without sample (I_o), and with sample (I).

4- The absorption coefficient of the samples for each wavelength was deduced by applying the Beer Lambert's law for each disk, using the following relations.

$$\alpha = \frac{2.303\ \log I/I_0}{t} \qquad (2.1)$$

$$T = \frac{I}{I_0} \qquad (2.2)$$

where α the absorption coefficient, t the thickness of the sample, and T the transmission.

5- Then, silver nitrate, with different ratios, was used to dope the PVA with the same thickness previously determined.

6- The above steps were repeated for the doped disks.

7- The absorption coefficients were calculated after measuring (I_o) and (I) for the doped materials.

8- The second setup was arranged as shown in figure (2-6) where the same monochromatic light sources were used, the intensity of each light source was measured without sample (I_0), and the reflected intensities (I_R) were measured in the presence of the samples.

9- Then, the refractive index was calculated for each sample using the following relations:

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \qquad (2.3)$$

$$R = \frac{I_R}{I_0} \qquad (2.4)$$

$$k = \frac{\alpha\lambda}{4\pi} \qquad (2.5)$$

where n the refractive index, R the reflectance, and k the extinction coefficient.

10- The above steps were repeated for the doped disks. And the refractive index was calculated after measuring (I_0) and (I_R).

CHAPTER THREE

RESULTS AND DISCUSSION

3-1 Introduction:

This chapter presents the results and discussion of the obtained data. These results represented the optical properties ofthe pure and doped PVA.

The conclusions and recommendations will be given at the end of this chapter.

3-2 The Results:

The results are classified as follows.

3-2-1The optical properties of the pure PVA:-

The transmission intensity as a function of wavelength was plotted for each disk thickness of the samples and then the absorption coefficients were calculated using Eq(2.1). The transmission spectrum is shown in figure (3-1)and the calculated values of the absorption coefficients are given in table 3-1, these values are plotted as a function of wavelength in figure (3-2).

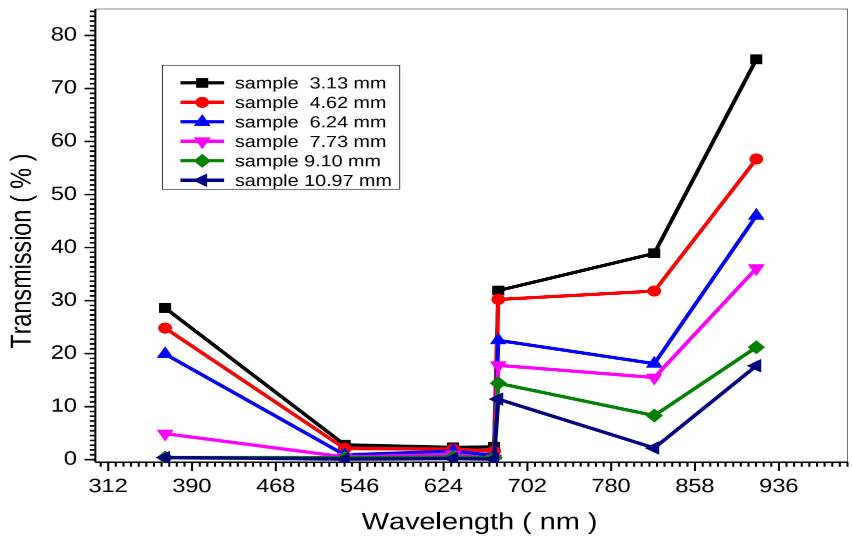


Figure (3-1):the transmission spectrum of pure PVA with different thicknesses.

Table 3-1: The calculated absorption coefficients of the pure PVA disks in different wavelengths.

λ (nm)	3.13mm	4.61mm	6.24mm	7.73mm	9.10mm	10.97mm
	α (cm^{-1})	α (cm^{-1})	α (cm^{-1})	α (cm^{-1})	α (cm^{-1})	α (cm^{-1})
365	3.99	3.0	2.6	3.9	6.0	5.0
532	11.37	8.3	7.4	6.7	6.1	5.9
632.8	11.98	8.4	6.7	5.9	5.8	5.4
671	11.96	8.9	7.6	7.5	5.9	5.9
675	3.64	2.6	2.4	2.2	2.1	2.0
820	3.03	2.5	2.7	2.4	2.7	3.4
915	.89	1.2	1.2	1.3	1.7	1.5

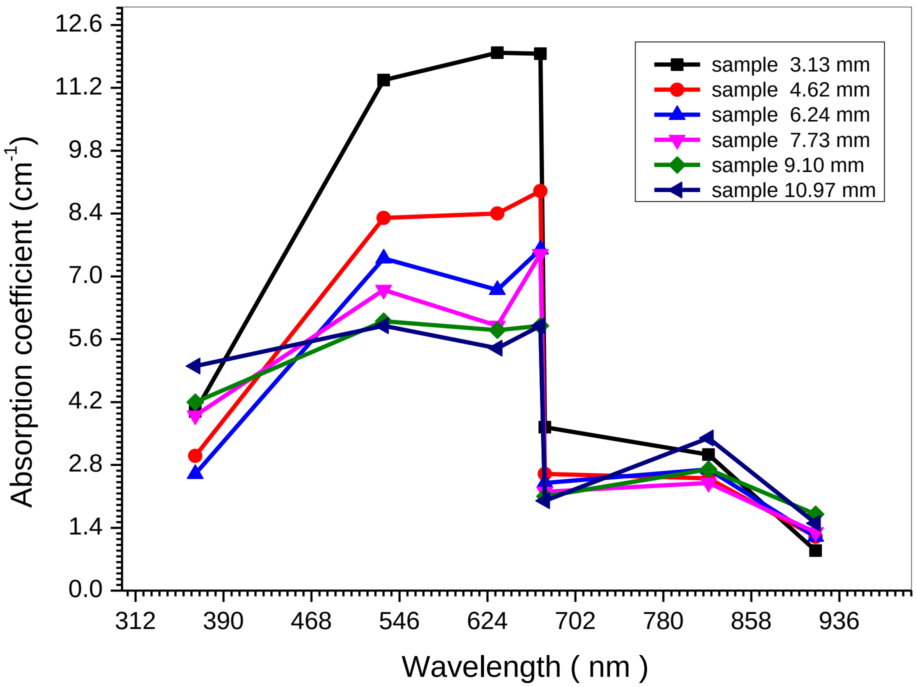


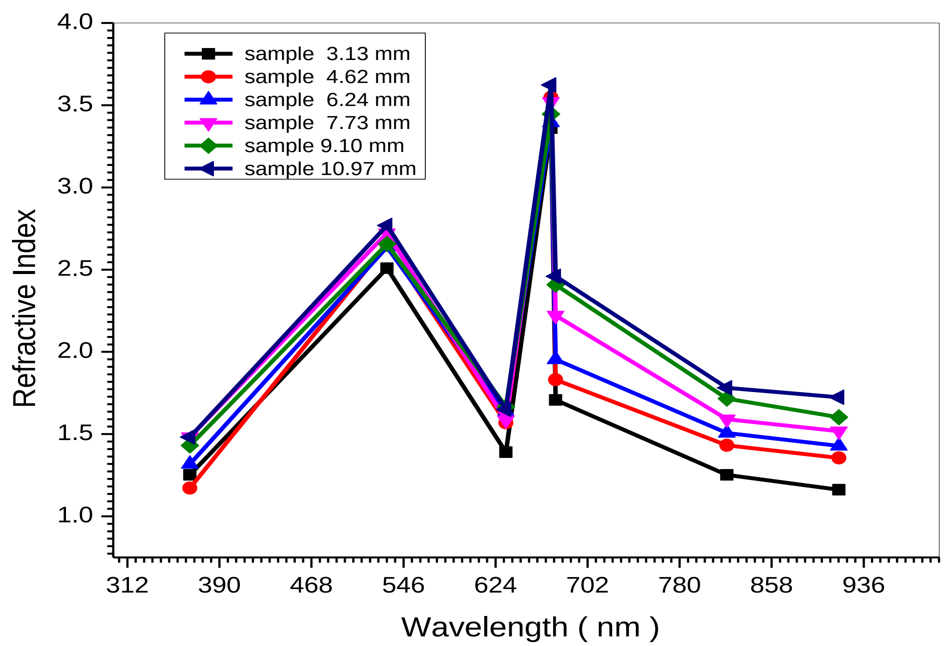
Figure (3-2): the absorption coefficient versus wavelength for pure PVA disks with different thickness.

From figure (3-1) it is clear that the pure PVA has a high transmission at wavelength 915 nm compared with other wavelengths. It is a good indicator to use this disk as an optical filter in this region. And the transmission decreased with increased the thickness. From figure (3-2) it is clear that the increment of the thickness decrease the absorption coefficient, which has high absorption coefficient at wavelength 671nm and that is a good indicator to use this material as an optical attenuator at this wavelength.

The refractive indices for the pure PVA were calculated using Eq(2.3) after measuring the reflected intensities of the samples, then calculating the extinction coefficient and the reflectance using Eq(2.4) and (2.5), respectively. The refractive index values are listed in table (3-2). These results are plotted as a function of wavelength in figure (3-3)

Table 3-2: the calculated refractive index for each wavelength for pure PVA with different thicknesses.

λ (nm)	3.13mm	4.61mm	6.24mm	7.73mm	9.10mm	10.97mm
	n	n	n	n	n	n
365	1.25	1.17	1.31	1.48	1.43	1.48
532	2.50	2.65	2.63	2.72	2.65	2.76
632.8	1.39	1.56	1.63	1.58	1.66	1.65
671	3.36	3.54	3.39	3.52	3.44	3.62
675	1.70	1.83	1.95	2.22	2.40	2.45
820	1.25	1.43	1.50	1.59	1.71	1.78
915	1.16	1.35	1.42	1.51	1.60	1.72



Figure(3-3): the calculated refractive index versus wavelength for pure PVA disks.

It is clear that the pure PVA has high refractive index at wavelength 671nm, and the increment of the thickness increase the refractive index.

3-2-2The optical properties of doped PVA:-

The fabricated samples of PVA were doped with different ratios of silver nitrate. The transmission spectrum of the new disks with different doping ratio of silver nitrate were plotted as a function of wavelength in figure (3-4) and the absorption coefficients were calculated using Eq(2.1). The absorption coefficients are listed in table 3-3, and plotted as a function of wavelength in figure (3-5).

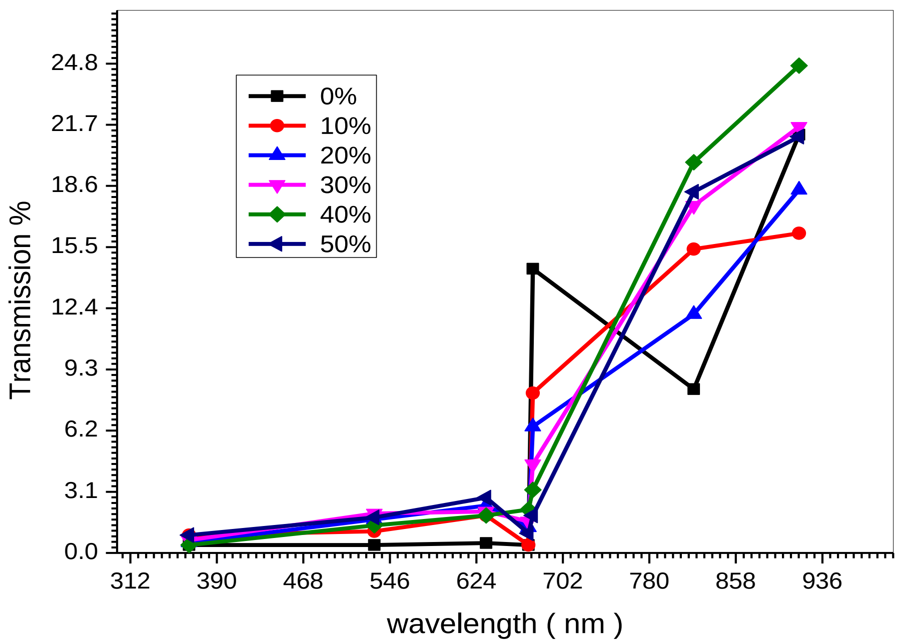


Figure (3-5):The transmission spectra of the doped PVA.

Table 3-3: The calculated absorption coefficients for the doped samples.

λ (nm)	0%	10%	20%	30%	40%	50%
	α (cm^{-1})	α (cm^{-1})	α (cm^{-1})	α (cm^{-1})	α (cm^{-1})	α (cm^{-1})
365	6.02	5.0	3.2	3.0	5.9	5.1
532	6.1	4.8	4.5	4.3	4.7	4.4
632.8	5.87	4.3	4.1	4.2	4.3	3.9
671	5.99	4.9	4.8	4.6	4.2	5.0
675	2.12	2.8	2.2	3.4	3.8	4.3
820	2.73	2.3	2.1	1.9	1.8	1.9
915	1.70	1.9	1.7	1.7	1.5	1.7

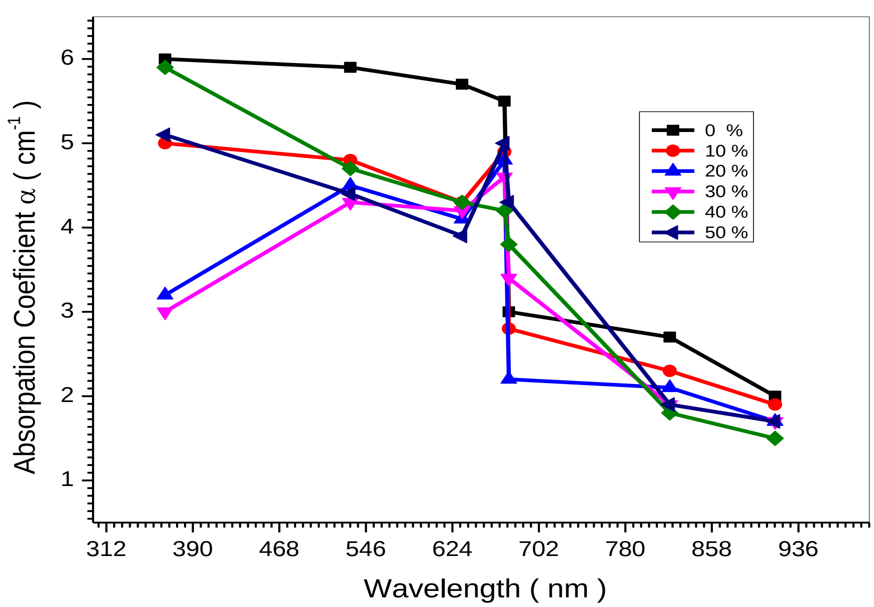


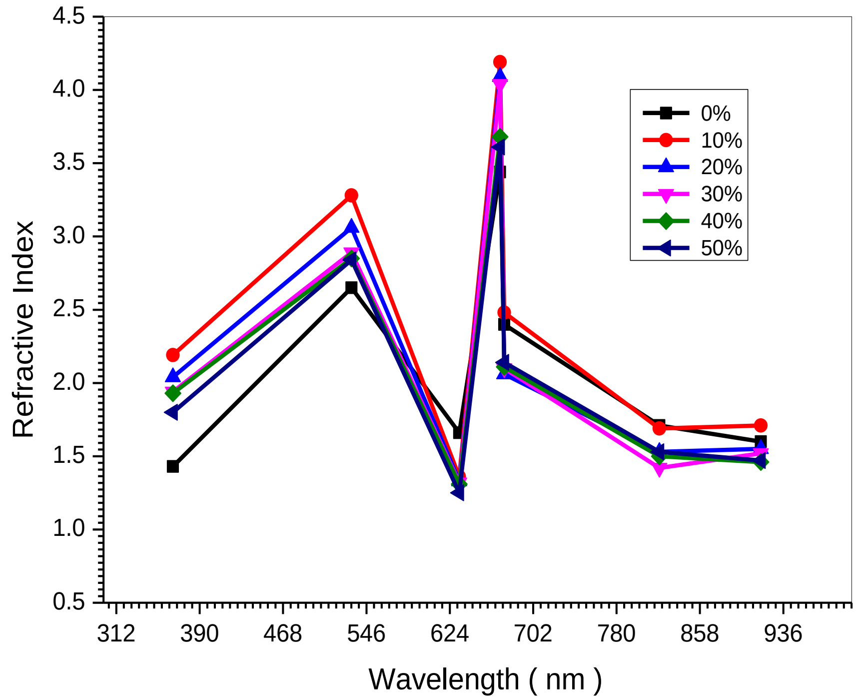
Figure (3-5): the calculated absorption coefficients versus wavelength for doped PVA with different ratios.

From Figure (3-4), it is clear that the transmission spectra of doped PVA samples increased with increasing wavelength. The increment of the concentration of $AgNO_3$lead to increases the localized state density which reduces the transmission values, and it’s noticed at wavelength 675nm. It can be seen from figure (3-5) that there is decrement in the absorption coefficients of doped PVA with increasing wavelength. Increasing the ratio of $AgNO_3$ decreased the absorption coefficient in the applied wavelength range.

The refractive indices for the doped PVA were calculated using Eq(2.3) after measuring the reflected intensities of the samples, then calculating the extinction coefficient and the reflectance using Eq(2.4) and (2.5), respectively. The refractive index values are listed in table 3-4. These results are plotted as a function of wavelength in figure (3-6)

Table 3-4:The calculated refractive index for each wavelength for doped PVA.

λ (nm)	0%	10%	20%	30%	40%	50%
	n	n	n	n	n	n
365	1.43	2.19	2.04	1.94	1.93	1.80
532	2.65	3.28	3.06	2.89	2.85	2.84
632.8	1.66	1.36	1.33	1.32	1.31	1.25
671	3.44	4.19	4.09	4.04	3.68	3.61
675	2.40	2.48	2.06	2.10	2.11	2.14
820	1.71	1.69	1.53	1.42	1.50	1.53
915	1.60	1.71	1.55	1.52	1.46	1.47



Figure(3-6): the calculated refractive index versus wavelength for doped PVA.

From figure (3-6) it is clear that the refractive index decreased with increasing the mass ratio of $AgNO_3$.

3-3 Conclusions:-

From the obtained results one can conclude that:

1- The pure PVA can be used as a filter at wavelength 915nm or as attenuator at wavelength of671nm.

2- Silver nitrates $AgNO_3$ can effectively doped PVA and change its optical properties. The presence of $AgNO_3$ leads to decrease in the absorption coefficient, increase in the transmission, and decrease in the refractive index.

3-4 Recommendations:

It is recommended to:

1- Use of other laser sources as assistance and different way of fabrication samples such as fabrication of thin film.

2- Investigate the ability of adding halides to the PVA to make remarkable change in their properties.

3- Investigate the ability of using PVA instead of any polymer to fabricate optical fiber such as PMMA.

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