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تصنيع وخصائص مزيج بوليمري PVA-PEG : تأثير معدل الوزن الجزيئي للبوليمر

بحث مقدم الى

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Fabrication and Characterization of PVA-PEG Polymeric Blend: Impact of Polymer Average Molecular Weight

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

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بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ

قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَا إِنَّكَ أَنتَ الْعَلِيمُ الْحَكِيمُ

صدق الله العظيم

(سورة البقرة: آية ٣٢)

Supervisor Certification

I certify that the preparation of this thesis, entitled **" *Fabrication and Characterization of PVA-PEG Polymeric Blend: Impact of Polymer Average Molecular Weight* ".** was made under my supervision by ***Hussam Raad Hamed*** at physics department the college of education for pure sciences university of Babylon in partial fulfillment of the requirements .

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Dedication

To Mesopotamia (Iraq) with honour and dignity…

To those, Who lost their lives in a war without committing any crime… To the heroes of ***Al Hashd Al Shaabi*** *and the* ***Security Forces***

To my first and dearest teacher my father…

To my mother whose love is planted in my heart…

To my brothers and sisters…

To my wife and kids

To my close friends

To my teachers

Who provide me the keys of success

Hussam✍

Acknowledgment

Praise be to Allah , the first before creation and the last after the annihilation of things, the All-Knowing, Who does not forget those who remember him, does not diminish from his thanks, does not disappoint those who call upon him, and does not cut off from his hope.

I would like to thank my supervisor, Professor **Dr. Fouad Shakir Hashim** . The least that I can offer is a thankful attitude that is unable to fulfill the meaning of this word for suggesting the topic of research and for the commendable efforts he provided me with valuable guidance and sound opinions throughout the research period, which paved the way for me to achieve it. He has my sincere appreciation and respect.

I also extend my heartfelt thanks to all my distinguished professors from the Physics Department and all dear colleagues for their support throughout the study period.

Hussam✍

Summary

The effect of adding average molecular weights of polyethylene glycol (PEG_S 4,8 and 20 K)on the morphology and optical properties of PVA considered as a main purpose of this study. The optical microscope (OM) images denote a network of paths charge transfer within the basics polymer (PVA) is formed when increasing the molecular weight of additive PEG up to 20k. The analysis of Fourier transformation infrared (FTIR) spectra confirms the presence of functional groups belonging to the polymer systems. Above 400 nm, the transmittance curves of all samples show a tendency towards saturation, and the highest rated average transmittance of the pure PVA film was ~ 95% in the Vis and NIR areas of spectrum, but it decreases almost gradually with the rising in the molecular weight of the additives, reaching ~ 55 at PEG_{20k}, which may be makes it convenient for UV shielding application. One of the most significant outcomes of this research is the reduction in the energy gap for indirect transition (allowed, and forbidden) with the rising the molecular weight of the additive PEG. All the other parameters under investigation were also influenced by the change in molecular weight.

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List of symbols

Symbol	Physical Meanings	Unites
A	Absorbance	%
T	Transmittance	%
α	Absorption Coefficient	cm^{-1}
n	Refractive Index	-
k_o	Extinction Coefficient	-
P	Polarization	-
I_o	the intensity of incident rays	Lux
I_T	The intensity of transmitted rays	Lux
T_g	Glass Transition Temperature	^oC
T_m	Melting Temperature	^oC
r	Exponential Constant	-
H	Planck Constant	J.s
E_{ph}	Energy of Phonon	eV
E	Energy	eV
c	Velocity of Light	m/s
R	Reflectance	%
T	Thickness of the film	µm
N	Complex refractive index	-
ε	Complex dielectric constant	-

List of Abbreviations

Abbreviations	Physical Meanings
RT	Room temperature
IR	Infrared
MW	Molecular weights
FTIR	Fourier transform infrared spectroscopy
OM	Optical microscope
PVA	poly(vinyl alcohol)
PEG	poly(ethylene glycol)

CHAPTER ONE

Introduction and Literature Review

1.1 Introduction

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

The polymers are classified into three categories: natural, industrial, and modified. Proteins, cellulose, starches, and rubber are examples of natural polymers; industrial polymers include poly (vinyl chloride), polyvinyl alcohol, nylons polyethylene, polypropylene, polyesters polycarbonate, Polyethylene glycol,…etc [2] .

polyvinyl alcohol (PVA) is classified as a basic polymer. It has a hydroxyl group that, through hydrogen bonding, can aid in the formation of an interpenetrating link in a polymer composite [3]. PVA a common type of thermoplastic polymer having the chemical formula $(C_2H_4O)_n$, is a semi-crystalline polymer[4]. PVA has some special qualities, like being environmentally friendly, non-toxic, water soluble, providing excellent optical characteristics, being chemically stable, getting excellent dielectric strength, and being able to store charges. Due to its outstanding thermo-stability, solubility in water, in height mechanical asset, chemical resistance, in height insulator asset, and superior film-forming capacity via solution casting, it makes a desirable hosting material for inorganic additions [5]. The thermoplastic polymer type poly (ethylene glycol) (PEG) has a flexible bond structure which this chemical formula $H-(O-CH_2-CH_2)_n-OH$. Additionally, PEG is acknowledged to be have mobility, is soluble in water, and is utilized as a binder in the creation of ceramic materials due to its well-known features, including its flexibility and lack of toxicity[6]. Polyethylene glycol (PEG) is an essential polymer with significant applications and can exhibit various Mw; PEG with a high Mw is called poly (ethylene oxide) (PEO)[7] . PEG and poly(vinyl alcohol) (PVA) have substantial properties, such as high solubility, low toxicity, biocompatibility and rapid biodegradability in water[8]; and they contain important functional groups, such as one hydroxyl and carbonyl per unit of the chemical chain[9]. These functional groups improve the material's compatibility with many other polymers, fillers and nanofillers to manipulate or enhance the characteristics of materials and make them attractive to scientists, engineers and researchers [10]. The above polymers have been experimentally and theoretically investigated for numerous applications, such as in photovoltaic cells and devices, optics, optoelectronics and electronics [11]. However, their distinctive properties are related to their internal components, which differ from the polymer net [12]. Despite all the characteristics of pure and mixed polymers, they suffer from weakness in most of their optical properties due to structural defects [13].

1.2 Polymer Blends

Polymer blends are defined as physical mixtures of two or more polymers that are different in structure interacting via secondary forces. Two or more existing polymers can be blended for different reasons and for a specific purpose. One of the reasons is to achieve a material that has a combination of component properties, for example a mixture of two polymers, one chemically resistant and the other hard. Another reason is cost savings by blending a high-performance polymer with a cheaper material, when any two materials are mixed together, or blended, the properties of the resulting mixture depend on the level at which intimate mixing takes place and on whether any chemical reactions between the components of the mixture take place [14]. For a homogeneous miscible blend, the Gibbs free energy of mixing requires a negative value. For high molecular weight polymer blends, the gain in entropy is negligible. Hence, the free energy of mixing can only be negative if the heat of mixing is negative. This means that the mixing must be exothermic, which usually requires specific interactions between the blend components. These interactions may range from strongly ionic to weak and non-bonding, including hydrogen bonding, ion-dipole, dipole-dipole, and donor-acceptor interactions. Based on the miscibility, three types of blends can be distinguished: (i) completely miscible blends, (ii) partially miscible blends (iii), and fully immiscible blends. Completely miscible blends consist of one homogeneous phase. This type of blend exhibits only one glass transition temperature (T_g), which is between the T_g of both blend components with a close relation to the blend composition. Partially miscible blends, in which a part of one blend component is dissolved in the other, exhibits normally good compatibility and fine phase morphologies. However, fully immiscible blends exhibit a coarse phase morphology having a sharp interface and a poor adhesion between both blend phases. This is the reason for often observed poor properties of immiscible blends, which strongly depend on the size and distribution of the phases[15].

1.3 Materials Used in the Study

1.3.1 Polyvinyl alcohol (PVA)

Poly-vinyl alcohol (PVA) is synthetic polymer employed since the early 1930s in a wide range of industrial, commercial, medical and food applications including resins, surgical threads, lacquers and food-contact applications [16]. Poly (vinyl alcohol) is a synthetic polymer that comes in the form of a granular powder that is odorless, transparent, tasteless, white, or cream-colored [17]. Polycarbonate (vinyl alcohol), which may be combined in water, has the benefit of being resistant to solvents and oils, as well as having outstanding characteristics [18]. PVA fiber has high tensile and compressive strengths, tensile modulus, and abrasion resistance due to its highest crystalline lattice modulus. Many researchers have looked at using PVA as a filler or in cross-linked products, additionally, it has been widely employed as a thermoplastic polymer to make nontoxic, harmless, and living tissues, among other things[19]. It has been used in a wide range of applications and is also widely used in semiconductor applications [20]. Figure (1.1) and (1.2) show the chemical structure of PVA and Fourier transform infrared spectroscopy (FT-IR) of pure PVA respectively, is a synthetic polymer that comes in the form of a granular powder that is odorless transparent, tasteless, white colored and amorphous [20]. Table (1.1) explain the physical properties of PVA [21].

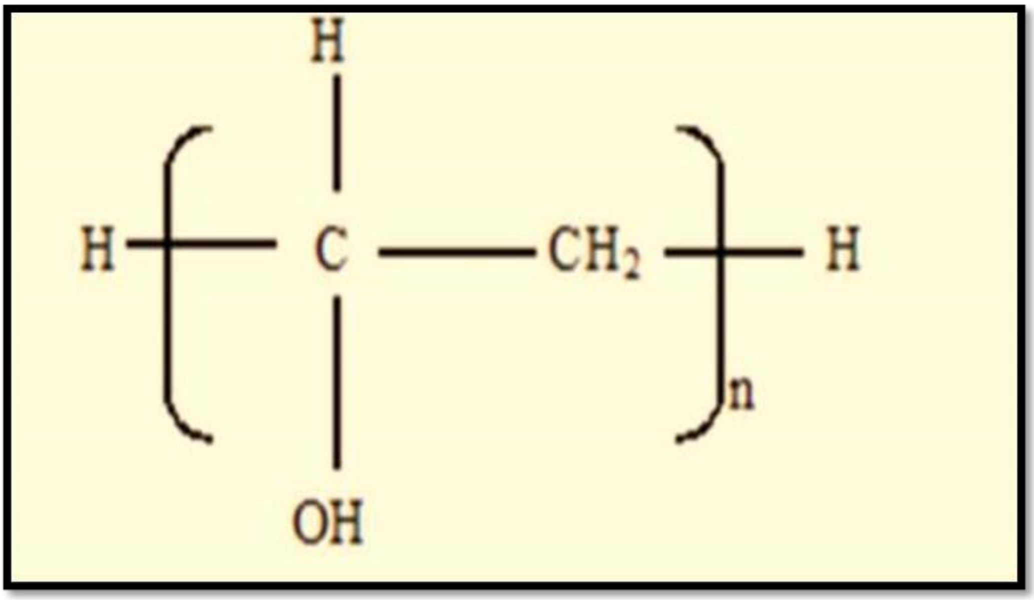

Fig. (1.1) The chemical structure of PVA[20].

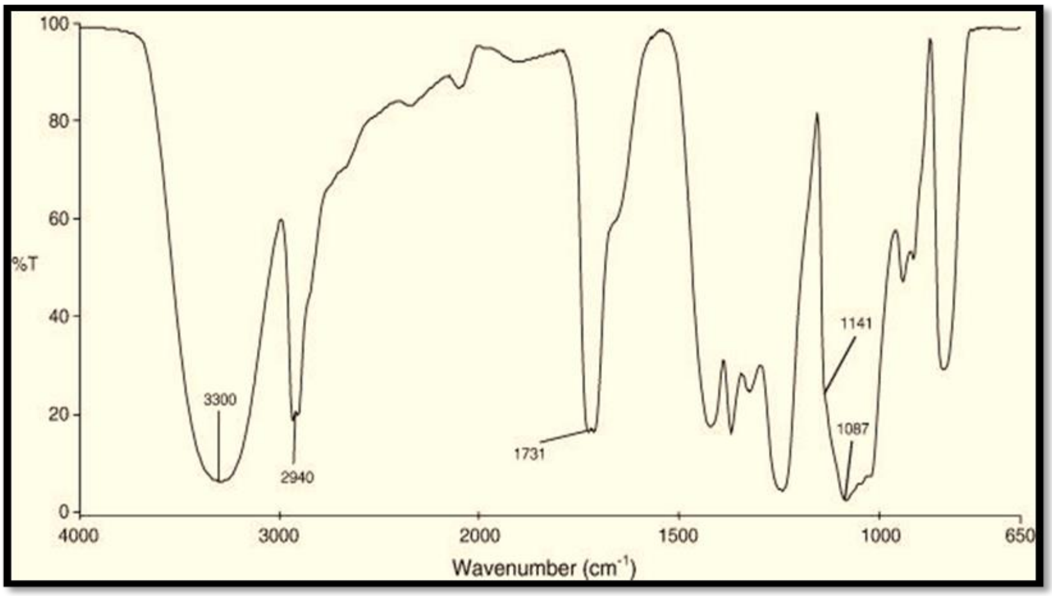

Fig. (1.2): FTIR spectra of pure PVA [20].

Table (1.1): Physical and chemical properties of poly(vinyl alcohol) (PVA)[21].

Property	Description
Appearance	White to an ivory white granular powder
Molecular formula	$(C_2H_4O)_n$
Solution PH	5- 6.5
Density	1.3 g/cm^3
Refractive index	1.55
Glass transition Temperature T_g	85 °C
Melting point	200 °C

1.3.2 Polyethylene glycol (PEG)

Polyethylene glycol is a polyether compound derived from petroleum with many applications, from industrial manufacturing to medicine. PEG is also known as polyethylene oxide (PEO) or polyoxyethylene , depending on its molecular weight[22]. Polyethylene glycol (PEG) is a water-soluble synthetic polymer widely used in pharmaceutical and cosmetic industries[23]. PEG has many attractive properties such as wide range of molecular weight, biocompatibility, low toxicity, and chain flexibility, and it has been used frequently in the production of polymer blends as it can improve the flexibility and ductility of rigid polymers. Figure (1.3) shows the chemical structure of PEG [24]. Table (1.2) explain some physical properties of PEG [25].

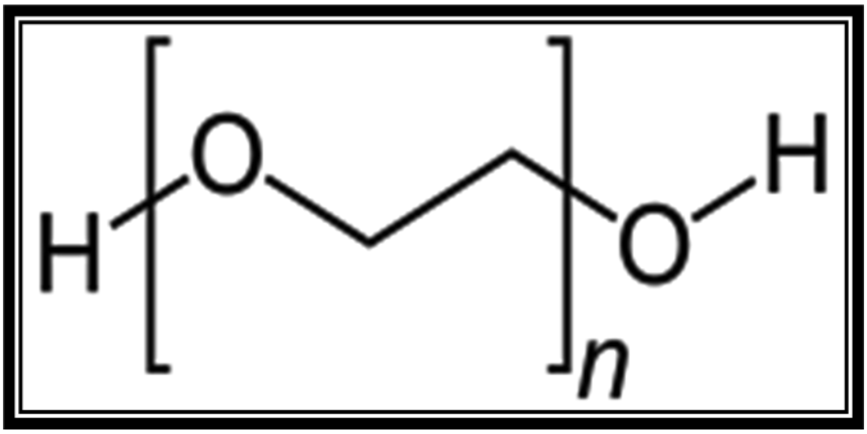

Fig.(1.3): The chemical structure of PEG [24].

Table (1.2): Physical properties of polyethylene glycol (PEG) [25]

Property	Description
Appearance	White to very pale yellow
Molecular formula	$C_{2n}H_{4n+2}O_{n+1}$
Solution PH	5.5 - 7
Density	1.27 g/cm^3 at 25 °C
Refractive index	1.469
Glass transition temperature T_g	55 °C
Melting point	250 °C

1.4 Literature Review

Fahad *et al.* in (2018)[26] studied the effects of PEG loads on blends of PVA/PEG was investigated. In an attempt to obtain cast films with good physical properties to be used for further research. In order to explore their effect on the mechanical properties of the PVA/PEG blend, the nanocomposites were also prepared as a nanofiller using graphene. by a solution mixing and casting process, water soluble polymers such as poly(vinyl alcohol) (PVA) and poly(ethylene glycol) (PEG) and their nanocomposites with graphene were prepared. To decide the optimal blend ratio, Using Fourier transform infrared spectroscopy (FTIR) . In addition, the mechanical parameters, such as tensile stress and elongation at break, were determined using a universal tensile measuring device. FTIR analysis results The creation of an H-bond between PEG and PVA has been proven. PEG has a significant plasticizing impact on PVA. Due to good compatibility as evidenced by FTIR and SEM data, as well as improved thermal characteristics

In (2019) Liu, *et al*. [27] studied a novel poly (vinyl alcohol) (PVA)/poly (ethylene glycol) (PEG) scaffold was carefully designed via thermal processing and subsequent supercritical fluid (SCF) foaming. Interestingly, a bimodal open-celled structure with interconnected networks was successfully created in the plasticized PVA (WPVA)/PEG scaffold. Large cells were produced from the nucleation sites generated in the PVA phase during rapid depressurization, while plenty of small pores generate in the cell walls of the big cells. The formation mechanism of this cellular structure was studied by considering the various phase morphologies and the diffusion behavior of the carbon dioxide (CO_2) in individual phases. In addition, the intermolecular interactions of the WPVA/PEG blend were studied using X-ray diffraction and FTIR analysis. The results demonstrate that various types of hydrogen bonds among the hydroxyl groups on the PVA chains, PEG and water molecules are formed in the blend system. The realization of thermoplastic foaming of the PVA/PEG blend benefits from the interactions of complexation and plasticization between water and PEG molecules.

In (2019) R.M. Ahmed , *et al*.[28] studied Enhancing the Optical Properties of Polyvinyl Alcohol by Blending It with Polyethylene Glycol. In the present research work a solution casting technique was utilized to fabricate various blends of polyvinyl alcohol (PVA)/polyethylene glycol (PEG). Embedding PEG in PVA resulted in obvious shifts in the absorption edge which points to a decrease in the energy gap values based on PEG content. Loss of the photon energy was a consequence of increasing the extinction coefficient at high wavelengths. The PEG content increased the refractive index of the PVA in the produced PVA/PEG blends. The direct and indirect energy gap values were decreased whereas the Urbach energy values were increased with increasing the PEG content. The exact electron transition which is responsible for the absorption process was determined successfully based on the complex optical dielectric functions. In addition, some other optical parameters were estimated to more understand fully the effect of embedding the PEG in the PVA. The Fourier transform infrared spectroscopy was used to determine the characteristic functional groups of both the PVA and the PEG.

In (2020) Jitender Paul Sharma, *et al*.[29] studied the drop cast films of (PVA), (PEG) and optimized. The absorption maxima is observed at 325 nm and 300 nm for the pure PEG and PVA samples, while it is found to shift to 320 nm for the polyblends. The value of indirect optical gap is found to be 1.75 eV, which is lower than the pure components.

In (2022) Rusul , *et al*.[30] studied the molecular weight (Mw) on the physicochemical properties of polymers and their matrices. This study focused on the impact of increasing the Mw of polyethylene glycol (PEG) (4, 8 and 20 K) mixed with polyvinyl alcohol (PVA). Graphene oxide (GO) nanosheets were employed to reinforce the polymer matrix by aquatic mixing-sonication-casting to prepare the nanocomposites and investigate their optical properties. Fourier transform infrared spectroscopy revealed strong interfacial interactions among the components and successful fabrication of the nanocomposites. Optical microscopy and scanning electron microscopy confirmed the fine homogeneity of the polymers and the excellent dispersion of nanosheets in the matrix. The absorption peak was located in the ultraviolet region related to GO. PEG Mw and GO additive significantly improved optical properties such as absorbance, real and imaginary dielectrics and the absorption coefficient constant up to 75%, 40%, 120% and 77%, respectively. An enhancement in the optical properties was also observed after the energy gap values for allowed and forbidden transitions were improved up to 90% and 375%, respectively.

1.5 The Aim of the Study

Studying the impact of average molecular weights of polyethylene glycol (PEG_S 4,8 and 20 K) on morphology and optical properties of fabricated PVA-PEG polymeric blend.

CHAPTER Two

Theoretical Part

2.1 Introduction

The general overview of the theoretical part of this chapter focused on the description of classification of polymer and laws used to describe the optical properties results.

2.2 Classification Based on the Structure of Polymers.

The physical properties of any polymer are depending on two molecular characteristics[31]

a) The length of the molecule

b) The functional group related with the repeating units.

By using different starting materials and processing techniques, it is possible to produce polymers having different molecular structures as the following.

1. Linear: The chains of polymer hold it together by many Vander Waals bonds. Examples of linear polymers are polyethylene, fluorocarbons, polystyrene, nylon, and polyvinyl chloride are shown in Figure (2.1 a).

2. Branched: Side-branch chains bond to the main ones during synthesis of the polymer. These reduce the packing efficiency, so lower density is shown in Figure (2.1 b).

3. Cross linked: Cross-linked polymers consist of smaller polymer chains which are bonded together. Each chain is bonded to many chains. Many of the rubber materials consist of polybutadiene cross linked with (S) atoms are shown in Figure (2.1 c).

4. Network: Mer units with three active covalent bonds are form 3D networks (e.g. epoxies) are shown in Figure (2.1 d).

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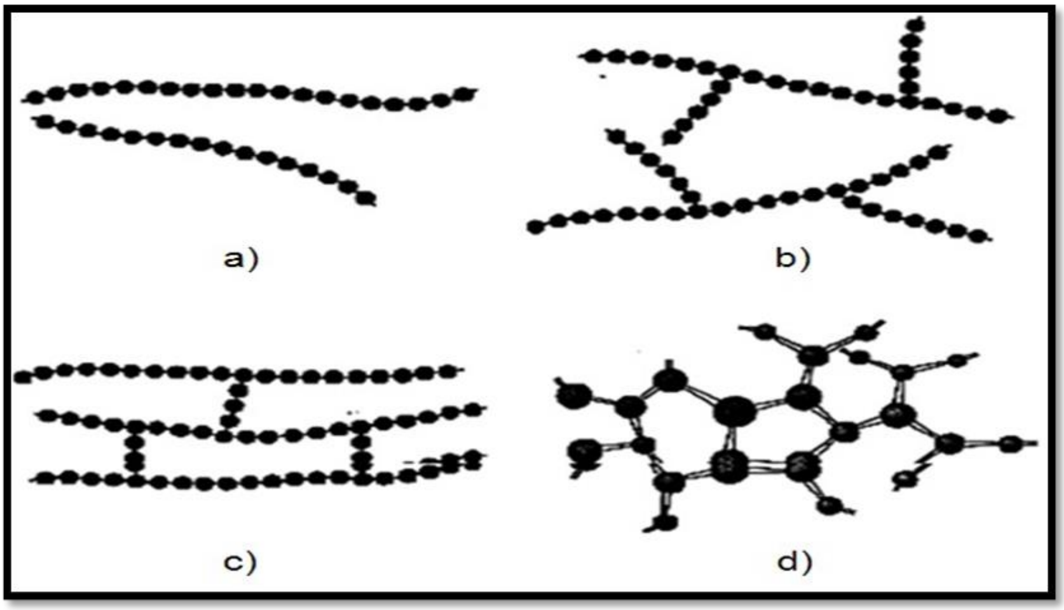

Fig (2.1): The type of polymers (a) Linear polymer, (b) Branched Polymer, (c) Cross-linked polymer, (d) Network polymer[31]

2.3 Comparison Between Thermoplastic and Thermosetting

Thermoplastics are lengthy polymer chains that have a high molecular weight. These chains can be crystalline or amorphous, depending on the thermoplastic. The high molecular weights of polymers are what give them their useful features, including as superior mechanical capabilities and the capacity to be molded into a wide variety of different kinds of parts (injection molded, extruded, etc). Thermoplastics can have no crystallinity, making them amorphous. This causes the lengthy chains to become entangled with one another, giving the impression that the material is "like a bowl full of spaghetti." Since the polymer chains are going through random Brownian motion and slithering past one another, the late Professor Garth Wilkes from Virginia Polytechnic Institute used to compare molten polymers (like linear amorphous) to a bowl full of snakes [32].

Thermosets are a type of polymer that start out as small molecules (monomers and oligomers), but through the process of a chemical reaction, they are able to polymerize into a network structure. In the fully cured and final condition, the crosslinks bind the chains together, which provides both strong mechanical qualities and dimensional stability, but thermosets will not flow (and are not dimensionally stable) above their T_g [33]. Figure (2.2) represents the thermoplastic and thermosetting.

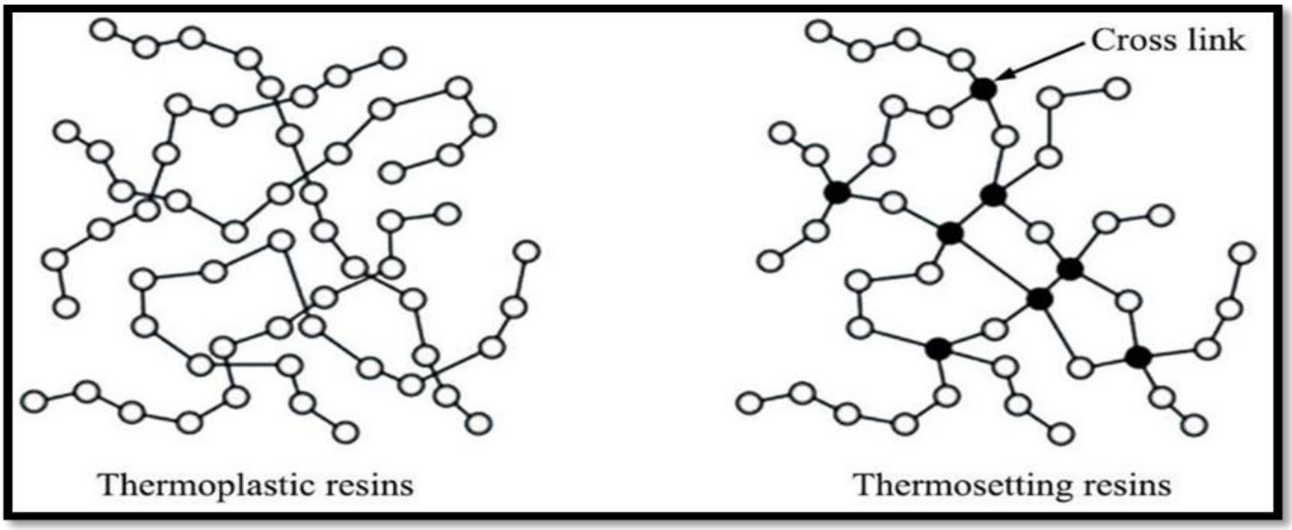

Fig (2.2): Difference between thermoplastic and thermoset polymers[33].

2.4 Measurements of Structural Properties

2.4.1 Optical microscope (OM)

One of the first techniques used to study the topography of a surface is optical microscopy, also called light microscopy, is a type of microscope that uses visible light and a system of lenses to magnify images of small samples.

Optical microscopes are the oldest design of microscope and were possibly designed in their present compound form in the 17th century. An optical microscope usually has a single eyepiece which can often be fitted with a camera for photography [34]. Traditional optical microscopes have a resolution restricted by the size of submicron particles approaching the wavelength of visible light (400–700 nm) include:

1. Transmission: beam of light passes through the sample.

2. Reflection: beam of light reflected off the sample surface.

An example is the polarizing or petrographic microscope for which the samples are usually fine powder or thin slices (transparent). Another example is the metallurgical or reflected light microscope which is used for the surfaces of materials, especially opaque ones [35].

2.4.2 Fourier Transform Infrared (FTIR) Spectroscopy

Chemical analytical spectroscopy is Fourier Transforms Infrared (FT-IR). It tests the sensitivity of infrared with the number of light waves. The wavenumbers consist of infrared light classified into three zones, far-infrared, mid-infrared and near-infrared, ranging from (4 ~ 400) cm^{-1}, (400 ~ 4,000) cm^{-1} and finally (4,000 ~ 14,000) cm^{-1}, respectively. The allowable use of this technology depends on detecting the vibration of the chemical functional group in a sample. Where, as the contact takes place between the infrared light and the substance, the chemical bonds will stretch. Here, independent of the rest of the molecule composition, the infrared radiation is captured by the chemical functional group at a particular wavenumber range, more complex molecules contain more than one bond. FT-IR spectroscopy is a powerful tool for identifying types of chemical bonds in a molecule applying to produce an infrared absorption spectrum as a molecular "fingerprint" the principle of this technique is that molecular bonds vibrate at various frequencies. Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. Since FT-IR provides information about the chemical bonding or molecular structure of materials without causing destruction, it could be used to identify unknown materials, detect the organic and some inorganic additives in the level of a few percent, also characterize the chemical structure change and solvent residue. Figure (2.3) get the configuration of the FTIR system [36].

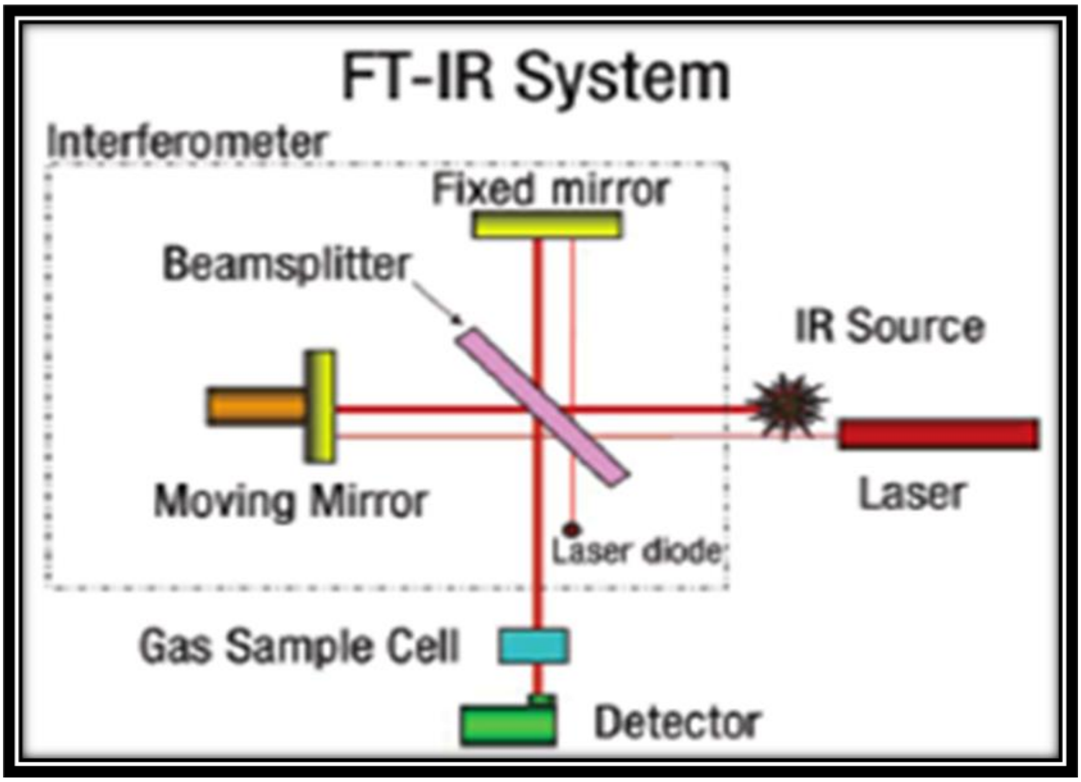

Fig (2.3): Scheme of the FTIR system[36]

2.5 Light in Matter

Matter can emit, absorb, transmit, and reflect (or scatter) light, usually, the effect of refraction is difficult to measure due to absorption and scattering, as shown in Figure (2.4). Interactions between light and matter determine the appearance of everything. light interacts with matter in ways such as emission and absorption. The photoelectric effect is an example of how matter absorbs light. What matter does with the energy from light depends on what kind of light it is and there is a whole spectrum of light called the Electromagnetic Spectrum. Despite the fact that light can travel through a vacuum, it cannot pass through all objects. Light can be transmitted, reflected, or absorbed when it strikes an object. The object is made up of molecules, and each molecule has electrons that can absorb energy and jump to higher energy levels. The electron will absorb this energy and re-emit it as heat if it corresponds to one of the electron energy levels. Transparent materials, on the other hand, do not absorb the photon's energy. The photon is able to travel right through since it is not absorbed. Some materials are partly transparent, allowing some photons to pass through while others are absorbed. Because it only passes specific hues of light, the material will seem colored [37]. In the presence of absorbance and scatter, the energy conservation law may be written as [38]:

$$T+R+(A+S)=1 \quad (2.1)$$

In general:

$$T+R+A=1 \quad (2.2)$$

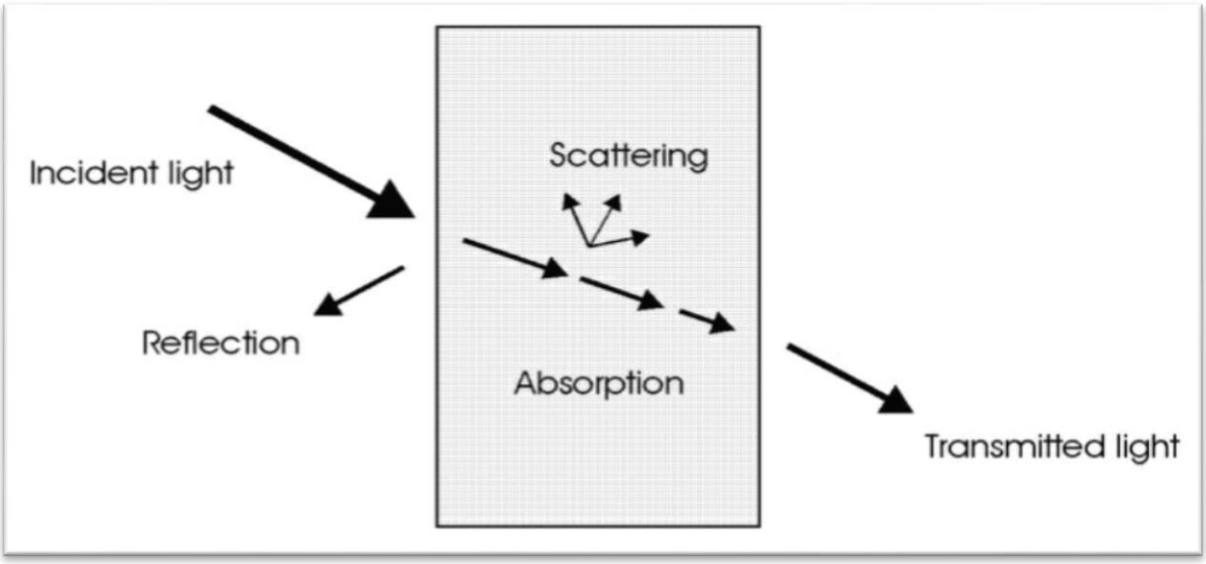

Fig (2.4): Definitions of T, R,A, and S.[38]

2.6 Optical properties

2.6.1 Absorbance (A)

The absorbance occurs when light passes through a material and the intensity is reduced based on the colors that are absorbed.

It can be defined as the ratio between absorbed light intensity (I_A) by material and the incident intensity of light (I_o)[39]:

$$A = \frac{I_A}{I_0} \qquad (2.3)$$

2.6.2 Transmittance (T)

The intensity of transmitted rays from the film (I_T) over the intensity of incident rays on the film (I_o) is called the transmittance (T), and can be obtained as follows[39] :

$$T = \frac{I_T}{I_0} \qquad (2.4)$$

2.6.3 Optical constants

There are many ways to find the optical constants of refractive index, extinction coefficient, optical conductivity, dielectric constant, and absorption coefficient.

2.6.3.1 Refractive index (n)

The refractive index can be defined as the ratio of the velocity of light in vacuum (c) to the velocity of light in the medium (υ) according to[40]:

$$n = \frac{c}{\upsilon} \qquad (2.5)$$

The relation can be used to calculate reflectance from absorption (A) and transmission (T) spectra in accordance with the conservation of energy law[41]

$$R + A + T = 1 \qquad (2.6)$$

The following equation can be used to calculate the refractive index[42]:

$$n = \frac{1+R}{1-R} + [\frac{2R}{1-R^2} - k^2]^{1/2} \qquad (2.7)$$

where: (k_0) is the extinction coefficient.
R: is the reflectance.

Depending on the refractive index, it can be determined the polarizability (P) by the relation [42]:

$$P = \frac{3}{4\pi}\left(\frac{n^2-1}{n^2+1}\right) \quad (2.8)$$

2.6.3.2 The absorption coefficient

It is defined as a ratio decrement in incident ray energy flux relative to distance unit in the direction of incident wave diffusion. The absorption coefficient (α) depends by the incident photon energy (hυ) and the properties of the sample. The following equation can be used to compute the absorption coefficient[42]:

$$\alpha = 2.303\left(\frac{A}{t}\right) \quad (2.9)$$

Where (t) represent a thickness of sample.

2.6.3.3 Dielectric constant

The dielectric coefficient (**ε**) can be determined using the refractive index (n), join complex dielectric coefficient (**ε**) with complex refractive index (N). From equations (2.9) and (2.10) real and imaginary complex dielectric coefficient can be written as in following equation[43]

$$\epsilon_1 = (n^2 - k_0^2) \quad (2.10)$$

$$\epsilon_2 = (2nk_0) \quad (2.11)$$

2.6.3.4 Extinction coefficient (k_o)

The electrical coefficient the amount of photons absorbed by the membrane, that is, the energy absorbed by the electrons of the material, and expresses the following relationship [44]:

$$k_o = \alpha\lambda/4\pi \quad (2.12)$$

Where (λ) is the wavelength of the incident light and (α) absorption coefficient.

2.6.4 Fundamental absorption edge

The fundamental absorption edge can be characterized as the quick increase in absorbance when the amount of energy absorbed is nearly equal to the band energy gap; Thus, the fundamental absorption edge denotes the less difference in the energy between up point in valance band to bottom point in conduction band[44]:

2.6.4.1 Absorption regions

The optical conductivity (σ_{op}) depends directly on the refractive index (n) and absorption coefficient (α) by the following relation.

$$\sigma_{op} = \alpha\, n\, c/4\pi \qquad (2.15)$$

c is the velocity of light, α is the absorption coefficient.

There are three different types of absorption regions:

A) High absorption region

This region is shown in Figure (2.5). In part (A), the absorption coefficient's magnitude (α) is greater than or equal to (10^4 cm^{-1}). The magnitude of the forbidden optical energy gap (E_g^{opt}) can be introduced from this region.

B) Exponential region

This region is shown as in Figure (2.5). In part (B), the absorption coefficient (α) equals ($1\ cm^{-1} < \alpha < 10^4\ cm^{-1}$). It describes the transition from extensive levels in the Valens band (V.B.) to local levels in the conductive band (C.B.) and vice versa, transitioned from local levels in (V.B.) to extended levels at the conductive band's bottom (C.B.).

C) Low absorption region

The absorption coefficient (α) is extremely small in this region. it is about ($\alpha < 1\ cm^{-1}$). The transition occurs in this region as a result of state density inside space motion caused by structural faults[45] , as in Figure (2.5,C), the part (C).

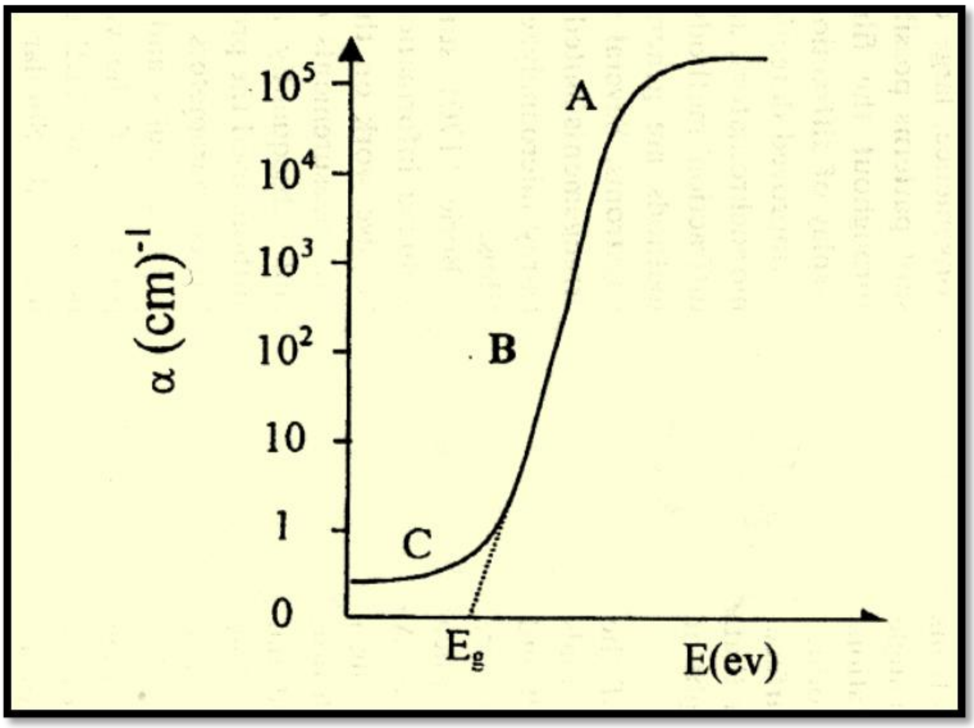

Fig (2.5): The variation of absorption edge with absorption regions [45].

2.6.4.2 The electronic transitions

There are two basic forms of electronic transition: direct and indirect transition. [46].

1) Direct transition

There are two kinds of direct transitions:

a. Direct allowed transition

This transition occurs from the top points in the (V.B.) and the bottom point in the (C.B.), as shown in Figure (2.6).

b. Direct forbidden transitions

This transition occurs from near top points of (V.B.) and the bottom points of (C.B.).

The absorption coefficient for this type of transition is equal to [47]:

$$\alpha h\upsilon = B(h\upsilon - E_g)^r \qquad (2.14)$$

Where E_g is the energy gap of direct transition.

B: the constant depended on the type of material

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

r =1/2 for the allowed direct transition.

r =1/3 for the forbidden direct transition.

2) Indirect transitions

In these transitions type, the bottom of (C.B.) is not over the top of (V.B.), in curve (E-K). The electron transits from (V.B.) to (C.B.) is not perpendicularly when the value of the electron's wave vector before and after the transition is not equal ($\Delta K \neq 0$), this transition type occurs with the help of a particle named Phonon. For conservation of the energy and momentum law. Indirect transitions are classified into two types [46], they are:

a. Allowed indirect transitions:

This type of transition occurs in a different region of K-space that is the electrons transmitted between the V.B. top and the C.B. bottom, as exposed in Figure (2.6).

b. Forbidden indirect transitions:

Forbidden indirect transitions are displayed between the nearest points in the top and the bottom of the valance and conductive bands respectively.

The equation (2.14) giving the transition absorption coefficient and the phonon absorption [48]:

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

E_{ph} is the phonon energy, where the sing (-) applied when phonon absorption, whereas the sing (+), used when phonon emission. The exponential constant is represented as r in the equation, in which its value is determined by the transition n=2 and n=3 for the allowed indirect, and forbidden indirect transitions, respectively.

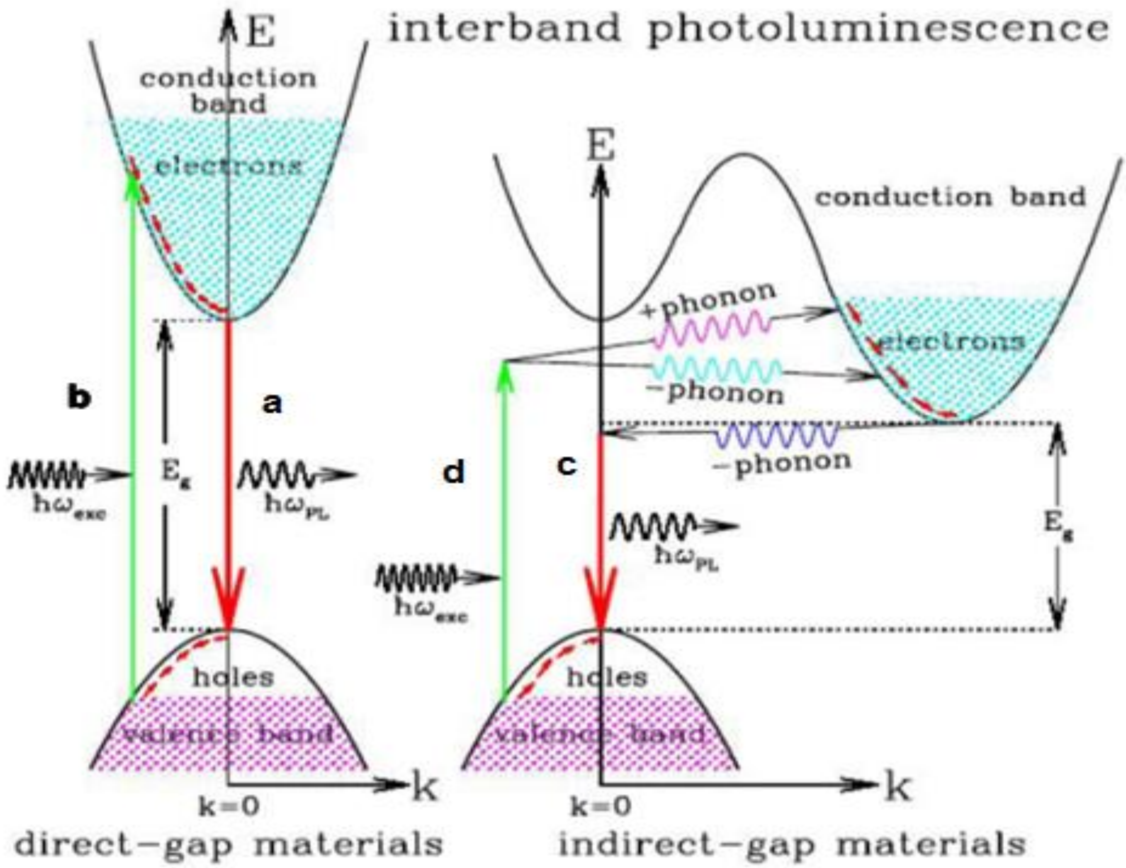

Fig (2.6): The electronic transition types (a) Allowed direct transition (b) Forbidden direct transition,(c)Allowed indirect transition and (d) Forbidden indirect transition[48]

CHAPTER Three

Experimental Part

3.1 Introduction

This chapter covers the preparation and processing steps of the sample, as well as a description of the equipment and methods used in the preparation and measuring process, such as, FTIR, OM, and optical spectrometer .

3.2 The Utilized Materials

The utilized materials in this study are:

3.2.1 Matrix material

Polymers: two types of polymers are used in this work:

- **Polyvinyl alcohol (PVA):** The polymer PVA could be obtained from (Alpha Chemika, India) with high average molecular weight 160,000 g mol^{-1} and high purity (99.98 %).
- **Polyethylene glycol (PEG):** The polymer PEG could be obtained from (Central Drug House, Ltd, Company, India) with average molecular weight 4000, 8000, and 20000 g/mol . The degree of hydrolysis equal 99%.

3.3 Purification of PVA and blended polymer PVA-PEGs $_{4k, 8k, 20k}$.

0.7 g of commercially available PVA in 40 ml deionize water (DW) with continuous stirring for 2 h. In the first hour, the mixing is done at room temperature (23^{o}C), and in the second hour, at a temperature 70-80^{o}C, then aqueous solution cooled to 40^{o}C and it is added 0.3g of PEG 4K or 8k or 20k to synthesis the polymer blend. The resulting solution was cast onto clean plastic Petri dish and kept to dry under air for 240h room temperature (RT) till the solvent gets completely evaporated. Structural and optical examinations were carried out as indicated in the Figure (3.1).

The method summarized in Table (3.1). The thicknesses of the produced films, as computed using a digital micrometer, was about (100 ± 5 µm).

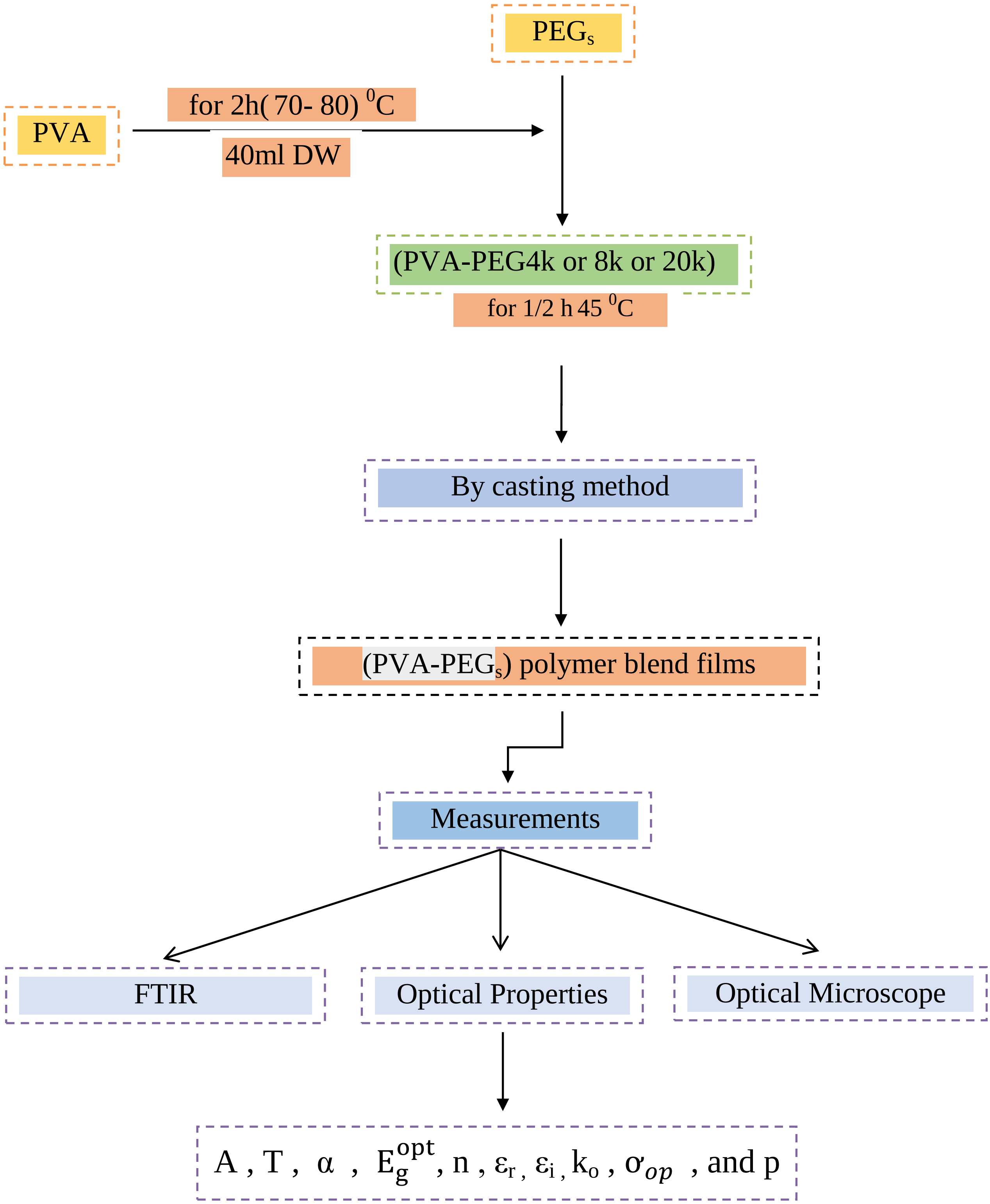

Fig (3.1): Scheme of experimental part.

Table (3.1): Summarized the purification of PVA, and PVA - PEGs films.

Sample	PVA (g)	PEG (g)
PVA	1	0
PVA-PEG_{4k}	0.7	0.3
PVA-PEG_{8k}	0.7	0.3
PVA-PEG_{20k}	0.7	0.3

3.4 Laboratory Equipment

3.4.1 Optical microscope (OM)

The change of surface morphology samples of pure PVA and PVA-$PEGs_{4k,\ 8k,\ 20k}$ as poly-blends were observed applying the optical microscope. This used OM was provided by Olympus (Top View, type Nikon-73346) , as shown in Figure (3.3), which contains an automatic controlled light intensity camera. OM has been introduced in the Physics Department/ Education College for Pure Science/ University of Babylon.

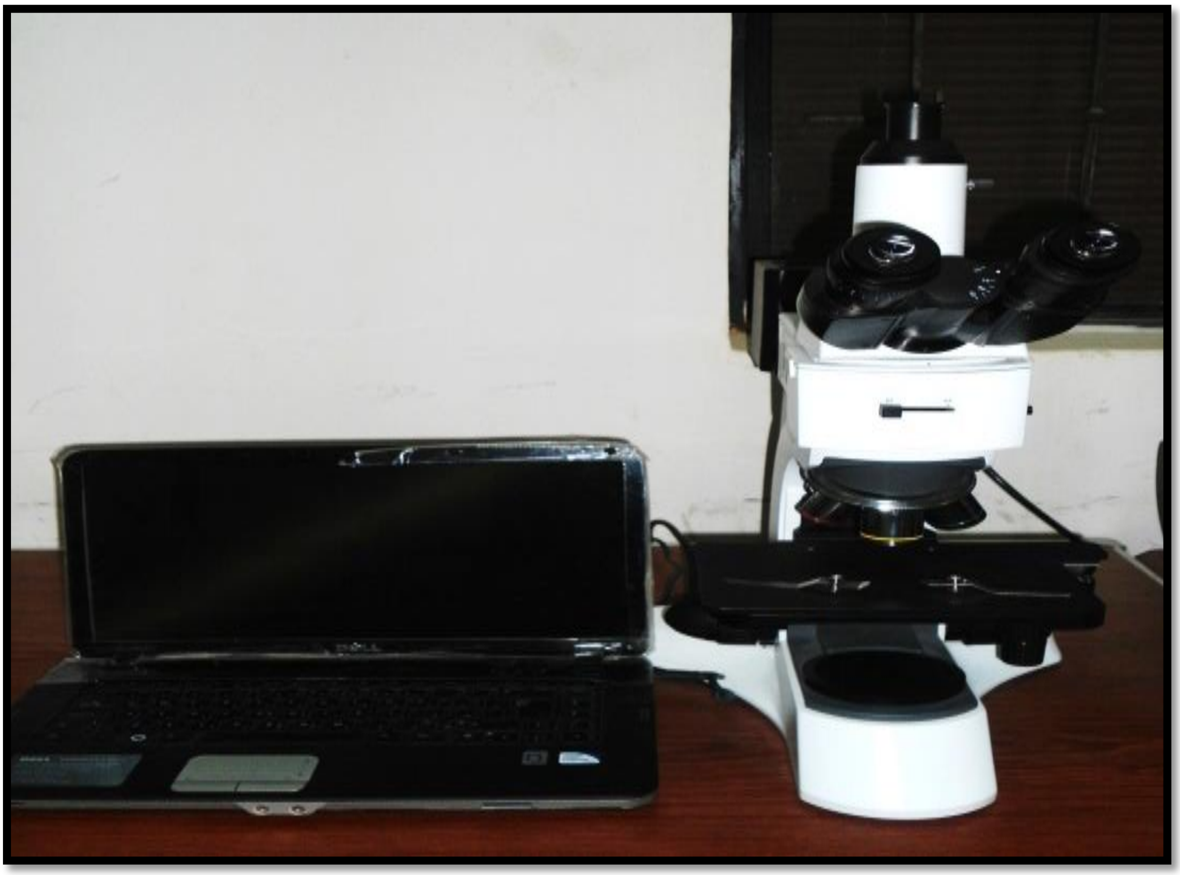

Fig (3.2): Photograph of the optical microscope.

3.4.2 Spectral characterization for FTIR

Spectra were captured using an FTIR (Bruker company type vertex -70, German origin), as shown in Figure (3.2). The spectrum of wave numbers considered is (500–4000) cm^{-1}. FTIR has been introduced in the Physics Department/ Education College for Pure Science/ University of Babylon.

Fig (3.3): Photograph of the FTIR device

3.5 Optical Properties Measurements.

The absorption spectrum of pure PVA and PVA-PEGs $_{4k,\ 8k,\ 20k}$ as poly-blends have been recorded in the wavelength range (200-1100) nm by using the double beam spectrophotometer (Shimadzu, UV-1800 Å), as shown in Figure (3.4). The absorption spectrum has been recorded at room temperature. A computer program (UV Probe software) was employed to obtain the absorbance, optical constants, transmittance, absorption coefficient, extinction coefficient, dielectric constant (real and imaginary parts), refractive index and energy gaps. It is implemented at the university of Babylon /college of education for pure sciences/ department of physics.

Fig (3.4): Photograph of the UV Spectrophotometer.

CHAPTER Four

Results and Discussion

4.1 Introduction

This chapter includes the results and discussion of morphological, and optical measurements for PVA and PVA/PEG $_{4k,8k,20k}$ as poly-blends

4.2 Optical microscopy

The surface of pure PVA and PVA-PEGs $_{4k,\ 8k,\ 20k}$ as poly-blends were characterized using optical microscopy at magnification power (10x) were seen in Figure (4.1) . Changes are observed on the surface of the PVA polymer with the change in the molecular weight of the PEG additive, and it is clear from the surface images of poly-blends has no pores. The figures show that the additive PEG are make aggregated randomly distributed on the films surface at the lower molecular weight. When increasing the molecular weight of PEG up to 20k, a network of routes within the polymer is formed, allowing charge carriers to move inside the basics polymer (PVA).

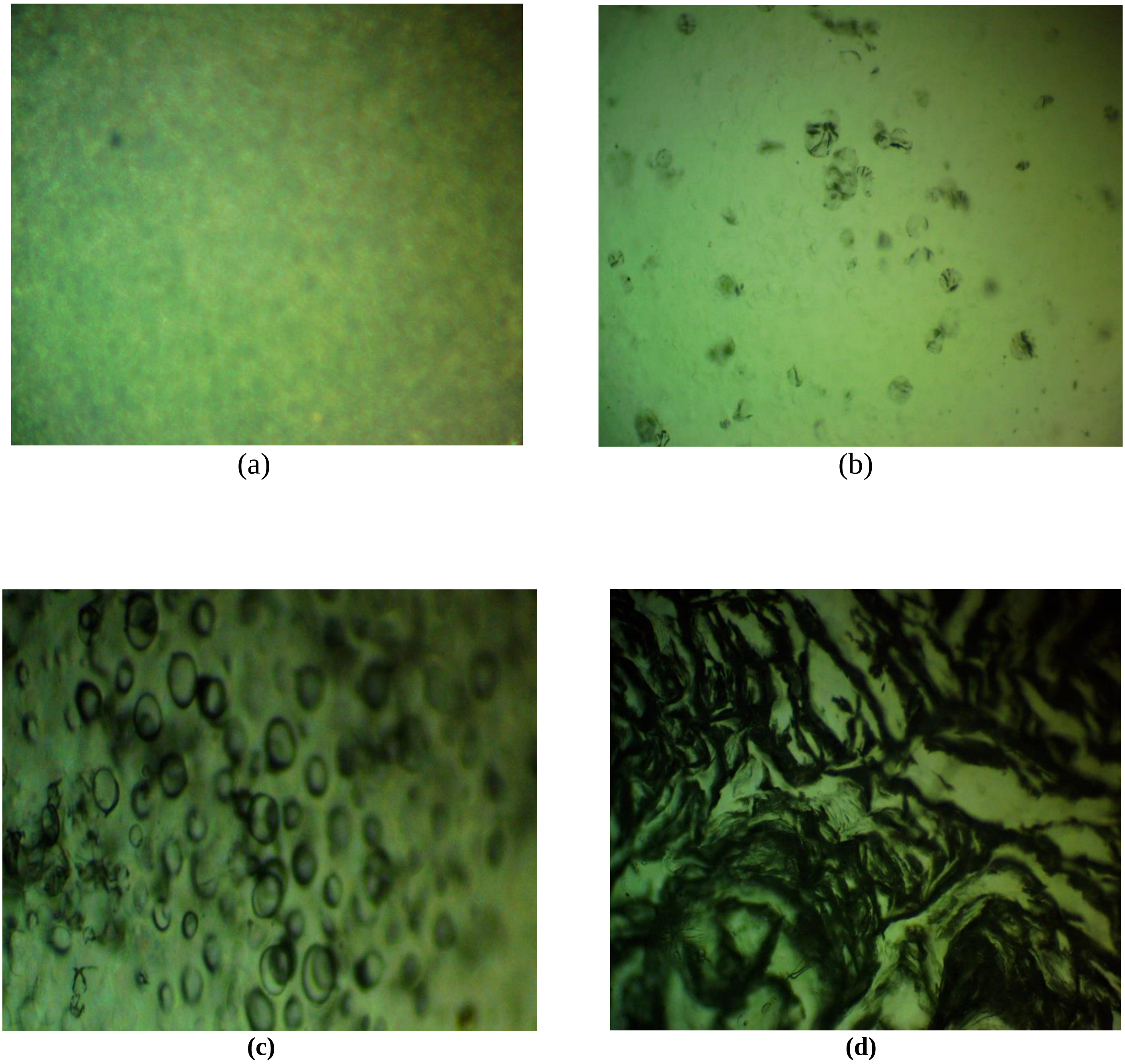

Fig (4.1): Photomicrographs (10X) of pure PVA (a) with, PEG_{4k} (b), PEG_{8k} (c), and PEG_{20k} (d).

4. 3 Fourier transform infrared (FTIR) of PVA/PEG blend

Fourier transform infrared (FTIR) is one of the important analytical techniques for researchers. It is considered as a tool for the simultaneous determination of organic components, including chemical bond, as well as organic content (e.g., protein, carbohydrate, and lipid) [49]. The absorption peaks of pure PVA and PVA-PEGs $_{4k,\ 8k,\ 20k}$ as poly-blends were characterized using FTIR spectra between 500 and 4000 cm^{-1}, as shown in Fig(4.2), Fig(4.3), Fig(4.4), and Fig(4.5), The spectrum that was recorded reveals distinctive bands that are caused by oscillations in the functional groups caused by elongation and twisting of the groupings of the produced film .The characteristics of the absorption peaks of PVA were found at 3283.21 , 2899.00 , 1733.74 , 1343.00, 1239.97, 1086.27, and 840.00 cm^{-1}. The broad peak at 3283.21 assigned to the stretching vibration of the alcohol group (OH) in the polymer matrix chain[50]. The intense peak at 2899.00, corresponds to the Methyl $C\text{-}H_3$ asymmetric[51]. Additionally, the peak at 1733.74 cm^{-1} corresponds to the C=O stretching band, which is actually attributed to carboxylic acid, aliphatic ketone, aldehyde, or quinine groups[52]. The peak at 1343.55 cm^{-1} is attributed to the deformation stretching vibration of the strong N-O . The peak at 1239.97 cm^{-1} is attributed to the deformation stretching vibration of the C-N link[51]. Moreover, the peaks observed at 1086.27, and 840.00 cm^{-1} could be attributed to the twisting vibration of strong C-O-C and medium C=C bending vibrations [53]. FTIR analysis of the polymeric blend revealed strong interfacial interaction bonds, particularly the –H bond, among the molecular chains of blended polymers . The intensity of the peaks was slightly affected by adding fixed proportions of PEGs $_{4k,\ 8k,\ 20k}$ to the original polymer PVA , as well as, it was mentioned a slight shift in peak positions toward higher wavenumbers. These findings were associated with the high solubility and good dispersion of the PVA/PEG polymer blend. All these factors have led to the successful production of blended polymers [30].

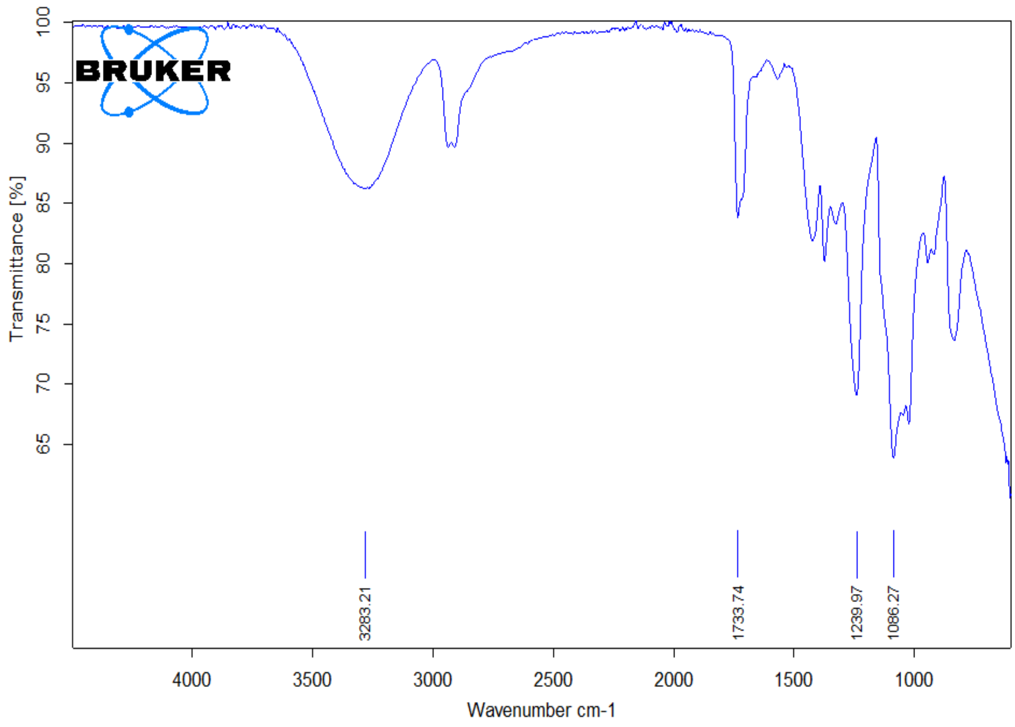

Fig (4.2): FTIR spectra of pure PVA

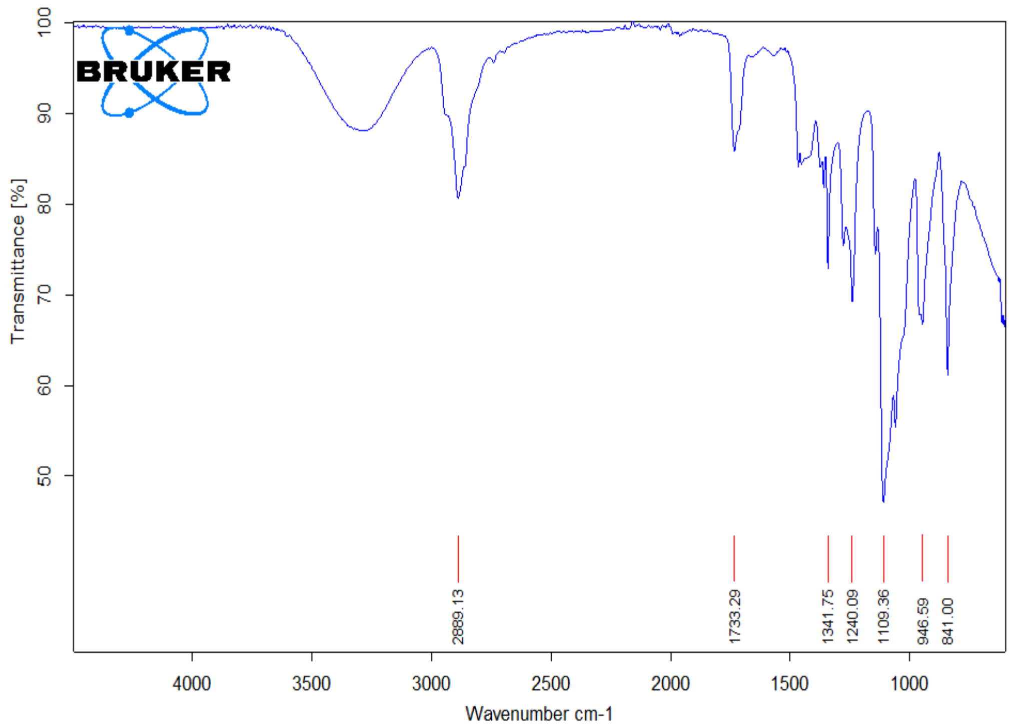

Fig (4.3): FTIR spectra of pure PVA with PEG_{4k}

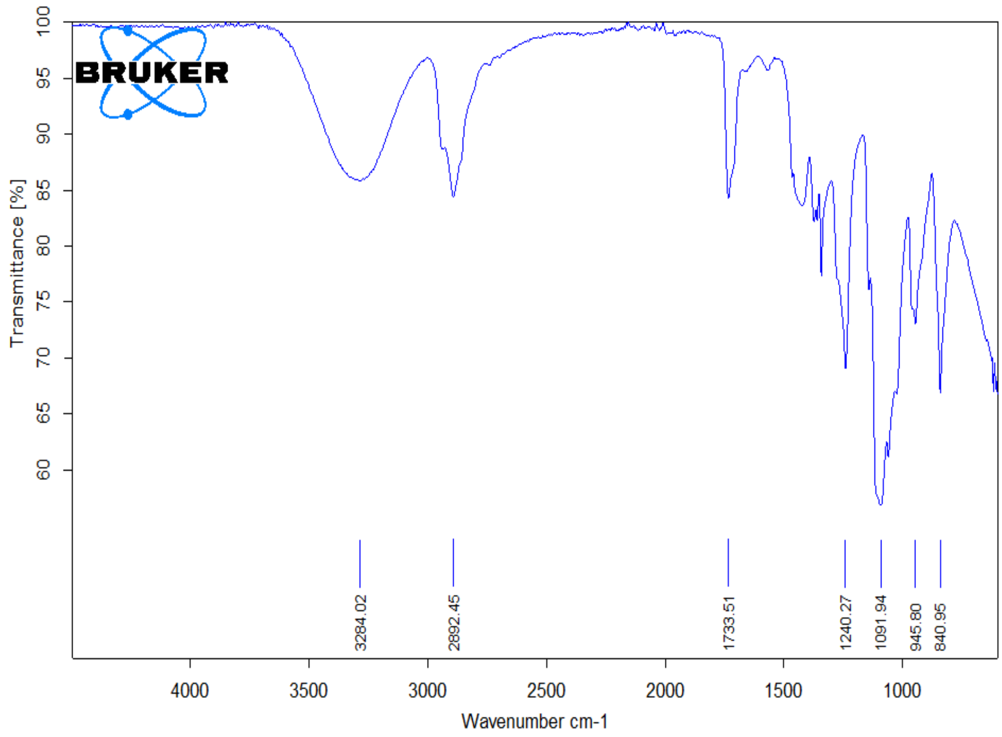

Fig (4.4): FTIR spectra of pure PVA with PEG_{8k}

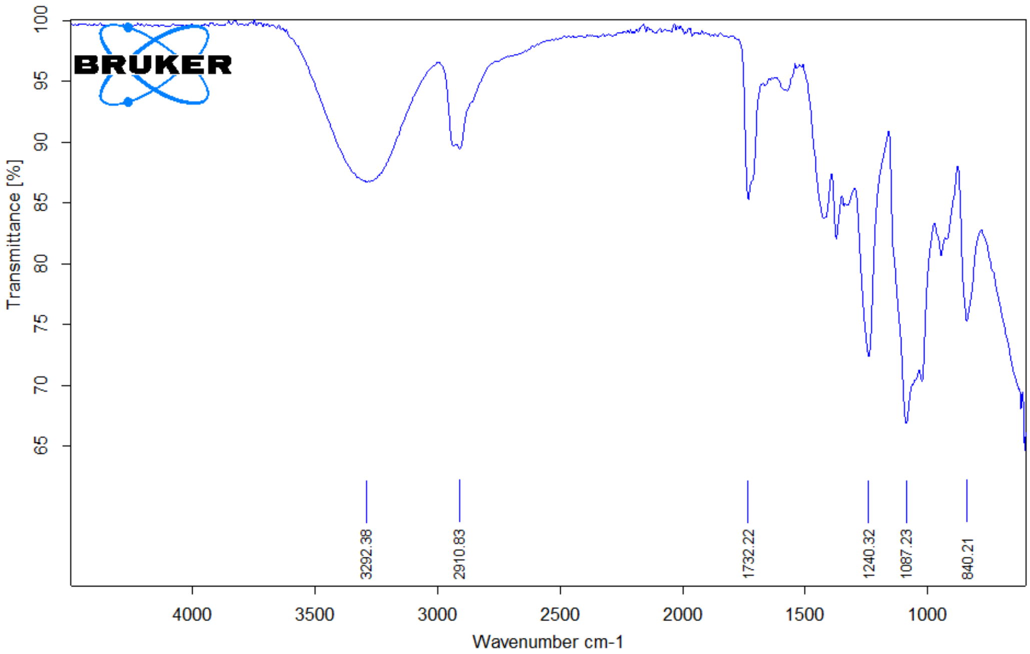

Fig (4.5): FTIR spectra of pure PVA with PEG_{20k}

4.4 The Optical Properties .

The effect of adding the PEGs 4k, 8k, and 20k on the optical properties of PVA considered as a main purpose of this study. The research covers the recording of the spectrum of absorbance at RT and calculating the absorption coefficient, extinction coefficient, as well as identifying the types of electronic transitions and calculating energy gaps.

4.4.1 The absorbance and transmittance

The optical absorbance spectra of pure PVA and blended polymer of different average molecular weights of PEGs 4k, 8k, and 20k as films for the wavelength (200-1100) nm are shown in Figure (4.6). In the ultraviolet region (UV) where films absorb a lot of light and then steeply descend as the wavelength increases, while the absorption spectra for all films show a minor drop in the visible and NIR regions and tend to steady at high wavelengths. This can be attributable to the incident photons' low energy, which prevents any interaction with the polymer structure. This implies that photons will transmit and scatter with high probability via polymer sheets.

The results show that the absorbance was increasing with the rising in the molecular weight of the additive PEG. In all films, the shift of absorption maxima towards greater wavelengths in the absorption edge indicates that the PEGs polymers possess different rheological properties.

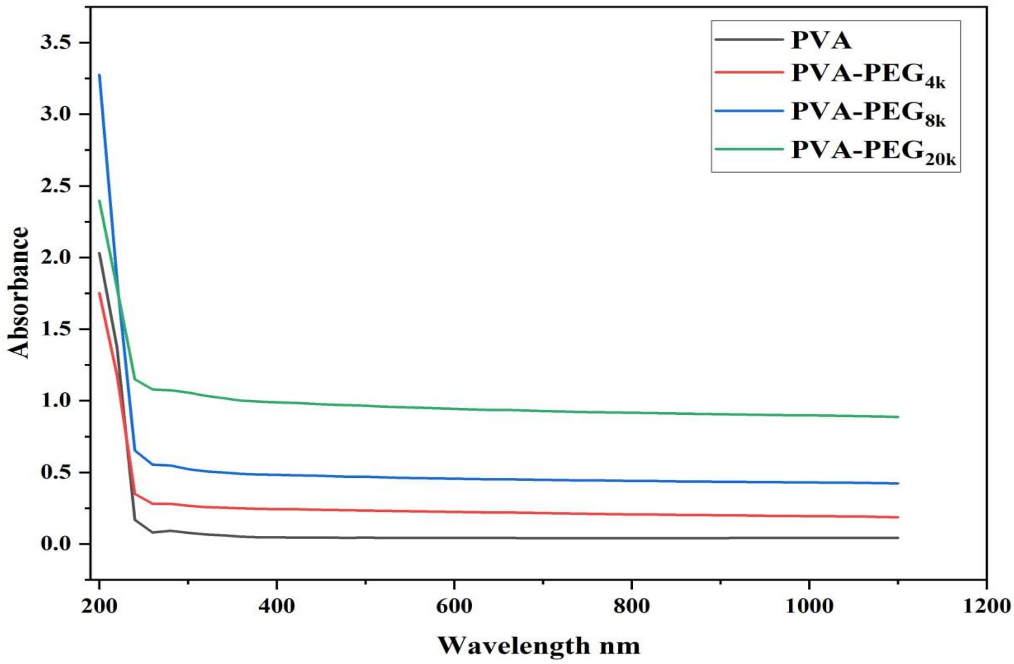

Fig (4.6): The absorbance of PVA and blended polymer PVA-PEGs $_{4k,\ 8k,\ 20k}$ with wavelength.

The optical transmittance spectra of pure PVA and blended polymer of different average molecular weights of PEGs 4k, 8k, and 20k as films for the wavelength (200-1100) nm are shown in Figure (4.7). Above 400 nm, the transmittance curves of all samples show a tendency towards saturation, and the highest rated average transmittance of the pure polymer film was ~ 95% in the Vis and NIR areas of spectrum, but it decreases almost gradually with the rising in the molecular weight of the additives, reaching ~ 55 at PEG_{20k}, which may be makes it convenient for UV shielding application. This feature was ascribed to the film surface morphology and the absorption.

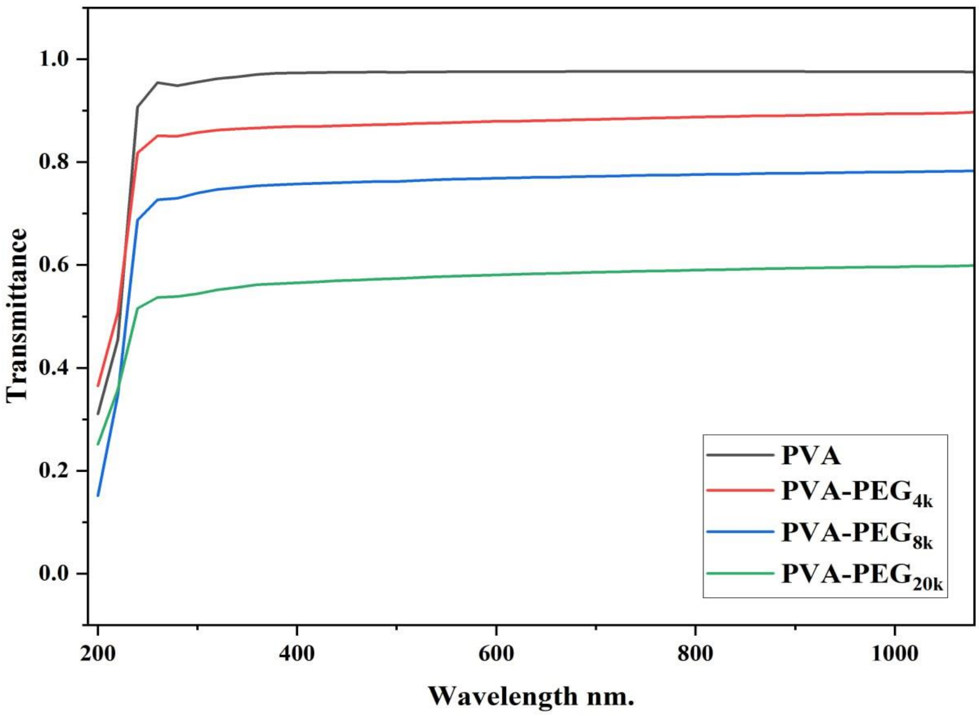

Fig (4.7): The transmittance of PVA and blended polymer PVA-PEGs $_{4k,\ 8k,\ 20k}$ with wavelength.

4.4.2 The absorption coefficient and energy band gap

The absorption coefficient of PVA and blended polymer PVA-PEGs 4k, 8k, 20k, as an inspection tool to ascertain the film's light-intensity attenuation, was shown in Figure (4.8). On the other hand, depending on the energy of the incident light, this is a sensitive physical way to give us vital information about the sorts of charges transported in a band and around the value of the band gap energy. At high energies, the electron absorption was excellent, with $\alpha \leq 104\ cm^{-1}$. This finding could be related to the high probability of indirect electronic transition. From such figure it was noted the shift in the absorption edge towards the longer wavelength with the rising in the molecular weight of the additives. This result reveals the decline of the optical energy gap as the molecular weight of the additive increases. This result agreed with a previous study [29 , 30].

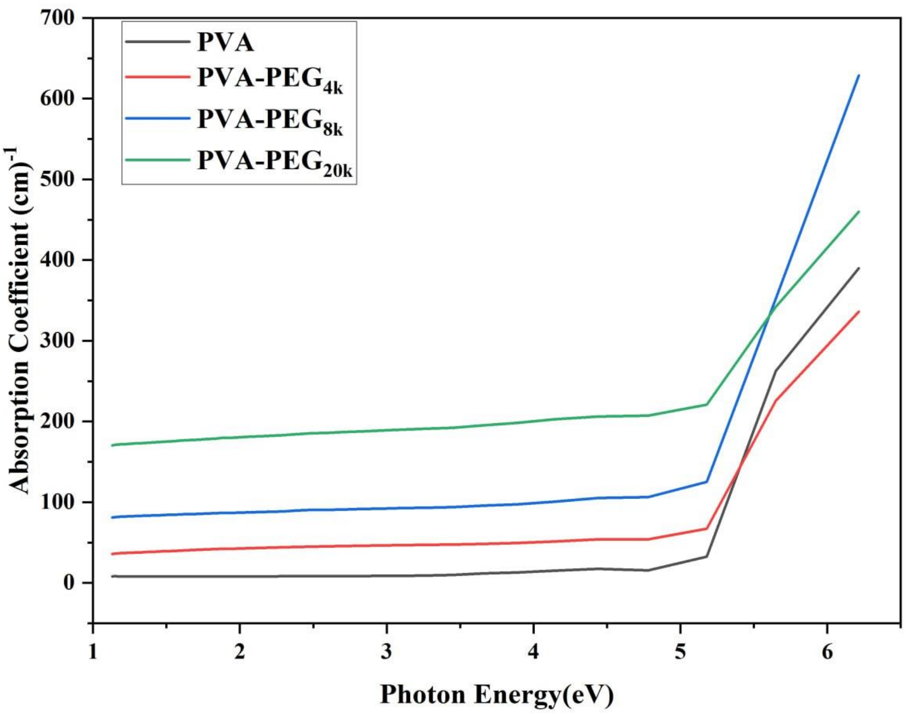

Figure (4.8): The absorption coefficient of PVA and blended polymer PVA-PEGs $_{4k, 8k, 20k}$ with wavelength.

The energy band gap is calculated using the classical relation for near edge optical absorption (2.15). The energies gap for allowed indirect transitions of pure PVA and blended polymer PVA-PEGs $_{4k, 8k, 20k}$ are shown in Figure (4.9). The energies gap for forbidden indirect transitions of pure PVA and blended polymer PVA-PEGs $_{4k, 8k, 20k}$ are shown in Figure (4.10). The indirect band gap obtained with procedure pure PVA and blended polymer PVA-PEGs $_{4k, 8k, 20k}$ films, calculated by projecting the linear portion of the curve to the hν axis. In the Table (4.1), the energies gap for allowed and forbidden indirect transitions are decreased with the rising in the molecular weight of the additive PEG. This result is probably due to the difference in the molecular weight values of PEGs 4k, 8k, and 20k , in addition to the nature of their diffusion on the surface of the films prepared according to the results of the optical microscope test.

As a result, it can soak up low-energy photons. These matches the lookup value.

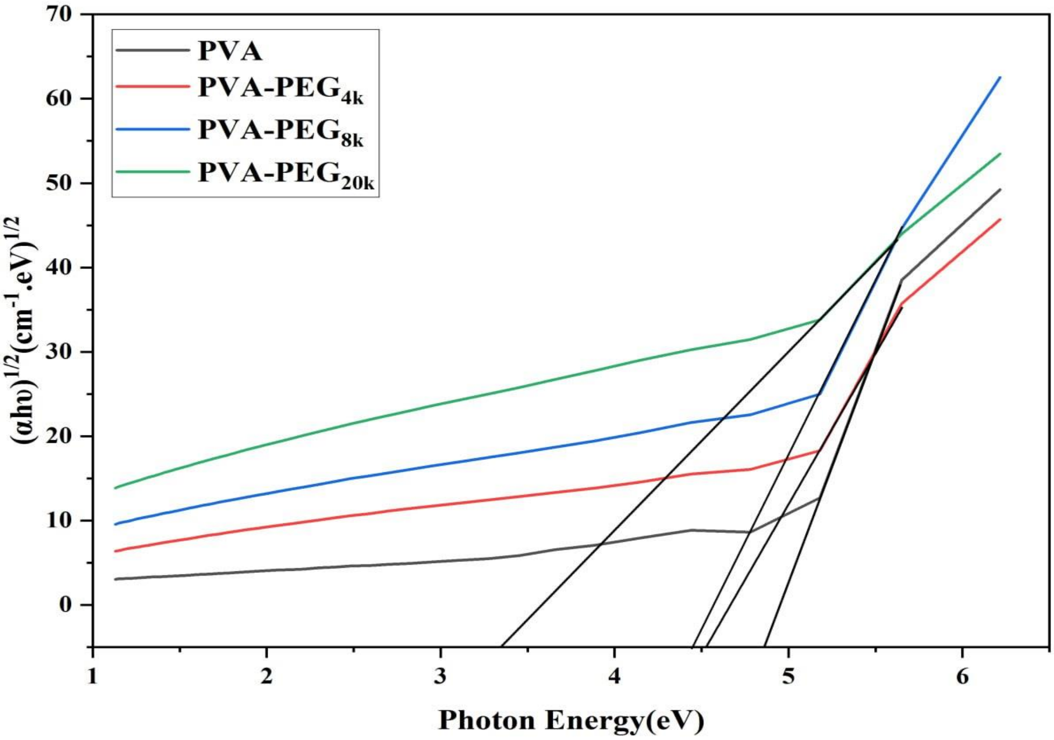

Figure (4.9): Variation of $(\alpha h\upsilon)^{1/2}$ for PVA and blended polymer PVA-PEGs $_{4k,\ 8k,\ 20k}$ with wavelength.

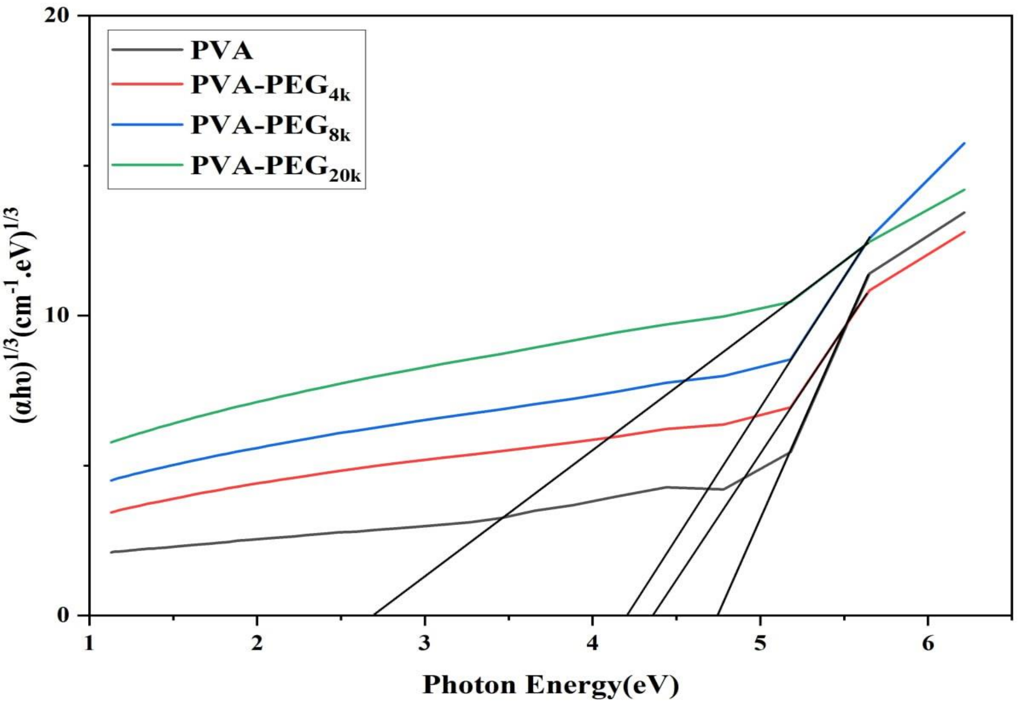

Figure (4.10): Variation of $(\alpha h\upsilon)^{1/3}$ for PVA and blended polymer PVA-PEGs $_{4k,\ 8k,\ 20k}$ with wavelength.

Table (4.1): E_g^{opt} values for the allowed and forbidden indirect transition of PVA and blended polymer PVA-PEGs $_{4k,\ 8k,\ 20k}$ with wavelength.

Sample	Allowed (eV)	Forbidden (eV)
PVA	4.82	4.72
PVA-PEG_{4k}	4.55	4.35
PVA-PEG_{8k}	4.47	4.2
PVA-PEG_{20k}	3.35	2.7

4.4.3 Index of refractive (n), polarizability (P) and extinction coefficient (K_o) of PVA and blended polymer PVA-PEGs $_{4k,\ 8k,\ 20k}$.

The index of refractive (n), polarizability (P) and extinction coefficient (K_o) of PVA and blended polymer PVA-PEGs $_{4k,\ 8k,\ 20k}$ films were considered from the equations 2.7, 2.8 and 2.9 respectively. The evaluation of the refractive index is believed to be a critical factor when developing a variety of electronic devices, such as electronic, optical, and photonic applications. Figure (4.11) shows the dependence of refractive index on different molecular weight of the additive PEG. The refractive index was found to be increased almost gradually with the rising molecular weight of the additive PEG. Also, the graph shows that as the wavelength of light increases (particularly in the UV region), the refractive index of the films decreases . This may be attributed to the effect of lattice absorption [54].

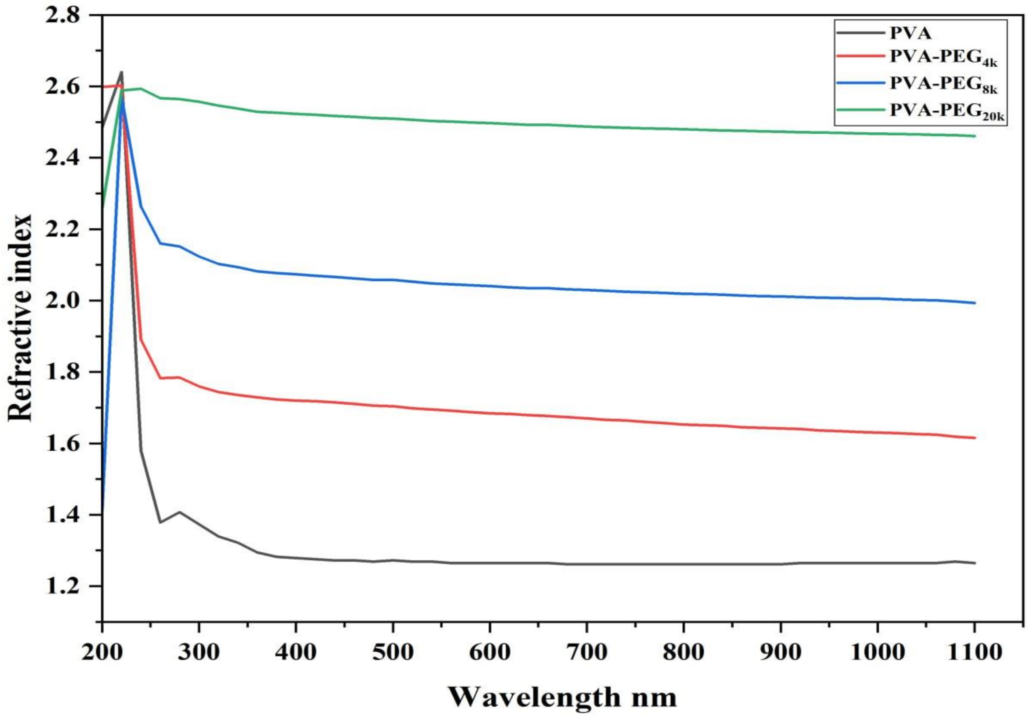

Figure (4.11): Variation of refractive index for PVA and blended polymer PVA-PEGs $_{4k,\ 8k,\ 20k}$ with wavelength.

According to the literature [55] the larger the polarizability, the greater the refractive index, and non-polarizing materials don't change the speed of light, and therefore n=1. Decreasing in the (E_g^{opt}) with the rising in the molecular weight of the additive PEG means that the electrons can move to other levels and thus an increase in the polarizability of the material , as shown in Figure (4.12) . A decrease in the polarization at UV region , towards increasing wavelength, is due to the inability of the dipoles formed to keep up with the high frequency (high energies).

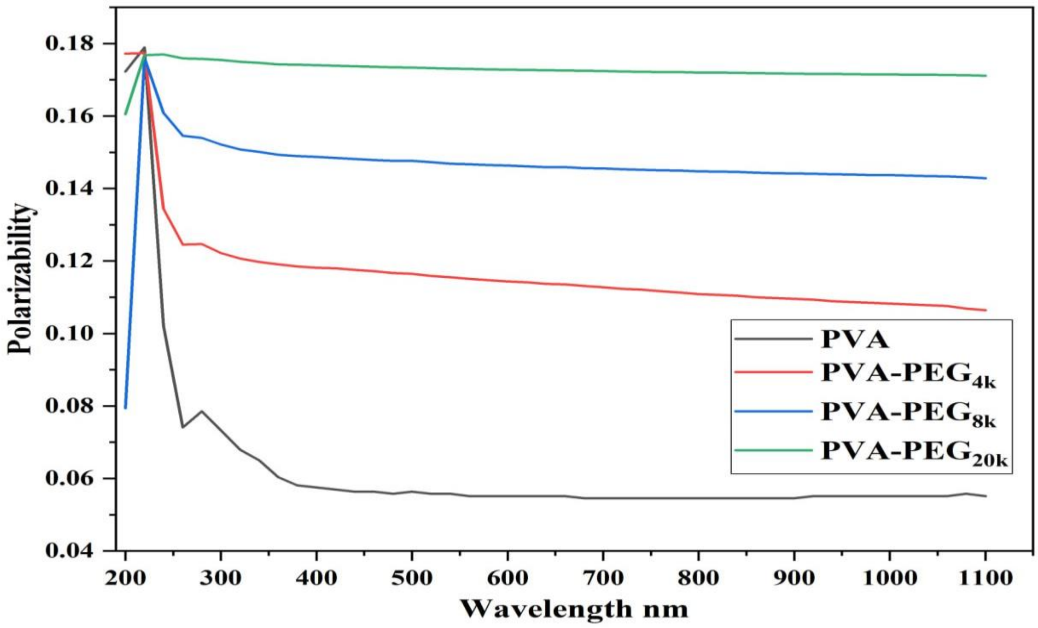

Figure (4.12): Variation of polarizability for PVA and blended polymer PVA-PEGs $_{4k,\ 8k,\ 20k}$ with wavelength.

Figure (4.13) shows the dependence of extinction coefficient on different molecular weight of the additive PEG. From observation of the figure, it can be notice that the extinction coefficient results of the blended polymer PVA-PEGs $_{4k,\ 8k,\ 20k}$ films are much larger than that of the pure polymer PVA in all regions. This result was directly depended on the absorption of light.

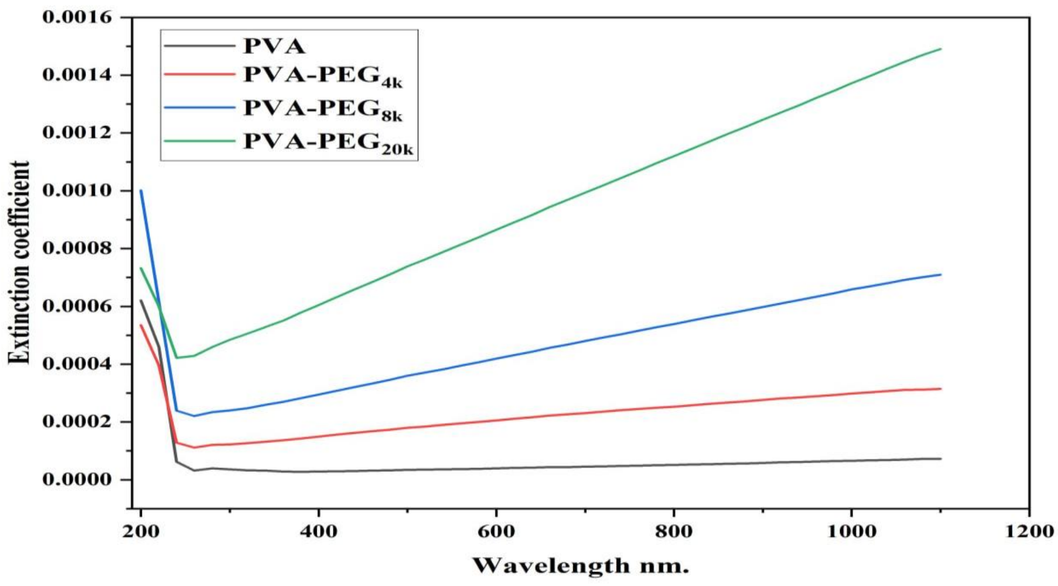

Figure (4.13): Variation of extinction coefficient for PVA and blended polymer PVA-PEGs $_{4k, 8k, 20k}$ with wavelength.

4.4.4 The real and imaginary parts of dielectric constant.

Dielectric constant of any solid is a measure of its polarizability [54]. The real and imaginary parts of dielectric constant are calculated using equations (2.10) and (2.11), respectively. The real part (ε_1) is attributed to the slowing down phenomenon of the speed of light in solid and the imaginary part (ε_2) pertains to dipole motion due to absorption of energy from electric field [56]. Figures (4.14) and (4.15) show the effect of adding the PEGs 4k, 8k, and 20k on the real and imaginary parts of dielectric constant of the prepared samples, respectively. For a given wavelength, ε_1 and ε_2 increasing with the rising in the molecular weight of the additive PEG in PVA film. As shown in the figures, the real and imaginary parts of dielectric constant were changed with the wavelength, this is due to the real part depending on refractive index and the imaginary part depends on extinction coefficient especially in the visible and NIR regions of wavelength where the refractive index is approximately constant while extinction coefficient increases with the increase of the wavelength.

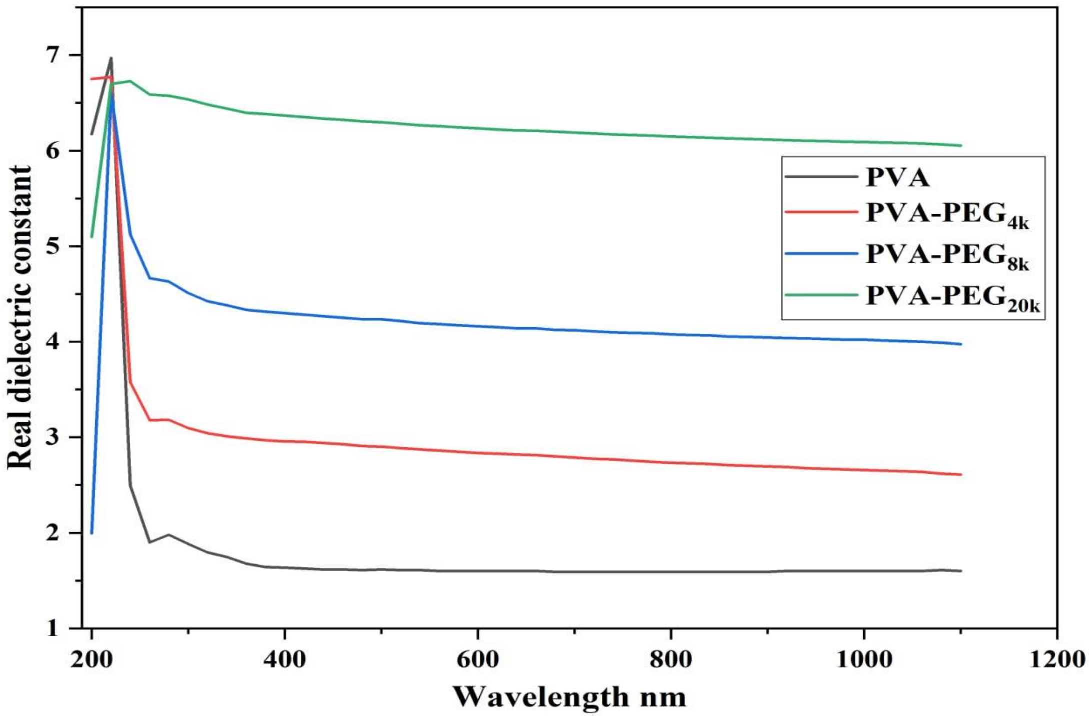

Figure (4.14): Values of real part of dielectric constant for PVA and blended polymer PVA-PEGs $_{4k,\ 8k,\ 20k}$ with wavelength.

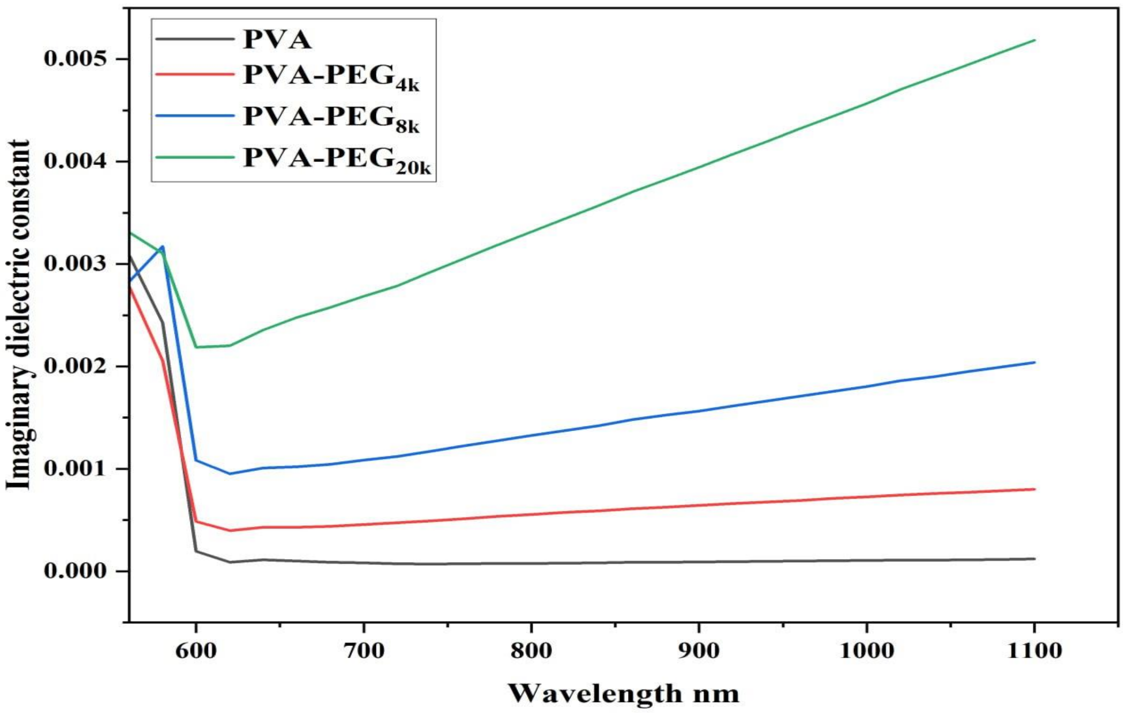

Fig (4.15): Values of imaginary part of dielectric constant for PVA and blended polymer PVA-PEGs $_{4k,\ 8k,\ 20k}$ with wavelength.

4.4.5 The optical conductivity

The study of a materials optical response is primarily focused on its optical conductivity. The optical conductivity (σ_{op}) is calculated using equation (2.13). Figure (4.16) shows the effect of adding the PEGs 4k, 8k, and 20k on the optical conductivity of the prepared samples, respectively. The results indicate that the optical conductivity of the prepared samples increases with the rising in the molecular weight of the additive PEG and reaches its highest value in the UV region. This tendency results from the band structure's localized stages becoming denser, which raises the absorption coefficient and, in turn, the optical conductivity.

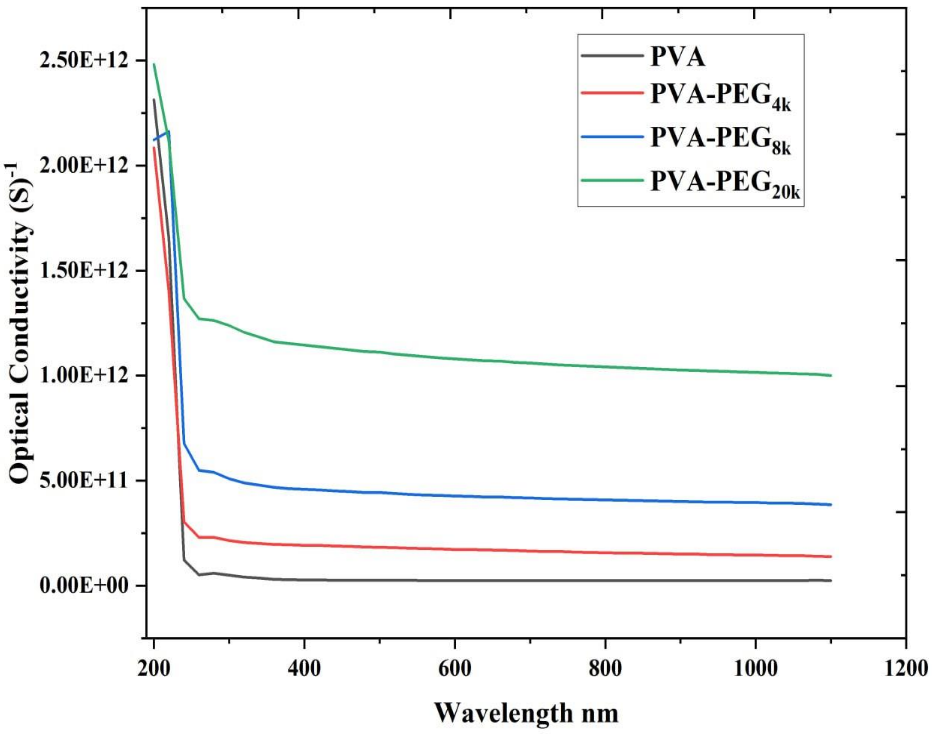

Fig (4.16): Variation of optical conductivity for PVA and blended polymer PVA-PEGs $_{4k, 8k, 20k}$ with wavelength.

4.5 Conclusions

At the end of the current study, the following conclusions are put forward:

1. The optical microscope images denote a network of paths charge transfer within the basics polymer (PVA) is formed when increasing the molecular weight of additive PEG up to 20k.

2. The analysis of FTIR spectra confirms the presence of functional groups belonging to the polymer systems.

3. Above 400 nm, the transmittance curves of all samples show a tendency towards saturation, and the highest rated average transmittance of the pure PVA film was ~ 95% in the Vis and NIR areas of spectrum, but it decreases almost gradually with the rising in the molecular weight of the additives, reaching ~ 55 at PEG_{20k}, which may be makes it convenient for UV shielding application.

4. One of the most significant outcomes of this research is the reduction in the energy gap for indirect transition (allowed, and forbidden) with the rising the molecular weight of the additive PEG. Important applications can come out of these resulted**.**

4.6 Future Works

Below are some ideas for future work to be conducted:

1. Study the rheological properties of polymeric blend PVA-PEG at different molecular weight.

2. Study the structural and electrical properties of polymeric blend PVA-PEG at different molecular weight.

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الخلاصة

يعتبر تـأثير إضـافة متوسط الأوزان الجزيئيـة للبـولي إيثيلـين جلايكـول ($_{4k \text{ ، } 8k}$ و $_{20k}$ PEGs) على الخصائص المورفولجيا والبصرية للـ PVA هو الهدف الرئيسي لهذه الدراسة. تشير صـور المجهر الضوئي (OM) إلى شبكة من مسارات نقل الشحنة داخل البوليمر الأساسي (PVA) الذي يتشكل عند زيادة الوزن الجزيئي لـ PEG الإضـافي حتـى 20k. يؤكد تحليل أطياف تحويل فورييـه للأشعة تحت الحمراء (FTIR) وجود مجموعات وظيفية تنتمي إلى أنظمة البوليمر. فوق 400 نانومتر، تُظهر منحنيات النفاذية لجميع العينات ميلًا نحو التشبع، وكان أعلى متوسط نفاذية مقدر لغشاء PVA النقي ~ 95% في مناطق Vis و NIR من الطيف، لكنه يتناقص تدريجيًا مع ارتفاع الوزن الجزيئي للمواد المضافة، حيث يصل إلى ~ 55 عند PEG_{20k}، مما قد يجعله مناسبًا لتطبيق الحماية من الأشعة فوق البنفسجية. من أهم نتائج هذا البحث هو تقليل فجوة الطاقة للانتقال غير المباشر (المسموح والممنوع) مع زيادة الوزن الجزيئي للبولي إيثيلين جلايكولPEG المضاف. كما تأثرت جميع العوامل الأخرى قيد البحث بالتغير في الوزن الجزيئي.