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تأثير ملح ($MnCl_2 \cdot 4H_2O$) على بعض الخصائص الفيزيائية للخليط
(PVA-PEO) المحضر بطريقة الصب

مرسالة مقدمة الى

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Effect of $(\text{MnCl}_2 \cdot 4\text{H}_2\text{O})$ Salt on Some Physical Properties of (PVA-PEO) Blend Prepared by Casting Method

A Thesis

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Abstract

In this study, films of pure [Polyvinyl Alcohol (PVA) - Polyethylene Oxide (PEO)] polymeric blends and reinforced by $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ salt with different weight ratios ((10, 20, 30, 40, and 50) wt%) were prepared using the solution casting method. Structural, optical, thermal, electrical (dielectric), mechanical, true density, apparent porosity, and water absorbency properties were studied for all polymeric blends films.

The effects of weight ratio of salt on structural properties for all reinforced polymeric blends films were studied, the X-ray diffraction results showed of pure polymer blend film [PVA-PEO] in the range ($2\theta=10^\circ-70^\circ$), shows well-defined broad peaks at around ($2\theta = 19.11^\circ$ and 23.32°), which indicates a semicrystalline nature. FTIR spectra were used to establish the interaction between the polymer (PVA) and the polymer (PEO) reinforced by $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ salt, which causes some changes in the vibration modes and the position of the bonds. All investigated samples exhibited broad bands at around (3310 cm^{-1}). The results showed the asymmetric vibration of O-H group in the polymers matrix. The peaks around (2880 cm^{-1}) can be attributed to the presence of C-H stretching vibration group. The C=C stretching vibration appears in the bonds at (1955 cm^{-1}). The peak at (1096 cm^{-1}) for all reinforced films is attributed to the stretching mode of C-O-C stretching. There is a shift of out-of-plane rings C-H bending vibration from (961.2 to 955 cm^{-1}). These indicate the chemical interactions of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ salt with the polymeric blend [PVA-PEO]. The two strong bands observed around (1471 cm^{-1} and 844 cm^{-1}) are assigned to the bending and stretching vibration of the CH_2 group, respectively. The change in the spectral

intensities of polymeric blend [PVA-PEO] involves a shift in some bonds due to the $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ salt addition.

The effects of weight ratio of salt on optical properties for all reinforced polymeric blends films were studied, as the transmittance and absorbance spectra were recorded within the range of wavelengths (190-1100) nm, and it was found that the energy gap value decreases with an increase of the added salt's weight ratio. Results showed that the indirect electronic transitions are allowed.

The effects of weight ratio of salt on thermal properties for all reinforced polymeric blends films were studied, and the practical results showed that the value of the thermal conductivity coefficient (k) increases at a weight ratio of (10 wt%) of added $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ salt, reaching a value of (0.000474 W/m.K). Afterward, it starts to decrease consistently with an increase in the weight ratio of added $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ salt, and test with a calorimeter differential analysis (DSC) for all reinforced polymeric blends films showed that the glass transition temperature (T_g) value begins to decrease irregularly with an increase in the weight ratio of added salt, and the crystalline melting temperature (T_m) value changes in an irregularly behavior compared to the pure polymeric blend film [PVA-PEO] with an increase in the weight ratio of added salt

Effects of salt's weight ratio on electrical (dielectrical) properties for all reinforced polymeric blends films were studied, and the practical results showed a decrease in the dielectric constant (ϵ') with an increase in frequency for all polymeric blends films, while the practical results also showed an increase in the alternating electrical conductivity ($\sigma_{a.c}$) with increasing frequency for all polymeric blends films, as well as an increase

Chapter One
Introduction & Literature
Review

(1.1) Introduction

Polymeric materials have been receiving great research attention due to their advantages, such as light-weight, low-cost, high flexibility, good mechanical properties, and ease of fabrication in thin film form [1]. These properties make them ideal materials for a broad range of applications in optical, biomedical, and electronic devices [2]. It has been established that the features of the polymeric materials depend mainly on the composition and attachment of monomers; therefore, many research groups have attempted to manipulate the characteristics of polymers to create materials with specific chemical, physical and biological properties for a particular application [3]. Currently, the research interests have been focused on the solid polymer electrode-based films, because of the possible application in organic solar cells, sensors, and electrochemical devices [1–3].

A composites material is a mixture of two or more distinct materials usually a binder material (matrix) and reinforcement. In general, resultant properties of composites materials are better than those of constituent materials and it has recognizable interphase. There are different types of composites material classification: macro-composites, micro-composites and an composites. Macro-composites are conventional composites such as glass, black carbon and Kevlar reinforced polymers. Macro composites are more superior to micro-composites but the nano composites are classified as new materials, it is defined as multiphase materials where at least one of the constituent phase has one dimensional less than (100 nm) [4-6].

(1.2) Polymers

Polymers constitute a wide range of materials which are derived at least in part from organic raw materials; they consist of repeating molecular units and

have special properties obtained by engineering the form of the molecular structures. Polymers are used as engineering materials in the neat form, i.e., as the pure material, or in combination with a large diversity of additives, both organic and inorganic. These additives may be, among others, plasticizers which reduce the rigidity or brittleness of the material, fillers which increase strength or stabilizers which protect the polymer against ultraviolet radiation [7,8].

(1.3) Classification of Polymers

(1.3.1) Thermal Classification of Polymers

Polymers are classified according to the effect of temperature to:

(1.3.1.1) Thermoplastic Polymers

The properties of these polymers are changed by the effect of temperature. When the temperature increases, they become flexible and sticky, by lowering the temperature, these polymers return to their original solid state. This is because the molecules in a thermoplastic polymer are connected by relatively weak intermolecular forces (Vander Waals forces). When heated, these molecules can slide over each other as in polystyrene, polyethylene, polypropylene, poly (vinyl alcohol) and poly vinyl chloride [9].

(1.3.1.2) Thermoset Polymers

These polymers are chemically changed when heated. Thermo sets are usually three-dimensional networked polymers in which there is a high degree of cross-linking between polymer chains. After being heated, these polymers become insoluble, hard, non-conductive of heat and electricity because molecules of these polymers are connected by strong covalent chemical bonds. Phenol formaldehyde resin and urea-formaldehyde resin are examples of this type of polymers [10,11].

(1.3.2) Chemical Classification of Polymers

Polymers are classified depending on the structural composition to [12]:

(1.3.2.1) Linear Polymers

The essential structural unit for these polymers is one molecular series of certain length connected with each other in a linear shape, it does not contain the branch except the totals twisted which are part of monomer, as in figure (1.1.a).

(1.3.2.2) Branched Polymers

Here the long chain is branching and it is characterized by this type of installation that the branches are as a ladder or a comb or as a crusader. The branches have different lengths, as in figure (1.1.b).

(1.3.2.3) Cross Linked Polymers

In this type, the chemical bonds are interwoven with each other in a complex way. The format string consists of three dimensional polymer chains linked together by more than one site, or when we use monomers containing effective totals rather than being included in two effective totals, as in the figure (1.1.c).

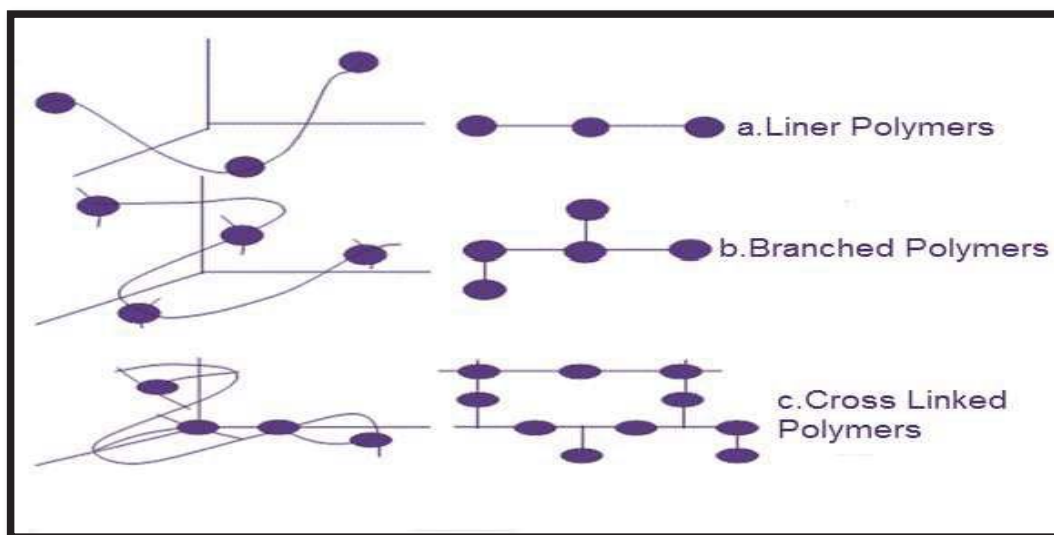


Figure (1.1): The different types of polymeric chains [13].

(1.4) Characteristics of Polymers

The characteristics of polymers are [14]:

- 1- Low density.
- 2- Low coefficient of friction.
- 3- Good corrosion resistance.
- 4- Good mould ability.
- 5- Excellent surface finish can be obtained.
- 6- Can be produced with close dimensional tolerances.
- 7- Economical.
- 8- Poor tensile strength.
- 9- Low mechanical properties.
- 10- Poor temperature resistance.
- 11- Can be produced transparent or in different color.

(1.5) Polymer Blends

Polymer blend is a mixture of two or more polymers in the required amounts, with no covalent bonds between them or that are not bonded to each other [15,16]. Two or more existing polymers may be blended for various reasons. One reason is to achieve a material that has a combination of the properties of the constituents, e.g. a blend of two polymers, one of which is chemically resistant and the other tough. Another reason is to save costs by blending a high – performance polymer with a cheaper material. A very important use of blending is the combination of an elastomer with a rigid polymer in order to reduce the brittleness of the rigid polymer. It is in the latter use that the self- organizing feature of some blends is seen to play a part. This feature arises when the components of the blend are incompatible, i.e. They do not mix, and they segregate into different regions within the

material [17]. Therefore, blending of polymers are excellent methods for modification and improvement of polymer properties. The most intimate form of mixing is at the molecular level, two substances that have mixed at this level may each be said to have dissolved in the other. If the molecules have similar sizes, each type of molecule is then surrounded, on average, by molecules of the two types in proportion to the component ratio of the two polymers in the mixture [18,19].

Polymer blends are often referred to by the contraction "Poly blends" and sometimes as "Alloys" to borrow a term from metallurgy [20]. Blends and alloys have revolutionized the plastic industry, as they offer new materials with properties never before available and materials that can be tailored for specific end uses [21]. Preparation of polymer blends can be accomplished by [22]:

- 1- Mechanical mixing.
- 2- Dissolution in co-solvent thin film casting freeze or spray drying.
- 3- Latex blending.
- 4- Fine powder mixing.
- 5- Use of monomer as solvent for another blend component then polymerization as in interpenetrating polymer networks "IPN's". Diverse other methods of IPN technology.

(1.6) Polymeric Composites

Polymeric composites are materials in which a second component with very different properties added to the polymer, so that both components contribute to the properties of the product . The second component which increases the strength or stiffness of the product called reinforcement material. Particulate materials such as carbon black are often used to reinforce elastomers, but fibers are usually used for reinforcing other types of polymer. Glass or

carbon fibers are often used, but polymeric fibers are appropriate for some applications, such as metallic filaments. The fibers are often aligned in one direction within a matrix of polymer, which gives the material anisotropic properties. Materials that are isotropic in one plane can be produced by using layers with the fibers aligned in different directions within the plane, or by using mats of chopped fibers as the reinforcement [18,23]. The composites are made up of matrix and reinforcement materials [24]. Doping of polymers attracted the scientific and technological researchers, because of their wide applications. The dopant in polymer can change the molecular structure and hence the microstructure as well as macroscopic properties of the polymer [25].

(1.7) Components of Composite Materials

There are two primary components of overlays:

(1.7.1) Matrix Material

The base material is the primary constituent of the overlaid material that encloses and keeps it in place with the reinforcement materials. Consequently, it stands in for the bonding material, as it helps to connect, and cohere the reinforcing material into an overlapping, and coherent system that can withstand the external forces acting against it. Base materials have an advantage over reinforcing materials due to their lower modulus of elasticity, hardness, and resistivity. The density, thermal, and electrical conductivity, thermal expansion ability, melting point, degree of transparency or opacity, ease of production, and relatively low cost are all factors that go into selecting the base material, which can be polymeric, metallic or ceramic [26,27].

(1.7.1.1) Polyvinyl Alcohol (PVA)

Polyvinyl alcohol (PVA) is the largest synthetic water soluble polymer produced in the world [28]. The physical characteristics of (PVA) are dependent on its method of preparation from the hydrolysis or partial hydrolysis process of polyvinyl acetate [29].

Because of (PVA) is a polymer obtained by the hydrolysis process, the (PVA) has particularly notable properties than other thermoplastic. Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer. Due to the characteristics of easy preparation, we have good biodegradability, excellent chemical resistance and good mechanical properties, also used on many biomaterial applications [30].

(1.7.1.2) Polyethylene Oxide (PEO)

Poly ethylene oxide (PEO) is one of the most intensely studied polymers in current materials science and biotechnology because of not only its unique behaviors in solution but also its wide applications [31,32]. The key properties of (PEO) are its soft semi-crystalline thermoplastic that displays a lot of interesting properties and finds many applications due to the wide range of molecular weight in which it is commercially available ($10^2 - 8 \times 10^6$ g/mol), chemical stability, solubility both in water and many organic solvents, non-toxicity, rapid clearance from the body, lack of immunogenicity and a Food and Drug Administration (FDA) approval for internal consumption. Films of high molecular weight (PEO) are tough, ductile, heat-sealable, and because of their high degree of crystallization, resist well to atmospheric moisture [33].

(1.7.2) Reinforcement Material

Reinforcement materials are additives used to improve the strength of a material without changing its molecular structure [25].

The support materials can be polymeric, ceramic, or mineral salt and the enhanced properties of these materials include increased thermal conductivity, decreased coefficient of thermal expansion and contraction, increased lifetime, increased hardness, wear resistance, modified electrical properties, increased chemical resistance, increased resistance to solvents, and the ability to impart color to the material [34,35]. It can be categorized as natural or artificial, organic or inorganic, fibers, particles, flakes or plates, or a network of these materials (cross-species hybridization). Alternatively, they are synthetic materials grafted upon natural ones, or vice versa [25,11].

(1.7.2.1) Manganese Chloride

Manganese (II) chloride is the dichloride salt of manganese, MnCl_2 . This inorganic chemical exists in the anhydrous form, as well as the dehydrate ($\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$) and tetra hydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$), with tetra hydrate being the most common form. Like many MN (II) species, these salts are pink, with the paleness of the color being characteristic of transition metal complexes with high spin d^5 configurations [36].

(1.8) Literature Review

❖ Elashmaw *et al.*, in (2014) studied the modification and development of electrical and magnetic properties of (PVA/PEO) incorporated with MnCl_2 , using a casting method, (PVA/PEO) films with different amounts of MnCl_2 were made, and their electrical and magnetic properties were studied. The magnetic properties of the material were looked at with electron spin resonance (ESR) and a vibrating sample magnetometer (VSM). Because of an increase in the number of mobile charge carriers of Mn^{+2} , the electrical conductivity was boosted, and this improvement depends on both

frequencies and temperatures. The correlated barrier hopping (CBH) model has been used to determine the A.C conduction process and conduction parameters. The (ESR) spectrum shows that at high concentrations, aggregated Mn^{+2} ions form, while at low concentrations, the ions remain separated. Due to the overlap of the Mn d-states with the valence band, the (VSM) reveals a paramagnetic nature for pure $MnCl_2$ and an anti-ferromagnetic nature for doped samples [37].

❖ **Abdullah et al., in (2015)** studied the complex formation in (PVA/PEO/ $CuCl_2$) solid polymer electrolytes was studied by casting method was used to make solid polymer electrolyte films from polymer blends of poly(vinyl alcohol) (PVA) and poly(ethylene oxide) (PEO) with different concentrations of copper (II) chloride ($CuCl_2$). FT-IR (Fourier transform infrared) and UV-Vis (ultraviolet-visible) spectroscopy were used for optical studies by changing the amount of $CuCl_2$, the optical features of these films were changed. The results show that as the salt concentration goes up, the absorption edge for electrolyte samples moves toward a lower energy region. This makes the band gap smaller. The results on the band gap energy showed that when $CuCl_2$ is added to a polymeric system, charge transfer complexes form in the blended polymer. These complexes increase the electrical conductivity by adding more charges to the lattice. In the wavelength range of (190 to 400 nm), the (PVA/PEO/ $CuCl_2$) solid polymer electrolyte plates are good at blocking (UV) light [38].

❖ **Abdelghany et al., in (2015)** studied the structural and thermal stabilization correlation of (PEO/PVA-AgCl) polymer composites, polyvinyl alcohol (PVA) and polyethylene oxide (PEO) with the same mass were used to make homogenous polymer mixes. Different concentrations of

AgCl were used to fill the polymeric matrix with the help of in situ preparation methods. Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and thermal analysis using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to study samples that had been filled. The samples were heated at a steady rate of (10 °C/min) in an inert gas atmosphere. FTIR bands were used to look at changes in the structure of (PVA/PEO) blends with up to (12%) AgCl and figure out what those changes mean. It has been found that the way characteristic temperatures change as a function of filler makeup is not a straight line. The results showed that AgCl works as a promoter that slows down degradation and makes the composite more stable as a whole. DSC thermograms showed that the second result was true [39].

❖ *Aziz et al., in (2017)* described the optical properties of pure and doped (PVA:PEO) based solid polymer blend electrolytes: two methods for band gap study, with the solution casting method, solid polymer-blend electrolyte sheets made from (PVA:PEO) have been made. It was seen that the absorption got stronger as the amount of aluminum salt got higher and moved to longer wavelengths. The fact that the absorption edge moved to a lower photon energy shows that the polymer blends and the aluminum salt respond well to each other, which means that the energy band gap should narrow. There has been a change in the refractive index of the treated samples. The linear link between the refractive index and the volume fraction of the added salt makes it easy to see how the aluminum salt can mix with the polymer blends. At high wavelengths, it was seen that the extinction rate went up [40].

❖ **Choudhary in (2017)** described the dielectric dispersion and relaxations in (PVA–PEO)–ZnO polymer nanocomposites, were prepared by the aqueous solution-cast method. The organic-inorganic nanocomposite materials were made by pouring zinc oxide nanoparticles into a mixture of poly(vinyl alcohol) (PVA) and poly(ethylene oxide) (PEO) in an aqueous solution. Dielectric relaxation spectroscopy (DRS) was used to study the dielectric dispersion and relaxation processes in (PVA–PEO) and (ZnO) films ($x = 0, 1, 3$ and 5 wt%) from (20 Hz to 1 MHz). ZnO effects on these (PNC) materials' complicated dielectric permittivity, electrical conductivity, electric modulus, and impedance have been investigated. ZnO content in the (PVA–PEO) mix matrix at ambient temperature greatly affects the polymers cooperative chain segmental motion dielectric permittivity and relaxation time values. The temperature-dependent relaxation periods and dc conductivity of (PVA–PEO/3wt% ZnO) film follow arrhenius. The film's dielectric permittivity varies linearly with temperature at radio frequencies but non-linearly at lower audio frequencies. X-ray diffraction shows that adding (1 wt%) from ZnO nanoparticles to the polymer blend matrix greatly reduces its crystalline phase. These (PNC) materials have low dielectric permittivity and electrical conductivity, making them suitable as novel flexible-type polymer nano dielectrics for microelectronic device insulation [41].

❖ **Mohamed *et al.*, in (2018)** studied the preparation and characterization of polymer blend (PVA/PEO) filled with methyl orange (MO) thin films, polymers blend (PVA/PEO) filled with different weight percent ratios of methyl orange was used to prepare films via casting method. Structural properties of the final thin films were carried out using (XRD) technique, (FTIR) and optical microscope. While the absorption

spectra of these films were measured using (UV-VIS) double beam spectrometer in the wavelength range of (190-1100 nm). The optical coefficients such absorption coefficient and extinction coefficient were calculated from the optical absorption. Direct and indirect allowed electronic energy transitions were studied under the influence of MO weight percent variation (0, 10, 20, 30, 40 and 50 wt %) [42].

❖ **Hashim *et al.*, in (2019)** studied the synthesis and characterization of flexible resistive humidity sensors based on (PVA/PEO/CuO) nanocomposites, were prepared by using casting method. The prepared humidity sensors have lightweight, low cost, flexible and high sensitivity compare with other humidity sensors. The results showed that the nanocomposites have high absorption in (UV) region. The absorbance of (PVA–PEO) blend increases with increase in CuO nanoparticles concentrations which may be used for solar cell, transistors, diodes and other electronic applications. The optical constants increase while the transmittance and energy gap decrease as CuO nanoparticles concentrations increase. The results of application showed that the (PVA–PEO–CuO) nanocomposites with different copper oxide nanoparticles concentrations have high sensitivity for relative humidity which may be used as sensors for different humidity ranges [43].

❖ **Hadi *et al.*, in (2020)** studied the structural, optical and electrical properties of (PVA/PEO/SnO₂) new nanocomposites for flexible devices, were prepared by solution casting method. The prepared nanocomposites have low cost, lightweight, flexible, high corrosion resistance, good optical and electrical properties. These properties of fabricated nanocomposites make it useful for different optoelectronics applications such as: sensors,

solar cells, transistors, diodes, capacitors, energy storage etc. The structural, optical and electrical properties of (PVA–PEO–SnO₂) nanocomposites have been studied. The experimental results of optical properties for (PVA–PEO–SnO₂) nanocomposites showed that the nanocomposites have higher absorbance in (UV) region at wavelength range (200–280 nm). This behavior makes the nanocomposites may be used for optoelectronics applications. The absorbance, absorption coefficient, extinction coefficient, refractive index, real and imaginary dielectric constants and optical conductivity of polymer blend are increased with the increase in SnO₂ nanoparticles concentrations while the transmittance and energy band gap are decreased with the increase in SnO₂ nanoparticles concentrations. The decrease in energy band gap is useful for different optoelectronics devices industries. Also, the results showed that the dielectric constant and dielectric loss decrease while the conductivity increases with the increase in frequency. The dielectric constant, dielectric loss and conductivity are increased with the increase in SnO₂ nanoparticles concentrations. The electrical properties showed that the (PVA–PEO–SnO₂) nanocomposites have good dielectric parameters which it may be used for different electronics applications [44].

❖ **Ahmed and Hashim in (2021)** studied the geometry optimization, optical and electronic characteristics of novel (PVA/PEO/SiC) structure for electronics applications, by using density functional theory (DFT), the electronic characteristic which contain total energy, cohesive energy, (HOMO, LUMO), ionization potential, energy gap, softness, electronic affinity, hardness, electronegativity and electrophilicity. The spectroscopic properties (IR, NMR and UV) for (PVA-PEO-SiC) (56 Atom) were investigated at the same large level of theory. DFT calculations of (1H

NMR) chemical shifts on (PVA-PEO-SiC) (56 Atom) showed a higher shielding of (PEO). The results indicate to the (PVA-PEO- SiC) have excellent optical and electronic properties with low energy band gap which make it suitable for various optoelectronics applications [45].

❖ **Ahmad *et al.*, in (2022)** studied the characterization of As-prepared (PVA-PEO/ZnO-Al₂O₃) NPs hybrid nanocomposite thin films, were prepared by solution casting method, optical, mechanical, and structural characterization of organic–inorganic nanocomposite thin films based on polyethylene oxide (PEO) and polyvinyl alcohol (PVA) polymers incorporated with (1:0), (0.75:0.25), (0.5:0.5), (0.25:0.75), and (0:1) content percentage ratios of ZnO-NPs:Al₂O₃-NPs nanoparticles are reported. The optical properties, including the absorption coefficient, refractive index, extinction coefficient, dielectric function, and optical band gap for the films, are investigated from the measured transmittance and reflectance using a newly derived mathematical model. The as-grown (PVA-PEO) polymeric thin films exhibit transmittance of (87%) while it decreases down to (75%) with ZnO-NPs and decreases in between by the addition of Al₂O₃-NPs. However, the refractive index increases from (2.0) with ZnO-NPs to (2.7) with Al₂O₃-NPs. The band gap energy is from (3.98 to 3.89 eV) accordingly. The dislocation density,, crystallite size, and average internal strain obtained from the X-ray diffraction (XRD) patterns exhibit abnormal behavior for equal ratio (0.5:0.5) of the two types of NPs compared with other ratios. Fourier transform infrared (FTIR) spectroscopy measurements to elucidate the major vibrational modes and bonding in the nanocomposite thin films. A redshift of the major peaks has been observed for all investigated compositional ratios indicating a shift of the absorption edge

confirming the band gap reduction. The scanning electron microscope (SEM) micrographs show a clear form of nanocomposites with (PVA-PEO/ZnO-NPs) compared to those when Al₂O₃-NPs or a combination of the two kinds of NPs are introduced to the complex matrix. Our detailed analysis of the physical properties of (PVA-PEO/ZnO-Al₂O₃) indicates their potential to be candidate materials for modern optical and optoelectronic devices [46].

❖ **Ragab in (2022)** studied the influence of graphene oxide on the optical, thermal, electrical and dielectric properties of (PVA/PEO) composite. Samples of polyvinyl alcohol and polyethylene oxide (PVA/PEO) loaded with different quantities of graphene oxide nanosheets (GO) were created using the casting technique. Various techniques were used to characterize the produced samples, including (XRD, FTIR, SEM, UV/Vis, DSC, TGA) and dielectric characteristics. XRD verified the semicrystalline structure of the (PVA/PEO) blend, with crystallinity decreasing as the GO nanosheets percentage increased. With the decreasing frequency and varied concentrations of GO nanosheets, the (FTIR) absorption spectra demonstrate a shift in peak locations and intensity fluctuations. The crystalline regions have a roughly spherical shape, as shown in (SEM) pictures. The optical band gap (direct and indirect) is calculated using (UV–Vis) spectra, which decreases with increasing dopant concentration. The single glass transition temperature (T_g) is seen in the (DSC) analysis, indicating that PVA and PEO are miscible. The inclusion of filler changes the amorphous phase, resulting in a variation in melting temperature (T_m). The dynamic ion activity of the produced samples was determined using the frequency-dependent composite films (A.C conductivity). At various concentrations and room temperatures (RT), the

dielectric constant (ϵ'), dielectric loss (ϵ''), and ($\tan\delta$) versus frequency graphs were also obtained. The ionic conductivity of composite (PVA/PEO/GO) samples increased at room temperature with the addition of graphene oxide reaching a maximum of (10^{-9} S/c) [47].

❖ **Elashmawi *et al.*, in (2022)** studied the structural, optical and dielectric modulus properties of (PEO/PVA) blend filled with metakaolin (MK). The (PEO/PVA) blend incorporated by different weight percentages ($\leq 10\%$) of metakaolin (MK) has been prepared by solution casting method. The (XRD) revealed a semicrystalline structure of pure (PEO/PVA) with peaks indicating the presence of silicon and aluminum in the MK composition. The addition of MK in the blend leads to a decrease in the diffraction peak intensities, confirming that the blend-MK interactions break some (PEO/PVA) blend domains. The (UV-Vis) transmittance and reflectance spectra were studied and used to determine optical parameters. The decrease in the band-gap values was demonstrated with the increase in MK to confirm the suitability of MK as a band-gap regulated the optical material in different applications. The obtained values of the optical band gap decrease with the increase of MK concentration due to the defect levels that correlate to the sample's density of localized states. The higher values of ϵ' found at a lower frequency related to the effect of the dominant contribution of the interfacial polarization due to the accumulation of charges, whereas the higher values of (ϵ'') at the lower frequency were related to an increase in the energy loss in the composite films. The Cole-Cole plot displays semicircles at the lower frequency range with a linear increase at the intermediate and higher frequency due to the grain boundary and the relaxation process. The values of the real part (σ') are lower than that of the corresponding values of the imaginary part (σ''). Applied an

electric field causes polarized films and the ability to store an electric charge [48].

❖ **Saber *et al.*, in (2023)** studied the Influence of Eu^{+3} on the structural, optical and electrical properties of (PEO–PVA) dual band gap materials for optoelectronic applications, ($\text{Eu}^3/\text{PEO–PVA}$) was prepared by solution casting. The impacts of Eu^{+3} content on the microstructure, chemical composition and complexation with the functional groups of the blend as well as on the film morphology were evaluated by (XRD), (FT-IR) spectroscopy and (FE-SEM) microscopy. It was revealed that the film's crystallinity and optical transmittance can be tailored by Eu^{+3} content. Tauc's method illustrated that the films exhibit dual band gaps on both the low energy side (2.0–2.8 eV) and the high energy side (4.0–4.38 eV). In addition, the refractive index and optical conductivity of (SPE) were greatly enhanced with increasing Eu^{+3} content. The current–voltage characteristic curves were recorded at an applied voltage range of (0–10 V), and temperature range of (30–100 °C). The materials exhibited non-Ohmic behavior. The DC conductivity (σ_{dc}) values of the pure and (6wt%) Eu^{+3} doped blend were in the range of (1.16×10^{-6} – 2.05×10^{-6} S/cm) and (1.73×10^{-6} – 3.36×10^{-6} S/cm), respectively. The relations between the current density and the electric field revealed that the schottky emission is the most suitable conduction mechanism [49].

(1.9) Aim of The Study

Preparation of a polymeric composite films based on a polymeric blend of [PVA-PEO] reinforced by manganese chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) salt with different weight ratios ((10, 20, 30, 40, 50) wt%) using the casting method. And study the effect of varying weight ratios of manganese chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) salt on: some structural properties, including (Fourier-transform

infrared spectroscopy (FTIR) and X-ray diffraction (XRD)), and some optical properties, including the optical energy gap (E_g), and some thermal properties, including (thermal conductivity coefficient (k), glass transition temperature (T_g), and crystalline melting temperature (T_m)), in addition, some dielectrical properties, including (dielectric constant (ϵ') and alternating electrical conductivity ($\sigma_{a.c}$)), and some mechanical properties, including (hardness, impact, and tensile), also the (true density, apparent porosity, and water absorbance).