



Fabrication, Structural and Optical Properties for (Polyvinyl Alcohol–Polyethylene Oxide– Iron Oxide) Nanocomposites



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NANOCOMPOSITES were usually used for different fields in an industrial applications with low cost and low weight. In this paper, nanocomposites from polyvinyl alcohol-polyethylene oxide- iron oxide nanoparticles have been fabricated. The iron oxide nanoparticles were added to polymer blend by different weight percentages are (2, 4 and 6) wt.%. The structural and dielectric properties of (PVA-PEO-Fe₂O₃) nanocomposites were studied. The results showed that the dielectric constant, dielectric loss and electrical conductivity of (PVA-PEO) blend are increased with the increase in iron oxide nanoparticles concentrations. The dielectric constant and dielectric loss are decreased while the electrical conductivity increases with the increase in frequency of applied electric field. The optical measurements showed the absorbance of (PVA-PEO-Fe₂O₃) nanocomposites is increased with increasing of the concentrations of iron oxide nanoparticles. The indirect energy gap (E_g) of (PVA-PEO) blend decreases with the increase of the concentrations of iron oxide nanoparticles. The optical constants such as absorption coefficient, extinction coefficient, refractive index, real and imaginary dielectric constants and optical conductivity of (PVA-PEO) blend varied with the increase of the weight percentages of iron oxide nanoparticles.

Keywords: Conductivity, Nanocomposites, Dielectric properties, Polymer blend, Iron oxide, Energy gap, Extinction coefficient.

Introduction

Composite materials based on a polymeric matrix with embedded metal nanoparticles have gain attention due to their properties such as electrical, mechanical, optical and chemical properties that can be used in the development of biomedical devices, solar cells, sensors, capacitors among others. A hybrid material consists of soluble polymers with inorganic component with excellent mechanical, optoelectronics and dielectric properties due to the combination of the organic and inorganic components, and it can be deposited as a thin film in different substrates. Therefore, the number of contributions in the development of hybrid composites based on polymers and nanoparticles with high permittivity, low cost, and easily tunable properties, have become a hot topic in the research of materials [1]. Usually, polymer materials have desirable high

breakdown strength and easy processability, but they have undesirable low dielectric permittivity and poor heat tolerance, caused by their covalent bond structures. Contrary to polymer materials, high-k ceramic materials have a favorable high permittivity and strong thermal resistance, but they have an undesirable low breakdown strength and high mechanical brittleness, that stems from their ionic bond structures. Nowadays, the hybridization strategy has been widely used to achieve high-performance materials. Therefore, the composite dielectric materials prepared via blending polymer and high-k ceramic have been largely developed to combine the advantages of both components. In these composite dielectrics, adding high-k ceramic with a higher Young's modulus compared to the polymer would improve the mechanical strength of the polymer and thus the electrical breakdown strength of the polymer.

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Furthermore, the processability of composite dielectrics would be well retained, attributed to a low Young's modulus (namely high flexibility) of the polymer component [2]. Polymers and particularly hybrid composites (organic–inorganic) are attracting increasing attention from researchers because of their use in many industrial sectors [3]. Polyvinyl alcohol is an essential polymer, due to its physical and chemical features and so it attracted researchers' attention over the years. This polymer can be a powder, film and fiber forms. It has a semi-crystalline nature arises from the role of OH group and the hydrogen bonds. Due to its low protein adsorption characteristics, biocompatibility and high water solubility, PVA is commonly used in medical devices [4]. Poly(ethylene oxide) is a semi-crystalline, biocompatible, biodegradable, nonionic and water-soluble polymer of considerable industrial significance, which finds applications in many different branches of industry. It is commercially available in a wide range of molecular weights (20000–8000000) [5].

Materials and Methods

Nanocomposites films prepared from polyvinyl alcohol- polyethylene oxide- iron oxide nanoparticles by using casting method by dissolving 1 gm of (PVA and PEO) in 20 ml of distilled water by using magnetic stirrer for 1 hour. The iron oxide nanoparticles were added to polymer blend with concentrations are (2, 4 and 6) wt.%. The dielectric properties of (PVA-PEO-Fe₂O₃) nanocomposites were measured in frequency range from 100 Hz to 5 × 10⁶ Hz by using LCR meter type (HIOKI 3532-50 LCR HI TESTER). To measure the optical properties of (PVA-PEO- Fe₂O₃) nanocomposites in range of wavelength (200-1100) nm, The UV/1800/ Shimadzu spectrophotometer device has been used. FTIR spectra for nanocomposites were recorded by FTIR (Bruker company, German origin, type vertex—70) in wave number range 400–4000 cm⁻¹.

The dielectric constant (ϵ') of nanocomposites is defined by the equation [6]:

$$\epsilon' = \frac{C_p}{C_o} \dots\dots\dots(1)$$

Where, C_p is parallel capacitance and C_o is vacuum capacitor

The dielectric loss (ϵ'') is given by the equation [6]:

$$\epsilon'' = \epsilon' D \dots\dots\dots(2)$$

where, D : is dispersion factor of nanocomposites.

The A.C electrical conductivity is determined by the following equation [7]:

$$\sigma_{A.C} = w \epsilon'' \epsilon_o \dots\dots\dots(3)$$

Where, w is the angular frequency.

Absorption coefficient (α) is calculated as the following equation:

$$\alpha = 2.303 (A/t) \dots\dots\dots(4)$$

A : is the absorbance. For amorphous polymers, indirect transition model can be computed as:[8].

$$\alpha h\nu = D(h\nu - E_g)^x \dots\dots\dots(5)$$

Where D is a constant, $h\nu$ is the photon energy, E_g is the optical energy band gap, $x = 3$ for forbidden indirect transition and $x = 2$ for allowed indirect transition.

Refractive index (n) is determined by following equation:

$$n = \dots\dots\dots(6)$$

Where R is the reflectance, can be got by :

$$R = 1 - A - T \dots\dots\dots(7)$$

The extinction coefficient (k) is determined by the following equation:

$$k = \dots\dots\dots(8)$$

Where λ is the wavelength of incident light. The dielectric constant is classified into two parts real (ϵ_r), and imaginary (ϵ_{im}). It can be computed each of the real and imaginary parts of dielectric constant (ϵ_r and ϵ_{im}) as the following equations:

$$\epsilon_r = n^2 - k^2 \dots\dots\dots(9)$$

$$\epsilon_{im} = 2nk \dots\dots\dots(10)$$

Optical conductivity (σ_{op}) can be determines as:[9].

$$\sigma_{op} = \dots\dots\dots(11)$$

Results and Discussion

Fig.1 show the photomicrographs for (PVA-PEO-Fe₂O₃) nanocomposites . The figure shows that the Fe₂O₃ nanoparticles is aggregated as a clusters at lower concentrations. When increasing the concentrations of Fe₂O₃ nanoparticles, the nanoparticles form a continuous network inside the (PVA-PEO) nanocomposites at concentration 4 wt% for nanocomposites.

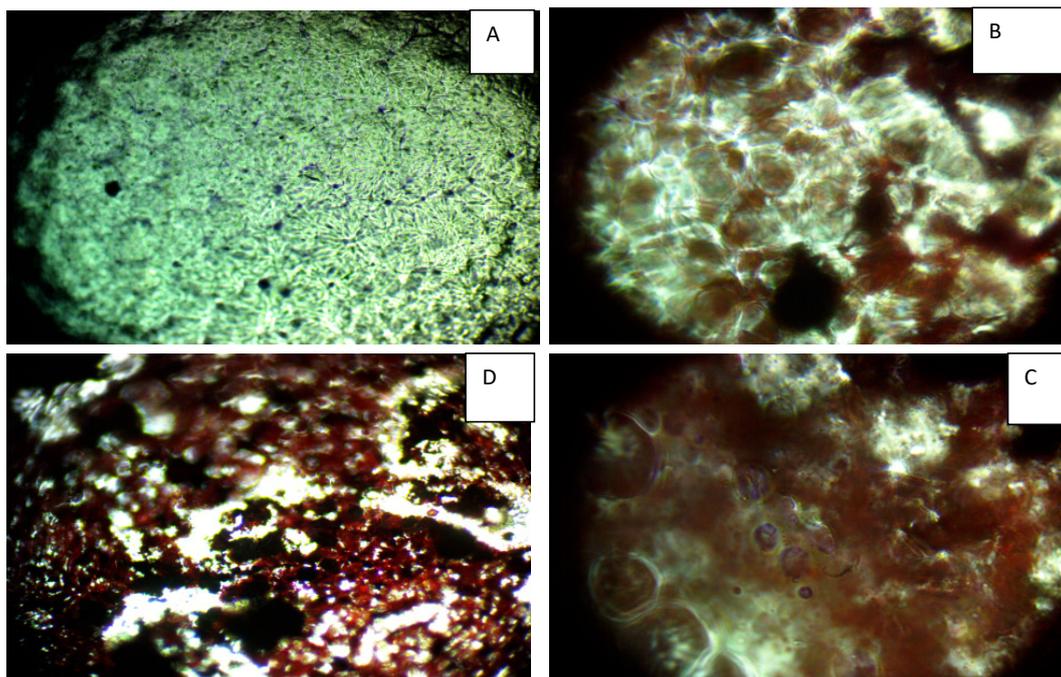


Fig.1. Photomicrographs (x40) for(PVA-PEO-Fe₂O₃) nanocomposites : (A) for pure (B) for 2 wt.% Fe₂O₃nanoparticles(C) for 4 wt.% Fe₂O₃ nanoparticles (D) for 6 wt.% Fe₂O₃ nanoparticles.

Figure 2 shows the FTIR spectra of (PVA-PEO-Fe₂O₃) nanocomposites. For all samples of nanocomposites are showed broad bands at around 3255.41 cm⁻¹ and 3648.3 cm⁻¹ are observed because of OH groups in the polymers matrix chain. The other bonds as (C-O-C) group can be noted in the bands at (1088) cm⁻¹ were attributed to the PVA film was not so transparent. Peaks at (2900- 2908) cm⁻¹ were due to the presence of C-H groups. The C=C stretching mode appear in the bands at (1708-1698) cm⁻¹.the peak at (1089-1096) cm⁻¹ the band be strong for all samples of nanocomposites this is due to the stretching mode of C-O group. The two strong bands observed at around (1418 cm⁻¹ and 842 cm⁻¹) are due to the stretching and bending modes of CH₂ group respectively[10].

The change in spectral of (PVA-PEO) involves shift in some bonds and change in the intensities due to iron oxide nanoparticles. The interaction between Fe₂O₃NPs and polymer blend causes these changes. From the FTIR studies note that there are no interactions between (PVA-PEO) blend and Fe₂O₃NPs. From figures are noted the transmittance decreases slightly with the increase of Fe₂O₃NPs concentrations because of the increase in density of nanocomposites [11].

The variation of dielectric constant and dielectric loss for (PVA-PEO-Fe₂O₃) nanocomposites

with frequency at room temperature are shown in Figure 3 and Figure 4. As shown in Figures, the dielectric constant and dielectric loss are decreased with the increase of frequency. High values of dielectric constant and dielectric loss at lower frequencies may be because the dipoles have sufficient time to get align to the electric field. Decrease in dielectric constant and dielectric loss at higher frequencies may be associated with the inability of dipoles to align rapidly with the rapidly changing applied field [12]. From Figures 3 and 4 the dielectric constant and dielectric loss are increased with the increase of iron oxide nanoparticles concentrations, this behavior attributed to increase of the charge carriers inside the nanocomposites [13], as shown in Figure 1.

Figure 5 shows that the variation of A.C electrical conductivity of nanocomposites with frequency. As shown in figure, the A.C electrical conductivity increases with the increase of frequency, this is due to the space charge polarization [14]. Also, the Figure 5 shows the electrical conductivity increases with the increase of iron oxide nanoparticles concentrations, this behavior attributed to the increase charge carrier numbers which are caused to decrease the resistivity and increase the conductivity of polymer blend [15].

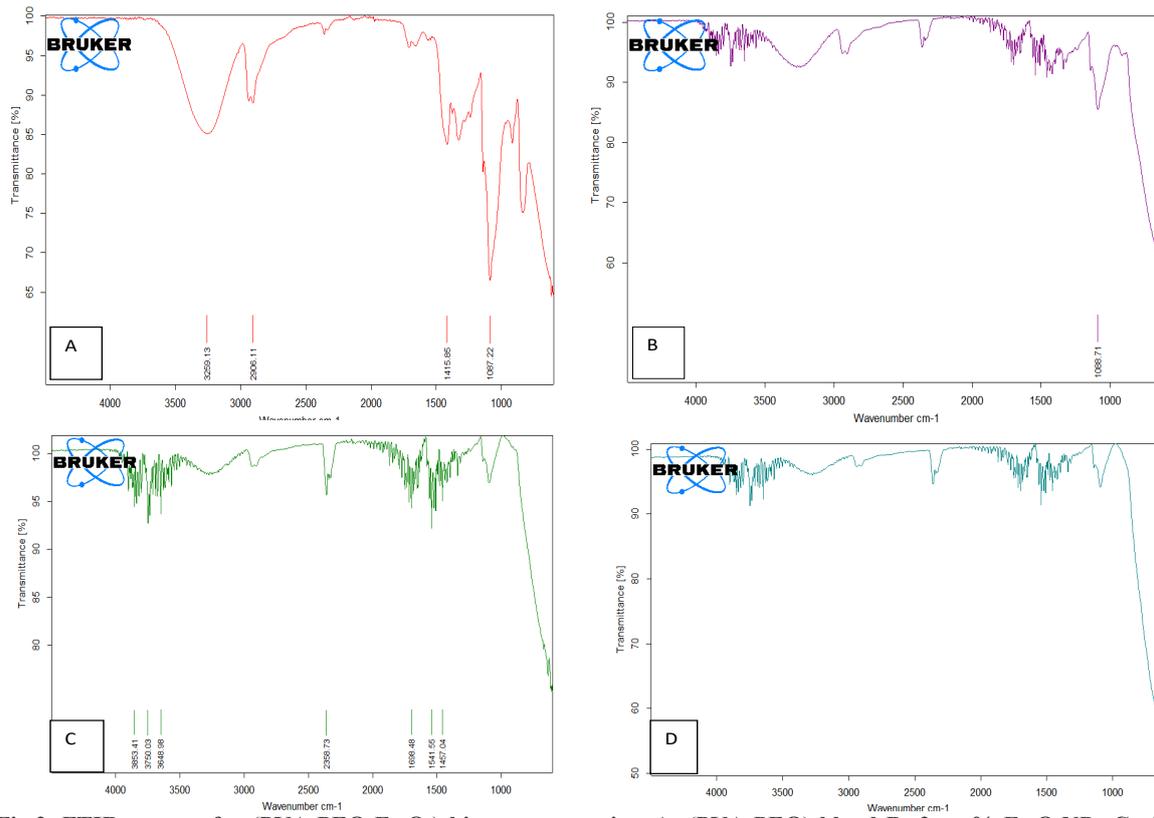


Fig.2. FTIR spectra for (PVA-PEO-Fe₂O₃) bionanocomposites A- (PVA-PEO) blend B- 2 wt.% Fe₂O₃NPs C- 4 wt.% Fe₂O₃NPs D- 6 wt.% Fe₂O₃NPs.

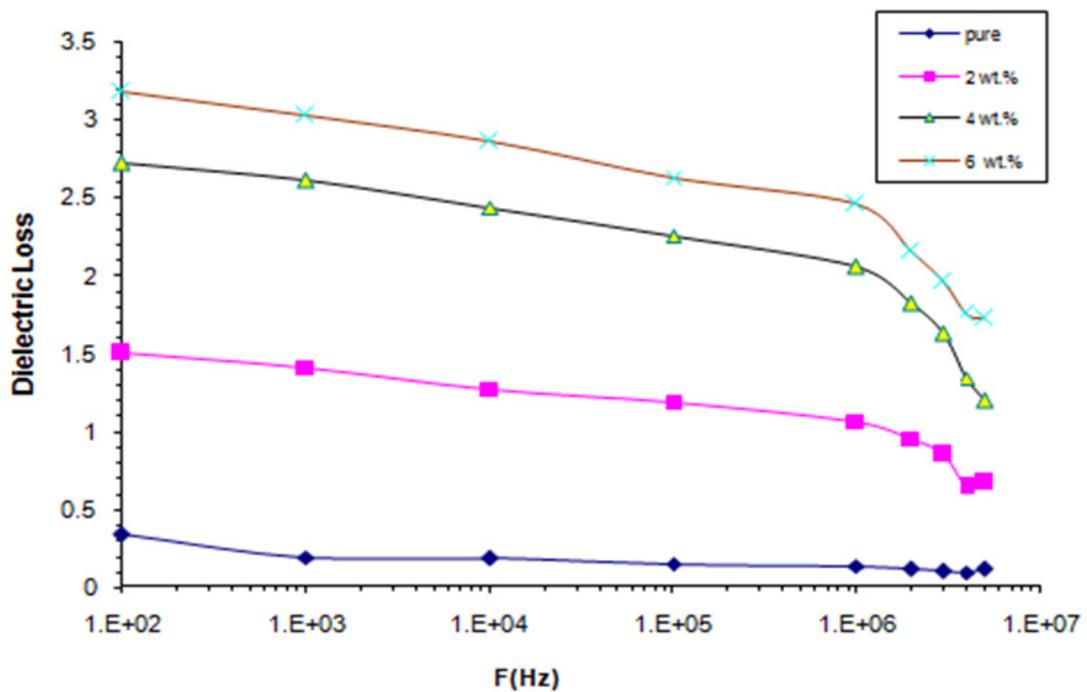


Fig.3. variation of dielectric constant for (PVA-PEO-Fe₂O₃) nanocomposites with frequency.

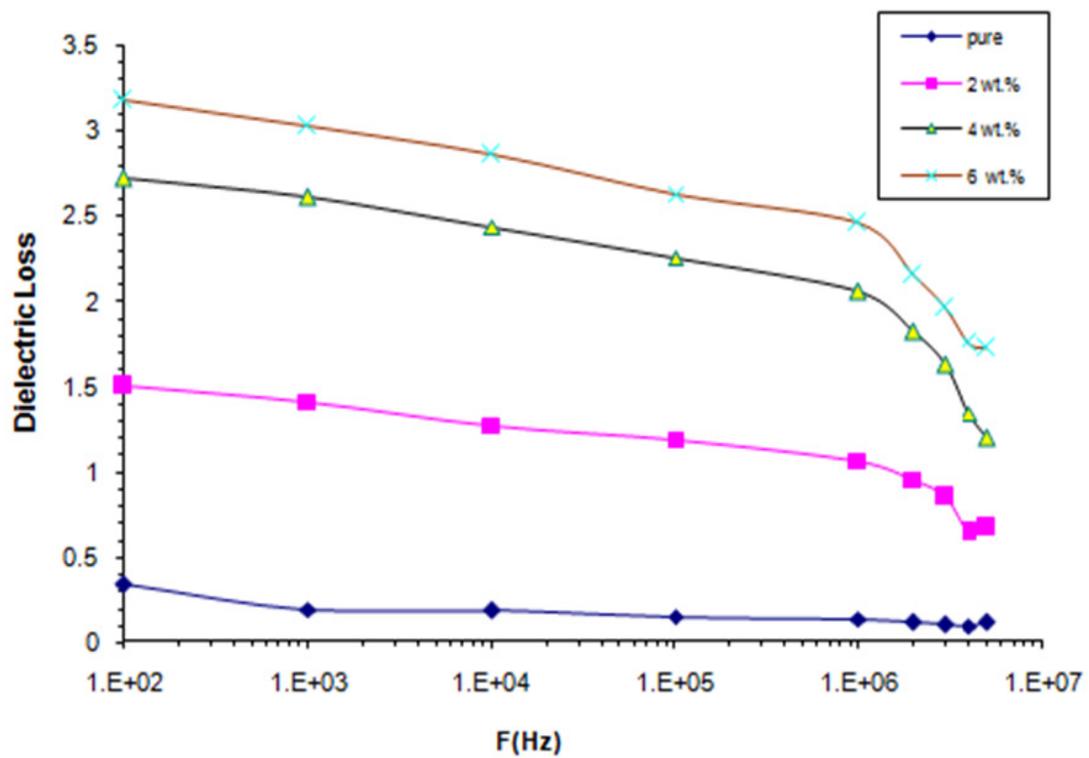


Fig.4. Variation of dielectric loss for (PVA-PEO-Fe₂O₃) nanocomposites with frequency.

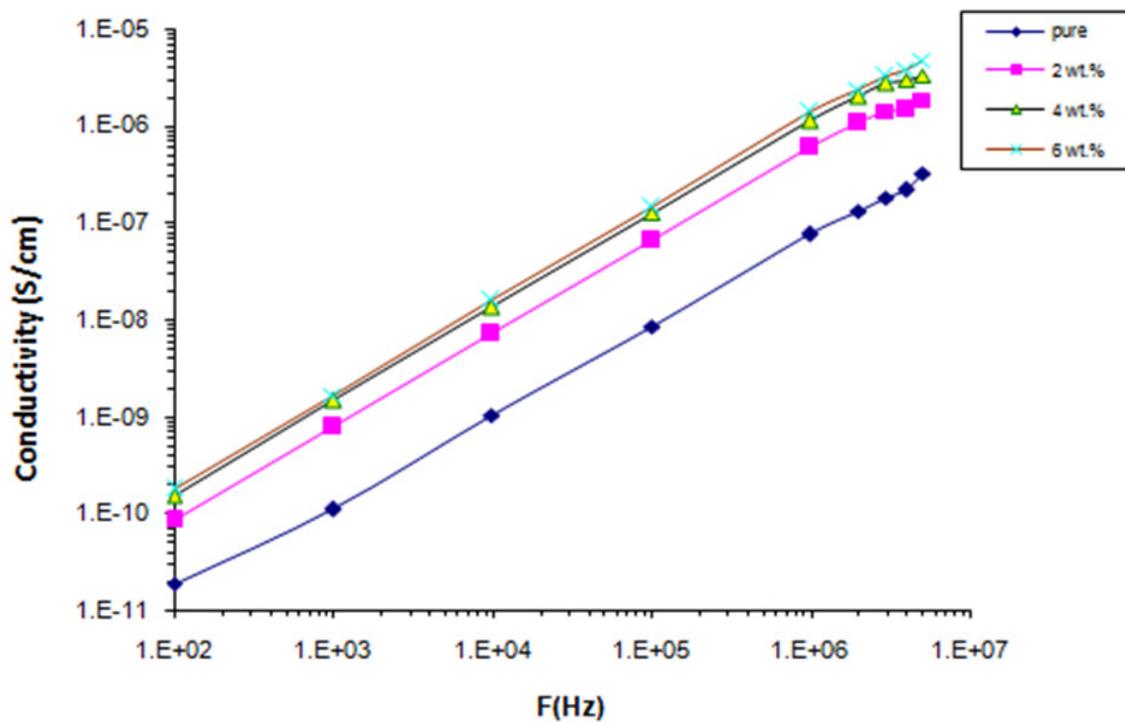


Fig. 5. Variation of A.C electrical conductivity of nanocomposites with frequency.

To know the effects of iron oxide filler on the optical properties of (PVA-PEO) blend, UV-visible absorption spectra for (PVA-PEO-Fe₂O₃) nanocomposites was measured.

Fig.6 shows the absorbance for (PVA-PEO-Fe₂O₃)nanocomposites . It's indicated that intensity of the peak increase with increases iron oxide filler [16]. The absorption band shifts due to specific weight Fe₂O₃ NPs and the formation of intermolecular hydrogen bonding existing between iron ions with the adjacent OH groups of the PVA and PEO main chain. Its note (PVA- PEO) blend has low absorbance because of the distance between valence and conduction bands is higher. The increase in iron oxide nanoparticles leads to the increase in absorption for (PVA-PEO-Fe₂O₃)nanocomposites [12,17].

Figure.7 shows the plot of absorption coefficient vs. incident photon energy for (PVA-PEO) blend with different percentages of iron oxide nanoparticles Fe₂O₃ NPs. It shows the absorption low when energy is low, this means the electrons transitions are low. In the high energy, absorption becomes large this indicate the high probability for electrons transitions. Absorption coefficient for (PVA-PEO-Fe₂O₃)nanocomposites is increased by increase of Fe₂O₃nanoparticles

additive [18]. The advantage of the absorption coefficient to conclude the transition electrons nature, when the value of absorption coefficient is high in the higher energy expected direct transition of electrons. The energy and momentum conservation can be by electrons and photons, when the value of absorption coefficient low expected indirect transition of electrons. The momentum conservation is by phonons only. From the results it's indicated absorption coefficient for (PVA-PEO-Fe₂O₃)nanocomposites has values are less than (10⁴ cm⁻¹) which mean it's have indirect energy band gap as shown in Fig.7[18].

Figure 8 shows the variations between absorbance edge $(\alpha h\nu)^{1/2}$ for (PVA-PEO-Fe₂O₃) nanocomposites as a function of photon energy. By take straight line from the upper part of the curve in direction axis (X) in value $((\alpha h\nu)^{1/2} = 0)$ it can be get indirect forbidden energy gap transition (allowed) [15]. It can be indicated that the values of forbidden energy gap (allowed) of (PVA-PEO-Fe₂O₃) nanocomposites are decreased with increasing iron oxide nanoparticles concentration this attribute to great localize levels in the forbidden energy gap. In addition to due to oxygen vacancies of Fe₂O₃ NPs which due to from non-stoichiometry [17]. Fig. 9 shows the variations between absorbance edge $(\alpha h\nu)^{1/3}$ for

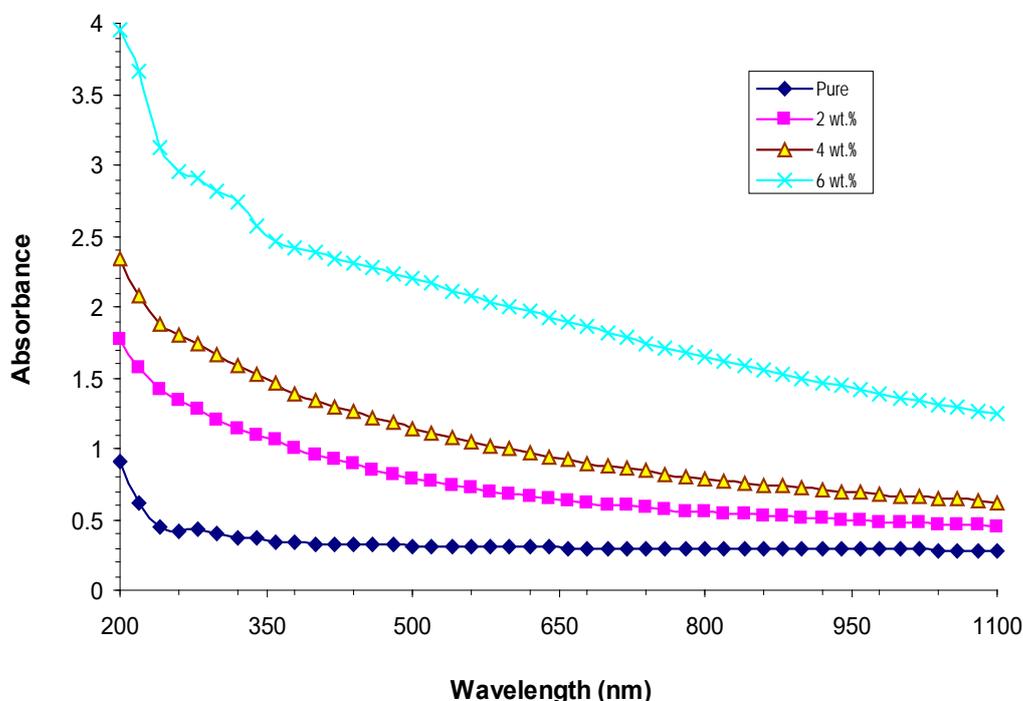


Fig. 6 . variation of absorbance for (PVA-PEO-Fe₂O₃) nanocomposites with wavelength.

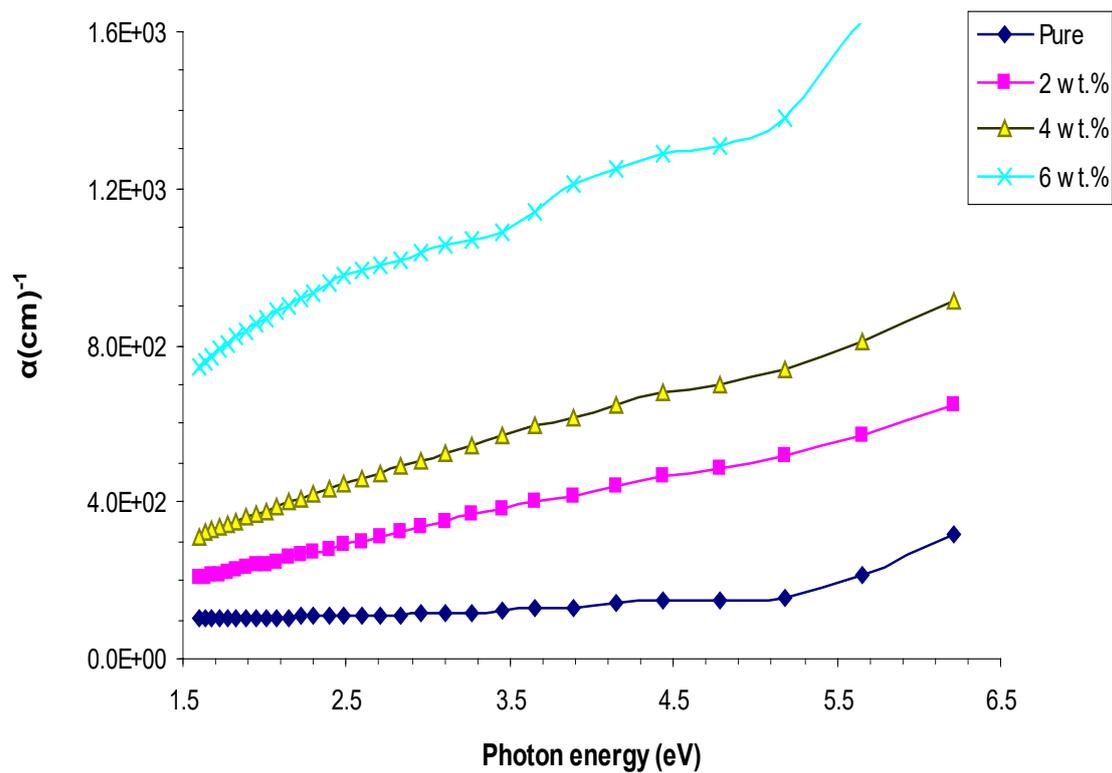


Fig.7. Variation of absorption coefficient (α) for (PVA-PEO-Fe₂O₃) nanocomposites with photon energy.

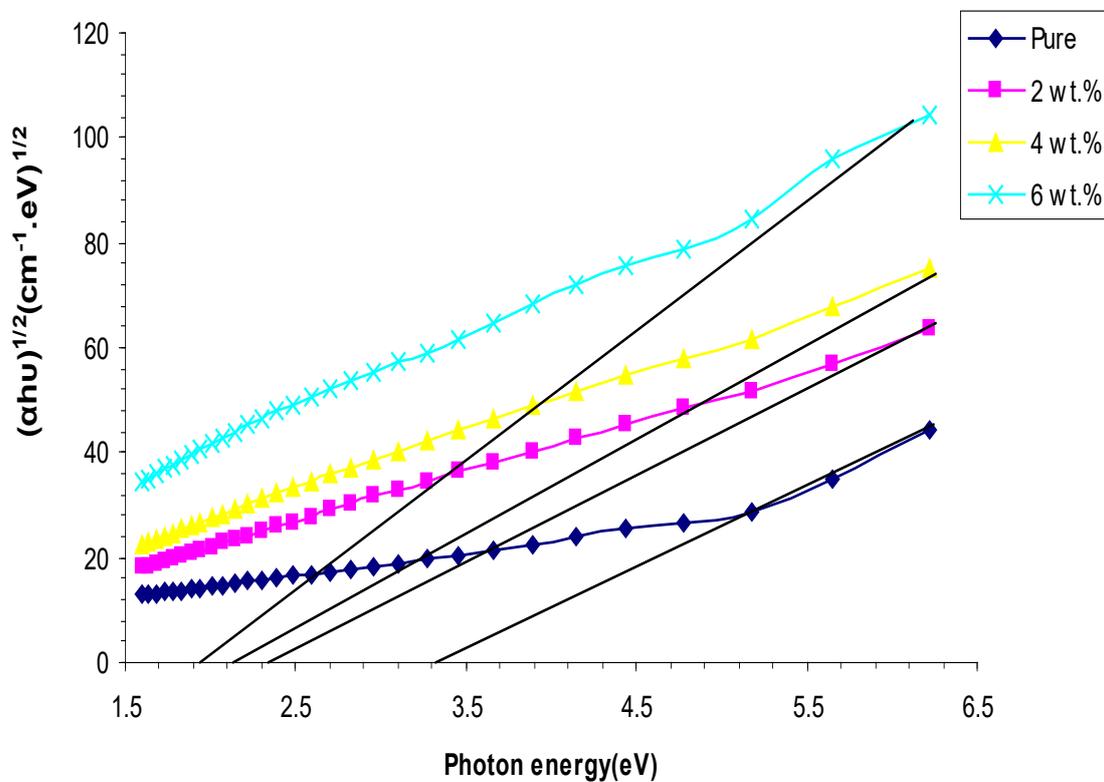


Fig.8. Variation of $(\alpha hu)^{1/2}$ for (PVA-PEO-Fe₂O₃) nanocomposites with photon energy.

(PVA-PEO-Fe₂O₃) nanocomposites as a function of photon energy. It indicates that the values of forbidden energy gap (prevent) for (PVA-PEO-Fe₂O₃) nanocomposites decrease with increasing iron oxide nanoparticles (Fe₂O₃NPs) concentration. This attribute forms new levels and the transition of electrons between the tails of localized levels made by the (Fe₂O₃NPs) additive [15,16].

To describe the attenuation of the waves, one must study the extinction coefficient. Fig. 10 shows the variations of extinction coefficient against wavelength for (PVA-PEO-Fe₂O₃) nanocomposites. It shows an increase in extinction coefficient with increasing iron oxide nanoparticles for (PVA-PEO) blend. The increasing of extinction coefficient is attributed to high absorption coefficient. Where iron oxide nanoparticles will modify the structure of the host (PVA-PEO) blend. An interesting result is that when the concentration of Fe₂O₃NPs increases, the absorbance in the visible region increases [17-19].

To describe the electromagnetic waves in the medium of propagation, one must study the refractive index. Fig. 11 illustrates the plot of the variations

of refractive index with wavelength for (PVA-PEO-Fe₂O₃) nanocomposites. The index of (PVA-PEO) blend increases with increasing the iron oxide nanoparticles, which is attributed to the increase in the scattering of incident photons, which causes an increase in reflectance. In addition to this, further addition of iron oxide nanoparticles causes an increase in intensity for (PVA-PEO-Fe₂O₃) nanocomposites [20].

Figure 12 and 13 show the variations of real and imaginary parts respectively versus wavelength for (PVA-PEO-Fe₂O₃) nanocomposites. It can be indicated that the real part is greater than the imaginary part, as the real part is mainly proportional to the square of the refractive index. In addition to the real part, it is increased with increasing (Fe₂O₃NPs) additive. Whereas the imaginary part is proportional to the extinction coefficient as shown in equation (11) and is increased with increasing iron oxide nanoparticles [21].

Figure 14 shows the optical conductivity with wavelength for (PVA-PEO-Fe₂O₃) nanocomposites. The optical conductivity is increased for (PVA-PEO-Fe₂O₃) nanocomposites due to iron oxide nanoparticles (Fe₂O₃NPs) being increased, which leads to an increase in the absorption coefficient [22].

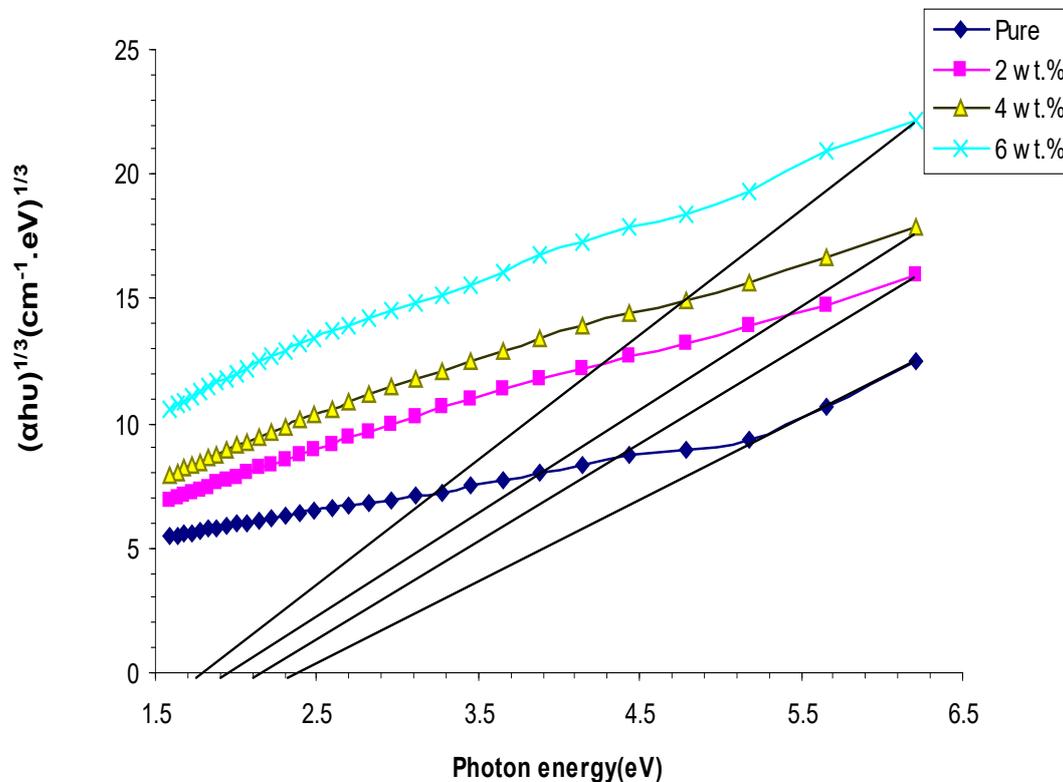


Fig. 9. Variation of $(\alpha hu)^{1/3}$ for (PVA-PEO-Fe₂O₃) nanocomposites with photon energy.

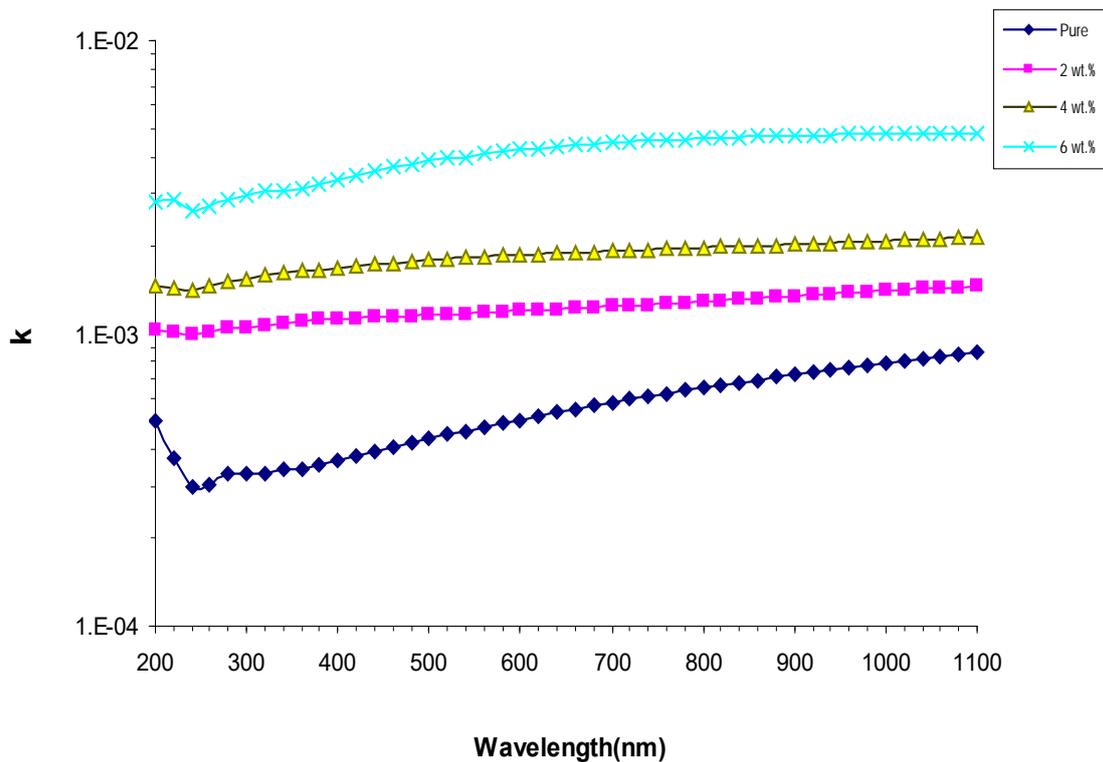


Fig. 10. Variation of extinction coefficient for (PVA-PEO-Fe₂O₃) nanocomposites with wavelength.

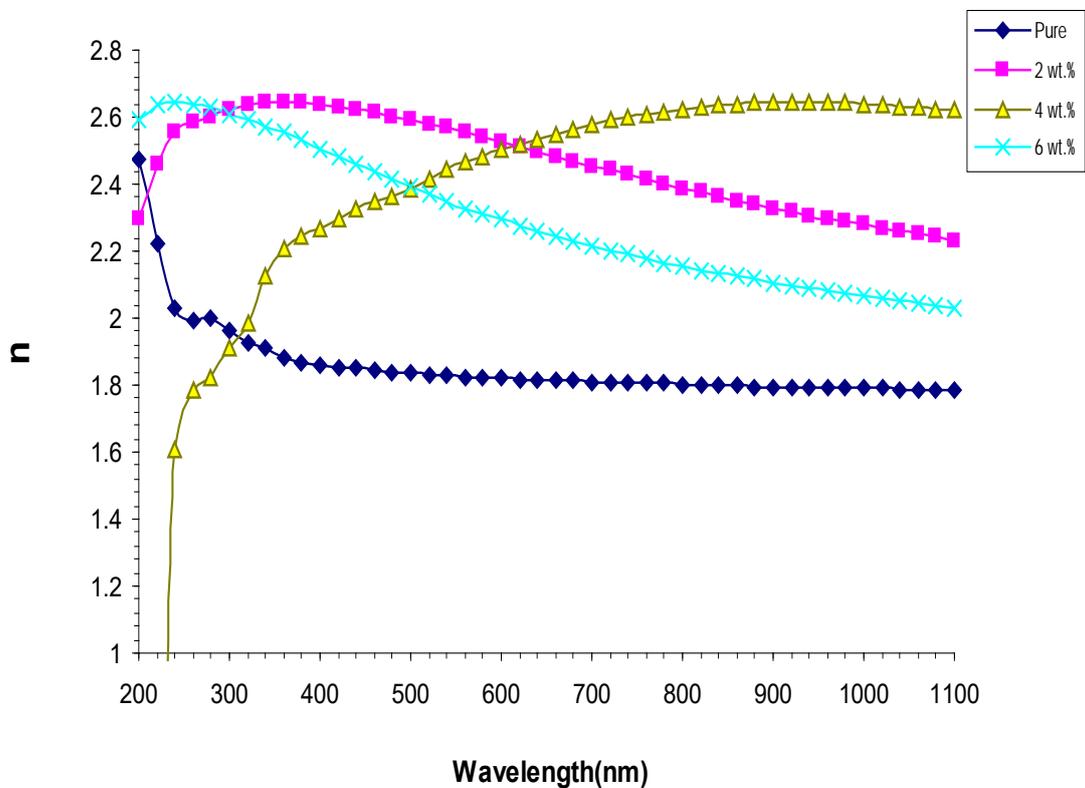


Fig. 11 . Variation of refractive index for (PVA-PEO-Fe₂O₃) nanocomposites with wavelength.

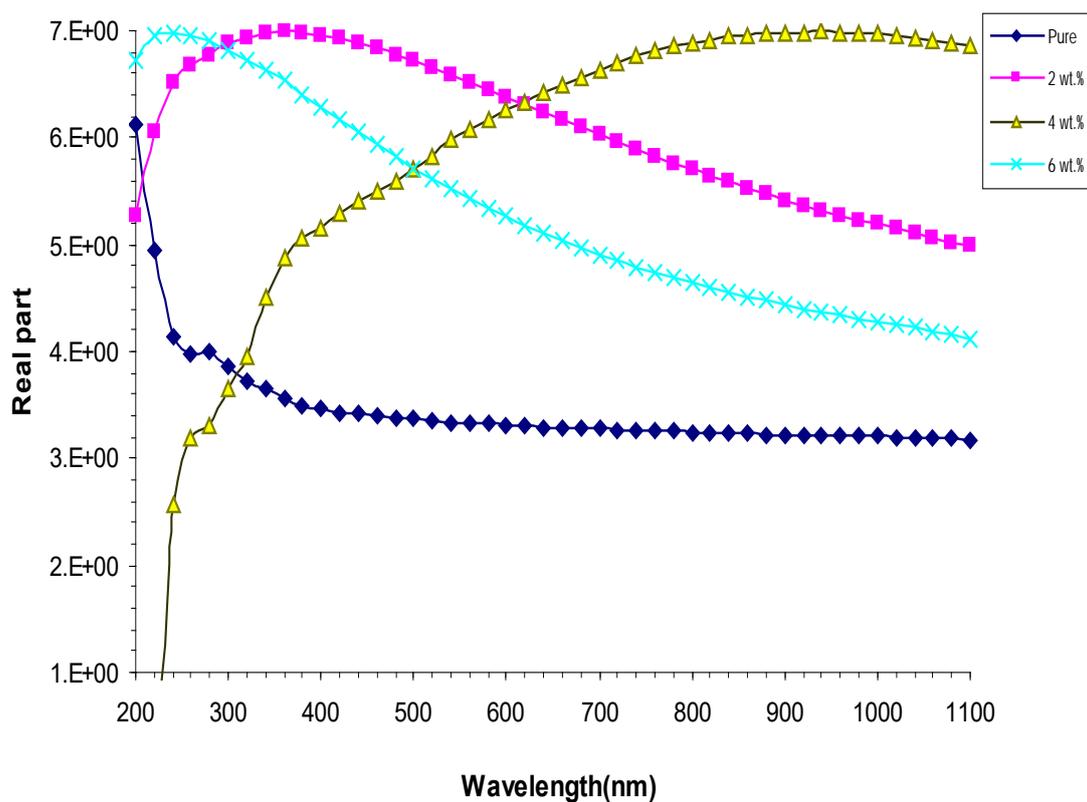


Fig. 12 . Variation of real part of dielectric constant for (PVA-PEO-Fe₂O₃) bionanocomposites with wavelength.

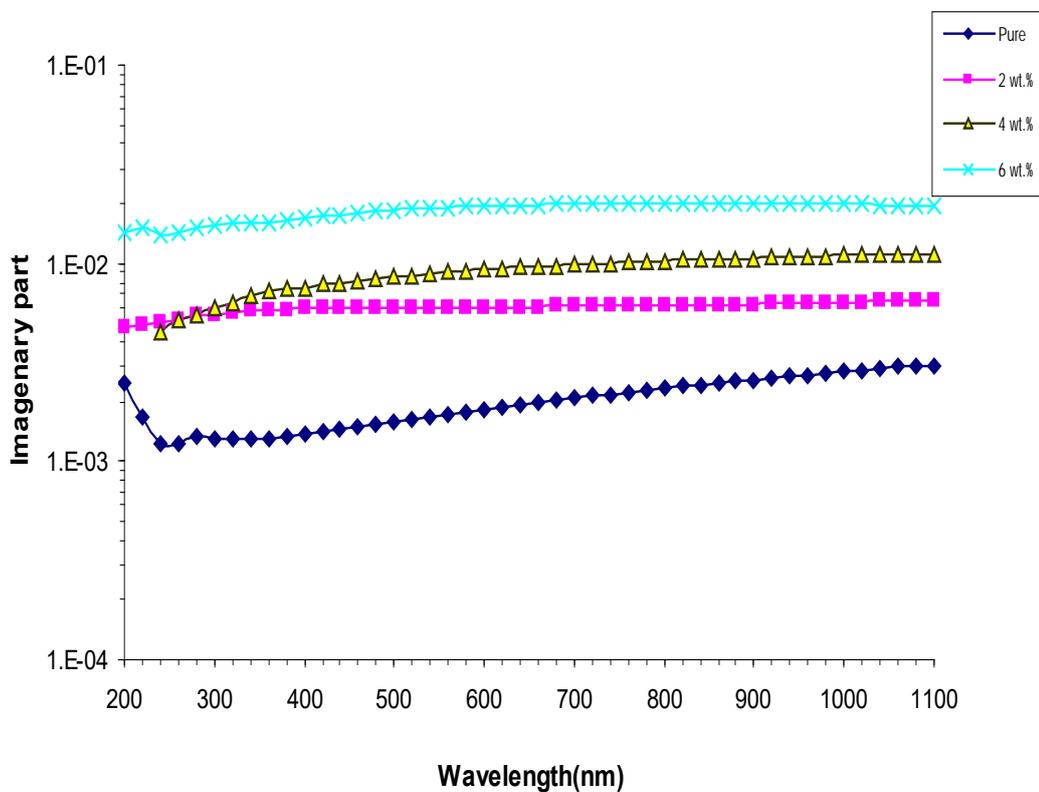


Fig. 13 . Variation of imaginary part of dielectric constant for (PVA-PEO-Fe₂O₃) nanocomposites with wavelength.

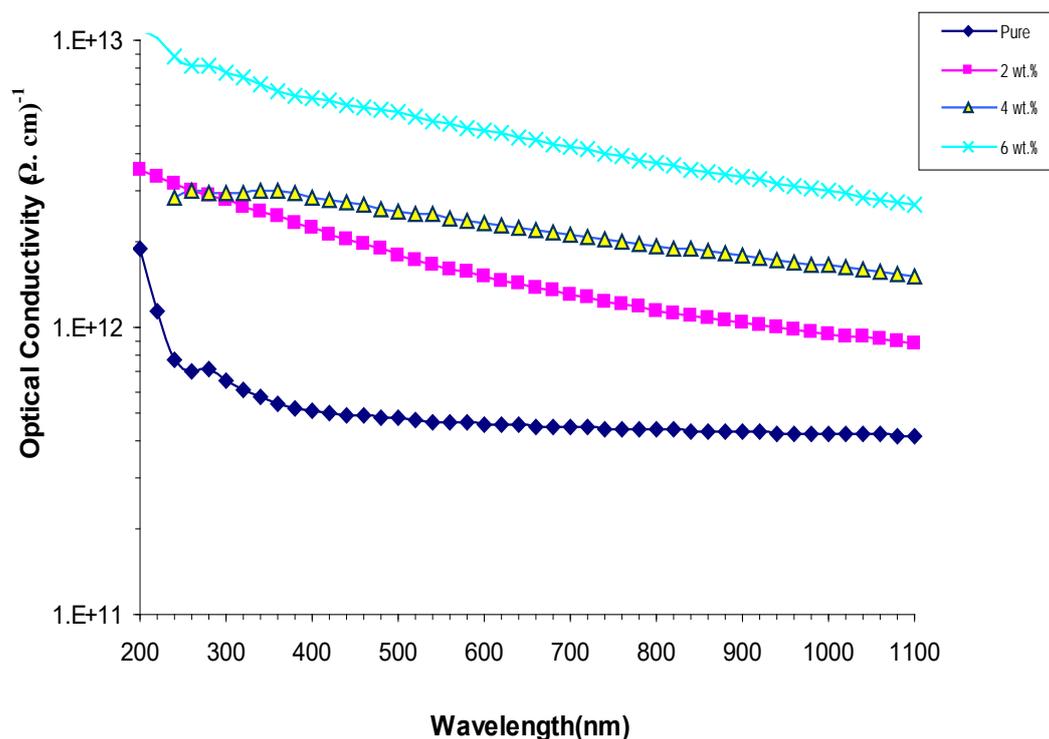


Fig. 14 . Variation of optical conductivity for (PVA-PEO-Fe₂O₃) bionanocomposites with wavelength.

Conclusions

1. The dielectric constant, dielectric loss and A.C electrical conductivity of (PVA-PEO) blend are increased with increase of the Fe₂O₃ nanoparticles concentrations which may be used it for different electronics applications.
2. The dielectric constant and dielectric loss of (PVA-PEO- Fe₂O₃) nanocomposites are decrease while the electrical conductivity increases with increase in the frequency. The results showed that the (PVA-PEO-Fe₂O₃) nanocomposites have good dielectric properties which can be used it for different applications in electronic industries.
3. The absorbance and optical constants (absorption coefficient, extinction coefficient, refractive index, real and imaginary dielectric constants and optical conductivity) of of (PVA-PEO) blend increase with an increase in weight percentages of iron oxide nanoparticles. The indirect energy gap (E_g) of (PVA-PEO) blend decreases with the increase of the concentrations of iron oxide nanoparticles. The results of optical properties showed that the the (PVA-PEO-Fe₂O₃) nanocomposites may be used for different optoelectronics applications.

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تحضير، الخصائص التركيبية والبصرية للمترابكات النانوية (بولي فينيل الكحول- بولي ايثيلين اوكسايد- اوكسيد الحديد)

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المترابكات النانوية تستعمل عادة في مجالات مختلفة في التطبيقات الصناعية مع قلة الكلفة و خفة الوزن. في هذا البحث، مترابكات نانوية من بولي فينيل الكحول- بولي ايثيلين اوكسايد- جسيمات اوكسيد الحديد النانوية تم تحضيرها. جسيمات اوكسيد الحديد النانوية تم اضافتها الى خليط البوليمر بنسب وزنية مختلفة هي (2، 4، 6) نسبة وزنية. درست الخصائص التركيبية والعزلية للمترابكات النانوية (بولي فينيل الكحول- بولي ايثيلين اوكسايد- جسيمات اوكسيد الحديد النانوي). بينت النتائج ان ثابت العزل الكهربائي، الفقدان العزلي، والتوصيلية الكهربائية للخليط (PVA-PEO) تزداد مع زيادة تراكيز جسيمات اوكسيد الحديد النانوية. ان ثابت العزل الكهربائي و الفقدان العزلي يقلان بينما التوصيلية الكهربائية تزداد مع زيادة تردد المجال الكهربائي المسلط. القياسات البصرية بينت ان الامتصاصية للمترابكات النانوية (PVA-PEO-Fe₂O₃) تزداد مع زيادة تراكيز جسيمات اوكسيد الحديد النانوية. فجوة الطاقة غير المباشرة (E_g) تقل مع زيادة تراكيز جسيمات اوكسيد الحديد النانوية. الثوابت البصرية (معامل الامتصاص، معامل الخمود، معامل الانكسار، ثوابت العزل الحقيقي والخيالي، و التوصيلة البصرية للخليط (PVA-PEO) تتغير مع زيادة النسب الوزنية لجسيمات اوكسيد الحديد النانوية.