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REGULAR PAPER

Structural, Optical and Electrical Properties of PVA/PEO/SnO_2 New Nanocomposites for Flexible Devices

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Abstract
Fabrication of polyvinyl alcohol (PVA)–polyethylene oxide (PEO) blend doped with tin dioxide (SnO_2) nanocomposites has been investigated for flexible electrical and optical applications. 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–SnO_2) nanocomposites have been studied. The experimental results of optical properties for (PVA–PEO–SnO_2) 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 SnO_2 nanoparticles concentrations while the transmittance and energy band gap are decreased with the increase in SnO_2 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 SnO_2 nanoparticles concentrations. The electrical properties showed that the (PVA–PEO–SnO_2) nanocomposites have good dielectric parameters which it may be used for different electronics applications.

Keywords Electronics · Optical properties · Nanocomposites · Dielectric · Blend · Tin dioxide

1 Introduction

Polymers are organic compounds have conjugated chain which exhibit high electrical conductivity, this because their properties as charge carrier by π-electrons, lead to charge mobility along the chain of the polymers backbone likewise, inorganic materials such as metals and metals oxide. Polymers properties are comparable with inorganic material but polymers have several pros, for examples being flexibility, processability, resistance to corrosion, low cost and lightweight. Inorganic materials also have valuable properties such as thermal stability and high mechanical strength. Therefore, polymer-inorganic hybrids are finding various applications in different field solar cell batteries, sensors and television sets [1]. Recently, several studies have been reported to composite various organic polymers for instances polyvinyl chloride (PVC), polyaniline (PANI), polypropylene (PP), polyvinyl alcohol (PVA) and polyethylene oxide (PEO) composite loaded with nanofillers inorganic material such as FeO, CdS, ZnO and CuO to identify their essential principles for their applications in different areas. Amongst the family of fabricating polymers, both polyvinyl alcohol (PVA)–polyethylene oxide (PEO) have been of particular interest due to their prperties [2]. Fore examples preparing proton-conducting polymer, preparation of nanocomposite polymer films and energy storage devices [3]. The fast improvement of power equipment and electronic products, functional materials with excellent electrical and thermal

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feature are highly desirable. Interesting electrical applications need the electrical conductivity of a polymeric matrix to be improved by the addition of nanoparticles. Particularly filled composites are commonly used in several applications. This is because introducing fillers, in particular nanoparticles, enhances the electrical and thermal possessions of the fabrication polymer. The addition of nanofillers conforms to the chain length of the polymer and then reduces Maxwell–Wagner–Sillar type interfacial polarization originated from the variances in dielectric permittivity of the polymer and filling. There is an interest in dielectric materials because of their varied range of uses in different field [4]. The subsequent chemical effect of hydroxyl groups lead to form hydrohen bonds, which gives this polymers special properties. Poly(ethylene oxide) (PEO) too is attracting interest as a biodegradable, water-soluble, nonionic biocompatible and semi-crystalline polymers that has the potential considerable industrial Both polymers are possible fabrication material employed in advanced technologies in the field of functional coatings with superior barrier properties. These nanocomposites exhibit the merits of blending the advantageous properties of metal oxides with the process ability and flexibility of polymers [5]. One metal oxide attracting attention is tin oxide in solar cell devices, optoelectronic devices and gas sensor due to special propertied such as optical, crystalline structure and magnetic properties. Given the photo catalysis behaviour associated with tin oxide is relatively clear, this compound identified as electrode material. Tin oxide nanoparticles can be synthesis through different ways, such as hydrothermal, sonochemical polymer, sol gel and co-precipitation and others [6]. There are many studies on properties of composites and nanocomposites such as: structural, DC and AC electrical [7–16], thermal and optical properties [17–26] and their applications for humidity sensors [27–34], radiation shielding [35–44], antibacterial [45–48] and thermal energy storage and release [49–52]. This paper deals with preparation of PVA/PEO/SnO_2 new nanocomposites and studying their structural, optical and electrical characteristics for flexible electrical and optical applications.

2 Materials and Methods

Films of polyvinyl alcohol (PVA)- polyethylene oxide (PEO) and polyvinyl alcohol- polyethylene oxide doped with tin dioxide nanoparticles (SnO_2) were synthesized via employing casting method. The polymer blend fabricated with concentration 90 wt% polyvinyl alcohol and 10 wt% PEO. Next, different tin oxide concentrations 2, 4 and 6 wt% were added to the polymer blend.

The nanocomposites samples were characterized using FTIR spectroscopy recorded using Bruker company German origin, type vertex - 70 in range (4000–500) cm^{-1}. UV–visible spectrophotometer of shimadzu, UV-1800 Å) in the range (200–800) nm. The dielectric measurements tested by using LCR meter type HIOKI 3532-50 LCR HI TESTER). The optical microscope was used to test the nanocomposites films.

The absorption coefficient (α) is given as [23, 53]:

$$\alpha = 2.303 * A/t \tag{1}$$

where t: thickness of the samples. A: represent the optical absorbance.

The Eq. (2) was employed to determine the non-direct transition model for amorphous materials [53]:

$$\alpha h\upsilon = B(h\upsilon - E_g)^r \tag{2}$$

B, hυ, E_g, and r are (constant, photon energy, energy band gab and allowed and forbidden indirect transition) respectively)

By using Eq. (3) the extinction coefficient (k) was determined [54]:

$$K = \alpha\lambda/4\pi \tag{3}$$

The refractive index (n) as function of reflectance (R) is given by the equation [54]:

$$n = \left(1 + R^{1/2}\right)/\left(1 - R^{1/2}\right) \tag{4}$$

Equations (5) and (6) showed parts of dielectric constant the imaginary (ε_2) and real (ε_1) respectively [55]:

$$\varepsilon_1 = n^2 - k^2 \tag{5}$$

$$\varepsilon_2 = 2nk \tag{6}$$

While Eq. (7) used to calculate the optical conductivity [55]:

$$\sigma = \frac{\alpha nc}{4\pi} \tag{7}$$

The dielectric constant (έ) of (PVA–PEO–SnO_2) nanocomposites is given by using the following equation [56]:

$$\varepsilon' = \frac{C_p}{C_\circ} \tag{8}$$

where C_o is vacuum capacitor and C_p is parallel capacitance.

The dielectric loss (ε˝) of (PVA–PEO–SnO_2) nanocomposites is given by following equation [56]:

$$\varepsilon'' = \varepsilon' D \tag{9}$$

where D: is dispersion factor.

The AC electrical conductivity were calculated via using Eq. (10) [57]:

$$\sigma_{A.C} = w\varepsilon''\varepsilon_o \quad (10)$$

W: represent the angular frequency.

3 Results and Discussion

Figure 1 represents the FTIR spectra which gives the information about the kind of the functional group of (PVA–PEO–SnO_2) nanocomposites. The frequency belong to OH groups in the nanocomposites appear at around 3255 cm^{-1}. The spectrum of the (PVA–PEO–SnO_2) nanocomposites shows peaks at (1086, 1420, 1700, 2905) cm^{-1}, which attributed to the C–O, C=C and C–H groups respectively in the nanocomposites [58, 59]. The absorbance spectra of (PVA–PEO–SnO_2) nanocomposites films are shown in Fig. 2. It is clear that the intensity of the peak increases with increasing of SnO_2 nanoparticles concentration because of the absorption of the incident radiation by SnO_2 nanoparticles free electrons. Figure 3 shows the

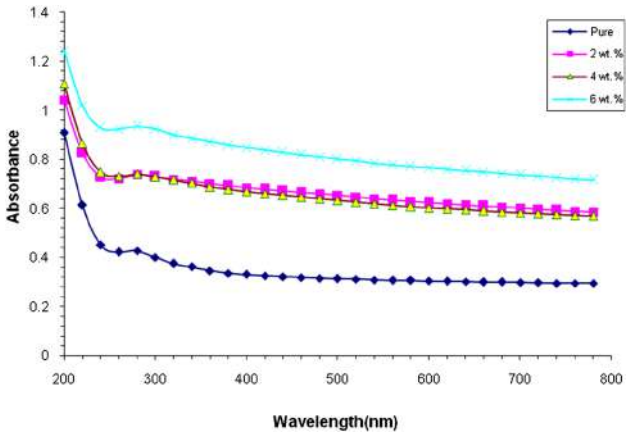

Fig. 2 Absorbance spectra of (PVA–PEO–SnO_2) nanocomposites films

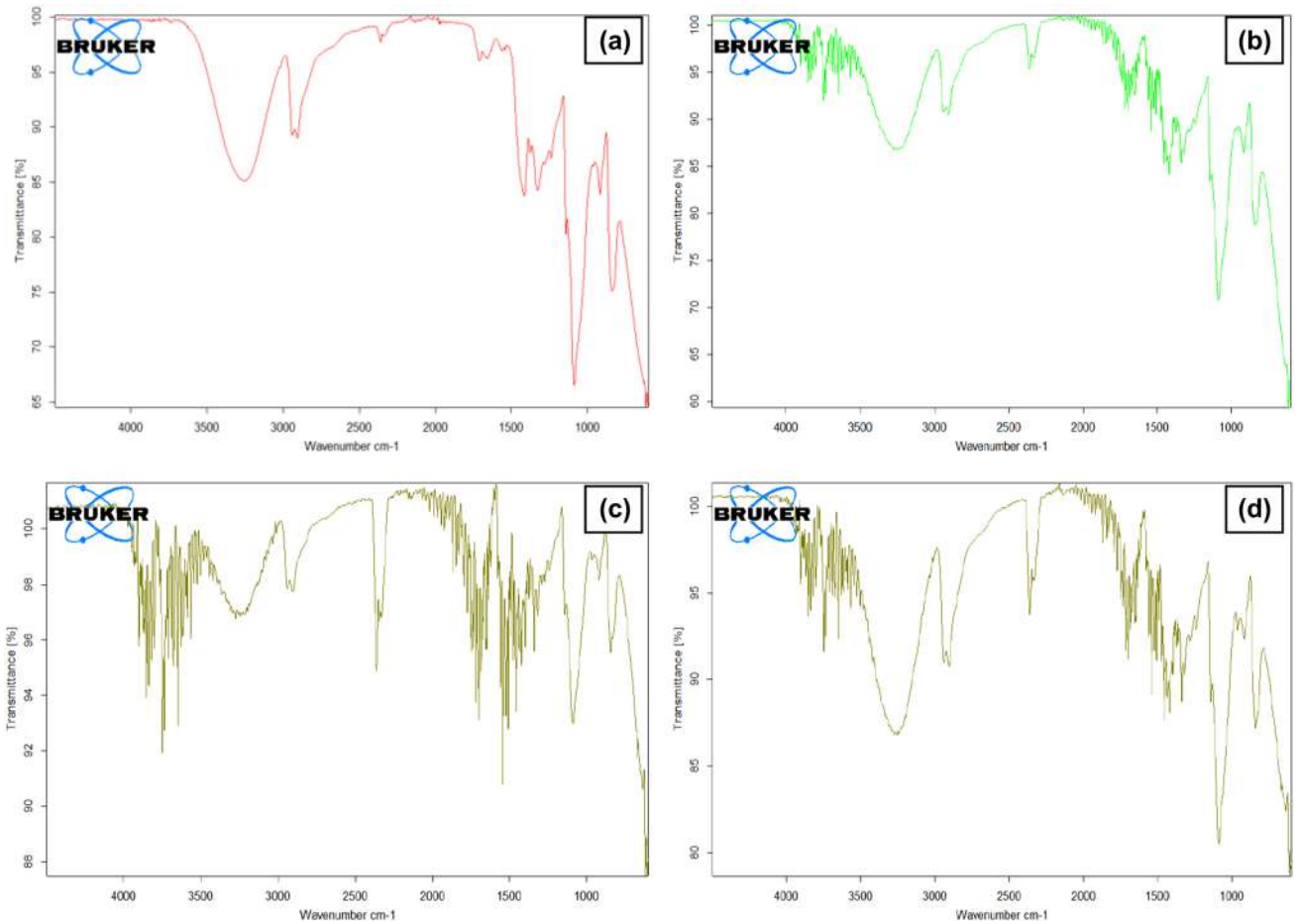

Fig. 1 Typical FTIR spectrum of the tin oxide loaded PVA/PEO hybrid nanocomposite with different SnO_2 content of **a** pure blend, **b** 2 wt%, **c** 4 wt% and **d** 6 wt%

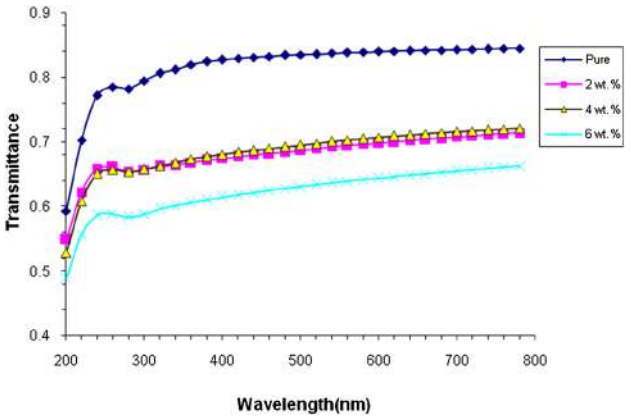

Fig. 3 Optical transmittance spectra of nanocomposites films for different SnO_2 nanoparticles concentration

optical transmittance spectra of nanocomposites films for different SnO_2 nanoparticles concentration. It is clear that the transmittance increases with increasing of the wavelength for different concentration and also it decreases with increasing of the SnO_2 nanoparticles doping concentration this is due to the fact that, SnO_2 nanoparticles absorb and scatter the incident light [60], as shown in Fig. 4.

Figure 5 shows the relationship between absorption coefficient and photon energy of the incident light. As shown in the figure, the absorption coefficient of all samples is high at high energies. This means that the electron transition has high possibility; i.e. the energy of incident photon is enough to transit the electron from the valence band to the conduction band which due to the energy of the incident photon is greater than the energy band gap. The absorption coefficient assists to know the nature of electron transition. When the values of the absorption coefficient of (PVA–PEO–SnO_2) nanocomposites are high ($\alpha > 10^4$) cm^{-1}, it is expected that direct transition of electron while, when the values of the absorption coefficient of material are low ($\alpha < 10^4$) cm^{-1}, it is expected that indirect transition of electron. The values of absorption coefficient of nanocomposites are low ($\alpha < 10^4$) cm^{-1}; the transition of electron is indirect. The absorption coefficient of nanocomposites increases with increase in SnO_2 nanoparticles concentrations, this is attributed to the increase in

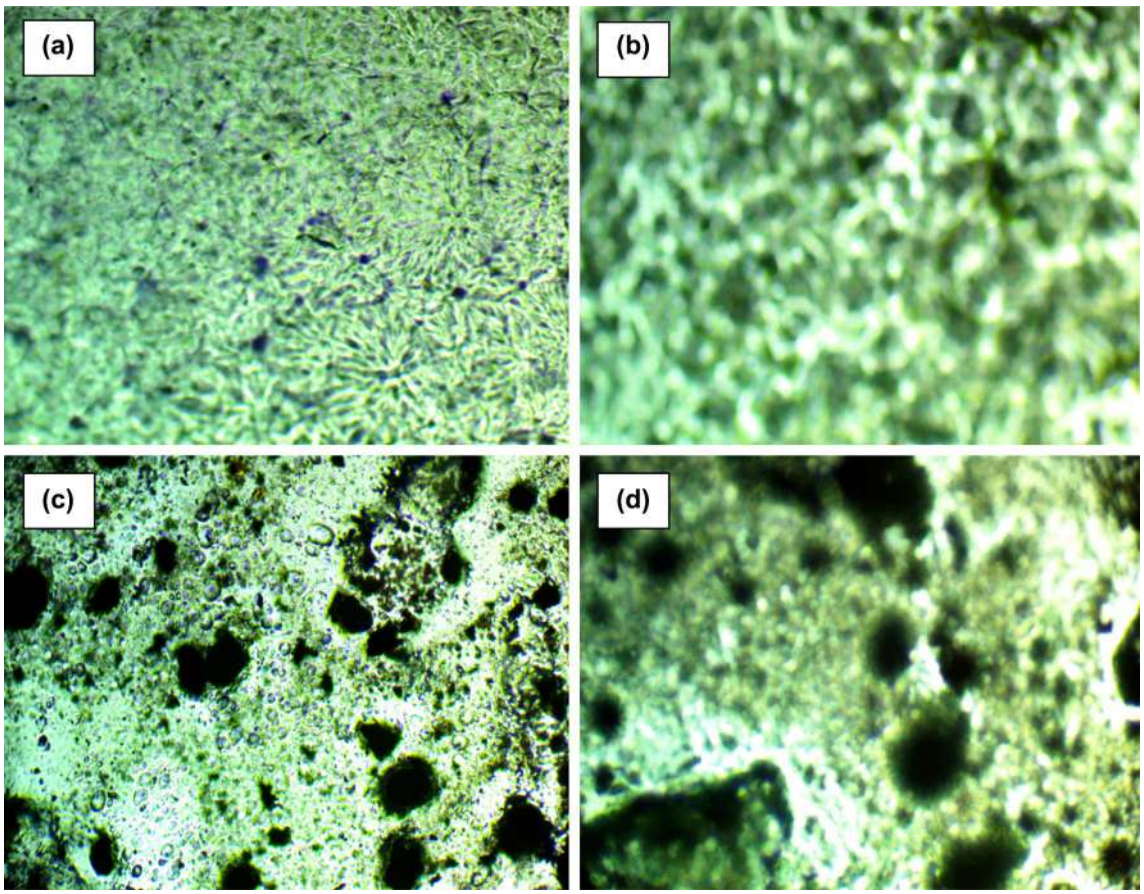

Fig. 4 Microscope images of the (PVA–PEO–SnO_2) nanocomposites: **a** pure blend, **b** 2 wt%, **c** 4 wt% and **d** 6 wt%

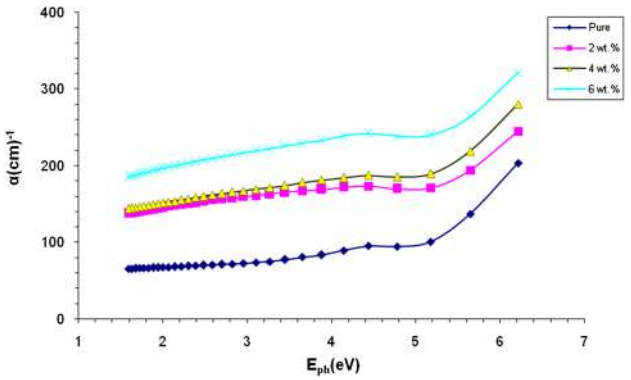

Fig. 5 Variation of absorption coefficient with photon energy of the incident light

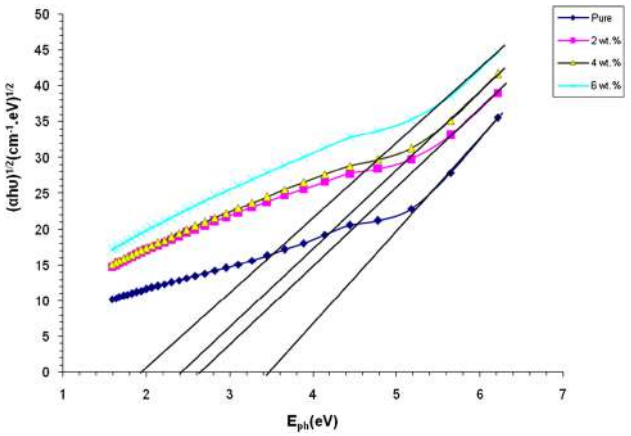

Fig. 6 The energies band gap values for allowed indirect transition

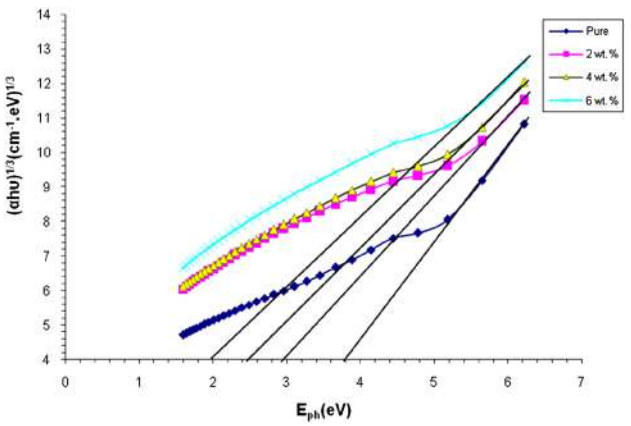

Fig. 7 The energies band gap values for forbidden indirect transition

number of charge carriers, hence, increase in absorbance and absorption coefficient for nanocomposites [61].

Figures 6 and 7 show the values of energies band gap for allowed and forbidden indirect transition respectively. The

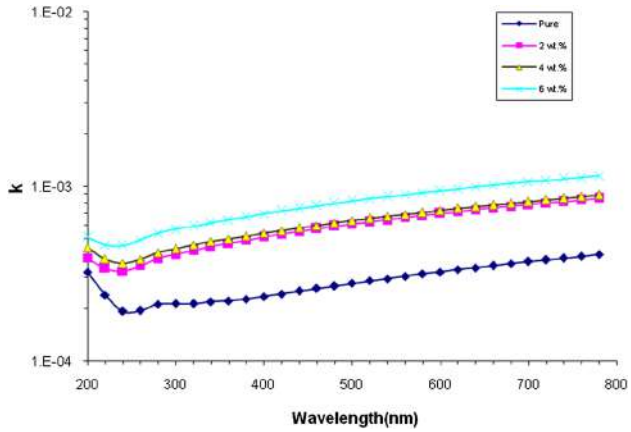

Fig. 8 Variation of extinction coefficient of (PVA–PEO–SnO_2) nanocomposites with wavelength

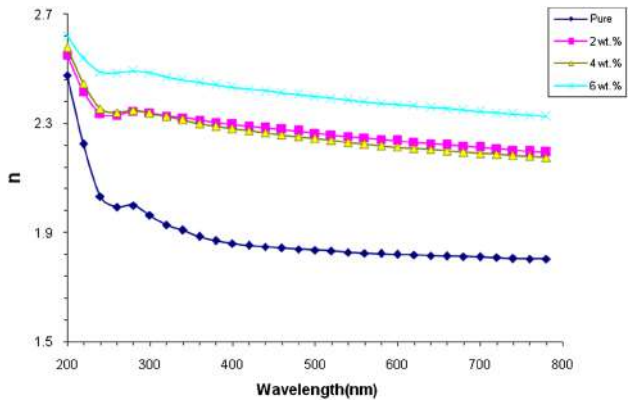

Fig. 9 Variation of refractive index for (PVA–PEO–SnO_2) nanocomposites with wavelength

figures is showed that the values of energy gap for allowed and forbidden indirect transition decrease with increasing tin dioxide nanoparticles concentration, this decrease because as tin dioxide nanoparticles content is responsible for the formation of some defects in the films. These defects produce the localized states in the optical band gap and overlap. These overlaps give an evidence for decreasing energy band gap when the tin dioxide nanoparticles content is increased in the polymeric matrix. In other words, the decreased in the optical gap reflects the increase in the degree of disorder in the films [62].

Figure 8 shows the variation of extinction coefficient for (PVA–PEO–SnO_2) nanocomposites with wavelength of the incident light. Extinction coefficient was increased for (PVA–PEO) blend films with increasing doping concentration; this is due to the increase in absorption coefficient, where the extinction coefficient depends on the absorption coefficient. Figure 9 shows the variation of refractive index

for (PVA–PEO–SnO_2) nanocomposites with wavelength of the incident light. As shown in figure, the refractive index decreases with increasing wavelength for (PVA–PEO–SnO_2) nanocomposites. The figure shows that the refractive index increases as a result of an increase in the weight percentage of SnO_2 nanoparticles; this behavior can be attributed to the increasing of the packing density as a result of filler content [63].

Figure 10 shows the variation of the real part of dielectric constant with the wavelength for (PVA–PEO–SnO_2) nanocomposites. The effect of SnO_2 nanoparticles concentrations on imaginary part of dielectric constant is shown in Fig. 11. The figures show that the real and imaginary parts of dielectric constant of (PVA–PEO) blend increase with increase in SnO_2 nanoparticles concentrations, this behavior attributed to the increase of electrical polarization due to contribution of SnO_2 nanoparticles concentration in the sample i.e., the increase in the dielectric constant of (PVA–PEO) blend represents a fractional increase in charges within the polymers. As shown in the figures, the real and imaginary parts of dielectric constant of (PVA–PEO) blend change with the wavelength, this is due to the real part of dielectric constant depends on refractive index because the effect of extinction coefficient is very small and the imaginary part of dielectric constant depends on extinction coefficient especially in the visible and near infrared regions of wavelength where the refractive index is approximately constant while extinction coefficient increases with the increase of the wavelength [64].

Figure 12 shows the variation of optical conductivity with the wavelength for (PVA–PEO–SnO_2) nanocomposites. The figure shows that the optical conductivity of nanocomposites are decreased with the increase of the wavelength, this behavior attributed to the optical conductivity depends strongly on the wavelength of the radiation incident on the samples of nanocomposites, the increased

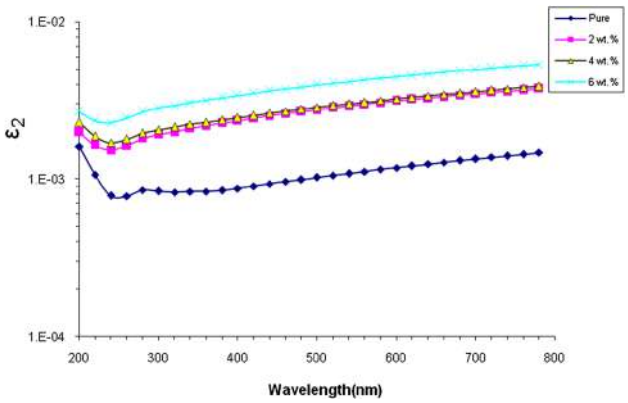

Fig. 11 Effect of SnO_2 nanoparticles concentrations on imaginary part of dielectric constant

optical conductivity at low wavelength of photon is due to high absorbance of nanocomposites in that region, hence, increase of the charge transfer excitations. The optical conductivity spectra indicated that the samples are transmittance within the visible and near infrared regions. Also, the optical conductivity of (PVA–PEO) blend is increased with the increase of SnO_2 nanoparticles concentrations, this behavior related to the creation of localized levels in the energy gap; the increase of SnO_2 nanoparticles concentrations increase the density of localized stages in the band structure, hence, increase of the absorption coefficient consequently increase the optical conductivity of nanocomposites [64].

Figures 13 and 14 show the observed variations of dielectric parameters (dielectric constant and loss) with frequency at room temperature. From the figures, it clear that at lower frequencies the values of both dielectric constant and dielectric loss are high because of the fact that in this region the dipoles have sufficient time to orient themselves in the

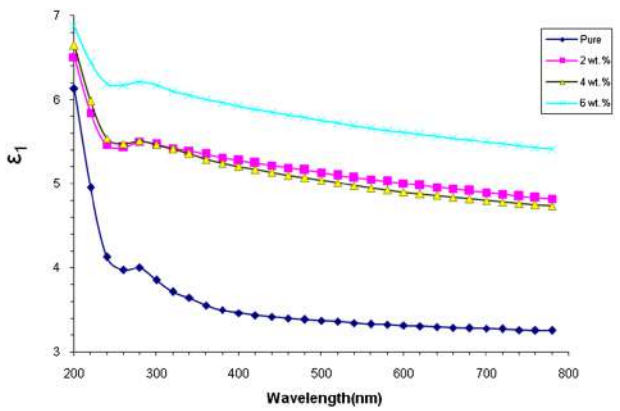

Fig. 10 Variation of real part of dielectric constant with wavelength for (PVA–PEO–SnO_2) nanocomposites

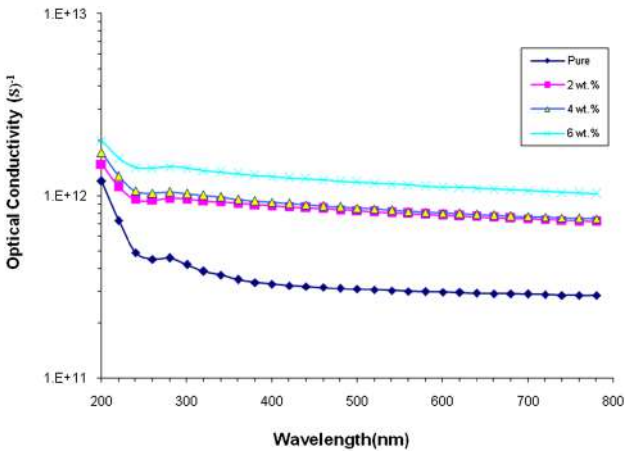

Fig. 12 Variation of optical conductivity with the wavelength for (PVA–PEO–SnO_2) nanocomposites

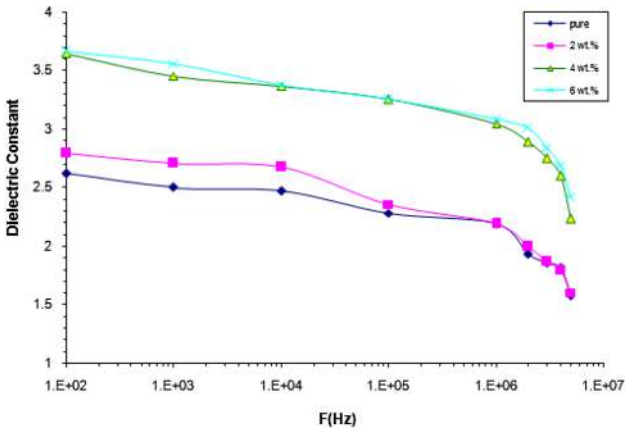

Fig. 13 Variation of dielectric constant for (PVA–PEO–SnO_2) nanocomposites with frequency

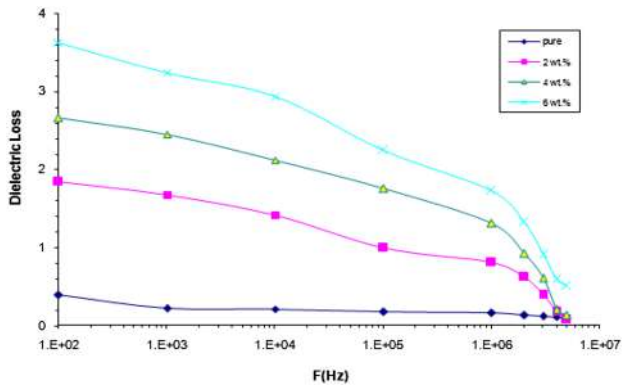

Fig. 14 Variation of dielectric loss for (PVA–PEO–SnO_2) nanocomposites with frequency

direction of the applied electric field. In addition to this, due to the electronic polarization effect (space charge polarization), charge carriers are accumulated at the electrode and electrolyte interface. As frequency increases dielectric constant and loss decreases monotonically and attains a constant value. This change in dielectric property is due to the fact that as the frequency increases, space charge polarization drops and more number of ions cannot diffuse in the direction of the applied electric field as a result the charge carriers are less contributed to the dielectric property. This change confirms the non-Debye type behavior of polymer electrolytes. Hence, due to insufficient time, the dipoles are unable to follow the field variation at higher frequencies [65].

Figure 15 shows the variation of conductivity with dopant concentration as well as frequency. As seen from FTIR results, the doping produce charge transfer complex (CTC) which results into the increase of flexibility of polymer chains and change in the band structure and chemical composition of the polymer. As frequency increases bonds

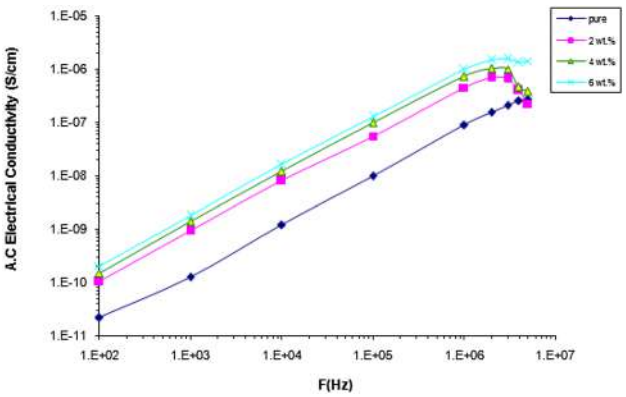

Fig. 15 Variation of conductivity with frequency for (PVA–PEO–SnO_2) nanocomposites

within the polymer starts to rotate with frequency and the flexible polar groups that are present in the polar bonds cause dielectric relaxation. Hence, conductivity increases with increase of frequency. Variation of conductivity with frequency showed two regions such as frequency-independent plateau region at low frequencies which is attributed to the long-range conduction process within the composites and frequency-dependent dispersion region at higher frequencies which corresponds to strong interaction of charge carriers. At lower frequency, due to the influence of space charge polarization in the nanocomposites, the charge carriers are accumulated at the electrode and electrolyte interface, due to this mobility of charge carriers is hindered [65]. Also, at low frequency, more charge accumulation occurred at the electrode and electrolyte interface, leading to a decrease in the number of mobile ions and electrical conductivity. The mobility of charge carriers was higher in the high-frequency region; hence the electrical conductivity increases with frequency [64]. From Figs. 13, 14 and 15, the dielectric loss, dielectric constant, and conductivity are increased with the increase in SnO_2 concentrations which can be explained by increasing in the number of charge carriers [66]. The enhancement of dielectric parameters of nanocomposites make them may be used in the different electronic devices industries.

The A.C electrical conductivity is given by the relation ($\sigma_{A.C} = A\ F^m$). The values of m are (0.785–0.897) for (PVA–PEO–SnO_2) nanocomposites which indicated to the nature and mechanism of conductivity is hopping mechanism.

4 Conclusions

The absorbance, absorption coefficient, extinction coefficient, refractive index, real and imaginary dielectric constants of (PVA–PEO) blend are increased with the increase

in SnO_2 nanoparticles concentration. The transmittance and energy band gap are decreased with the increase in SnO_2 nanoparticles concentration. The (PVA–PEO–SnO_2) nanocomposites have higher absorbance in the UV-region. The dielectric constant, dielectric loss and A.C electrical conductivity of (PVA–PEO) blend are increased with the increase in SnO_2 nanoparticles concentrations. The dielectric constant and dielectric loss of nanocomposites are decreased with the increase in frequency while the A.C electrical conductivity is increased with the increase in frequency. From the studies on optical and dielectric properties of (PVA–PEO–SnO_2) nanocomposites, the (PVA–PEO–SnO_2) nanocomposites may be used in a optoelectronics applications such as: sensors, solar cells, capacitors, transistors, diodes, etc.

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