

Effect of Carbon Black Nanoparticles on the Optical Properties of poly (ethylene oxide) Films

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Abstract

The optical properties of thin films made of poly (ethylene oxide) dispersed with dopants of fixed amount of carbon black (0.1 wt%). The prepared films by casting method have been optically investigated as a function of the carbon black fillers, and UV-visible wavelength ranges from (300 to 800) nm. The absorption coefficient, energy gap, refractive index, extinction coefficient, dielectric constants, and optical conductivity have been determined. The results obtained showed that the optical constants change with doped 0.1wt.% carbon black complexes.

Keywords: PEO, carbon black, optical, energy gap, refractive index, extinction coefficient, dielectric constants, optical conductivity.

INTRODUCTION

Many research works have been focused on increasing the observed ionic and electrical conductivities of solid polymer electrolytes(SPE) for the purpose of producing thin films to be used in promising electrical industry. Such applications of these SPE films include solid batteries, smart sensors, transistors, and other solid – state electrochemical devices. Among the polymers used as basic materials to manufacture polymeric electrolytes thin films are poly(ethylene oxide) and polyacrylonitrile which contribute in a significant development in batteries technology [1-5].

Electrical properties of polymers can be tailored to a specific requirement by addition of suitable conducting elements or dopant substances. Poly(ethylene oxide) has good thermal and electrical insulation properties, it is white solid with melting point around 65 °C, low toxicity, low glass transition temperature (-65 °C) which allows transport the ion at surrounding temperature. PEO is the best polymer used, because its large solvating power with ions, good process ability and outstanding mechanical properties [6-8].

Carbon black, when doped in polymers, may reside at various sites, It may go substitution-ally into the polymer chains and composed charge transfer complexes (CTC), or may exist in the form of molecular aggregates between the polymer chains [9].

Carbon black (CB) is a non-crystalline form of carbon, it is conductive and largely composed of carbon atoms or aggregates of nearly spherical shape. The most important purpose of (CB) used as a filler in polymers to impart

electrical and thermal conduction, i.e., conductive polymer composites [10-13].

The optical, electrical, thermal, and mechanical characterization is an essential for the industrial development of thin films of new polymers, blends, composites and advanced materials that can be used as optical devices, filters, polarizers, total reflectors, and narrow pass-band filters [14]. This paper is an extension study to previously published short communication by Zihlif et.al. [15] which contains preliminary data concern optical properties of PEO films (undoped). While in the present comprehensive paper the studied PEO thin films are doped with carbon black nanoparticles, i.e., hybrid films. Also, this paper covers optical absorption and energy transport processes occur in doped thin films. The optical properties studied in UV-visible wavelength range (300nm-800nm). A number of measured quantities as optical energy gap, energy tails, refractive index, optical conductivity, and dielectric constant.

EXPERIMENTAL WORK

In this study the material examined is (poly ethylene oxide) thin films doped with carbon black as dopant neat PEO sample for contrast the noticed consequences.

Preparation of thin films

PEO and carbon black powders were blended together in methanol as a convenient solvent. Then for two days the mixture was mixed by using a rotary magnet to get a homogeneous mixture. On to a glass mould the mixture was directly casted to delicate films. At room temperature by waiting for two days the methanol was permitted to evaporate perfectly. All samples were dried in the oven at temperature 40°C for two days.

The thickness of the synthesized composites was measured by a sensitive digital vernier caliper. Least count of the instrument is 0.001 mm. The thickness of all thin films were measured at six different spot places, chosen randomly, and then their average is taken. The obtained values of thicknesses are given in table 2.1

Table 2.1 Thickness values of polymer thin films

Polymer Composite Film	Thickness(μm)
Pure PEO	70
PEO + 0.1 % CB	120

Measurements of optical properties

Using the ultraviolet visible spectrophotometer shown in Figure (2.1), existing at Jordan University in the Chemistry Department, the reflectance (R) spectra and optical absorbance (A) of the thin films were assembled in the range of λ : (200 – 800) nm .

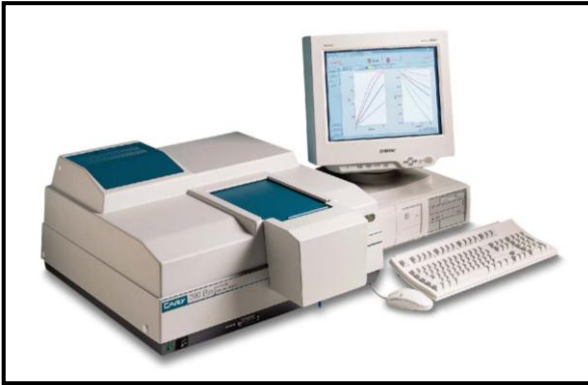


Figure 2.1: Cary spectrophotometer

The absorption coefficient $\alpha(\omega)$ is

$$\alpha(\omega) = \frac{1}{x} \log \left\{ \frac{(1-R)^2}{2T} + \frac{(1-R)^2}{\sqrt{(2T)^2 + R^2}} \right\} \quad (2.1)$$

where T is the optical transmittance, x is the sample thickness and R is the reflectance.

The refractive index (n) can be calculated from [16]

$$n = \left\{ \left[\frac{4R}{(R-1)^2} - k^2 \right]^{1/2} - \frac{R+1}{R-1} \right\} \quad (2.2)$$

where k is the extinction coefficient which is related to with the wavelength and the coefficient of absorption (α) by:

$$k = \frac{\alpha \lambda}{4\pi} \quad (2.3)$$

The dielectric constant (ϵ') and dielectric loss (ϵ'') are determined from the equations:

$$\epsilon' = n^2 - k^2 \quad \text{and} \quad \epsilon'' = 2nk \quad (2.4)$$

RESULTS AND DISCUSSION

Optical Results

The optical properties of PEO thin films doped with carbon black (0.1 wt. %), by weight were studied through measurements and determination of some physical parameters such as the optical gap, the energy gap tails, refractive index, dielectric constant and optical conductivity.

Solids absorbed an amount of the incident light of intensity I_0 and consequently optical transitions start when the energy of

photon absorbed is a quantity higher than or equals to the forbidden energy gap. If the required energy is almost equal to the difference between the lowest level of conduction band and the highest level of valence band, electrons will transfer from the valence band to conduction band. At high absorption coefficient levels, where $\alpha(\omega) > 10^4 \text{ cm}^{-1}$, the absorption coefficient α for non – crystalline materials can be related to the energy of the incident photon energy ($\hbar\omega$) according to the following formula:

$$\alpha \hbar\omega = \left(\frac{4\pi\sigma_0}{nc\Delta E} \right) (\hbar\omega - E_g)^r = \beta (\hbar\omega - E_g)^r \quad (3.1)$$

where the factor β is a constant depends on the refractive index of the material and the probability of absorption. The exponent r is an index determined by the type of electronic transition causing the optical absorption and can take values 1/2, 3/2 for the direct and 2, 3 for the indirect forbidden transitions [17] , [18].

($r = 1/2$ for allowed direct transitions and $r = 2$ for allowed indirect transitions), and E_g is the optical band gap. The optical absorption spectra of all films were recorded at room temperature, by using the UV-visible spectrophotometer in the wavelength range (200-800) nm.

Figure (3.1) represents the UV absorption spectra obtained for the prepared films. It shows clearly that the optical absorption increases when PEO sample fixed content of carbon black of concentration (0.1 wt.%), and decreases rapidly with increasing the incident photon wavelength ($<350\text{nm}$), i.e. below the absorption edge.

Tauc's plots were plotted and depicted in Figure (3.2) where the $(\alpha\hbar\omega)$ represents the product of the absorption constant and photon energy. From the graph, it is seen that the optical energy gap value decreases with doped 0.1wt.% carbon black as compared to that case of the un doped film.

The drawn straight lines obtained with $r = 1/2$ indicate that the electron transition process is direct in k-space. Extrapolation of the linear portion of these curves gives the optical energy gap (E_g) value [19] , [20].

A decrease in the energy band gap value may be attributed to an increase in structural disorder of the polymer doped films. The decrease dependence in optical energy gap on doping may be explained on the basis of the fact that the incorporation of small amounts of carbon black particles forms free electrons disorder in the host polymer lattice. The absorption studies have led to a variety of interesting thin film optical phenomenon, which have thrown considerable light on the band structure of solids and phonic states [21].

The reduction in the band energy gap is also due to carbon black particles dopants incorporated into the polymer chains and, thereby, extending the density of states more into the visible region of the electromagnetic spectrum as compared to that case of the un doped film. The decrease in the value of the optical energy gap indicates enhancement of the semiconducting level of the prepared doped films, and existing of the conductive carbon black particles.

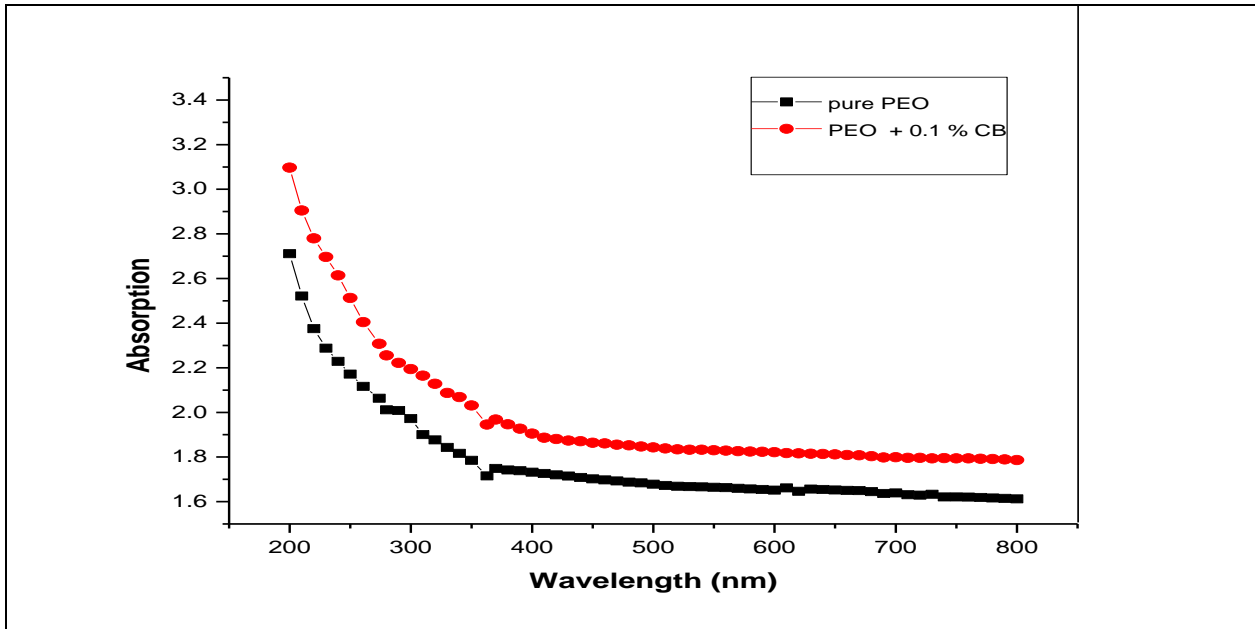


Figure 3.1 : Absorption spectra for PEO/ CB composites

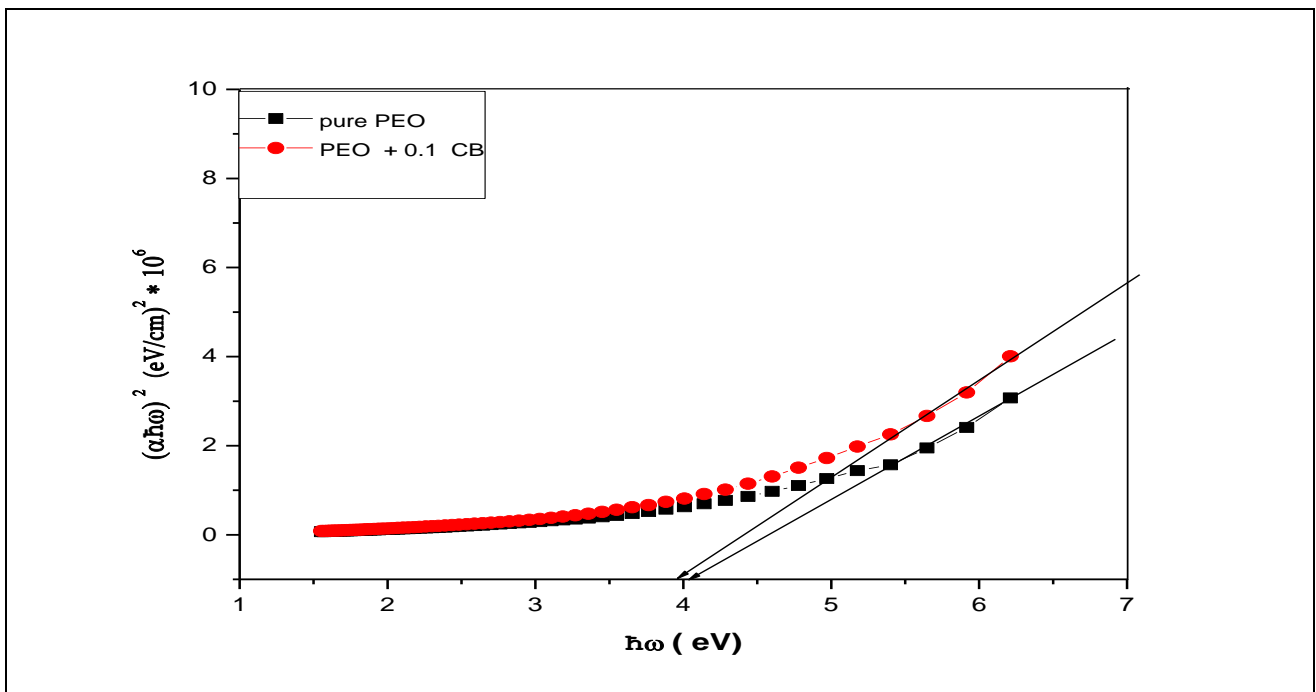


Figure 3.2: $(\alpha\hbar\omega)^2$ versus the photon energy for PEO/CB composites

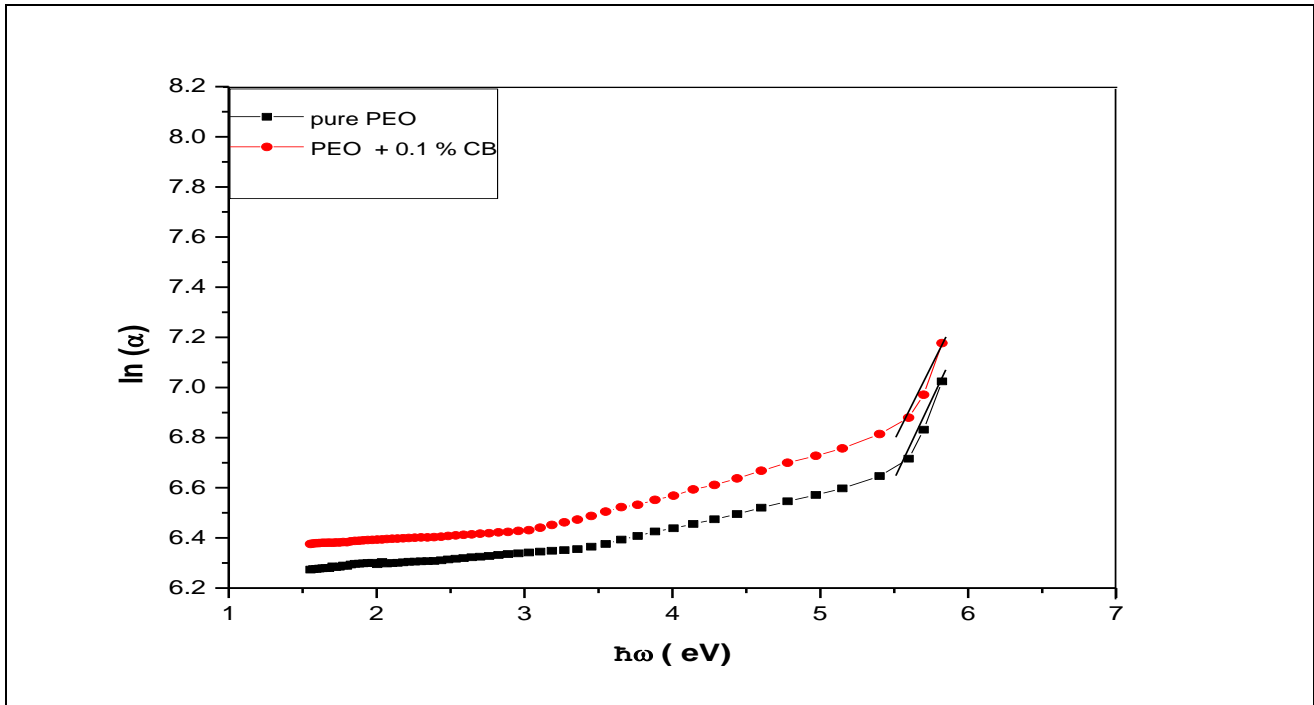


Figure 3.3: Urbach plots of $\ln(\alpha)$ versus the photon energy for PEO/CB composites

Table 3.1: Optical energy results for PEO/CB composite films

Thin film	Optical band gap E_g (eV)	ΔE (eV)	Single-oscillator energy parameter E_0 (eV)	Dispersion energy parameter E_d (eV)
Pure PEO	4.09	0.89	6.81	10.81
PEO doped with 0.1wt.% carbon black	4.02	0.85	6.89	14.32

Table (3.1) includes the determined values of (E_g) which decrease with doped 0.1wt.% carbon black. The optical absorption coefficient $\alpha(\omega)$ is described by Urbach formula [22]:

$$\alpha(\omega) = \alpha_0 \exp(\hbar\omega / \Delta E) \quad (3.2)$$

where α_0 is a constant and ΔE is the energy gap tails interpreted as the width of the tail of localized states in the forbidden band gap [23]. Figure (3.3) represents the Urbach plots for the thin films. The extrapolated tail width values (ΔE) listed in table (3.1), were determined by using the slope of the linear part of each curve and equation (3.2):

$$\ln(\alpha) = \hbar\omega / \Delta E + \ln(\alpha_0) \quad (3.3)$$

The exponential dependence of $\alpha(\omega)$ on photon energy ($\hbar\omega$) indicates that the absorption processes taking place in the studied thin films obey Urbach rule. These energy tails become smaller as un doped film, which is consistent with that variation of the optical energy gap (E_g) [23].

The increments of the energy tail widths can be explained by the fact that doping the carbon black content may lead to the creation of ionic complexes, free electrons, disorder, and imperfections in the structure of the composites, a case that may increase localized states within the forbidden energy gap. The energy tails have smallest values due to neatness of the PEO structure and scanty impurities, which lead to decrease localized states within the forbidden band gap. This usually contributes to the increase in the optical energy gap [19].

The extinction coefficient (k) value can be obtained from the relation between the absorption coefficient and wavelength, equation (2.3). Extinction Coefficient represents the imaginary part of complex refractive index and it can be defined as the amount of energy loss as a result of interaction between the light and the charge of medium [24].

For the PEO thin films, they are shown in figure (3.4). The figure shows that the extinction coefficient (k) increases with increasing the wavelength, because (k) is directly proportional to the absorption coefficient as see in equation (2.3). The value of extinction coefficient increases with doped 0.1wt.% carbon black because it is directly proportional to the absorption coefficient. Extinction coefficient values exhibit changes with 0.1wt.% carbon black, and are associated with processes of scattering, reflection, and optical absorption taking place on the thin film surfaces [25].

Figure (3.5) shows the variation of the refractive index (n) obtained from equation (2.2). On the other hand, when the refractive index and the extinction coefficient are known, the real and the imaginary parts of dielectric constant of the composites can be estimated. The real and the imaginary parts of complex dielectric constant are expressed in equation (2.4). The real part is associated with the term that shows how much it will slow down the speed of light in the material. The imaginary part shows how a dielectric absorbs energy from an electric field due to dipole motion in the PEO polymeric matrix [26].

Figure (3.5) shows the variation of the refractive index (n) for pure PEO thin film and PEO doped with (0.1 wt.%) carbon

black, the (n) value was calculated from equation (2.2) and (2.3) which relate the refractive index (n) with the absorption coefficient (α) and the extinction coefficient (k). Figure (3.5) shows that the refractive index decreases with increasing the applied wavelength, i.e. dispersion behavior. The refractive index values ranged from 1.65 for pure PEO to 1.82 for PEO doped with (0.1 wt.%) carbon black composite estimated at wavelength 600 nm. The variations of refractive index with the wavelength show that some interactions take place between photons and electrons. Refractive index changes with variation of the wavelength of the incident light beam are due to these interactions [27].

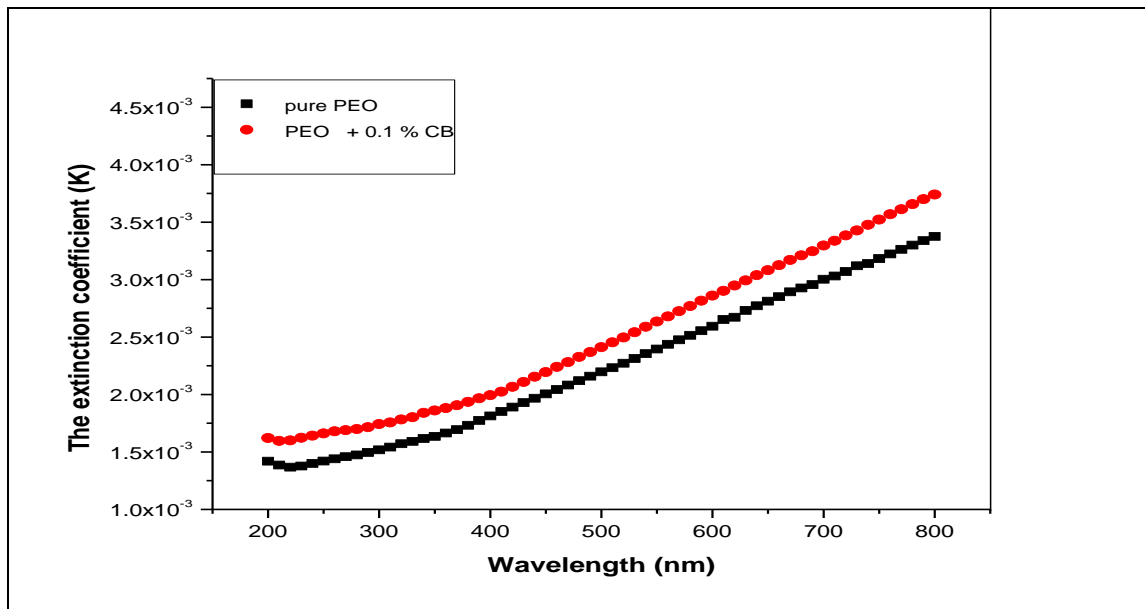


Figure 3.4: The variation of extinction coefficient with the photon wavelength

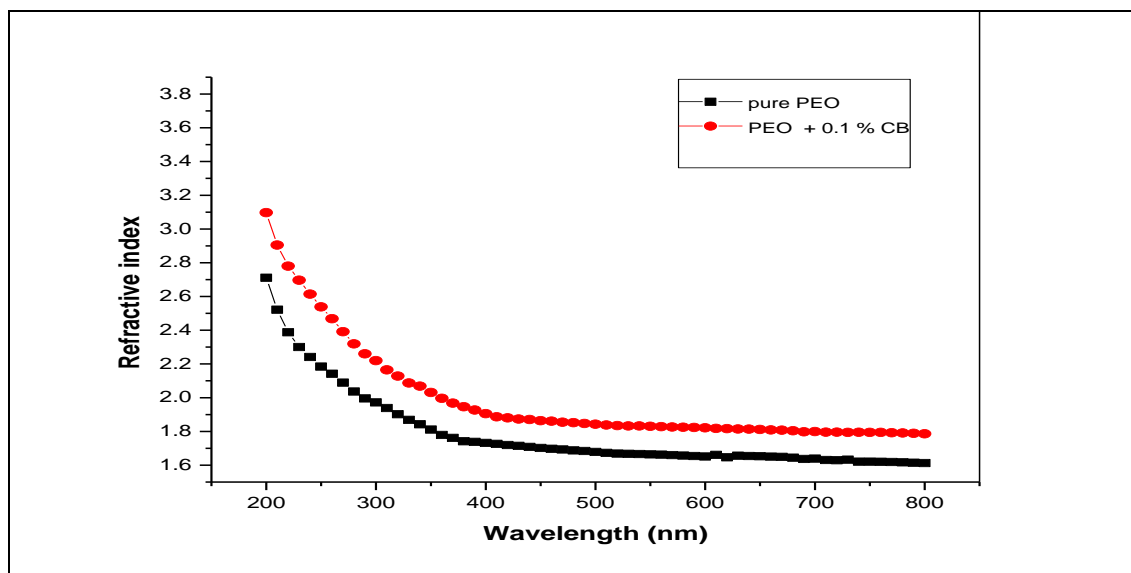


Figure 3.5: Refractive index versus the incident wavelength

The variations of the real and imaginary components of the complex permittivity of the composites with the incident wavelength are shown in figures (3.6) and (3.7), respectively. The curves follow the same dispersive pattern in the UV-wave length as shown in the (n) behavior.

The dielectric constant value of PEO composites is greater for doped with 0.1wt.% carbon black and is attributed to

interfacial polarization, a phenomenon that appears in heterogeneous media consisting of phases with different ionic conductivity [28], that is, PEO composites with carbon black particles dispersed in the PEO resin. PEO becomes more heterogeneous as carbon black is added to it, because of accumulation of charges at the interfaces between the dispersed phase and the PEO matrix.

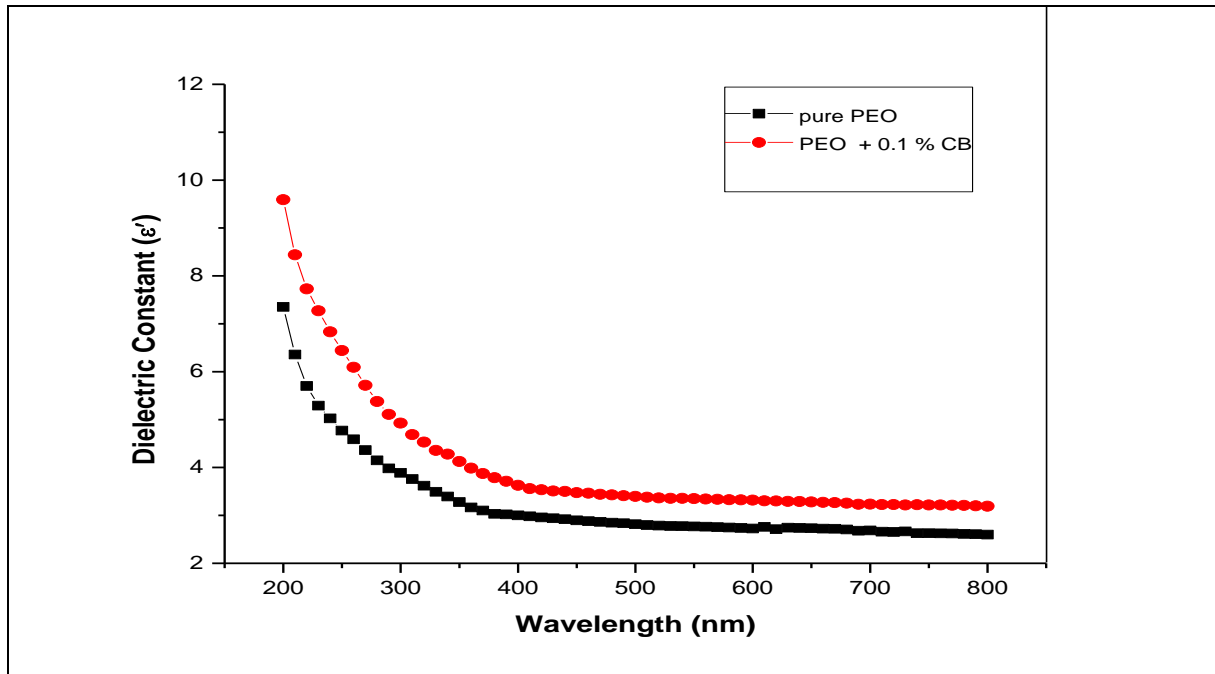


Figure 3.6: The dielectric constant versus the wavelength

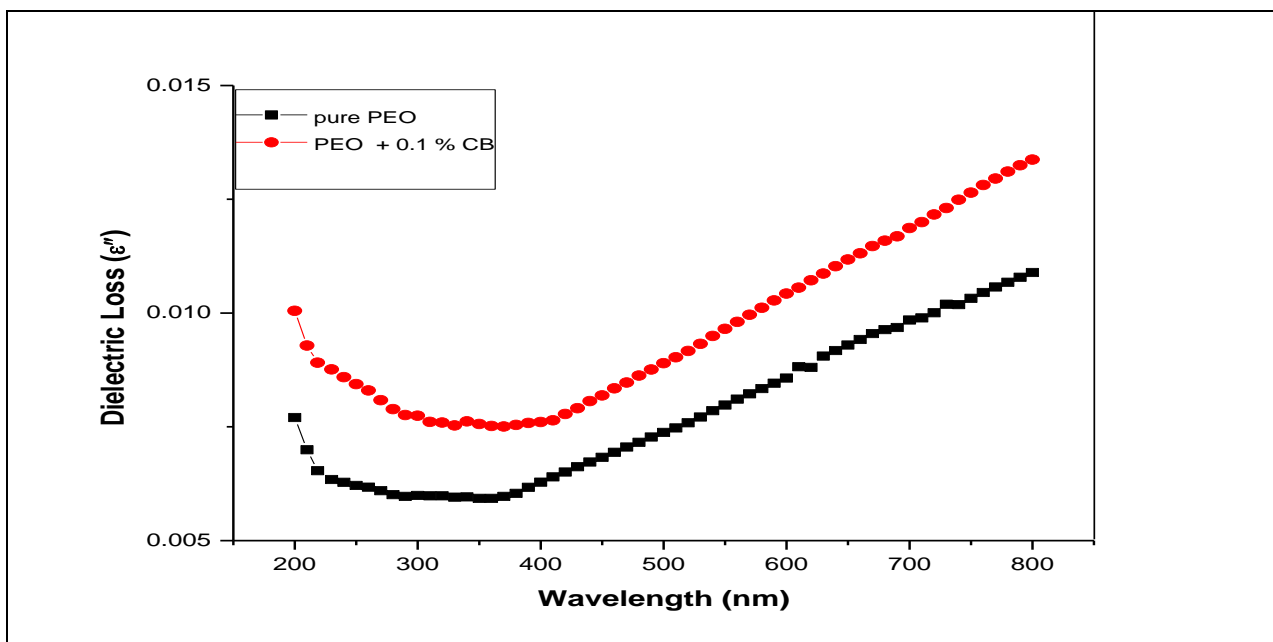


Figure 3.7: The dielectric loss versus the wavelength

The Wemple–DiDomenico relationship can fit the dispersion energy values of the refractive index of the thin films [29]. The refractive index is related to energy of the photon ($\hbar\omega$) based on the relation:

$$n^2 = 1 + \frac{E_0 E_d}{E_0^2 - (\hbar\omega)^2} \quad (3.4)$$

where E_d is the dispersion energy and E_0 is the single-oscillator energy [30]. E_d represents the dispersion energy associated with the average strength of the optical transitions and E_0 simulates the excitation of electrons [31]. The dispersion energy E_d , which is a measure of the inter-band optical transition intensity, is a significant factor to calculate the thin films dispersion parameters [32]. Plotting $(n^2-1)^{-1}$ versus $(\hbar\omega)^2$ for the polyethylene oxide/carbon black composites, we have got straight lines as seen in figure (3.8). According to the relation:

$$(n^2 - 1)^{-1} = \frac{E_0}{E_d} - \frac{1}{E_0 E_d} (\hbar\omega)^2 \quad (3.5)$$

the (E_0) and (E_d) quantities were calculated from the slope and the intercept (E_0/E_d) on the vertical axis. Table (3.1) shows that E_0 and E_d quantities increased with doped 0.1wt.% carbon black as the optical band gap decrease. The increase in dispersion energy is usually associated with the evolution of the thin films microstructure to a more ordered phase [33].

The optical conductivity (σ) is a powerful tool for studying the electronic states in materials. If a system is subjected to an

external electric field then, in general, a redistribution of charges occurs and currents are induced. At low fields, the optical conductivity is determined by:

$$\sigma = \frac{\alpha n c}{4\pi} \quad (3.6)$$

where c is the light speed, n is refractive index and α is the absorption coefficient.

Figure (3.9) shows plots of optical conductivity versus $(\hbar\omega)$ for the different prepared thin films. It is seen that the optical conductivity increases with thin film doped 0.1wt% carbon black [34]. The behavior of optical conductivity with energy of photon is seen in figure (3.9), it can be seen that, at pure PEO and PEO doped 0.1wt% carbon black, $(\hbar\omega)$ has low values which is due to interface scattering of discontinuous metal particles, carbon black form small isolated islands embedded in PEO matrix. As the carbon black content doped, which represents the moment when there is enough conductive particles present to make a continuous network, the islands grow and continuous carbon black - paths extending through PEO are established[24].

Optical conductivity $(\hbar\omega)$ of the thin films doped with carbon black was increased with energy corresponding to the band gap energy, which due to electrons excited by photon energy and due to large absorption coefficient for these composite.

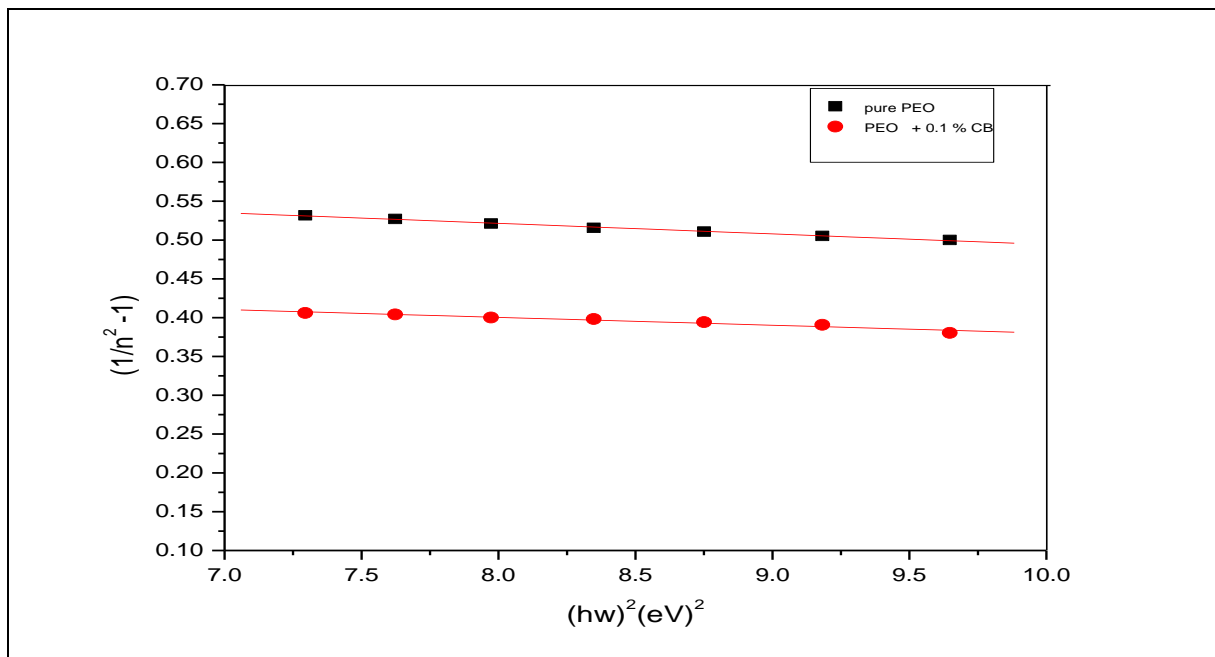


Figure 3.8: The variation of $(n^2 - 1)^{-1}$ with $(\hbar\omega)^2$

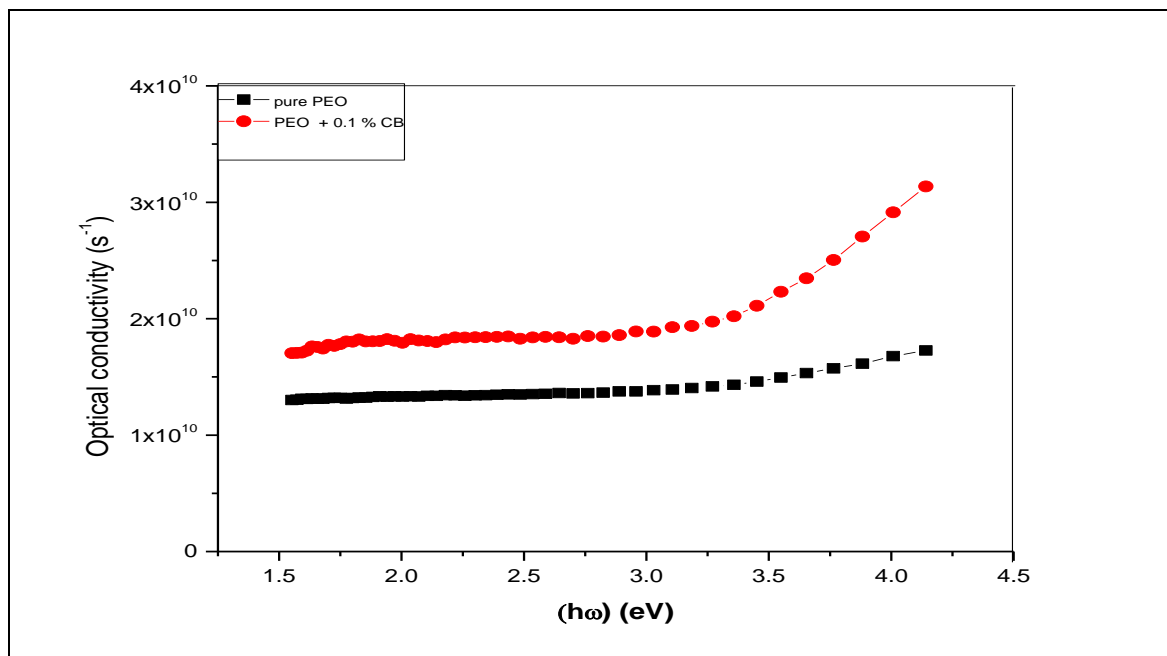


Figure 3.9: The variation of the optical conductivity versus the photon energy

CONCLUSIONS

The optical properties of PEO thin films doped with carbon black were studied. By studying the results, we deduced that:

1. Analysis of the optical energy results illustrate that the electron transitions is direct in k-space.
2. Doping the carbon black content, the optical energy gap in the samples decreases.
3. The dielectric constant and refractive index of composites increase with doped 0.1wt.% carbon black complex.
4. The dielectric constant (ϵ') and the dielectric loss (ϵ'') of the composites decrease with frequency and with doping carbon black.
5. Fitting the observed data to proposed empirical physical laws seems to be reasonable.

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