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Tuning the Morphological and Optical Characteristics of SnO_2/ZrO_2 Nanomaterials Doped PEO for Promising Optoelectronics Applications

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ABSTRACT

In this work, the casting method was utilized to form the PEO/SnO_2/ZrO_2 nanocomposite to improve its structural and optical characteristics. The formation network path inside the polymeric matrix at the higher concentration of nanoparticles was confirmed by the optical microscope (OM). The nanocomposite of PEO/SnO_2/ZrO_2 has a higher absorbance in the UV region, which proved from the optical measurements that it can be used as an optoelectronic device. Increasing the concentration of SnO_2 and ZrO_2 NPs alters several properties. For example, the refractive index, optical conductivity, absorbance, extinction coefficient, and real and imaginary dielectric constants all increase, but the transmittance and energy optical band gap decrease. For the permitted and prohibited indirect transitions separately, the energy gap shrank from 3.68 eV to 3.4 eV and 3.66 eV to 3.35 eV, respectively. The narrowing of the energy band gap is very useful for many fields that work with optical devices.

1. INTRODUCTION

Nanotechnology is a nascent technology. The current generation is exerting a big impact on the global economy by developing innovative and substantial products, enhancing product utilization, and implementing more efficient production methods. Nanotechnology yields several types of nanoparticles, encompassing metallic, metal oxide, doped metallic, and undoped metallic and metal oxide particles. Nanoparticles are materials with dimensions between 1 and 100 nanometers in at least one direction. Within that narrow range, materials display distinct mechanical, chemical, and physical properties [1]. Due to their unique properties, polymer nanocomposites are becoming more popular [2]. Metal and semiconductor nanoparticles have excellent optical and electrical properties, making polymers good host materials [3]. Due to their remarkable features and new methods, nanocomposites with inorganic and organic components have gained technological strength in linear and nonlinear optics and solar cells [4]. Polymers behave like inorganic materials. However, polymers offer flexibility, simplicity of processing, corrosion resistance, affordability, and a lightweight composition. Thermal stability and structural integrity are also advantages of inorganic materials. In solar cell batteries, sensors, and TVs, polymer-inorganic hybrids find application [5].

The distinctive properties and wide range of applications of polyethylene oxide (PEO), a well-known synthetic polymer, have piqued the interest of researchers all over the globe. At the very end of each polymer chain are hydrogen and hydroxyl groups. Hydrophobic ethylene groups and hydrophilic oxygen groups form a hydrogen bond site in the repeating unit [6]. Combining PEO with a catalyst achieves polymerization, resulting in PEO [7]. Because it is hydrophilic, linear, and lacks cross-links, it dissolves effectively in organic and water-based solvents [8]. At temperatures below 100°C, PEO dissolves easily in water, irrespective of the polymerization ratios or levels [9]. The properties of polyethylene oxide (PEO) include not being ionic, not being poisonous, not irritating, being biodegradable, and being biocompatible. Not only that, but the material is cheap [10]. There's a chance that PEO is a hybrid polymer with both amorphous and crystalline parts [11]. The physical features of this substance are exceptional, and they include qualities like high viscosity, low melting point (69°C), glass transition temperature (-50°C), flexibility, high ionic conductivity, and outstanding chemical stability [12].

Recently developed composites include carbides, metals, oxides, ionic materials, and biomaterials [13]. Tin oxide, a widely used and studied crystalline n-type semiconductor with a wide band gap, has been extensively researched. Researchers have extensively studied tin oxide gas sensors, dye-sensitized solar cells, optical, optoelectronic, and hybrid microelectronic devices [14]. Recent research suggests the chemical could be a lithium cell and photocatalysis electrode [14]. This oxide is a popular white pigment for conducting coatings due to its semi-conductive transparency. Tin oxide nanoparticles are synthesized using co-precipitation, hydrothermal, sol-gel, nonchemical polymer, and precursor techniques [15]. An n-

type semiconductor oxide, tin dioxide, has a wide bandgap. As a catalyst, catalytic support, biological and pharmaceutical gas sensor, rechargeable Li battery, and optical electronic device, tin dioxide (SnO_2) has received attention. Gold-tin dioxide catalytic activity has garnered attention recently. In the research of Xavier et al. [16], nanocomposites showed excellent catalytic activity for CO oxidation at low temperatures. Tin dioxide (SnO_2) finds wide applications as a catalyst, catalytic support, biological material, medicinal substance, gas sensor, rechargeable lithium battery component, and optical electronic gadget, contributing to its popularity. Gold-tin dioxide catalytic activity has garnered attention recently. In CO oxidation at low temperatures, nanocomposites were highly catalytic [17].

Zirconium oxide (ZrO_2) is one of the most extensively studied transition metal oxides in the field of optics. In the visible and near-infrared spectrum, ZrO_2 films exhibit remarkable transparency, a large optical band gap, and a high refractive index [18]. Zirconia, or ZrO_2, is a mineral with remarkable physical and chemical characteristics. Some of its many applications include catalysts, fuel cells, gas sensors, optoelectronics, and materials that resist corrosion [19-23]. ZrO_2 exhibits both illumination and high transparency [24]. Its large surface area, oxygen vacancies, and bandgap of more than 5 eV make it a promising photocatalytic candidate. Crystals in this material can be either cubic or tetragonal. Factors such as flaws, synthesis, particle size, and calcination temperature cause these variations in structure. The occurrence of phases at various calcination temperatures has been the subject of contradictory research [25].

Many studies have examined the optical characteristics of polymer composites with PEO as the host material. Al-Mehmadi et al. [26] added several proportions of tungsten trioxide (WO_3) nanoparticles to PEO-NaAlg's research, which indicates that the presence of WO_3 leads to a decrease in the optical band gap. Al-Harbi et al. [27] did an independent study that showed that adding ZnO/GO nanostructured additives to PEO/CMC host polymers results in a substantial decrease in the bandgap. Moreover, previous studies have discovered changes in the optical band gap and refractive indices of PEO when it is filled with various dopants. The metal oxide had been into polymers to improve their optical properties [28-34].

The goal of this study is to make PEO/SnO_2/ZrO_2 nanocomposites and look into their structure and optical properties so that they can be used in different optical areas, like photodetectors.

2. MATERIALS AND METHODS

To investigated the (PEO/SnO_2/ZrO_2) nanocomposites, 30 mL of distilled water added 1 gm of PEO with continuous magnetic stirrer for 30 minutes and temperature 70°C to ensure more homogenous solution and then added (0, 2, 4 and 6) wt.% from SnO_2 and ZrO_2 NPs to PEO solvent completely. The casting method was used to prepare of (PEO/SnO_2/ZrO_2) nanocomposites. The Olympus (Top View) type (Nikon 73346) with an automatically controlled camera under a (10 x) magnification was employed to define the films' surface for the examined surface film. using spectrophotometer (UV-1800 ^{0}A-Shimadzu) to investigate the optical measurements.

The coefficient of absorption (α) is provided as Eq. (1) [35]:

$$\alpha = 2.303 * A/d \quad (1)$$

The absorbance is denoted by A and the sample thickness is measured by d. The photon energy (hv) and the α are dependent on the indirect E_g^{opt}, as demonstrated in the Eq. (2) [36].

$$\alpha hv = B\left(hv - E_g^{opt} \pm E_{ph}\right)^r \quad (2)$$

The band tailing parameter B and the type of optical transition r for the materials being studied are defined by the equation (r = 2 for permissible indirect transitions). The formula for the refraction index is Eq. (3) [37].

$$n = \frac{1 + R^{\frac{1}{2}}}{1 - R^{\frac{1}{2}}} \quad (3)$$

Indicate R represent the reflectance, the extinction coefficient (k) is illustrate by Eq. (4) [38].

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

λ indicate the wavelength. The component real (ε_1) and imaginary (ε_2) parts of dielectric constant are assumed by Eqs (5) and (6) [38].

$$\varepsilon_1 = n^2 - k^2 \quad (5)$$

$$\varepsilon_2 = 2nk \quad (6)$$

The conduction for the optical (σ_{op}) is definite by Eq. (7) [39].

$$\sigma_{opt.} = \alpha nc/4\pi \quad (7)$$

c indicates to the speed of light.

3. RESULTS AND DISCUSSION

The optical microscope (OM) reveals changes in the surface morphology of (PEO-SnO_2-ZrO_2) nanocomposites. Figure 1 depicts the optical microscope of the (PEO-SnO_2-ZrO_2) nanocomposites at a 10 x magnification. Image (A) depicts a homogeneous phase with no phase separation. The image (B-E) in Figure 1 unambiguously illustrates the homogeneous dispersion of SnO_2 and ZrO_2 NPs on the PEO polymer film's surface. However, at lower concentrations, the SnO_2 and ZrO_2 NPs incline to collective and formula collections. Increasing the concentrations of SnO_2 and ZrO_2NPs in the PEO polymer results in the formation of a network of pathways within the PEO. These pathways allow charge carriers to flow, causing a modification in the material characteristics, which can be observed. This process offered an appropriate approach for fabricating nanocomposite films. This behavior is consistent with [40-47].

Figure 2 shows the correlation between the wavelength and the absorbance characteristics of nanocomposites made of (PEO-SnO_2-ZrO_2). Because they have a lot of energy, photons can connect with atoms and help electrons move from lower to higher energy levels. This is the reason why all of the samples absorb a lot of ultraviolet (UV) light. This is because the photons coming in don't have enough energy to interact successfully with the material's atoms, which is why the

nanocomposite's spectra show less absorption in the near-infrared range. The screen absorption effect is more noticeable at shorter wavelengths and less noticeable as the wavelength gets longer. The absorbing effect is directly linked to the amount of SnO_2 and ZrO_2 nanoparticles present. It has also been seen that the number of charge bearers has increased. While impurity atoms are present between the conduction and valence bands, they cause a distribution of energy levels that explains the observed behaviors [48-52]. This result agrees with the researches of Kock et al. [53] and Jasim et al. [54].

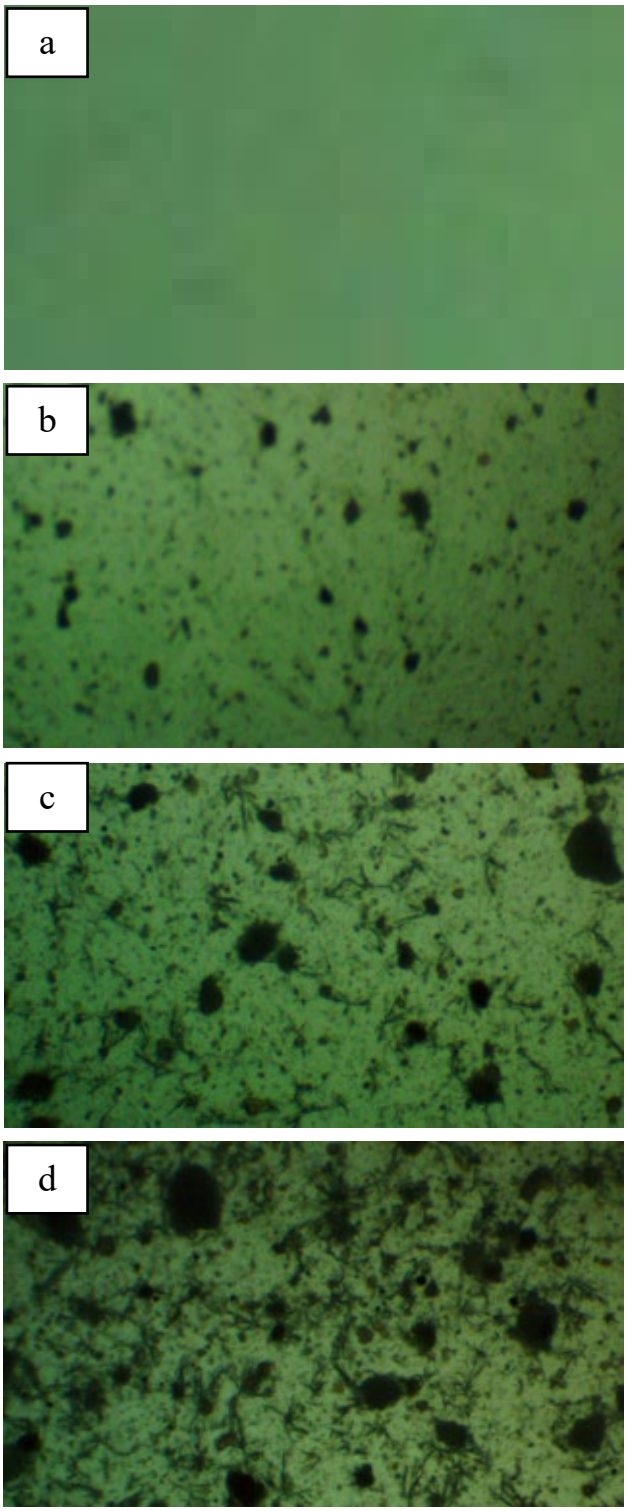

Figure 1. Photomicrographs for (PEO-SnO_2-ZrO_2) nanocomposites:(a) for (PEO) blend; (b) for 2 wt.% SnO_2 and ZrO_2 NPs; (c) for 4 wt.%SnO_2 and ZrO_2 NPs; (d) for 6wt.%SnO_2 and ZrO_2 NPs

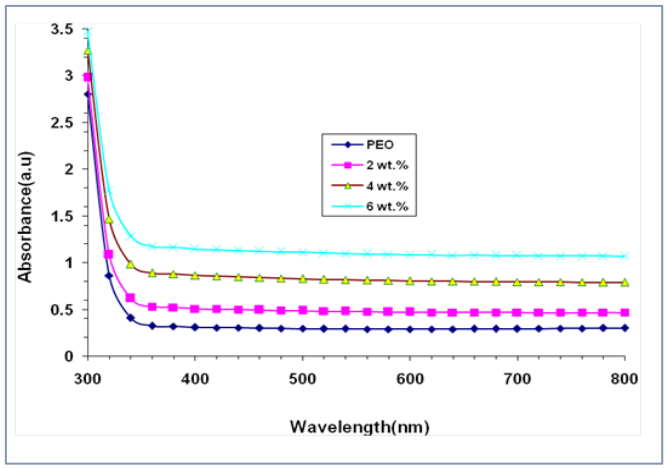

Figure 2. Absorbance of (PEO-SnO_2-ZrO_2) nanocomposites varies with wavelength

Figure 3 shows the correlation between the wavelength and the transmittance spectra of films made of (PEO-SnO_2-ZrO_2). Graphs of spectra showing varying concentrations of SnO_2 and ZrO_2 nanoparticles are displayed. The graph clearly shows that the transmittance decreases as the concentrations of SnO_2 and ZrO_2 increase. The capacity of the electrons in the outermost shells of SnO_2 and ZrO_2 to absorb the electromagnetic energy of the incident light and migrate to higher energy levels explains the observed behaviors. The material can absorb all incoming light and block its transmission because the moving electron occupies energy locations in each band [55].

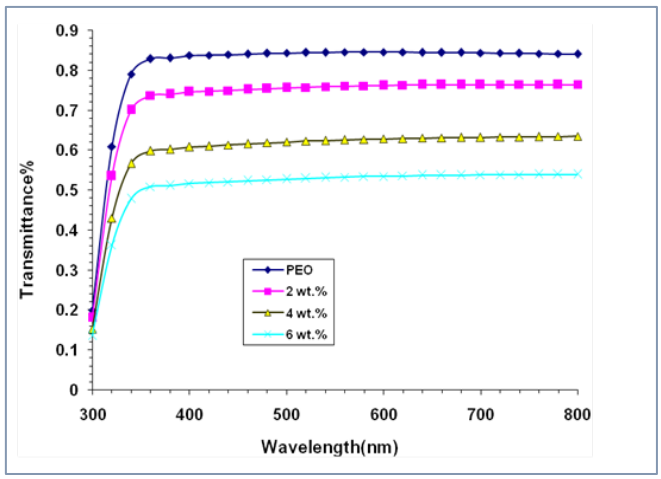

Figure 3. Nanocomposites of (PEO-SnO_2-ZrO_2) and how their transmittance spectra change with wavelength

Figure 4 shows how photon energy affects (PEO-SnO_2-ZrO_2) nanocomposites' absorption coefficient. As wavelengths grow and energy decrease, absorption coefficients visually decrease. Low energy photons ($hv < E_g$) are unlikely to produce electron displacement, as per reference [56]. This study shows how absorption coefficient affects electron transition. We expect the absorption coefficient to exceed $10^4 cm^{-1}$ at high energies. Electrons and photons conserve energy and momentum during direct electron transitions. In contrast, at low energy levels, the absorption coefficient is about $10^4 cm^{-1}$, indicating indirect transitions where phonons boost electric momentum [57]. PEO-SnO_2-ZrO_2 nanocomposites absorb below $10^4 cm^{-1}$. Along with previous findings, this shows an indirect electron transition.

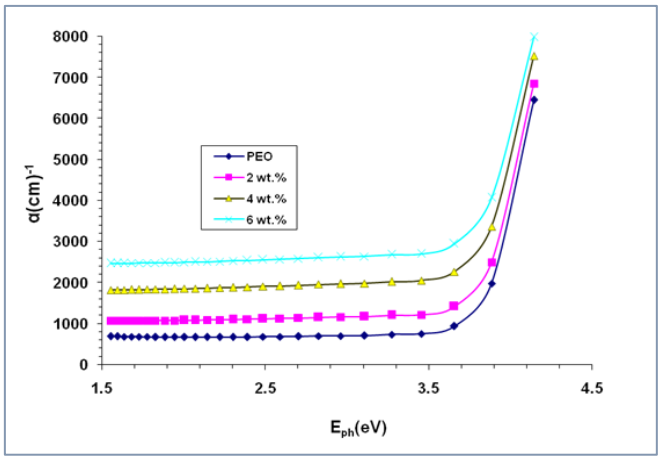

Figure 4. The photon energy dependence of the absorption coefficient of (PEO-SnO_2-ZrO_2) nanocomposites

The extinction coefficient measures how much an electromagnetic wave's intensity drops when it travels through a material. Figure 5 shows the relationship between wavelength and the extinction coefficient graphically. Extinction coefficient values are positively correlated with SnO_2 and ZrO_2 nanoparticle concentrations, as seen in the figure. A possible explanation for the enhanced film absorbance is the presence of pollutants within the energy gap, which generate a high concentration of energy levels [58].

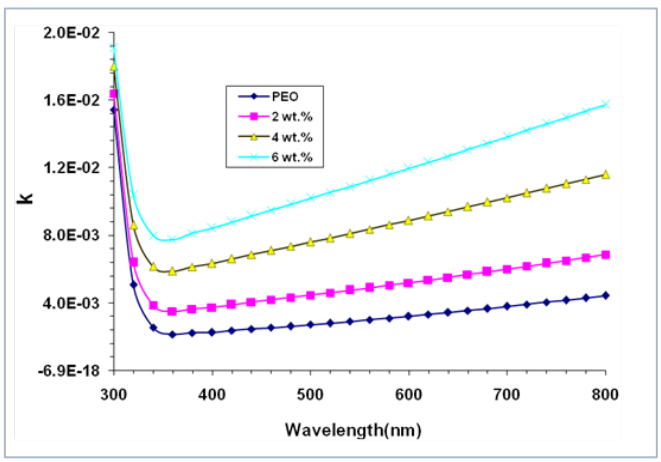

Figure 5. Distinction between the extinction coefficient and wavelength of (PEO-SnO_2-ZrO_2) nanocomposites

Figure 6 shows the wavelength-refractive index relationship. PEO-SnO_2-ZrO_2 nanoparticles directly affect refractive index, as seen in the graphic. Doping drugs change the direction of incident rays, creating extra energy levels. This increases the strength of reflected rays, raising the refractive index. Due to low transmittance (T) in the UV, the UV has a high refractive index. According to the standard, the visible and near-infrared (IR) ranges have low refractive index values due to high transmittance (T). SnO_2 and ZrO_2 presence increases nanocomposites' density and n values [59-63].

The energy gaps for permissible and forbidden indirect transitions are shown in Figures 7 and 8. Draw a linear line from the curve peak to the x-axis at $(\alpha h\nu)^{1/2} = 0$ to get the allowed energy gap. Conversely, the forbidden energy gap is identified when $(\alpha h\nu)^{1/3}$ is zero. Observations show that SnO_2 and ZrO_2 nanoparticles lower energy gaps. Doping creates energy levels within the energy gap, causing the decline. After leaving the valence band, electrons proceed to the energy gap's local levels and then to the conduction band [64-68].

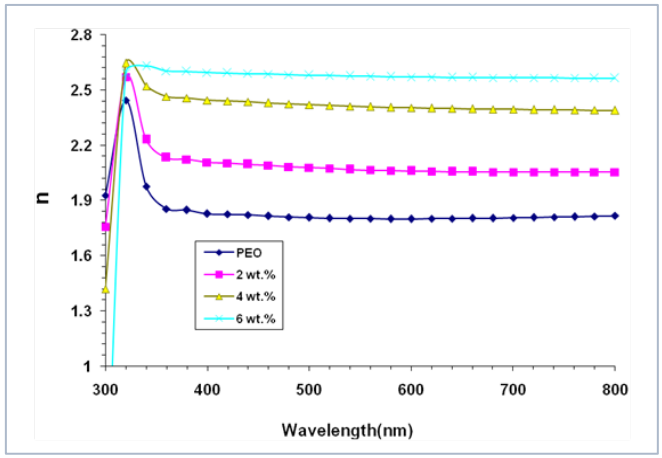

Figure 6. Fluctuations of the refractive index of (PEO-SnO_2-ZrO_2) nanocomposites as a function of wavelength

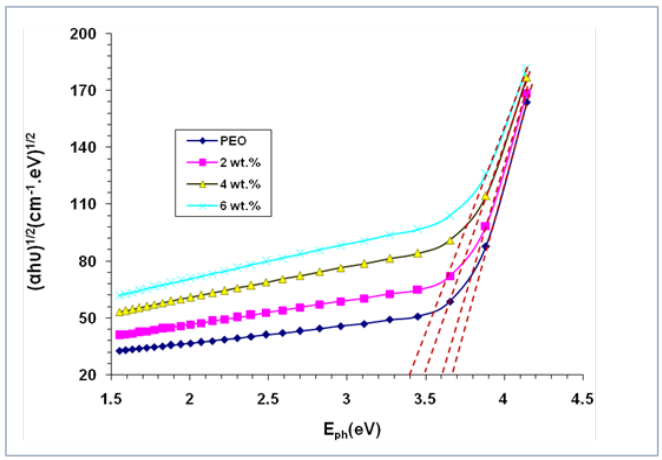

Figure 7. Division of $(\alpha h\nu)^{1/2}$ for (PEO-SnO_2-ZrO_2) nanocomposites with photon energy

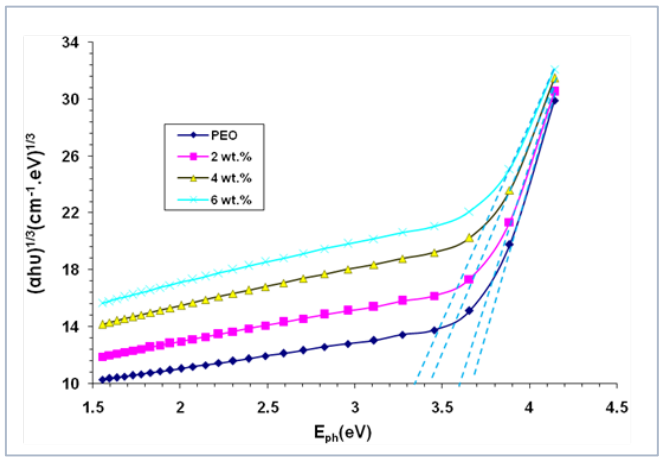

Figure 8. Division of $(\alpha h\nu)^{1/3}$ for (PEO-SnO_2-ZrO_2) nanocomposites with photon energy

A substance's dielectric constant measures its electromagnetic radiation-induced polarization. The phenomenon is commonly described using two components: the real (ε_1) and imaginary (ε_2) dielectric constants. PEO-SnO_2-ZrO_2 nanocomposites' real and imaginary dielectric

constants vary with wavelength, as shown in Figures 9 and 10. The study found a correlation between SnO_2 and ZrO_2 nanoparticle proportions and real and imaginary dielectric constants. Nanoparticles increase electric polarization, explaining the observed behavior. Electric polarization increases dipole concentration and dielectric constant. The true dielectric constant curves in Figure 8 closely mirror the refractive index curves, demonstrating a significant link. The refractive index (n) affects the dielectric constant more than the extinction coefficient (k), especially when squared, explaining the observed resemblance. Figure 9 shows the wavelength-hypothetical dielectric constant correlation. In the infrared and visible bands, the restraining coefficient affects the imaginary component of the dielectric constant. Despite the refractive index being roughly constant in the defined sites, the extinction coefficients increase with longer wavelengths [69].

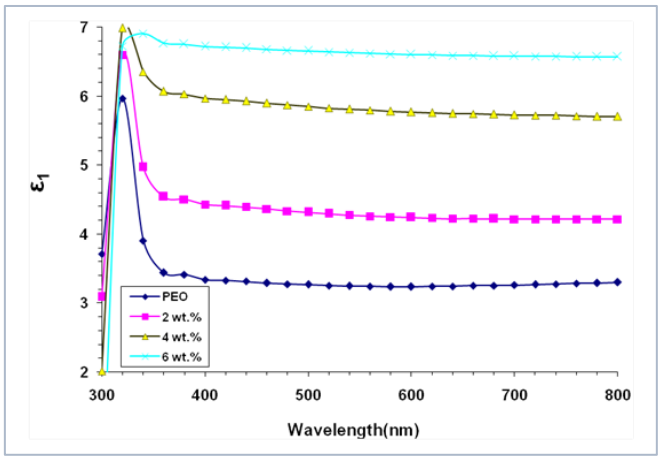

Figure 9. Experimental results of the dielectric constant for nanocomposites of for (PEO-SnO_2-ZrO_2) with wavelength

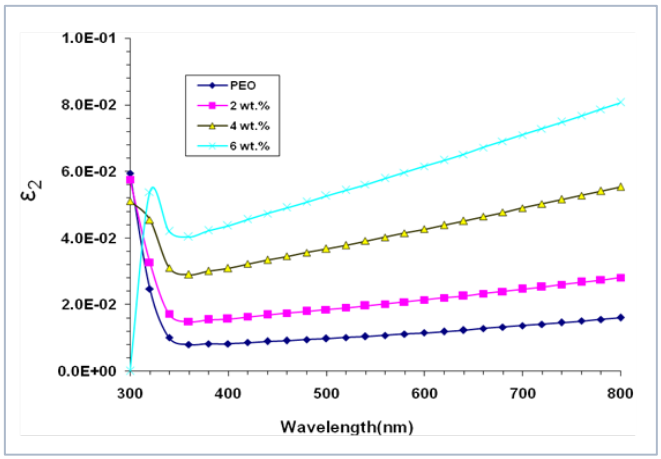

Figure 10. Presentation of (PEO-SnO_2-ZrO_2) nanocomposites with wavelength imaginary part of dielectric constant

The optical conductivity of PEO-SnO_2-ZrO_2 nanocomposites is shown in Figure 11. All nanocomposite samples show a decrease in optical conductivity with increasing wavelength and an increase at shorter wavelengths. All nanocomposite materials absorb more light in this range, which explains their increased optical conductivity at shorter photon wavelengths. This causes charge transfer excitations to rise. Visible and near-infrared light transmission is high in the spectrum data. Furthermore, optical conductivity is directly related to SnO_2 and ZrO_2 nanoparticle concentration. Energy gaps create specific energy levels, causing this occurrence [70-74].

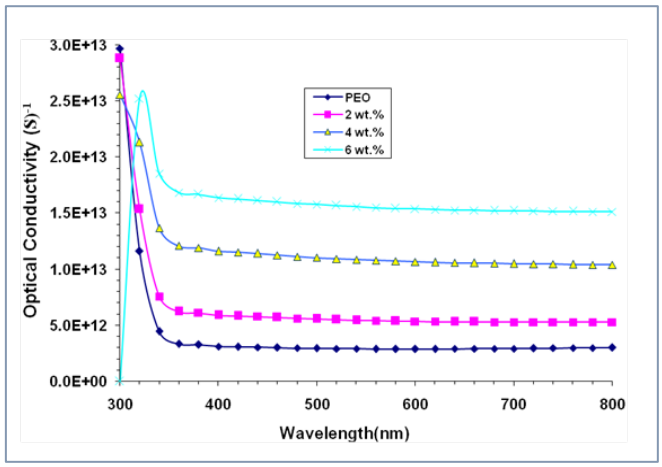

Figure 11. Disparity of optical conductivity for (PEO-SnO_2-ZrO_2) nanocomposites with wavelength

4. CONCLUSIONS

The present study cast (PEO-SnO_2-ZrO_2) nanocomposites films. With increasing nanoparticle concentrations, optical microscope (OM) pictures showed electrically charged channels inside the polymeric matrix. PEO-SnO_2-ZrO_2 nanocomposites have increased UV absorption based on their optical characteristics. Nanocomposites with this behavior show potential for optoelectronics. Increases in the quantities of SnO_2 and ZrO_2 nanoparticles lead to an increase in the optical conductivity, refractive index, extinction coefficient, absorbance, and real and imaginary dielectric constants of the resulting nanocomposites. The transmittance of these nanocomposites decreases proportionally with nanoparticle concentration. Both allowed and disallowed indirect transitions have a lower optical energy gap at 6wt.%. For authorized transitions, the energy gap reduces from 3.68 to 3.4 eV, and for banned transitions, from 3.66 to 3.35. Many optoelectronic device manufacturers benefit from the energy band gap reduction.

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