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Synthesis and Improving the Characteristics of Polymeric Blend Doped with Inorganic Nanoparticles for Optoelectronics Devices

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In present paper, the structural, optical and electronic characteristics of PVP/PEO blend doped with silicon carbide and titanium oxide are studied for various optoelectronic applications like sensors, transistors, solar cell, photocatalysts and photovoltaic cell. Results show that absorption of blend increases about 78.3% and 77% when ratios rise in SiC and TiO₂ to 4.5 wt.% at $\lambda = 400$ nm. The energy band gap of blend decreases from 3.6 eV to 3.3 eV and 3.31 eV when the contents of SiC and TiO₂ nanoparticles reach to 4.5 wt.%. The results concerning the electronic characteristics indicated to the excellent values of electronics parameters with the increase in SiC and TiO₂ contents. Finally, the obtained results concerning the PVP/PEO/SiC and PVP/PEO/TiO₂ nanocomposites have good structural, optical and electronic characteristics, which can be suitable for photonics and electronics fields with low cost, lightweight and flexibility.

У даній роботі структурні, оптичні й електронні характеристики суміші полівінілпіролідон/оксид поліетилену, леговані карбідом кремнію й оксидом Титану, вивчаються задля різних оптоелектронних застосувань, таких як датчики, транзистори, сонячні батареї, фотокаталізатори та фотоелектричні елементи. Результати показують, що поглинання сумішшю збільшується приблизно на 78,3%, 77%, коли співвідношення зростають із SiC і TiO₂ до 4,5 ваг.% при $\lambda = 400$ нм. Ширина енергетичної зони суміші зменшується з 3,6 еВ до 3,3 еВ і 3,31 еВ, коли вмісти наночастинок SiC і TiO₂ сягають 4,5 ваг.%. Результати щодо електронних характеристик вказують на відмінні значення параметрів електроніки зі збільшенням вмісту SiC і TiO₂. Нарешті, одержані результати щодо нанокompatитів полівінілпіролідон/оксид поліетилену/SiC і полівінілпіролідон/оксид поліетилену/TiO₂ мають хороші структурні, оптичні й електронні характеристики, які можуть підходити для сфер застосування фотоніки й електроніки з низькою вартістю, легковагістю та гнучкістю.

Key words: SiC, polymer blend, nanocomposites, flexibility, optical properties.

Ключові слова: SiC, полімерна суміш, наноккомпозити, гнучкість, оптичні властивості.

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1. INTRODUCTION

Polymer matrix nanocomposites doped with semiconductor nanoparticles have acquired an interest lot related to the phases' particular characterization as well as the better, new characterization emergence by merging the phases of inorganic and organic. In specific, there are some enhanced in electrical and optical characterization are observed, as appeared by the inclusive range of potential roles of such nanocomposite in the type of semiconductor/polymer materials [1].

Organic polymers based on inorganic nanoparticles include attracted mounting attention due to their particular characterization promising from the combination of inorganic and organic hybrid materials. Usually, the resulting nanocomposites show improved optoelectronic, magnetic, mechanical and optical characterization. Consequently, the nanocomposites have been usually used in the different applications such as electronics, military equipment, optical devices, safety, automotive, protective garments and aerospace. These field applications always require additional characterization and roles such as high mechanical characterization, chemical resistance, flame retardation, UV resistance, water repellence, electrical conductivity, environmental stability, radar absorption, magnetic field resistance, *etc.* [2]

Polyvinylpyrrolidone (PVP) has a good steady environment, modest electrical conductivity and easy processing. It has a large range of fields like as electrochemical machines [3]. PVP has excellent film producing and behaviour of adhesive on several solid substrates and its display excellent optical eminence (high transmittance in visible region) and mechanical strength necessary for applications. The PVP amorphous structure also gives a low loss of scattering, which creates it as a perfect polymer for nanocomposite for various fields [4]. Polyethylene oxide (PEO) explains excellent high surface and chemical resistance and presents high light transparency [5]. Silicon carbide has a large energy gap, which is a good performance for the UV photodetectors in conditions of its ability to function in hard environments and resist the damaging causes for ionizing rays [6]. As an optical substance, SiC is used for high reflectance in the extreme ultraviolet (EUV; $\lambda < 190$ nm), mostly in the 50 to 180 nm [7]. Titanium oxide (TiO₂) as thin film or powder

has been widely examined related to their low cost, good photochemical stability and nontoxicity. The pure TiO_2 reacts only to UV region, which includes 4% of the full sunbeam. The absorption forms in the UV-region relate to huge energy gap (3.2 eV), which finally restricts its useful fields in organic pollutants degradation like pesticides, detergents, dyes, *etc.* Because of low resistivity and diamagnetism, TiO_2 has become a worry in the application of devices of multistate memory, sensors and resistors. These determinations have potential studies to improve photocatalytic activity, raise resistivity and induce the TiO_2 magnetism [8].

This paper deals with the effect of the SiC and TiO_2 nanoparticles on PVP/PEO blend to use it for detectors and photonics devices.

2. MATERIALS AND METHODS

The PVP/PEO/SiC and PVP/PEO/ TiO_2 nanocomposites films were synthesized using casting method. The silicon carbide and titanium oxide nanoparticles were obtained as powders (US Research Nanomaterials, high purity 99%, 20–30 nm). The blend was prepared by dissolving 0.5 g of PVP and PEO in 40 ml of distilled water with ratios 66 wt.% PVP and 34 wt.% PEO. Then, the SiC and TiO_2 nanoparticles were added to PVP/PEO blend with weight percentages of 1.5, 3 and 4.5 wt.%. The samples prepared with thickness (10 μm). The homogeneity of nanoparticles inside the PVP/PEO blend was tested by optical microscope (Nikon-73346). The optical properties of (PVP/PEO/SiC) and (PVP/PEO/ TiO_2) nanocomposites samples were measured by using spectrophotometer (UV-1800A-Shimadzu).

3. RESULTS AND DISCUSSION

Figure 1 represents the absorbance of PVP/PEO/SiC and PVP/PEO/ TiO_2 films with wavelength. The PVP/PEO/SiC and PVP/PEO/ TiO_2 nanocomposites samples have high values of absorbance for the UV radiation with attributed to the electrons excitation at UV light [9]. The absorption values of (PVP-PEO) blend rise with rising in SiC and TiO_2 nanoparticles' ratios, which may be related to the absorption and scattering the photons by the charge carriers of SiC and TiO_2 nanoparticles as shown in Fig. 2.

Figure 2 shows the SiC and TiO_2 nanoparticles' distribution inside the (PVP/PEO) blend where the photons of incident light are absorbed, hence the transmission decreases as represented in Fig. 3 showing the variation of transmission spectra of PVP/PEO/SiC and PVP/PEO/ TiO_2 nanocomposites with photons' wavelength. As seen from the absorbance and transmittance spectra of the nanocompo-

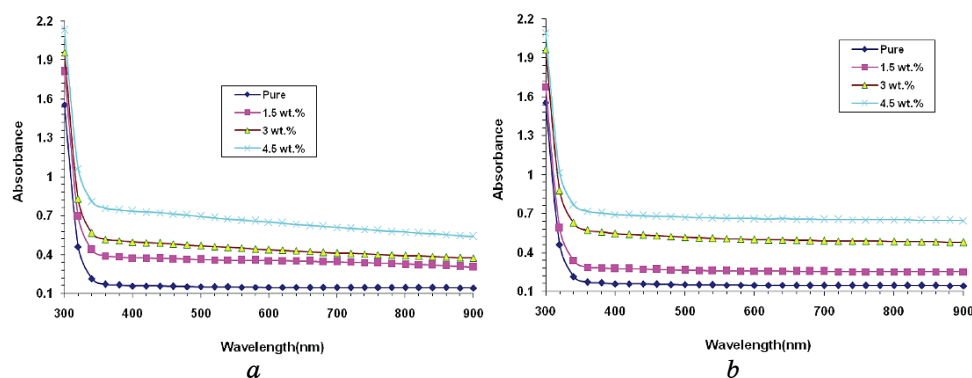


Fig. 1. Absorbance spectra: *a*—for (PVP/PEO/SiC) nanocomposites; *b*—for (PVP/PEO/TiO₂) nanocomposites.

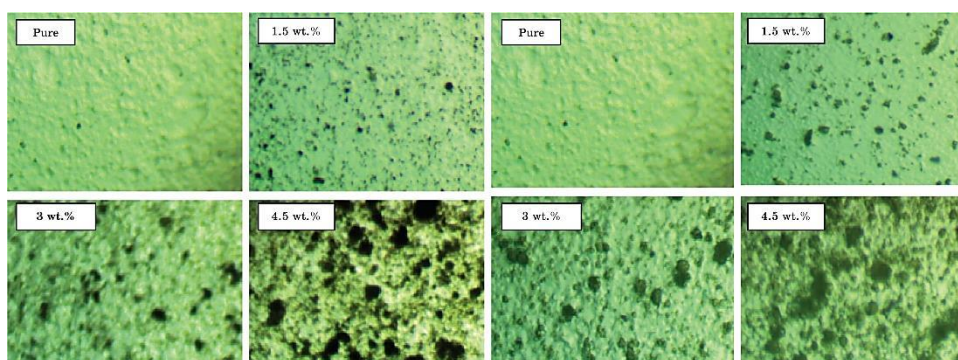


Fig. 2. Optical microscope images (×10): *a*—for (PVP/PEO/SiC) nanocomposites; *b*—for (PVP/PEO/TiO₂) nanocomposites.

sites, the absorbance of PVP/PEO blend increases 78.3% and 77% with rising in SiC and TiO₂ ratios to 4.5 wt.% at $\lambda = 400$ nm, while the transmittance of polymer blend decreases 28.8% and 26.6% with increase in SiC and TiO₂ content to 4.5 wt.% at $\lambda = 360$ nm. The obtained results showed that these nanocomposites could be used for different photonics and detectors devices.

The absorption coefficient α of PVP/PEO/SiC and PVP/PEO/TiO₂ nanocomposites is determined by using [10]:

$$\alpha = 2.303A/t, \quad (1)$$

where A represents the absorbance, t represents the thickness.

Figure 4 shows the behaviour of α for the (PVP/PEO/SiC) and (PVP/PEO/TiO₂) nanocomposites with photons' energies. The ab-

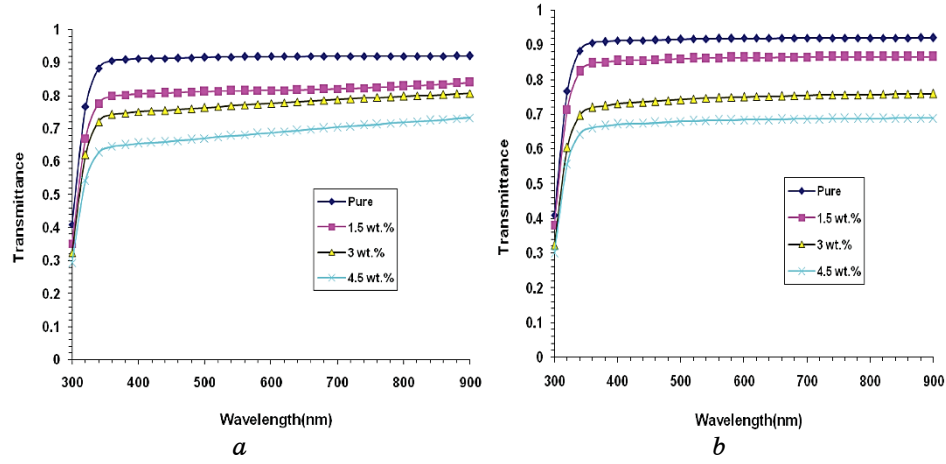


Fig. 3. Transmittance spectra: *a*—for (PVP/PEO/SiC) nanocomposites; *b*—for (PVP/PEO/TiO₂) nanocomposites.

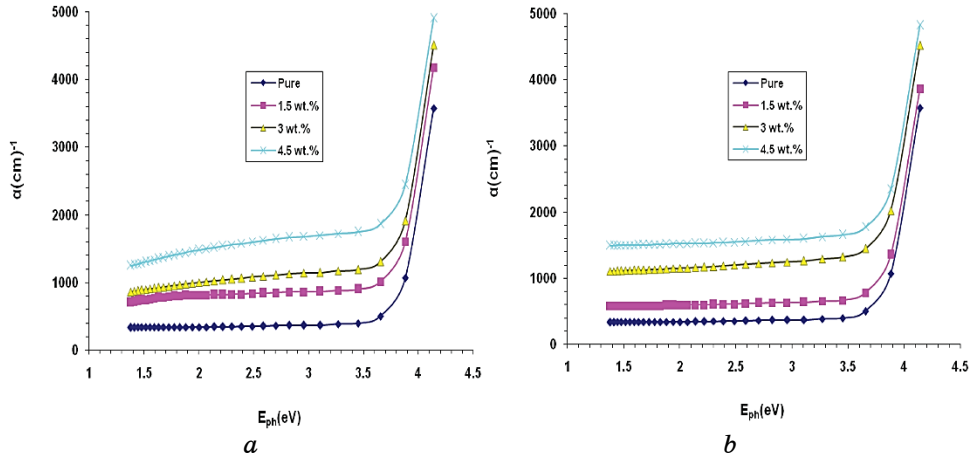


Fig. 4. Behaviour of α with energy of photon: *a*—(PVP/PEO/SiC) nanocomposites; *b*—(PVP/PEO/TiO₂) nanocomposites.

sorption coefficient values raise with raising the SiC and TiO₂ nanoparticles' contents, which are attributed to the creating of energy levels between the valence and conduction bands [10].

The energy band gap of nanocomposites is calculated by using [11]:

$$\alpha h\nu = B(h\nu - E_g)^m. \quad (2)$$

The energy gaps of (PVP/PEO/SiC) and (PVP/PEO/TiO₂) nanocom-

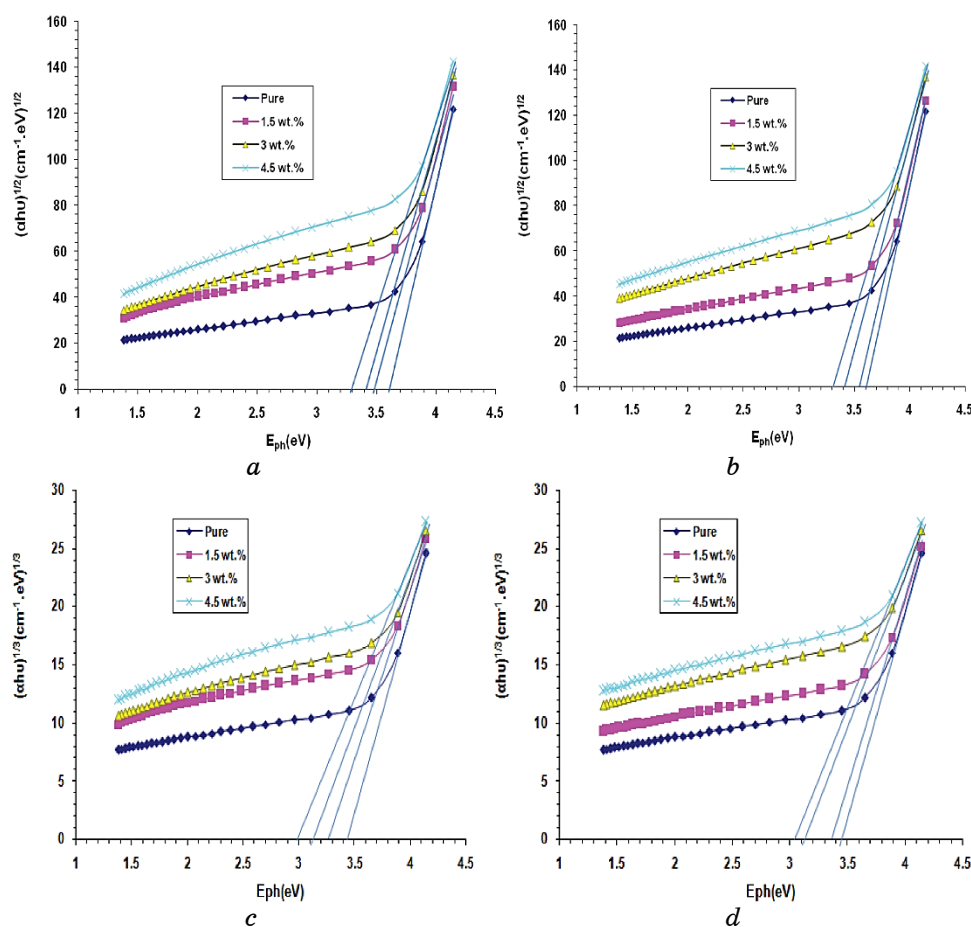


Fig. 5. Energy gap: *a*—allowed indirect transition of (PVP/PEO/SiC) films; *b*—allowed indirect transition of (PVP/PEO/TiO₂) films; *c*—forbidden indirect transition of (PVP/PEO/SiC) films; *d*—for forbidden indirect transition of (PVP/PEO/TiO₂) films.

posites are represented in Fig. 5. The energy gap of blend reduces as the SiC and TiO₂ nanoparticles' contents raise. The reducing of energy band gap may be due to the form the trap levels between the energy states and causing the decrease of energy gap [11].

The extinction coefficient (k) was calculated by means of the relation [12]:

$$k = \alpha\lambda/(4\pi). \quad (3)$$

Figure 6 shows the behaviour of extinction coefficient for the

(PVP/PEO/SiC) and (PVP/PEO/TiO₂) nanocomposites with photon wavelength. The extinction coefficient values increase as SiC and TiO₂ nanoparticles' contents increase due to increasing the absorbing and scattering [12].

The refractive index n of the (PVP/PEO/SiC) and (PVP/PEO/TiO₂) nanocomposites can be determined by means of the relation [13]:

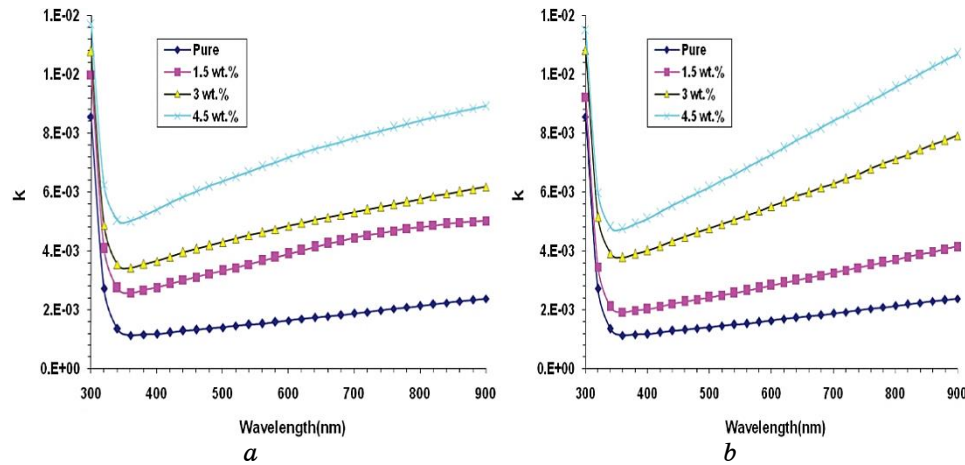


Fig. 6. Behaviour of K with wavelength: a —(PVP/PEO/SiC) nanocomposites; b —(PVP/PEO/TiO₂) nanocomposites.

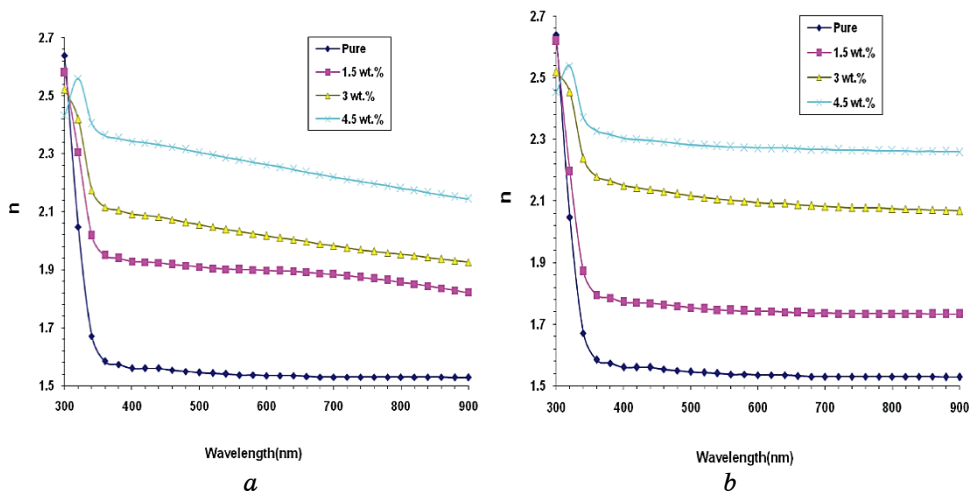


Fig. 7. Variation of refractive index with wavelength: a —for (PVP/PEO/SiC) nanocomposites; b —for (PVP/PEO/TiO₂) nanocomposites with wavelength.

$$n = (1 + R^{1/2}) / (1 - R^{1/2}). \quad (4)$$

The behaviour of refractive index for the (PVP/PEO/SiC) and (PVP/PEO/TiO₂) nanocomposites with doping concentrations is shown in Fig. 7. The values of refractive index for both nanocomposites raise with raising the SiC and TiO₂ nanoparticles' contents that is related to increase the refraction, and consequently the films refractivity will raise hence the refractive index increase [13, 14].

The real/ ϵ_1 and imaginary/ ϵ_2 dielectric constants are given in [15]:

$$\epsilon_1 = n^2 - k^2, \quad (5)$$

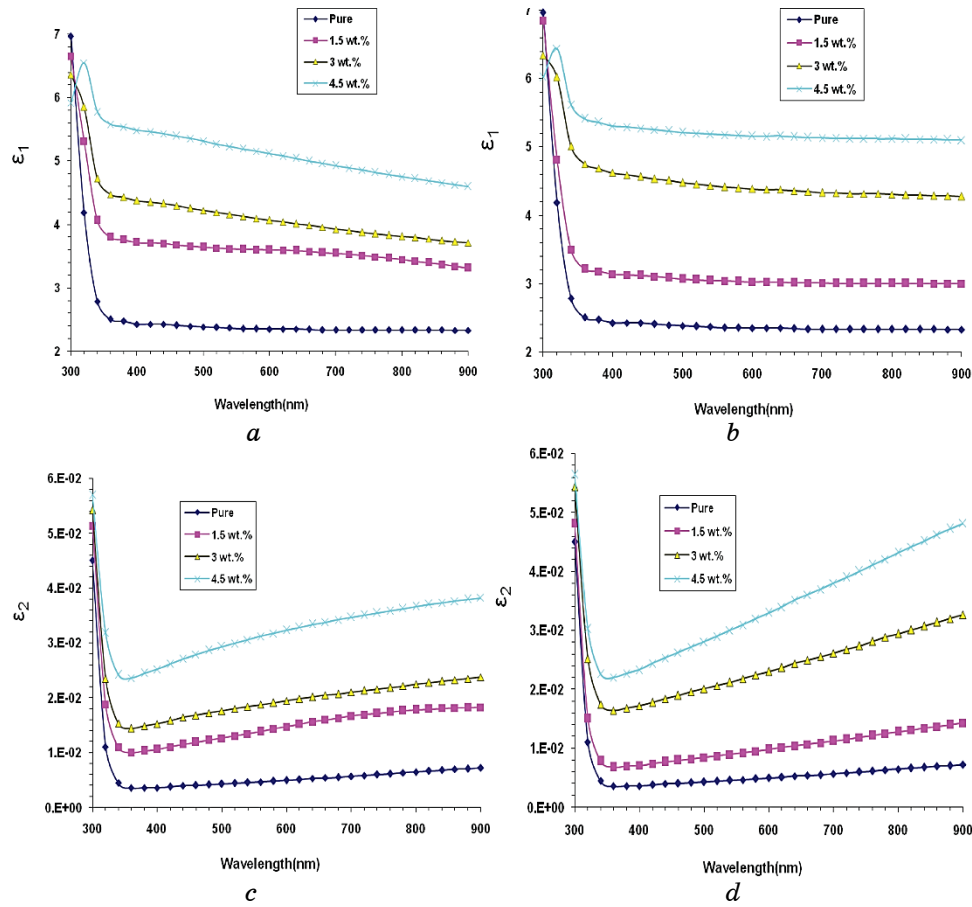


Fig. 8. *a*—real dielectric constant of (PVP/PEO/SiC) films; *b*—real dielectric constant of (PVP/PEO/TiO₂) films; *c*—imaginary dielectric constant of (PVP/PEO/SiC) films; *d*—imaginary dielectric constant of (PVP/PEO/TiO₂) films.

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

Figure 8 shows the real and imaginary of dielectric constants variation for (PVP/PEO/SiC) and (PVP/PEO/TiO₂) nanocomposites with photons wavelength. The real part is attributed to the dispersion. The imaginary part describes the rate of dissipative of electromagnetic wave propagation in the medium. The real part mainly depends on values of n^2 , while imaginary part depends on the n and k values [15].

The optical conductivity ($\sigma_{\text{opt.}}$) is given by means of the relation [16]:

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

Figure 9 represents the optical conductivity behaviour of the (PVP/PEO/SiC) and (PVP/PEO/TiO₂) nanocomposites with wavelength of photon for different ratios of SiC and TiO₂ nanoparticles. The σ_{opt} of blend rises with increasing in SiC and TiO₂ nanoparticles' contents due to creating the localized states or defect states in the band structure of polymer blend [16–19].

The Urbach energy is given by the formula [16]:

$$\alpha = \alpha_0 \exp\left(\frac{E}{E_u}\right), \quad (8)$$

where α_0 is a constant and E_u is the Urbach energy, which is related to the width of band tail of the localized states in the energy band gap.

The values of E_u of nanocomposites were obtained from Fig. 10. The E_u values for the (PVP/PEO/SiC) nanocomposites are of 2.47 eV, 3.37 eV, 3.23 eV and 3.69 eV for blend, 1.5% SiC, 3% SiC and 4.5% SiC. The Urbach energy values for the (PVP/PEO/TiO₂) nanocomposites are 3.22 eV, 4.04 eV and 5.29 eV for 1.5% TiO₂, 3% TiO₂ and 4.5% TiO₂. The Urbach energy of (PVP–PEO) blend raises with the raising of the SiC and TiO₂ nanoparticles' contents that is attributed to the various defects in optical band gap of the nanocomposites where the SiC and TiO₂ nanoparticles change the width of localized levels in the energy gap of nanocomposites, hence energy gap is opposite to the Urbach energy [20].

The skin depth was calculated by the following relation [21]:

$$\delta = 1/\alpha. \quad (9)$$

Figure 11 represents the behaviour of δ for the (PVP/PEO/SiC) and (PVP/PEO/TiO₂) films with wavelength. The skin depth of (PVP/PEO/SiC) and (PVP/PEO/TiO₂) films decreases with the increase in energy of photon that is due to increase of the absorption

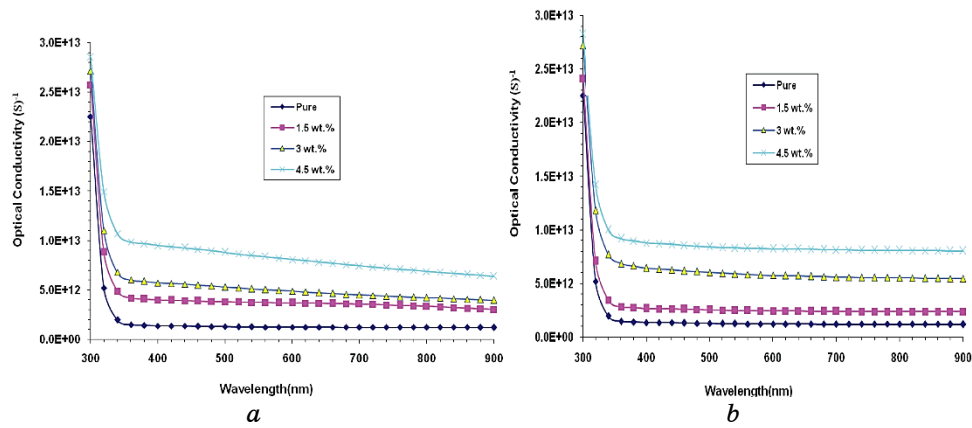


Fig. 9. Behaviour of optical conductivity with wavelength: *a*—to (PVP/PEO/SiC) films; *b*—to (PVP/PEO/TiO₂) films.

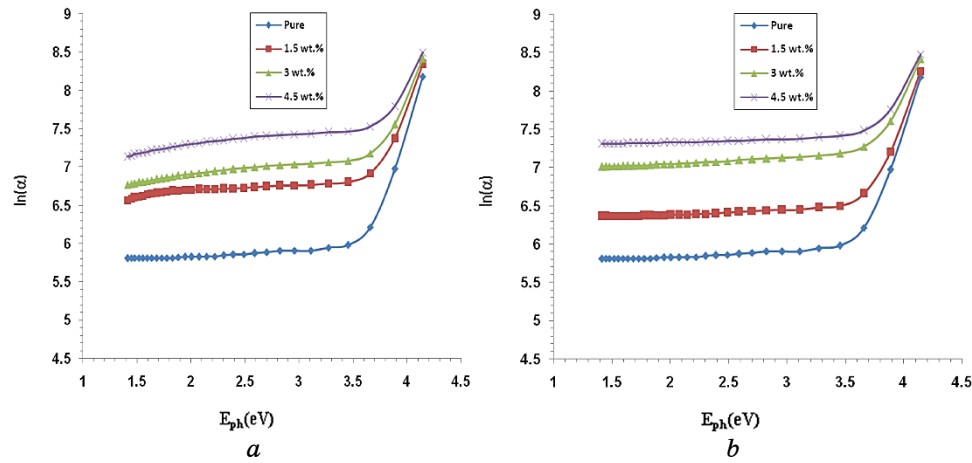


Fig. 10. Behaviour of $\ln(\alpha)$ with energy: *a*—(PVP/PEO/SiC) nanocomposites; *b*—(PVP/PEO/TiO₂) nanocomposites.

possibility [21].

The absorption coefficient due to free carriers can be determined by the following relation [22]:

$$\alpha = k\lambda^p, \quad (10)$$

where p depends on the mechanism of scattering and doping ratio. For the acoustic-phonon scattering, $p \approx 1.5$; for the optical-phonon scattering, $p \approx 2.5$, and for impurity scattering, $p \approx 3.5$ [22]. The p

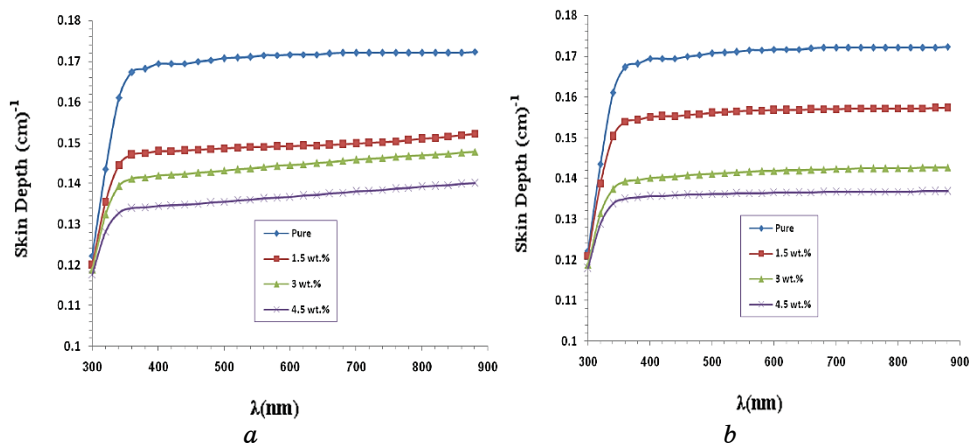


Fig. 11. Skin depth behaviour against wavelength: *a*—(PVP/PEO/SiC) nanocomposites; *b*—(PVP/PEO/TiO₂) nanocomposites.

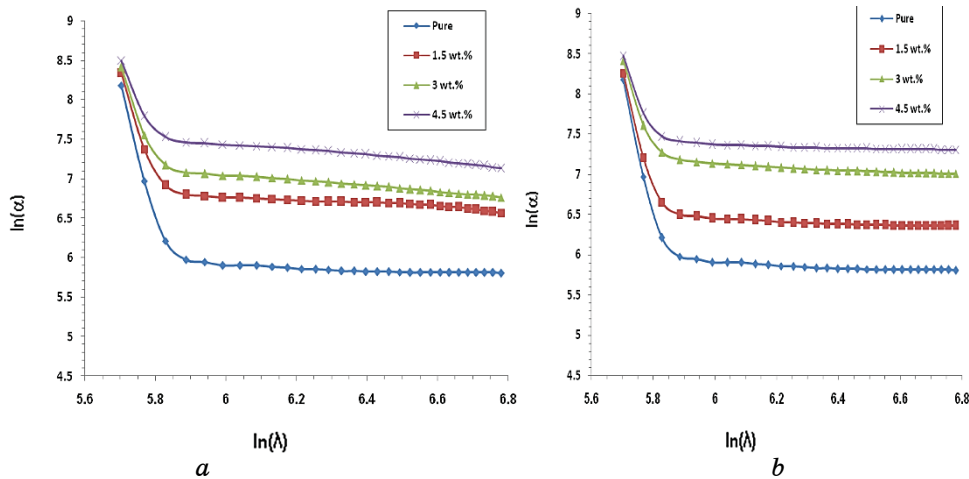


Fig. 12. The $\ln(\alpha)$ against $\ln(\lambda)$: *a*—(PVP/PEO/SiC) nanocomposites; *b*—(PVP/PEO/TiO₂) nanocomposites.

values were calculated as shown in Fig. 12 for the (PVP/PEO/SiC) and (PVP/PEO/TiO₂) nanocomposites. The p values are of 3.2, 2.1, 1.8 and 1.4 for blend, 1.5% SiC, 3% and 4.5% SiC, respectively. In addition, p values are of 2.5, 1.7 and 1.4 for 1.5% TiO₂, 3% TiO₂ and 4.5% TiO₂, respectively; these values of p are calculated at wavelength range 300–500 nm.

The free-carrier electric susceptibility can be calculated by using the relation [23]:

$$\varepsilon_1 = \varepsilon_\infty - \frac{e^2}{\pi c^2} \frac{N}{m^*} \lambda^2 = -4\pi\chi_e. \quad (11)$$

Figure 13 shows the dielectric constant variation with (λ^2) of (PVP/PEO/SiC) and (PVP/PEO/TiO₂) to calculate the numbers of charge carriers. From this Figure, the N value is the same for all

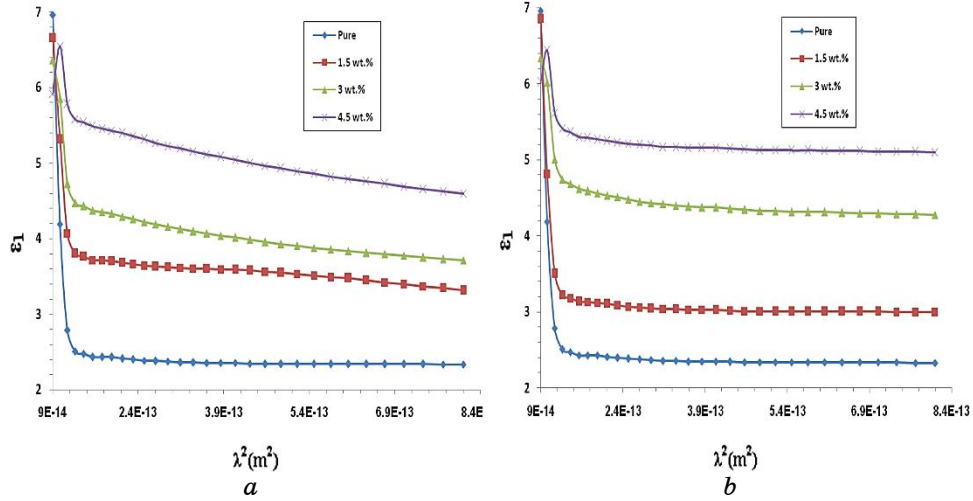


Fig. 13. Dielectric constant behaviour with λ^2 : *a*—for (PVP/PEO/SiC) nanocomposites; *b*—for (PVP/PEO/TiO₂) nanocomposites.

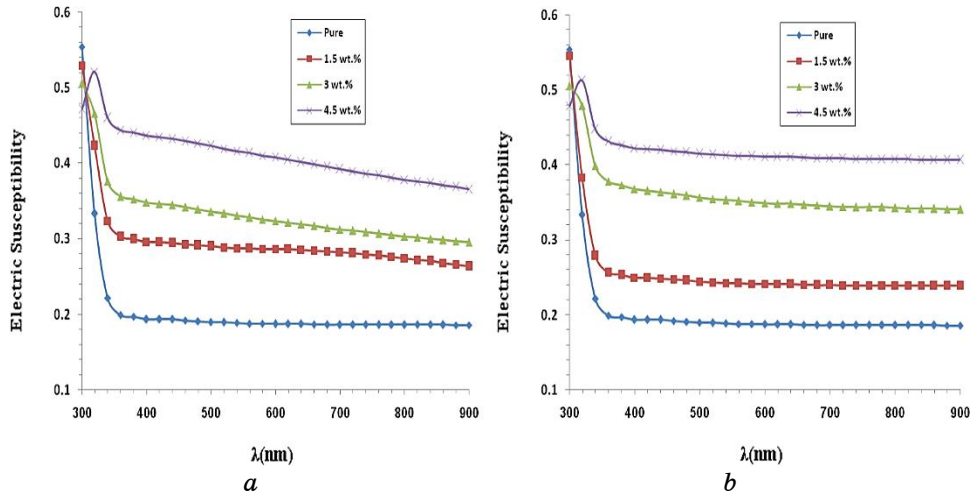


Fig. 14. Electric susceptibility against wavelength: *a*—(PVP/PEO/SiC) nanocomposites; *b*—(PVP/PEO/TiO₂) nanocomposites.

concentrations of SiC nanoparticles that is $2.23 \cdot 10^{27} \text{ m}^{-3}$. The values of N for the (PVP/PEO/TiO₂) nanocomposites are of $2.23 \cdot 10^{27} \text{ m}^{-3}$, $2.23 \cdot 10^{27} \text{ m}^{-3}$, $1.11 \cdot 10^{27} \text{ m}^{-3}$ and $8.93 \cdot 10^{26} \text{ m}^{-3}$ for pure blend, 1.5% TiO₂, 3% TiO₂ and 4.5% TiO₂, respectively.

Figure 14 represents the electric susceptibility behaviour with photon wavelength. The χ_e values increase as the SiC and TiO₂ nanoparticles' contents increase that is related to increasing the charge-carriers' numbers in nanocomposites.

The dispersion data of the refractive index may be expressed by a single-oscillator model, where E_0 and E_d are single-oscillator constant [24]:

$$n^2 = 1 + \frac{E_d E_0}{E_0^2 - E^2}, \quad (12)$$

where E_0 represents the single oscillator energy and E_d represents the dispersion energy. Figure 15 shows the calculated values of E_0 and E_d . The values of E_0 are of 7.16 eV, 15.43 eV, 17.25 eV and 26.9, while the values of E_d are of 5.37 eV, 6.4 eV, 6.4 eV and 7.4 eV to blend, 1.5% SiC, 3% SiC and 4.5% SiC, respectively. The E_0 values are of 11.94 eV, 23.56 eV and 44.72 eV, while the E_d values are of 5.97 eV, 7.06 eV and 11.18 eV for 1.5% TiO₂, 3% TiO₂ and 4.5% TiO₂.

The electrical conductivity (σ_{el}) is calculated using the relation [25]:

$$\sigma_{el} = \frac{2\lambda\sigma_{opt}}{\alpha}. \quad (13)$$

Figure 16 shows the electrical conductivity behaviour *vs.* wavelength. The electrical conductivity values raise with rising SiC and TiO₂

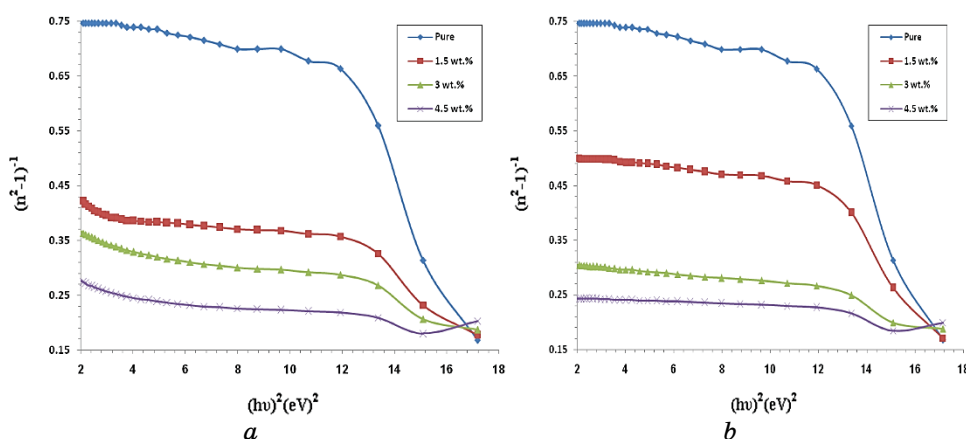


Fig. 15. The $(n^2 - 1)^{-1}$ against $(h\nu)^2$: *a*—(PVP/PEO/SiC) nanocomposites; *b*—(PVP/PEO/TiO₂) nanocomposites.

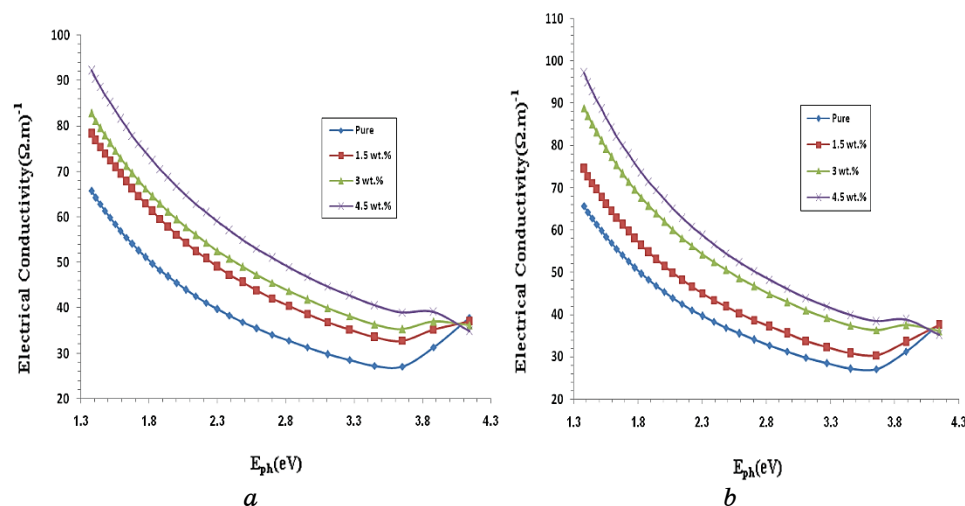


Fig. 16. Electrical conductivity against energy: *a*—(PVP/PEO/SiC) nanocomposites; *b*—(PVP/PEO/TiO₂) nanocomposites.

nanoparticles' contents that may be related to rising in localization of charge-carriers' density leading to the higher conductivity [26].

4. CONCLUSIONS

The results indicated that the (PVP/PEO/SiC) and (PVP/PEO/TiO₂) prepared nanocomposites may be considered promising for the electronics and photonic devices.

The structure, optical and electronic characteristics of films indicated that both nanocomposites might be used for various fields in solar cells, transistors, gates, sensors, *etc.* The absorbance of PVP/PEO blend rises about 27.1% and 25.8% at $\lambda = 300$ nm, while the transmission and energy gap reduce with rising in SiC and TiO₂ NPs contents, which make it suitable for optoelectronics applications.

The optical constants, dispersion parameters and electronics parameters of blend are improved by adding the SiC and TiO₂ nanoparticles' contents.

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