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Influence of MnO_2 Nanoparticles' Addition on Optical Properties of PVA/PEG Blend

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This work is aimed to fabricate the PVA/PEG/MnO_2 nanostructure to be used in many applications in electronics and optics. The optical properties of PVA/PEG/MnO_2 nanostructure are studied at wavelength range from 200 nm to 800 nm. The experimental results show that the absorbance of PVA/PEG blend increases with the increase in MnO_2 nanoparticles' concentration that may be used for various electronic applications. The extinction coefficient, refractive index, real and imaginary parts of dielectric constants, and optical conductivity of PVA/PEG blend are also increased with the increase in MnO_2 nanoparticles' concentration. The transmittance and energy band gap are decreased as MnO_2 concentration increases.

Цю роботу спрямовано на виготовлення наноструктури полівініловий спирт/поліетиленгліколь/MnO_2, яка буде використовуватися в багатьох застосуваннях в електроніці й оптиці. Вивчаються оптичні властивості наноструктури полівініловий спирт/поліетиленгліколь/MnO_2 в діяпазоні довжин хвиль від 200 нм до 800 нм. Результати експерименту показують, що поглинання сумішшю полівініловий спирт/поліетиленгліколь збільшується зі збільшенням концентрації наночастинок MnO_2, що може бути використано для різних електронних застосувань. Коефіцієнт згасання, показник заломлення, реальна й уявна частини діелектричних проникностей, оптична провідність суміші полівініловий спирт/поліетиленгліколь також збільшуються зі збільшенням концентрації наночастинок MnO_2. Коефіцієнт пропускання та ширина забороненої зони зменшуються зі збільшенням концентрації MnO_2.

Key words: optical properties, polymer blend, nanocomposites, MnO_2, nanostructures.

Ключові слова: оптичні властивості, полімерна суміш, нанокомпозити, MnO_2, наноструктури.

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1. INTRODUCTION

In recent years, optical properties of polymers are drawing great interest because of their scope for application in optical devices. The versatility and dependability of polymers is established from the fact that they have attractive properties like lightweight, good mechanical and optical properties. Polymers are also considered good host materials where dopant can modify the physicochemical properties. The optical band gap and refractive index are the fundamental parameters of an optical material, because these are directly linked to the electronic properties of the material. High refractive index of optical materials is needed in various fields including optical waveguides, LED encapsulation materials, *etc.* [1].

Blending polymer products is the latest technique for optimizing different polymer matrices and is a valuable method for producing substances with an extensive diversity of characteristics. Polymer characteristics may be improved by combining two or more polymers and/or adding organic/inorganic fillers for use in various applications. The melt blending and solvent casting routes are the most common ways for the manufacturing of polymer blends or composites [2].

Polymer blending with another material can be used as an effective method to alter the resulting film blend properties. An insulating polymer such as polyvinyl alcohol (PVA) can be turned conductive by blending with other materials to diversify its applications. Previous studies have shown that polymer-based synthetic materials can be applied into electrical and optical devices, such as photovoltaic devices, rechargeable batteries and nonlinear optical devices, and light-emitting diodes (LEDs). Moreover, conductive polymers have also been applied in the health sector, including as a biosensor and a coating agent for detecting cancer cells [3].

PVA is a widely used commercial polymer owing to its high transparency, hydrophilicity, and adhesive properties. Furthermore, its strong oxygen barrier capabilities and mechanical and biodegradable properties promote the application of PVA in fibre manufacturing, food packaging, and biomedicine [4]. MnO_2 (manganese dioxide) attracted large research care due to their characteristic physical and chemical properties and wide applications in energy storage, biosensor, ion exchange and catalysis. MnO_2 has been considered as a hopeful electrode material for supercapacitors because of its low cost, environmental benignity, and excellent capacitive performance in aqueous electrolytes [5]. The present work is aimed to studying the effect of MnO_2 nanoparticles addition on optical properties of PVA/PEG blend to use in many optoelectronics applications.

2. MATERIALS AND METHODS

Films of PVA/PEG/MnO_2 nanocomposites were synthesized using casting method. The PVA/PEG films were prepared by dissolving of 0.5 g of polyvinyl alcohol and polyethylene glycol (PEG) in 25 ml of distilled water with ratio 80 wt.% PVA and 20 wt.% PEG. The MnO_2 nanoparticles (NPs) were added to PVA/PEG blend with concentrations of 1.8, 3.6 and 5.4 wt.%. The optical properties of PVA/PEG/MnO_2 nanocomposites were measured by using UV-double beam spectrophotometer (Shimadzu, UV-1800 Å) in the wavelength range 280–800 nm.

The absorption coefficient (α) is determined by relation (1) [6, 7]:

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

Here, A and t are the absorbance and sample thickness, respectively.

The energy gap of nanocomposite can be calculated by Eq. (2) [8]:

$$\alpha h\nu = B(h\nu - E_g)^r, \quad (2)$$

where B is constant, E_g is photon energy.

The refractive index (n) is given by Eq. (3) [9, 10]:

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

where R is the reflectance.

The extinction coefficient (k) is determined by Eq. (4) [11, 12]:

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

The real (ε_1) and imaginary (ε_2) parts of dielectric constant are given by Eqs. (5) and (6), respectively [13, 14]:

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

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

The optical conductivity (σ) is determined by Eq. (7) [15]:

$$\sigma = \alpha nc/(4\pi). \quad (7)$$

3. RESULTS AND DISCUSSION

Figure 1 shows the behaviour of absorbance for PVA/PEG/MnO_2 nanocomposites with wavelength of the incident light. The absorption for all samples of nanocomposites increases at UV region; this is related to the excitations of donor level electrons to the conduction band at these energies. The high absorbance of nanocomposites at UV region due to the energy of photon enough to interact with atoms; the electron is excited from a lower to higher energy level by absorbing a photon of known energy.

The changes in the absorbed and transmitted radiation may decide the types of possible electron transitions. Fundamental absorption of absorbance spectra refers to band-to-band or excitation transition. At visible and near infrared regions, the absorbance of nanocomposites has low values; this behaviour is due to the energy of incident photons, which do not have sufficient energy to interact with atoms. Thus, the photons will be transmitted when the wavelength increases. The transmittance of nanocomposites increases as shown in Fig. 2, which represents the variation of the transmittance for nanocomposites with wavelength of the incident light.

In Figures 1 and 2, the absorbance increases, while the transmittance decreases with the increase in MnO_2 nanoparticles' concentration. This is related to both the agglomeration of nanoparticles with increasing concentration and the increase of the number of charge carriers [16].

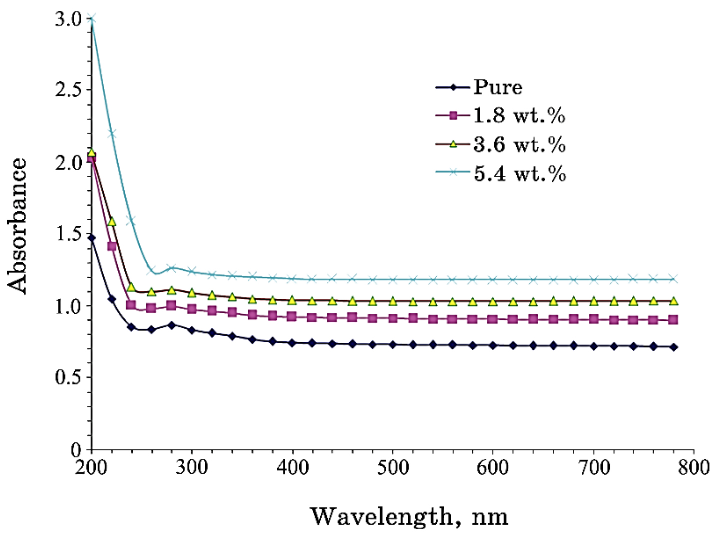

Fig. 1. Behaviour of absorbance for PVA/PEG/MnO_2 nanocomposites with wavelength.

Figure 3 shows the variation of absorption coefficient with photon energy of the incident light. The absorption coefficient assists to know the nature of electron transition. When the values of the absorption coefficient are high, $\alpha > 10^4$ cm^{-1}, it is expected the direct transition of electron, while, when the values of the absorption coefficient of material are low, $\alpha < 10^4$ cm^{-1}, it is expected the indirect transition of electron. The values of absorption coefficient of PVA/PEG/MnO_2 nanocomposites are low: $\alpha < 10^4$ cm^{-1}; the transi-

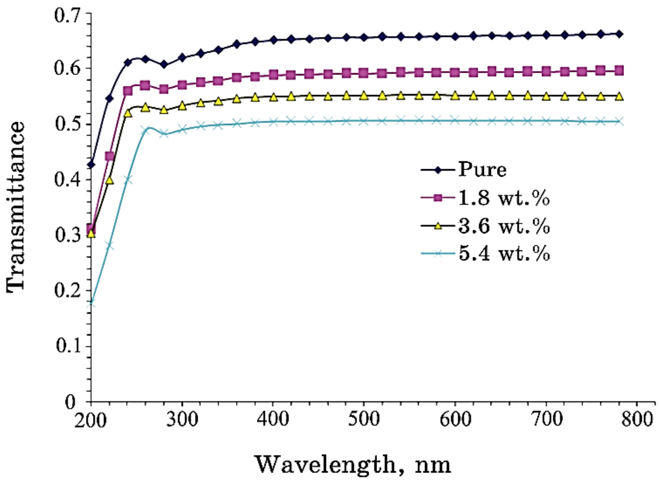

Fig. 2. Variation of transmittance for PVA/PEG/MnO_2 nanocomposites with wavelength.

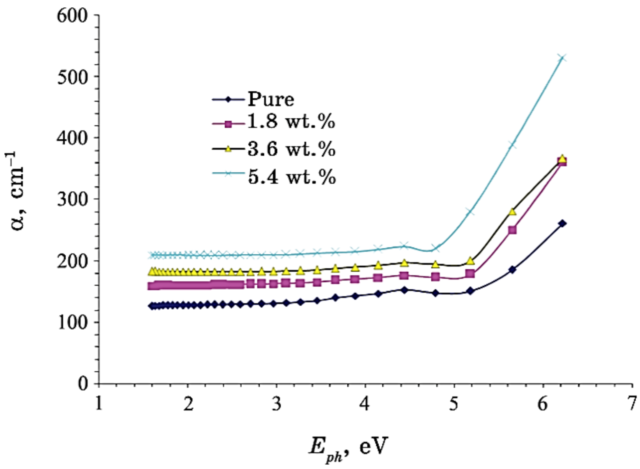

Fig. 3. Variation of absorption coefficient with photon energy of the incident light.

tion of electron is indirect. The absorption coefficient of PVA/PEG blend increases with the increase in MnO_2 nanoparticles' concentration; this is attributed to the increase in number of charge carriers, hence, the increase in absorbance and absorption coefficient [17].

The energy band gap values of PVA/PEG/MnO_2 nanocomposites are represented in Figs. 4 and 5 for allowed and forbidden indirect transitions. As shown in these figures, the energy band gap of

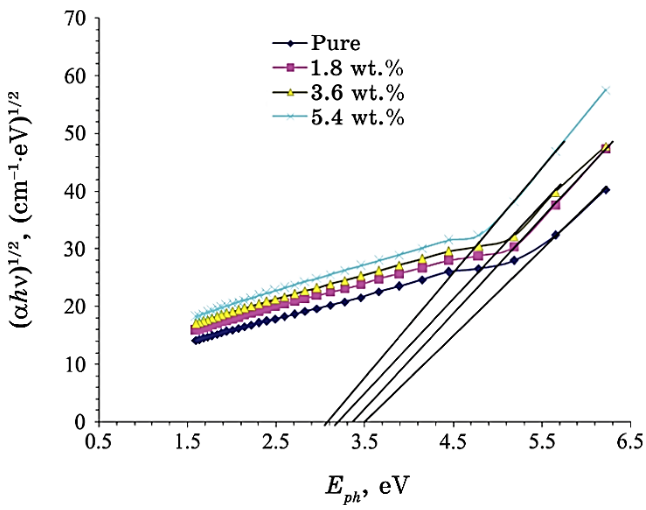

Fig. 4. Energy gap values of PVA/PEG/MnO_2 nanocomposites for allowed indirect transition.

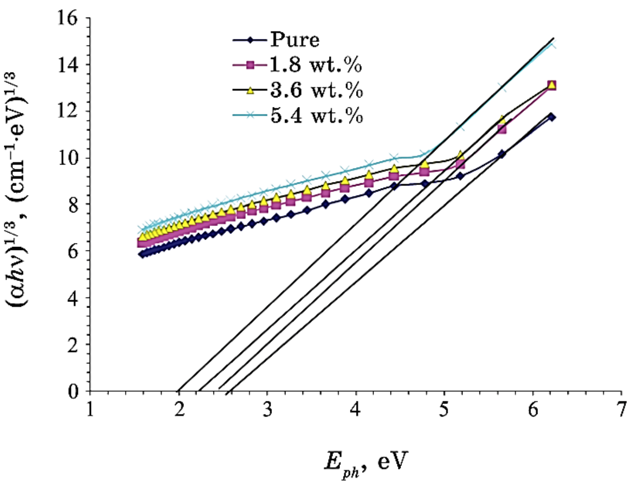

Fig. 5. Energy gap values of PVA/PEG/MnO_2 nanocomposites for forbidden indirect transition.

PVA/PEG/MnO_2 nanocomposites decreases with the increase of MnO_2 nanoparticles' concentration; this is related to the formation of some defects in the films. These defects produce the localized states in the optical band gap and overlaps. These overlaps give an evidence for decreasing energy band gap [18].

Figures 6 and 7 show the behaviour of refractive index and extinction coefficient, respectively, with photon wavelength for different MnO_2 nanoparticles' concentration. From these figures, it can be seen that the refractive index and extinction coefficient are

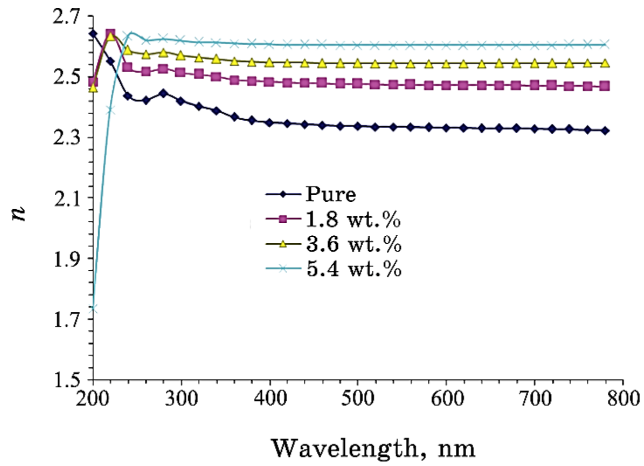

Fig. 6. Behaviour of refractive index with photon wavelength for different MnO_2 nanoparticles' concentration.

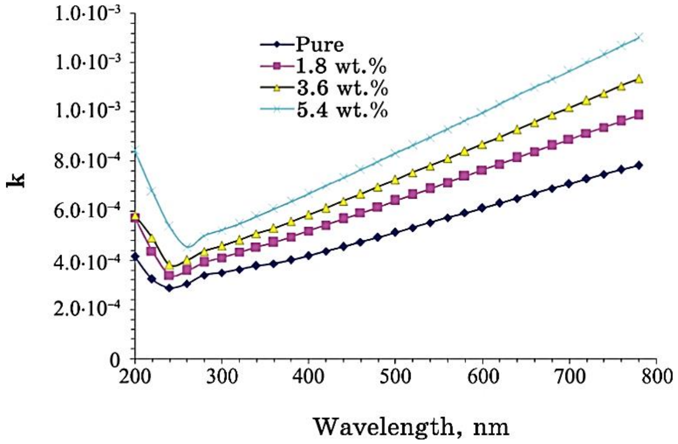

Fig. 7. Behaviour of extinction coefficient with photon wavelength for different MnO_2 nanoparticles' concentration.

increased with the increase in MnO_2 NPs' concentration that may be attributed to the increase of the density of nanocomposite and absorption coefficient [19].

The real and imaginary parts of dielectric constant for PVA/PEG/MnO_2 nanocomposites are shown in Figs. 8 and 9, respectively. From these figures, it is clear that high MnO_2 NPs' concentration leads to the increase of absorption coefficient and refractive index, which leads to increase of the real and imaginary parts of dielectric constant [20].

Figure 10 shows the optical conductivity variation of

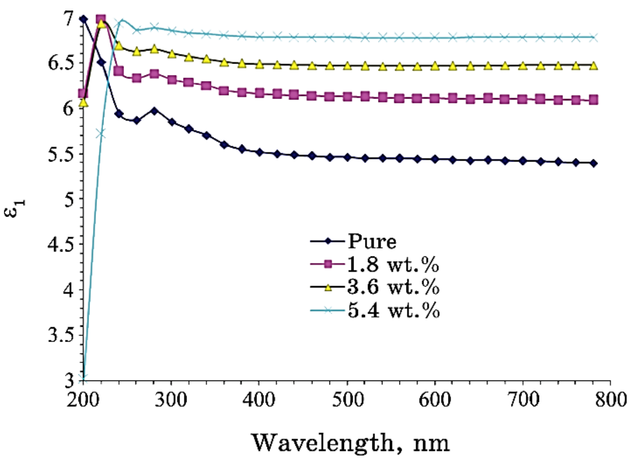

Fig. 8. Real part of dielectric constant for PVA/PEG/MnO_2 nanocomposites.

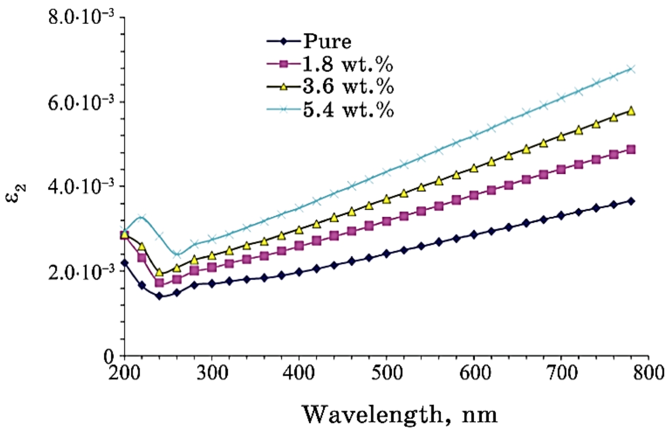

Fig. 9. Real part of dielectric constant for PVA/PEG/MnO_2 nanocomposites.

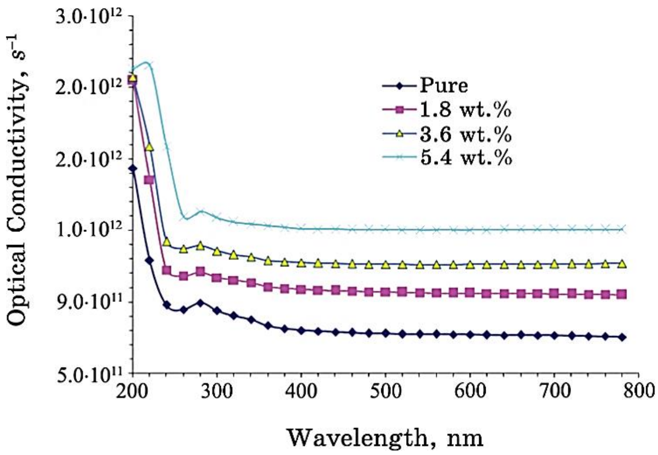

Fig. 10. Optical conductivity variation of PVA/PEG/MnO_2 nanocomposites with wavelength.

PVA/PEG/MnO_2 nanocomposites with wavelength. This figure shows that the optical conductivity of PVA/PEG/MnO_2 nanocomposites is decreased with the increase in wavelength; this behaviour of the optical conductivity depends strongly on the radiation incident wavelength. The increase of the optical conductivity at low photon wavelength is related to both high absorbance of PVA/PEG/MnO_2 nanocomposites in that region and, therefore, the increase of the charge transfer excitations. The optical conductivity of PVA/PEG/MnO_2 nanocomposites is increased with the increase in MnO_2 NPs' concentration that is due to the localized levels' creation in the energy gap; the increase of MnO_2 NPs' concentration leads to the increase of the density of localized states in the band structure. Therefore, the absorption coefficient will increase that leads to the increase in the optical conductivity [21–23].

4. CONCLUSIONS

In the present paper, the PVA/PEG/MnO_2 nanostructures were prepared to use in many electronics and optics applications. The results indicated that the absorbance of PVA/PEG blend increases with the increase in MnO_2 nanoparticles' content. The absorption coefficient, extinction coefficient, refractive index, real and imaginary parts of dielectric constants and optical conductivity of PVA/PEG blend are increased with the increase in MnO_2 NPs' content. The transmittance and energy band gap are decreased as MnO_2 concentration increases. Finally, the optical-properties' results show that the PVA/PEG/MnO_2 nanostructures may be used for different optics and electronics applications.

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