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**Influence of MnO\textsubscript{2} Nanoparticles Addition on Structural, Optical and Dielectric Characteristics of PVA/PVP for Pressure Sensors**

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Films of PVA/PVP/MnO\textsubscript{2} nanostructures were fabricated for pressure sensors fields with lightweight, flexible and low cost compare with other sensors. The structure, dielectric and optical characteristics of PVA/PVP/MnO\textsubscript{2} nanostructures have been studied. The results showed that the dielectric constant, dielectric loss and A.C electrical conductivity of PVA/PVP blend are enhanced with the increase in MnO\textsubscript{2} NPs content. The dielectric constant and dielectric loss decrease while the A.C electrical conductivity increases with the increase in frequency. The optical characteristics of PVA/PVP/MnO\textsubscript{2} nanostructures showed that the absorbance was rise with increasing of the MnO\textsubscript{2} NPs content. The indirect energy gap of PVA/PVP blend was reduced with increase in MnO\textsubscript{2} NPs content. The optical constants of blend are changed with the increase in MnO\textsubscript{2} NPs content. The pressure sensor application results of PVA/PVP/MnO\textsubscript{2} nanostructures showed that the electrical capacitance ($C_{el}$) increases with the rise in applied pressure.

**Keywords:** MnO\textsubscript{2}, pressure sensors, energy gap, dielectric constant, conductivity.

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**Introduction**

The new polymer nanocomposites production has been commonly studied by the modern fields on nanoscale inorganic additive in the food packaging approaches, barrier fields, coatings, antimicrobial, sensors, antballistic products, conductive, and other materials. The novel generation of these nanocomposites includes carbides (B\textsubscript{C}, SiC, WC), nitrides (BN CrN, TiN, ZrN), borides (CrB\textsubscript{2}, ZrB\textsubscript{2}, WB, TiB\textsubscript{2}), metal oxides (Y\textsubscript{2}O\textsubscript{3}, MgO, Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2}, CeO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, TiO\textsubscript{2}), cellulose nanofibrils, carbon nanotubes, and other nanoparticles types as scatter phase. The properties and characteristics of the new nanomaterials are affected by the kind of additive employed by the polymer matrix. The applications include many fields like electronics, aerospace, military, vehicles, marine and medicine [1]. The transition metals oxides are an significant group of semiconductors have functions in solar energy transformation, magnetic storage media, catalysis and electronics [2]. MnO\textsubscript{2} is promising green matter has involved large interests in good quality of its excellent environmental compatibility, low cost, and broad structural diversity combined with especial chemical and physical characteristics. The important fields of MnO\textsubscript{2} nano-scale contain alkaline batteries, gas sensors, photocatalyst, electrochemical capacitors, and smart windows [3]. Polyalvyl alcohol is an important polymer, relate to its chemical and physical features. This polymer may be a film, powder, and fiber forms. PVA has a semi-crystalline nature due from the hydrogen bonds and the OH group role. Relate to its low protein adsorption properties, excellent water solubility and biocompatibility, PVA is usually employed in medical devices. Polyvinyl-pyrrolidone has an excellent stable environment, moderate electric conductivity and easy processing. PVP has a broad applications range like electrochemical devices. PVA/PVP interactions have unique characteristics which
combine the characteristics of both polymers [4]. The present work aims to prepare the PVA/PVP/MnO nanostructures films to use as lightweight and low-cost pressure sensors.

I. Materials and Methods

Nanocomposites films of polyvinyl alcohol (PVA)-polyvinyl pyrrolidone (PVP)- manganese oxide (MnO) was fabricated by using casting method. The solution of PVA/PVP blend was prepared by the 0.5 gm of PVA and PVP with ratio 77 wt.% PVA: 23 wt.% PVP were dissolved in distilled water (20 ml) of. The MnO NPs added to the blend with ratios are 1.5 %, 3 % and 4.5 %. The optical characteristics measured in range of wavelength (220 - 820) nm by spectrophotometer (UV/1800/ Shimadzu). The dielectric characteristics of films measured in frequency range (100 Hz - 5 ×10⁶ Hz) by LCR meter type (HIOKI 3532-50 LCR HI TESTER). The pressure sensor testing investigated by measuring the capacitance between two electrodes on the top and bottom of the sample for various pressures range (80 - 200) bar. The absorption coefficient (α) is given by [5,6]:

\[
α = 2.303 \text{ (A/t)},
\]

where A: absorbance and t: sample thickness.

The energy band gap can be determined by [7]:

\[
\alpha \hbar \nu = B(\hbar \nu - E_0)^k
\]

where B: constant, hν: photon energy, E_0: energy band gap, r = 3 for forbidden indirect transition and r = 2 for allowed indirect transition.

The refractive index (n) is given by [8]:

\[
n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}}
\]

where R is the reflectance.

The extinction coefficient (k) is defined by [9]:

\[
k = \frac{\alpha \lambda}{4 \pi}
\]

where λ is the wavelength of incident photon.

The dielectric constant parts: real (ε_1), and imaginary (ε_2) are calculated by the equations [10]:

\[
ε_1 = n^2 - k^2
\]

\[
ε_2 = 2nk
\]

The optical conductivity (σ_{op}) can be calculated by the equation [11].

\[
σ_{op} = \frac{αnc}{4\pi}
\]

The dielectric constant (ε') can be calculated by using [13]:

\[
e^{-} = \frac{ε'}{ε_0}
\]

where, C_p is parallel capacitance and C_o is vacuum capacitor.

The dielectric loss (ε”) can be calculated by using [14]:

\[
ε^{-} = \frac{ε'}{ε_0}
\]

The AC electrical conductivity can be determined by using [14]:

\[
σ_α = w ε^{-} ε_0,
\]

where w – angular frequency.

II. Results and Discussion

Figure 1 shows the FTIR measurements of PVA/PVP/MnO nanostructures. As shown in Figure 1, there is no interactions between the blend and the MnO NPs. It shows broad bands at around 3257 cm⁻¹ are observed related to OH groups in the blend chain. The peaks at around 1647 cm⁻¹ due to the presence of such free C=O groups. The bands at around 1289 cm⁻¹ due to the other bonds (C-O-C) [15].

The behavior of absorbance of pure polymeric blend and PVA/PVP/MnO nanostructures with wavelength is shown in Figure 2. The absorbance of blend is rise with the increase in MnO NPs content; this is relate to rise of the charges carries numbers [16,17].

The absorption coefficient is useful to show the electron transition nature. The PVA/PVP/MnO nanostructures has values of absorption coefficient less than (10⁴ cm⁻¹) as shown in Figure 2. The absorption coefficient of PVA/PVP/MnO nanostructures is rise with the rise of MnO NPs content which related to rise the charges carries numbers [18], as shown in Figure 3. Figure 3 indicates that the nanoparticles shape a continuous arrangement within the polymeric blend at high ratios [19,20]. The absorption coefficient values indicate to the PVA/PVP/MnO nanostructures have indirect energy gap. Figures 4 and 5 represent the energy gap for allowed indirect and forbidden indirect transitions respectively. As shown in Figures, the energy gap are reduced with the rise in MnO NPs ratio which is due to the some defects formation in the samples. These defects create the localized positions in the optical band gap and overlap. These overlaps offer evidence for reducing energy band gap when the MnO NPs ratio rise in the polymeric blend [21].

The variation of extinction coefficient and refractive index with wavelength of films are shown in Figures 6 and 7 respectively. The figures indicate that the extinction coefficient and refractive index of blend are rise with the rise in MnO NPs ratio. The rise of extinction coefficient and refractive index of blend related to rise the absorption coefficient and the samples density [22-25].

Figures 8 and 9 indicate to the real and imaginary of dielectric constant behavior with wavelength respectively. The real part mostly depends on n² because
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Fig. 1. FTIR spectra of PVA/PVP/MnO₂ nanostructures: A – pure blend, B – 1.5 wt.% MnO₂ NPs, C – 3 wt. MnO₂ NPs, D – 4.5 wt.% MnO₂ NPs.

Fig. 2. Absorbance behavior of PVA/PVP/MnO₂ nanostructures with wavelength.
the $k^2$ values are small as compared to the $n^2$ values while imaginary part generally depends on the $k$ values [26].

Figure 10 represents the optical conductivity variation of PVA/PVP/MnO$_2$ nanostructures with wavelength. The optical conductivity of blend rises with the increase in MnO$_2$ NPs ratio and photon energy. The rise in optical conductivity as MnO$_2$ NPs ratio increase due to reduce the energy gap [27-28].

Fig. 3. Photomicrographs (x10) of PVA/PVP/MnO$_2$ nanostructures: A – pure blend, B– 1.5 wt.% MnO$_2$NPs, C – 3 wt. MnO$_2$NPs, D – 4.5 wt.% MnO$_2$NPs.

Fig. 4. Energy gap of allowed transition.
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Fig. 5. Energy gap of forbidden transition.

Fig. 6. Extinction coefficient variation with wavelength.

Fig. 7. Refractive index variation with wavelength.

Fig. 8. Real dielectric constant behavior with wavelength.

Fig. 9. Imaginary dielectric constant behavior with wavelength.

Fig. 10. Optical conductivity behavior of films with wavelength.

Figures 11-13 show the variation of dielectric constant, dielectric loss and A.C electrical conductivity of PVA/PVP/MnO$_2$ nanostructures with frequency respectively. From the Figures, the dielectric constant, dielectric loss and electrical conductivity of blend rise with rise in MnO$_2$ NPs ratio which is relate to rise of the charge carrier density in blend [29, 30]. The dielectric constant and dielectric loss reduce while the conductivity rises with the rise in frequency; this is due to the polarization effects [31]. The variation of capacitance for PVA/PVP/MnO$_2$ nanostructures films with pressure is shown in Figure 4. The figure indicates that the
capacitance rises with the rise in pressure. When the pressure is applied to film, it led to mechanical deformation and charges displacement. An electric field will produce and consequently voltage may be detected on the lower and upper film surface. When stress is removed, the voltage will disappear. This fact is called direct piezoelectric effect. Conversely, the internal production of mechanical strain of the film resulting from an applied electrical field is called reverse piezoelectric effect [32].

**Conclusions**

The results of optical characteristics showed that the optical absorbance of PVA/PVP blend rises with the rise in the MnO$_2$ NPs ratio. The energy gap of blend reduces with the rise in MnO$_2$ NPs content. The optical constants (absorption coefficient, extinction coefficient, refractive index, dielectric constants parts and optical conductivity) of PVA/PVP blend are rise with increasing of the MnO$_2$ NPs content. The dielectric constant, dielectric loss and A.C electrical conductivity of PVA/PVP blend rise with the rise in MnO$_2$ NPs content. The dielectric constant and dielectric loss of PVA/PVP/MnO$_2$ nanostructures reduce while the conductivity rises with the rise in frequency. The results of PVA/PVP/MnO$_2$ nanostructures application for pressure sensors indicated that the nanostructures films have highly sensitive for pressure.

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Влияние введения наночастиц MnO2 на структурные, оптические и диэлектрические характеристики PVA/PVP для датчиков тиску

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Наноструктурированные пленки PVA/PVP/MnO2 были получены для использования в качестве датчиков тиску, как гибкие и недорогие, по сравнению с другими датчиками. Исследованы структура, диэлектрические и оптические характеристики наноструктур PVA/PVP/MnO2. Исследования показали, что диэлектрическая проницаемость, диэлектрические потери и электропроводность переменного тока для структуры PVA/PVP увеличиваются с увеличением содержания наночастиц MnO2. Диэлектрическая проницаемость и диэлектрические потери уменьшаются, тогда как электропроводность переменного тока увеличивается с увеличением частоты. Оптические характеристики наноструктур PVA/PVP/MnO2 показали увеличение коэффициента зеркальной отражаемости с увеличением содержания MnO2. Ширина непрямой энергетической запрещенной зоны PVA/PVP уменьшается с увеличением содержания MnO2. Результаты исследований показывают, что электрическая емкость (Cp) увеличивается с увеличением приложенного давления.

Ключевые слова: MnO2, датчик давления, запрещенная зона, диэлектрическая константа, проводимость.