Наносистеми, наноматеріали, нанотехнології
Nanosistemi, Nanomateriali, Nanotehnologii
2021, т. 19, № 2, сс. 353–362

PACS numbers: 07.07.Df, 07.60.Pb, 78.20.Ci, 78.30.Jw, 78.40.Me, 78.67.Sc, 82.35.Np

Synthesis of PVA/PVP/SnO_2 Nanocomposites: Structural, Optical, and Dielectric Characteristics for Pressure Sensors

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Nanocomposites' films are prepared from PVA/PVP blend with various ratios of SnO_2 by using the casting method. The structural, optical, and dielectric characteristics of nanocomposites are studied for pressure sensors' applications. The results indicate to the optical characteristics of PVA/PVP/SnO_2 nanocomposites improved with the rise in SnO_2-nanoparticles' ratios. The dielectric characteristics show that the dielectric parameters of PVA/PVP blend enhance with rise in SnO_2-nanoparticles' ratios. The pressure-sensor results for nanocomposites show that the capacitance increases with an increase in pressure.

Плівки нанокомпозитів готуються з суміші ПВА/ПВП з різними співвідношеннями SnO_2 за допомогою методи лиття. Структурні, оптичні та діелектричні характеристики нанокомпозитів вивчаються задля застосування давачів тиску. Результати вказують на те, що оптичні характеристики нанокомпозитів ПВА/ПВП/SnO_2 поліпшилися зі зростанням співвідношення наночастинок SnO_2. Діелектричні характеристики показують, що діелектричні параметри суміші ПВА/ПВП поліпшуються зі зростанням співвідношення наночастинок SnO_2. Результати давача тиску для нанокомпозитів показують, що ємність збільшується зі збільшенням тиску.

Key words: pressure sensors, tin oxide, energy gap, conductivity, dielectric properties.

Ключові слова: сенсори тиску, оксид Стануму, енергетична щілина, провідність, діелектричні властивості.

(Received 30 May, 2020; in revised form, 19 June, 2020)

1. INTRODUCTION

In recent years, the electrical and optical characteristics' studies of polymers include attracted greatly attention in their approaches' view in devices (optical, electronic ones). The electrical characteristics are aimed to know the charge transport prevalent nature in these substances, while the optical characteristics are aimed to anti-reflection, achieving better reflection and polarization characters. Optical and electrical characteristics of the polymers may be suitably customized by the dopant addition, depending on their reactivity with the polymer matrix. Moreover, the polymer materials advantages such as good mould ability, high strength and flexibility might be combined with the great characteristics of inorganic substances like heat stability, heat strength, high strength, and chemical resistance during producing composite substances. The large-range fields of nanofillers like filters, tissue engineering, catalysis, scaffold, sensors and wound dressing might be extended with improving their electrical, mechanical, magnetic, optical, and thermal characteristics by incorporating organic and inorganic constituents in their structures [1].

The creation of polymer composites by means of polymer matrix, which can offer high tensile strength and non-toxicity, will be appropriate for food packaging and biomedical applications. Polyvinyl alcohol (PVA) offers the property of biocompatibility, non-toxicity, water solubility, superior tensile strength and is gradually replacing other non-biocompatible plastics like polyethylene, polypropylene, HDPE, *etc.* in many fields [2].

Polyvinyl alcohol is semi-crystalline, with low electrical conductivity. PVA has certain physical characteristics resultant from crystal/amorphous interfacial effects. Its electrical characteristics may be modified to an exact requirement by the suitable doping substance addition [3]. Poly(N-vinylpyrrolidone) (PVP) attracts particular attention between the polymers that is related to its excellent stability of environmental, appropriate electrical conductivity and easy processability. The reactive pyrrolidone group of PVP easily forms complexes with many inorganic salts, synthetic or natural functional polymers, biomolecules and biomacromolecules [4].

Improved characteristics of semiconducting metal oxides create them to find approaches in several applications. Between the semiconducting metal oxides, tin oxide (SnO_2) has been generally inves-

tigated due to its large band gap of 3.6 eV and its potential fields in different approaches like liquid-crystal displays, gas sensors, photovoltaic cells, and solar cells [5]. SnO_2-nanostructures' multifunctionality arises relating to their large band gap, high surface to volume ratio, high exciton binding energy of 130 meV at room temperature (300 K), variation of remarkable resistivity in gaseous environment, chemical, mechanical and thermal stabilities, *etc*. Optoelectronic characteristics of SnO_2 depend on the impurities' presence and its stoichiometry with respects to oxygen [6].

2. MATERIALS AND METHODS

PVA–PVP–SnO_2 nanocomposites were prepared by casting technique. The solution of polymers was prepared by dissolving of 0.5 gm of PVP + PVA in distilled water (20 ml) with ratio 77 wt.% PVA:23 wt.% PVP. The SnO_2 nanoparticles were added to blend solution with ratios 1.5, 3 and 4.5 wt.%. The optical characteristics were tested in wavelength range 220–820 nm by using spectrophotometer (UV/1800/Shimadzu). The dielectric characteristics were measured in frequency range 100 Hz–5 MHz by LCR meter type (HIOKI 3532-50 LCR HI TESTER). The pressure-sensor application was tested by measuring the parallel capacitance (C_p) between two electrodes on the top and bottom of film with different pressures' range 80–200 bar. Absorption coefficient, α, is given by [7, 8]:

$$\alpha = 2.303A/t; \tag{1}$$

A is absorbance, and t is sample thickness. The energy gap is determined by the equation [9, 10]

$$Ah\nu = B\left(h\nu - E_g\right)^r, \tag{2}$$

where B is constant, $h\nu$ is photon energy, E_g is energy gap, $r = 3$ for forbidden indirect transition, and $r = 2$ is allowed indirect transition. Refractive index, n, is given by the equation [11]

$$n = (1 + \sqrt{R})/(1 - \sqrt{R}); \tag{3}$$

here, R is reflectance. The extinction coefficient, k, is defined by

$$k = \alpha\lambda/(4\pi), \tag{4}$$

where λ is wavelength [12]. The parts of dielectric constant, real, ε_1, and imaginary, ε_2, ones are calculated by [13]:

$$\varepsilon_1 = n^2 - k^2, \tag{5}$$

$$\varepsilon_2 = 2nk. \tag{6}$$

The optical conductivity, σ_{op}, may be calculated by the equation [14, 15]

$$\sigma_{op} = \alpha nc/(4\pi)\,. \tag{7}$$

The dielectric constant, ε', is given by [16]:

$$\varepsilon' = C_p/C_o \tag{8}$$

where C_p is capacitance and C_o is capacitance of vacuum. The dielectric loss, ε'', can be calculated by using [17]:

$$\varepsilon'' = \varepsilon' D, \tag{9}$$

where D is dispersion factor. The A.C. conductivity can be determined by using [18]:

$$\sigma_{ac} = \omega\varepsilon''\varepsilon_o, \tag{10}$$

where ω is angular frequency.

3. RESULTS AND DISCUSSION

Figure 1 explains the FTIR test of nanocomposites. The FTIR tests of PVA/PVP/SnO_2 nanocomposites show the nanocomposites' interactions. From Figure 1, it is seen bands at around 3256 cm^{-1}, which are related to OH groups. The peaks at around 1652 cm^{-1} are due to C=O groups. The bands at around 1290 cm^{-1} are due to the other bonds (C–O–C) [19, 20].

Figure 2 represents the absorbance variation of blend with wavelength. The absorbance of blend rises with rising of the SnO_2-nanoparticles' ratios that is due to the rise in number of charge carries in nanocomposites [21–26], as exposed in Fig. 3, which shows the SnO_2-nanoparticles' distribution in PVA/PVP blend. The absorption-coefficient variation with energy of photon is shown in Fig. 4. Absorption coefficient of PVA/PVP blend rise with rising of the SnO_2 nanoparticles' ratios that is related to rise of the absorbance [27]. The absorption coefficient shows the nature of energy gap. From the α values, the energy gap is indirectly corresponding, as shown in Figs. 5 and 6, to allowed and forbidden transitions, respectively. The energy gap for transitions (allowed and forbidden ones) is reduced with rise in SnO_2-nanoparticles' ratios that is related to creating the localized levels in the optical band gap [28, 29].

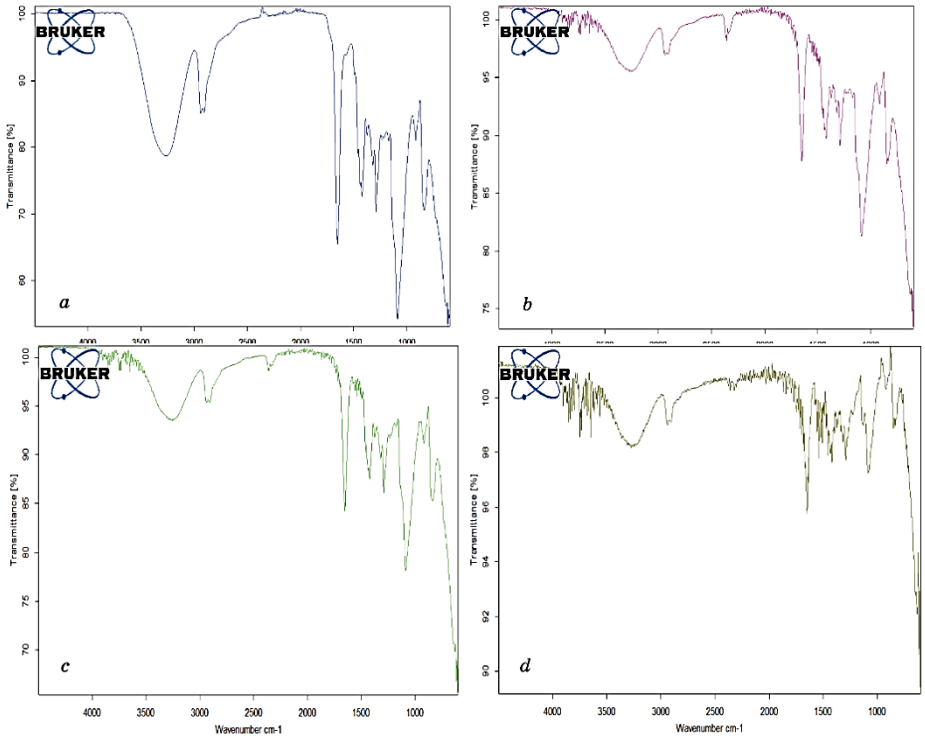

Fig. 1. FTIR test of PVA/PVP/SnO_2 nanocomposites: *a*—blend; *b*—1.5 wt.% SnO_2; *c*—3 wt.% SnO_2; *d*—4.5 wt.% SnO_2.

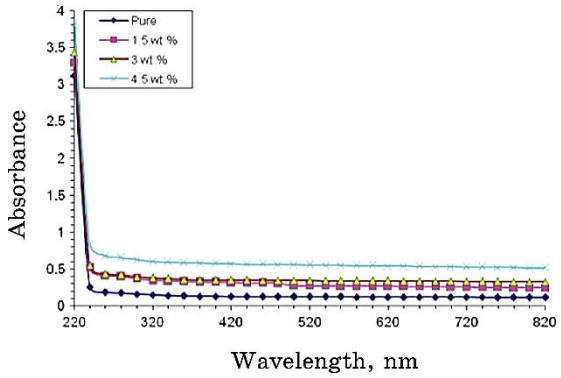

Fig. 2. Relationship between the absorbance of PVA–PVP blend and wavelength.

The variations of *n* and *k* with wavelength are shown in Figs. 7 and 8, respectively. The refractive index and extinction coefficient are increased with rise in SnO_2 content that is due to rise in absorp-

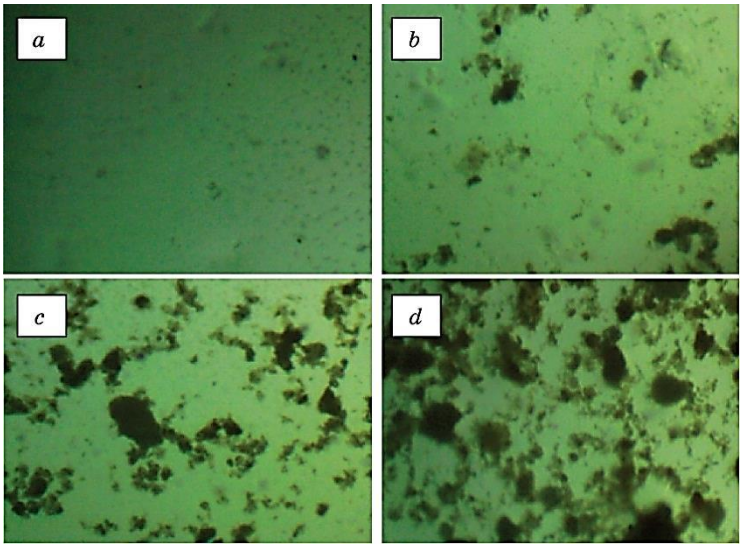

Fig. 3. Microscope images of PVA/PVP/SnO_2 nanocomposites: *a*—blend; *b*—1.5 wt.% SnO_2; *c*—3 wt.% SnO_2; *d*—4.5 wt.% SnO_2.

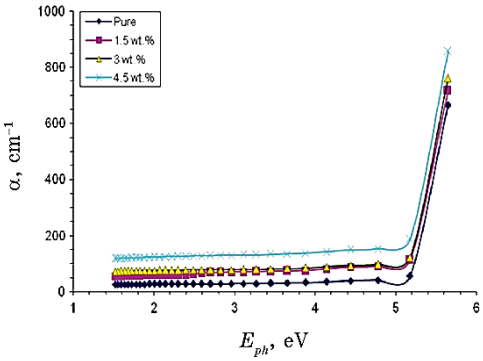

Fig. 4. Absorption-coefficient variation with energy of photon.

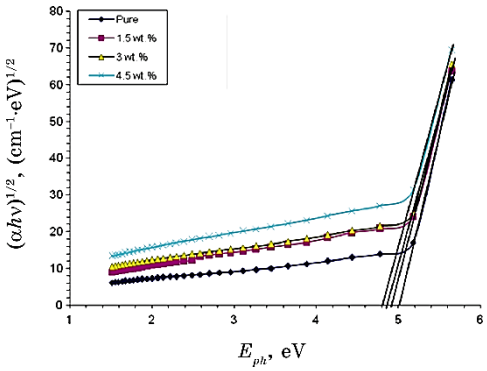

Fig. 5. Energy gap for allowed indirect transitions.

tion and density of nanocomposite [30].

Figures 9 and 10 show the variations of ε_1 and ε_2 of PVA/PVP/SnO_2 with wavelength, respectively. ε_1 and ε_2 rise with rise in SnO_2 that is related to the real part dependent on n^2 because the values of k^2 are small as compared to values of n^2, while imaginary part mainly depends on the values of extinction coefficient [31].

Figure 11 explains the optical conductivity variation for PVA/PVP/SnO_2 films with wavelength.

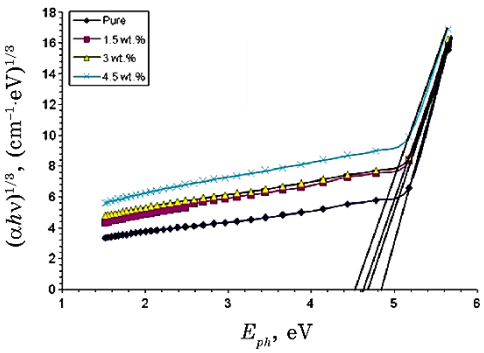

Fig. 6. Energy gap for forbidden indirect transitions.

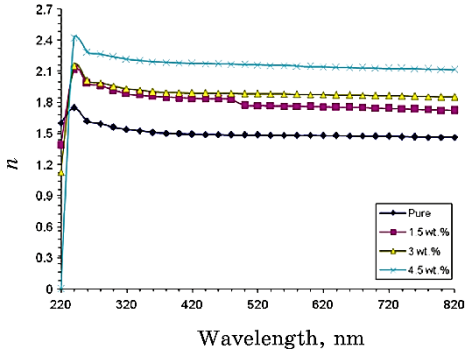

Fig. 7. Variation of refractive index with wavelength.

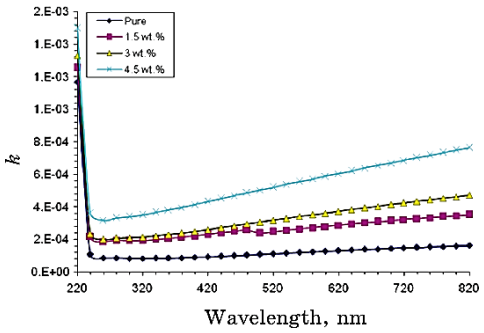

Fig. 8. Variation of extinction coefficient with wavelength.

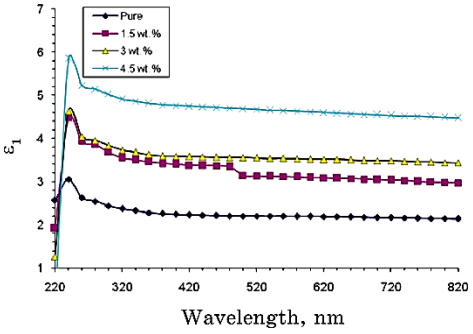

Fig. 9. Variation of ε_1 for PVA/PVP/SnO_2 with wavelength.

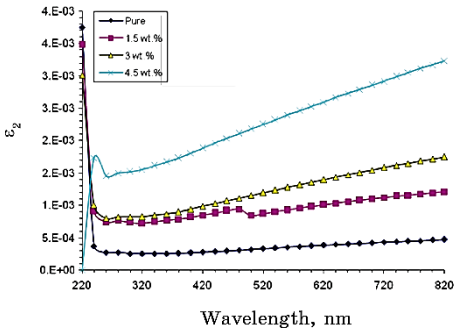

Fig. 10. Variation of ε_2 for PVA/PVP/SnO_2 with wavelength.

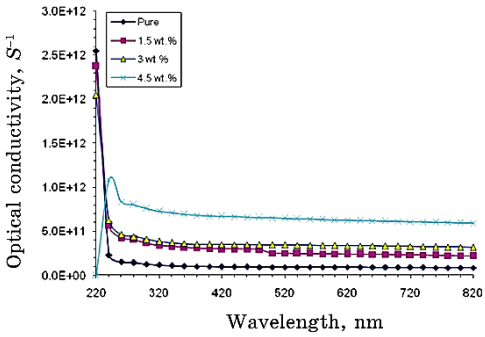

Fig. 11. Optical conductivity variation for PVA/PVP/SnO_2 nanocomposites with wavelength.

The optical conductivity of PVA/PVP blend increases with rise in

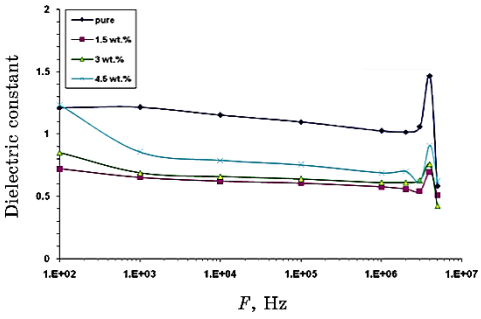

Fig. 12. Relationship between dielectric constant and frequency.

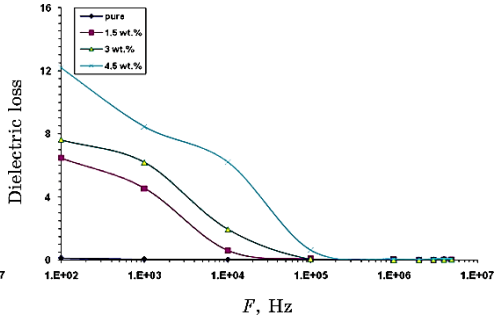

Fig. 13. Relationship between dielectric loss and frequency.

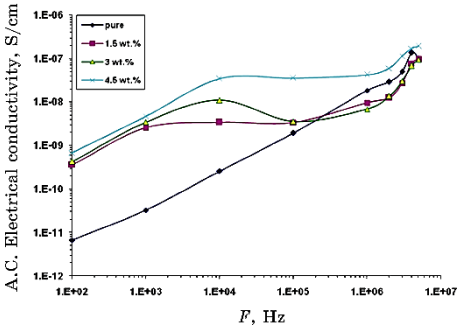

Fig. 14. Relationship between A.C. electrical conductivity and frequency.

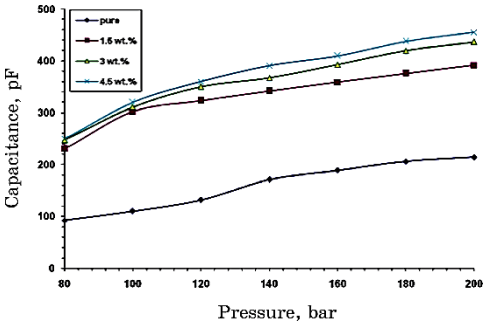

Fig. 15. Variation of capacitance for nanocomposites with pressure.

SnO_2-nanoparticles' ratios that is attributed to decrease in energy band gap and rise in the α and n values [32–35].

Figures 12–14 show the relationship between ε', ε'', $\sigma_{A.C.}$ and frequency, respectively. The dielectric parameters of PVA/PVP blend rise with rising of SnO_2 ratios that is due to increase of the charge-carriers' density in blend [36]. The dielectric constant and loss also increase, while the conductivity decreases with rise in frequency; this behaviour is related to polarization effects [37, 38].

Figure 15 shows the capacitance variation for nanocomposites' samples with pressure (compression stress). As from Figure 15, the capacitance increases with increase in pressure. This behaviour may be due to the crystal consisting of many interlocking domains, which contain negative and positive charges. These domains are symmetrical inside the crystal with the result that the crystal has a net charge of zero. When a pressure is applied to the crystal, this symmetry is broken, and in order to restore the symmetry, these domains realign themselves, and through the realignment, generate

a current that causes the increase in capacitance [39].

4. CONCLUSIONS

The results indicate to the optical characteristics of PVA/PVP blend, which are improved with a rise in tin oxide content.

The dielectric properties show that the dielectric parameters enhance with rising of the SnO_2-nanoparticles' ratios.

The results of pressure sensors indicate that the PVA/PVP/SnO_2 nanocomposites have excellent sensitivity for pressure.

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