Novel Metal-Oxide-NPs-Doped Polymers: Structural and Dielectric Properties for Flexible Pressure Sensors

Ahmed Hashim and Ali Jassim

College of Education for Pure Sciences,
Department of Physics,
University of Babylon,
Hillah, Iraq

Biodegradable polymer blend−inorganic metal-oxide nanoparticles' semiconductor for novel pressure sensors with low cost, lightweight and good sensitivity is investigated. Biodegradable blend prepared from polyvinyl alcohol and starch with following weight percentage: polyvinyl alcohol (85 wt.% PVA) and starch (15 wt.% ST). The influence of lead-oxide nanoparticles' concentration on the structural and dielectric properties of (PVA−ST) blend is studied. The dielectric properties of (PVA−ST−PbO$_2$) nanocomposites are studied in frequency range from 100 Hz to 5 MHz. The results show that the dielectric constant and dielectric loss of (PVA−ST−PbO$_2$) nanocomposites decrease with increasing of frequency of applied electric field. The A.C. electrical conductivity of (PVA−ST−PbO$_2$) nanocomposites increases with increase in frequency. The dielectric parameters of (PVA−ST) blend (dielectric constant, dielectric loss, and A.C. electrical conductivity) increase with increase in lead-oxide nanoparticles' weight percentage. The nanocomposites are tested for pressure sensors. The experimental results show that the (PVA−ST−PbO$_2$) nanocomposites have high sensitivity for pressure, and the electrical resistance of nanocomposites decreases with increases in applied pressure.

Досліджено здатну до біологічного розкладання полімерну суміш із неорганічними металооксидними наночастинками напівпровідника для нових датчиків тиску з низькою вартістю, легкістю та хорошою чутливістю. Суміш, яка розкладається мікроорганізмами, приготовано з полівінілового спирту (ПВС) та крохмалю з наступними ваговими відсотками — полівініловий спирт (85 ваг.% ПВС) і крохмаль (15 ваг.% Кр). Досліджено вплив концентрації наночастинок оксиду плюмбуму на структурні та діелектричні властивості суміші (ПВС−Кр). Діелектричні властивості нанокомпозитів (ПВС−Кр−PbO$_2$) вивчаються в діапазоні частот від 100 Гц до 5 МГц. Результати показують, що діелектрична постійна та діелектричні втрати нанокомпозитів (ПВС−Кр−PbO$_2$) змен-

шуються зі збільшенням частоти прикладеного електричного поля. Електропровідність змінного струму нанокомпозитів (ПВС–Кр–PbO$_2$) збільшується зі збільшенням частоти. Діелектричні параметри суміші (ПВС–Кр) (діелектрична постійна, діелектричні втрати й електропровідність змінного струму) збільшуються зі збільшенням вагового відсотка наночастинок оксиду плюмбуму. Нанокомпозити тестуються на датчики тиску. Експериментальні результати показують, що нанокомпозити (ПВС–Кр–PbO$_2$) мають високу чутливість до тиску, а електричний опір нанокомпозитів понижується зі збільшенням застосованого тиску.

Key words: metal oxide, polymer, biodegradable nanocomposite, electrical and dielectric properties, pressure sensor.

Ключові слова: оксид металу, полімер, нанокомпозит, який розкладається мікроорганізмами, електричні та діелектричні властивості, датчик тиску.

1. INTRODUCTION

Nanocomposites of organic and inorganic semi-conductors dispersed in polymer matrices are multifunctional materials often suggested as elements of nonlinear optical devices and for development of plastic solar cells. The increasing interest in their possible use is caused by their plasticity, simple preparation techniques, and an opportunity to tune their properties by changing the concentration and the nanoparticle size in the matrix. A polymeric nanocomposite should possess high optical and photochemical stability [1]. Nanocomposites on base of semi-conductor nanoparticles and polymer matrix are prospective materials for application in optoelectronics, for creation of luminescent materials, sensor, *etc.* Introducing semi-conductor nanoparticles into polymer matrix bulk changes physico-chemical properties of the system. The properties of the obtained structures depend on a semi-conductor particle type, dimensions of particles. Furthermore, the physicochemical properties of the system will be under influence of the effects of interaction of nanoparticles with polymer matrix, polymer–nanoparticle interphase phenomena [2–5].

Ceramic materials are typically brittle, possess low dielectric strength and, in many cases, are difficult to be processed requiring high temperature. On the other hand, polymers are flexible, can be easily processed at low temperatures and exhibit high dielectric breakdown fields [6]. Polymers are considered as a good choice as host materials, because they normally exhibit long-term stability and possess flexible reprocessability, and they can be designed to

yield a variety of bulk physical properties. This new class of organic−inorganic composites or hybrid materials may afford potential applications in molecular electronics, photoelectrochemical cells, optics, solvent-free coatings, *etc.* [7]. Polyvinyl alcohol (PVA) has been intensively investigated because of its excellent characteristics and its applications. PVA is the good potential material, which is having high storage capacity, high dielectric strength, and electrical properties. It has a carbon chain backbone with hydroxyl group attached to methane carbons. These O−H groups can be source of hydrogen bonding and, therefore, assist the formation of polymer complex. It has good mechanical properties and shows ionic conduction [8].

Sensor technology is one of the widely used technologies for applications in the industry and medicine. It can be used to measure pressure, temperature, quality and amount of energy, and to monitor health. High performance electrochemical devices such as sensors require good semi-conductor properties, lightweight nature and enhanced energy storing capabilities. Various types of sensors have been fabricated from polymer matrices such as pressure, thermal (infrared), vapour, humidity, gas, electrical and temperature (thermal) sensors. The most important parameters in sensor technology are response time and sensitivity [9]. Saygh *et al.* [9] fabricated a novel flexible-nanocomposite pressure sensor with a tensile strength of about 47 MPa. A hybrid composite was prepared by incorporating the nanolayers of titanium dioxide TNL (2.5 wt.%) with reduced graphene oxide (*r*GO) (2.5 wt.%) synthesized by improved graphene-oxide synthesis to form a polyvinylidene fluoride (PVDF)/*r*GO−TNL composite. A comparison between PVDF, PVDF/*r*GO (5 wt.%), PVDF/TNL (5 wt.%) and PVDF/*r*GO−TNL (total additives—5 wt.%) samples is analysed for their sensing, thermal and dielectric characteristics. As found, the flexible material shows good sensing properties with high response in short time [9].

2. EXPERIMENTAL PART

Biodegradable blend of polyvinyl alcohol (85 wt.%) and starch (15 wt.%) prepared by dissolving 1 gm of polyvinyl alcohol and starch in 20 ml of distilled water by using magnetic stirrer to mix the polymers for 1 hour to obtain more homogeneous solution. The lead-oxide nanoparticles were added to blend with concentrations of 1, 2 and 3 wt.%. The pressure-sensor films of (PVA−ST−PbO_2) nanocomposites casted in the template (Petri dish has diameter of 10 cm). The samples were prepared with thickness range 120−142 μm. The (PVA−ST−PbO_2) nanocomposite films were examined by using the optical microscope (supplied from Olympus name (ToupView)

type (Nikon-73346)) with magnification ×10. The dielectric properties of nanocomposites were measured in frequency range from 100 Hz to $5\cdot10^6$ Hz by using LCR metre type (HIOKI 3532-50 LCR HI TESTER). The pressure sensor test of (PVA−ST−PbO$_2$) nanocomposites were examined by measuring the electrical resistance by using the Keithley electrometer type 2400 of source matter between two electrodes on the top and bottom of the sample for different pressures within the range 80−200 bar.

The dielectric constant (ε') of nanocomposites is defined by the following equation [10]:

$$\varepsilon' = C_p/C_o,\tag{1}$$

where C_p is parallel capacitance and C_o is vacuum capacitor.

The dielectric loss (ε'') of nanocomposites can be written by the equation [10]:

$$\varepsilon'' = \varepsilon'D,\tag{2}$$

where D is dispersion factor of (PVA−ST−PbO$_2$) nanocomposites.

The A.C. electrical conductivity of (PVA−ST−PbO$_2$) is calculated by the following equation [11]:

$$\sigma_{\text{A.C.}} = w\varepsilon''\varepsilon_o,\tag{3}$$

where w is the angular frequency.

3. RESULTS AND DISCUSSION

The variation of dielectric constant of (PVA−ST−PbO$_2$) nanocomposites with frequency is shown in Fig. 1. This figure shows that the dielectric constant of nanocomposites decreases with the increasing of frequency of the applied field. This may be attributed to the tendency of dipoles in nanocomposite samples to orient themselves in the direction of the applied electric field and decreasing of space-charge polarization to the total polarization [12, 13].

The dielectric constant of (PVA−ST) blend increases with the increasing of the concentration of PbO$_2$ nanoparticles. This behaviour could be interpreted from interfacial polarization inside the nanocomposites in applied alternating electric field and increasing of the charge carriers [14−19], as shown in Fig. 2.

The variation of dielectric loss of (PVA−ST−PbO$_2$) nanocomposites with frequency is shown in Fig. 3. The dielectric loss of nanocomposites decreases with the increase in frequency of applied electric field. This behaviour is attributed to the decrease of the space-
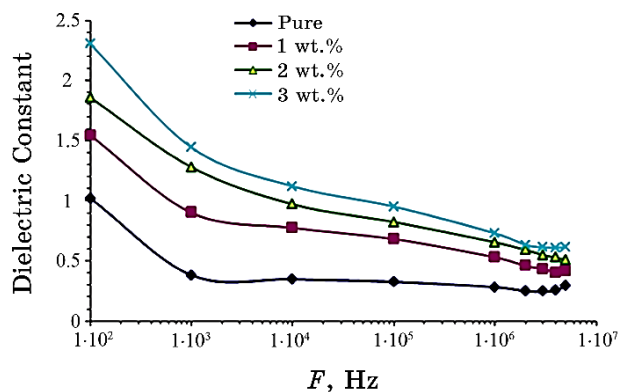
Fig. 1. Variation of dielectric constant of (PVA–ST–PbO$_2$) nanocomposites with frequency.
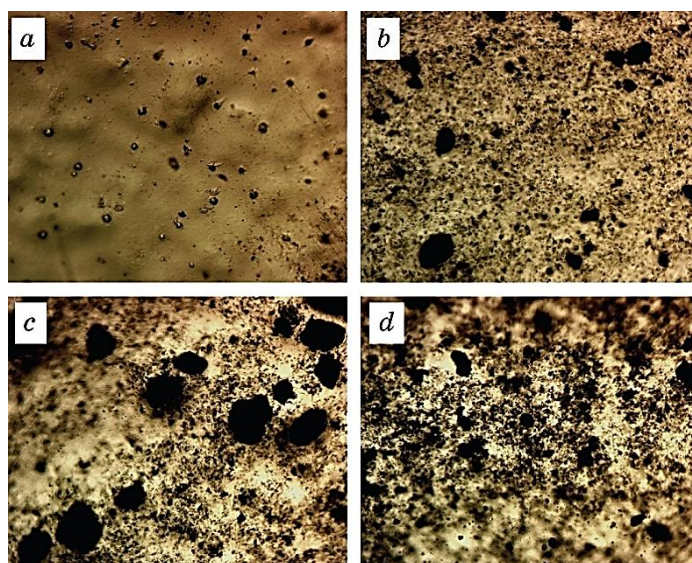

Fig. 2. Photomicrographs (×10) for (PVA–ST–PbO$_2$) nanocomposites: (*a*) for pure (PVA–ST) blend; (*b*) for 1 wt.% PbO$_2$ nanoparticles; (*c*) for 2 wt.% PbO$_2$ nanoparticles; (*d*) for 3 wt.% PbO$_2$ nanoparticles.

charge polarization contribution.

From Figure 3, the dielectric loss is high at low frequency, and it decreases, when the frequency increases. This is because the electric dipoles have sufficient time to align with the applied electric field before the electric field changes its direction; consequently, the dielectric constant of nanocomposites is high. At high frequencies, the dielectric constant value decreases due to the shorter time available
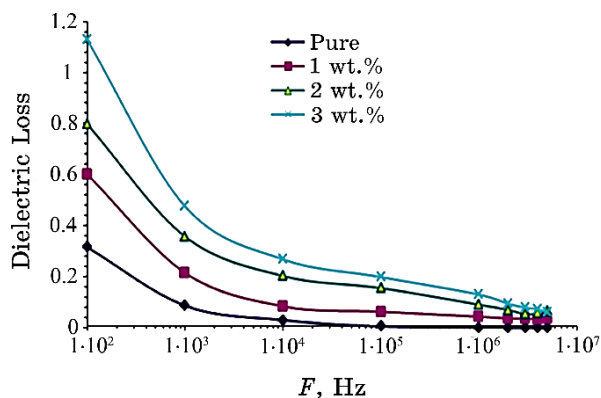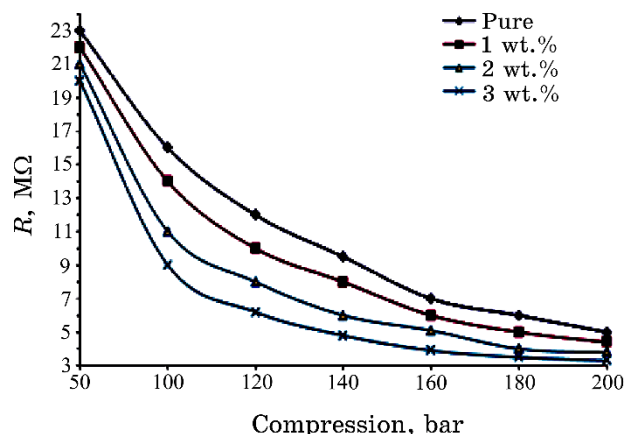
Fig. 3. Variation of dielectric loss of (PVA–ST–PbO₂) nanocomposites with frequency.
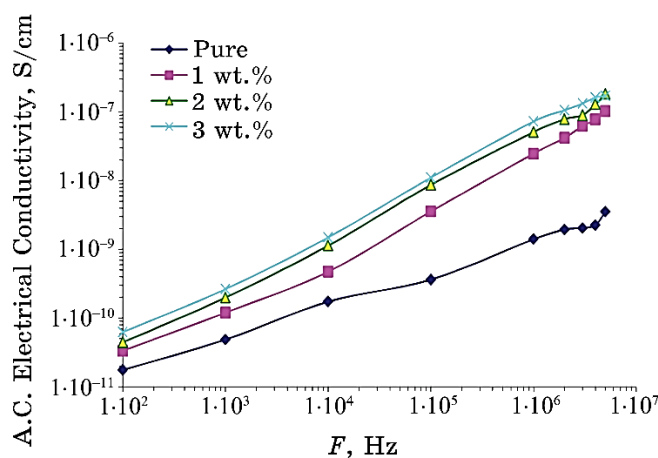
Fig. 4. Variation of A.C. electrical conductivity of (PVA–ST–PbO₂) nano-composites with frequency at room temperature.

for the dipoles to align [20]. Figure 3 shows that the dielectric loss of (PVA–ST) blend increases with the increasing of the PbO₂ nano-particles' concentration. The increase of dielectric loss of (PVA–ST) blend with the increasing concentration of PbO₂ nanoparticles is re-lated to the increase of the charge-carriers' number [21−24].

Figure 4 shows the variation of A.C. electrical conductivity of (PVA–ST–PbO₂) nanocomposites with frequency at room tempera-ture. The A.C. electrical conductivity increases with increase in frequency of electric field. This behaviour is attributed to the mo-bility of charge carriers and the hopping of ions from the cluster. At the low frequency, more charge accumulation is occurred at the

Fig. 5. Variation of electrical resistance of (PVA–ST–PbO$_2$) nanocomposites under different pressure at room temperature.

electrode and electrolyte interface, leading to a decrease in the number of mobile ions and electrical conductivity [25]. The mobility of charge carriers was higher in the high-frequency region; hence, the electrical conductivity increases with frequency [26] for (PVA–ST–PbO$_2$) nanocomposites. In addition, this figure shows that the A.C. electrical conductivity of (PVA–ST) blend increases with the increase of the PbO$_2$ nanoparticles' concentration. The increase of conductivity is caused by the increase in the number of charge carriers due to dopant-nanoparticles' composition, which reduces the resistance of nanocomposite and increases the A.C. electrical conductivity. At high concentration of nanoparticles, the nanoparticles form a network in the nanocomposite [27–31], as shown in Fig. 3.

Figure 5 shows the variation of electrical resistance of (PVA–ST–PbO$_2$) nanocomposites under different pressure at room temperature. As shown in figure, the electrical resistance of nanocomposites decreases with pressure increasing. The decrease of electrical resistance can be explain as follows: the agglomeration of nanoparticles in the matrix does not allow formation of conducting paths; when pressure is applied to the sample, the agglomerated additives follow the movement of the polymer chains and cause forming conducting networks of the sample. The largest improvement in the hybrid composite can be attributed to the less agglomeration in the matrix and better dispersion [9].

4. CONCLUSIONS

The dielectric constant, dielectric loss and A.C. electrical conductiv-

ity of (PVA−ST) blend increase with an increase in lead-oxide nanoparticles' concentration.

The dielectric constant and dielectric loss of (PVA−ST−PbO$_2$) nanocomposites decrease with increase in frequency, while the A.C. electrical conductivity increases with an increase in frequency.

The electrical resistance of (PVA−ST−PbO$_2$) nanocomposites decreases with increase in pressure. In addition, the (PVA−ST−PbO$_2$) nanocomposite films have high sensitivity for pressure with low cost and lightweight.

REFERENCES

1. P. Lutsyk, L. Dzura, A. Kutsenko, Ya. Vertsimakha, and J. Sworakowski, *Quant. Electro. & Optoelectronics*, **8**, No. 3: 54 (2005).
2. I. R. Agool, K. J. Kadhim, and A. Hashim, *Int. J. of Plastics Technol.*, **20**, Iss. 1: 121 (2016); https://doi.org/10.1007/s12588-016-9144-5
3. I. R. Agool and K. J. Kadhim, and A. Hashim, *Int. J. of Plastics Technol.*, **21**, Iss. 2: 444 (2017); https://doi.org/10.1007/s12588-017-9196-1
4. A. Hadi and A. Hashim, *Ukrainian J. of Phys.*, **62**, No. 12: 1044 (2017); doi:10.15407/ujpe62.12.1044
5. A. Hashim and Q. Hadi, *J. of Inorganic and Organometallic Polym. and Mater.*, **28**, Iss. 4: 1394 (2018); https://doi.org/10.1007/s10904-018-0837-4
6. S. Devikala, P. Kamaraj, and M. Arthanareeswari, *Chem. Sci. Trans.*, **2**: S1 (2013).
7. I. R. Agool, K. J. Kadhim, and A. Hashim, *Int. J. of Plastics Technology*, **21**, Iss. 2: 397 (2017); https://doi.org/10.1007/s12588-017-9192-5
8. A. Hashim, M. A. Habeeb, A. Khalaf, and A. Hadi, *Sensor Letters*, **15**: 589 (2017); https://doi.org/10.1166/sl.2017.3856
9. A. Al-Saygh, D. Ponnamma, M. A. AlMaadeed, P. Vijayan P, A. Karim, and M. K. Hassan, *Polymers*, **9**, No. 2: 33 (2017).
10. A. Hashim and A. Hadi, *Ukrainian J. of Phys.*, **62**, No. 12: 1050 (2017); doi:10.15407/ujpe62.12.1050
11. T. V. Kosmidou, A. S. Vatalis, C. G. Delides, E. Logakis, P. Pissis, and G. C. Papanicolaou, *eXPRESS Polym. Letters*, **2**, No. 5: 364 (2008).
12. H. N. Chandrakala, Shivakumaraiah, H. Somashekarappa, R. Somashekar, S. Chinmayee, and Siddaramaiah, *Indian J. of Adv. in Chem. Sci.*, **2**: 103 (2014); IJACS-MSP90.pdf (ijacskros.com)
13. D. Pradhan, R. N. P. Choudhary, and B. K. Samantaray, *Inter. J. Electrochemical. Sci.*, **3**: 597 (2008).
14. A. Qureshi, A. Mergen, and B. Aktas, *J. of Phys.: Conf. Ser.*, **153**: 1 (2009).
15. A. Hashim and A. Hadi, *Sensor Letters*, **15**, No. 12: 1019 (2017); doi:10.1166/sl.2017.3910
16. A. Hashim and A. Hadi, *Ukrainian J. of Phys.*, **63**, No. 8: 754 (2018); https://doi.org/10.15407/ujpe63.8.754
17. A. Hashim and Q. Hadi, *Sensor Letters*, **15**, No. 11: 951 (2017); doi:10.1166/sl.2017.3892
18. M. A. Habbeb, A. Hashim, and Abdul-Raheem K. AbidAli, *European Journal of Scientific Research*, **61**, No. 3: 367 (2011).

19.   A. Hashim, M. A. Habeeb, A. Hadi, Q. M. Jebur, and W. Hadi, *Sensor Letters*, **15**: 998 (2017); doi:10.1166/sl.2018.3935

20.   S. C. Mishra, *Global J. of Eng. Sci. and Res.*, **1**, No. 9: 32 (2014).

21.   A. L. Saroj and R. K. Singh, *J. of Phys. and Chem. of Solid*s, **73**: 162 (2012).

22.   X. Huang, S. Wang, M. Zhu, K. Yang, P. Jiang, Y. Bando, D. Golberg, and Chunyi Zhi, *J. of Nanotechn.*, **26**: 1 (2015).

23.   D. Hassan and A. H. Ah-yasari, *Bulletin of Elec. Eng. and Informatics*, **8**, Iss. 1: 52 (2019); doi:10.11591/eei.v8i1.1019

24.   D. Hassan and A. Hashim, *Bulletin of Elec. Eng. and Informatics*, **7**, Iss. 4: 547 (2018); doi:10.11591/eei.v7i4.969

25.   P. Vasudevan, S. Thomas, K. Arunkumar, S. Karthika, and N. Unnikrishnan, *J. of Mat. Sci. and Eng.*, **73**: 1 (2015).

26.   I. Tantis, G. Psarras, and D. Tasis, *J. of eXPRESS Polym. Lett.*, **6**, No. 4: 283 (2012).

27.   Hojjat Amrollahi and Mahmood Borhani, *Inter. J. of Eng. Res.*, **4**, No. 2: 69 (2015); http://www.i-scholar.in/index.php/IJER/article/view/159807

28.   O. Abdullah, G. M. Jamal, D. A. Tahir, and S. R. Saeed, *Inter. J. of Appl. Phys. and Math.*, **1**, No. 2: 101 (2011).

29.   A. Hashim, I. R. Agool, and K. J. Kadhim, *Journal of Materials Science: Materials in Electronics*, **29**, Iss. 12: 10369 (2018); https://doi.org/10.1007/s10854-018-9095-z

30.   A. Hadi, A. Hashim, and Y. Al-Khafaji, *Transactions on Electrical and Electronic Mater.*, **21**: 283 (2020); https://doi.org/10.1007/s42341-020-00189-w

31.   H. Ahmed and A. Hashim, *Egypt. J. Chem.*, **63**, No. 3: 805 (2020); doi: 10.21608/EJCHEM.2019.11109.1712