

doi: 10.15407/ujpe62.12.1050

A. HASHIM,<sup>1</sup> A. HADI<sup>2</sup><sup>1</sup> University of Babylon, College of Education for Pure Sciences, Department of Physics  
(Babylon, Iraq)<sup>2</sup> University of Babylon, College of Materials, Department of Ceramics and Building Materials, Iraq  
(Babylon, Iraq; e-mail: ahmed\_taaay@yahoo.com)

## SYNTHESIS AND CHARACTERIZATION OF NOVEL PIEZOELECTRIC AND ENERGY STORAGE NANOCOMPOSITES: BIODEGRADABLE MATERIALS–MAGNESIUM OXIDE NANOPARTICLES

PACS 28.41.Qb, 81.07.-b

*Sensors based on piezoelectric polymer nanocomposites have high sensitivity, low weight, flexibility, low cost, etc. We have studied a novel piezoelectric sensor made of the carboxymethyl cellulose, polyvinyl pyrrolidone–magnesium oxide nanocomposite. The electric conductivity and dielectric properties of the nanocomposite are studied at room temperature. The dielectric properties of the nanocomposite are examined in frequency range (100 Hz–5 MHz). The DC electric conductivity, dielectric constant, and dielectric losses increase with the concentration of magnesium oxide nanoparticles. The dielectric constant and dielectric losses decrease, as the frequency increases. The AC electrical conductivity increases with the concentration of magnesium oxide nanoparticles and the frequency. The nanocomposite was tested for the piezoelectric application in the pressure interval (80–200) bar. The experimental results show that the electric resistance is decreased, as the compaction stress increases. The nanocomposite has high sensitivity to the pressure. The nanocomposites is tested for the thermal energy storage and release. The results indicate that the times of the melting and solidification in the thermal energy storage and release decrease, as the concentration of magnesium oxide nanoparticles increases.*

*Keywords:* compaction stress, sensitivity, carboxymethyl cellulose, piezoelectric, conductivity, energy storage.

### 1. Introduction

Polymers have induced a considerable interest in the device fabrication because of their extraordinary inherent properties, like the easy processability, flexibility, high mechanical strength, *etc.* The electrical and optical properties of polymers can be tailored to a desired limit through a suitable doping. Further, polymers, on the doping with noble metal nanoparticles, show novel and distinctive properties obtained from a unique combination of the inherent characteristics of polymers and novel properties of metal nanoparticles. Due to this exclusive combination, polymer–metal nanocomposites are considered as advantageous candidates for device applications in various fields, like optics, mechanics, electronics, *etc.* This opens a new gateway in developing the materials with improved performance in many potential applications like optical devices, biomed-

cal sciences, coating materials and SERS based sensors *etc.* [1]. Polymer nanocomposites have recently attracted the great attention of scientists. Researches have shown that nanofillers can improve the dielectric breakdown strength, enhance the voltage endurance, depress the space charge formation, and weaken the partial discharge degradation of the pristine polymers more significantly than the micro-sized fillers. These improvements are of importance for the electrical insulation applications and shed light on the further advancement in dielectric materials. The dispersion of nanoparticles in the polymer matrix and the property of the interface between nanoparticles and a polymer are regarded as key factors affecting the electric insulating properties of nanocomposites [2]. The dielectric properties of heterogeneous polymer materials play an important role in device applications such as high performance capacitors, electrical cable insulation, electronic packing and components. From the fundamental point of view, the dielectric relaxation spec-

troscopy has been widely used to realize the microscopic dynamical relaxation process in complicated systems. The detailed investigation of the dielectric losses, as well as the electrode and interfacial polarization effect of polymers, is of great importance. Polymer blending is a useful technique for designing materials with a wide variety of properties. An important commercial advantage is that polymer blends offer a way to produce new materials by using the already existing polymers, which thus reduces development costs. Polyvinyl pyrrolidone (PVP) deserves a special attention among the conjugated polymers because of good environmental stability, easy processability, moderate electrical conductivity and the rich physics in charge transport mechanisms. A local modification of the chemical structure induces drastic changes in electronic properties. The composite materials consisting of a conducting medium in the insulating polymer matrix provide satisfactory mechanical, as well as electrical, properties [3]. PVP is an amorphous polymer and possesses high  $T_g$  values up to 170 °C because of the presence of the rigid pyrrolidone group. In solutions, it has excellent wetting properties and readily forms films. This makes it good as a coating or an additive to coatings. It is commonly used in medicine because of its extremely low cytotoxicity. Its other applications can be found in controlled drug-release technology and electrochemical devices (batteries, displays) [4]. The impressive widespread of the use of composite materials at present could be explained, among other arguments, by the possibility to predict composite's properties on the basis of the volumic content and the corresponding properties of the matrix and the reinforcement. In fact, the user can get a new material that is tailored by his demands. Measurements of the electrical properties of polymers are one of the most convenient and sensitive methods for studying the polymer structure. The presence of a filler affects both electrical and mechanical properties. In most of their industrial applications, elastomers are used as composite materials [5, 6]. In addition, they are used as conducting adhesives in electronics packaging flip-chips, cold solders, switching devices, static charge dissipating materials, and devices for surge protection [7, 8]. Polymeric composites have high strength and stiffness, low weight, and high corrosion resistance [9]. The studies of metal oxide nanoparticles-polymer nanocomposites are generating the increasing inter-

est due to their potential applications in household electronics, recording heads, memory and microwave devices. The addition of inorganic nanoparticles to polymers allows a modification of the polymer physical properties, as well as the implementation of new features in the polymer matrix. Nanocomposites on the base of semiconductor nanoparticles and a polymer matrix are promising materials for applications in optoelectronics, for the creation of luminescent materials, sensor electronics, *etc.* [10]. Critical infrastructures, including highways, buildings, bridges, aircraft, ships, and pipelines, form the lifeline of economic and industrial hubs and are sometimes subjected to severe loading conditions due to extreme events such as earthquakes, hurricanes, and other natural disasters during their lifetime. To prevent catastrophic failures and subsequent loss of life, it is essential to continuously monitor the state of the structure and to identify any initiation of damages in real time by using the structural health monitoring (SHM) techniques, in particular, strain sensing. SHM provides an autonomous way of tracking changes in the system in real time using a combination of instrumentation systems and analytical methods. Instrumentation systems consist primarily of transducers to measure physical quantities such as strain, displacement, and acceleration, which can give insight into the behavior of structures. Among the quantities of interest for SHM, strain is a local direct measure of the state of the structure and is, thus, widely used as a reliable indicator of a damage induced in the structure. Hence, strain sensors are used extensively in SHM applications. Strain gauges or transducers can be broadly classified into optical sensors, resistance-based sensors, and piezoelectric sensors. Among them, resistance-based sensors form the major portion of commercially available foil strain-gauge sensors. Piezoelectric materials have the ability to convert mechanical energy into electrical energy and have long been used for strain sensing. Among other types of sensors, piezoelectric sensors have the lowest power requirements, and the charge output from piezoelectric sensors lies within the range of measurement capabilities of commercially available analog/digital sensors [11].

## 2. Materials and Methods

Piezoelectric nanocomposites films were prepared with different concentrations of carboxymethyl cel-

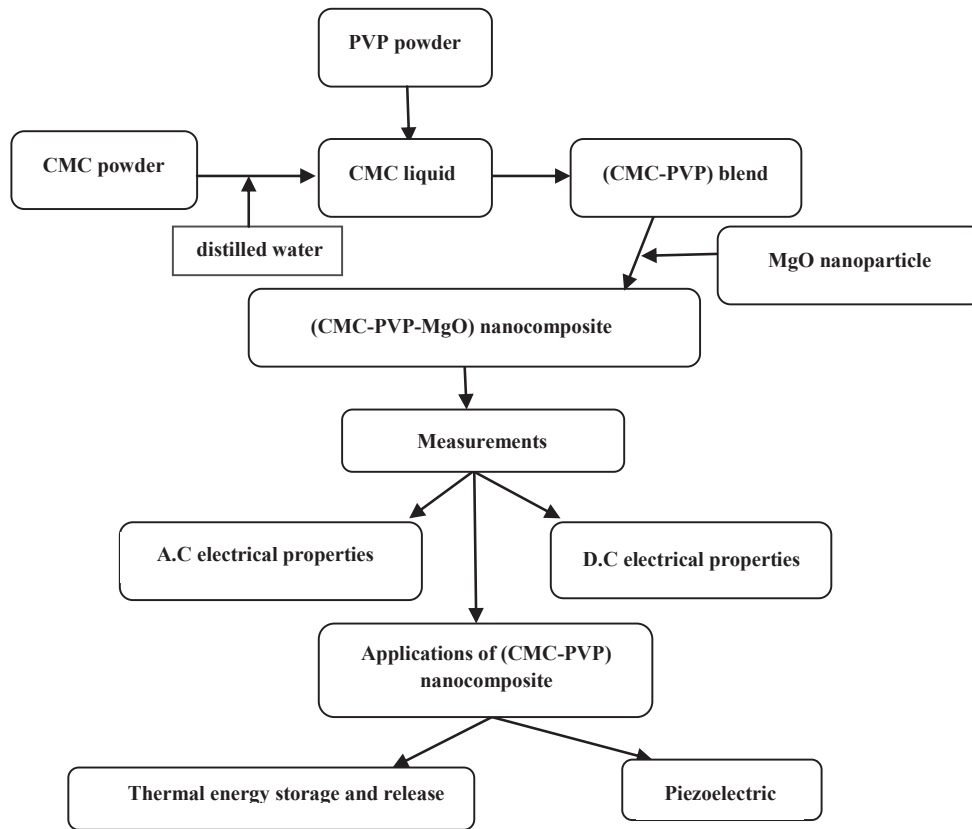


Fig. 1. Diagram of the experimental work

lulose, polyvinyl pyrrolidone, and magnesium oxide nanoparticles. The piezonanocomposite was synthesized with different concentrations of carboxymethyl cellulose (78 wt.%), polyvinyl pyrrolidone (22 wt.%), and MgO nanoparticles were added to the blend in different concentrations (0, 2, 4, and 6 wt.%), by using the casting method. The dielectric properties of the (carboxymethyl cellulose, polyvinyl pyrrolidone-magnesium oxide nanoparticles) nanocomposite were examined in the frequency range (100–5×10<sup>6</sup>) Hz by using an LCR meter (HIOKI 3532-50 LCR HI TESTER). The piezoelectric properties of the nanocomposite were investigated by measuring the electrical resistance between two electrodes on the top and bottom of the nanocomposite films in the pressure range (80–200) bar. The thermal energy storage and release of the nanocomposite include analyzing the melting and solidification characteristics during the heating and cooling processes. Water and nanofluids were used as the heat-transfer nanofluid,

whose temperature can be varied from 14 °C to 100 °C with a stirrer and measuring the temperature of nanofluids during the heating and cooling processes by a digital device. Figure 1 shows the experimental work diagram. The DC electrical conductivity ( $\sigma_V$ ) of the nanocomposite can be determined for a sample with the length ( $L$ ), a constant area ( $A$ ), and electrical resistance ( $R$ ) by the relation [12]

$$\sigma_V = \frac{l}{RA}. \quad (1)$$

The dielectric constant of the nanocomposite is given by the relation [13]

$$\varepsilon' = \frac{C_p}{C_0}, \quad (2)$$

where  $C_p$  is the parallel capacitance, and  $C_0$  is the vacuum capacitor, which is given by [13]

$$C_0 = \varepsilon_0 A/t, \quad (3)$$

where  $\epsilon_0$  is the vacuum permittivity,  $A$  is the area of a capacitance plate, and  $t$  is the distance between two plates.

The dielectric loss ( $\epsilon''$ ) is given by relation [14]

$$\epsilon'' = \epsilon' D, \tag{4}$$

where  $D$ : is dispersion factor.

The AC electrical conductivity is given by the relation [14]

$$\sigma_{A.C} = W \epsilon'' \epsilon_0. \tag{5}$$

### 3. Results and Discussion

Figure 2 shows the variation of the dielectric constant of the (CMC–PVP–MgO) nanocomposite in the frequency range (100–5 × 10<sup>6</sup>) Hz at room temperature. It is observed that the dielectric constant decreases, as the frequency increases, i.e., the dielectric constant has higher values in the low-frequency range, then it decreases, as the frequency increases. This situation has been attributed to the fact that there are all types of polarizations; electronic, ionic, dipolar, and space charge polarization (Maxwell–Wagner polarization) in the low-frequency range. The situation in the high-frequency range due to the fact that the electric dipoles cannot follow up the frequency of the applied electric field is quite different [15]. The variation of dielectric losses of the (CMC–PVP–MgO) nanocomposite with the frequency at different concentrations of MgO nanoparticles is shown in Fig. 3. It is clear from this figure that the dielectric losses decrease, as the frequency increases, which can be attributed to the fact that, at low frequencies, the value of dielectric losses is due to the migration of ions in the material. At moderate frequencies, the dielectric loss is due to the contribution of ion jumps, conduction losses under the migration of ions, and ion polarization loss. At high frequencies, ion vibrations may be the only source of the dielectric loss. So, the dielectric loss has the minimum value. The large value of dielectric losses in the low-frequency range is also due to the motion of free charge carriers within the material. As a result, the power-law dispersion in dielectric losses is observed, and it does not reveal any peak in the measured frequency range [16].

Figure 4 shows the variation of the AC electrical conductivity of the (CMC–PVP–MgO) nanocomposite in the frequency range (100–5 × 10<sup>6</sup>) Hz at room

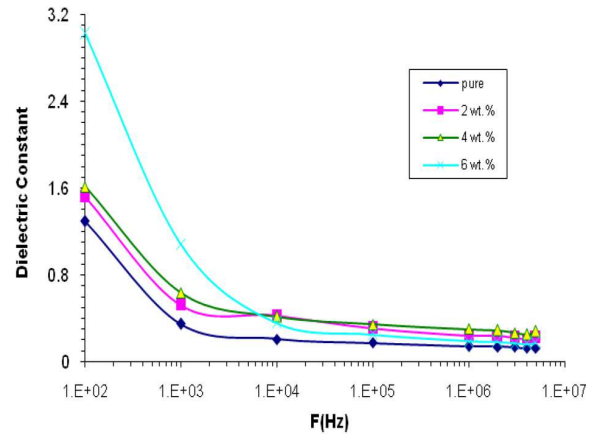


Fig. 2. Variation of the dielectric constant of the (CMC–PVP–MgO) nanocomposite with the frequency

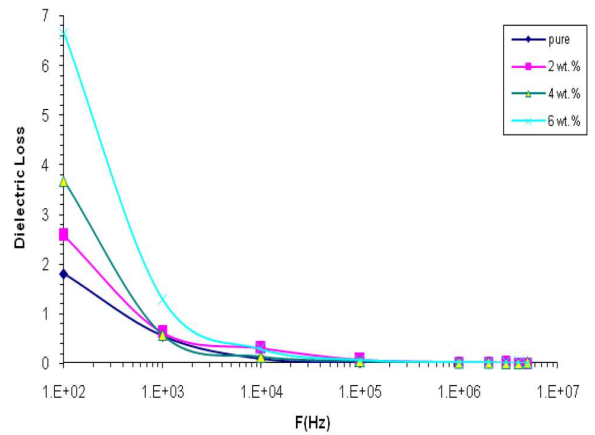


Fig. 3. Variation of dielectric losses of the (CMC–PVP–MgO) nanocomposite with the frequency

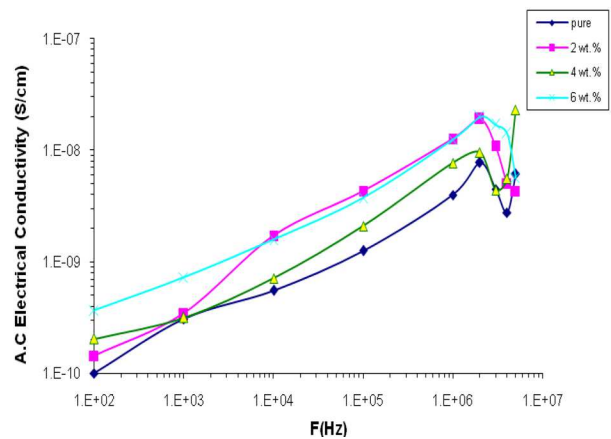


Fig. 4. Variation of the AC electrical conductivity of the (CMC–PVP–MgO) nanocomposite with the frequency

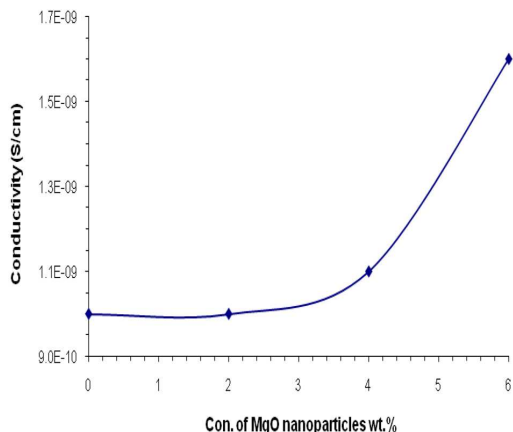


Fig. 5. Variation of the DC electrical conductivity of the (CMC-PVP) blend with the concentration of MgO nanoparticles

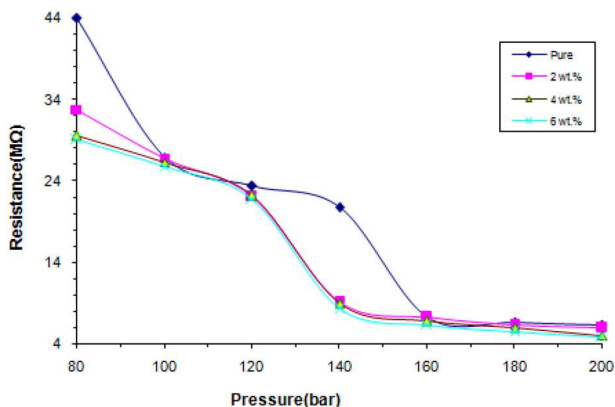


Fig. 6. Effect of the pressure on electrical resistance of the (CMC-PVP-MgO) nanocomposite for different concentrations of MgO nanoparticles

temperature. As the frequency decreases, the more and more charge is accumulated at the electrode and electrode interface, which leads to a decrease in the number of mobile ions and, eventually, to a drop in the conductivity at low frequencies. In the high-frequency region, the conductivity increases with the frequency due to the mobility of charge carriers and the hopping of ions from the infinite cluster. As a result, the ion exchange process occurs effectively in the high-frequency region [16].

As shown in Figs. 2–4, the dielectric constant, dielectric losses, and AC electrical conductivity of the (CMC-PVP) blend increase with the concentration of MgO nanoparticles. This result can be attributed to an increase in the conductivity as a result of the increase in the charge carrier density in the polymer

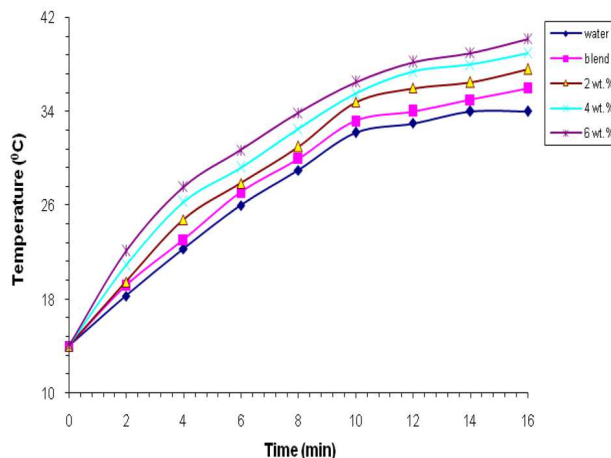


Fig. 7. Melting curves of the (CMC-PVP-MgO) nanocomposite

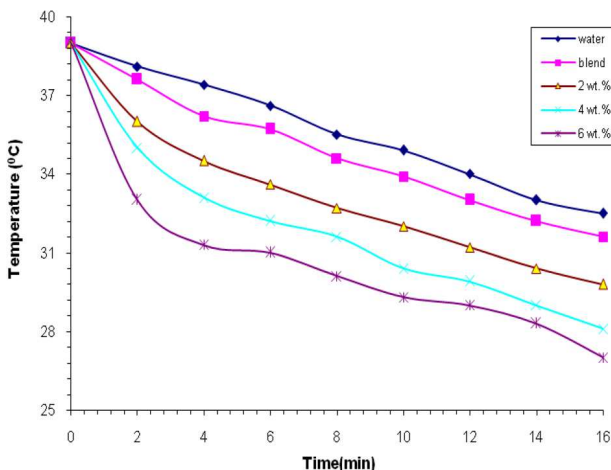


Fig. 8. Solidification curves of the (CMC-PVP-MgO) nanocomposite

matrix and the space charge polarization contribution [17]. Figure 5 shows the dependence of the DC electrical conductivity of the (CMC-PVP) blend on the concentration of MgO nanoparticles. As is seen, the DC electrical conductivity of the (CMC-PVP) blend increases with an increase in the concentration of MgO nanoparticles, which is attributed to an increase in the number of free charge carriers [18].

Figure 6 shows the effect of a pressure on the electrical resistance of the (CMC-PVP-MgO) nanocomposite for different concentrations of MgO nanoparticles. We see that the electrical resistance decreases with an increase in the pressure. In this case, the

nanocomposite is deformed, its surfaces are rubbed against each other, which causes them to deflect and generates a potential difference (or piezoelectric potential). The ion displacement due to this strain creates a difference of potential along the film. The potential difference that drives the current from one electrode to another one is in the nanocomposite film [11].

The thermal energy storage and release were investigated during the melting and solidification processes, as shown in Figs. 7 and 8. From the figures, the melting and solidification times decrease with an increase of the concentration of MgO nanoparticles. We see that there is an apparent heat transfer enhancement effect by introducing MgO nanoparticles into the (CMC–PVP) blend, because MgO nanoparticles improve the thermal storage/release performance of the (CMC–PVP) blend. Based on the aforementioned results, (CMC–PVP–MgO) can be considered as a potential building thermal energy storage material to keep comfort indoor environment and save energy [19].

1. The dielectric constant, dielectric losses, and AC electrical conductivity of the (CMC–PVP–MgO) nanocomposite are increased with the concentration of MgO nanoparticles. The dielectric constant and dielectric losses of the (CMC–PVP–MgO) nanocomposite decrease, as the frequency increases. The AC electrical conductivity increases with the frequency.

2. The DC electrical conductivity of the (CMC–PVP–MgO) nanocomposite increases with the concentration of MgO nanoparticles.

3. The (CMC–PVP–MgO) nanocomposite has higher sensitivity to a pressure, low weight, flexibility, low cost, etc.

4. The melting and solidification times for the thermal energy storage and release applications decrease with an increase of the concentration of MgO nanoparticles.

1. R.P. Chahal, S. Mahendia, A.K. Tomar, S. Kumar. Optical and structural properties of gamma irradiated PVA/Ag nanocomposite films. *Appl. Sci. Lett.* **2**, No. 2, 55 (2016).
2. S. Ju, M. Chen, H. Zhang, Z. Zhang, Dielectric properties of nanosilica/low-density polyethylene composites: The surface chemistry of nanoparticles and deep traps induced by nanoparticles. *J. Express Polymer Lett.* **8**, No. 9, 682 (2014).
3. Ch.V. Subba Reddy, Xia Han, Quan-Yao Zhu, Li-Qiang Mai, Wen Chen. Dielectric spectroscopy studies on (PVP + PVA) polyblend film. *Microelect. Engin.* **83**, 281 (2006).
4. A.M. Abdelghany, E.M. Abdelrazek, D. Rashad. Impact of in situ preparation of CdS filled PVP nano-composite. *J. Spectrochim. Acta Part A: Molec. Biomolec. Spectrosc.* **130**, 302 (2014).
5. B.H. Rabea, A. Hashim. Dielectric properties of (PS–BaSO<sub>4</sub> · 5H<sub>2</sub>O) composites. *Eur. J. Social Sci.* **32**, No. 3, 316 (2012).
6. A.J. Kadham Algidsawi, H.J. Kadham Algidsawi, A. Hashim, G.A.A.W Ali. The dielectric properties of (PVC–Zn) composites. *Australian J. Basic Appl. Sci.* **5**, No. 11, 1463 (2011).
7. B. Hussien, A. Hashim, A. Jewad. Electrical properties of polyvinylchloride – Zinc composite. *Eur. J. Social Sci.* **32**, No. 3, 225 (2012).
8. Z. Al-Ramadhan, A. Hashim, A.J. Kadham Algidsawi. The D.C electrical properties of (PVC–Al<sub>2</sub>O<sub>3</sub>) composites. *AIP Conf. Proceed.* **1400**, No. 1, 180 (2011).
9. A. Hashim, A.J. Kadham Algidsawi, H. Abduljalil, S. Hadi. Mechanical properties of (PVA–CoNO<sub>3</sub>, BaSO<sub>4</sub> · 5H<sub>2</sub>O) composites. *Eur. J. Scient. Research* **65**, No. 2, 163 (2011).
10. I.R. Agoool, K.J. Kadhim, A. Hashim. Preparation of (polyvinyl alcohol–polyethylene glycol–polyvinyl pyrrolidone–titanium oxide nanoparticles) nanocomposites: Electrical properties for energy storage and release. *Inter. J. Plastics Technol.* **20**, No. 1, 121 (2016).
11. H. Gullapalli, V.S.M. Vemuru, A. Kumar, A. Botello-Mendez, R. Vajtai, M. Terrones, S. Nagarajaiah, P.M. Ajayan. Flexible piezoelectric ZnO–paper nanocomposite strain sensor. *Small* **6**, No. 15, 1641 (2010).
12. H. Abduljalil, A. Hashim, A. Jewad. The effect of addition of titanium dioxide on electrical properties of polymethyl methacrylate. *Eur. J. Sci. Research* **63**, No. 2, 231 (2011).
13. B. Hussien, A.J. Kadham Algidsawi, A. Hashim. The A.C electrical properties of (PVC–Sn) composites. *Australian J. Basic Appl. Sci.* **5**, No. 7, 933 (2011).
14. R. Divya, M. Meena, C.K. Mahadevan, C.M. Padma. Investigation on CuO dispersed PVA polymer films. *J. Engineer. Research Applic.* **4**, Iss. 5, 1 (2014).
15. A.F. Mansour, S.F. Mansour, M.A. Abdo. Enhancement of structural and electrical properties of ZnO/ PVA nanocomposites. *IOSR J. Appl. Phys.* **7**, Iss. 2, 97 (2015).
16. P. Vasudevan, S. Thomas, K. Arunkumar, S. Karthika, N. Unnikrishnan, Synthesis and dielectric studies of poly (vinyl pyrrolidone)/titanium dioxide nanocomposites. *J. Mater. Sci. Engineer.* **73**, 1 (2015).
17. M.A. Habbab, A. Hashim, A.-R.K. AbidAli. The dielectric properties for (PMMA–LiF) composites. *Eur. J. Sci. Research* **61**, No. 3, 367 (2011).
18. C. Srikanth, C. Sridhar, B.M. Nagabhushana, R.D. Mathad. Characterization and DC conductivity of novel CuO doped polyvinyl alcohol (PVA) nano-composite films. *J. Engineer. Research Applic.* **4**, Iss. 10, 38 (2014).

19. J. Huang, S. Lu, X. Kong, S. Liu, Y. Li. Form-stable phase change materials based on eutectic mixture of tetradecanol and fatty acids for building energy storage: Preparation and performance analysis. *J. Mater.* **6**, 4758 (2013).

Received 23.06.17

A. Хашим, А. Хаді

СИНТЕЗ І ВЛАСТИВОСТІ НОВИХ  
НАНОКОМПОЗИТІВ ДЛЯ АКУМУЛЮВАННЯ  
ЕНЕРГІЇ: БІОДЕСТРУКТИВНІ  
МАТЕРІАЛИ–НАНОЧАСТИНКИ  
ОКИСУ МАГНІЮ

Р е з ю м е

Сенсори на основі п'єзоелектричних полімерних нанокон-  
полімерів мають високу чутливість, малу вагу, гнучкість, не-  
дорогі і т.п. Ми досліджували новий п'єзоелектричний сен-

сор з наноконполімером, що складається з карбоксиметил цел-  
люлози, полівініл піролідона і окису магнію. Його діеле-  
ктричні властивості і провідність виміряні за кімнатною  
температурою. Діелектричні властивості вивчені в діапа-  
зоні частот 100 Гц–5 МГц. Провідність по постійному стру-  
му, діелектрична константа і діелектричні втрати ростуть  
з концентрацією наночастинок окису магнію. Діелектри-  
чна константа і діелектричні втрати зменшуються з ро-  
стом частоти. Провідність по змінному струмі зростає з  
концентрацією наночастинок окису магнію і частотою. Для  
п'єзоелектричних застосувань наноконполімер вивчений в ін-  
тервалі тисків 80–200 бар. Експеримент показує, що опір  
зменшується зі збільшенням стискаючого тиску, що свід-  
чить про високу чутливість наноконполімера до тиску. Про-  
ведено випробування наноконполімера на накопичення і ви-  
вільнення енергії. Показано, що часи плавлення і затвер-  
діння наноконполімера зменшуються з ростом концентрації  
наночастинок окису магнію.