Synthesis, characterization and USW sensor of PEO/PMMA/PVP doped with zirconium dioxide nanoparticles

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Abstract
The piezoelectric phenomena uses in various helpful applications, such as printing of piezoelectric inkjet, the detection of sound and the production of high voltage electricity in different electronic devices. In present research, polyethylene oxide (PEO), poly(methyl methacrylate) (PMMA) and poly(N-vinyl pyrrolidone) (PVP) were separately dissolved in deionized water. These polymers were mixed with ratio of 0.6:0.2:0.2 wt%, respectively before loaded with 0.0, 0.02, 0.04 and 0.06 wt% of zirconium dioxide nanoparticles (ZrO$_2$NPs) via casting method to prepare nanocomposite (NCs) films. The optical microscope (OM) showed good diffused of the NPs into matrix with homogenous distribution. The functional groups of k1 specimen were diagnosed via Fourier transformation infrared (FTIR). The ultrasonic wave (USW) properties were studied for k1 specimen with various frequencies (25, 30, 35, 40 and 45) kHz. The USW coefficients were clearly affected by the frequency varied. The USW coefficients decreased with increasing the frequency except the compressibility. The dielectric constant of the k1 sample was notable improved up to 85% with increasing of applied load. The k1 specimen was succeeded to be used as USW sensor. New NCs film presented as promising material for wide electrical and mechanical applications.

Keywords ZrO$_2$ · PVP · USW sensor · Optical microscopy · Piezoelectric effect

1 Introduction

The piezoelectric effect or USW sensor, known as the direct piezoelectric effect, is an electricity generating phenomena which occurs when a material exposed to external pressure, mechanical stress or applied force. polyethylene oxide (PEO), which is synthesized from polyether polymer (PE) [1], has many important applications in treatment of water, pipes industries, physical, medical and engineering purposes [2]. PMMA is, on the other hand, a tough and lightweight polymer with a density between 1.17 and 1.20 g/cm$^3$ [3]. PMMA has a promising impact strength, comparing with polystyrene and glass [3]. The white colored PVP is considered as stable materials in different temperature range applications, hygroscopic, completely soluble in water and capable of incorporation with various materials [4]. ZrO$_2$NPs, in another point of view, have a quite interesting physical and chemical properties such as heat and chemical resistance, hardness and strength. Furthermore, it is mostly used in catalysts industrializations, piezoelectricity, gamma shielding and solid fuel batteries [5]. the optical, mechanical, morphological and structural properties of NCs films usually affected by the smallest ZrO$_2$NPs diameter [6–8]. The major aim of present work is study the influence of loadings ZrO$_2$NPs on morphological, USW properties and pressure sensitivity of PEO/PMMA/PVP polymer blend.

2 Material and characterizations

2.1 Materials

PEO (Mw=6 kDa and assay purity=99.8%) was supplied from Reagent World, PMMA (Mw=5 kDa and assay purity=99%) was purchased from DIDACTIC, PVP (Mw=40 kDa and assay purity=99.9%) was purchased from Central Drug House, and ZrO$_2$NPs was purchased from (US Research Nanomaterials, Inc.) with average grain size of (40 nm) and assay purity of (99.9%).
2.2 Synthesis of NCs

The PEO, PMMA and PVP polymer powders were separately dissolved in 50 mL deionized water (DI) and stirred at 60°C via magnetic stirrer. The process continued for 1 h before getting on homogeneous mixture. In the doping process, four different ZrO$_2$NPs ratios were separately added to the polymer blend. The process then continued for another 3 h. The composite mixtures were then casted in 5 cm Petri dish. Thereafter, samples have been left to dry for 7 days. The specimens thickness were in the range between 80 and 95 μm. The method of preparation was listed in Table 1.

2.3 characterizations

The morphological properties were investigated using Nikon, Olympus 73,346 camera. Vertex 701, Bruker spectrometer has been utilized to study the chemical functional groups of k1 specimen. The density was measured using Matsu Maku GP/120S. The viscosity was measured using Brookfield viscometer. The USW properties were measured by using SV-DH-7 A/SVX-7 ultra sound instrument.

3 The experimental study

3.1 The OM and FTIR images:

Figure 1 represents the OM photomicrographs of k0, k1, k2 and k3 samples. The magnification power was (100X). Figure (1-A) shows the PEO/PMMA/PVP blend has acceptable and homogenous dissolving. The (B, C, and D) parts in the same Figure show the diffusion process of ZrO$_2$NPs in the blend. The some weak agglomerations of ZrO$_2$NPs were clearly appeared in (C and D) parts. The explanation of that related to the interaction that happens among ZrO$_2$NPs because these NPs occupies a high surface area in small volume [6]. OM is generally used to study the compatibility or surface morphological properties among various constituents of the polymer electrolytes. The micrograph indicates with the loaded of ZrO$_2$NPs, the surface clearly shows a uniformly distributed area. The micro/macro structural indications were good agreement with previous results that have referred an improvement in the amorphous phase after loading [6]. Furthermore, the OM images refer to good diffusion of NPs, homogeneity and surface roughness of raw material/ZrO$_2$NPs composites.

Figure 2. represents the FTIR spectrum of k1 specimen in the wave number range between 500 and 4500 cm$^{-1}$. From the figure, it can obviously be seen that, the chemical functional groups that respectively appeared in the computed optical range. These functional groups were alcohol/phenol (OH) stretching which appeared at 3284.56 cm$^{-1}$, and (C=C) stretching at 1662.29 cm$^{-1}$. The bands at 1437.15 cm$^{-1}$, 1289.84 cm$^{-1}$, and 1099.92 cm$^{-1}$ are corresponded to the symmetric bending of CH$_2$, the CH wagging, and (C-O) stretching of primery alcohol respectively [6, 7]. The (OH) wagging which appeared at 540 cm$^{-1}$ is accountable to the existence of ZrO$_2$NPs. There is many physical interactions happened between the polymer blend

| specimen ID | Ratio of weight percentages % | Mixing Time h |
|-------------|-------------------------------|---------------|
| PEO | PMMA | PVP | NPs |
| k0 | 0.600 | 0.200 | 0.200 | 0.00 | 1 |
| k1 | 0.588 | 0.196 | 0.196 | 0.02 | 3 |
| k2 | 0.576 | 0.192 | 0.192 | 0.04 | 3 |
| k3 | 0.564 | 0.188 | 0.188 | 0.06 | 3 |

Fig. 1 The OM images (100X) of (A) k0, (B) k1, (C) k2 and (D) k3 specimens

Fig. 2 The FTIR spectrum of k1 specimen
This behavior returns to the structural relaxation that happened between the PEO/PMMA/PVP polymer blend and ZrO$_2$NPs contents in various frequency values. A collide at rest has internal characteristics similar to solid. When the USW propagate, different periodic molecules flow among lattice spaces and causes a compressing. In the final the molecules return to the original position. The USW velocity has been directly proportional with the amount of ZrO$_2$NPs, but inversely proportional with frequency. This is because the USW causes various physical interaction between PEO/PMMA/PVP polymer blend and ZrO$_2$NPs molecules, lead to increase the velocity. The increasing of frequency led to decrease the USW velocities [12]. Figure 5. shows that, the relationship between the relaxation time and amplitude and frequency. The relaxation amplitude ($D$) was theoretically calculated by [13]:

$$D = \frac{\alpha}{f^2}$$

The values of relaxation time and amplitude decreased with the increasing of frequency and ZrO$_2$NPs contents. The increasing of these coefficients with ZrO$_2$NPs led to higher fraction between the composition layers that examined by moment of inertia [14].

The compressibility of PEO/PMMA/PVP doped with ZrO$_2$NPs were theoretically calculated by Laplacian equation [15], so the values raised with higher frequency:

$$\beta = \left(\rho v^2\right)^{-1}$$

The Young modulus (K) was calculated by [16]:

3.2 The USW measurements

The solution density of PEO/PMMA/PVP polymer blend against various ZrO$_2$NPs contents was measured at room temperature and shown in Fig. 3. Figure 3. represents the densities of all aqueous solutions increased with the increasing of the ZrO$_2$NPs contents, because the ZrO$_2$NPs formed across linked (networks) among the molecules of PEO/PMMA/PVP that occupies the spaces among molecules. Furthermore, the density of each materials increased with increasing of doping materials [9].

The USW properties were applied for testing in the region between the sender and receiver. The receiver converts USW pulses to the electrical pulses then received by oscilloscope. The apparent signal in first channel contains positive peak which represents the incident USW or initial amplitude ($A_0$) and the negative part in the second channel refers to receiver amplitude ($A$). The USW transmittance waves (T) have been computed by the following equation [10]:

$$T = \frac{A}{A_0}$$

Figure 4. represents the relationship between the USW velocity and the frequency. It's clear from the Figure that, the USW velocity of PEO/PMMA/PVP polymer blend decreased with the increasing of frequency. The USW velocity computed by the following equation [11]:

$$V = \frac{X}{t}$$

This behavior returns to the structural relaxation that happened between the PEO/PMMA/PVP polymer blend and ZrO$_2$NPs contents in various frequency values. A collide at rest has internal characteristics similar to solid. When the USW propagate, different periodic molecules flow among lattice spaces and causes a compressing. In the final the molecules return to the original position. The USW velocity has been directly proportional with the amount of ZrO$_2$NPs, but inversely proportional with frequency. This is because the USW causes various physical interaction between PEO/PMMA/PVP polymer blend and ZrO$_2$NPs molecules, lead to increase the velocity. The increasing of frequency led to decrease the USW velocities [12]. Figure 5. shows that, the relationship between the relaxation time and amplitude and frequency. The relaxation amplitude ($D$) was theoretically calculated by [13]:

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The compressibility of PEO/PMMA/PVP doped with ZrO$_2$NPs were theoretically calculated by Laplacian equation [15], so the values raised with higher frequency:
The density is very smaller than velocity. The USW absorption coefficient was calculated by the law of Lambert-Beer \[19\] :

\[
\frac{A}{A_0} = e^{-\alpha x}
\]  

Figure 7 represents the relationship between the dielectric constant and applied load for k1 specimen. From this Figure, the values of dielectric constant were increased with the increasing of applied load. The specimens are display a high polarizability and capability to orient the dipoles of molecular. The charges of space and polarization of orientation are responsible for the piezoelectric effects in this polymer composite film. The (PEO/PMMA/PVP)-ZrO\(_2\)NPs film has a high flexibility. Moreover, the increasing of the dielectric constant perhaps because the increasing of ZrO\(_2\)NPs contents \[24\]. This is due to of just each atom of oxygen has the same distance with the zirconia atoms. The variance in the atoms position due to mechanical stress leads to creation of an electric field and polarization respectively \[25, 26\]. The researchers have been studied various mechanical USW properties of materials in order to enhanced the ability to absorb USW \[27–33\].

4 Conclusions

Novel (PEO/PMMA/PVP)-ZrO\(_2\)NPs NCs films were successfully prepared via casting method. The OM images showed a fine diffusion of ZrO\(_2\)NPs in the mixtures. The FTIR peaks refers strong interfacial interactions between the raw material and ZrO\(_2\)NPs. The results revealed an enhancement of the physical properties by the increasing the ratio of ZrO\(_2\)NPs contents. The enhancing of density, viscosity, USW velocity and USW absorption coefficient of the polymer blend was associated with increasing of ZrO\(_2\)NPs. The addition of ZrO\(_2\)NPs controlled an increase the
Fig. 8 The dielectric constant vs. applied load for k1 specimen

compressibility of USW of polymer blend and thus became more tolerable to environmental conditions. Additionally, it was found that the best frequency value is 25 kHz), which showed the best mechanical results. The dielectric constant of the k1 specimen was 85% improved with increasing the applied load. An promising USW sensors can be made from (PEO/PMMA/PVP)-ZrO\textsubscript{2}NPs film.

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References

1. J.E. Mark (1999) Polymer Data Handbook. New York: Oxford university.2nd ed. ISBN: 9780195181012
2. Bailey and Koleske (1976) Poly(Ehtylene Oxide). Academic Press. ISBN:0120732505
3. A. Jenkins (2013) Polymer Science: A material Science Handbook. North Holland Publishing. Kindle ed. ASIN: B01DY7XF70
4. B. Kutscher (2020) Dermatologicals (D), 4. Antiseptics and Disinfectants (D08), Anti-Acne Preparations (D10), and Other Dermatological Preparations (D11). Ullmann’s Encyclopedia of Industrial Chemistry. 1–22
5. J. Fathima, A. Pugazhendhi, R. Venis (2017) Synthesis and characterization of ZrO2 nanoparticles- antimicrobial activity and their prospective role in dental care. Microb. Pathogenesis 110, 245–251.
6. A. Karar (2022) Structural, Morphological, and Gamma Ray Shielding (GRS) Characterization of HVCMC/PVP/PPEG Polymer Blend Encapsulated with Silicon Dioxide Nanoparticles. Silicon. 14, 6–10. https://doi.org/10.1007/s12633-022-01678-8
7. J. Jeevananandam, A. Barboum, Y. Chan, A. Duformsne, M. Dan- quah (2018) Review on nanoparticles and nanostructured mate- rials: history, sources, toxicity and regulations. Beilstein J. Nanotech 9, 1050–1074
8. I. Agool, K. Jawad, A. Hashim (2017) Fabrication of new nano- composites: (PMMA-PEG-PVP) blend-zirconium oxide nanoparticles for humidity sensors. IJPT J. 21, 397–403
9. S. Kulkarni, U. Khadke (2016) Effect of Solvents on the Ultra- sonic Velocity and Acoustic Parameters of Polyvinylidene Fluoride Solutions. Indian Journal of Materials Science. 2016: 1–6
10. B. Dipak (2000) Dictionary of pure and applied physics. Taylor& Francis. ISBN: 9780849328909
11. J. Karar Abdali, Abdulkareem, A. Majeed (2015) Enhancement of Some Mechanical Properties of Polyethylene Glycol by Adding Carboxymethyl Cellulose as a Blends and Applied in Wood Glue. World Sci. News J. 21, 12–23.
12. R. Li, A. Kolesnikov, M. Kiba (2017) Parameters of ultrasonic dispersion of polymer-composite solutions. Polym. Sci. Ser. D J. 10(2), 185–188
13. A. Upmanyu, D. Singh (2014) Ultrasonic Studies of Molecular Interactions in Polymer Solution of the Polyisobutylen (PIB) and Benzene. Acta Acustica unied with Acustica 100(3), 434–439
14. J. Ali, S. Ali, K. Abdali, R. Shirren, O. Abdulazeez (2017) Synthesis of hyperbranched polymers and study of its optical proper- ties. J. Eng. Appl. Sci. 12(6), 7800–7804
15. K. Hassina, P. Frederic, D. Jean, D. Hakim (2009) Measurements under High Pressure of Ultrasonic Wave Velocity in Glyc- erol. IEEE: International Ultrasonic Symposium Proceedings. 8: 1567–1570
16. D. Rao, A. Krishnaiah, P. Naidu. Excess thermodynamic prop- erties of liquid ethylenediamine + anorganic hydrocarbon. Acta Chim. Academiae Scientiarum Hung. 107(1), 49–55 (1981)
17. S. Ravichandran, K. Ramanathan, U/S Investigations of MnSO\textsubscript{4}, NiSO\textsubscript{4}, and CuSO\textsubscript{4} in PMMA Solution at 303 K. Rasayan J. 3(2), 375–384 (2010)
18. P. Nikam, M. Hasan, Ultrasonic velocity and apparent molar compressibility of trichloroacetic acid in aqueous ethanol. Asian J. Chem. 5(2), 319–321 (1993)
19. W. Zong, L. Dong (2011) Method of improved scattered size estimation without Attenuation known a priori. Bioinformatics and Biomedical Engineering (ICBBE), 4th International Conference, IEEE. 8(10), 1–4
20. Karar Abdali, Shireen R., Ali J (2019) Mechanical Ultrasonic Properties of (Polymethylene Oxide-TiO\textsubscript{2}) Polymer Composite Gel. J. Eng. Appl. Sci. 14(5), 6002–6005.
21. A. Karar (2017) Acoustical Properties of (Chitin/nano-TiO\textsubscript{2}) Bio- Composite Polymer Composite Gel. J. Univ. Babylon Pure Appl. Sci. 25(5), 1762–1766
22. Karar Abdali (2015) Enhancement of some physical properties of polyethylene glycol by adding some polymeric cellulose derivatives and its applications. Ph.D. thesis, College of Science, Baby- lon University, Iraq
23. A. Al-Khalaf, K. Abdali, A. Obaid, M. Zghair (2019) Preparation and structural properties of liquid crystalline materials and its transition metals complexes. Asian J. Chem. 31(2), 393–395

24. T. Kim (2015) Characterization and applications of piezoelectric Polymers. Electrical Engineering and Computer Sciences. University of California at Berkeley. M.Sc. thesis

25. M. Qayssar, H. Ahmed, A. Majeed (2019) Structural, A.C electrical and Optical properties of (Polyvinyl alcohol–Polyethylene Oxide–Aluminum Oxide) Nanocomposites for Piezoelectric Devices. Egypt. J. Chem. 62, 719–734

26. A. Hashim, A. Hadi (2018) Novel Pressure Sensors Made From Nanocomposites (Biodegradable Polymers–Metal Oxide Nanoparticles): Fabrication and Characterization. Ukrainian J. Phys. 63(8), 754

27. N. Bouhamed, S. Souissia, P. Marechalb, M. Amara, O. Lenoirb, R. Legerc, A. Bergeret (2020) Ultrasound evaluation of the mechanical properties as an investigation tool for the wood-polymer composites including olive wood flour. Mech. Mater. 148, 103445

28. J. Merotte, L. Duigou, A. Bourmaud, K. Behlouli, C. Baley (2016) Mechanical and acoustic behavior of porosity controlled randomly dispersed flax/PP, biocomposite Polymer. Test. 51, 174–180

29. M. Kariminejad, D. Tormey, S. Huq, J. Morrison, M. McAfee (2021) Ultrasound Sensors for Process Monitoring in Injection Moulding. Sensors. 21(15), 5193

30. A. Maiorano, G. Napolitano, D. Annunziata, E. Rocca (2021) Experimental measurements through ultrasounds for viscoelasticity analysis. IOP Conference Series: Materials Science and Engineering. 1048(1), 012005

31. A. Khan (2021) Effect of Ultrasonic Vibration on Structural and Physical Properties of Resin-Based Dental Composites. Polymers. 13(13), 2054

32. M. Abutalib, A. Rajeh (2021) Enhanced structural, electrical, mechanical properties and antibacterial activity of Cs/PEO doped mixed nanoparticles (Ag/TiO$_2$) for food packaging applications. Polym. Test. 93, 107013.

33. S. Abdullah, M. Abdul kadhim, E. Al-Bermany (2021) Graphene-Reinforced the Structure and Mechanical Properties of New PMMA-PVA Hybrid Nanocomposites. IOP Conf. Series: Materials Science and Engineering. 1094, 1–15

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