The Effect of Heat Treatment on Crystalline, Electrical and Optical Properties of ZnO/PVA Nanocomposites

Abrar Ismardi[1*], Muhammad Nasir[2], Nor Hakimin Abdullah[3], Wan Rizti Fadila[1], Erina Fitri Shentya[1], Santika Ratnaduhita[1], Diki Ribut Wahyudi[1]

[1]Department of Engineering Physics, Telkom University, Jl. Telekomunikasi No.1 Terusan Buah Batu, Bandung, 40257, Indonesia
[2]Loka Penelitian Teknologi Bersih LIPI, Jl. Cisitu Lama, Dago, Kecamatan Coblong, 40135, Bandung, Indonesia
[3]Faculty of Bioengineering and Technology, Universiti Malaysia Kelantan Jeli Campus, Locked Bag No. 100, 17600, Jeli, Kelantan, Malaysia

*E-mail: abrarselah@telkomuniversity.ac.id

Abstract- ZnO/PVA nanocomposites have been successfully synthesized using the spin coating method by using synthesized ZnO, ZnO nanoparticles as filler, and PVA as a matrix. The synthesized films were treated at temperatures of 70, 90, and 120 °C. Some characterizations, such as I-V, UV-Vis, XRD, and SEM, have been carried out to study the electrical, crystalline, and optical properties of ZnO/PVA nanocomposites. The characterization of electrical properties using I-V measurements showed that $ZnO_{synthesized}$/PVA had a high current value of 1.55 nA, while ZnO_{nano}/PVA had a smaller current value of 1.49 nA when treated at 120 °C. In addition, the higher the treatment temperature, the greater the resistance of $ZnO_{synthesized}$/PVA and ZnO_{nano}/PVA. UV-Vis characterization showed that ZnO_{nano}/PVA experienced a red shift when the temperature increased, while $ZnO_{synthesized}$/PVA and ZnO_{nano}/PVA when treated at 120 °C experienced a blue shift. XRD characterization of ZnO_{nano}/PVA showed that the higher the given temperature, the lower the crystallinity, from 45.77 to 34.81%. SEM characterization showed that ZnO_{nano}/PVA at room temperature agglomerated and formed larger particles.

Keywords: Absorbance, Heat Treatment, Thin Film, Wavelength, ZnO/PVA Nanocomposite

1. INTRODUCTION

Nanocomposites are inorganic (polymer) or organic composites that are nanometer in size and act as fillers and matrices [1, 2, 3]. The development of nanocomposites is currently widely found in biomedicine, sensors, and computing. Because they have a small size and the nanocomposites have different properties to adjust the material [4].

The polymer used in this study was polyvinyl alcohol (PVA). PVA is a polymer made of polyvinyl esters or polyvinyl ethers by going through a transesterification reaction using methyl or ethyl alcohol, such as polyvinyl acetate. It is known that polyvinyl acetate is crystalline and has a relatively small and adjacent hydroxyl group size, so this polyvinyl alcohol is easily soluble in water [5]. In addition, PVA also has the ability to form films with high optical qualities, judging by their luminescent properties, which can be used for nonlinear optical devices and optical sensors. In this study, the filler used was zinc oxide (ZnO). ZnO is currently emerging as a promising material for semiconductor, piezoelectric and optoelectronic devices, due to its optical and electrical properties. In addition, ZnO has a wide band gap (3.3 eV) and a large excitation binding energy (60 meV) [6]. The combination of ZnO and PVA nanoparticles results in better electrical, mechanical, and optical properties [7, 8].

Research on ZnO/PVA nanocomposites has been widely carried out for the application of optical sensors. One of them is a study conducted by Kandulna where ZnO/PVA nanocomposites with various concentrations are used as electron transfers in OLED [9]. In the study, ZnO/PVA nanocomposites were fabricated into new hybrid materials with low band gaps, high dielectric permittivity, high voltage breakdown, and energy storage density for applications in OLEDs and capacitors as electrical energy storage devices. It is known that concentration can affect the physical properties of ZnO/PVA nanocomposites. However, only a few of the studies reported on the thermal treatment of the ZnO/PVA nanocomposite. The thermal effect of synthesized ZnO/PVA can alter the properties of the nanocomposite. It is necessary to study the thermal treatment of ZnO/PVA nanocomposites to degrade thermo-mechanical and thermo-oxidative materials and increase the solubility of PVA during and after the ZnO/PVA nanocomposite synthesis process [10, 11]. This mechanism can control the size of ZnO and PVA nanocomposite particles [12]. The change in the properties of the nanocomposite after the thermal treatment can also change its optical properties. It is indicated that this has the potential to be applied as the optical sensor in flexible devices.

2. EXPERIMENTAL METHOD

This research was conducted to determine the effect of heat treatment on the crystalline, electrical, and optical properties of ZnO/PVA nanocomposites. The research begins with the preparation of tools, substrates, and solutions. The process is continued by using two types of ZnO: synthesized ZnO, which is ZnO synthesized using simple chemical methods, and ZnO nanoparticles (Sigma Aldrich) that have been purchased in the market. The two types of ZnO were used to make ZnO/PVA nanocomposites using the in situ method. Then, the nanocomposite is given a temperature treatment after going through the synthesis process, and the solution has been printed on the glass substrate. After being given temperature treatment, the thin films were characterized by their physical properties (crystal, morphological, electrical, and optical properties).

In the synthesis of ZnO, a simple chemical method was used. 0.1 M zinc acetate is stirred into 100 ml of methanol at room temperature with a magnetic stirrer until it dissolves, then 0.2 mM NaOH is added with a pipette. The stirring process was carried out for 2 hours, then filtered using filter paper. Then it is dried in an oven at 50 °C for 5–6 hours [13].

The in-situ method was used to synthesize the ZnO/PVA nanocomposite. 0.1g of synthesized ZnO and 0.1 ZnO nanoparticles were dissolved in 10 ml of distilled water each, then sonicated for 30 minutes. After that, mix the ZnO solution with 10% w/v PVA nanocomposite and stir using a magnetic stirrer for 2 hours at room temperature or 80°C. Then, the ZnO/PVA solution was sonicated for 30 minutes. After sonication, the solution is deposited onto a glass substrate and leveled. In forming a thin film from a room-temperature ZnO/PVA solution, drying is carried out at room temperature in a closed room for 24–48 hours. As for the ZnO/PVA solution at certain temperatures (70°C, 90°C, and 120°C), drying is carried out with a hot plate stirrer for 10 minutes at 80°C. Giving heat treatment at this temperature is carried out based on the PVA thermal degradation area at 70°C–120°C, where evaporation of O bonds occurs [14].

After the ZnO/PVA nanocomposite synthesis process, the thin films were then characterized by their properties. It is characterized by its crystal structure, electrical properties, morphology, and optical properties. The crystal structure of ZnO/PVA was then characterized by XRD analysis, in which the pattern was taken using an X-ray diffractometer (Cu K = 0.154 nm) [7, 9]. The electrical properties of the ZnO/PVA nanocomposite were then characterized by measuring the current-voltage (I-V) characteristics using a Keithley 2400 [15]. Morphological analysis of ZnO/PVA nanocomposite thin films was used by SEM to study the morphology of the samples and the particle size distribution using a particle size analyzer [7]. The optical properties of the ZnO/PVA nanocomposite were then studied by using UV-Vis analysis with a wavelength range of 200–800 nm [9].

3. RESULT AND ANALYSIS

In this result, we will have studied the samples that are categorized into two types: the first is the samples using the ZnO synthesis ($ZnO_{synthesis}$) and the ZnO nanoparticles from Sigma Aldrich (ZnO_{nano}). The electrical properties of ZnO/PVA nanocomposite thin films used in ZnO_{nano}/PVA and $ZnO_{synthesis}$/PVA samples are shown in Figure. 1 below. The I-V curve can be divided into two

regions, namely the ohmic(high resistance) and non-ohmic (low resistance) regions. The particle size of the synthesized ZnO/PVA nanocomposite is related to the electrical properties; the smaller the particle size resulting from the higher temperature treatment given during the annealing process, the more effectively it improves the electrical properties [16].

Synthesis of ZnO/PVA samples (A4, A5, A6) and ZnO_{nano}/PVA samples (B4, B5, B6) show an ohmic curve where each sample has a lower current (nA) and the current increases linearly with the increase in the applied voltage. This is indicated to be caused by the electron mobility, which is based on the electron-hole recombination process (increasing hole charge carriers) in the presence of ZnO in the PVA matrix. This conduction mechanism of polymer nanocomposites is slightly different from the intrinsic semiconductor's phenomenon [9]. The thin films $ZnO_{synthesis}$/PVA and ZnO_{nano}/PVA had the highest currents of 1.55 nA at a voltage of 5.01 V, which obtained a resistance of 3.23 G, and 1.49 nA at a voltage of 5.03 V, which obtained a resistance of 3.37 G, respectively. This result is clearly depicted in the thin film that was treated at 120^0 C, as shown in Figure 1. From these results, the particle size of the nanocomposite made using the as-synthesized ZnO is larger than the ZnO nanoparticles. For analysis of induced electrical properties, temperature treatment on $ZnO_{synthesis}$ and PVA samples decreased resistance when given a temperature of 900 °C (A5), whereas in the ZnO_{nano} and PVA sample it increased. The higher the temperature given, the higher the resistance.

The growth process and post-deposition treatment have strong effects on the structure and properties of ZnO/PVA nanocomposite, which can also significantly affect their electrical and piezoelectric properties [19]. In figure 1, the I-V result does not start at V = 0, as predicted by the piezoelectric properties resulting for the research. Beside that, it is also due to the possibility of thermal agitation caused by the internal nature of ZnO, which is a piezoelectric material that occurs at room temperature.
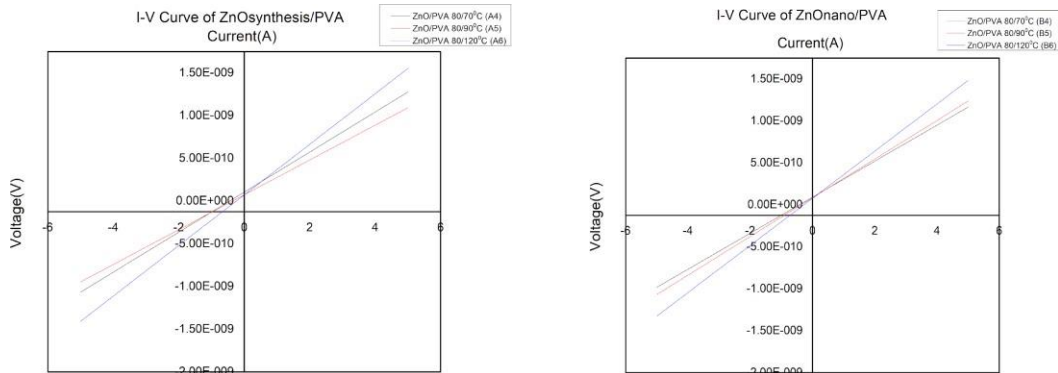
Figure 1. (a) $ZnO_{synthesis}$/PVA ohmic curves; (b) ZnO_{nano}/PVA I-V ohmic curves

The optical properties of ZnO/PVA nanocomposite thin films using samples of ZnO_{nano}/PVA 70°C (B4), 90°C (B5), 120°C (B6) and $ZnO_{synthesis}$/PVA 120°C (A6) are shown in Figure 2 below.
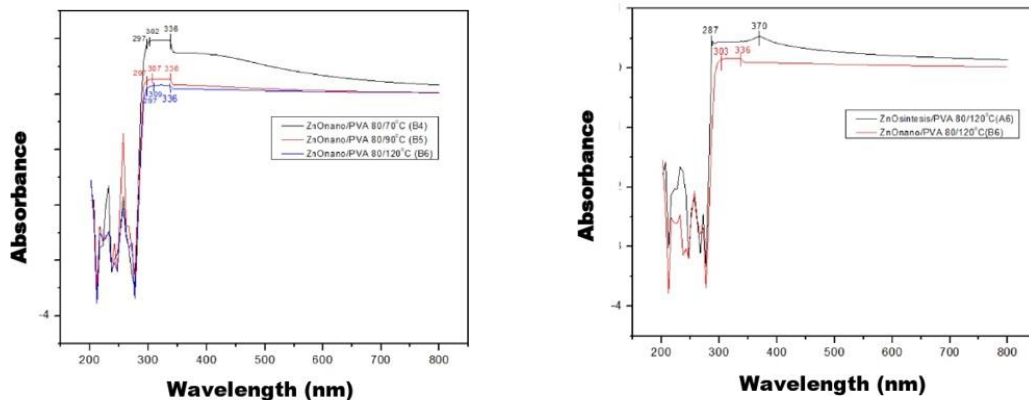
**Figure 2.** (a) UV-Vis results of samples B4, B5, and B6; (b) UV-Vis comparison of samples A6 and B6.

Due to the decrease in particles that is caused by the varying temperatures and semiconductor quantum confinement effects, the absorbance edge will shift to a higher energy [12, 17]. Therefore, the band gap energy of all the samples can be obtained from the UV-Vis spectra. In ZnO_{nano}/PVA (B4, B5, and B6), the band gap energy decreased from 4.10 to 4.01 eV with an increased wavelength of 302–309 nm. For the synthesized ZnO (A6), it can be seen from the smaller band gap energy of 3.35 eV with a wavelength of 370 nm compared to ZnO nanoparticles (B6). It is clearly shown that the shifting at the absorption edge is caused by the quantum confinement effect. Therefore, the average particle size can be determined from the inflection point in the absorbance spectrum with the wavelength [17]. The calculation of the band gap energy is shown in Table 1 below.

Table 1. Band gap energy and particle size of ZnO_{nano}/PVA (B4, B5, B6) and $ZnO_{synthesis}$/PVA (A6) thin film samples

Sample	λ_c (nm)	Band gap energy (eV)	Particle size (nm)
$ZnO_{synthesiss}$/PVA 120^0C (A6)	370	3.35	5.47
ZnO_{nano}/PVA 70^0C (B4)	302	4.10	2.68
ZnO_{nano}/PVA 90^0C (B5)	307	4.04	2.77
ZnO_{nano}/PVA 120^0C (B6)	309	4.01	2.81

In table 1, the higher the treatment temperature, the larger the particle size, it is indicated the absorption wavelength peaks on ZnO_{nano}/PVA thin films (B4, B5, and B6).

The XRD analyses were studied for the samples synthesized in room temperature ZnO/PVA (B) and annealed at 120°C ZnO/PVA samples (B6). The purpose of XRD results is to determine crystallite size and crystallinity and to be compared with the standard diffraction pattern of JCPDS No. 36-1451, which corresponds to the structures of pure ZnO and PVA [18]. In the XRD results of samples B and B6, each has seven main peaks, which correspond to the hkl field and JCPDS peak No. 36-1451. From the XRD pattern, it has the FWHM for obtaining the size of the crystallite using the Scherrer equation, and the results are shown in Table 2.
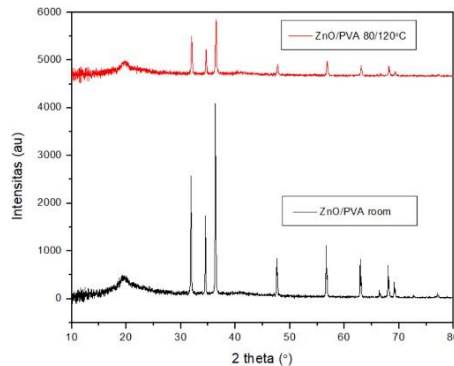
Figure 3. XRD spectra of the samples synthesis in the room temperature ZnO_{nano}/PVA (B) and annealed at120°C ZnO_{nano}/PVA samples (B6)

Table 2. Crystal size of samples synthesis in the room temperature ZnO$_{nano}$/PVA (B) at 120°C ZnO$_{nano}$/PVA samples (B6)

No	JCPDS No 36-1451		ZnO/PVA at room temperature (B)			ZnO/PVA 120° (B6)		
	hkl	2θ (°)	FWHM	2θ (°)	D (nm)	FWHM	2θ (°)	D (nm)
1.	(100)	31.96	0.15201	31.845	54.35	0.2159	32.006	38.28
2.	(002)	64.67	0.15731	34.487	52.88	0.2069	34.649	40.23
3.	(101)	36.44	0.16471	36.232	50.77	0.2339	36.484	35.76
4.	(102)	48	0.19219	47.619	45.19	0.2752	47.76	31.57
5.	(110)	58.86	0.10558	56.665	85.49	0.2943	56.796	30.69
6.	(103)	63.12	0.10614	62.908	87.58	0.17	63.07	54.83
7.	(112)	68.2	0.1035	67.991	92.59	0.2828	68.153	33.92
			Average		66.978	Average		37.987

From Table 2 above, the average of crystallite size of the ZnO/PVA thin film sample at room temperature (B) is ≈ 66.978 nm while the ZnO/PVA at temperature 120°C (B6) is ≈ 37.897 nm. From this result the average crystallite size of B is almost twice bigger than sample B6. The crystallinity of ZnO/PVA can be calculated by comparing the area of the crystal peaks with the total integrated area of all peaks. The area calculation can be measured using the origin software. The crystallinity showed clearly in the equation (1) below. From the calculation it is found that sample B and B6 have a crystallinity of 45.77% and 34.81 %, respectively.

$$Crystallinity\ (\%) = \frac{The\ total\ integrated\ area\ of\ the\ crystal\ peaks}{Total\ integrated\ area\ of\ all\ peaks} \times 100\% \qquad (1)$$

According to Kandulna, there is a correlation between FWHM and crystallinity index with ZnO/PVA nanocomposites by incorporation of ZnO in the PVA polymer matrix [9]. It is clearly seen that the higher the temperature treatment the crystallinity of ZnO nano/PVA decreases. This is due to the thermal degradation of PVA which has decreased in mass when it is given heat treatment at 70°C-120°C. It causes the evaporation of H_2O bonds which are physically weak and chemically strong [17]. In addition, the results of the crystallinity of ZnO$_{nano}$/PVA showed that ZnO nanoparticles had a semi-crystalline structure and distribution of ZnO nanoparticles on the PVA surface.

The SEM results of ZnO$_{nano}$/PVA for samples B and B6 are shown in Figure 4. From these results, it is shown that the particles when treated at a given room temperature (B) are larger than at 120°C (B6). For particle measurements from SEM results using the image software shown in Table 3. This is caused by the surface energy in sample B, which causes the particles to tend to agglomerate and form larger particles [7].
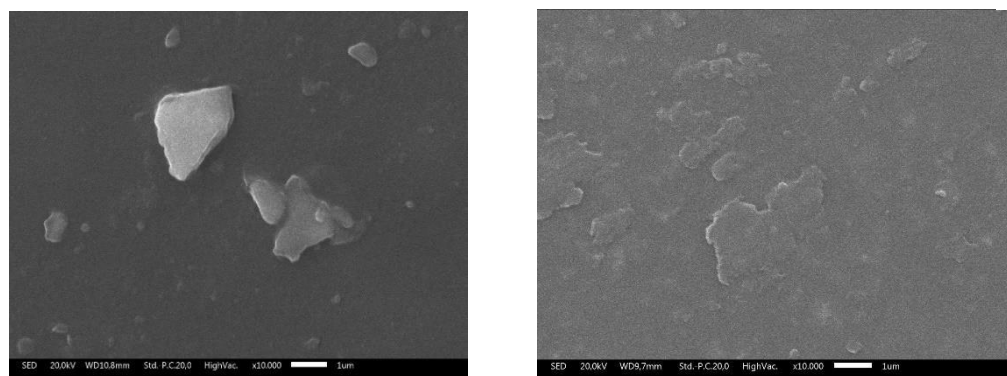

Figure 4. SEM results of ZnO$_{nano}$/PVA thin films at (a) room temperature and (b) 120°C

Table 3. Particle measurements results of ZnO/PVA at room temperature (B) and 120°C (B6)

No.	ZnO/PVA at room temperature (B)		ZnO/PVA at 120°C (B6)	
	Width	Particle Size (μm)	Width	Particle Size (μm)
1	0.005	0.474	0.018	1.821
2	0.004	0.38	0.006	0.579
3	0.003	0.328	0.005	0.493
4	0.02	1.966	0.006	0.606
5	0.009	0.898	0.007	0.643
6	0.013	1.297	0.006	0.58
7	0.002	0.22	0.003	0.267
8	0.006	0.546	0.005	0.455
9	0.002	0.177	0.002	0.179
10	0.001	0.1	0.004	0.405
Average	0.007	0.639	0.006	0.603

The average particle size of the ZnO/PVA nanocomposite at room temperature is 639 nm, while at 120°C is 603 nm. For crystallinity, the calculation is carried out using the largest particle sizes, 1966 nm (B) and 1821 nm (B6), resulting in the crystallinity of 30.77% at room temperature and 29.03% at 120°C, respectively. Figure 5 depicts the results of the EDS spectra of the ZnO_{nano}/PVA for samples B and B6, with C, O, and Zn atomic compositions in the thin film and the percentage of each component shown in Tables 4 and 5.
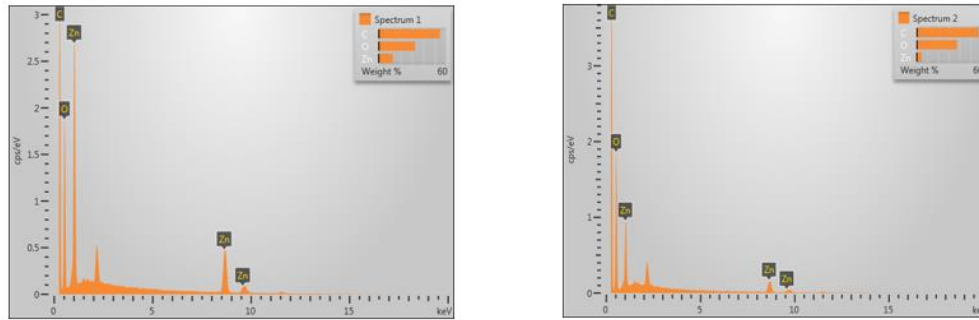
Figure 5. EDX results of sample B (a) and sample B6 (b)

Table 4. EDX ZnO_{nano}/PVA Measurement results at room temperature (B)

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label
C	K series	25.42	0.25416	54.64	0.33	67.05	C Vit
O	K series	25.42	0.08552	32.66	0.49	30.09	SiO_2
Zn	K series	20.04	0.20039	12.70	0.33	2.86	Zn
Total				100.00		100.00	

Table 5. EDX ZnO_{nano}/PVA 120°C (B6) Measurement Results

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label
C	K series	31.55	0.31551	57.89	0.53	66.62	C Vit
O	K series	25.23	0.08489	37.50	0.52	32.40	SiO_2
Zn	K series	6.40	0.06401	4.61	0.24	0.98	Zn
Total				100.00		100.00	

The percentage of Zn atoms in ZnO$_{nano}$/PVA decreased from 2.86% (table 4) to 0.98% (table 5) and the percentage of C atoms in ZnO$_{nano}$/PVA decreased from 67.05% to 66.05% because of the temperature treatment.

4. CONCLUSION

From the result, it shows that film ZnO$_{synthesis}$/PVA has a larger particle size than ZnO$_{nano}$/PVA, which, in terms of the electrical properties of ZnO$_{synthesis}$/PVA has the highest current of 1.55 nA. ZnO$_{nano}$/PVA has a current of 1.49 nA when given a temperature of 120°C. There was a decrease in resistance when given a temperature of 90 °C, while for ZnO$_{nano}$/PVA (B4, B5, and B6), the resistance increased with the higher temperature treatment. ZnO$_{synthesis}$/PVA (B6) has a band gap energy of 3.35 eV, which is smaller than the band gap energy of ZnO$_{nano}$/PVA (B6), while the particle size of ZnO$_{synthesis}$/PVA (B6) is larger. The absorbance spectra were shifted to the blueshift region. For the film of ZnO$_{nano}$/PVA thin films, crystal size and crystallinity decreased from 66.978–37.897 nm and 45.77–34.81% when given room temperature (B) and 120 °C (B6), respectively. Therefore, it can be seen from the SEM results that sample B undergoes agglomeration and forms larger particles. This result has the potential to be applied as an optical sensor for flexible devices, such as pulse oximeter that is usually applied in medical applications.

REFERENCES

[1] S. Komarneni, "Nanocomposites," *Mater. Chem,* vol. 2, no. 12, pp. 1219-1230, 1992.

[2] I. Sriyanti, "Nanocomposite prepared by simple mixing method," in *PROCEEDING OF THE THIRD INTERNATIONAL SEMINAR ON SCIENCE EDUCATION "Challenging Science Eduction in The Digital Era"*, Bandung, 2009.

[3] Niranjan Karak, Elsevier. "Fundamentals of Nanomaterials and Polymer Nanocomposites,Nanomaterials and Polymer Nanocomposites". Science Article, pp. 1-45, 2019

[4] Kim Hung Huynh, Xuang Hung Pham. "Synthesis, Properties, and Biological Applications ofMetallic Alloy Nanoparticles". Metal Nano/Microparticles for Bioapplications, vol 21, 2020.

[5] Ning Zhang, Yong Pang, LuZong. "Rubber-like and biodegradable poly (vinyl alcohol) composites with triple networks for high-efficiency solvent barrier". Composites Science and Technology, Volume 231, 2023.

[6] Hajar Benali, Fatima Lmai. "Synthesis and characterization of Mg-doped ZnO thin-films for photovoltaic applications". Materials today: Proceedings, vol 66, pp. 212-216, 2022.

[7] G. A. Elham, H. A.-F. Mohammad, S. Nasser, K. Mehdi and M. Parisa, "PREPARATION AND CHARACTERIZATION OF PVA/ZnO NANOCOMPOSITE," *Food Processing and Preservation,* vol. 39, no. 6, pp. 1442-1451, 2014.

[8] Saeid Asadpour, Ahmad Raeisi Vanani. "A review on zinc oxide/poly(vinyl alcohol) nanocomposites: Synthesis, characterization and applications". Journal of Cleaner Production, vol 362, 2022.

[9] R. Kandulna and R. B. Choudhary, "Concentration-dependent behaviors of ZnO-reinforced PVA–ZnO nanocomposites as electron transport materials for OLED application," *Polymer Bulletin,* vol. 75, no. 7, pp. 3089-3107, 2017.

[10] B. Luigi, P. L. M. Francesco, C. Manuela and C. M. Maria, "Effect of processing temperature and mixing time on the properties of PP/GnP nanocomposites," *Polymer Degradation and Stability,* vol. 181, pp. 1-10, 2020.

[11] A. Ravve, Principles of Polymer Chemistry, Niles, USA: Springer, 2012.

[12] S. Zandi, P. Kameli, H. Salamati, H. Ahmadvand and M. Hakimi, "Microstructure and Optical Properties of ZnO Nanoparticles Prepared by a Simple Method," *Physica B: Condensed Matter,* vol. 406, no. 17, pp. 3215-3218, 2011.

[13] P. P. Jeeju, S. Jayalekshmi and K. Chandrasekharan, "Nonlinear optical properties of ZnO/poly (vinyl alcohol) nanocomposite films," in *AIP Conference Proceedings*, 2014.

[14] G. Xinghou, T. Chak Yin, P. Ling, H. Zhonghua and T. Chi Pong, "Characterization of poly(vinyl alcohol) (PVA)/ZnO nanocomposites prepared by a one-pot method," *Composites: Part B,* no. 60, pp. 144-149, 2014.

[15] A. Roberto, C. Amanda, L. M. Maria, d. l. T. Karla, T. Richard, M. Mario, V. Hector, F.Javier and V. Israel, "Polymeric Nanocomposites Membranes with High Permittivity Based on PVA-ZnO Nanoparticles for Potential Applications in Flexible Electronics," *Polymers,* vol. 10, no. 12, pp. 1-17, 2018.

[16] A. A. Khalaf, A. Sahar, Z. Jean and S. Chafic, "Sythesis of ZnO Nanopowders By Using Sol- Gel and Studying Their Structural and Electrical Properties at Different Temperature," *Energy Procedia,* vol. 119, pp. 565-570, 2017.

[17] S. M. Soosen, B. Lekshmi and K. C. George, "OPTICAL PROPERTIES OF ZnO NANOPARTICLES," *SB Academia Review,* vol. 16, no. 1 & 2, pp. 57-65, 2009.

[18] A. F. Mansour, S. F. Mansour and M. A. Abdo, "Improvement Structural and Optical Properties of ZnO/ PVA Nanocomposites," *IOSR Journal of Applied Physics,* vol. 7, no. 2, pp.60-69, 2015.

[19] Q. C. Bui, B. Salem, H. Roussel, et al., "Effects of Thermal Annealing on the Structural and Electrical Properties of ZnO Thin Films for Boosting Their Piezoelectric Response," Journal of Alloys and Compounds, 2021.