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Polymeric nanocomposites membranes with high permittivity based on PVA - ZnO nanoparticles for potential applications in flexible electronics

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Abstract: In this study is reported the optical, structural and dielectric properties of Poly (vinyl alcohol) thin films membranes with embedded ZnO nanoparticles (PVA/ZnO) obtained by solution casting method at low temperature of deposition. Fourier Transform Infrared spectra showed the characteristics peaks, which correspond to O-H and Zn-O bonds present in the hybrid material. The X-ray diffraction patterns indicated the presence of ZnO structure into the films. The composite material showed low absorbance and a wide band gap energy from 5.6 to 5.9 eV. The surface morphology for the thin films of PVA/ZnO was studied by Atomic Force Microscopy and Scanning Electron Microscopy. The dielectric properties of the nanocomposites were measured from low to high frequencies, the results showed a high dielectric constant (ε) in the order of 10^4 at low frequency and values from ε≈2000 to 100 in the range of 1KHz-1MHz respectively, the properties of PVA/ZnO such as the high permittivity and the low temperature of processing make it a suitable material for potential applications in the development of flexible electronic devices.

Keywords: solution process; thin films; composite material; dielectric constant

1. Introduction

Composite materials based on a polymeric matrix with embedded metal nanoparticles have gain attention due to their properties such as electrical, mechanical, optical and chemical properties that can be used in the development of biomedical devices, solar cells, sensors, capacitors among others [1] [2]. A hybrid material consists of soluble polymers with inorganic component with excellent mechanical, optoelectronics and dielectric properties due to the combination of the organic and inorganic components, and it can be deposited as a thin film in different substrates. Therefore, the number of contributions in the development of hybrid composites based on polymers and nanoparticles with high permittivity, low cost, and easily tunable properties, have become a hot topic in the research of materials [3]. Recently, some works have been reported the integration of thin films based on polymeric materials such as Polyvinyl alcohol (PVA) as a gate dielectrics for the development of organic Thin Film Transistors (TFT), due to the high dielectric constant which enhances the gate capacitance, with the advantages of solution processable material, at low cost, non-

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toxic, with flexible hydrophilic network and low temperature of deposition [4] [5]. PVA is a poor electric conductor, water soluble, it has carbon chain backbone with OH groups and it is eco-friendly, and its physical properties may be adapted to a specific requirement in conjunction with inorganic materials [6]. On the other hand, nanoparticles of Zinc oxide (ZnO Nps) have been used in memory devices, gas sensors, thin film devices, and flexible electronic devices [7], [8]. Furthermore, the utilization of ZnO as semiconductive filler to prepare high dielectric constant polymer composites has been reported [9]. Related to hybrid materials, few studies have investigated the dielectric properties of PVA with embedded ZnO nanoparticles into the polymeric matrix. J.J. Mathen et al. synthesized membranes of PVA/ZnO for developed of an UV-A sensor on an ITO substrate showed the interfacial interaction between the filler and the matrix resulting in a large improvement in the dielectric, optical and mechanical properties [1]. P. I. Devi et al. studied the dielectric properties of a hybrid composite based on Polyvinylidene fluoride PVDF-ZnO for microwave frequencies, it showed a decrease in dielectric constant and dielectric loss with the frequency, and the ZnO composition has a great influence on the trend and magnitude of dielectric properties [10]. Sugumaran et al. obtained a hybrid poly (vinyl alcohol)-indium zinc oxide (PVA-InZnO) thin films by a simple dip coating method with dielectric constant values around 6 to 20 [11]. Recently, a nanocomposite polymer films based on PVA and TiO_2 nanoparticles have been reported with relative high permittivity [12] . Therefore there is an interest in order to obtain a composite material with a high dielectric constant which to meet the requirements for flexible electronics such as low temperature of deposition, stability, flexibility and low cost. In this work, is reported the synthesis and characterization of a Poly(Vinyl Alcohol) thin films with embedded ZnO nanoparticles (ZnO Nps) by solution casting method, taking the advantage that the electrical and optical properties can be tuned by adding ZnO nanoparticles into a polymeric matrix. The nanocomposites have been characterized using Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM), UV-vis spectroscopy to determine band gap, and Atomic Force Microscopy (AFM) for surface roughness of the membranes. The dielectric properties of PVA–ZnO nanocomposites were measured from low to high frequencies. The results show high dielectric constant (ε) at low frequencies, even at high frequencies ε is higher than other related composites materials, thus the hybrid PVA-ZnO Nps make it a suitable for potential applications in electronic devices.

2. Materials and Methods

2.1 Materials

For the synthesis was used Polyvinyl Alcohol (PVA) from sigma aldrich with an average molecular weight M_w=130,000 and 99% hydrolyzed to obtain the membranes. A solution of PVA was prepared using 2.5g powder in 50 ml of distilled water and stirred at 90°C in order to obtain a homogenous solution. For ZnO Nps, Sodium Dodecyl Sulfate (SDS), Zinc chloride ($ZnCl_2$), Acid Citric ($C_6H_8O_7$), Potassium Hydroxide (KOH) and Ammonia (HN_4) were used to form ZnO nanoparticles. The general process is depicted in Figure. 1.

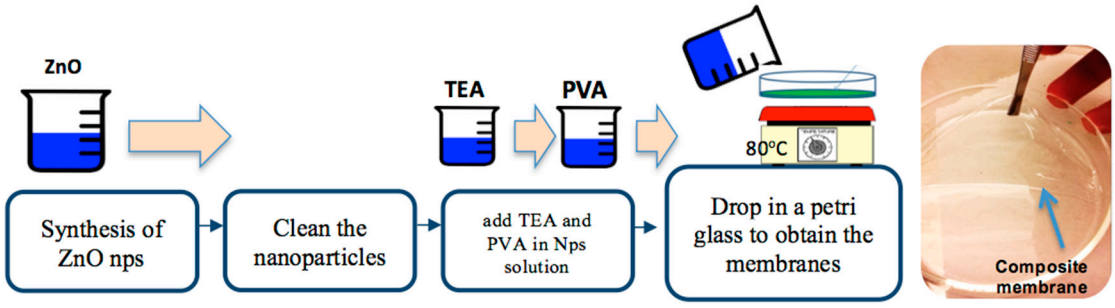

Figure 1. General sequence of synthesis of PVA/ZnO membranes

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2.1.2 Preparation of PVA/ZnO membranes

The membranes as thin films were prepared by solution casting method, following the next steps: firstly, the solution of ZnO nanoparticles was cleaned with distilled water. The next step was to add 0.3 ml of trietanolamyne (TEA) (1M) in 3 ml of nanoparticles solution; then 19.2 ml of PVA that was previously prepared was added. Finally, the solution was deposited on glass petri dishes and it was heating at 80°C for 40 minutes to obtain the membranes. The quantities for the precursors in the synthesis of ZnO nanoparticles are listed and labeled in Table 1.

Table 1. Details of the solutions to synthetize ZnO nanoparticles

Sample Name	SDS	$ZnCl_2$	$C_6H_8O_7$	Solution
Z1	5 ml	1 ml	1 ml	NH_4
Y1	5 ml	1 ml	1 ml	KOH
Z4	5 ml	2.5 ml	1.2 ml	NH_4
Y4	5 ml	2.5 ml	1.2 ml	KOH

2.2. Characterization

The ZnO Nps were chemical, optical and structural characterized using the methods of Fourier Transform Infrared Spectroscopy (FTIR), Ultra Violet-Visible spectra measured by UV- Vis, model 6850 jenway spectrometer, and morphology by Scanning Electron Microscopy (SEM) as well as Energy Dispersive Spectroscopy (EDS) was included for the composition analysis of the thin films and the structure was determined by X-ray diffraction (XRD 20 to 80 θ).
For the dielectric properties of the material, firstly, the solutions of PVA/ZnO Nps were measured using the open-ended coaxial probe technique [13]. This technique was implemented using a Keysigtht Vector Network Analyzer and the open-ended coaxial performance probe (Keysight N1501A Dielectric Probe Kit). The Figure 2 shows the setup of the open-ended coaxial probe technique. The measurements were performance in a frequency range from 0.5GHz to 20GHz and the system was calibrated using air and distilled water.

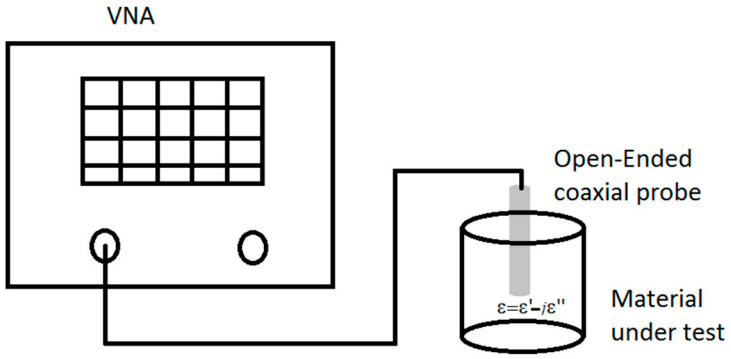

Figure 2. Setup of the open-ended coaxial probe technique for dielectric measurements in the solution of PVA/ZnO Nps

Using the equation (1) where ε′ is the dielectric constant and ε′′ is the loss factor is possible to obtain the conductivity and the tangential loss (tanδ) which is determined by the equations (2) and (3)

$$\varepsilon = \varepsilon' - j\varepsilon'', \quad (1)$$

$$\sigma = 2\pi f \varepsilon'' \varepsilon_0, \quad (2)$$

$$tan\delta = \frac{\varepsilon''}{\varepsilon'}, \quad (3)$$

where *f is* the frequency in Hz and ε_0 is the permittivity in the vacuum.
Later a Metal-Insulator-Metal structure was fabricated on the membranes using aluminum as top and bottom electrodes. Aluminum circular contacts with a diameter of 2000 μm and a thickness of 300nm were deposited by e-beam evaporation through a shadow mask. The dielectric constant of the PVA/ZnO membranes was carried out using the MIM structure and LCR impedance analyzer (HIOKI LCR model 3536) at room temperature and a constant voltage of 1 Vrms in the frequency range from 500 Hz to 1 MHz.

3. Results and discussion

3.1 FTIR analysis

In order to determine the chemical bonds in the PVA and ZnO nanoparticles, the FTIR spectrum was measured in the membranes, which is showed in fig. 3. The peak at 3267 cm^{-1} is due to OH groups in the polymer backbone, the peaks at 2906 cm^{-1} and 918 cm^{-1} are due to CH_2 asymmetric and symmetric stretching, respectively. The peak observed around 1420 cm^{-1} is due to C-C stretching which is in accordance to reference [14]. Furthermore, the band observed at 420-417 cm^{-1} is due to Zn-O stretching, this suggest the presence of ZnO into the membranes.

The interaction of PVA bonds with the addition of ZnO nanoparticles is attributed by the intermolecular interaction between OH groups by PVA and the surface of the nanoparticles [15]. The hydroxyl groups of PVA have a strong tendency to form a charge transfer complex with ZnO nanoparticles through chelation [16]. The addition of TEA in the solution allows the complete interaction between the nanoparticles and the polymer and also provides a dispersion of the nanoparticles avoiding agglomerates. The bands of PVA are more or less pronounced depending if KOH or NH_4 is employed in the synthesis, and also it depends of nanoparticles concentration into the polymer (PVA) matrix, thus the intensity of the OH bonds are decreasing as the amount of ZnO increases. Hydroxyls groups are the most representatives to analyze the chemical changes due to evident reduction intermolecular interactions to provide the composites formation. The chemical reaction of PVA with ZnO and it precursors is shown in the inset of Figure. 3. PVA can be chemically or thermally cross-linked at their hydroxyl groups generate water as a by-product [17].

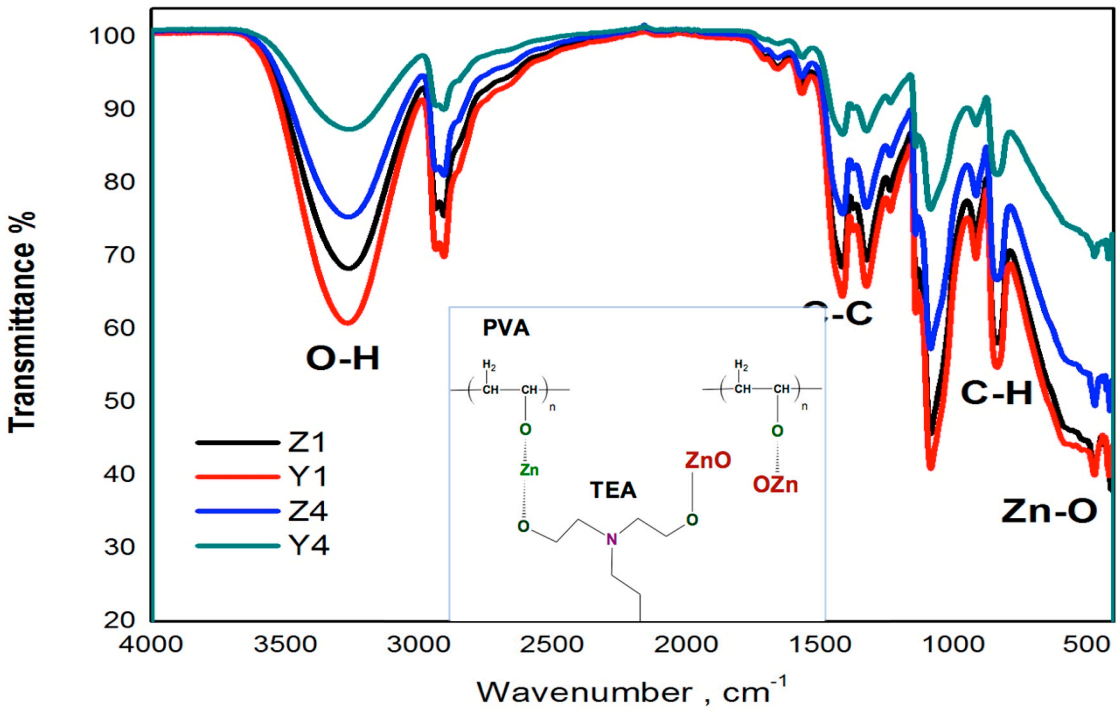

Figure 3. FTIR spectra of PVA matrix with ZnO nanoparticles, the inset shows the reaction of PVA and ZnO.

3.1. Absorbance characteristics and optical band gap

The UV-Vis absorbance spectra for the ZnO Nps is shown in fig. 4, in the samples there is a peak at 339 nm, close to 385nm which corresponds to the bulk ZnO [18], it is identified due to the addition of ZnO nanoparticles, consequently, this is an indication of the interaction between PVA and ZnO, the inset of Figure. 4 is a SEM image for the ZnO Nps corroborating the aspheric morphology and the completely formation of the nanoparticles. Prior to embedded the ZnO into the PVA, the Tauc´s method was used to calculate the ZnO band gap (Eg), obtaining a mean value of 3.9 eV, that is a high value for ZnO obtained from a chemical method. Figure 5a shows the UV–Vis absorbance spectra in the region from 200 to 1100 nm for PVA/ZnO Nps membranes. From the spectra is possible to observe that the absorption for all films decreased with increasing wavelength, while for the samples Y4 and Z4, the absorption increased with increasing ZnO content. This is in agreement with the reported by reference [16], where the absorption is proportional to the number of absorbing molecules and it increases with increasing weight % of ZnO.

In Figure 5b is plotted the band gap (Eg) of the PVA/ZnO membranes, The Eg values are in the range from 5.6 to 5.9 eV, the samples prepared from the NH_4 (sample Z4) showed the high value due to the agglomeration of nanoparticles, however the Eg values are very closed to each another, which is and indicative that there are no significantly changes in the structure of the hybrid material and a good dispersion of the ZnO Nps is presented into the polymeric matrix.

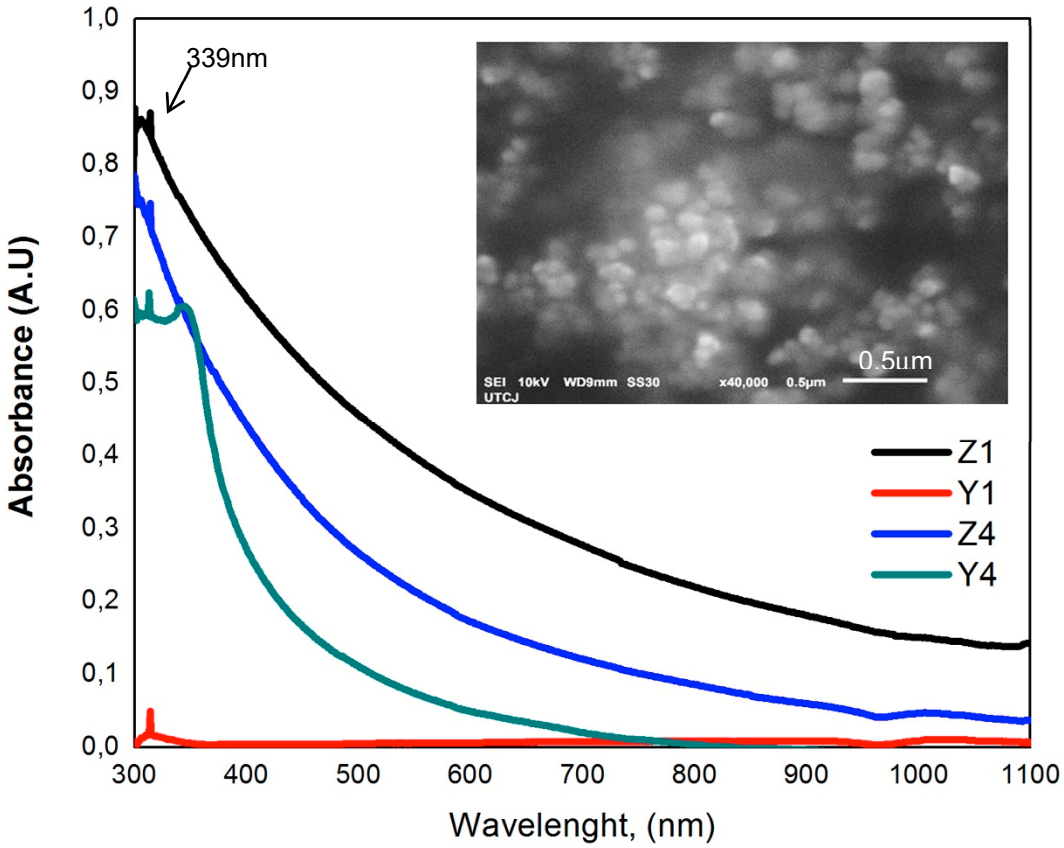

Figure 4. UV-Vis absorbance spectra of ZnO nanoparticles synthesized at different contents, the inset shows a SEM image for one of the ZnO nanoparticles agglomeration.

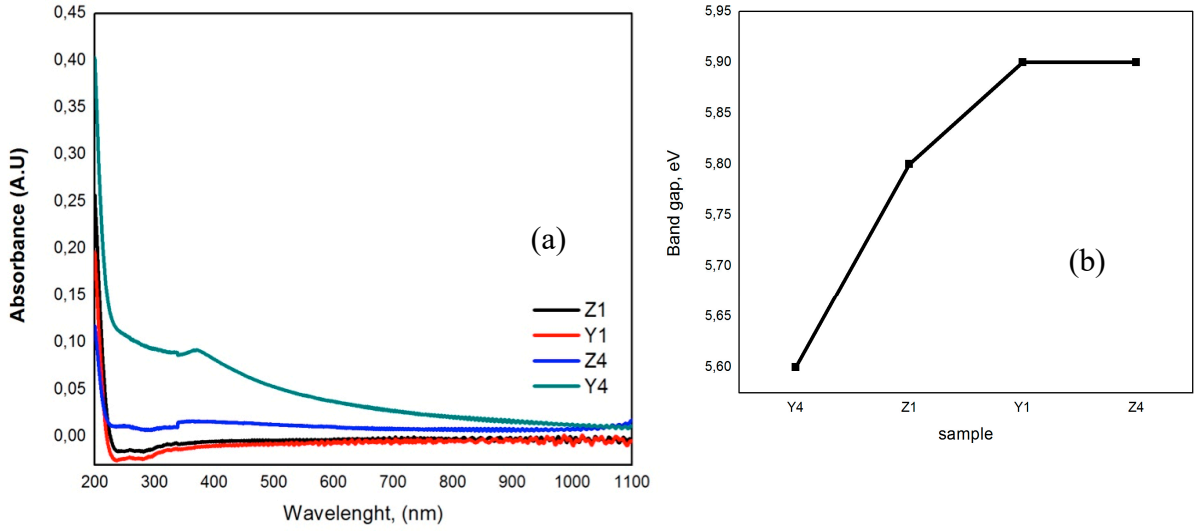

Figure 5. (a) Absorbance spectra of PVA-ZnO Nps; (b) Band gap obtained for the samples.

3.3 Surface morphology

In Figure 6a is shown the surface morphology for two samples with different concentration of ZnO nanoparticles into the membranes. In the Figure. 6b is showed the variation of the average roughness of the film as a function of the precursors NH_4 or KOH for ZnO Nps. The membranes prepared with low ZnO nanoparticles concentration showed low roughness (samples Z1 and Y1), is possible to observe that all samples have a homogeneous topography and low roughness.

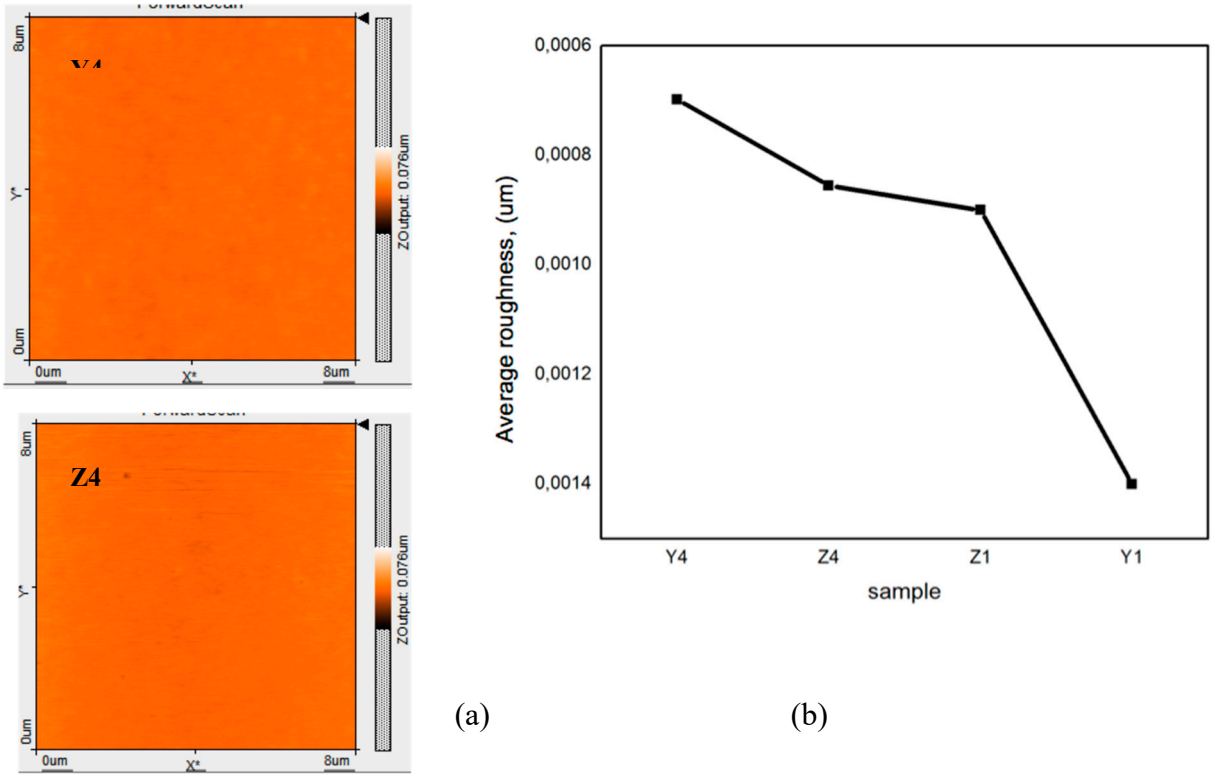

Figure 6. (a) AFM topography for samples Z4 and Y4; (b) Average roughness for PVA-ZnO membranes.

The Scanning electron micrographs of PVA/ZnO Nps membranes are shown in Figure. 7 (a-d). SEM images showed ZnO nanoparticles distribution in the polymer membrane. The formation of agglomerates is observed when the ZnO concentration increases for samples Y4 and Z4, however homogeneous agglomeration distribution is obtained in all samples. This distribution is attributed to the wet chemistry process used to obtain ZnO nanoparticles in solution where the ZnO Nps are compatible with the process to obtain the polymer. The ZnO nanoparticles synthetized by sol gel-method showed a size of 100 nm from samples obtained with the use of KOH or NH_4 precursors.

3.4 Structural analysis

The X-ray diffraction pattern (XRD) for PVA/ZnO membranes is showed in Figure 8. The broad diffraction peak located at $2\theta = 21.53°$ is due to amorphous PVA [11]. Peaks located at $2\theta = 29.5$ °, 36.1 °, 39.5 °, 43.2 °, 47.6 ° and 48.6 ° corresponding to (100) (100) (102) (110) and (103) respectively, the reflection plane of ZnO, showing the presence and hexagonal structure of the nanoparticles, and c-axis orientation, in addition to well-defined diffraction peaks indicating complete crystal formation [1] [19]. The values of interplanar spacing (d), the average of lattice parameters and the unit cell (u)

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in the membranes were obtained by Bragg law, resulting as follows d= (3.0201Å, 3.0206 Å) and u= (76 and 69 nm) respectively.

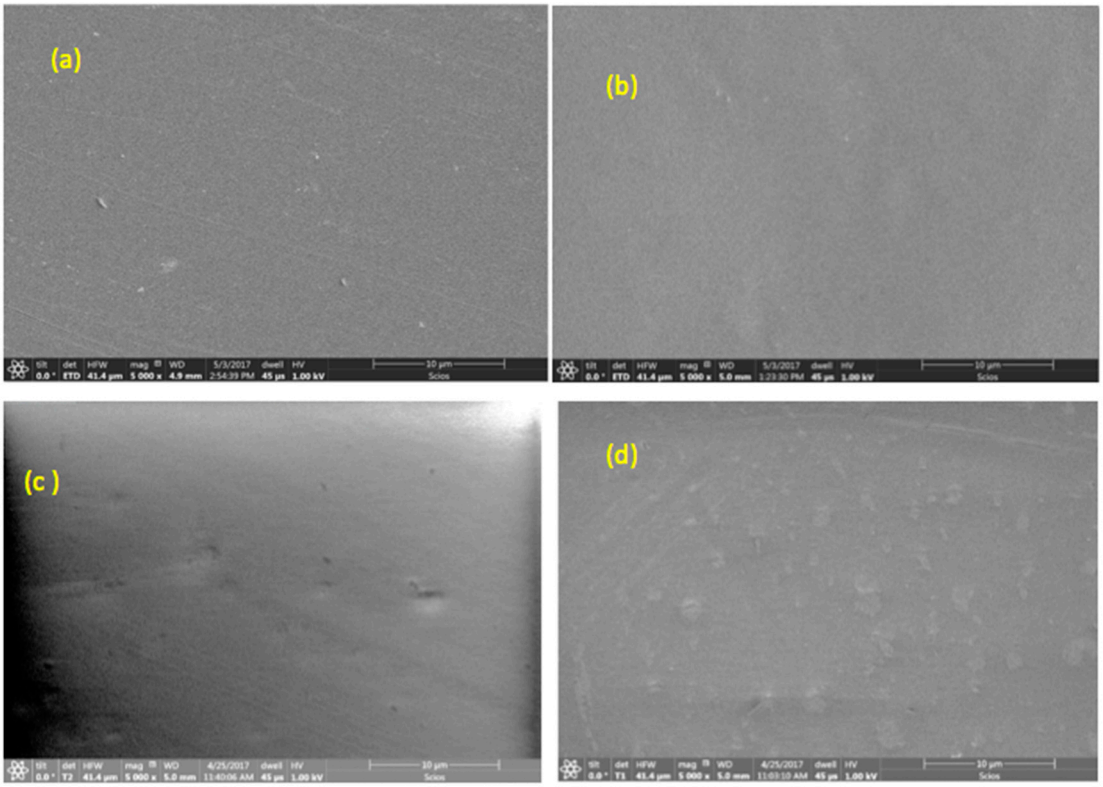

Figure 7. SEM images for PVA-ZnO membranes: a) Z1, b) Y1, c) Z4, d) Y4.

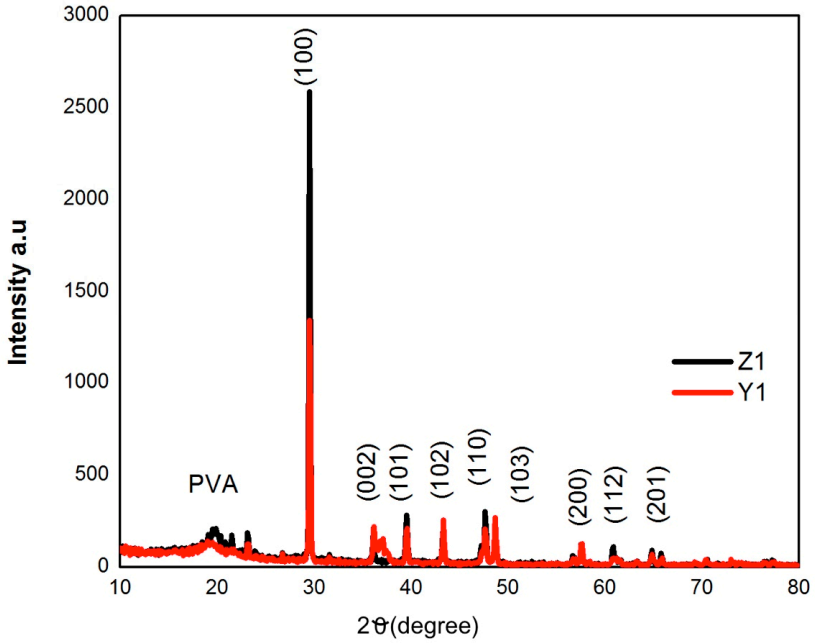

Figure 8. XRD pattern of PVA/ZnO Nps membranes

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3.4 Dielectric properties

For the analysis of dielectric properties, firstly the solution of PVA/ ZnO Nps was analyzed with the technique that was described in the experimental section, for this study distilled water was used as dielectric reference and also for the calibration, the measurements were performed in the range from 0.5-20 GHz at room temperature. The relative permittivity of water is ε'≈80, as is shown in the Figure 9(a), therefore the dielectric constant (ε) values of PVA/ ZnO Nps are closer to the permittivity of water at 500MHz, this is due to the water component in the PVA solution. In addition, Figure 9(a) and (b) show the variation in the dielectric constant (ε'), and loss factor (ε'') with frequency for different content of ZnO Nps, in the insets of figures is possible to observe the variations, the dielectric constant for the solution of the PVA with ZnO nanoparticles which decreases as frequency increases, this is in accordance with the reported by Yeow et al, and could be explained due to the dipoles which are not able to follow the variation field at higher frequencies [19]. At relative low frequencies in the range for microwave applications the solution for the membranes showed a high dielectric constant, and it is related to electrode polarization of the polymer [20].

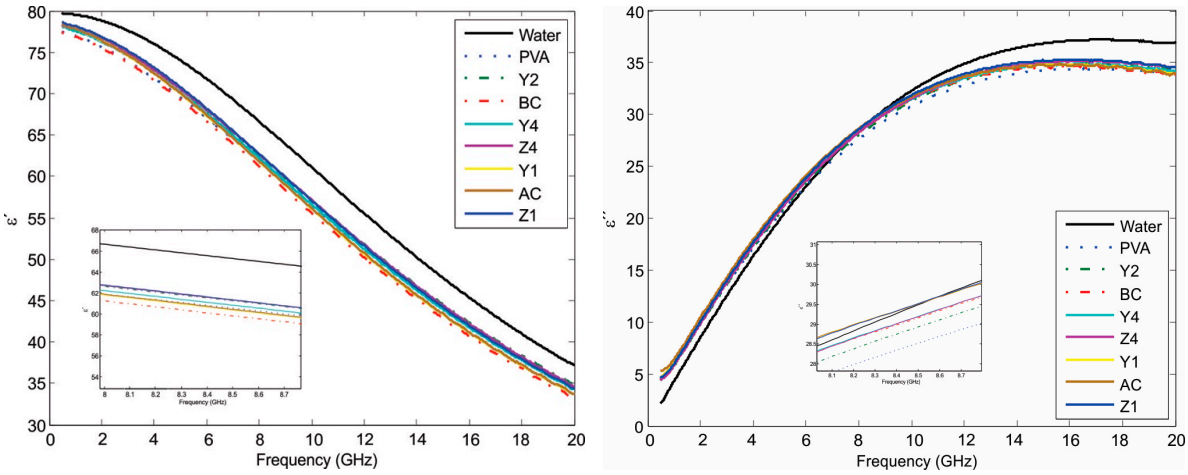

Figure. 9. (a) The dielectric constant ('); and (b) loss factor ('') as a function of the frequency for various ZnO nanoparticles content in PVA solution.

Figure 10 shows the dielectric constant as a function of frequency for the PVA membranes with different content of ZnO Nps, the measured capacitance with the LCR equipment was used to calculate the dielectric constant in the films, the inset in the figure 10 shows one of the samples used for the characterization. From the figure 10 is possible to observe the influence at low frequency on the dielectric constant, which is high for all samples, and the value decrease with frequency increases, this trend is similar to the reported by other authors, however the maximum value of ε=11468 obtained for the sample Y4 at 500Hz is higher than the reported by other works, in table 2 is showed a comparison with materials, methods and permittivity values [5]. At lower frequencies, all the free dipolar functional groups present in PVA polymeric chain can align themselves resulting higher permittivity values [20]. For frequencies up to 1KHz, the bigger dipolar groups find difficulty to orient at the same pace as the alternating field, so the contributions of this dipolar group decrease and also the permittivity [16]. The permittivity in ZnO nanoparticles also decreases when increases frequency of the applied field, this is due to ZnO is a polar ceramic material with relatively high permittivity therefore, the ε values of the nanocomposites are also found higher [21]. In addition, the ZnO Nps embedded in the PVA matrix enhances the dielectric permittivity of the composite, because ZnO exhibits a strong ionic polarization due to Zn^{2+} and O^{2-} ions and has a high value of static permittivity [22]. Therefore, the samples Z4 and Y4 presented the higher value, further, the increasing of ε values in the composites obtained at low frequencies can be attributed to the interfacial

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polarization, which exhibits due to the difference in the permittivity values of the ZnO and the PVA matrix.

Table 2. Comparison of permittivity values with related works of Polymer matrix/ZnO

Material	Deposition method and Temperature	Permittivity (ε) Frequency	Reference
PVA/ZnO membranes	Solution casting/ 50°C	17,8 at 100 Hz	[1]
PVDF/xGnPs	Solution mixing process	2,080 at 10^3Hz (4.1 vol%)	[2]
PVDF/ZnO composites	combination of solution blend, sequential precipitation, and hot-press processes/ °60C	100 at 500HZ	[9]
PVA/ZnO nanocomposites	Solution casting/ 40 °C	500 at 10^2 Hz 10^2 at 10^6 Hz	[14]
PVDF/ZnO nanowires clusters	Microemulsion / 80°C	113 at 10^2 Hz	[23]
Ag/TiO_2/ polytetrafluoroethylene (PTFE)	solution blended process 80°C	100AT 10^3Hz	[26]
PVA/ZnO	Solution casting method 80°C	≈10^4 at 500Hz	This work

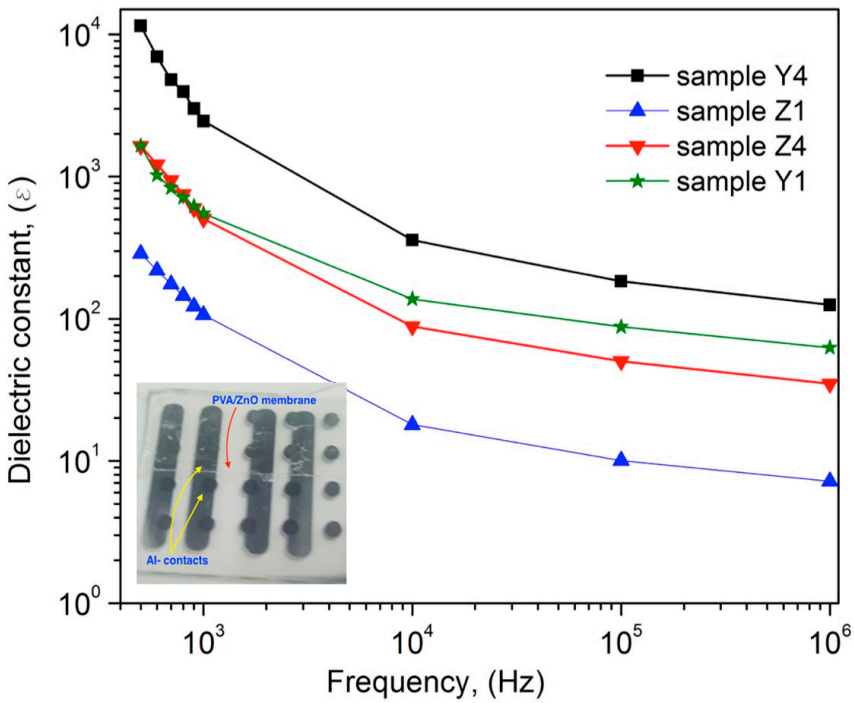

Figure 10. Variation of dielectric constant with frequency for the membranes of PVA with different content of ZnO Nps. The inset is a picture of one the fabricated capacitors over glass substrates.

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Capacitance-Voltage (C-V) curves were measured as an additional characterization in order to corroborate the high dielectric constant of the composites, the data were obtained with 4200A Keithley semiconductor parameter analyzer at 1 KHz with a voltage sweeping from -1V to 1 V, the Figure 11 shows the C-V plot for the samples Y1 and Z1 identifying the three regions: accumulation, depletion and inversion, from accumulation region the dielectric constant was extracted with a value ε~1079 which is close to the obtained with the impedance analyzer and the value reported here is one of the highest using ZnO semiconductor nanoparticle for the composite.

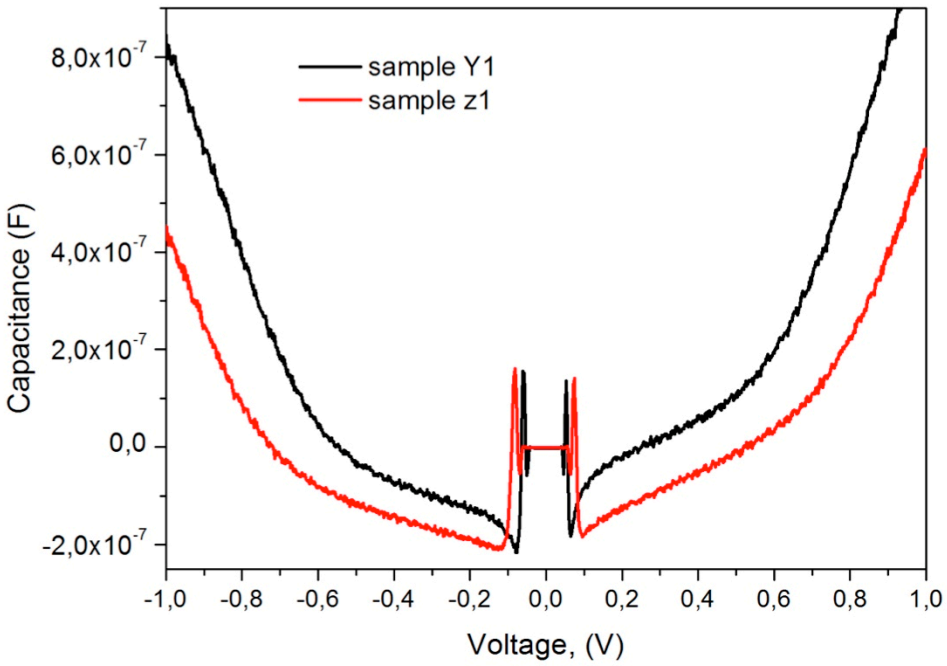

Figure. 11. C-V measurements for the samples Y1 and Z1 (PVA/ZnO)

The introduction of conductive or semiconductive inorganic particles into the polymer matrix has resulted in dielectric composites with an effective permittivity that is much higher than that of the matrix. Relative permittivity (εr) values of up to 10^5 have been reported in some composite systems [24]. Large dielectric constant can be achieved in composites; the physical reason for the critical behavior of the dielectric constant near percolation is the existence of microcapacitor networks. Each microcapacitor is formed by the neighboring conductive filler particles and a very thin layer of dielectric in between and contributes an abnormally large capacitance mainly due to the introduction of nanofiller [25]. Further studies are necessaries to investigate the effect of the filler shape on dielectric constant and breakdown strength of the PVA/ZnO composites, however the higher dielectric values in these membranes are very attractive for applications as an insulator in TFT for flexible electronics due to the compatible process for the semiconductor materials and also its low temperature of processing. For future work, we are taking in account to fabricate electronic devices such as thin film transistor to obtain some basic digital gates using a complete process with the integration of the dielectric material and semiconducting materials obtained in solution process in flexible substrate .

4. Conclusions

Composites polymers based in membranes of PVA/ZnO NPs were prepared by solution casting process. The thin films were studied by the structural, optical and dielectric characterization. The

FTIR analysis demonstrated a good interaction between PVA matrix and the ZnO Nps, in samples with more ZnO Nps the O-H groups decrease, while in the samples prepared using NH_4 as the precursor a reduction in the O-H groups is observed. The UV–vis analysis showed that the addition of ZnO nanoparticles affect the absorbance close to the UV region and the maximum band gap is 5.9eV for the sample with the higher ZnO content. The XRD analysis showed that the crystal structure of ZnO is presented in the PVA matrix. The surface morphology of the PVA/ZnO obtained by AFM showed a smoother surface with average roughness close to 1nm, and the SEM images presented an uniform dispersion of ZnO nanoparticles in the PVA. In general structural and chemical analysis confirmed that the ZnO nanoparticles were embedded into the PVA matrix. The dielectric properties of PVA depend on frequency and also in the ZnO content, thus in this work was obtained a hybrid material using semiconductive nanoparticles with the highest dielectric constant due to the interaction of nanoparticles, therefore these nanocomposites thin films are very promising material for applications in the develop of transistors for flexible electronics.

Author Contributions: Dr. R. Ambrosio, Dra. A. Carrillo and Dr. M. Mota prepared and designed the experiments. Karla de la Torre performed the experiments . R. TorreAlba determined the dielectric properties at High Frequencies. J. Flores and H. Vazquez analyzed the data. M. Moreno and I. Vivaldo measured the structural properties and morphology of the materials. All of the authors contributed to the writing of this article.

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Conflicts of Interest: "The authors declare no conflict of interest."

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