Fabrication and Characterization of PZT-PAni/PVDF Based Nanocomposite

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***Abstract*-This work presents the preparation and characterization of PZT ceramic obtained by the polymeric precursor method (PPM). The influence of the synthesis method on the grain size and the morphology are also object of study. The fabrication and characterization of composite films with 0-3 connectivity, immersing nanoparticles of PZT into the non-polar poly(vinylidene fluoride) – PVDF as the polymer matrix were presented. For comparison there are results obtained with composite samples made of ceramic particles unrecovered and recovered with a conducting polymer, the polyaniline (PAni).**

Keywords—PZT; composite; PVDF; PAni; polymer precursor method

I. INTRODUCTION

The concept of energy harvesting must be related to capture the ambient energy and convert it into usable electrical energy without environment attack i.e., a clean electric energy. Although there are a number of sources of harvestable ambient energy, such as solar energy and energy from wind, piezoelectric materials are very interesting due to their ability to convert applied strain energy into usable electric energy [1].

Perovskite lead zirconate titanate (PZT) based materials exhibit various properties, such as pyroelectric, piezoelectric and ferroelectric depending on the chemical compositions, type of synthesis, hence is used in several applications like sensors [2], actuators[3] ultrasonic transducers and electro-optic devices [4].

Piezoelectric materials can be classified in piezoelectric ceramics, piezoelectric polymers, and piezoelectric composites [5]. However, the piezoelectric ceramics has better electromechanical coupling coefficient (K), high piezoelectric strain coefficient (d_{33}) as well as rapid response. On the other hand, the piezoelectric polymers low acoustic impedance, low piezoelectric factor and electromechanical coupling coefficient [5]. Nevertheless it has a good flexibility and suppleness. Some polymers such as PVDF in alpha phase, it is not have piezoelectric properties, so the formation of the composite has the flexibility afforded by the polymer matrix together with the ferroelectric and piezoelectric properties provided by the PZT ceramics. In the study by composites is important to refer to the connectivity that is as the phases are arranged in the composites. Among the patterns can be highlighted 0-3 connectivity, which is a simpler model and have been studied in the literature [6, 7] which the polymeric matrix that is self-connected the three dimensions. There is no contact between the ceramic grains[8]. This study we aimed to optimize the processing to obtain the composite PZT/PVDF with connectivity 0-3 and included a third phase in this composite, the polyaniline (PAni) as conducting polymer.

II. EXPERIMENTAL PROCEDURE

A. Synthesis methods:

Powder of $Pb(Zr_{0,52}Ti_{0,48})O_3$ (PZT) was prepared by polymeric precursor method (PPM) as previously described in the paper submitted [9]. Pure PZT was prepared from the metal citrate complex which was polyesterified in ethylene glycol. Most of the organic matter was subsequently eliminated at temperatures as low as 300 °C, and a dark residue containing reactive oxides with well-controlled stoichiometry was formed. The formed porous product was crushed and heated in an alumina crucible at 800 °C for 4 hours to eliminate organic material residues and a perovskite-structured material was obtained.

B. Coating of PZT with the conductive polymer PAni

To do the coating of PZT particles was used 60 mL of hydrochloric acid 1 $mol.L^{-1}$, 3 mL of distilled aniline and 10g PZT. This mixture stayed for 3 minutes at ultrasound to promote homogenization and after that was added in a beaker containing 0,096 g of ammonium persulfate oxidant, 40 ml of hydrochloric acid 1 $mol.L^{-1}$ under stirring and controlled temperature of 2 °C for a period of 2 hours. The green color characteristic of protonated PAni is observed. It was then washed with ammonium hydroxide 0.1 $mol.L^{-1}$ (deprotonation) and then these particles were added in a solution with a pH around 3.7 with stirring for a period of 16 hours to reprotonation. These particles of PZT-Pani-rp were dried at room temperature.

C. Preparation of composite PZT-PAni-rp/PVDF

The PZT-PAni-rp particles were mechanically mixed with PVDF powder and after that hot pressed at 190°C between sheets of Kapton using about 11.4 MPa for 2 minutes. In this way we got composites with a thickness about 200 μm. To carried out the electrical characterizations gold electrodes were deposited by sputtering on both side of composite.

D. Characterizations

The materials were characterized by XRD (Rigaku, model D/Max-2500/PC) using CuKα radiation in the 2θ range from 20° to 80° with 0.02°/min, FE-SEM (JEOL, JSM-7500F). The diffuse reflectance spectra were obtained from solid samples using spectrophotometer Cary UV-vis NIR 500. For hysteresis measurements (Equipment Radiant Technology RT6000 HVA using an amplifier with the maximum potential difference of 4000 volts)

III. RESULTS AND DISCUSSION

Figure 1 show diffraction patterns of the thermally treated powders at temperatures 800°C/4h. XRD pattern peaks can be consistently indexed by the tetragonal structure (card JCPDS #33-0784) and also by the rhombohedral structure of the PZT (card JCPDS #73-2022). This result was expected for Zr/Ti (52/48) molar ratio used in this work because it is in the morphotropic phase boundary [10] which ensures the coexistence of the two crystalline structures of PZT.

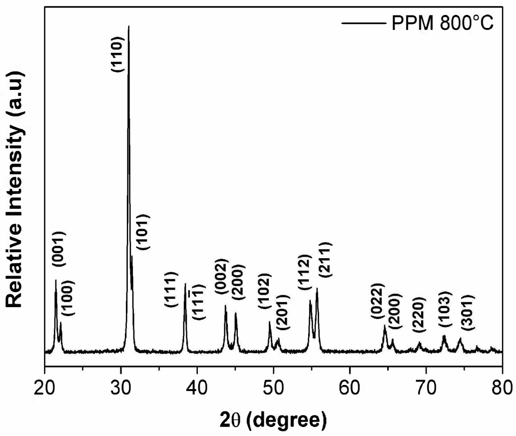

Figure 1. XRD patterns of PZT powder (48/52) obtained by the PPM at 800ºC/4h.

Figure 2(a) shows FE-SEM images of PZT powders obtained by PPM calcinated at 800°C. Figure 2(b) b the PZT is coating with polyaniline. The powder prepared by PPM is composed of micro-sized rounded particles; this structure forms large agglomerates. Figure 2(c) can be observed to cutting the composite film cross section and the optimum thickness was found for this study of approximately 200 microns. The Figure 2(d), it is possible to observe the PZT particles coated with PAni immersed in the PVDF matrix.

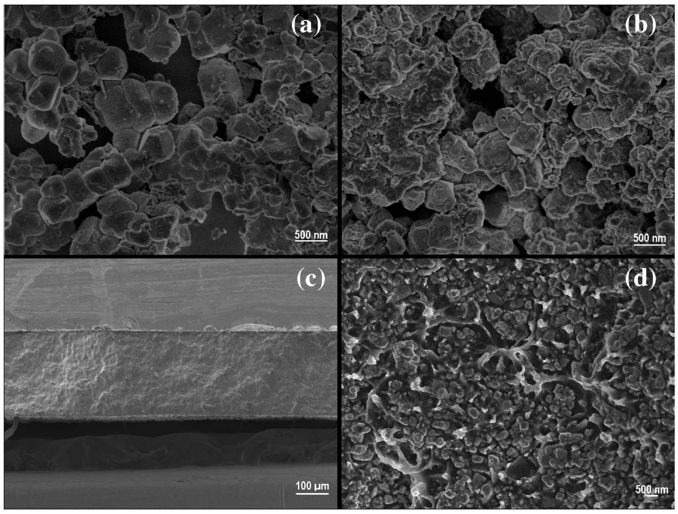

Figure 2. (a) SEM images of PZT powder obtained by PPM calcined at 800°C/4h; (b) SEM images of PZT particles coated with PAni; (c) General vision for cross section of composite film; (d) Composite film PZT/PAni/PVDF.

Figure 3 indicate the values of the optical band gap were obtained based on Kubelka-Munk theory [11, 12] from data of UV-Vis absorbance spectra. The main reason to measure the band gap was to compare the values for PZT-PAni with PZT without PAni because the aim is to make the polymer less resistive without modify the piezoelectric characteristics of PZT particles. There was not observed significant variation in band gap value indicating that the coating with PAni not changes the piezoelectric properties of the particle.

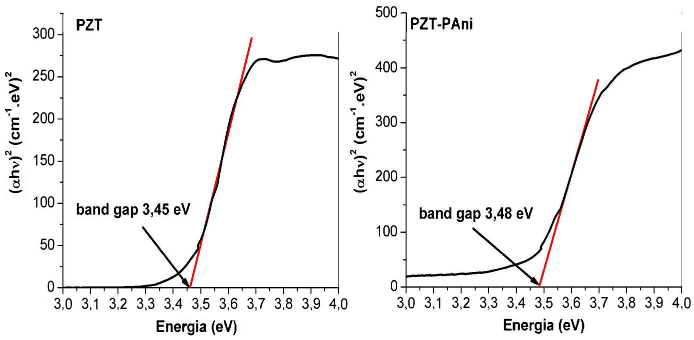

Figure 3. Absorbance Spectra in the UV–vis to PZT powder obtained by PPM (a) PZT without PAni; (b) PZT- PAni

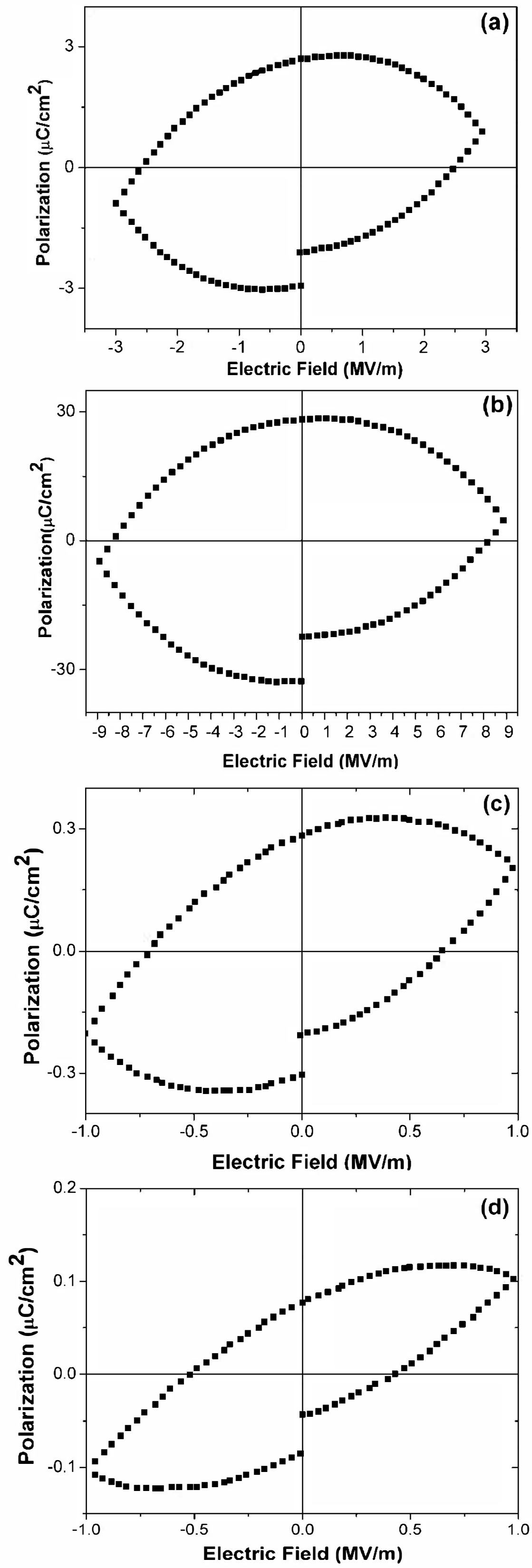

Figure 4. P x E hysteresis loops for PZT-PAni/PVDF composite. The Electric field applied in (a) 3 MV/m, (b) 9 MV/m. Electric field fixed 1 MV/m and frequency applied (c) 2.5 Hz and (d) 20 Hz.

Figure 4 shows the hysteresis loop acquired after to apply alternating electric field. In the Figure 4(a, b) the electric field applied was 3MV/m and 9 MV/m and we can see that remnant polarization, Pr, increases also from 2.7 $\mu C/cm^2$ to 28.2 $\mu C/cm^2$, respectively. The opposite effect can be observed when the field is kept fixed at 1MV/m and the values of frequency was 2.5 Hz and 20 Hz, Fig. 4(c, d).Therefore, when electric field is kept fixed increasing the frequency is observed the remnant polarization decrease. Charges have a relaxation time which must be considered, therefore, the use of lower frequencies that lead to a longer cycle with longer relaxation time, it promotes an increase in Pr. It was observed Pr = 0.28 $\mu C/cm^2$ and 0.08 $\mu C/cm^2$ value, respectively.

IV. CONCLUSIONS

In this study, were possible obtained PZT powders from PPM and to form the composite with PVDF polymer matrix. XRD patterns confirm PZT phases co-exist in the morphotropic phase boundary. FE-SEM images showed that particles with round forms were obtained by PPM. Based on the UV–vis absorbance spectra the PZT powders had not influence on the band gap energy with the coating of PAni. The ferroelectric properties were observed and charge carriers contributed to the rounding of the hysteresis loops.

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