

Pb(Zr,Ti)O₃ nanofibers produced by electrospinning process

Ebru Mensur Alkoy, Canan Dagdeviren and Melih Papila

Faculty of Engineering and Natural Sciences, Sabanci University, 34956, Tuzla, Istanbul, Turkey

ABSTRACT

Lead zirconate titanate (PZT) nanofibers are obtained by electrospinning a sol-gel based solution and polyvinyl pyrrolidone (PVP) polymer, and subsequent sintering of the electrospun precursor fibers. The PVP content of the precursor solution is critical in the formation of the fully fibrous mats. Scanning electron microscope (SEM) is used to examine the morphology of the precursor fibers and annealed PZT nanofibers. The diameters of the precursor PZT/PVP green fibers have increased with the aging of the precursor solution along with an increase in the viscosity. The viscosity of 500 mPa results in successful fibrous mats, yielding green PZT/PVP fibers with a diameter of 400 nm. The fiber mats are then sintered at 700°C. X-ray diffraction (XRD) pattern of the annealed PZT fibers exhibits no preferred orientation and a pure tetragonal perovskite phase. Preparation of piezocomposites by infusion of epoxy into the nanofiber mat facilitates successful handling of the fragile mats and enables measurements of dielectric properties.

INTRODUCTION

PZT is the most widely used ferroelectric material in ultrasonic transducers, non-volatile random access memory devices, microelectromechanical devices, sensor and actuator applications due to its high dielectric constant, high electromechanical coupling coefficient, and large remnant polarization [1,2]. This material can be processed into various forms such as bulk ceramics, thin films and fibers depending on application area. PZT in fiber form is appealing because of its increased anisotropy, improved flexibility and strength over monolithic PZT ceramics. Micron-scale PZT fibers are usually incorporated into a polymer matrix to obtain smart piezocomposite structures [3]. They can also be used as individual fibers in novel actuator and sensor devices, such as energy harvesting and self-powered in-vivo medical devices, high-frequency transducers, non-volatile ferroelectric memory devices [4]. Nano-scale PZT fibers are also expected to find wide applications particularly in nano-electronics, photonics, sensors and actuators [5].

There are a few methods to obtain PZT in fiber form. Sol-gel, dicing of the bulk ceramic, and extrusion, for instance, are applied to produce PZT fibers typically in the micron scale [6,7,8]. Electrospinning technique has recently gotten attention because the fibers at micro- and even nanoscale can be produced by this method. Nano-scale PZT fibers have been also produced by electrospinning method [9,10,11]. Zhou et al. [12] have produced PZT nanofibers and found that these fibers exhibit significant reversible piezoelectric strains under applied electric field. The level of this strain was measured to be about 4.2% which is reportedly six times larger than that observed in thin films.

The objectives of this study are to investigate the processing conditions in electrospinning of polymeric pre-cursor fiber mats followed by annealing for PZT nanofibers, to examine the

phase and morphology of these nanofibers prior and posterior to annealing process and to characterize the dielectric properties of the resultant PZT/epoxy composite.

EXPERIMENTAL

The PZT sol-gel precursor solution was prepared from lead acetate trihydrate, titanium isopropoxide and zirconium n-butoxide in n-butanol. 2-methoxyethanol was used as the main solvent [13]. Final concentration of the solution was 0.4 M and Zr/Ti ratio was 0.5:0.5. The process flow chart for the preparation of the sol-gel solution is given in Figure 1(a). Addition of two alternative polymers, namely, polyvinyl pyrrolidone (PVP) and polyvinyl alcohol (PVA) was investigated. Each polymer choice at various concentrations was added to the sol-gel solution. A home-made, electrospinning set-up allowing computer controlled polymer solution flow rate, as depicted in Figure 1(b), was used to prepare the pre-cursor nano-fiber mats. The PZT/ polymer precursor solution was electrospun on an aluminum foil collector and randomly oriented green fibers were collected. The applied voltage (12 kV) and the distance between the tip of the needle and the collector (10 cm) resulting in electrostatic field of 1.2 kV/cm were kept fixed after preliminary screening experiments. The effect of electrospinning parameters, such as the type of the polymer (PVP versus PVA) and associated polymer solution concentration (6 – 34 wt%), on the morphology of the green precursor fibers and mats were investigated in detail. Annealing regime ($T=700^{\circ}\text{C}$, heating rate= $0.5\text{-}5^{\circ}\text{C}/\text{min}$) was another crucial parameter studied in order to control the crystallinity and the final sintered morphology of the mats.

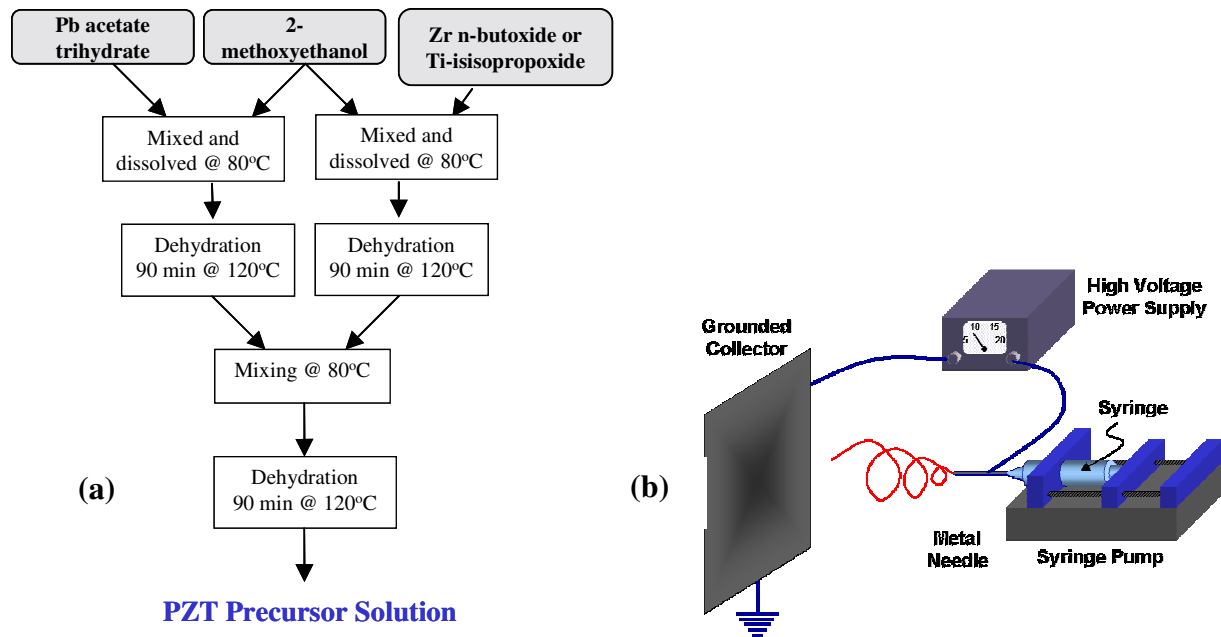


Figure 1. a) The process flow chart for the preparation of the precursor sol-gel solution and (b) schematic representation of the electro-spinning setup.

Thermo Gravimetric Analysis (TGA) was used to identify the crucial steps in the pyrolysis and sintering processes. Sintered PZT mats were characterized by X-ray diffraction

(XRD) and scanning electron microscopy (SEM). Dielectric properties of the PZT/resin composites were also measured by Impedance Analyzer.

DISCUSSION

Microstructural features of green fiber mats

The as-prepared green and sintered nanofiber mats were examined by scanning electron microscope (SEM). Images of the green PZT/PVA mats corresponding to various PVA ratios indicated that no uniform fibers could be collected; instead the mats were predominantly composed of nanoscale beads. In fact, using PVA as a transfer polymer has only led to a spray coating. As a result, PVA was not used as a carrier polymer in the rest of the study.

Figure 2 shows the PZT/PVP green mats by electrospinning at various PVP content in the solution. From Figure 2 (a) and Figure 2(b), small amount of PVP, such as 6wt% or 12wt%, was clearly seen to be insufficient to obtain fiber formation. On the other hand, the concentration of the PVP polymer in the solution exceeding 22wt% appears to result in fibrous mat with reasonable amount of beads. In particular, 28wt% PVP ratio resulting viscosity of 290 mPa was considered to be optimal as the bead-free uniform green PZT/PVP fibers were collected (Figure 2 (d)).

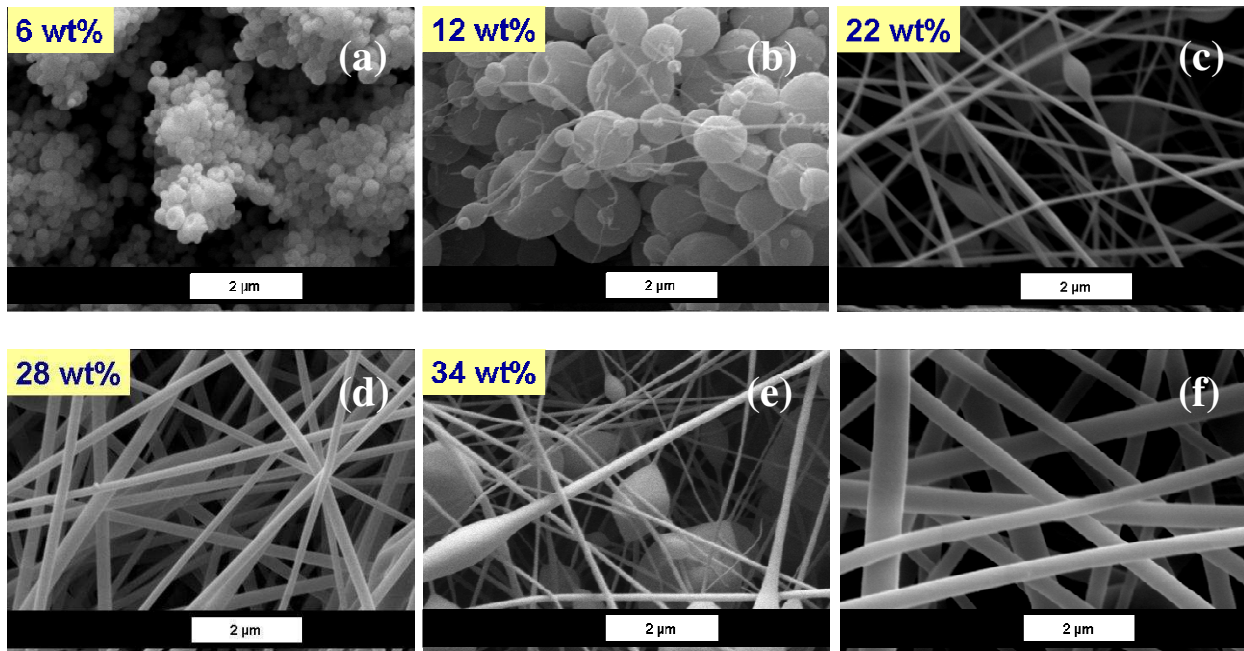


Figure 2. PZT/PVP green fibers from as-prepared solution with (a) 6wt%, (b) 12wt%, (c) 22wt%, (d) 28wt%, (e) 34 wt% PVP content and (f) PZT/PVP green fibers from 72 hour aged solution with 22wt% PVP content.

Additional viscosity measurements and investigation were carried out on the PZT precursor solution of 22wt% PVP in order to explore the effect of aging. The average diameters of the fibers prepared from aged solutions were also measured by SEM. Figure 3 shows the diameter of the PZT/PVP green fibers and viscosity of the precursor solution as a function of

aging time. It appears that aging the electrospinning solution for several days led to an increase in viscosity along with an increase in fiber diameters. From Figure 2(c), (f) due to correlation between the viscosity and the PVP content along with Figure 3, it is clearly seen that the viscosity of the solution has significant effect on formation of fibers and their size.

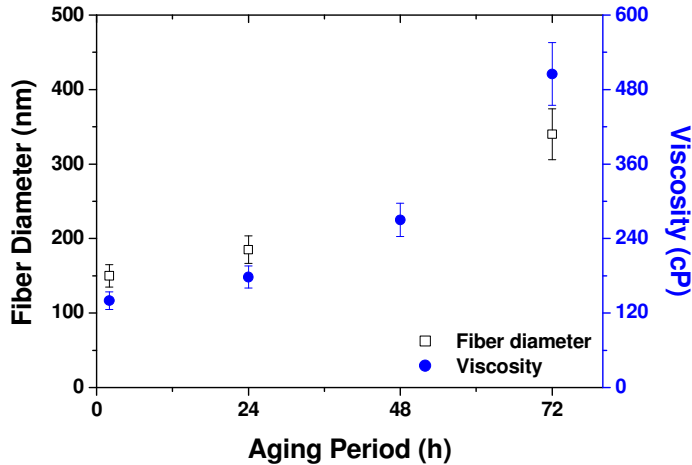


Figure 3. The effect of aging of the precursor solution prior to electrospinning

XRD study and microstructure of the sintered PZT fibers

The phase identification of the PZT nanofibers was performed using XRD. The XRD pattern of the PZT fibers annealed at 700°C for 1 hr indicates that these nanofibers are crystallized in the tetragonal pure perovskite phase with no preferred orientation (see figure 4).

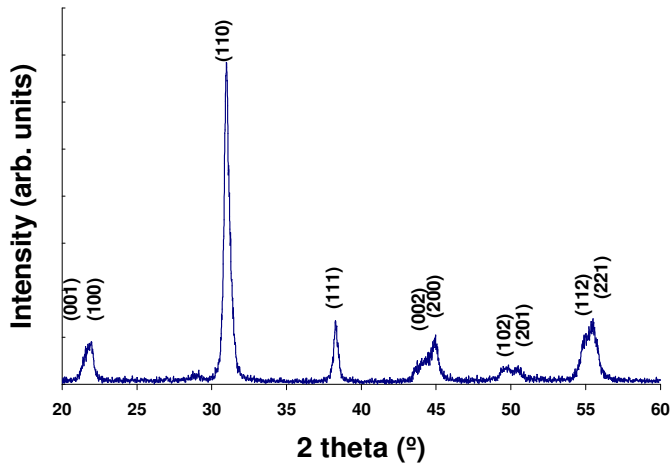


Figure 4. XRD pattern of the PZT nano-fiber mat sintered at 700°C for 1 hour.

Various annealing regimes (temperature = 600-700°C and heating rate = 0.5 – 5°C/min) were investigated to obtain dense PZT nanofiber mats. As depicted from Figure 2, precursor fibers have uniform cylindrical geometry with average diameter varying in the range of 200-350 nm, depending on electrospinning process parameters. After sintering, however, branching occurred between the fibers and the typical diameter shrunk to 100-250 nm range. **Figure 5(a)** and **(b)**

present the morphology of the annealed fibers prepared from the PZT precursor solution with 28 wt% PVP content sintered at 700°C using 5°C/min and 0.5°C/min heating rates, respectively. It is clear that heating regime has significant effect on the microstructure of the fibers.. At the slow heating regime (0.5°C/min) all organics are removed, leaving behind a uniform microstructure with fiber diameters varying between 120-160 nm, whereas fast heating regime (5°C/min) yields a more complex microstructure with a mixture of fibers and platelet-like grains.

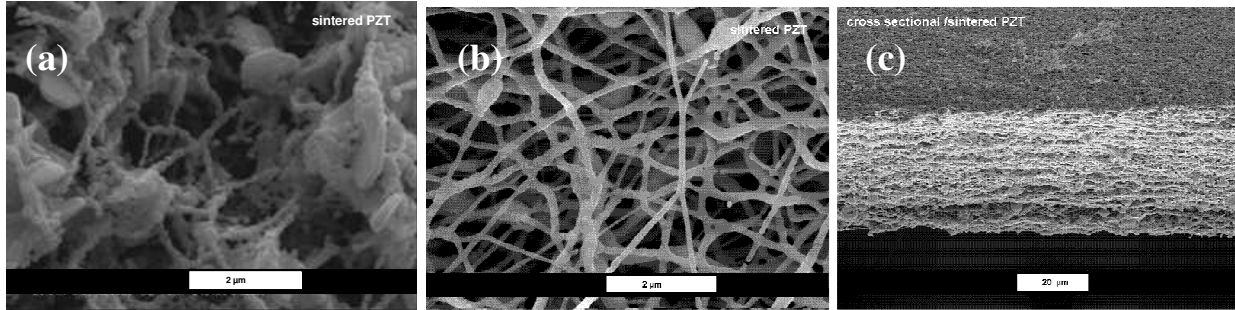


Figure 5. The micrographs of PZT fibers sintered at 700°C for 1 hour with (a) 5°C/min, (b) 0.5°C/min heating regime and, (c) Cross sectional view of the sintered PZT fiber mat.

Dielectric properties of the PZT nano-fiber/resine composites

After obtaining the PZT fibers, PZT/polymer matrix composite samples were prepared. T676NA vinyl ester, Accelerator D (styrene 10wt%, N-N dimethylaniline with >89 wt %), Accelerator G (styrene >80wt %) and Butanox LPT (methyl-ethyl ketone peroxide in diisobutyl phthalate) were mixed to obtain the polymer matrix of the composite. This solution was poured on to the sintered PZT fiber mat and the sample was dried 10 hours at room temperature. The dielectric constant and loss of the PZT/vinylester composites were then measured from 10 kHz to 1 MHz using an HP 41494A Impedance Analyzer (Figure 6).

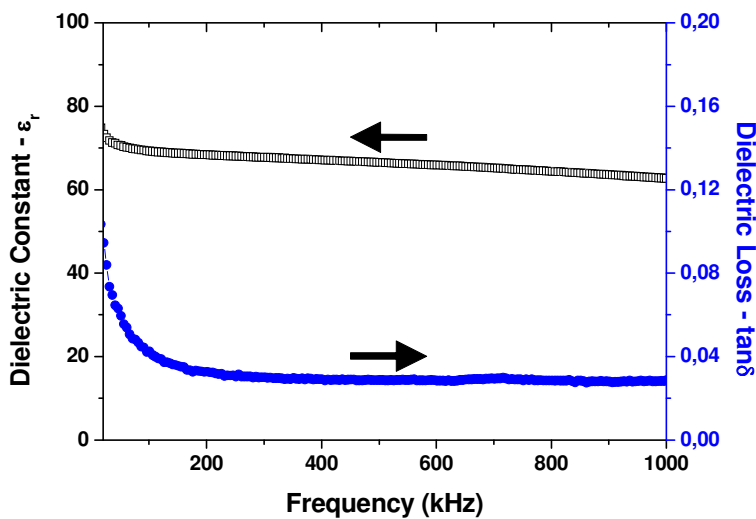


Figure 6. Dielectric constant and of the PZT/resin sample as a function of frequency at the room temperature.

Figure 6 shows dielectric behavior of the PZT/vinylester composite sample. The dielectric constant was found to be fairly stable and vary from 72 to 62 within the measurement range. This value is more than an order of magnitude higher than the dielectric constant of the resin itself. Comparing with bulk PZT [14], however, the composite has much lower dielectric constant. This is expected due to the low PZT fiber ratio in the composites. It may also be related to insufficient embedding or wetting of the fibers by the polymer matrix that may lead to voids within the composite.

CONCLUSIONS

In summary, PZT nanofibers were successfully obtained by electrospinning based process. Processing conditions and the annealing regime was found to have significant influence on the morphology of the PZT nanofiber mats. The dielectric constant and dielectric loss measured at room temperature is order of magnitude higher than polymer matrix. It is however much lower than bulk PZT values, indicating the fiber mat was not thoroughly embedded within the matrix. Improving the composite making procedure will further be studied.

ACKNOWLEDGMENTS

We kindly acknowledge the support for this work from The Scientific and Technological Research Council of Turkey - TÜBİTAK Grant 106M364 and post doctoral fellowship of Turkish Academy of Sciences.

REFERENCES

1. R. Maeda, J.J. Tsaur, S.H.Lee and M. Ichiki, *J. Electroceram.* **12**, 89 (2004).
2. N. Setter and R. Waser, *Acta Mater.* **48**,151 (2000).
3. J. Ouellette, *The Industrial Physicist* **2**, 4, 10 (1996).
4. S. Xu, Y. Shi and S. Kim, *Nanotechnology* **17**, 4497 (2006).
5. X.Y. Zhang, X. Zhao, C.W. Lai, X.G. Tang, and J.Y. Dai., *Appl. Phys. Lett.* **85**, 18, 4190 (2004).
6. R. Meyer Jr., T. Shrout and S. Yoshikawa, *J. Am. Ceram. Soc.* **81**, 861-868 (1998)
7. M. Zhang, I.M.M. Salvado and P.M. Vilarinho, *J. Am. Ceram. Soc.* **90**, 358-363 (2007)
8. K. Kitaoka, *J. Am. Ceram. Soc.* **81**, 1189-1196 (1998)
9. Y.Wang, R. Furlan, I.Ramos, J.J. Santiago-Aviles, *Appl. Phys. A* **78**, 1043-1047 (2004)
10. N. Dharmaraj, C.H. Kim, H.Y. Kim, *Mat. Lett.* **59**, 3085-3089 (2005)
11. S. Xu, Y. Shi, S. Kim, *Nanotechnology* **17**, 4497-4501 (2006)
12. Z.H. Zhou, X.S. Gao and J. Wang, *Appl. Phys. Lett.* **90**, 052902 (2007)
13. E. Mensur Alkoy, S. Alkoy and T. Shiosaki, *Jpn. J. Appl. Phys.*, **44**, 12, 8606 (2005).
14. P. K. Sharma, Z. Ounaies, V. V. Varadan and V. K. Varadan, *Smart Mat. And Str.*, 10, 878-883, (2001).