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Dielectric Parametric Study in Electrospun PLZT/PVDF Nanocomposite Membranes

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ABSTRACT

Electrospun lead lanthanum zirconate titanate (PLZT)/polyvinylidene fluoride(PVDF) nanocomposite-based membranes were fabricated using a traditional electrospinning process. Scanning electron microscopy (SEM) was utilized to observe the surface morphology of the electrospun nanofiber membrane. The dielectric parameters of the nanocomposite membranes, such as permittivity, electric modulus, ac conductivity, and Impedance in the frequency range of 10^3-10^6 Hz, were measured via an LCR measurement system. All-important electrical parameters were calculated from experimental measurements of capacitance and dissipation factor at ambient temperature. Frequency-dependent of, the above-cited parameters are presented.

Keywords

Electrospinning, Membrane, Nanofiber, Nanocomposite, PLZT, PVDF.

Introduction

Electroactive polymers (EAPs) and nanocomposite materials, as well as their potential applications, have been extensively studied by researchers in more recent years due to their relatively low-cost, ease of fabrication, and mechanical strength. Conventional or archaic energy methods have proven to be finite and hazardous, calling for more sustainable, cost-effective, and environmentally friendly energy solutions. There is an increased need for more effective and smaller-sized power systems that can be implemented in hostile, organic, or difficult-to-reach areas with the latest advancements of microelectronic systems. Nanocomposite research has provided researchers with a more remarkable ability to fabricate, enhance, modify, and optimize materials to meet the specific needs of various systems and ambient environments. PVDF is a highly non-reactive thermoplastic and semi-crystalline fluoropolymer. It is one of the more popular and extensively researched EAPs, exhibiting some of the best electroactive properties such as piezoelectric, pyroelectric, ferroelectric, and optoelectronic [1-3]. PVDF, in particular, has a piezoelectric coefficient 10x higher than other polymers. PVDF can be readily formed into a thin film profile using various fabrication methods and tends to serve as an excellent matrix polymer for dopants such as metals, oxides, carbon nanotubes, or other electroactive materials. PLZT/PVDF, in particular, is an impressively performing nanocomposite in dielectric behavior and is usually fabricated by solution casting techniques. However, there is a need for very flexible and nanocomposite thin films for use in biomedical and infrared sensors. This investigation examines the electrical parameters of nanocomposite MPLZT/PVDF fabricated using the electrospinning technique. Electrospinning can create sub-micron to nano-scale fibers, and some benefits include a large surface area to volume ratio, flexibility in surface functionalities, superior mechanical performance, and greater porosity [4,5]. A notable advantage of this particular electrospun nanofiber and membrane is the elimination of the need for electrical poling, as the applied voltage to the polymer solution during the electrospinning process allows for the direct formation of PVDF in its electroactive and ferroelectric β phase.

Experimental

Nanoparticles Fabrication

A proprietary Nanomiser(device is used to produce huge quantities of aerosols with controllable as well as narrow droplet size distributions. The modified PZT nanoparticles (named MPLZT) were procured and prepared by a propriety method to produce a variety of high purity ceramics, mixed metal oxides, and metal nanopowder utilizing a nanospray process from Micro-coating Inc., Georgia, USA. The micrograph below in Figure 1 exhibits the agglomeration of said particles. The particles themselves are less than 30 nm with relatively equal size.

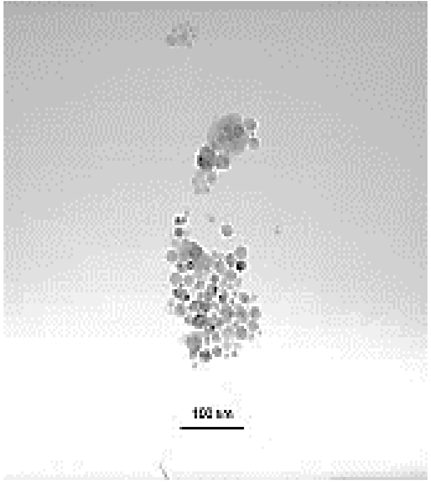

Figure 1: A transmission electron micrograph (TEM) of nanoparticles of MPLZT ($Pb_{0.93}La_{0.07}Zr_{0.3}Ti_{0.7}O_3$)

Fabrication of Electrospun Nanocomposite Membrane

PVDF powder (MW 534000, Sigma-Aldrich) was dissolved in dimethylformamide to yield a polymer solution with a 20 wt. %. The solution was then mechanically stirred and agitated for 3 hours at a constant velocity of 100 rpm on a 60 °C hot plate. The electrospinning solution was carried out with an Inovenso laboratory-scale electrospinning setup. A constant 20 kV voltage with the negative polarity was applied to an 18 gauge stainless steel -Teflon needle at a distance of 18 cm from a grounded collector plate. Flow rate of the polymer solutions for all samples was 6 mL/hr^{-1}, and the approximate time of total electrospinning was 60 min [6]. The ambient temperature during electrospinning was approximately 25 °C, with ambient humidity at roughly 60%. Nanofibers were collected on an aluminum foil collector plate and then removed. The resulting membranous nanofibers were cut to appropriate sizes, and copper tape with conducting adhesive (Kapton film) was applied to the film to form a full-face electrode capacitor ready for electrical testing. The composition of the PVDF-nanocomposite solution is tabulated in Table 1, including sample terminology.

Table 1: Composition of PVDF solution, DMF = Dimethylformamide, MEK = Methyl Ethyl Ketone, and SWCNT = single-walled carbon nanotubes.

PVDF (grams)	DMF/MEK (mL)	PLZT (grams)	Sample code
2.0	30	0.00	PVDF
2.0	30	0.074	MPLZT-2
2.0	30	0.212 +SWCNT	MPLZT-4

AC Parametric Characterization

The fabricated nanocomposites were placed in a copper sample holder. Electrical constants such as capacitance (Cp) and dissipation factor (tan δ) were measured in the frequency range of 10Hz to 1MHz at exponential frequency steps with the applied signal of 10V/cm at interval temperatures using a Quadtech 1920 LCR bridge setup interfaced with LABView software on a desktop CPU via general purpose interface (GPIB) connection [7]. Experimental values for capacitance (Cp) and dissipation factors (tanδ) were utilized for the calculation of other electrical parameters of the nanocomposite membranes.

Impedance

The real part of Impedance (eq. a) and the imaginary part of Impedance (eq. b) was calculated directly from experimental data obtained from our laboratory LCR system, providing measurements of capacitance (C_p) and dissipation factor (tanδ) using the following equations:

(a) $Z' = 1/(\omega x C_p x \tan\delta)$

(b) $Z'' = -1/(\omega x Cs)$

where $Cs = Cpx(1+\tan^2\delta)$ and signal frequency is represented by ω.

Permittivity

The real part of the dielectric constant (eq. c) as well as the imaginary part of the dielectric constant (eq. d) are calculated from the following equations and readings for permittivity:

(c) $\varepsilon' = (Cpxd)/(\varepsilon_0 xA)$

(d) $\varepsilon'' = \varepsilon' x\tan\delta$

where Cp, ω, tanδ, A, and d are the parallel plate capacitance of the sample, signal frequency, dielectric loss, electrode area, and thickness, respectively. The permittivity of vacuum is $\varepsilon_0 = 8.854\times10^{-12}$ F/m.

Electric Modulus

Electric Modulus, the real part (eq. e) as well as the imaginary component (eq. f) are calculated from the following equations and readings for permittivity:

(e) $M' = \varepsilon'/(\varepsilon'+\varepsilon'')$

(f) $M'' = \varepsilon''/(\varepsilon'+\varepsilon'')$

AC Conductivity

AC conductivity (g) is calculated using the following equations and readings for imaginary dielectric constant and permittivity of vacuum:

(g) $\sigma_{AC} = \varepsilon o x \omega x \varepsilon''$

where the permittivity of vacuum is $\varepsilon_0 = 8.854\times10^{-12}$ F/m.

Surface Morphology

Fabricated fibers were coated with a thin film of gold and examined at an accelerating voltage of 2kV with 5000X magnification. Scanning electron microscopy (SEM) was utilized to observe the surface morphology of the electrospun nanofiber membrane [6]. An SEM image of the electrospun PVDF fiber can be seen below in Figure 2. The fibers are randomly oriented and form a web of nanofibers, primarily due to the Taylor cone dispersion of the polymer during the electrospinning process.

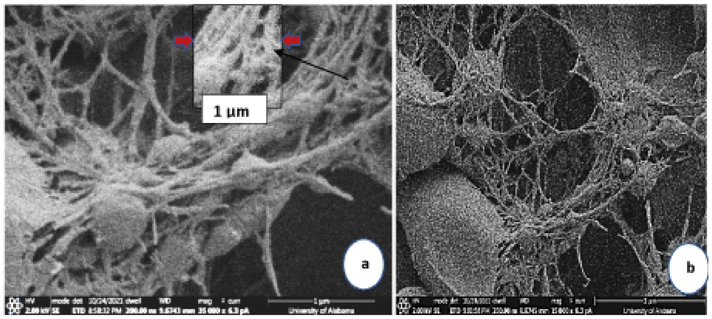

Figure 2: Scanning electron micrographs of electrospun nanocomposite membranes (a) PVDF (b) MPLZT-4.

Results and Discussion

Impedance

The pure PVDF nanomembrane in Figure 3 exhibits the most significant magnitude impedance for all of the developed films. All films show a general decrease in Impedance with the increase in the magnitude of frequency [8].

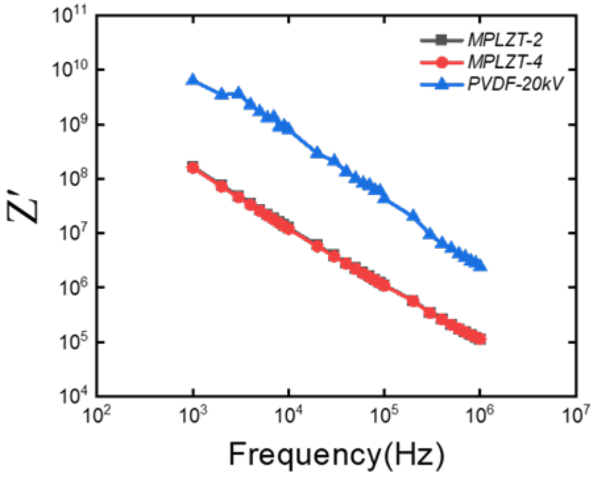

Figure 3: Real part of relative Impedance of MPLZT and PVDF—20kV electrospun nanocomposite membrane.

Permittivity

The results for the real part of the dielectric constant of the electrospun films are presented in Figure 4. The pure PVDF-20kV film shows the lowest value of this parameter in particular. Next in order of increasing value is the MPLZT-2 nanomembrane. MPLZT-4 proves to be the highest performing film in terms of real dielectric constant. The nanomembranes with added electroactive material to the PVDF matrix exhibit a slight downward linear trend while the pure membranes remain more consistent. These results suggest that, with an increasing load of dopants, the most primary dielectric constant can be increased.

The results for the imaginary dielectric constant found in Figure 5 follow the same general order of magnitude as the real part. However, a slight linear trend appears to be reversed as the doped membranes have a slight trend upwards this time. These results reflect the real part of the dielectric constant of these films and are therefore complementary, which is a good indicator of proper electrical activity in the membranes we have fabricated via electrospinning.

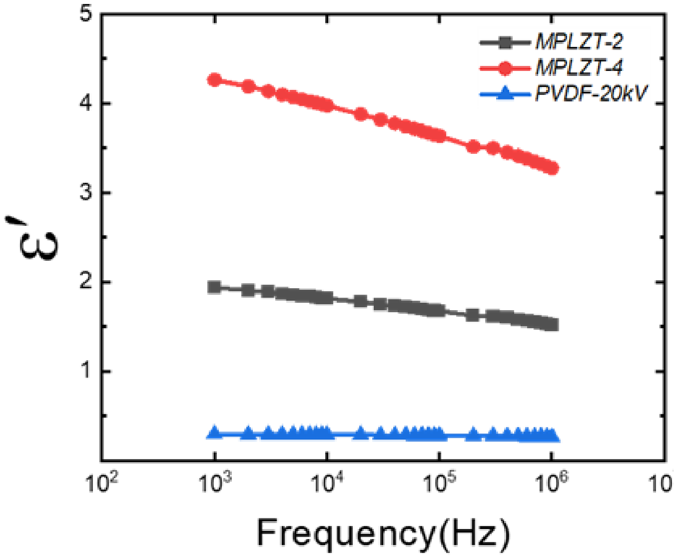

Figure 4: Real part of relative permittivity of MPLZT and PVDF—20kV electrospun nanocomposite membrane.

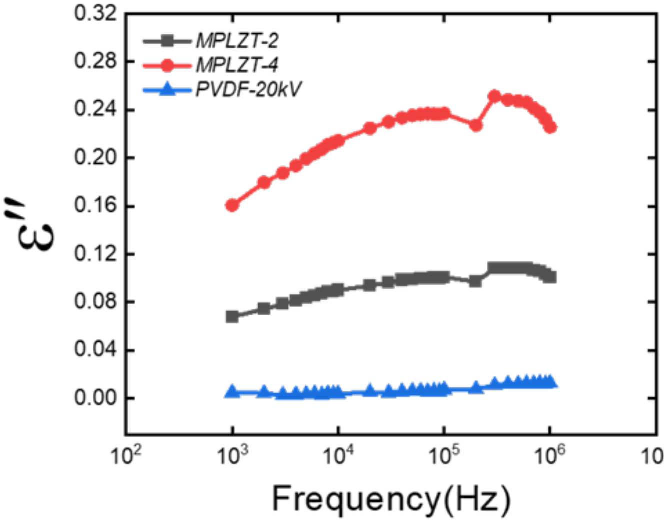

Figure 5: Imaginary part of relative permittivity of MPLZT and PVDF—20kV electrospun nanocomposite membrane.

Electric Modulus

The data obtained for both the real and imaginary parts of the electric modulus can be found in Figure 6 and Figure 7 respectively. The PVDF-20kV films shows the largest values for both real and imaginary electric modulus.

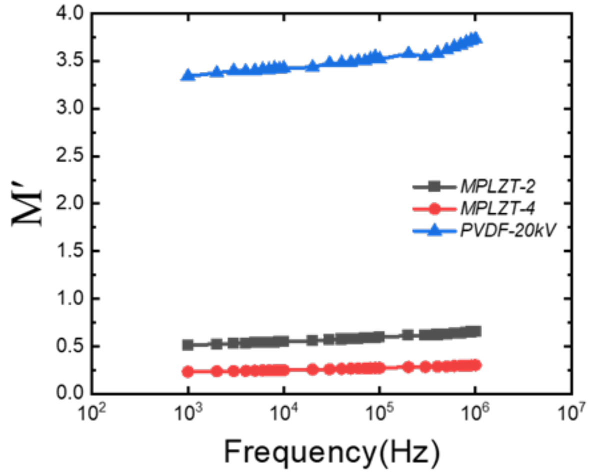

Figure 6: Real part of the complex electric modulus of MPLZT and PVDF-20kV nano-spun films.

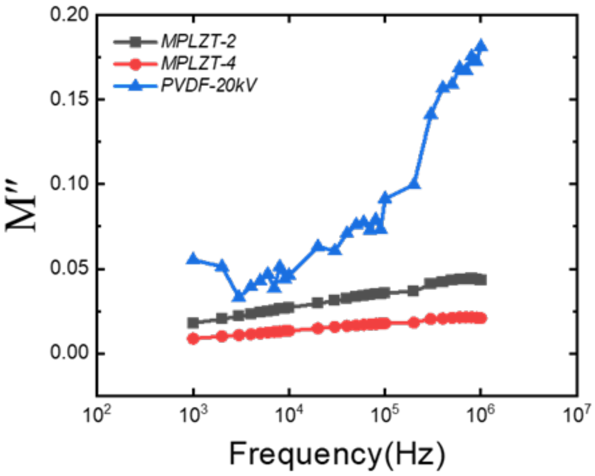

Figure 7: Imaginary part of the complex electric modulus of MPLZT and PVDF-20kV nano-spun films.

AC Conductivity

Favorable values were obtained for alternating current conductivity for the electrospun membranes, as presented in Figure 7. The data plots for all of the analyzed nanomembranes exhibit an increasing and one-to-one linear relationship in the experimental frequency range and at relative ambient body temperature. An increase in AC conductivity with the addition of lead zirconate titanate into a PVDF polymer matrix can also be observed as the highest performing membrane is MPLZT-4. It is worth mentioning that the conductivity of the nanocomposite depends on the microscopic and macroscopic conductivities. The microscopic conductivity depends upon the doping level, conjugate length, or chain length. The macroscopic conductivity depends upon the composite membranes' inhomogeneities and the embedded nanoparticles' orientation [8-10].

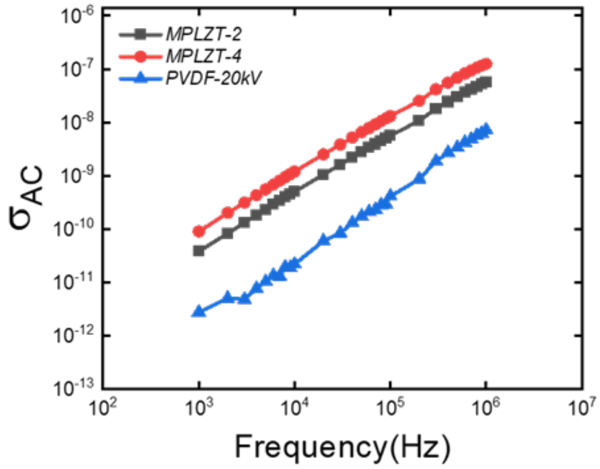

Figure 8: AC conductivity of MPLZT and PVDF-20kV nanocomposite membranes.

Conclusion

For the present investigation, the traditional electrospinning process produced PLZT/PVDF nanocomposite membranes. PVDF is an extensively researched electroactive polymer known for its impressive mechanical and dielectric performance and applications such as sensors, transducers, and energy harvesters. However, no data exists in the literature on doped nanocomposites membranes. In general, investigation shows that the addition of PLZT to the polymer matrix of PVDF matrix enhances the dielectric response of the nanocomposite films. Electrospun films in particular, resemble biological tissue as they are more membranous in terms of internal structure and exhibit greater porosity than other conventional electroactive polymers fabricated by different methods. The study of dielectric and alternating current behavior of electrospun nanocomposite films such as PLZT/PVDF can prove useful in the development of more advanced biomedical applications in the form of tactile sensors or energy harvesters developed with the ambient human body in mind.

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Institutional Review Board

Human subjects were not involved in this study.

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