Investigation on characteristics of PVDF/ZnO nanocomposite films for high-k capacitors

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ABSTRACT

Aims: To investigate the dielectric and electrical properties of nanocomposite films for their application as high-k capacitors

Study design: The ferroelectric polymer PVDF is doped with ZnO nanoparticles (ZnO-NP) to study the dielectric properties

Place and Duration of Study: Material Science laboratories at the Department of Physics, Chemistry and Mathematics at Alabama A&M University during the months from February 2013 to December 2013

Methodology: In this work, homogeneous ceramics-polymer nanocomposites consisting of zinc oxide (ZnO) nanoparticles as fillers and poly(vinylidene fluoride) (PVDF) polymer as matrix have been prepared using a solution casting process. The temperature dependency of the dielectric permittivity of the nanocomposite films suggests that the introduced ZnO phase and interface areas contribute to the improvement of the dielectric response.

Results: In comparison with pure PVDF film, dielectric permittivity of the nanocomposite with a small amount of filler volume fraction (8.6%) significantly improved by two times. Thus, it can be predicted with higher concentrations of ZnO nanoparticles, composite films will have higher dielectric constants and warrants in applications as high-k capacitors for printed organic electronics.

Conclusion: The nanocomposites thick films by embedding ZnO-NPs in PVDF matrix have been successfully fabricated. The nanocomposite displayed better dielectric properties than the pristine PVDF specimens did. As expected, the effective dielectric constant of PVDF increased when it was mixed with ZnO-NPs over the entire temperature range investigated. However, as the concentration of ZnO-NPs increased, the dielectric constant for the PVDF/ZnO-NPs nanocomposite doubled over that of pure PVDF. It can be concluded nanocomposites fabricated with higher concentration of ZnO-NPs have a potential to meet both present and future technological demands of high-*k* dielectrics and embedded capacitors/organic substrates.

Keywords: Poly(vinylidenedifluoride), Zinc Oxide, Dielectric Constant and Capacitors

1. INTRODUCTION

The thermal attributes of physical systems have been a major topic of investigation for centuries. With the advent of nanophysics and nanotechnologies, including microelectronics, high-speed data processing techniques, energy storage, thermal sensing and imaging have become useful diagnostic tools in medical, environmental, industrial, and military arenas [1].

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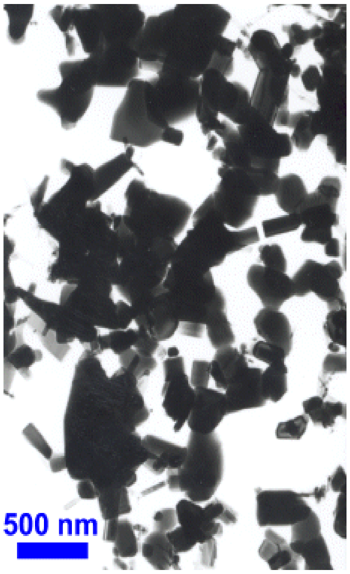
Composite materials containing metal nanoparticles have attracted great attention due to their unique chemical, thermal and physical properties, which make them applicable in various walks of science such as embedded capacitor [2], electronic packaging [3], capacitors/piezoelectric transducers [4], multilayer ceramic capacitors [5], microwave substrate applications [6], piezo-sensitive and chemocapacitive sensors [7, 8]. Depending upon the requirement of users, the dielectric constant of the composites can also be tailored by varying type of matrices. Polymer matrix composites containing ferroelectric ceramic powder are widely studied because of their tailored dielectric, thermal, mechanical properties and easy processing [9]. Poly(vinylidene fluoride) (PVDF) is chemically, thermally, and mechanically very stable material which has excellent ferroelectric, pyroelectric, and piezoelectric properties [10, 11]. PVDF could be applied to motion and infrared sensors, supercapacitors, actuators, and memory devices because of these properties [12, 13]. Nanocomposites of electroactive ceramic and a ferroelectric polymer are very appropriate for many applications as their properties can be easily tailored to suit particular performance requirements [14]. To achieve various performance objectives, high-dielectric constant ferroelectric ceramics have been used as fillers in polymers by researchers such as lithium tantalite ($LiTaO_3$) in P(VDF-TrFE) [15], Barium Titanate ($BaTiO_3$) in PMMA [16], Lead Zirconate Titanate (PZT) in PVA and PVDF [17], and Carbon nanotubes (CNT) in PVDF [18].

The ferroelectric polymers doped with metallic fillers possess higher dielectric constants making them effective in their applications as high-k capacitors with higher dielectric loss [19]. Higher dielectric loss is not desirable in electronic and charge storage devices. In order to enhance the dielectric constant filler with high dielectric constant is desired. The systematic study on PVDF (with low dielectric constant)/ZnO (with high dielectric constant) has been not carried out so far. The ferroelectric PVDF when doped with zinc oxide nanoparticles (ZnO-NPs) can yield better dielectric properties and improved capacitances due to unusual physical and chemical properties resulting from the nano-size and ultra-large surface area. Thus, it was thought worthwhile to investigate PVDF/ZnO-NPs nanocomposite. In the present work, the dielectric properties of the PVDF/ZnO-NPs nanocomposite films were measured as a function of temperature and filler volume fraction. High dielectric constant and low dissipation factor in the nanocomposite is realized with negligible frequency dependence that ensures a promising application for the embedded capacitors/organic substrates.

2. EXPERIMENTAL DETAILS

2.1 Materials - For this research, the ferroelectric polymer material used was PVDF, and the ceramic material was zinc oxide nanoparticles (ZnO-NPs, with a diameter of ~50nm), obtained from sigma Aldrich and MTI Corporation respectively. Both materials are dielectric, but with quite different characteristics. PVDF has a low density (ρ = 1.78 gm/cm^3) compared to the ZnO (Purity: 99.9+%, APS: 50 nm, SSA: 4.9 - 6.8 m^2/g, Color: white, Morphology: irregular as shown in TEM micrograph (Fig.1a), Bulk density: 0.25 - 0.4 g/cm^3, True density: 5.606 g/cm^3). Fig. 1b shows the X-ray diffractogram of ZnO NPs depicting hexagonal crystallographic system.

2.2 Fabrication - The polymer-composite films were fabricated via solution-cast technique. Firstly, the PVDF was dissolved in a suitable amount of methyl-ethyl-ketone (MEK) or dimethylformamide (DMF) at 60ºC. A requisite amount of composite materials ZnO NPs (with diameter ~50nm) was then added to form polymer-composite matrix. This mixture was ultrasonically agitated for several hours to break-up the agglomerates and disperse the guest concentrations uniformly. The obtained composite solution was then poured into petri dishes for the solvent to evaporate. The films were annealed for 4-5 hours in air at room temperature. To form a parallel plate capacitor, silver conducting electrodes were deposited on opposite faces of the composite film, and were cut into 10 mm x 10 mm sized element for testing. The electroded samples were poled at 100°C with 5 kV/cm voltages for 2 hours. After the poling process, the samples were short-circuited and annealed at 50°C for 2 hours. A detailed fabrication process of the composite films is compiled in Table 1.



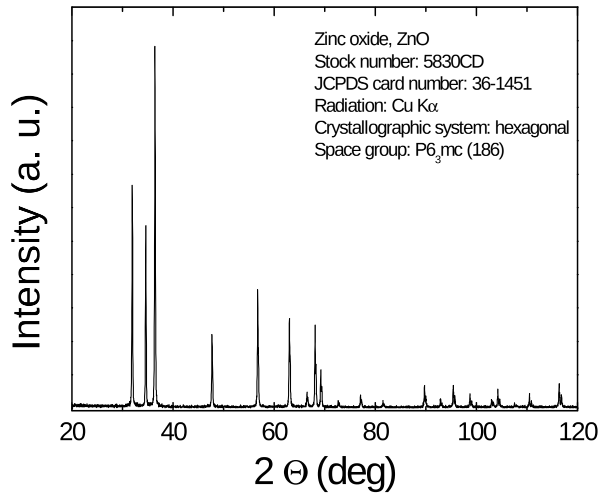


Fig 1. (a) TEM image of ZnO NP, (b) XRD spectra of ZnO NP

Table.1. A Nanocomposite Film (PVDF + ZnO NPs) fabrication processes

Specimen	ZnO (g)	PVDF (g)	DMF (ml)	Volume Fraction (Φ)	Stir (hrs)	Temp (℃)	Thickness (cm)
PVDF-1		1	10	0	4.5	60	0.071
ZnO-2	0.1	1	10	3.17%	4.5	60	0.079
ZnO-3	0.2	1	10	5.9%	4.5	60	0.0682
ZnO-4	0.3	1	10	8.6%	4.5	60	0.089

2.3 Characterization - Labview interfaced Quadtech LCR Bridge network was used to conduct the dielectric study, and Nicolet 10 FTIR to study the normal vibrational modes of PVDF and nanocomposites. The real and imaginary parts of the dielectric permittivity (ε' and ε'') were obtained by measuring terminal parallel capacitance C_P and loss tangent at a fixed measurement frequency of 1KHz using Quadtech 1920 LCR meter. The LCR meter is equipped with home-made three terminal sample holder having large thermal capacity ans measurements were taken during heating run with Barnant temperature controller. A K-type thermocouple was installed near the sample and temperature was measured with the help of HP 34970A digital multi-meter. The complete experimental set-up is shown in Fig.2.

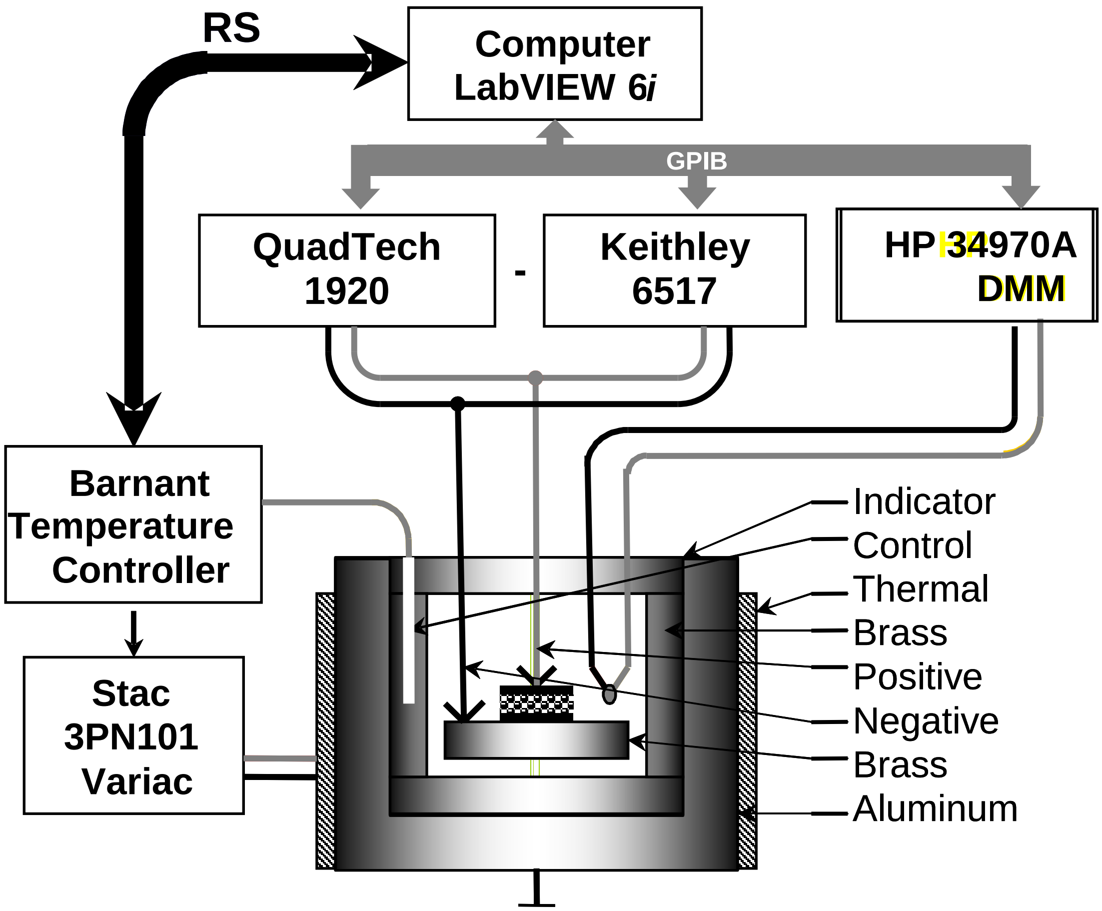


Fig 2. Experimental Set-up for dielectric measurement

3. RESULTS AND DISCUSSION

Figure 3 shows the temperature dependence of the dielectric constant of the composite with various wt% of ZnO-NP in PVDF polymer. The figure depicts that all the poled samples were functional. The variations of dielectric permittivity with temperature are described at 1KHz for various concentrations of ZnO-NPs. These observations prove that the electric properties of the polymer improve by adding ZnO-NPs. The increase in the dielectric constant of ZnO is due to the conductive properties of ZnO-NPs. The specimens, ZnO-2 and ZnO-3 are observed to have closer dielectric constants due to their thicknesses. Table 1 describes the thickness of ZnO-2 as 0.079cm and ZnO-3 measures at 0.0682cm, which justifies that greater concentration of ZnO-NP yields higher dielectric constants, notwithstanding the dielectric permittivity's directly proportionality to thickness. However, upon optimizing the fabrication procedure for thickness, the similar properties between ZnO-2 and ZnO-3 can be mitigated. It is evident from fig 3, that dielectric constant increases with the increase of ZnO wt% in the polymer. PVDF:ZnO, the composite with the highest wt% among the three samples investigated, shows the highest dielectric constant at a given temperature. From the variation of dielectric permittivity with temperature with various wt% of ZnO-NP in PVDF polymer, it was also evident that the dielectric permittivity of all the composites is higher than pure PVDF. The permittivity variations of the PVDF and ZnO doped PVDF composites as a function of frequency, with temperature and volume fractions are detailed. These results indicate that the introduced ceramic fillers and interface areas have positive influences on the structure of the polymer matrix and contribute to the enhancement of the dielectric responses and energy storage properties of the nanocomposites. The dielectric properties were studied as a function of ZnO-NPs loading and frequency.

Table 2. PVDF, PVDF/ZnO-NPs specimen dimensions and electrical properties at 1KHz

Specimen	Thickness (cm)	Area (cm^2)	Є', at 23^0C	Capacitance (pF), at 23^0C
PVDF -1	0.071	0.713	7.75	6.88
ZnO - 2	0.079	0.795	11.89	10.58
ZnO - 3	0.0682	0.743	12.68	12.22
ZnO - 4	0.074	0.784	15.45	14.48

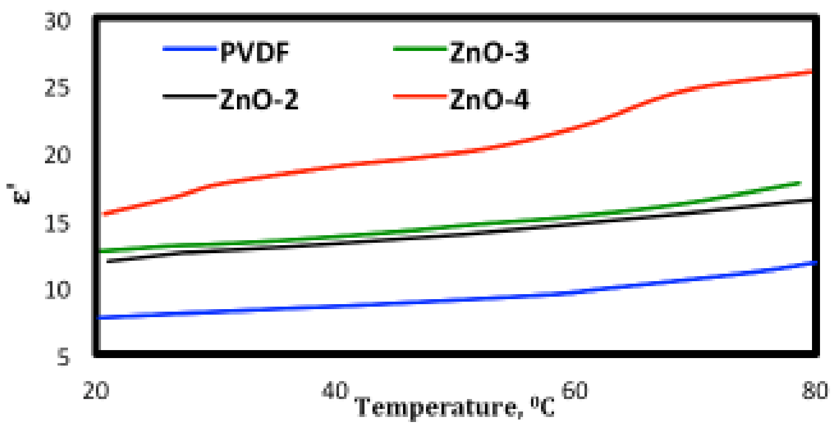


Fig 3. Dielectric constant vs. temperature for various concentrations of ZnO

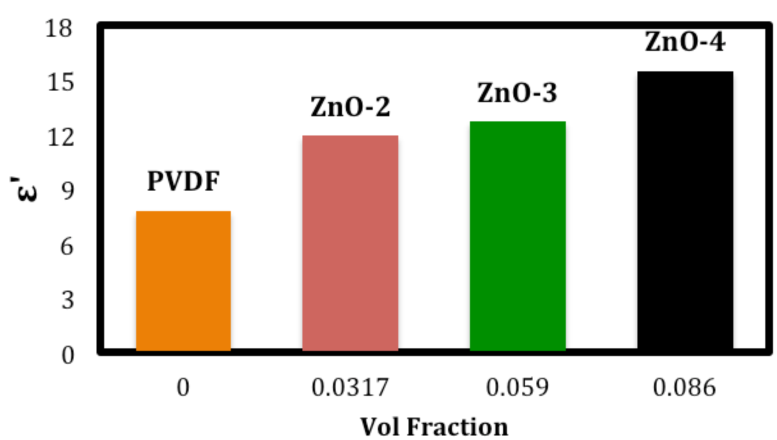


Fig 4. Dielectric constants for composites as a function of volume percent of ZnO

To measure the permittivity of the nanocomposites, initially they were electroded with silver paint and cured at 60^0C for 1h. The dielectric constants were measured as a function of frequency from 20^0C to 80^0C and the capacitance (C) was evaluated from

$$C= \varepsilon_o \varepsilon_r A/d, \quad (1)$$

where ε_o is the permittivity of vacuum and ε_r is the dielectric constant, d is the thickness of the film, and A is the area of the film. A mechanical profiler measured the thickness of the films. The results of dielectric constant and capacitance are presented in the table 2, which pave way for nanocomposite based high k capacitors.

The Table 2 shows the dielectric constant of the PVDF/ZnO-NPs composites as a function of filler ZnO-NP content. It can be seen from the figure 4 that the dielectric constant of the composites increases with increasing content of ZnO-NP in the PVDF matrix. The increased dielectric constants are due to the higher polarization of ZnO than that of PVDF matrix. And dielectric constant (ε') steadily increases with the increase of ZnO-NP content, which can be ascribed to a higher dielectric constant of filler relative to the polymer matrix. The dielectric constant and dissipation factor of 45 vol.% composite measured at 1 KHz are 12.638 and 0.0779 respectively. With well-controlled morphology, dielectric constant has been increased from 7.5 to 15 at 1KHz at room temperature, with the loading of ZnO-NPs. The PVDF+ZnO-NPs possess double the dielectric constant (ε^{l} =15.45) than that of the pristine PVDF (ε^{l}= 7.75) at 1kHz at room temperatures.

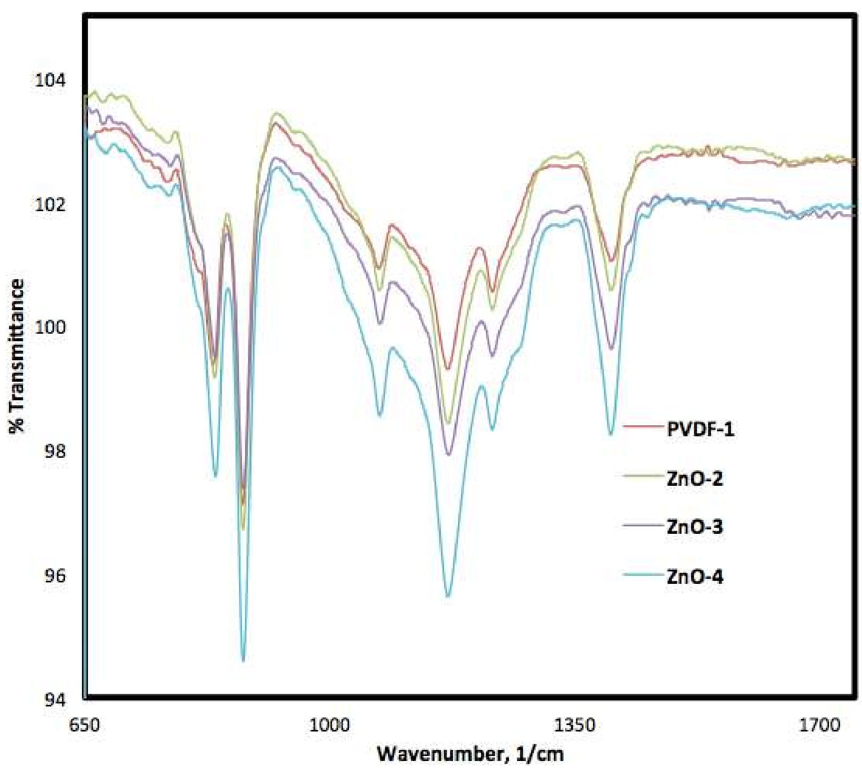


Fig 5. FTIR spectra of PVDF and PVDF/ZnO nanocomposites

The IR spectra of ZnO nanocomposites shown in the figure 5, has the identified reigns and are informative on the conformational isomerism of the chain, providing information on α and β phase content. A stretching frequency band appearing at 831cm^{-1} can be attributed to C-N band of DMF. The strong band appearing at 875 cm^{-1} can be correlated to C-O stretching, which could be due to delocalization of non-bonded electron pair from nitrogen atom that reduces double bond character of C=O stretching. A shoulder peak with low intensity appearing at 1066 cm^{-1} is attributed to the out-of-plane (C-H) bending. A sharp peak at 1162 cm^{-1} with high intensity corresponds to C-F band of PVDF. The peak with low intensity at 1225 cm^{-1} is confirmed for CH_2 rocking band. Another sharp peak with medium intensity appearing at 1396 cm^{-1} for CH_2 bending vibrations corresponds to CH_2 in plane bending. Since the concentration of ZnO is low in comparison with PVDF and DMF, the peaks for ZnO stretching and bending between 360 cm^{-1} to 420 cm^{-1} appear to be suppressed.

4. CONCLUSION

The nanocomposites thick films by embedding ZnO-NPs in PVDF matrix have been successfully fabricated. The nanocomposite displayed better dielectric properties than the pristine PVDF specimens did. As expected, the effective dielectric constant of PVDF increased when it was mixed with ZnO-NPs over the entire temperature range investigated. However, as the concentration of ZnO-NPs increased, the dielectric constant for the PVDF/ZnO-NPs nanocomposite doubled over that of pure PVDF. It can be concluded nanocomposites fabricated with higher concentration of ZnO-NPs have a potential to meet both present and future technological demands of high-*k* dielectrics and embedded capacitors/organic substrates.

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AUTHORS' CONTRIBUTIONS

" 'Dr. Chilvery', performed the statistical analysis, and wrote the first draft of the manuscript. 'Dr. Batra' designed the study, wrote the protocol and 'Mr. Thomas' managed the analyses of the study. All authors read and approved the final manuscript."

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