Investigation on characterisitcs 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 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 thru 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 ZnONPs 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/ZnONPs nanocomposite doubled over that of pure PVDF. It can be concluded nanocomposites fabricated with higher concentration of ZnONPs 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

Poly(vinylidene fluoride) (PVDF) is chemically, thermally, and mechanically very stable material which has excellent ferroelectric, pyroelectric, and piezoelectric properties. PVDF could be applied to motion and infrared sensors, supercapacitors, actuators, and memory devices because of these properties[1]. 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 [2]. To achieve various performance objectives, high-dielectric constant ferroelectric ceramic have been used as fillers in polymers by researchers such as lithium tantalite ($LiTaO_3$) [3], Barium Titanate ($BaTiO_3$) [4], Lead Zirconate Titanate (PZT) [5], and Carbon nanotubes (CNT) [6].

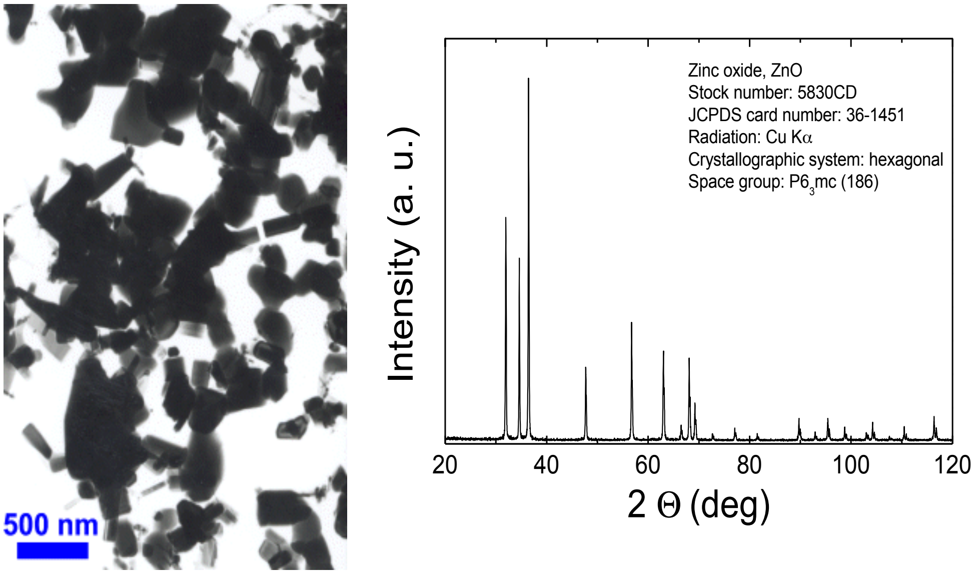
The ferroelectric polymers doped with metallic fillers possess higher dielectric constants making them effective in their applications as high-k capacitors. Ferroelectric polymers, like PVDF when doped with zinc oxide nanoparticles (ZnONPs) can yield better dielectric properties and improved capacitances due to unusual physical and chemical properties resulting from the nano-size and ultra-large surface area. In the present work, the dielectric properties of the PVDF/ZnONPs nanocomposite films were measured as a function of temperature and filler volume fraction.

With well-controlled morphology, dielectric constant has been increased from 7.5 to 15 at 1KHz in room temperatures, 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. The frequency dependence of the electrical properties of the PVDF+ZnO nanocomposite thin films was studied in the frequency range of 10Hz to 100KHz. The permittivity of the PVDF, various concentrations of ZnO doped PVDF as a function of frequency, and the variations of AC conductivity of the nanocomposites with temperature and volume fractions of ZnO 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 loading and frequency. The high dielectric constant and low dissipation factor obtained with negligible frequency dependence ensures a promising application for the embedded capacitors/organic substrates.

2. EXPERIMENTAL DETAILS

2.1 Materials - For this research, the polymeric material used to prepare the nanocomposite thick a film was PVDF, and the ceramic material was zinc oxide nanoparticles (ZnO-NPs, with a diameter of ~50nm), both 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. Silver electrodes were deposited on the composite film, and were cut into 10 mm x 10 mm sized element for testing. The electroded samples were poled at 100^0C with 5 kV/cm voltages for 2 hours. After the poling process, the samples were short-circuited and annealed at 50^0C for 2 hours. A detailed fabrication processes are compiled in Table 1.



(a) **(b)**

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 (gm)	PVDF (gm)	DMF (ml)	Volume Fraction (Φ)	Stir (hrs)	Temp (°C)	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 Instrumentation - 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.

3. RESULTS AND DISCUSSION

The variations of dielectric permittivity with temperature are described at 1KHz for various concentrations of ZnO. These observations prove that the electric properties of the polymer improve by adding ZnO. The increase in the dielectric constant of ZnO is due to the conductive properties of ZnO-NPs.

Table 2. PVDF, PVDF+ZnO NPs specimen dimensions and dielectric 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

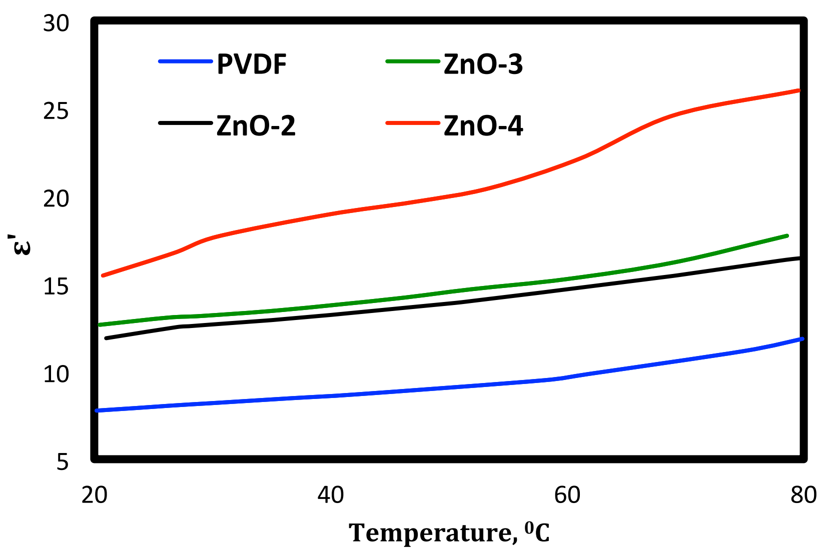


Fig 2. Dielectric constant vs. temperature for various concentrations of ZnO

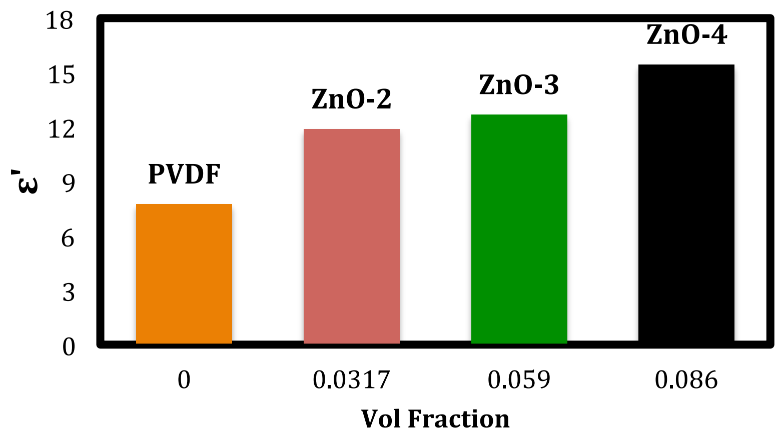


Fig 3. Dielectric constants for composites as a function of volume percent of ZnO

To measure the permittivity of the PVDF-ZnO NPs was 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

$$C= \varepsilon_o \varepsilon_r A/d, \tag{1}$$

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 volume fractions of nanocomposites were also considered to study their impact on dielectric constant and conductivity. The volume fraction (Φ) can be obtained by the below equation:

$$M^C = M^P (\rho^C / \rho^P) (\Phi/1- \Phi) \tag{2}$$

where M^C and M^P are the concentrations of ceramic and polymer respectively, and ρ^C and ρ^P are densities of ceramic and polymer respectively. The Table 2 shows the dielectric constant of the PVDF/ZnO composites as a function of ZnO content. It can be seen from the figure 3 that the dielectric constant of the composites increases with increasing content of ZnO in the PVDF matrix. The increased dielectric constants are due to the higher polarization of ZnO than that of PVDF matrix. The dielectric constant and dissipation factor of 45 vol.% composite measured at 1 KHz are 12.638 and 0.0779 respectively.

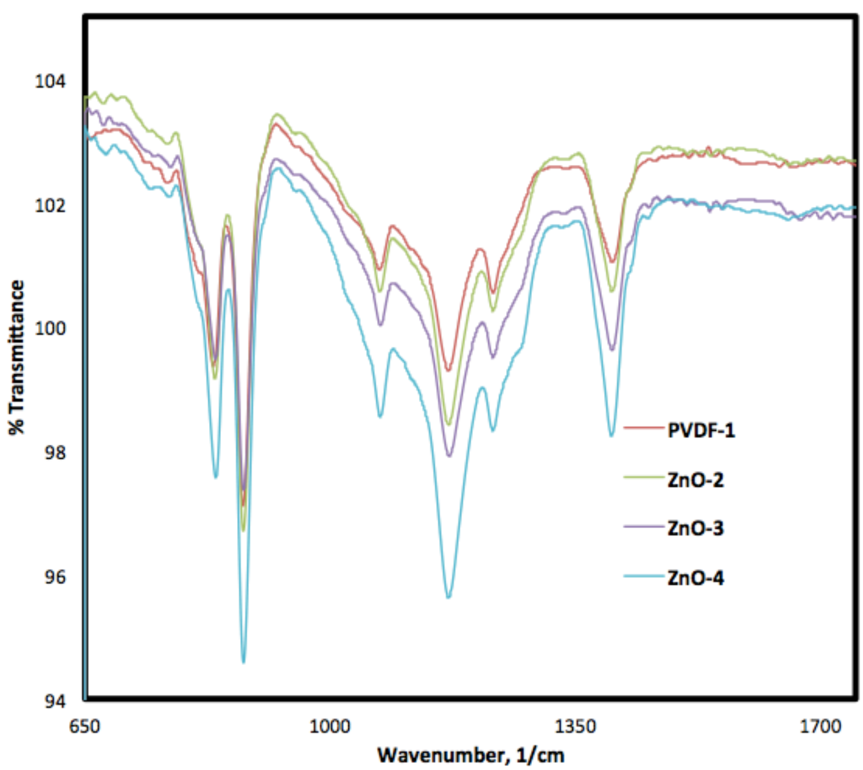


Fig 4. FTIR spectra of PVDF and PVDF/ZnO nanocomposites

The IR spectra of ZnO nanocomposites shown in the figure 4, 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 ZnONPs 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/ZnONPs nanocomposite doubled over that of pure PVDF. It can be concluded nanocomposites fabricated with higher concentration of ZnONPs have a potential to meet both present and future technological demands of high-*k* dielectrics and embedded capacitors/organic substrates.

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