Electrical Conduction Mechanism Of Volume And Surface Resistivities Of Multi-Walled Carbon Nanotubes Doped Polyvinyl Alcohol (PVA) And The Pyroelectric Behavior Of Polyvinylidene Difluoride (PVDF) Thin Films

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Outline

Introduction and Background

Motivation

Objectives

Experimental

Results

Summary/Conclusion

Acknowledgements
we have reported measurements of the temperature-dependent surface resistivity of pure and multi-walled carbon nanotubes doped Polyvinyl Alcohol (PVA) thin films.

In the temperature range from 22 °C to 40 °C, with a humidity-controlled environment, we have found the surface resistivity to decrease initially but to rise steadily as the temperature continued to increase.

we report recent volume resistivity measurements and address the electrical conduction phenomenon that contributes to both surface and volume resistivities of pure and doped PVA thin films.

we have measured the temperature-dependent pyroelectric coefficient of doped PVDF thin films.
Motivation

- To Continue property characterization doped polyvinylidene difluoride (PVDF) thin films for pyroelectricity/IR sensors
- To measure bulk and surface resistivity of PVDF as a function of temperature
- To consider doped polyvinyl alcohol (PVA) thin films and measure their resistivity properties as well
- To consider the application of the electrical temperature coefficient for sensing
Dielectric thin film samples have been prepared with the solvent evaporation procedure as shown in Fig. 1a and 1b.

**Fig. 1a.** Image of samples

**Fig. 1b.** UV-VIS spectrograph of Ag-nano-particles in PVA film
Figure 1c. Pure And Doped PVA Films And Commercial Paper
For testing purposes, we have used Keithley Model 6517 Electrometer and Keithley Model 8009 resistivity test fixture with the Amprobe wireless thermometer when using the J-type thermocouple.

Humidity, another important factor in surface resistivity measurements, was monitored with a commercial grade humidifier.

In this research, we specified humidity as normally low, normally medium or normally high.

All of our reported measurements were made at normal medium humidity at approximately 70%.
Fig. 2a. Experimental setup #1

Fig. 2b. Interior view of fixture with commercial PVA film

Fig. 2a, 2b, 2c and 2d show our setup resistivity measurements, consisting of a combined Keithley electrometer and Keithley test fixture, with the Amprobe wireless thermometer
**Fig. 2c.** Illustration of current path with sample and electrodes

**Fig. 2d.** Close-up showing circular electrodes with dimensions
Figure 2e. Experimental Setup #2, Dielectric Constant, Dielectric Loss, and Other Measurements
• Table 1 that follows gives important conduction mechanisms in dielectrics.

• The methods to distinguish these conduction mechanisms are essential because there are several conduction mechanisms that may all contribute to the current through the dielectric or on its surface at the same time.
Table 1. Important Conduction Mechanisms In Dielectrics
See Fig. 3a – 4b below, which show the temperature dependent surface resistivity measurements of PVA for the commercial films, for the doped Ag nano-particles or for the doped MWCNT, and the copier paper films.

All of the resulting graphs have the same characteristic behavior: the surface resistivity is only slightly high at low temperatures, but decreases initially as the temperature increases reaching a minimal resistivity value where upon the surface resistivity increases as the temperature continues to increase to our experimental limit of 40°C.
Figure 3a. Doped Sample: Current Density Vs. Electric Field

\[ y = 42.449x + 1.1113 \]

\[ R^2 = 0.98371 \]
Figure 3b. Undoped Sample: Current Density Vs. Electric Field

Current Density- Electric Filed Plot at T=25°C

\[ y = 13.306x - 0.1789 \]

\[ R^2 = 0.99916 \]
Figure 3c. Commercial Copier Paper: Current Density Vs. Electric Field
Fig. 4a. Surface resistivity graphs of commercial film and copier paper

Fig. 4b. Surface resistivity graphs of Ag nano-particle and MWCNT
Discussions and Conclusions For PVA Films

- The preliminary experimental results obtained from this investigation can be summarized as:

- PVA thin films, doped and commercial, can be developed with the solvent evaporation method.

- The combined system of Keithley Model 6517 electrometer, Keithley Model 8009 test fixture and the amprobe thermometer can be used readily to measure surface resistivity of commercial PVA films, of Ag nano-particle or MWCNT doped PVA films and of copier-paper films, but cannot in the present configuration be used to measure the surface resistivity of PVDF films.

- Surface resistivity of Ag nano-particle doped PVA films is generally higher in value than that of commercial PVA and varies the most greatly in the temperature range from 22°C to 40°C, followed in order of that of MWCNT PVA films and copier-paper.
PVDF Films

◆ The authors have determined the dielectric and conductance properties of multi-wall carbon nano-tubes (MWCNT) in polyvinylidene fluoride (PVDF) nanocomposite thin films as a function of temperature and frequency.

◆ Film Thickness was from ranging from 15 – 280 microns and measurements were made in the temperature range from room temperature to 20 to 90°C and frequencies from 50Hz to 110MHz.

◆ The samples were prepared by the solution casting technique.

◆ Measures indicate that at constant temperatures, the real dielectric constant decreases at lower frequencies, stays steady at low frequencies but rise at higher frequencies over towards the strong resonance.

◆ The dielectric loss decreases also at lower frequencies but rise at higher frequencies with a steeper slope in each case.

◆ The pyroelectric coefficient in the same temperature range, compared the pyroelectric coefficient results with previous measures made on silver nanoparticle in PVDF thin films.

◆ MWCNT:PVDF thin films yield higher figures of merit than that indicated by pure PVDF thin films and results indicate a usage of MWCNT:PVDF thin films in infrared uncooled sensors and vidicon technology.
Methods to Measure The Pyroelectric Coefficient

- Direct Techniques (Byer & Roundy)  
  (Present Method at AAMU)

- Dynamic Method (A.G. Chynoweth)

- Charge Integration Method (A. M. Glass)

- All-Optical Technique (Jacopo Parravicini)
The real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of dielectric constant were calculated by measuring capacitance $C_p$ and dielectric loss $D (= \tan \delta)$.

$$\varepsilon' = C_p \varepsilon_0 \left( \frac{d}{A} \right), \quad \varepsilon'' = \varepsilon' D$$

$d$ is the film thickness, and $A$ is the electrode area.

The pyroelectric current $I_p$ was measured, and the pyroelectric coefficient ($p$) was calculated using the relationship:

$$p = \left( \frac{I_p}{A(dT/\text{dt})} \right)$$

where $A$ is the electrode area (identical areas for the opposite electrodes used in each sample) and $dT/dt$ is the rate of temperature change with time, which was kept to $1^\circ \text{C/minute}$.

Pyroelectric Coefficient from the Effective Medium Approach:

$$p = \left( \frac{\varepsilon' - \varepsilon_m}{\varepsilon_i - \varepsilon_m} \right) p_i + \left( \frac{\varepsilon_i - \varepsilon'}{\varepsilon_i - \varepsilon_m} \right) p_m$$

$\varepsilon'$ for the composite, $\varepsilon_i$ the inclusion, $\varepsilon_m$ the matrix.
Figure 1. Summary of Composite Film Fabrication Process:

- P(VDF-TrFE) + MEK = PMix
- MWCNT + PMix = nPMix (Ultrasonic Dispersion)
- nPMix Film Spin Coating (or) Solution Casting
- Annealing
- Testing
- Poling
- Silver Electroding
PYROELECTRIC CRYSTAL SHOWING THE CHANGE IN POLARIZATION
Basic Pyroelectric Detector Element

\[ i_p = Ap \frac{dT}{dt} \]
Room-temperature Properties of Various Pyroelectric Detector Materials and Some Figures of Merit" for Detector Operation.

<table>
<thead>
<tr>
<th>Material</th>
<th>$p$ (nCcm$^{-2}$K$^{-1}$)</th>
<th>$\varepsilon'/\varepsilon_0$ (Jcm$^{-3}$K$^{-1}$)</th>
<th>$c_p$ (nAcmW$^{-1}$)</th>
<th>$p/c_p$ (Vcm$^{-2}$J$^{-1}$)</th>
<th>$p/(c_p\varepsilon')$ (cm$^3$J$^{-1}$)$^{1/2}$</th>
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<tr>
<td>TGS</td>
<td>30</td>
<td>50</td>
<td>1.7</td>
<td>17.8</td>
<td>4000</td>
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<tr>
<td>LiTaO$_3$</td>
<td>19</td>
<td>46</td>
<td>3.19</td>
<td>6.0</td>
<td>1470</td>
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<tr>
<td>Sr$<em>{1/2}$Ba$</em>{1/2}$Nb$_2$O$_6$</td>
<td>60</td>
<td>400</td>
<td>2.34</td>
<td>25.6</td>
<td>720</td>
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<td>PLZT(6/80/20)</td>
<td>76</td>
<td>1000</td>
<td>2.57</td>
<td>29.9</td>
<td>340</td>
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<tr>
<td>PVDF</td>
<td>3</td>
<td>11</td>
<td>2.4</td>
<td>1.3</td>
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Figure 2. Pyroelectric Coefficient Vs Temperature of PVDF Film
Figure 3 Pyroelectric Coefficient Vs Temperature of PVDF/MWCNT Film
Figure 4. Real Part of Dielectric Constant ($\varepsilon'$) Vs Temperature of PVDF and PVDF/MWCNT Films
Figure 5. Imaginary Part of Dielectric Constant ($\varepsilon''$) Vs Temperature of PVDF and PVDF/MWCNT Films
Table 1. Dielectric, pyroelectric and figures-of-merit of PVDF and composites films

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pyroelectric Coeff. (p); $F_i$ (nC/cm² °C)</th>
<th>Dielectric Cont. ($\varepsilon''$)</th>
<th>Dielectric Loss ($\varepsilon''$)</th>
<th>Pyroelectric-voltage (V)</th>
<th>$FM_p = p/\varepsilon''$ (nC/cm² °C)</th>
<th>$FM_{vol} = p/((\varepsilon''_v)^{1/2}$ (nC/cm² °C)</th>
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<tbody>
<tr>
<td>PVDF Film</td>
<td></td>
<td></td>
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<tr>
<td>35</td>
<td>0.1175</td>
<td>12.924</td>
<td>0.4702</td>
<td>3.16</td>
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<td>0.4345</td>
<td>13.540</td>
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<td>2.1629</td>
<td>3.92</td>
<td>1.7665</td>
<td>7.0674</td>
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<td>PVDF:MWCNT Film</td>
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<td>968.41</td>
<td>49.767</td>
<td>55.724</td>
<td>19.38</td>
<td>19.4752</td>
<td>137.2829</td>
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<tr>
<td>P(VDF-TrFE) Film</td>
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</tr>
<tr>
<td>60</td>
<td>0.28</td>
<td>17.58</td>
<td>2.21</td>
<td>-</td>
<td>0.02</td>
<td>0.07</td>
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<tr>
<td>70</td>
<td>0.637</td>
<td>18.97</td>
<td>3.35</td>
<td>-</td>
<td>0.03</td>
<td>0.15</td>
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<td>P(VDF-TrFE)+LT+Ag Nanoparticles Film</td>
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<td></td>
</tr>
<tr>
<td>60</td>
<td>44.9</td>
<td>40.99</td>
<td>29</td>
<td>-</td>
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<tr>
<td>70</td>
<td>132</td>
<td>48.28</td>
<td>40.73</td>
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<td>18.99</td>
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</table>
Figure 16. Comparison of pyrovoltaic generated for PVDF and PVDF- via 1°C increase in temperature
Figure 9. Figure-of-Merit for Detector Applications Vs Temperature of PVDF Film
Figure 10  Figure-of-Merit for Vidicon Application Vs Temperature of PVDF/MWCNT Film
Figure 11. Figure-of-Merit for Vidicon Application Vs Temperature of PVDF Film
Summary/Conclusions

Flexible And Homogeneous Films Have Been Prepared— LT Or MWCNT Composites;

The Incorporation Of MWCNT Have Enhanced Both Dielectric Constants And The Pyroelectric Coefficient;

Further Work Is In Progress To Grow Thinner Films With Larger Amounts Of MWCNT Or LT In PVDF;

Phenomenal And Synergistic Understanding Of The Effects Of MWCNT In Composite Thin Films;

Resolve Issues of Using Parallel Plates Versus Electrode Metallic Coating

Development Techniques to Reduce Internal Stress In The Films;

Development of IR Devices Remain To Be Completed.
Further Studies

- Further study is needed on PVA to ascertain the surface resistivity temperature dependence in greater temperature ranges, and to determine conduction mechanisms that are involved as a function of temperature.

- Further study is needed on PVDF films to ascertain surface resistivity properties more conclusively than what are reported here.

- Further studies are needed to determine sensors and other detection applications.
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Some References


Additional References


