



# Piezoelectric Carbon Nanotube Tape for use in Sensor Technology

Dr. Dennis S. Tucker

EM32

Marshall Space Flight Center



# Co-Investigators

- John Rakoczy and Dr. Pedro Capo-Lugo/EV41
- Angela Shields/ES43
- Professor Yuntian Zhu/NCSU
- Dr. Mohan Sanghadasa/AMRDEC



# Purpose of Program

- Purpose of research is to develop piezoelectric CNT tape for use as sensing elements in vibration gyroscopes and accelerometers for small satellites
- CNT/P(VDF-TrFE) tape has potential to be robust with high strength and superior thermal properties



# Background

- Carbon nanotubes (CNT) have been of intense interest since discovery in 1991
- They exhibit superior mechanical and thermal properties as well as unique electrical properties
- CNTs can be either single-wall or multi-wall



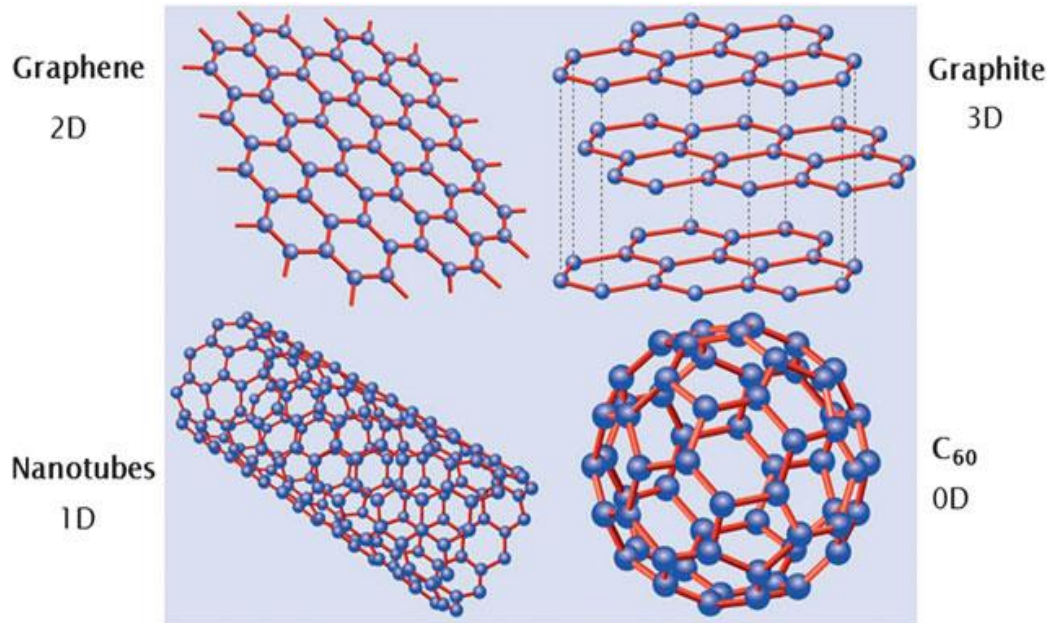
# Background

- Synthesis techniques include:
  1. Arc Discharge
  2. Laser Ablation
  3. Plasma Torch
  4. Chemical Vapor Deposition (CVD)



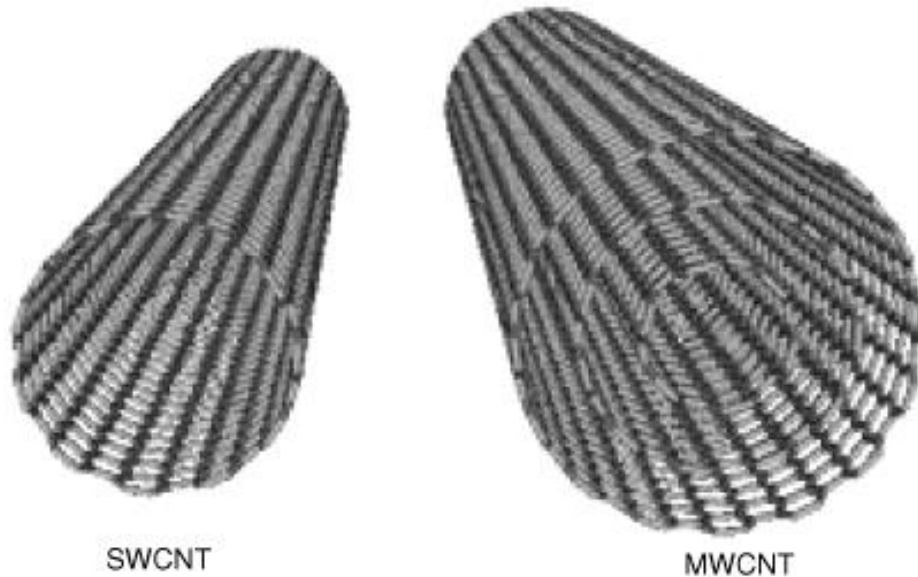
# Background

CNT is one allotrope of carbon





# Background





# Background

CNTs Being Investigated for Various Sensors Including:

1. Pressure Sensors
2. Flow Sensors
3. Acoustic Sensors
4. Chemical Sensors
5. Temperature Sensors





# Background

- We are interested in sensor applications for spacecraft including:
- Gyroscopes
- Accelerometers
- Structural Health Monitoring
- These will use CNT Tape as Active Elements

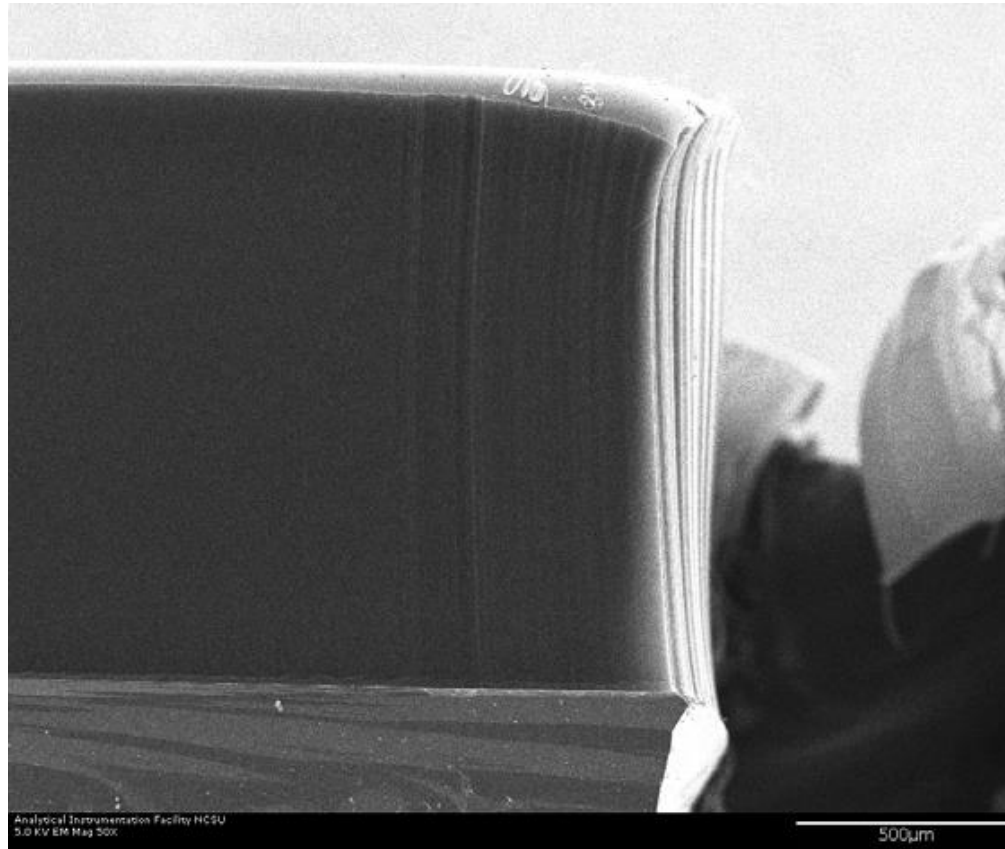


# Experimental

- P(VDF-TrFE) (70/30) Copolymer dissolved in DMSO, 0.2 w/o, 5 w/o and 10 w/o
- Solution sprayed onto CNT tape as it is wound onto take-up reel; 100 micrometers thick
- Tape removed from reel and dried in vacuum oven at 100C for 24 hours
- Tape removed and pressed using glass weight above Curie Temperature to induce beta phase growth; 90 micrometers thick
- Beta phase is most polarizable of all the phases
- 10 w/o BaTiO<sub>3</sub> added to solution to increase piezoelectric response
- Piezoelectric Effect measured using Radiant Technologies Tester



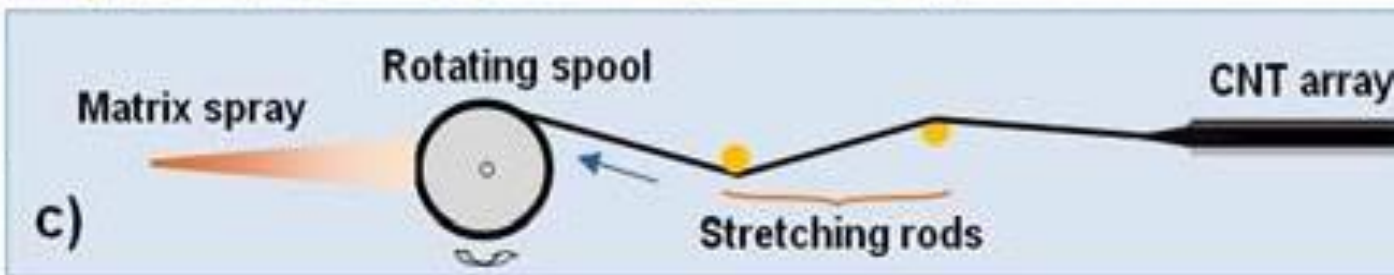
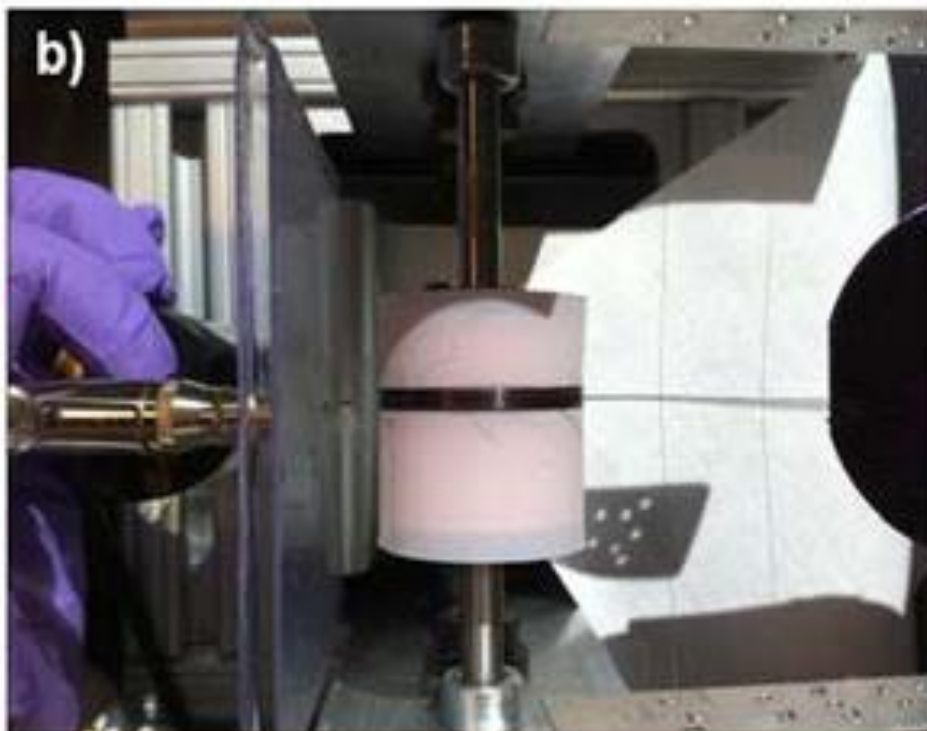
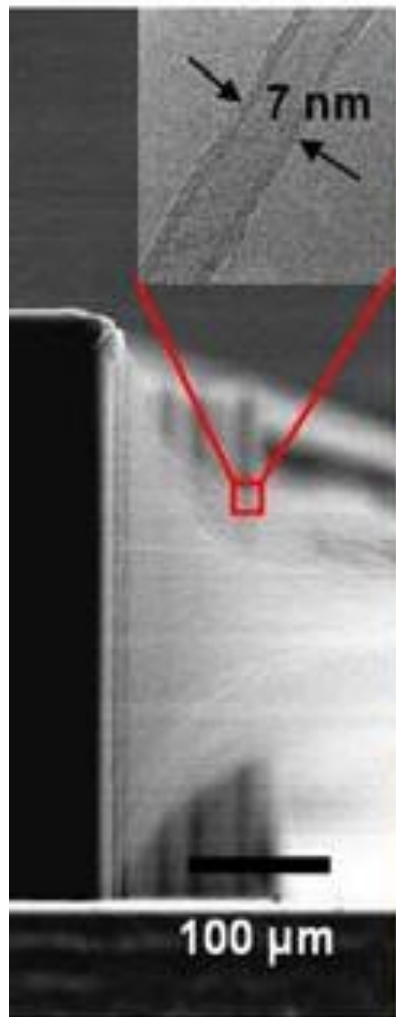
# Experimental



**1.5 millimeter tall vertically aligned carbon nanotube array grown on a silicon substrate.**



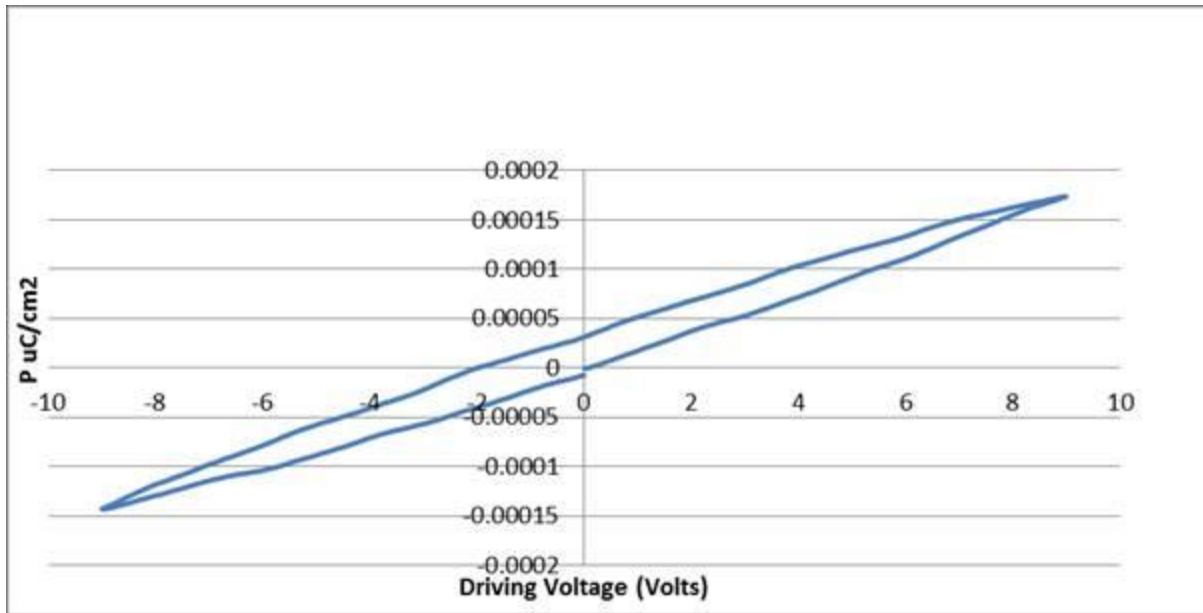
# Production of CNT Tape





# Results

Initial Hysteresis Curve for CNT/P(VDF-TrFE) 0.2 w/o  
Pr = 16  $\mu\text{C}/\text{cm}^2$  – Measured with Radiant Tester

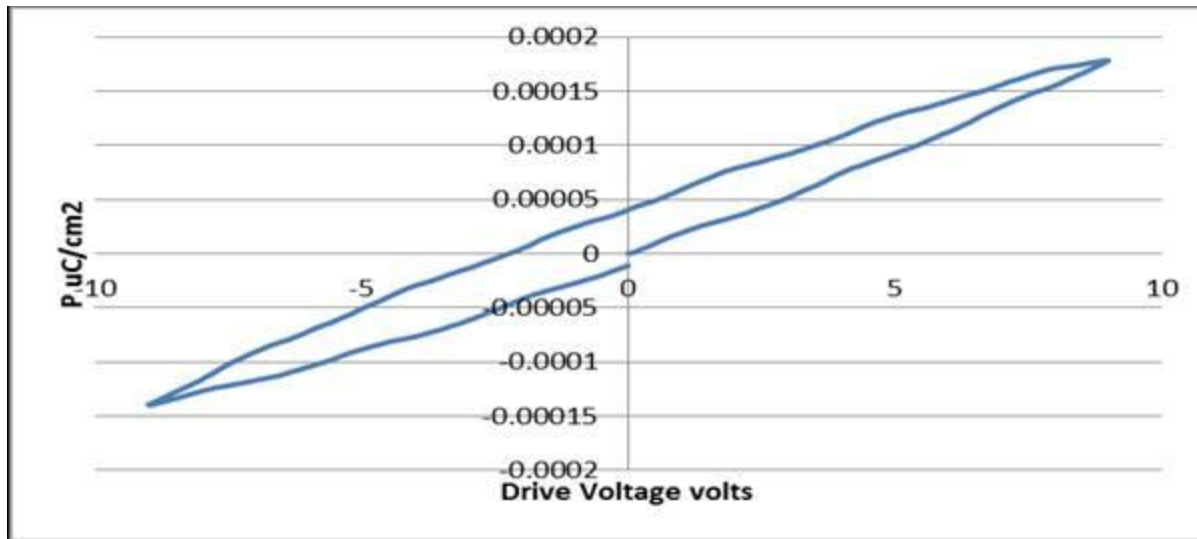




# Results

Sample in Previous Slide Direct Poled at 10 Volts for 10 Minutes

$P_r = 22 \text{ uC/cm}^2$

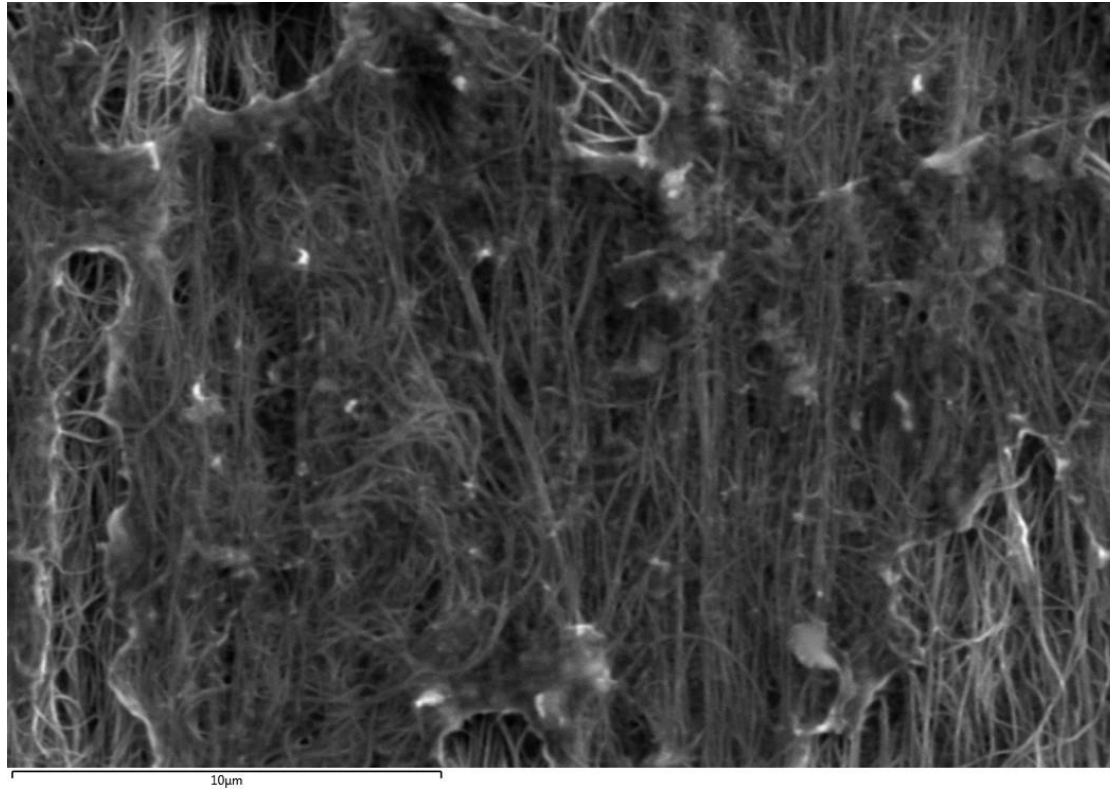




# Results

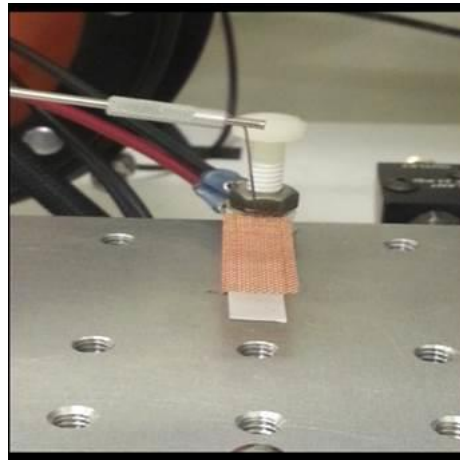
SEM of 0.2w/o P(VDF-TrFE) CNT Tape

500X – SEM Image





# Corona Poling

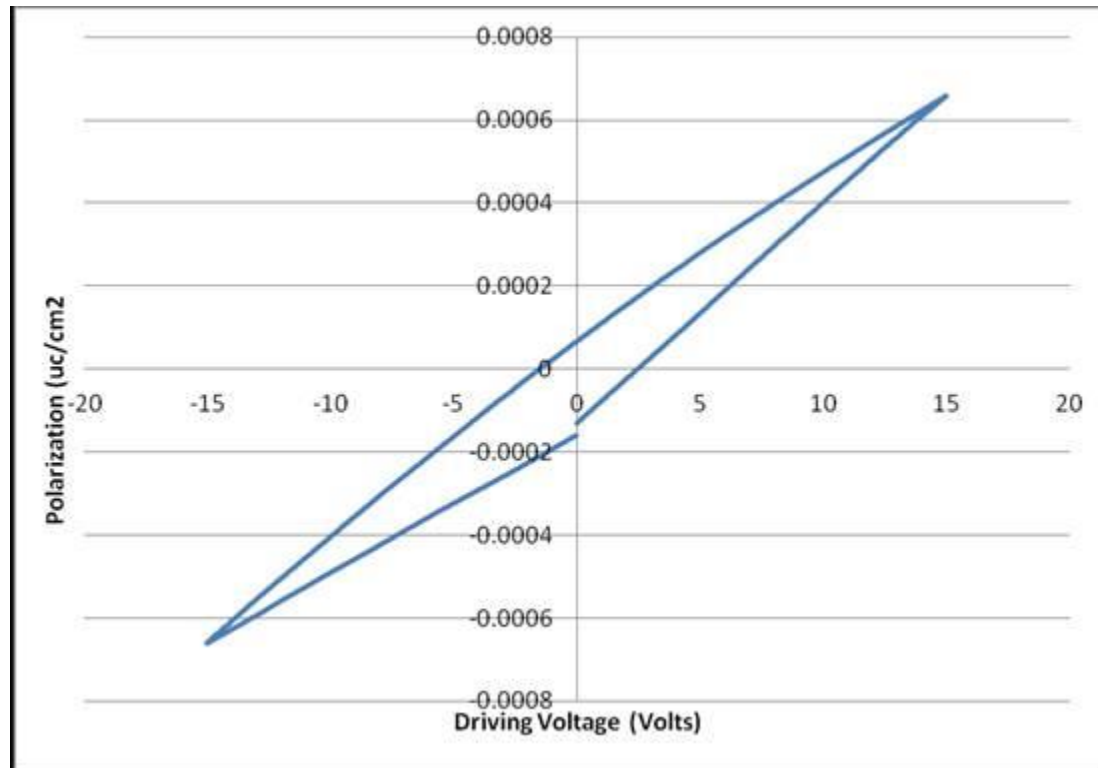






# Results

CNT/P(VDF-TrFE)/BaTiO<sub>3</sub> (10 w/o) Corona Poled at 2500 V for 20 Minutes  
Pr = 61  $\mu\text{C}/\text{cm}^2$

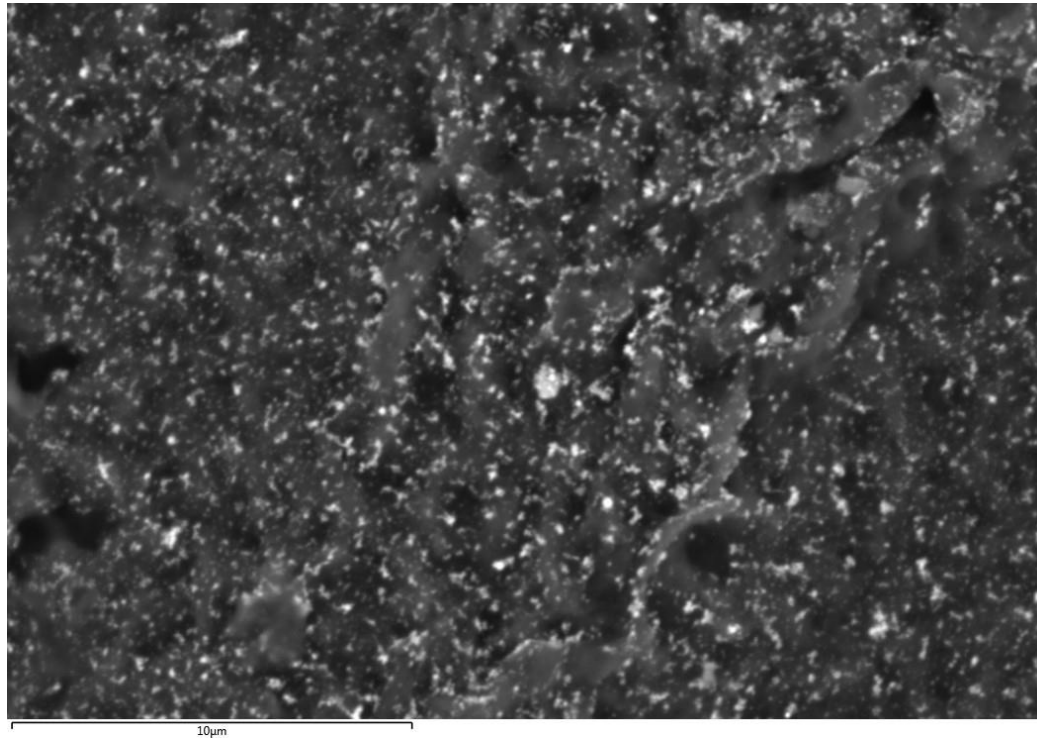




# Results

## SEM CNT/P(VDF)TrFe10/BT10

500X – SEM Image





# Piezoelectric Constitutive Equations

- $S_{ij} = s_{ijkl}^E T_{kl} + d_{kij} E_k$
- $D_i = d_{ikl} T_{kl} + \epsilon_{ik}^T E_k$

Where:

- $S_{ij}$  = strain components
- $T_{ij}$  = Stress components
- $E_k$  = electric field components
- $D_k$  = displacement components
- $d_{kij}$  = constants of the displacement matrix
- $\epsilon_{ij}$  = constants of electric field matrix



# Piezoelectric Response Matrix

For PVDF Materials displacement matrix elements are:

- $d_{31}$ ,  $d_{32}$ ,  $d_{33}$ ,  $d_{25}$  and  $d_{15}$
- The matrix is not fully populated due to the anisotropic nature of PVDF
- $d_{ij}$  for our study: ratio of the strain in the  $j$ -axis to electric field applied along  $i$ -axis

**Figure 1.6** Directions of forces affecting a piezoelectric element

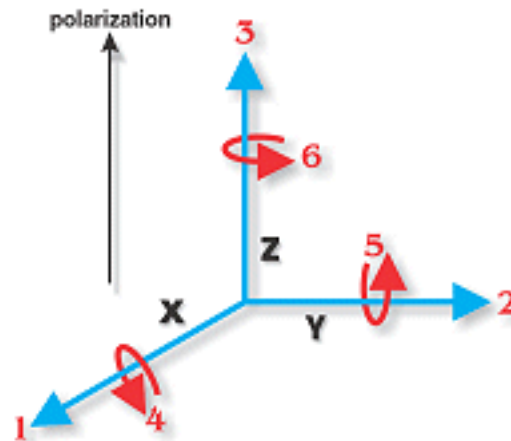


Diagram Source: APC Inc.



# Results



Orientation of CNT Tape for Piezoelectric Measurements of  $d_{33}$

Apply voltage along 3 direction and Measure Response along 3 direction



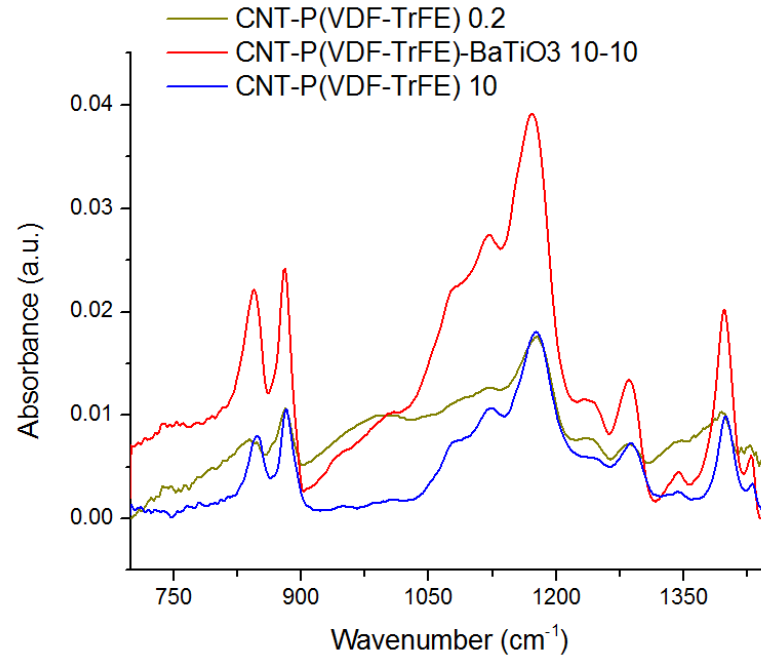
# Results

- CNT/P(VDF-TrFE)/BT showed  $d_{33}$  of 140 pm/V
- Lit shows values from 1 – 34 pm/V
- Differences not only due to material but also sample thickness and polarization voltage
- Thin films with high voltage show highest values
- CNT/P(VDF-TrFE) films had  $d_{33}$  of 70 pm/V compared to 32-35 pm/V for pure P(VDF-TrFE) commercial film
- Due to Maxwell-Wagner-Sillars polarization – buildup of charges at interface of materials of different conductivity
- Dielectric constant of CNT/P(VDF-TrFE) was 161
- Lit values approximately 16 – These only had small w/o cnts (0.1 or less)
- These tapes had a tensile strength of 120 MPa and Young's Modulus of 17.8 GPa (Lit values of 68 MPa strength and 1.4 GPa Young's Modulus)



# Results

## FTIR Data



Beta Phase Wavenumbers: 840 and 1280



# Results

Material	Dielectric Constant	$d_{33}$ (pm/V)
CNT/P(VDF-TrFE)	161	70
P(VDF-TrFE)/BT	204	140
CNT/P(VDF-TrFE)/BT	76	81

$g_{33} = d_{33}/\epsilon$  (N/C) This gives idea of sensor value

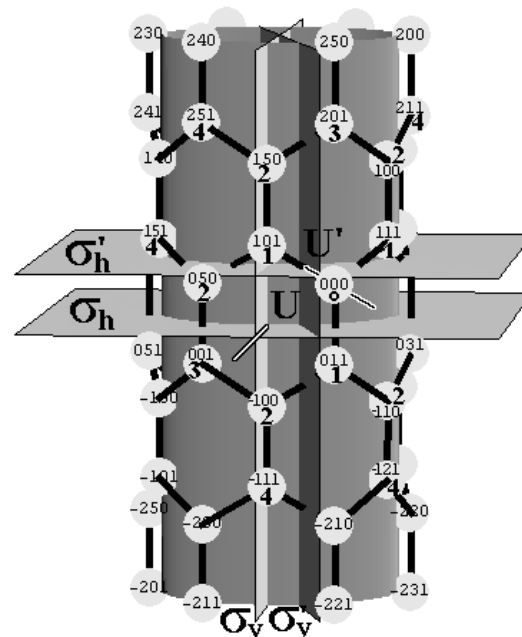
Last material is only one with value  $> 1$  so should be investigated further; also PZT as additive should be investigated





# Future Work

- Achiral SWCNTs show mirror symmetries





# Inducing Piezoelectricity in CNTS

- Theoretically, it is possible to induce piezoelectric effect in CNTS
- Break mirror symmetry by adsorbing ions on one end or side of CNTS – Will try ion implantation
- Will try potassium initially on one end of vertical array
- Draw into CNT sheets and reinforce with BMI: Previous testing showed Tensile Strength of 3.8 GPa and Thermal Conductivity of 40 W/m K
- Also will take sheets and ion implant one side
- Test for Piezoelectric Effect