Carbon Nanotube/Polymer Nanocomposites Flexible Stress and Strain Sensors

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MRS Spring Meeting 2008

Conformable stress and strain sensors are required for monitoring the integrity of airframe structures as well as for sensing the mechanical stimuli in prosthetic arms. For this purpose, we have developed a series of piezoresistive single-wall carbon nanotube (SWCNT)/polymer nanocomposites. The electromechanical coupling of pressure with resistance changes in these nanocomposites is exceptionally greater than that of metallic piezoresistive materials. In fact, the piezoresistive stress coefficient (π) of a SWCNT/polymer nanocomposite is approximately two orders of magnitude higher than that of a typical metallic piezoresistive. The piezoresistive stress coefficient is a function of the nanotube concentration wherein the maximum value occurs at a concentration just above the percolation threshold concentration (Φ ~ 0.05 %). This response appears to originate from a change in intrinsic resistivity under compression/tension. A systematic study of the effect of the modulus of the polymer matrix on piezoresistivity allowed us to make flexible and conformable sensors for biomedical applications. The prototype haptic sensors using these nanocomposites are demonstrated. The piezocapacitive properties of SWCNT/polymer are also characterized by monitoring the capacitance change under pressure.

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Outline

1. Introduction
2. Materials
3. Stress and Strain Sensing Capabilities

    I: Piezoresistance (SWCNT concentration, Modulus of Matrix)

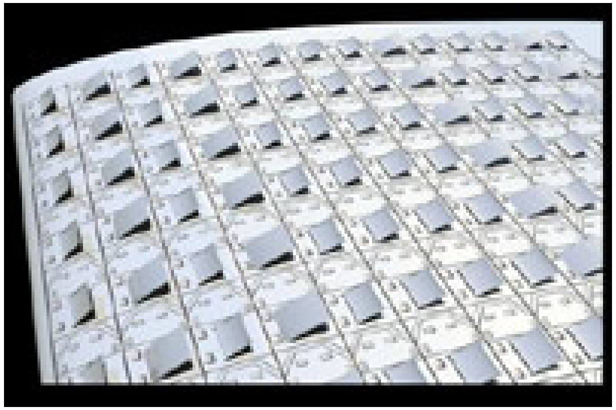
    II: Piezocapacitance

4. Demonstration of a Prototype Sensor
5. Summary

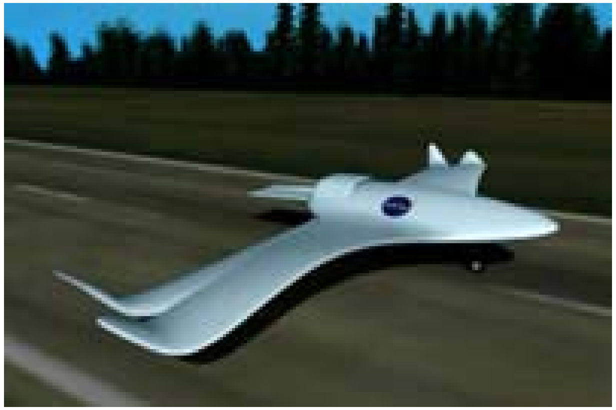
Introduction

Motivation

To develop structural, sensing, actuating materials for aerospace applications



1. Electro-Active Sensing Polymer (EASP) advantages
    - Lightweight
    - Tailorable
    - Conformable



2. State of the art EASP limitations
    - Thermal instability
    - Low sensitivity
    - High drive voltages required

→ ***Polyimide + SWNT***

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http://www.spectrum.ieee.org/jan08/5864

Sensitive Synthetic Skin in the Works for Prosthetic Arms

By Prachi Patel-Predd

PHOTO: OAK RIDGE NATIONAL LABORATORY

4 January 2008—By combining carbon nanotubes with a specially designed polymer, researchers are making a material that looks, feels, and functions like human skin. The synthetic skin could lead to next-generation prosthetic arms with which users can feel a light touch, shake hands, cook, and type naturally.

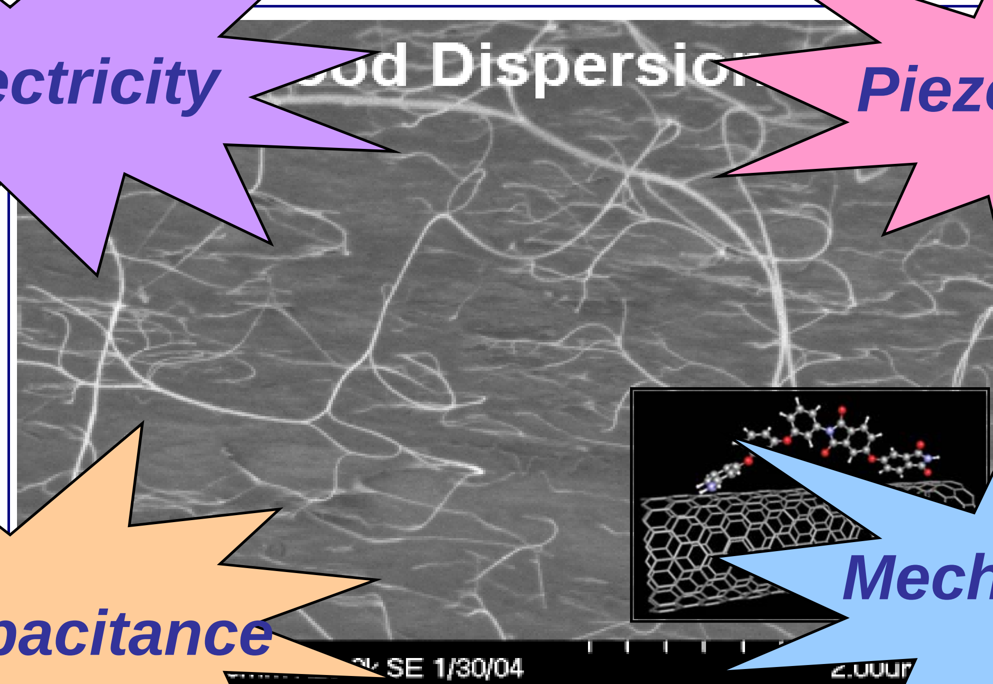
Researchers at Oak Ridge National Laboratory (ORNL), in Tennessee; NASA; and the nonprofit National Institute of Aerospace (NIA), in Hampton, Va., plan to have a 6-square-centimeter patch of the synthetic skin ready by the end of next year. "With this technology, the artificial limb will come much closer to its human counterpart," says ORNL researcher and Defense Advanced Research Projects Agency (DARPA) liaison Art Clemons.

The project is part of DARPA's Revolutionizing Prosthetics program, which aims to build by 2010 a strong, lightweight mechanical arm that can touch and feel just like the real thing, send signals to amputees' brains, and respond to direct brain control.

Stress and Strain Sensing Methodology

Piezoelectricity

Piezoresistance



Piezocapacitance

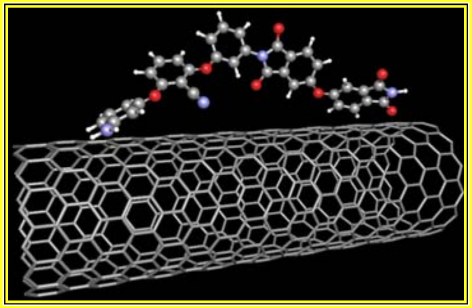
Mechano-optical

CNT types, concentrations
Polymeric matrix (modulus, and etc)

Materials

(1) CNTs

• HiPco SWCNT (CNI)   (from 0% to 10%)



(2) Polymeric Matrices

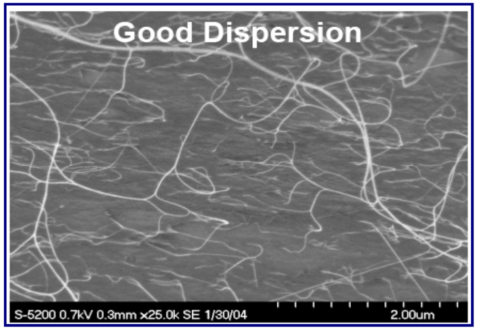
• Polyimide

- LaRC EAP (High Modulus)

  2,6-bis(3-aminophenoxy)benzonitrile ((β-CN) APB)

  4,4'-oxidiphthalic anhydride (ODPA)

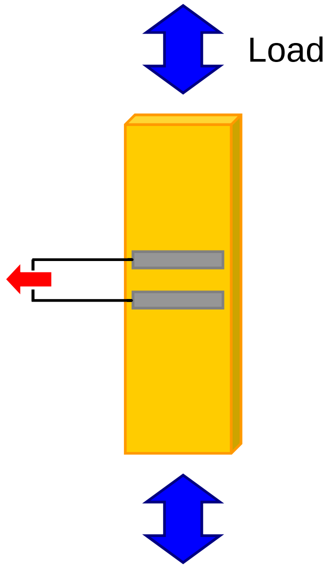
- *n*-LaRC EAP (Low & Medium Modulus)

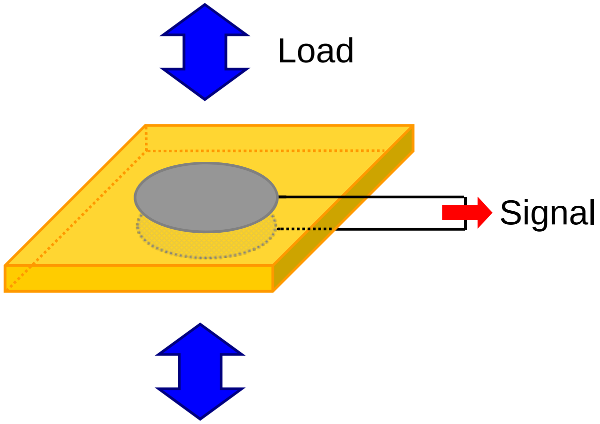


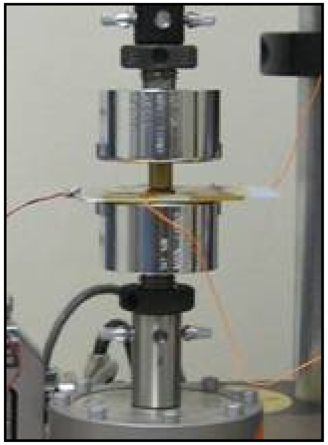
via in-situ polymerization under ultra-sonication

C.Park et al., Chem. Phys. Lett. 364, 303 (2002)

Stress & Strain Sensing







Surface Sensing Mode

Thickness Sensing Mode

Piezoresistance Stress Coefficient (π)

$$\pi = \frac{\Delta R}{R_0 \sigma}$$

Piezoresistance Strain Coefficient (Gauge Factor, G)

$$G = \frac{\Delta R}{R_0 \varepsilon}$$

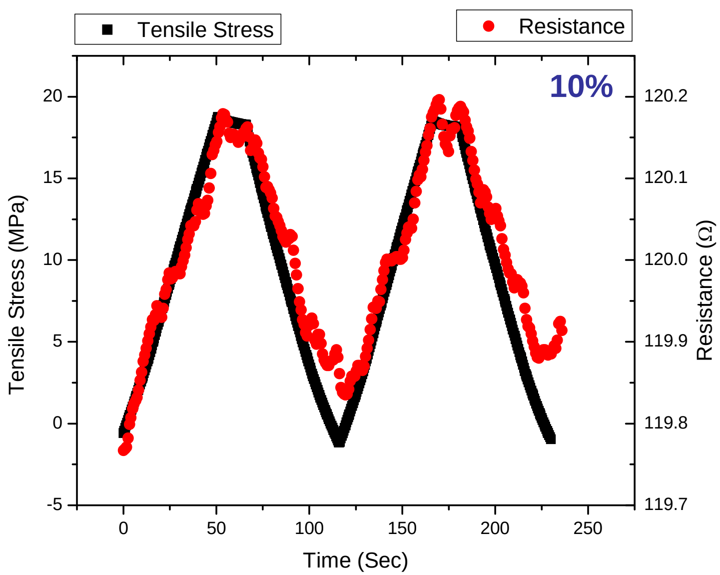
** R: resistance; σ: stress; ε: strain*

Stress Sensing vs CNT Concentration

Surface-Sensing by Piezoresistance

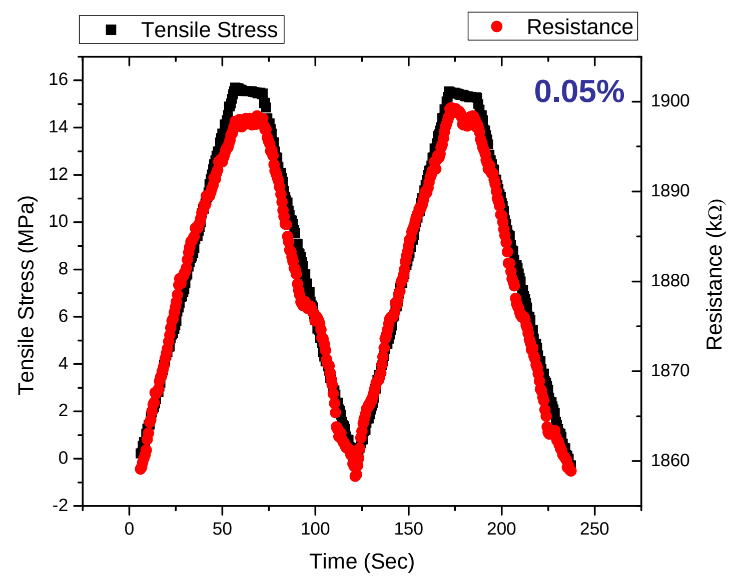
Piezoresistance Stress Coefficent (π) $\pi = \Delta R/(R_o \cdot \Delta\sigma)$

10% SWNT / LaRC EAP



$\pi = 2.27\times10^{-4}$ ($\pm$ 8.05×10^{-5}) MPa^{-1}

0.05% SWNT / LaRC EAP



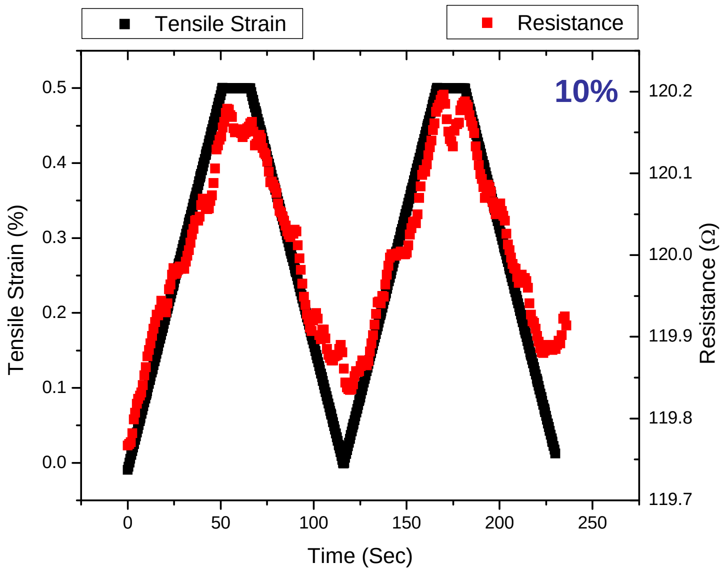
$\pi = 1.52 \times10^{-3}$ ($\pm$ 2.17×10^{-4}) MPa^{-1}

Strain Sensing vs CNT Concentration

Surface-Sensing by Piezoresistance

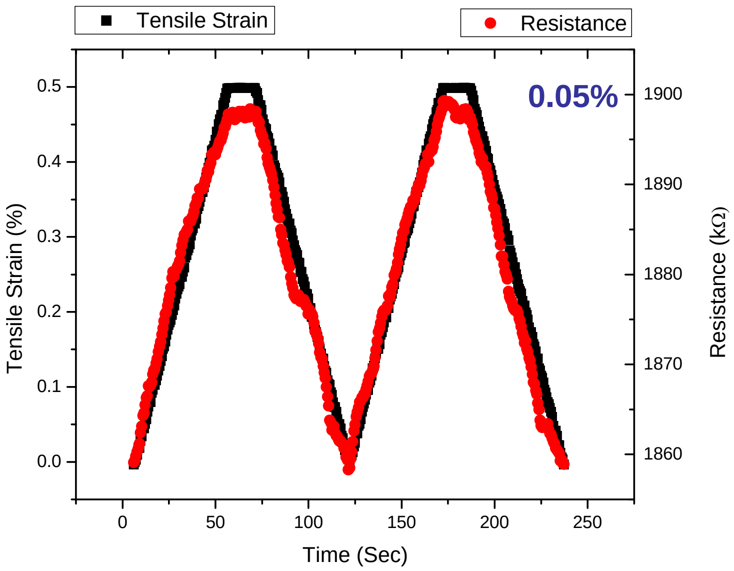
Piezoresistance Strain Coefficient (*G*) $G = \Delta R/(R_o \cdot \Delta\varepsilon)$

10% SWNT / LaRC EAP



$G \sim 0.885\ (\pm\ 0.31)$

0.05% SWNT / LaRC EAP

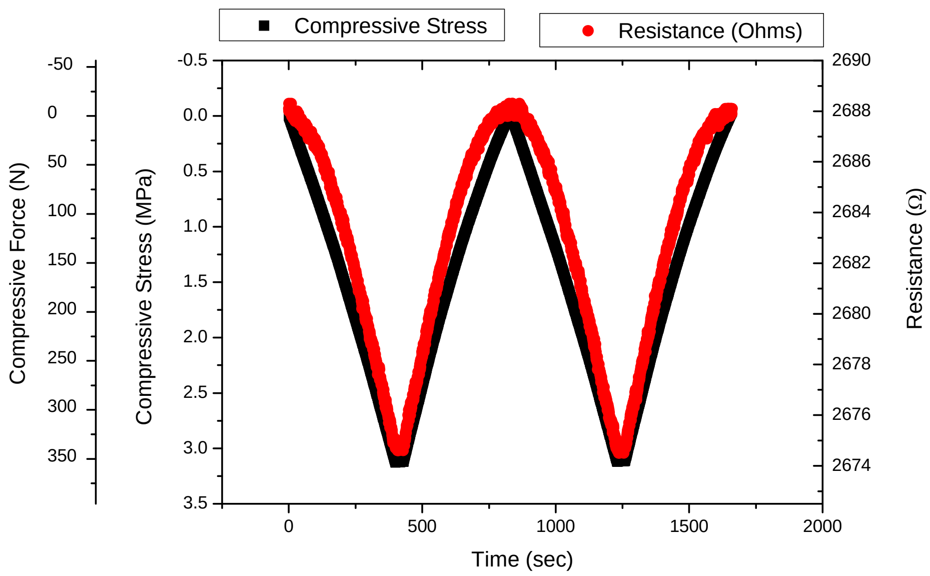


$G \sim 4.21\ (\pm\ 0.27)$

Stress Sensing vs Modulus of Matrix

Thickness-Sensing by Piezoresistance

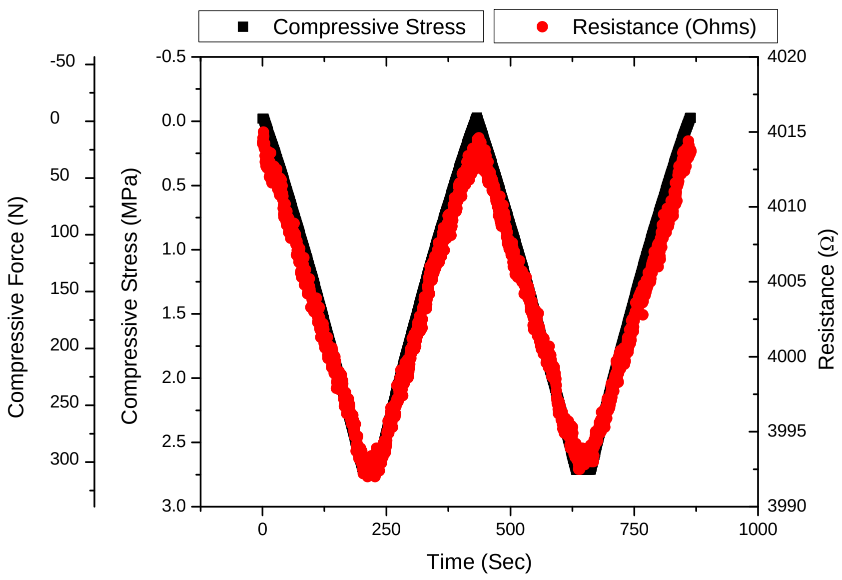
0.1% SWNT / LaRC EAP



$\pi = -7.58\times10^{-4}$ ($\pm$ 7.85×10^{-5}) MPa^{-1}

Modulus: ~ 3.3 GPa

0.1% SWNT / n-LaRC EAP



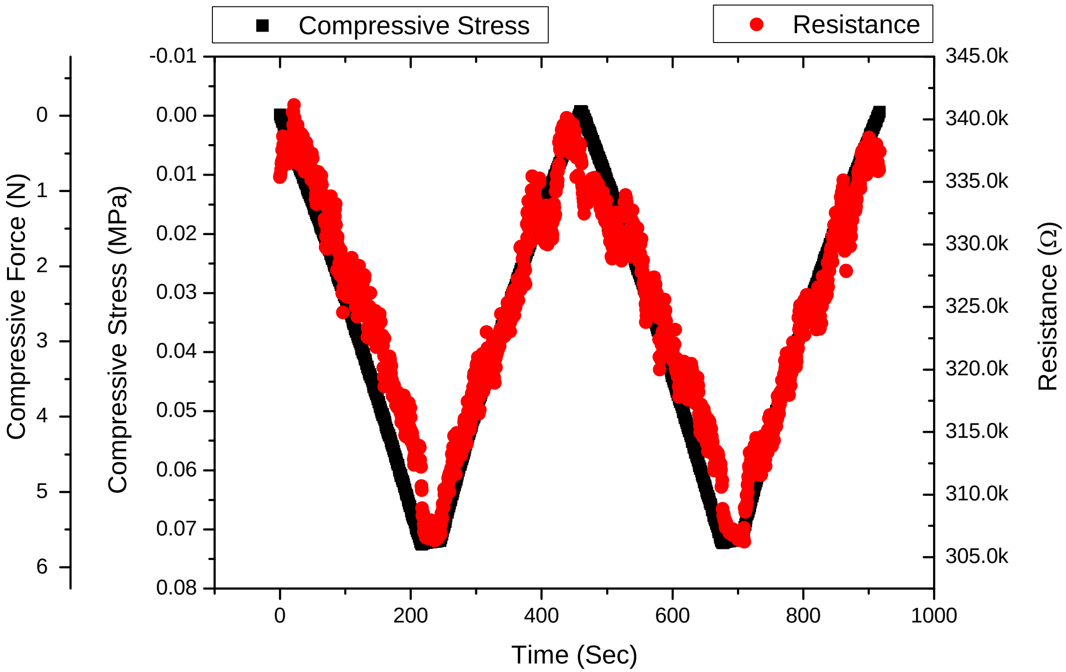
$\pi = -2.02\times10^{-3}$ ($\pm$ 6.42×10^{-5}) MPa^{-1}

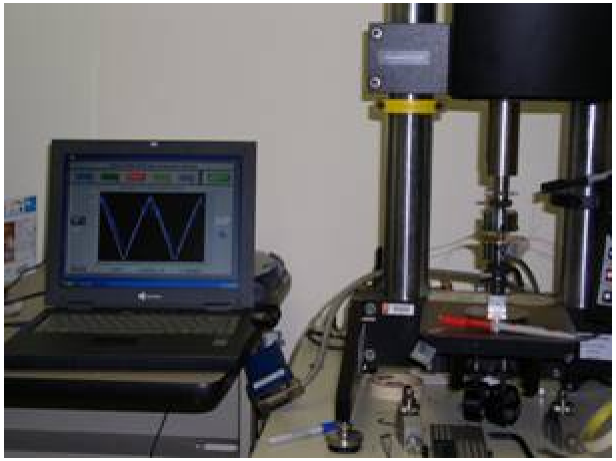
Modulus: 1.14 GPa

Stress Sensing vs Modulus of Matrix

Thickness-Sensing by Piezoresistance

0.1% SWNT/n-LaRC EAP (n100)





$\pi \sim -1.19\ (\pm\ 1.14\times10^{-1}\ \mathrm{MPa}^{-1})$

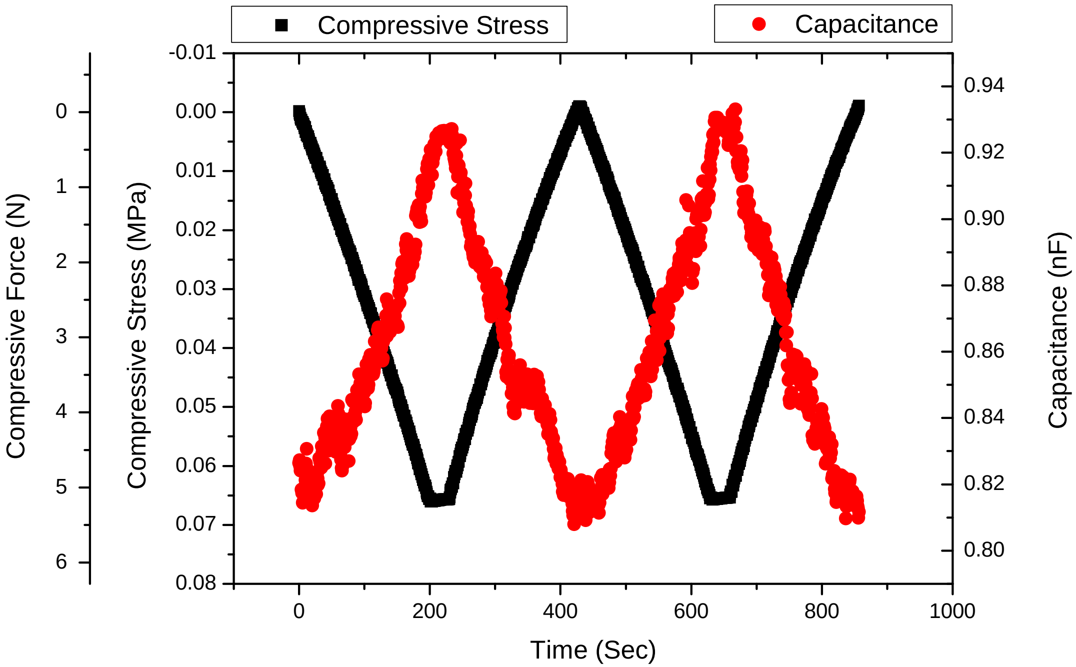
Modulus: ~ 2.03 MPa

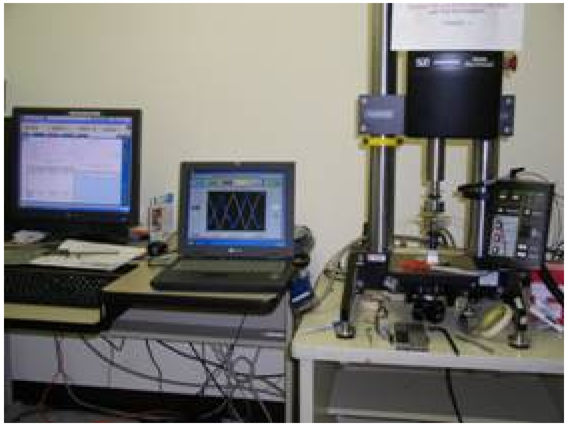
N100: PDMS 100%

Piezocapacitive Characteristics

Thickness-Sensing by Piezocapacitance

0.1% SWNT/*n-LaRC EAP (n100)*





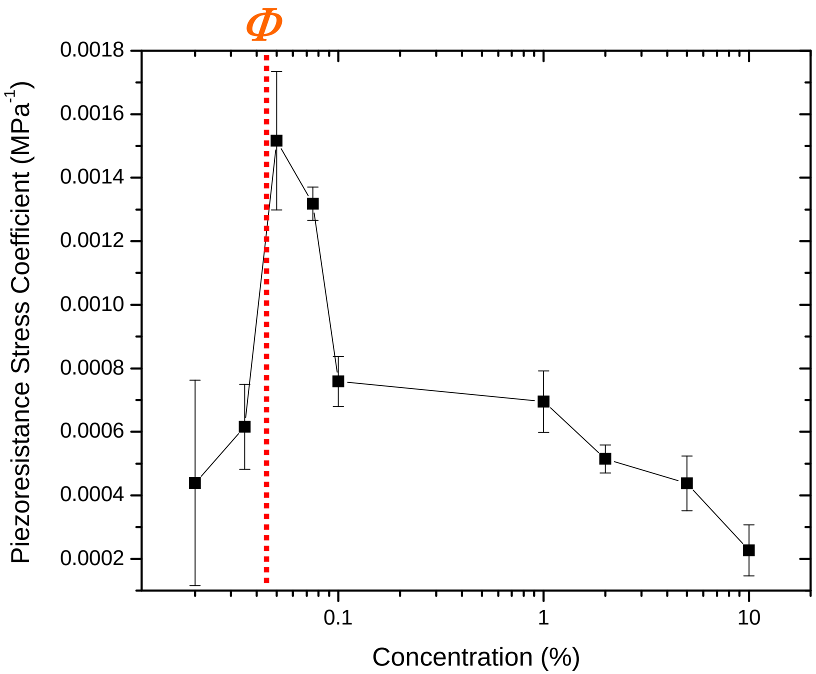
Piezocapacitance Coefficient:

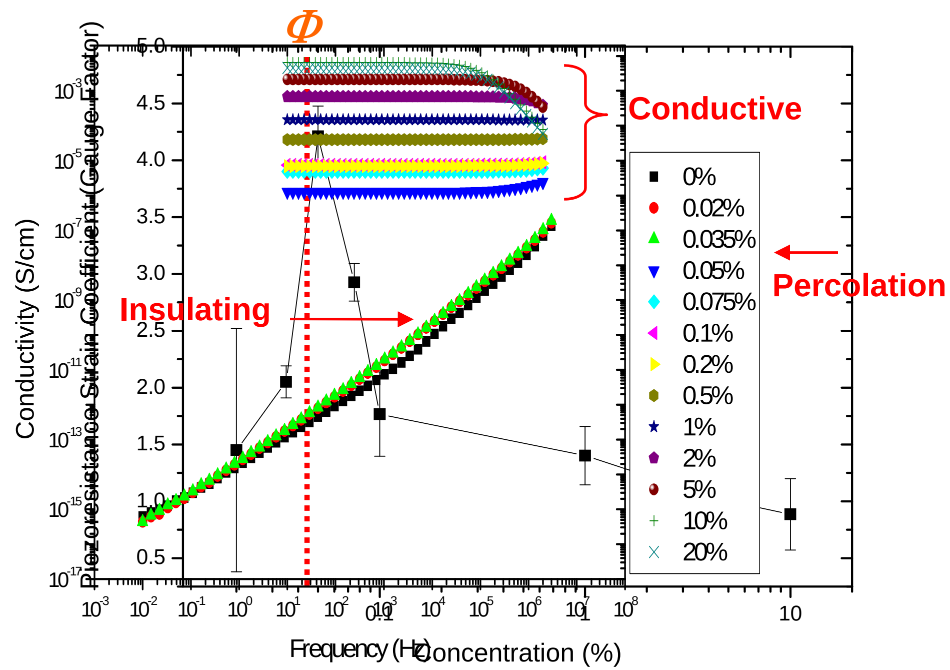
~ 1.99 (± 1.91×10^{-1} MPa^{-1})

Summary of Stress & Strain Sensing

Surface-Sensing by Piezoresistance

*note: overlapped graphs are an animation display





Comparison with other material

Materials	**Piezoresistance Stress Coefficient** (MPa^{-1})
SWNT (conc. dependent)/LaRC EAP (*n*-LaRC EAP)	1~10^{-3}
Aluminum	~10^{-5}

Mechanism for Piezoresistive Response

$$G = \frac{\Delta R}{R_0 \varepsilon} = G(\Delta R_D) + G(\Delta R_I) = (1 + n\nu) + \left(\frac{\Delta \rho}{\rho \varepsilon}\right) \qquad (n = 1, 2)$$

Where n is 1 for a surface sensing mode, and 2 for a through-thickness sensing mode, respectively, ν *is Poisson's ratio of film,* ρ *is resistivity, and* ε *is strain*

$$R_I = \frac{L_T}{S_T} R_T + \frac{L_B}{S_B} R_B = A_T\left(\exp\left(\frac{E_a}{k_B T}\right)\right) + A_B\left(1 + \exp\left(\frac{E_g}{k_B T}\right)\right)$$

Where R_I *is intrinsic resistance of the SWCNT/polyimide nanocomposite,* R_T *is the tunneling resistance and* R_B *is the band-gap change dependent SWCNT resistance.*

$$\frac{R(\varepsilon)}{R_0} = \exp(2\alpha d_0 \varepsilon) \qquad \alpha = \frac{2\pi}{h}(2m\varphi)^{1/2}$$

where *R(*ε*)* and R_0 are the composite resistance under *tensile strain (*ε*)* and the original resistance at *e =0,* d_0 is the tunneling distance between SWCNTs, *h* is the Planck's constant, *m* is the mass of the charge carriers, and φ is the tunneling barrier height.

1. Angelidis, N. et al. Composites. ***35****:1135-1147. 2004.*
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3. J. Cao, Q. Wang and H. Dai, Phys. Rev. Let., 90, 157601 (2003).
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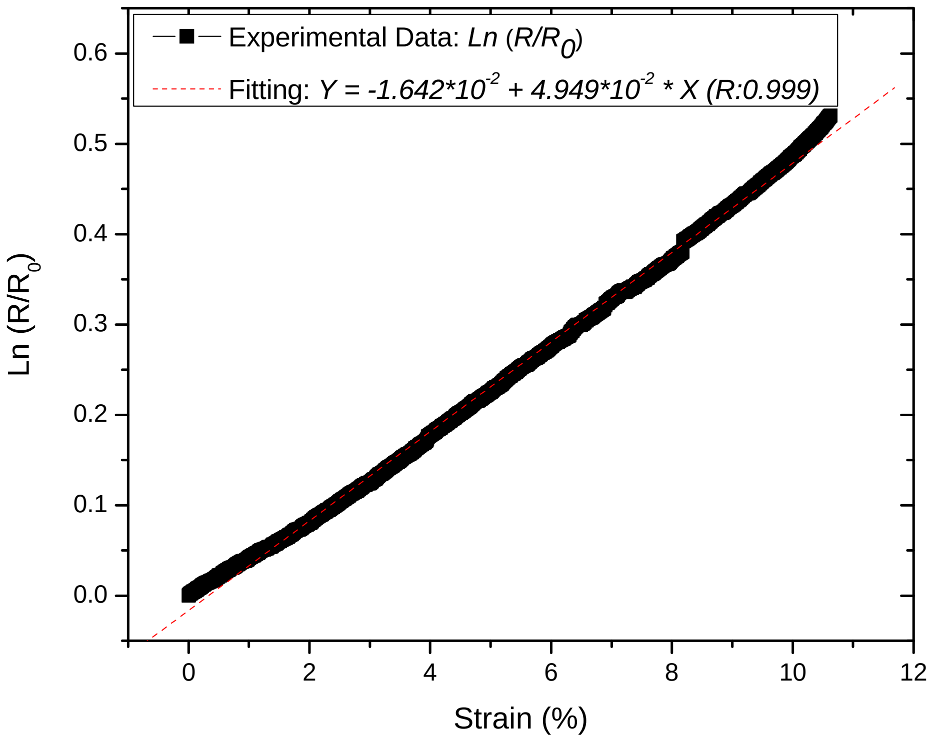
Mechanism for Piezoresistive Response



$$\frac{R(\varepsilon)}{R_0} = \exp(2\alpha d_0 \varepsilon)$$

$$\alpha = \frac{2\pi}{h}(2m\varphi)^{1/2}$$

$$\alpha d_0 = 2.475 > 1$$

if, $\Phi_{SWCNT} = 4.8 – 5.0$ *eV,*

$\Phi_{PI} = 5.1$ *eV,*

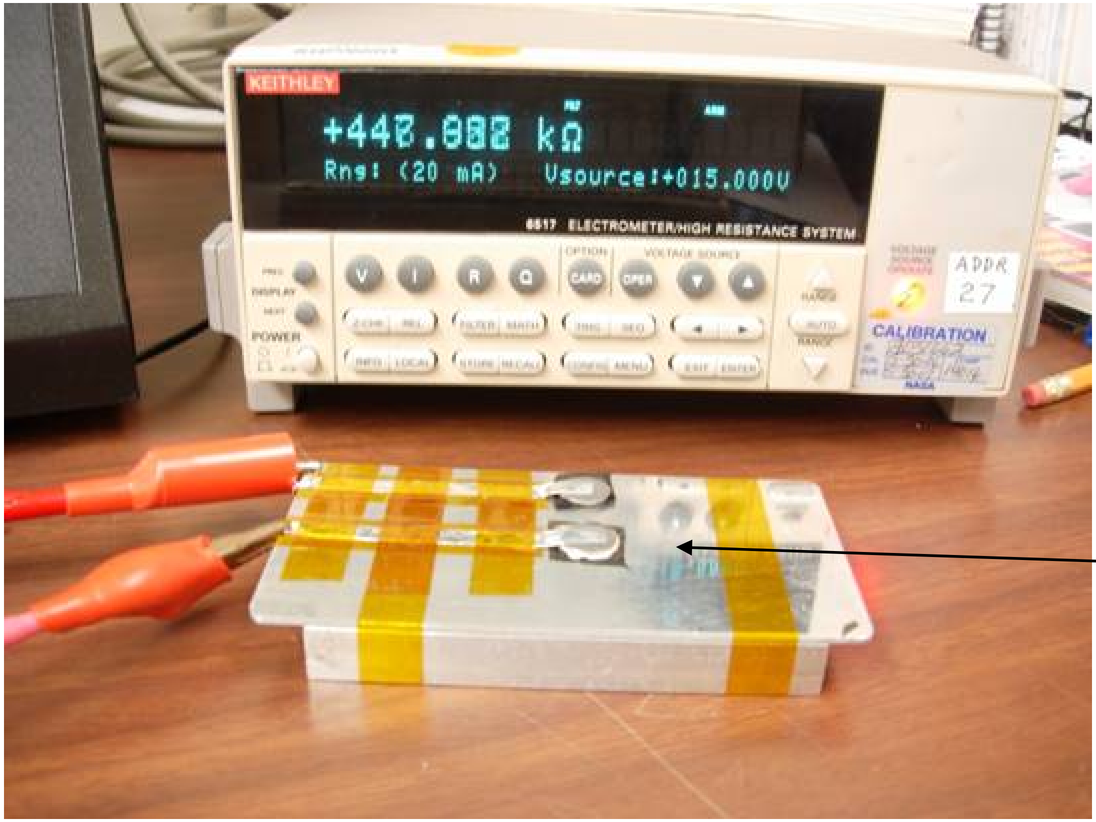
$\varphi = 0.1 – 0.3$ *eV*

$\therefore$ ***d_0 = 0.9 ~ 1.5 nm***

K. Ohe et al., Jpn. J. Appl. Phys. 10, 99 (1971).
K. E. Wise et al., Chem. Phys. Lett. 391, 207 (2004).

Demonstration of a Prototype Stress Sensor

Resistance change under stress

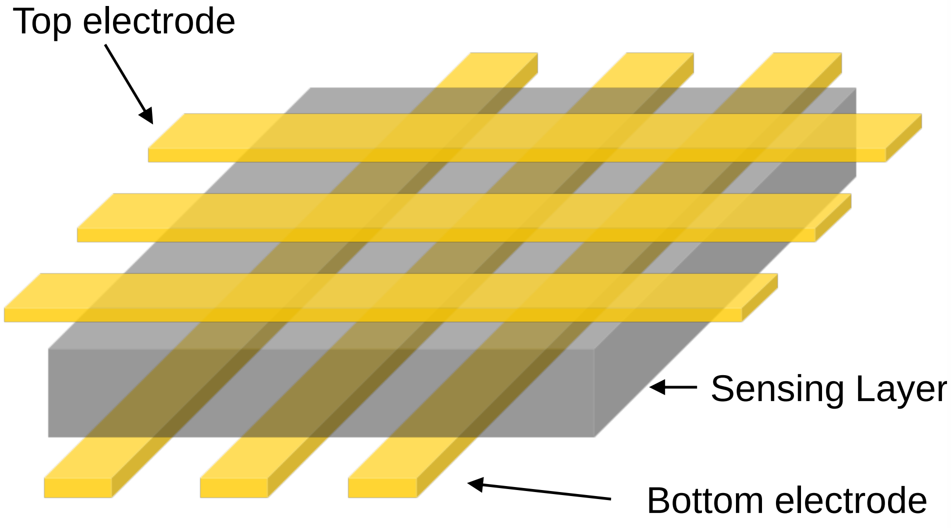


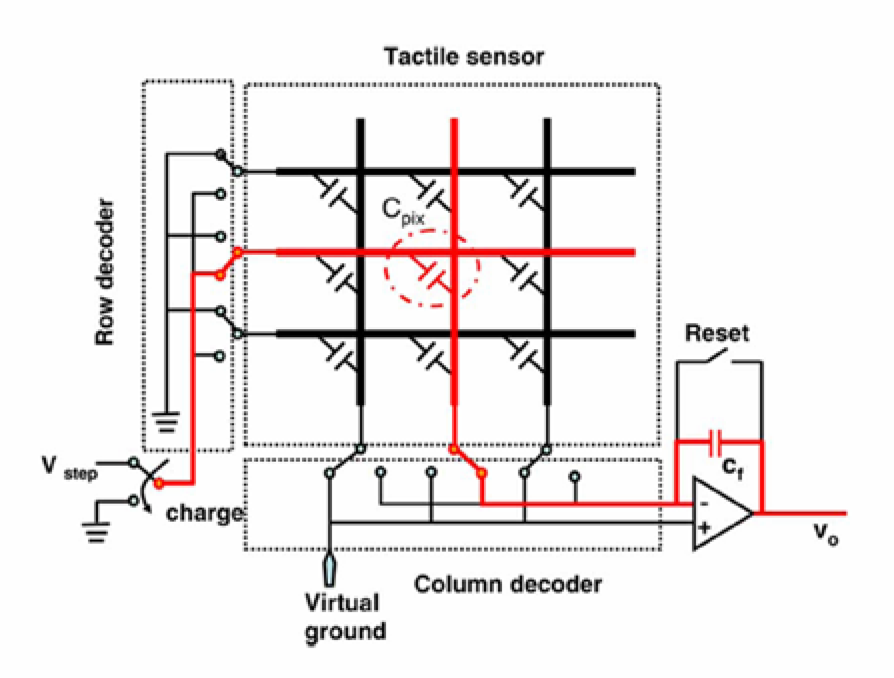
Prototype
stress sensor

0.1% CNT/*n*-LaRC EAP (*n*:100)

Ongoing project - Passive Matrix Pressure Sensor

Sensing Pressure and Location

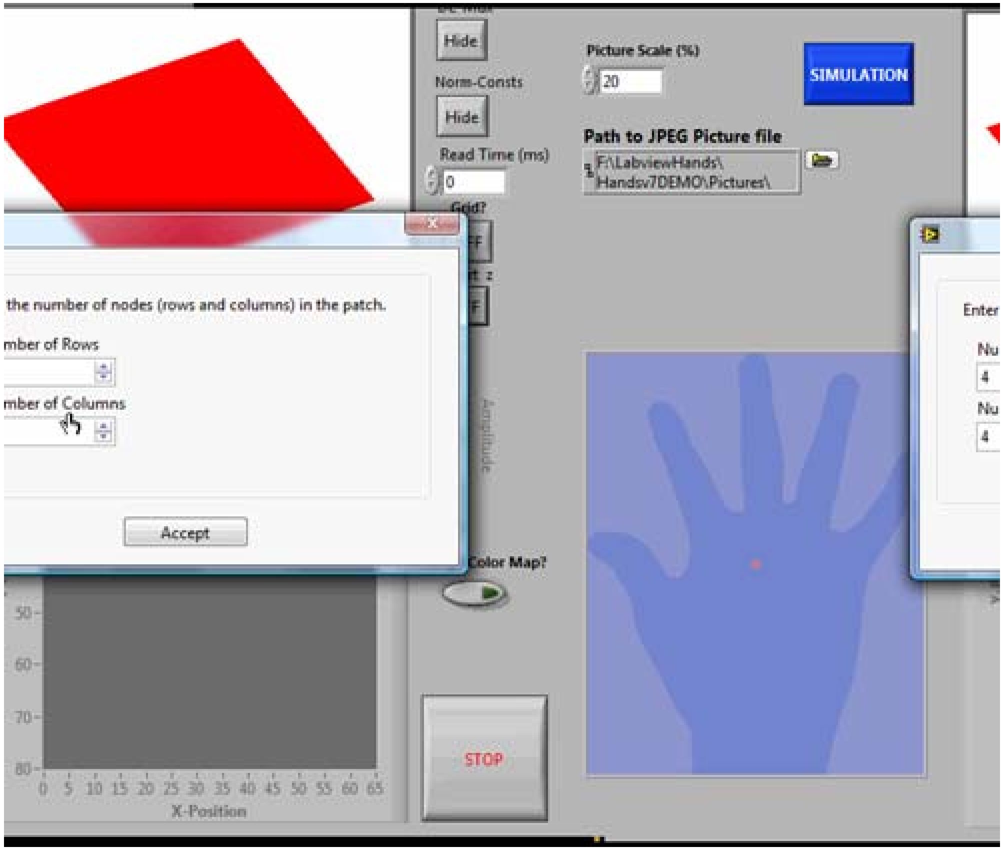




H.-K. Lee et al., J. MEMS, 15, 1681 (2006).

Ongoing project – Demonstration of Haptic Sensor

Sensing Pressure and Location



LaRC-Haptic Sensing Program

Summary

(1) SWCNT/polymer nanocomposites can provide a **new design space** for the development of stress and strain sensing materials.

(2) Small loadings of SWCNT (around percolation threshold conc.) into the polymer matrix showed an enhanced **piezoresistance response**.

(3) The sensing capabilities of mechanical stress and strain for the SWCNT/polyimide nanocomposite were demonstrated via **piezoelectric, piezoresistance and piezocapacitance response.**

(4) These overall property enhancements can lead to **improved sensors** for biomedical, aerospace and other applications

Thank You