

Temperature effects on polymer-carbon composite sensors: evaluating the role of polymer molecular weight and carbon loading

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Abstract

We report the effect of environmental conditions (temperature) coupled with varying polymer properties (molecular weight) and carbon loadings on the performance of polymer-carbon black composite film, used as sensing medium in the JPL Electronic Nose (ENose). While bulk electrical properties of polymer composites have been studied, with mechanisms of conductivity described by connectivity and tunneling, it is not fully understood how environmental conditions and intrinsic polymer and filler properties affect polymer composite sensor characteristics and responses. Composites of polyethylene oxide (PEO)-carbon black (CB) considered here include PEO polymers with molecular weights of 20K, 600 K and 1M. The first sets of experiments were performed to evaluate the effects of polymer molecular weight on the percolation threshold of PEO-carbon composites. The second set of experiments performed on the ENose focused on investigating the incremental sensor temperature effects (28-36°C in steps of 2°C) on PEO-carbon sensor response for baseline conditions (with air and no solvent) with varying polymer molecular weight and carbon loadings. Results show a correlation between the polymer molecular weight and percolation threshold. Noticeable changes in sensor properties at varying sensor temperatures are also observed for different carbon loadings that could be explained by a change in conduction mechanism.

Keywords

Polymer-composite, Electronic Nose, Temperature, Conduction mechanism

INTRODUCTION

The enhancement in electrical conductivity of insulating polymers, by mixing them with specific conductive fillers, such as metallic particles/powder/fibers, carbon black, ionic conductive polymers, and intrinsically conductive polymeric powders have found wide range of applications including EMI (Electromagnetic Interference)/RFI (Radio

Frequency Interference) shielding applications (computer and cellular phone housings, etc) to automobile tires to sensing [1].

Polymer-carbon composites used as sensing medium in the Electronic Nose (ENose) built at JPL [2-7] will be the focus of this work. An electronic nose is an array of chemical sensors, which respond when exposed to vapors. The response of the sensor to an analyte is determined by the relative change in resistance $\Delta R/R_0$ (discussed in the following section). Each sensor is non-specific to any one vapor. Upon exposure to a vapor, the sensors respond (conductivity change), creating a pattern across the array. The pattern of distributed response may be deconvoluted, and the contaminants identified and quantified using a software analysis program such as pattern recognition and/or neural network or principal component analysis. There are however various external or environmental conditions that may enhance or compromise sensor characteristics. Some external factors are pressure, humidity, and temperature.

The various possible mechanisms used to describe the conductivity behavior (electron or charge transport) of polymer-carbon composites include percolation theory, quantum mechanical tunneling and thermal expansion [1, 8-12]. The percolation theory explains the formation and structure of three dimensional conducting networks when the conductive filler is added to the polymer matrix. On increasing the amount of the conducting filler in the polymer matrix, the resistivity of the composite decreases and the composite experiences an insulator-to-conductor transition at certain critical content of the filler. This sharp break reflects the aggregation of conducting particles to form networks. This is usually defined as the percolation transition, and the critical weight (or volume) fraction of the filler is the threshold dividing the composite into insulator and conductor. The percolation threshold in polymer-carbon composites is a complex phenomenon. It depends on the physico-chemical properties of both the polymer and filler (particle size, porosity, surface area etc.) as well as the

composite processing conditions (temperature, solvent type, mixing etc) [1].

The mechanisms of tunneling or hopping and thermal expansion could be grouped together as they normally reflect temperature effects. Tunneling is commonly known to occur at low temperatures (1-100 K) and also on the application of high electric field [1]. Variable range hopping models have also been used to describe temperature dependence of conductivity in the ranges 80-300 K [12]. Thermal expansion resulting from temperature increase causes greater separation between the conductive particles causing an increase in resistivity (positive temperature coefficient (PTC) phenomenon). The PTC phenomenon for crystalline and semi crystalline polymers filled with carbon black has received considerable attention, while amorphous polymers have shown smaller PTC effect [13,14]. The PTC phenomenon for the crystalline and semi crystalline polymer-carbon black composites occurs near about the polymer melting point following which the resistivity decreases as the temperature increases, called as negative temperature coefficient (NTC) phenomena.

In the present work, we have investigated the effects of polymer molecular weight on polymer-carbon percolation threshold and the sensor temperature effects on ENose polymer-carbon black composite sensors. Two sets of experiments were performed. In the first set, polymer-carbon percolation threshold dependence was studied for polyethylene oxide-carbon composites at different polyethylene oxide molecular weights of 20K, 100K and 1M. In the second set, sensor responses for baseline conditions (with air and no solvent) were recorded for sensor temperatures in the range 28-36°C. Each sensor was held at 28°C baseline temperature and stepped 2°C to 36°C. Studies for using temperature as a variable for pattern identification is discussed elsewhere [15]. In the following discussion, the polymer and the carbon black will be abbreviated as PEO and CB, respectively and the PEO with different molecular weights will be referred to as PEO_20K, PEO_600K and PEO_1M.

EXPERIMENTAL

The PEO polymers were purchased from PolySciences. The carbon black used for the composite films was Black Pearls 2000, a furnace black made by the Cabot Corporation. All of the solvents used to dissolve the polymers and disperse the carbon black were reagent grade solvents from J. T. Baker and were used as received. Both the polymers and the carbon black were also used as received.

The polymer-carbon black solutions were prepared by mixing solutions of polymer and CB. The homogeneous polymer solution concentration (polymer/solvent) was varied between 0.5-2%. The solvent used in this study was 1,3-

Dioxolane. Protocols for film casting have been published previously [1-7].

The resistivity measurements for the percolation study were performed by depositing composite films at 4-6 positions on alumina substrates. The depositions were made between two gold contacts separated by 1 mm. The gold contacts were made on the substrates by sputtering gold on a thin layer of chromium. The film thickness (*h*) was measured by DEKTAK profilometer [16] using a standard hill and valley mode. The film resistance was measured using a FLUKE multimeter [17], which could measure resistances up to 100 M ohm.

ENose sensing films were deposited on ceramic substrates, which had eight Au-Pd electrode sets. The sensor substrate is 25 mm x 10 mm; each sensing film covered an electrode set with an area of 2mm x 1 mm. Four sensor substrates were used in the device, for a total of 32 sensors. A detailed description of the sensor chip and device operation can be found else where [7].

ENose operation involves establishing baseline resistance for each sensor film by flowing air prior to analyte exposure. Sensor data is recorded as resistance versus time and the events (exposure to an analyte or a change in temperature) are analyzed as normalized changes in resistance ($\Delta R/R_0$). The program calculates the $\Delta R/R_0$ values from the processed data. This value is more accurately described in equation:

$$\Delta R/R_0 = (R_t - R_0)/R_0$$

R_t : sensor resistance at plateau of the response

R_0 : resistance prior to the event

The percolation studies were performed for all the PEO-carbon composites (PEO_20K, PEO_600K and PEO_1M), while the temperature effect studies were done only for PEO_20K and PEO_1M. For the temperature studies, PEO-CB sensors with varying carbon loading were held at 28°C and stepped 2°C to 36°C. The sensor baseline was then established by flowing dry air. Raw sensor data for PEO_20K-carbon sensors is shown in Figure 1. The spikes at the beginning of each temperature event are directly correlated with temperature. The temperature control loop used on the sensor substrates tends to overshoot when it first changes temperature. The resistance measurement, R_t , used to calculate the sensor response is taken at the end of the temperature event, after the temperature of the substrate has equilibrated.

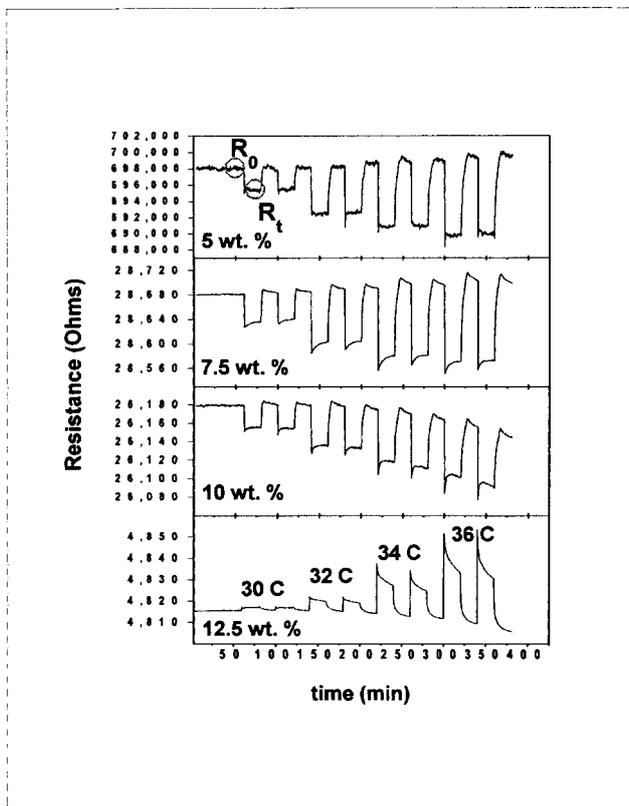


Figure 1: Raw data of resistance of PEO_20K sensors as a function of temperature. Each sensor temperature was held at 28°C (baseline with dry air) and stepped 2°C to 36°C.

RESULTS AND DISCUSSION

Percolation threshold-polymer molecular weight dependence

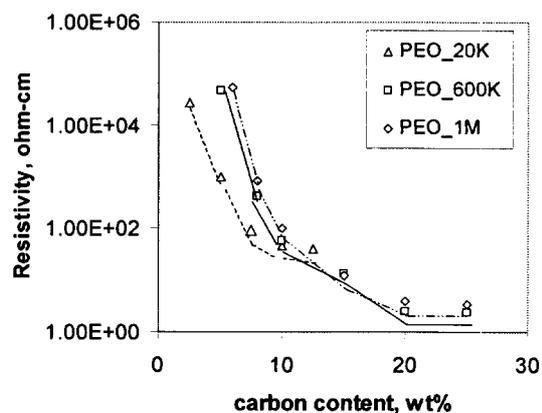
The resistivity of the polymer-carbon film, ρ , is calculated using the equation

$$\rho = RA/L$$

Where R, A and L are the resistance, cross sectional area and length of the composite film, respectively. The area (A) is determined from the width (w) and the film thickness (h). In this study, w and L were fixed at 2.5mm and 1mm, respectively.

The percolation curves for PEO-carbon black composites at different molecular weights of the polymer are shown in Figure 2.

It can be seen that the polymers with high molecular weights (600K and 1M) show higher percolation threshold value (point at which the resistivity plateaus out) as compared to the low molecular weight polymer (20K).



gies (polymer-polymer, polymer-carbon black, and carbon black-carbon black) has been developed that tries to explain the percolation threshold dependence on polymer molecular weight [18]. The high molecular weight polymers have long chains that are highly intermingled or spaghetti like in morphology as compared to the low molecular weight polymer that have shorter chains. More carbon black is needed to coat the high molecular weight polymers as well as form network structures through the polymer matrix.

Sensor temperature effect on sensor baseline response

The sensor temperature effects on sensor baseline response were measured for PEO-carbon sensors by flowing dry air and varying sensor temperatures in the range 28-36°C. Each sensor was held at 28°C baseline temperature and stepped 2°C to 36°C. PEO_20K and PEO_1M composites with carbon loadings 5-20 wt% were used for this study.

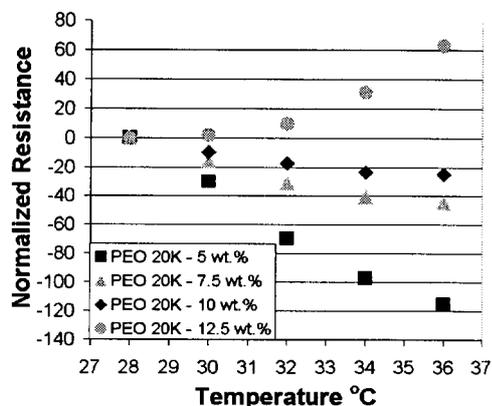


Figure 3: Baseline resistance of PEO_20K-carbon sensors as a function of temperature for varying carbon loadings. Each sensor temperature was held at 28°C (baseline with dry air) and stepped 2°C to 36°C.

The normalized baseline resistance as a function of temperature for varying carbon loadings for PEO_20K-carbon sensors is shown in Figure 3. PEO_20K sensors with 5 to 10 wt% carbon loading show a decrease in baseline resistance with an increase in temperature. Whereas, the highest carbon loaded sensor exhibit an increase in baseline resistance with an increase in temperature

This decrease in resistance with increasing temperature for carbon loading 5 to 10 wt% is similar to amorphous polymer-carbon composites, which show smaller PTC behavior but a NTC behavior with temperature increase [13,14]. We also believe that the polymers used in this work are amorphous in nature and we see similar effects. Since the glass transition temperature of PEO is very low (-63°C, from the manufacturer), hence for a low molecular weight PEO_20K containing 5 wt% carbon, an increase in temperature could result in increased polymer chain mobility and also causing more increased movement of the carbon particles that adhere (coat) to the polymer or are near the polymer chain trying to form percolation network. Hence a decrease in composite resistance (or increase in conductance) may be caused by more tunneling contribution as compared to percolation networks that would seem to be incompletely formed at such low content and would get disrupted with increasing temperature. As the carbon loading increases from 5 to 10 wt%, more three dimensional percolation networks slowly are being formed; hence an increase in temperature results in lesser mobility of the chains. In this scenario, even though some percolation networks may be disrupted to cause a decrease in conductance but the overall the tunneling contributions may still dominate and the response curves still decrease with increasing temperature for carbon loadings 7.5 and 10 wt%. The curves for 7.5 and 10 wt% carbon loadings shift with respect to the 5 wt% composite film curve. At the highest carbon loading for PEO_20K-carbon composite, the contribution to the conduction is through the percolation networks. An increase in carbon black content hinders the mobility of the polymer chains. Hence as an increase in temperature causes more breaking of the networks and hence causing an increase in the resistance.

The PEO_1M-carbon sensors show almost similar temperature effects as the PEO_20K-carbon sensors. The difference in morphology between a high and low molecular weight polymer has known to result in different disper-

sion of carbon black in the polymer matrix [19,20]. The high molecular weight polymers have long chains that are highly intermingled or spaghetti like in morphology as compared to the low molecular weight polymer that have shorter chains. More carbon black is needed to coat the high molecular weight polymers as well as to form interconnecting network structures through the polymer matrix. It could be possible that for a high molecular weight polymer, it is difficult for the carbon to penetrate the polymer matrix to form interconnected network and hence resulting in most of carbon to just coat the polymer unless composite processing conditions (temperature, solvent type, mixing etc) are adjusted appropriately. The contributions due to tunneling may still be dominant over the carbon loadings in this case. Hence for the PEO_1M-carbon composites, an increase in temperature causes less movement of the polymer chains. The shifting of the PEO_1M sensor response curves with increased carbon loading and temperature may indicate that the contributions for resistance increase caused by the disruption of percolation networks slowly comes into the picture. Figure 4 shows the temperature dependence of the baseline resistance for the PEO_1M-carbon sensors.

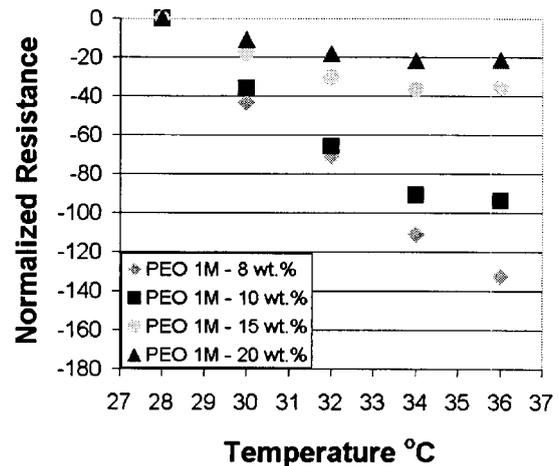


Figure 4: Baseline resistance of PEO_1M-carbon sensors as a function of temperature for varying carbon loadings. Each sensor temperature was held at 28°C (baseline with dry air) and stepped 2°C to 36°C.

ACKNOWLEDGMENTS

The research reported in this paper was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration. Research was supported by NASA Code U.

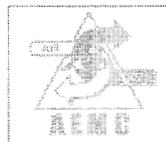
REFERENCES

- [1] E.K. Sichel, ed., *Carbon Black-Polymer Composites*, Marcel Dekker, New York (1982).
- [2] M. A. Ryan, M. L. Homer, M. G. Buehler, K. S. Manatt, B. Lau, D. Karmon, and S. Jackson, "Monitoring Space Shuttle Air for Selected Contaminants Using an Electronic Nose," *28th International Conference on Environmental Systems*, Danvers, Massachusetts, USA, 1998.
- [3] M. A. Ryan, M. L. Homer, H. Zhou, K. S. Manatt, V. S. Ryan, and S. P. Jackson, "Operation of an Electronic Nose Aboard the Space Shuttle and Directions for Research for a Second Generation Device," *Proceedings of the 30th International Conference on Environmental Systems*, Toulouse, FRANCE, 2000.
- [4] M. A. Ryan, M. L. Homer, M. G. Buehler, K. S. Manatt, F. Zee, and J. Graf, "Monitoring the Air Quality in a Closed Chamber Using an Electronic Nose," *27th International Conference on Environmental Systems*, Lake Tahoe, Nevada, USA, 1997.
- [5] M. G. Buehler and M. A. Ryan, "Temperature and Humidity Dependence of a Polymer-Based Gas Sensor," *Electro-Optical Technology for Remote Chemical Detection and Identification II*, Orlando, Florida, USA, pp. 40-48, July 1997.
- [6] M. A. Ryan et al., *Proceedings of the International Conference on Environmental Systems*, Society of Automotive Engineers (1997).
- [7] M. A. Ryan, H. Zhou, M. G. Buehler, K. S. Manatt, V. S. Mowrey, S. P. Jackson, A. K. Kisor, A.V. Shevade and M. L. Homer, "Monitoring Space Shuttle Air Quality Using the JPL Electronic Nose", submitted to *IEEE Sensors Journal*.
- [8] J.C. Huang, "Carbon black filled conducting polymers and polymer blends", *Advances in Polymer Technology*, 21 (4): 299-313 (2002).
- [9] Balberg I, "A comprehensive picture of the electrical phenomena in carbon black-polymer composites", *Carbon*, 40 (2) 139-143 (2002).
- [10] J.C. Dawson, and C.J. Adkins, "Conduction mechanisms in carbon-loaded composites", *Journal of Physics Condensed Matter*, 8 (43): 8321-8338 (1996).
- [11] D. Vanderputten, J.T. Moonen, H.B. Brom, J.C.M. Brokkenzipp, and M.A.J. Michels, "Effect of Fractality on the Hopping Conduction in Carbon-Black/ Polymer Composites", *Synthetic Metals*, 57 (2-3): 5057-5062 (1993).
- [12] M.G. Alexander, "Anomalous temperature dependence of the electrical conductivity of carbon-poly(methyl methacrylate) composites" *Materials Research Bulletin*, 34 (4): 603-611 (1999).
- [13] XJ He, LJ Wang, and XF Chen, "PTC effect in carbon black-filled ethylene-propylene-diene terpolymer systems", *Journal of Applied Polymer Science*, 80 (9): 1571-1574 (2001).
- [14] J. Fournier, G. Boiteux, G. Seytre, and G. Marichy, "Positive temperature coefficient effect in carbon black/epoxy polymer composites", *Journal of Materials Science Letters*, 16(20): 1677-1679 (1997).
- [15] M.L. Homer, J.R. Lim, K. Manatt, A. Kisor, L. Lara, A. D. Jewell, A. V. Shevade, S.P.-S.Yen, H. Zhou and M.A.Ryan, "Using Temperature Effects on Polymer-Composite Sensor Arrays to Identify Analytes", submitted to *IEEE Sensors proceedings (2003)*.
- [16] DEKTAK is a profile measuring system from Veeco Metrology Group, Santa Barbara CA.
- [17] FLUKE multimeter from John Fluke Mfg. Co., Inc.
- [18] M.L. Homer, J.R. Lim, K. Manatt, A. Kisor, L. Lara, A. D. Jewell, A. V. Shevade, S.P.-S.Yen, H. Zhou and M.A.Ryan, *manuscript in-preparation to be submitted to IEEE Sensors Journal (2003)*.
- [19] Y. Bin, C. Xu, Y. Agari, and M. Matsuo, "Morphology and electrical conductivity of ultrahigh-molecular-weight polyethylene-low-molecular-weight polyethylene-carbon black composites prepared by gelation crystallization from solutions", *Colloid and Polymer Science*, 277 (5): 452-461 (1999).
- [20] Rwei SP, Ku FH, and Cheng KC, "Dispersion of carbon black in a continuous phase: Electrical, rheological, and morphological studies", *Colloid and Polymer Science*, 280 (12): 1110-1115 (2002).

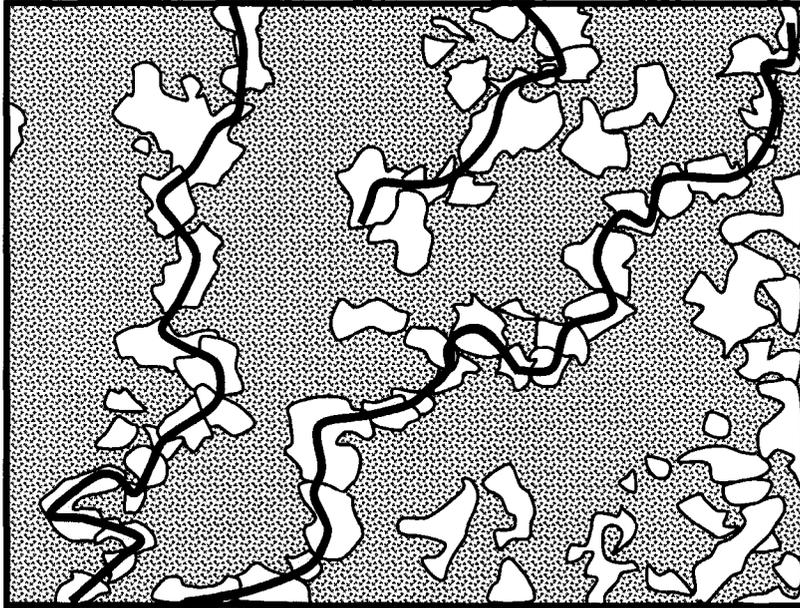
Temperature Effects on Polymer-carbon Composite Sensors: Evaluating the Role of Polymer Molecular Weight and Carbon Loading

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Conduction in Polymer-Carbon Composites

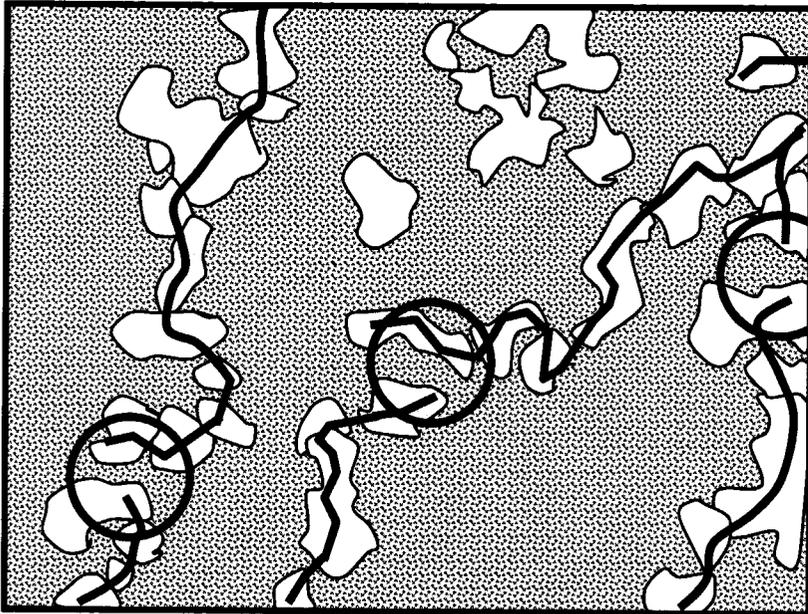


Conduction through pathways formed by carbon particles. Conduction may be through connected particles or by tunneling.

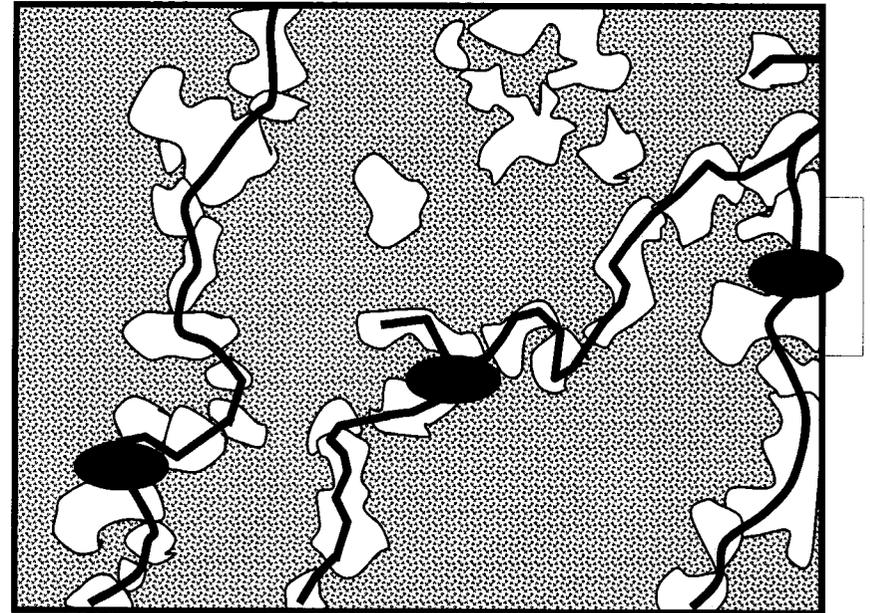


Conduction interrupted when polymer matrix swells, pushing carbon particles apart.

Conduction in Polymer-Carbon Composites



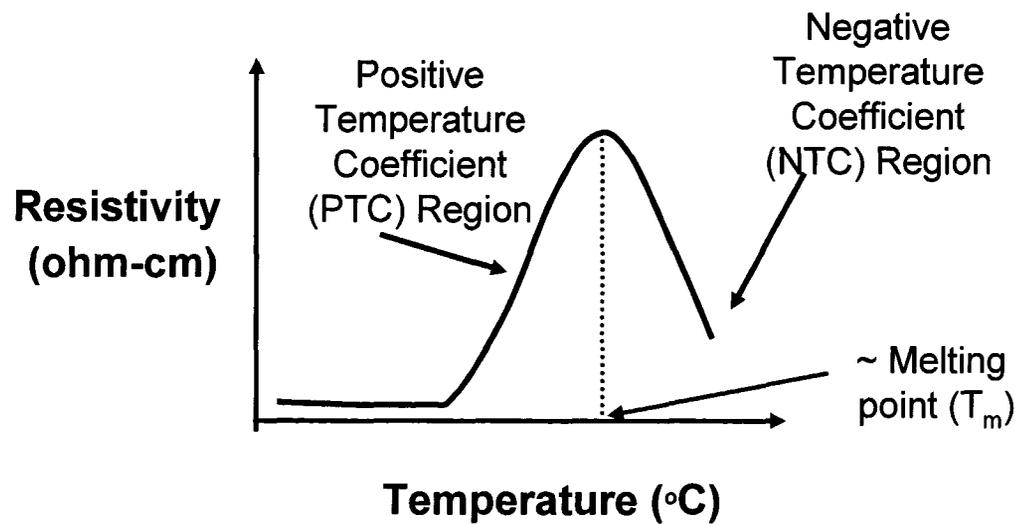
Conduction interrupted by breaks in carbon particle path



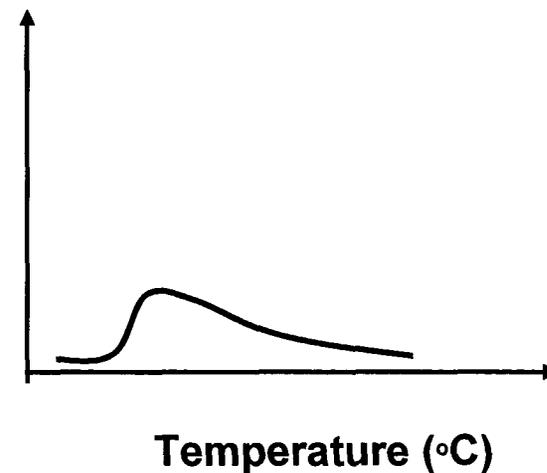
Conduction enhanced by ionically conducting solution to fill breaks in carbon particle path

Resistivity of Polymer-Carbon Composite versus Temperature

Composites of crystalline and semicrystalline polymers

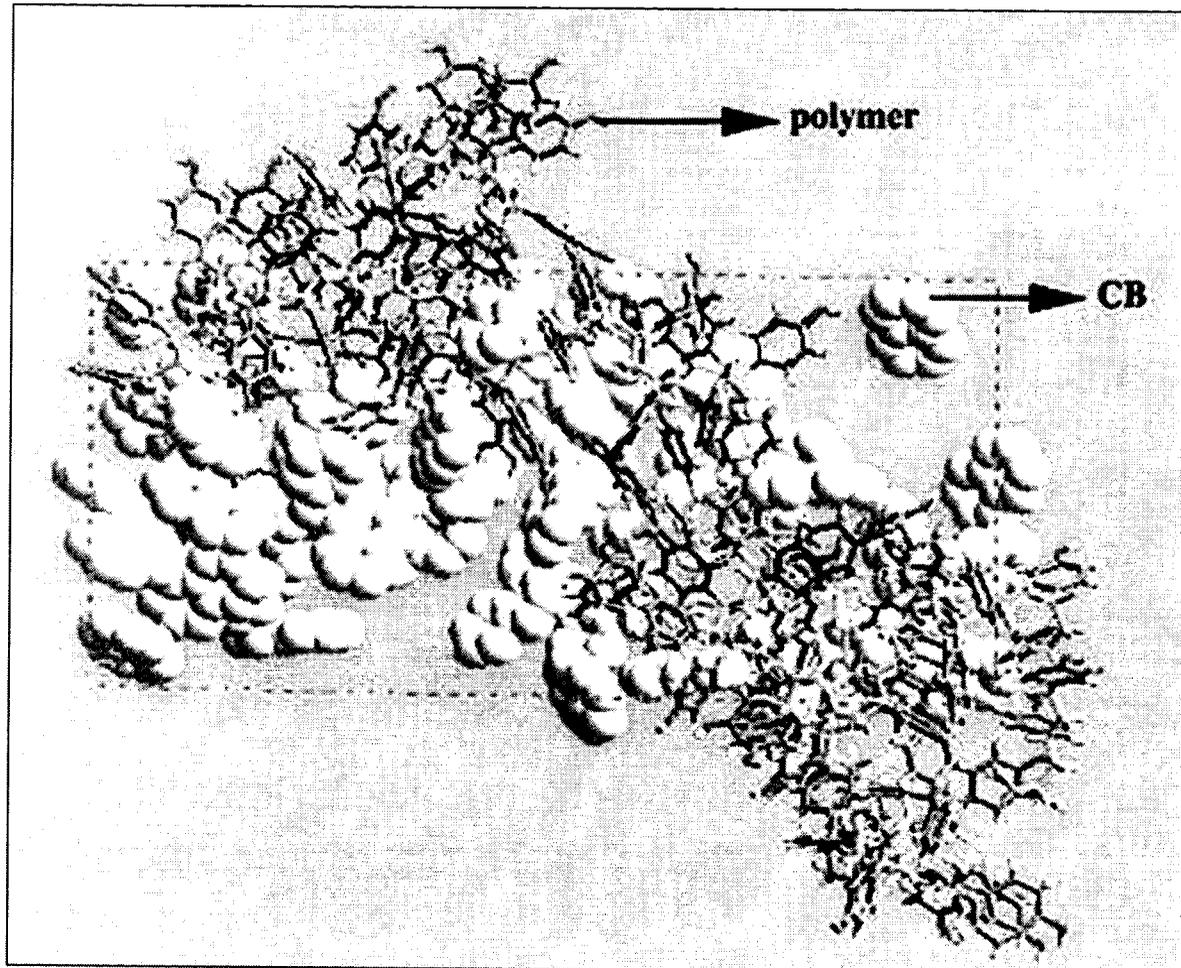


Composites of amorphous polymers

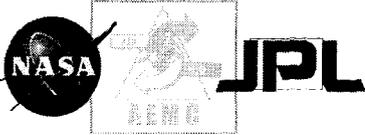


PTC effect is less pronounced in composites of amorphous polymer

Polymer-Carbon Black Composite Film



Structure of poly(4-vinylphenol)-CB composite film; structure equilibrated using molecular dynamics. Van der Waals, electrostatic and H-bonding energy terms will be analyzed in this structure in the presence of analyte molecules.



Objectives

- ❖ To evaluate the effects of polymer molecular weight on the percolation threshold of polyethylene oxide-carbon composites

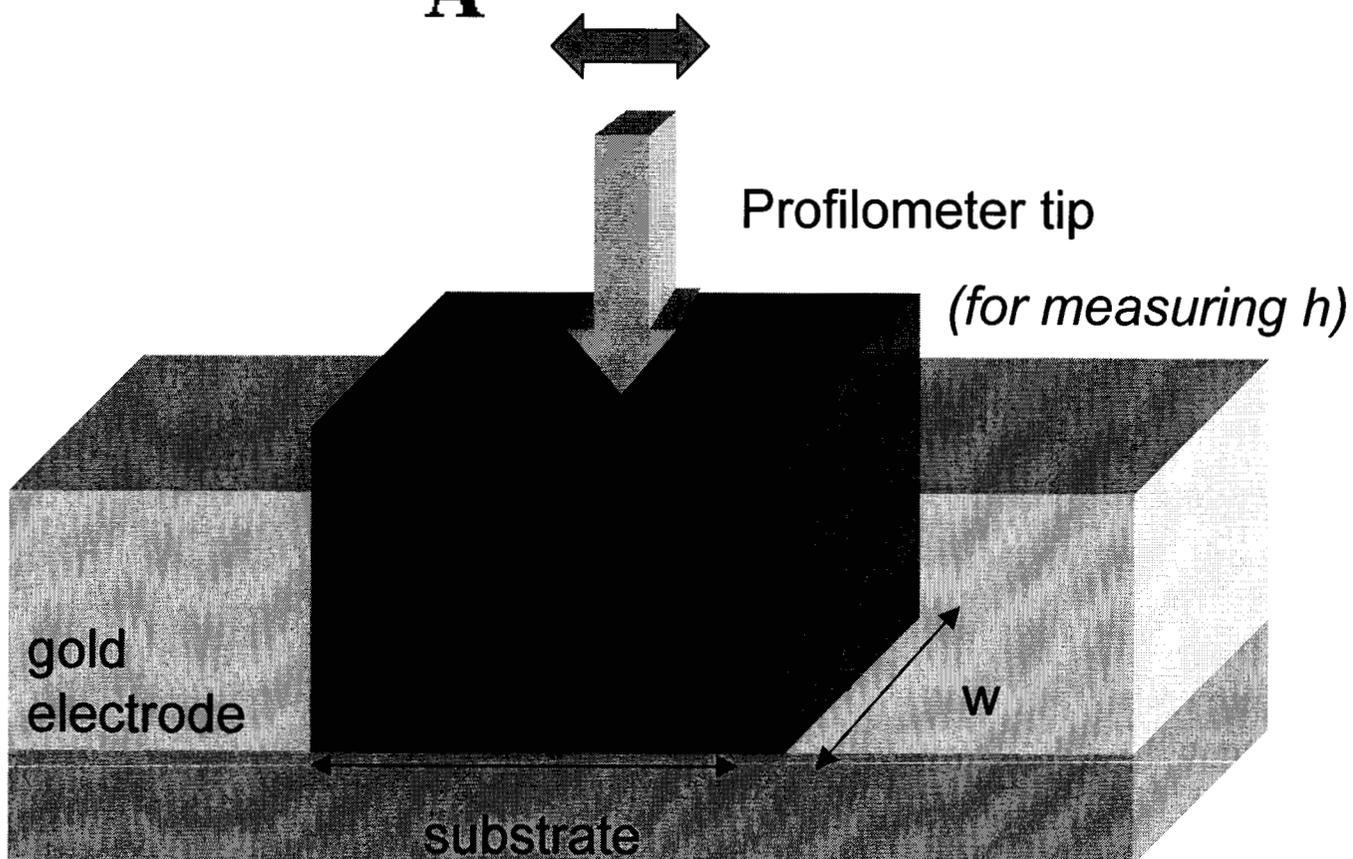
Polyethylene oxide (molecular weight: 20K, 600 K, 1M)
Carbon black (5-25 wt%)

- ❖ To investigate the incremental sensor temperature effects (28-36°C in steps of 2°C) on ENose) PEO-carbon sensor response for baseline conditions (air and no solvent)

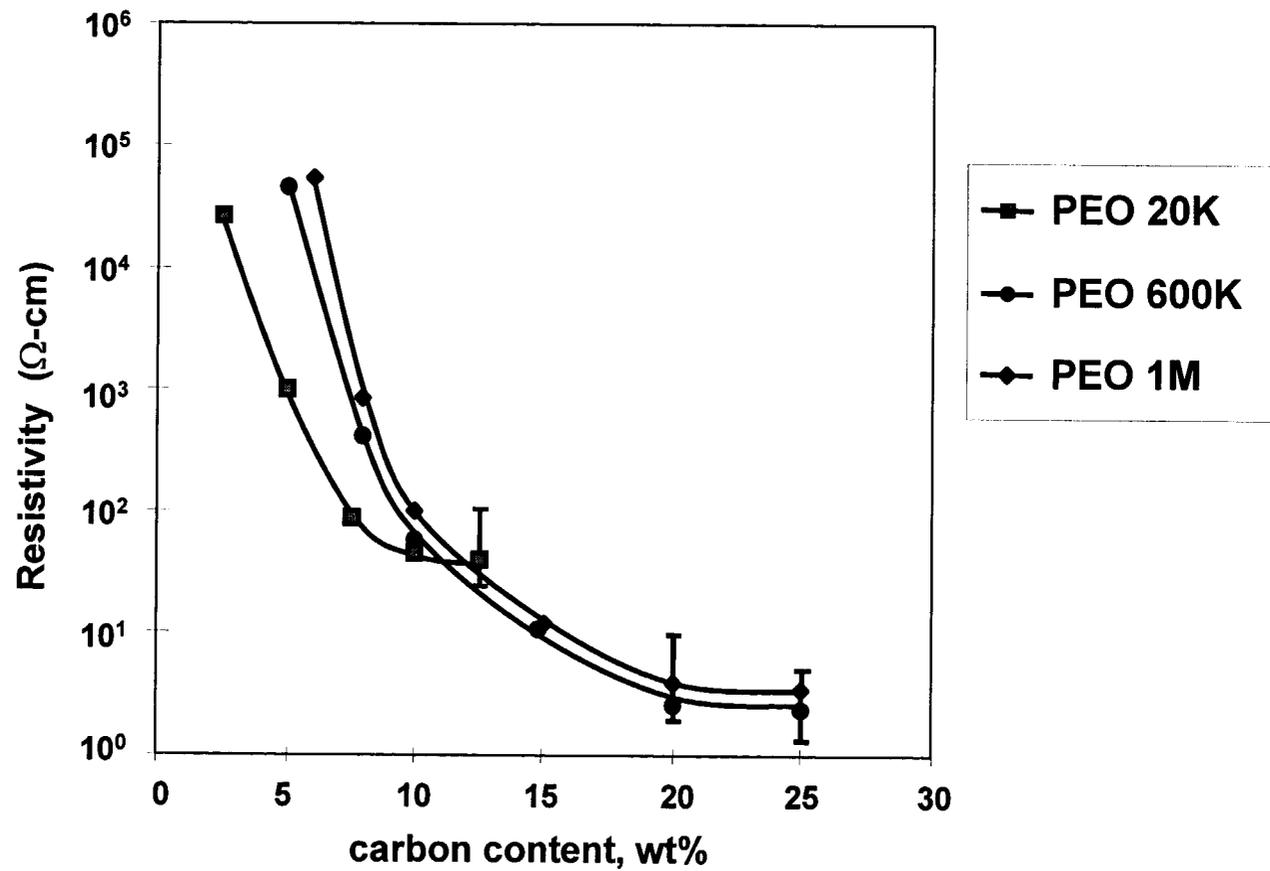
Resistivity Measurements

Resistance $R = \frac{\rho L}{A}$

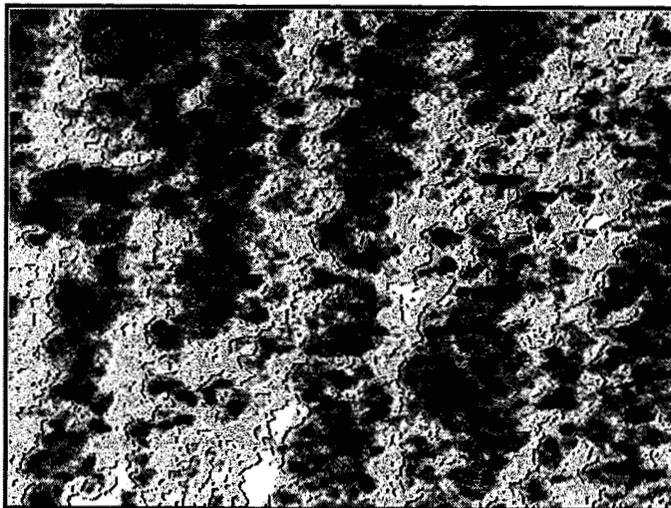
ρ = resistivity
 L = length
 A = cross sectional area



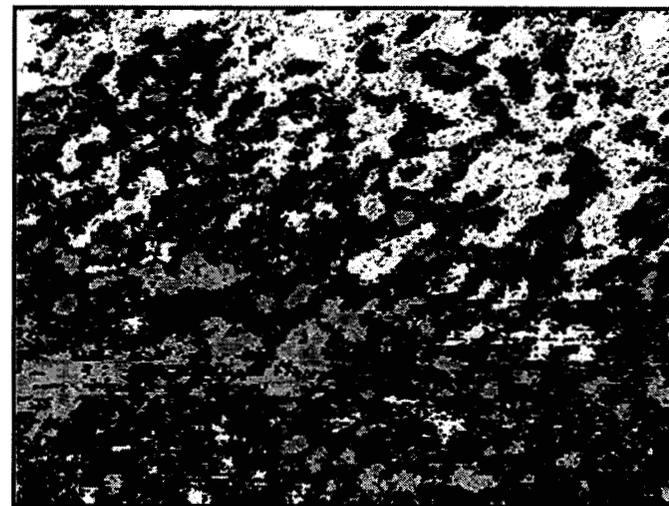
Percolation Threshold



Polyethylene oxide (1M)
carbon black = 10 wt%



Polyethylene oxide (1M)
Carbon black = 15 wt%



 polymer

 carbon black



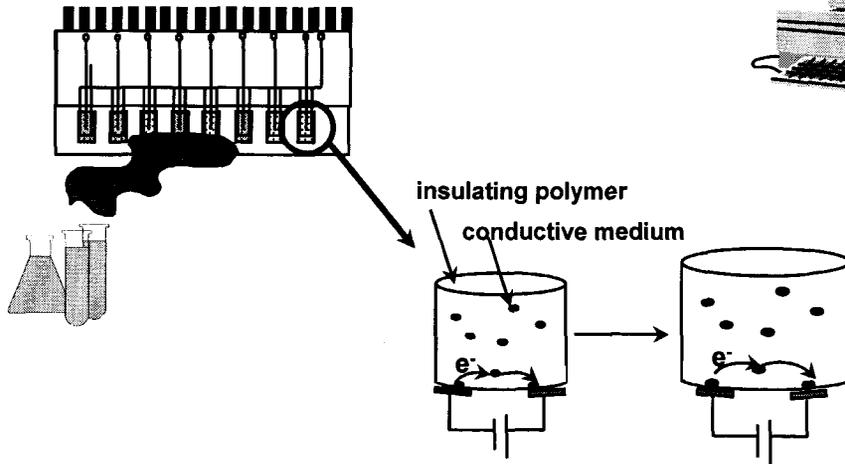
JPL

What is an Electronic Nose (ENose)?

An array of non-specific chemical sensors, controlled and analyzed electronically, which mimics the action of the mammalian nose by recognizing patterns of response

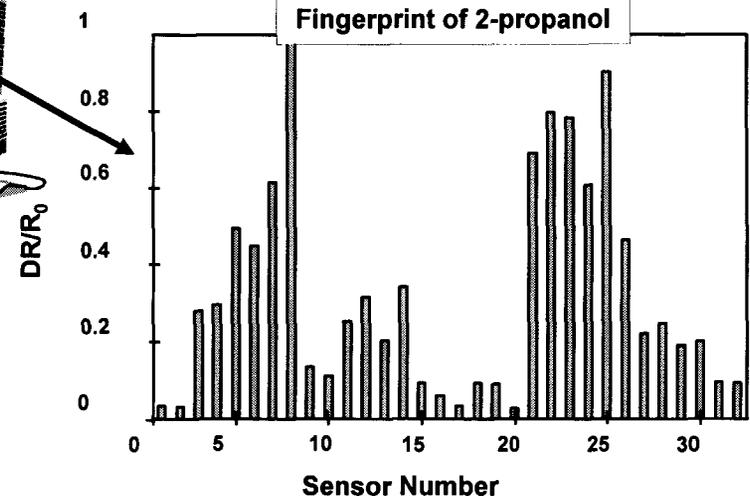
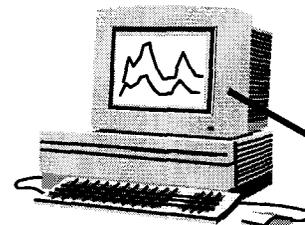
1. ENose measures background resistance in each sensor and establishes R_0 .

2. Contaminant comes in contact with sensors on the sensing head.



3. The sensing media, polymer films loaded with a conductive medium such as carbon black, change resistance by swelling or shrinking as air composition changes.

4. Resistance is recorded by a computer, the change in resistance is computed, and the distributed response pattern of the sensor array is used to identify gases and mixtures of gases



5. Responses of the sensor array are analyzed and quantified using software developed for the task.

propanol 300 ppm

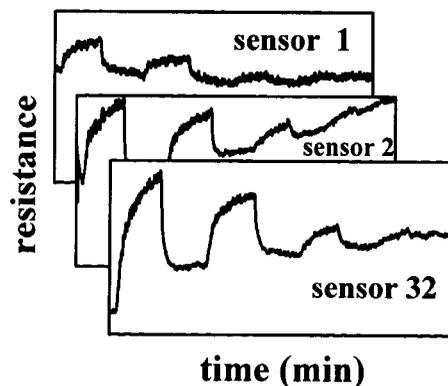
Sensor Calibration and Characterization

- Training Sets: Generate time-series resistances for sensors with known gases and concentrations
- Preprocess resistance data: Convert time-series resistance data to resistance response pattern
- Establish “fingerprints” for analytes

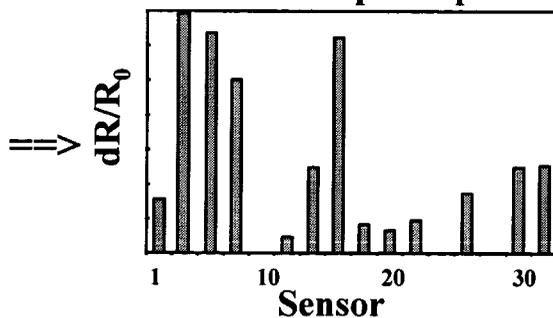
Identification and Quantification of Analytes

- Testing Sets: Generate time-series resistances for sensors with unknown gases and concentrations
- Preprocess resistance data: Convert time-series resistance data to resistance response pattern
- Deconvolute response pattern by pattern recognition using Levenberg-Marquardt Nonlinear Least Squares Fits (LMNLS)

time-series resistance data



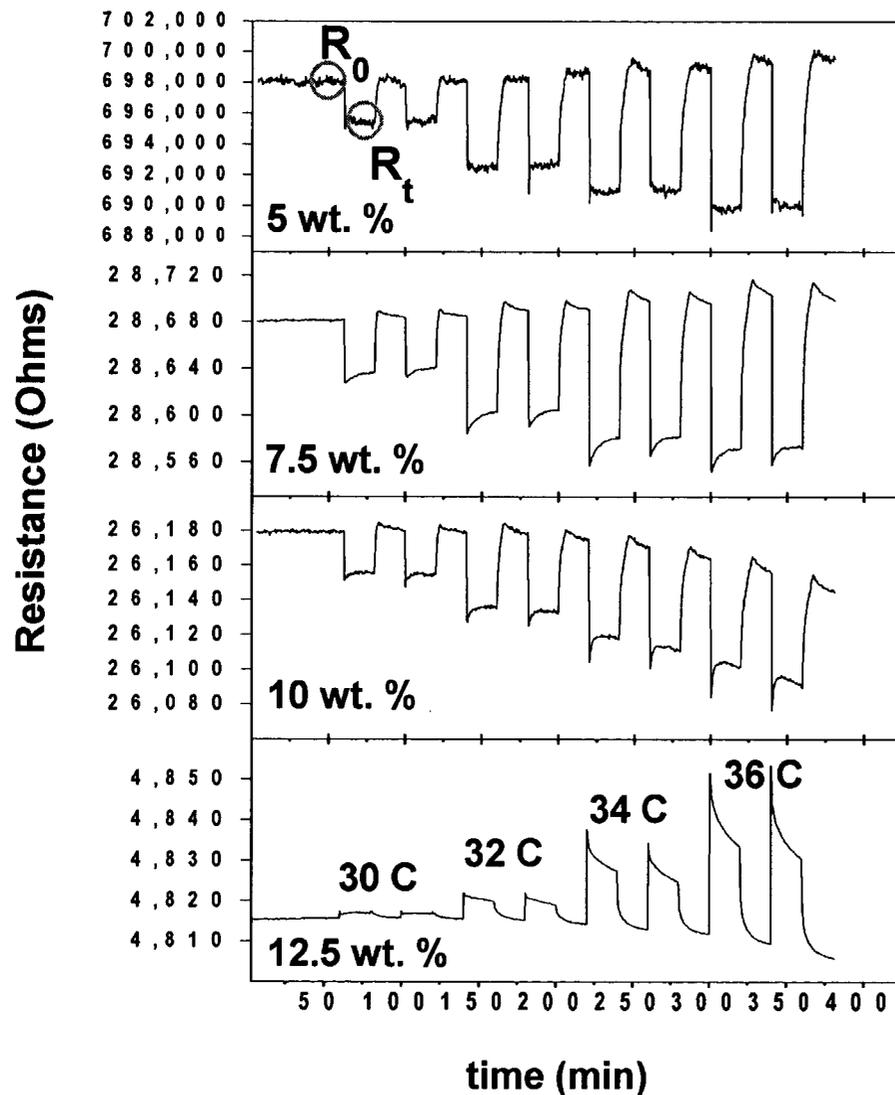
resistance response pattern



software analysis result

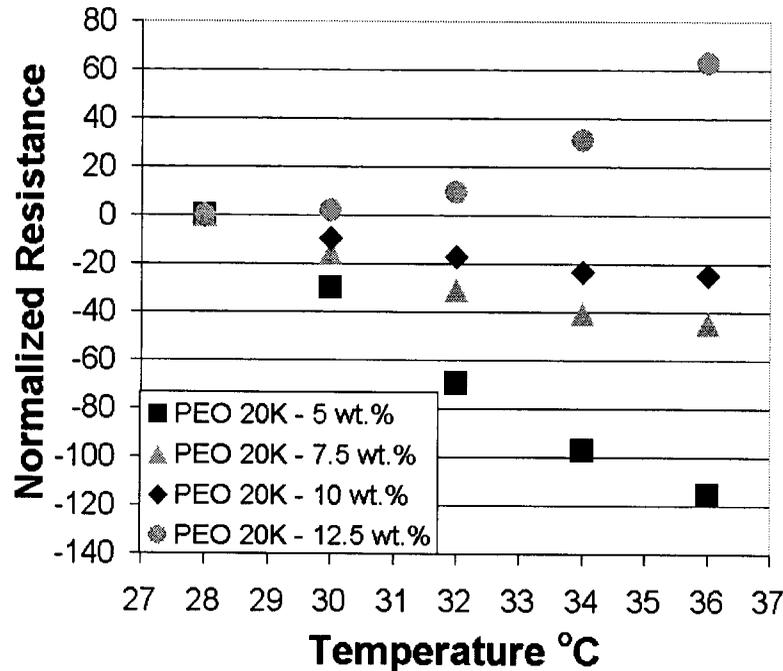
⇒ 35 ppm toluene +
50 ppm benzene

Sensor Response to Changes in Temperature



Raw data of PEO (M.W. = 20K) sensors baseline resistance as a function of temperature. Each sensor temperature was held at 28°C (baseline with dry air) and stepped 2°C to 36°C.

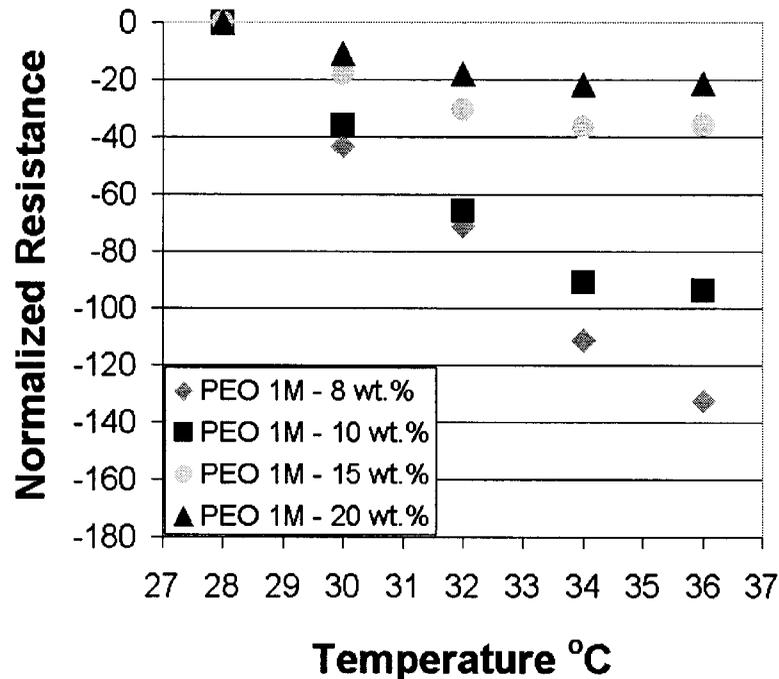
Sensor Response to Changes in Temperature



- NTC behavior at 5-10 wt%
- PTC behavior at 12.5 wt%
- As temperature increases higher polymer mobility at low carbon loadings
- Conducting mechanism:
 - *tunneling at low carbon loadings*
 - *Percolation network contribute more at high carbon loading*

Baseline resistance of PEO -carbon sensors (PEO molecular weight 20K) as a function of temperature for varying carbon loadings. Each sensor temperature was held at 28°C (baseline with dry air) and stepped 2°C to 36°C.

Sensor Response to Changes in Temperature



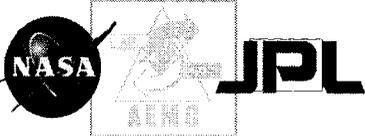
- NTC behavior
- Conducting mechanism:
 - *predominantly by tunneling*
 - *percolation network contribute more at high carbon loading*

Baseline resistance of PEO -carbon sensors (PEO molecular weight 1 M) as a function of temperature for varying carbon loadings. Each sensor temperature was held at 28°C (baseline with dry air) and stepped 2°C to 36°C.



Conclusions

- Percolation threshold in polyethylene oxide-carbon composites was found to increase with the molecular weight of the polymer.
- Noticeable changes in sensor properties at varying sensor temperatures are also observed for different carbon loadings that could be explained by a change in conduction mechanism.



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