

# 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 temperature coupled with varying polymer molecular weight and carbon loadings on the performance of polymer-carbon black composite films, used as sensing media 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 effects of polymer molecular weight on the percolation threshold of PEO-carbon composite and incremental sensor temperature effects on PEO-carbon sensor response were investigated. Results show a correlation between the polymer molecular weight and percolation threshold. Changes in sensor properties as a function of temperature are also observed at different carbon loadings; these changes may 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 has found applications ranging from EMI (Electromagnetic Interference)/RFI (Radio Frequency Interference) shielding in computer and cellular phone housings, to automobile tires to chemical and physical sensing [1].

Polymer-carbon composites used as sensing media 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  $\Delta R/R_0$  (*vide infra*). Each sensor is non-specific to any one vapor. Upon exposure to a vapor, the sensors respond with a 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, neural network or principal component analysis. There are however various external or environmental conditions that may enhance or compromise sensor characteristics. Some of these 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]. 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 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, such as particle size, porosity, surface area as well as the composite processing conditions, such as temperature, solvent type [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. A composite exhibiting an increase in resistivity with increased temperature is described as having a positive temperature coefficient (PTC). The PTC phenomenon for crystalline and semi crystalline polymers filled with carbon black has received considerable attention, while amorphous polymers have shown smaller PTC effects [13,14]. The PTC phenomenon for crystalline and semi crystalline polymer-carbon black composites occurs near the polymer melting point, above which the resistivity decreases as the temperature increases, known as the negative temperature coefficient (NTC) phenomenon.

In the present work, we have investigated the effects of polymer molecular weight on the polymer-carbon percolation threshold and the temperature effects on ENose polymer-carbon black composite sensors. Two sets of experiments were performed. In the first set, the dependence of polymer-carbon percolation threshold on polymer molecular weight was studied for polyethylene oxide-carbon composites at different polyethylene oxide (PEO) molecular weights of 20K, 600K and 1M. In the second set, sensor responses for baseline conditions (air and no analyte) 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 called as PEO and CB, respectively and PEO with different molecular weights will be referred to as PEO\_20K, PEO\_600K and PEO\_1M.

## EXPERIMENTAL

The PEO polymers were purchased from Poly-Sciences. 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.

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].

Composite films for resistivity measurements for the percolation study were made by depositing PEO-CB solutions at 4-6 positions on alumina substrates. The films were made between two gold contacts separated by 1 mm. The gold contacts were made on the substrates by sputter-

ing 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 elsewhere [7].

ENose operation involves establishing baseline resistance for each sensor film by flowing air 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

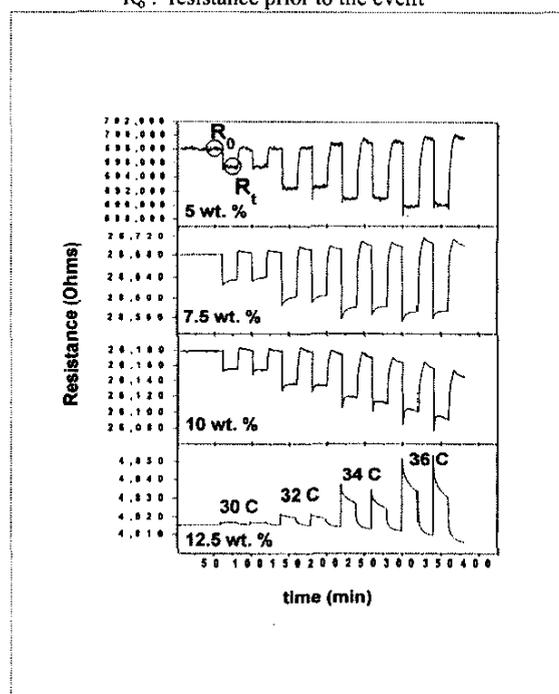


Figure 1: Raw data of resistance of PEO\_20K sensors as a function of temperature. Each sensor temperature was held at 28°C (baseline with dry air) and stepped 2°C to 36°C.

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.

## RESULTS AND DISCUSSION

### Percolation threshold-polymer molecular weight dependence

The resistivity of the polymer-carbon film,  $\rho$ , 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). A thermodynamic percolation model for polymer-carbon composites based on molecular modeling interaction energies (polymer-polymer, polymer-carbon black, and carbon black-carbon black) has been developed to explain the percolation threshold dependence on polymer molecular weight [18].

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.

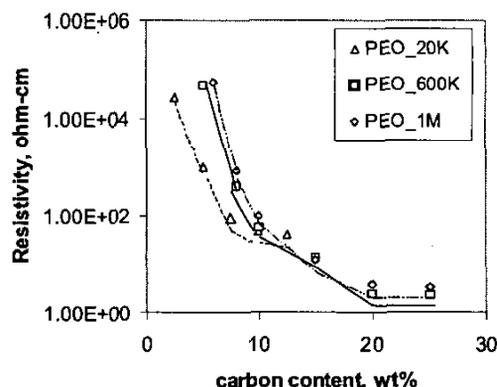


Figure 2: Percolation curves for PEO-carbon composites at different molecular weights of PEO.

### Effect of sensor temperature on sensor baseline response

Effects of sensor temperature on sensor baseline response were measured for PEO-CB sensors by flowing dry air over the sensors 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.

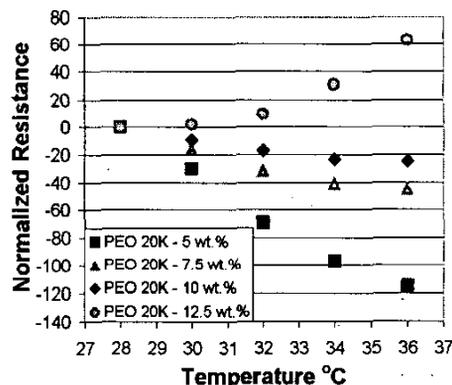


Figure 3: Baseline resistance of PEO\_20K-carbon sensors as a function of temperature for varying carbon loadings. Each sensor temperature was held at 28°C (baseline with dry air) and stepped 2°C to 36°C.

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 sensor with highest carbon load exhibits an increase in baseline resistance with an increase in temperature

This decrease in resistance with increasing temperature for carbon loadings of 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 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 (-67°C, from the manufacturer), for a low molecular weight PEO\_20K containing 5 wt% carbon, an increase in temperature could result in increased polymer chain mobility. At the same time, increasing temperature can cause increase 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 contributions 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 lowered mobility of the chains. In this scenario, even though some percolation networks may be disrupted to cause a decrease in conductance overall the tunneling contributions will dominate and the response curves decrease with increasing temperature for carbon loadings 7.5 and 10 wt%. As from in Figure 3, 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. An increase in temperature causes more breaking of the networks, causing an increase in the resistance.

The PEO\_1M-carbon sensors show similar temperature effects as the PEO\_20K-carbon sensors. The difference in morphology between a high and a low molecular weight polymer is known to result in different dispersion 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.

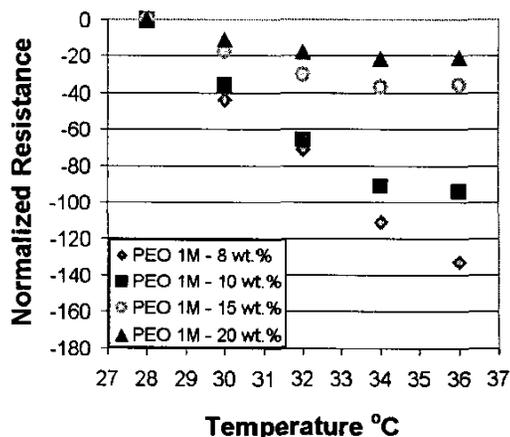


Figure 4: Baseline resistance of PEO\_1M-carbon sensors as a function of temperature for varying carbon loadings. Each sensor temperature was held at 28°C (baseline with dry air) and stepped 2°C to 36°C.

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