Modeling Chemiresistor Sensors 1: Conductivity Model

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Abstract

Chemiresistor sensors made from carbon black – polyisobutylene composite, perform based on the change of the resistivity of the composite when they swell in the analytes. Two models are necessary to describe the mechanism of carbon-polymer chemiresistors theoretically: the conductivity model and the thermodynamic model. In this work, the conductivity model was studied. Sixty-four chemiresistors representing 8 different carbon concentrations (8 to 60 vol% carbon) were constructed by depositing thin films of a carbon black/polyisobutylene composite onto concentric spiral platinum electrodes. The impact of carbon concentration and geometry on the measured resistance and derived resistivity of the polymer composite was determined. The thickness and surface topography of each sensor was measured with a mechanical profilometer. The derived resistivity data fit the general effective media (GEM) model adequately, and the fitted parameters predicted values for percolation threshold and carbon resistivity that were consistent with published literature. Finite element modeling showed that resistivity was a strong function of composite composition and thickness, but was relatively insensitive to the surface roughness of the composite on the sensor. The correlations developed can be used in reverse to calculate the thickness of the composite polymer film deposited on the solid substrate from a measurement of resistance in dry air.

1. Introduction

Sensors made from conductive carbon black dispersed in various polymers have been developed and studied extensively. The response of the sensor to a chemical is measured as a change in the resistance of the sensor, thus this type of device is named “chemiresistor”. As the analyte diffuses into the polymer composite, the polymer swells, which causes the dispersed conductive carbon particles to move further apart from each other, which in turn decreases the conductivity or increases the resistance of the sensor. An array of polymer composite sensors can be constructed from a wide variety of polymers that differ in their responses to various analytes. By selecting polymers with a varied range of responses, one aspires to develop an array of sensors that can detect nearly any vapor and calculate concentrations of individual analytes in a mixture of vapors. One still has to process the various signals from all the sensors, but there are statistical methods available to calculate individual analyte concentrations from the integrated responses to mixtures of vapors.

Although empirical methods have been used to analyze sensor responses, much less work has been done to describe the conductive carbon–polymer chemiresistor theoretically. To describe the physics of such a sensor, two models are necessary: a thermodynamic model and a conductivity model. The thermodynamic model gives the relationship between the concentrations of each component in the vapor phase and those in the polymer phase. This governs how much the polymer swells and how far the conductive particles move from each other as a function of gas-phase composition. The conductivity model describes the relationship between the concentration (and thus interparticle distance) of the conductive carbon in the polymer phase, and the resistivity of the composite film. Combining these two models produces a relationship between the concentration of analyte(s) in the vapor, and the change in conductivity (or resistivity) of the composite of the sensor. This paper focuses on the conductivity model.

2. Theory

2.1 General Effective Media Model

The general effective media (GEM) equation was developed by combining effective media theory and percolation theory [2-6] and was used as the conductivity model for chemiresistor sensors. The GEM model relates the composite resistivity to the concentration of the various components [1]:

$$\frac{f\left(\rho_c^{-1/k}-\rho_m^{-1/k}\right)}{\rho_c^{-1/k}+A\rho_m^{-1/k}}+\frac{(1-f)\left(\rho_p^{-1/k}-\rho_m^{-1/k}\right)}{\rho_p^{-1/k}+A\rho_m^{-1/k}}=0 \tag{1}$$

where

$$A=\frac{1-f_c}{f_c}$$

f_c is the critical volume fraction of the low resistance (carbon) component, or percolation threshold; ρ_c is the resistivity of the low resistance (carbon black) phase; ρ_m is the resistivity of composite mixture; ρ_p is the resistivity of the high resistance (polymer) phase; f is the volume fraction of the low resistance (carbon) phase; k is an exponent.

2.2 Measurement of Resistivity

Resistivity is an intrinsic property of a material, independent of material geometry, whereas resistance is highly dependent upon geometry. In rectangular sample geometries with flat electrodes attached to opposite sides of the sample (instead of on the bottom), the resistivity is related to the resistance by

$$\rho=\frac{RA}{L}=\frac{VA}{IL}=\frac{V}{iL} \tag{2}$$

where R is the resistance, A is the cross section of the material perpendicular to the current flow, L is the length between source electrodes, V is the voltage between source electrodes, I is the current flow and i is the current density. In the present research, spiral electrodes are used to increase the area available for conductance between electrodes while minimizing the footprint. The increased area has been shown to reduce the variance in the baseline resistances of the chemiresistors [7]. However, it is not trivial to relate the resistivity to resistance in the polymer deposited on the spiral electrodes because A, L and i are no longer simple parameters. Figure 1 illustrates our model of current flow in the conductive composite above the spiral electrodes. Figure 1A shows the 2-turn spiral electrodes which alternate positive and negative polarity inside the spiral. The current flows from the electrode upward and sideways through the composite, and then down to the adjacent electrode. By straightening the curved electrodes, one has the model shown in Figure 1B with parallel adjacent electrodes. In this symmetrical model, current flows to both the left and right from the positive electrodes to the adjacent negative electrodes. Thus one can further subdivide the electrical model into "half-electrodes" 15 µm wide on the bottom sides of a strip of conductive polymer, with a spacing of 50 µm between the electrode edges, as shown in Figure 1C. The thickness, t, of this strip of conductive polymer determines the shape of the lines of current flow between the two electrodes. Figure 1D shows a cross section of the polymer strip with lines illustrating the flow of current. Thus the current flow in 3-D has been reduced to a simplified model of current flow in 2-D that is much more easy to calculate. The current distribution and potential distribution in the 2-D model must satisfy the LaPlace potential equation [8]:

$$\nabla^2\Phi = 0 \tag{3}$$

in which Φ is the electrostatic potential and ∇ is the del operator. The solution of the LaPlace equation for this geometry gives a potential distribution and current distribution (lines of current are perpendicular to equipotential surfaces) that is non-uniform, as illustrated in Figure 1D.

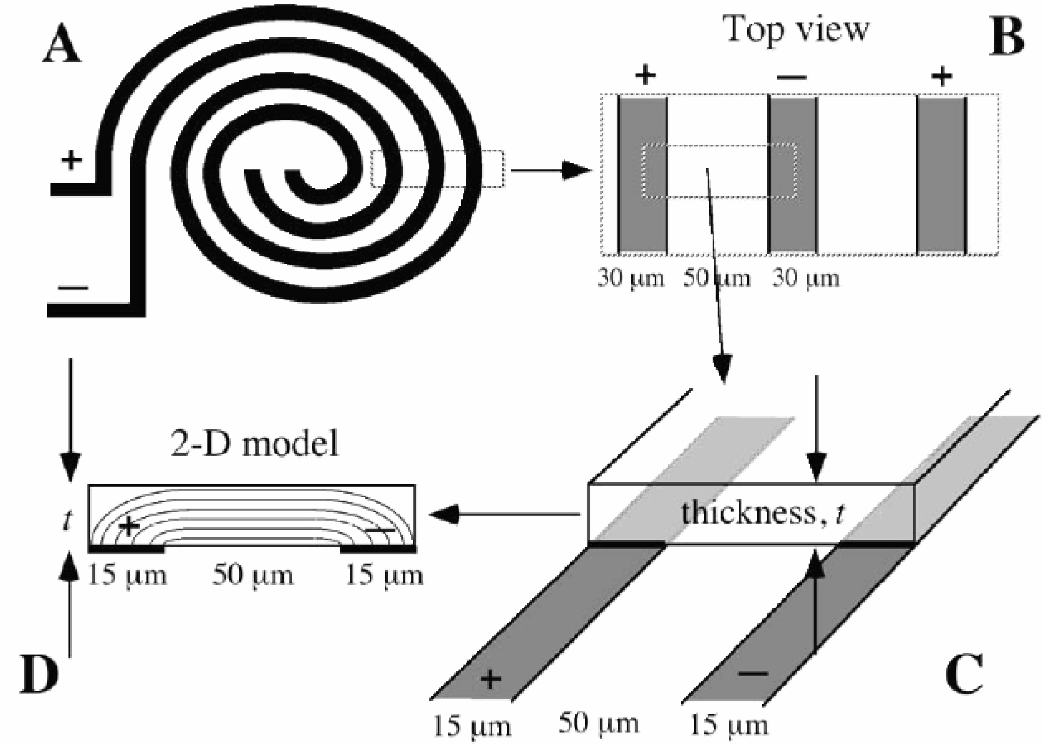

Figure 1. Illustration of the relationship between the chemiresistor electrode and the 2-dimensional model of current flow in the polymer composite deposited on the electrode. A: Top view of the spiral electrodes used to measure resistance in the conductive polymer. B: Expanded top view of a section of spiral electrodes having 30 µm line width with 50 µm spacing. C: Cutaway view of a section of adjacent electrodes covered with a layer of conductive polymer of thickness *t*. D: 2-dimensional representation of lines of current flow in a section of polymer of thickness *t* above the electrodes.

3. Methods and Materials

Substrates for the chemiresistors were prepared by depositing platinum traces on a silicon wafer using a custom-designed mask. The line widths of the platinum electrodes are 30 µm, and the spacing between electrodes is 50 µm. Each chip has 4 concentric spirals that act as the conductive electrodes of the chemiresistor.

Resistive inks were created by weighing a known mass of polymer and dissolving it in a solvent. The polymer used in this study was polyisobutylene (PIB, 400,000 MW, Scientific Polymer Products, Ontario, NY) and the solvent was trichloroethylene (TCE, Fisher, Pittsburg, PA). A known mass of PIB was measured and placed in a vial. Five mL of TCE were added to the vial and then the polymer/solvent mixture was placed on a hotplate set to 40 °C, which dissolved the PIB within an hour of heating. A measured mass of partially graphitized carbon black (#23164-1, Polysciences, Warrington, PA) was added to the mixture. The vials containing the mixture of carbon, polymer, and solvent were then sonicated in a water bath for an hour. The inks were manually deposited onto the spiral traces of each chemiresistor with a micropipette. Each chip received four depositions of the same carbon volume fraction. A total of 16 chips were created for this study with two chips for each of the eight carbon volume fractions. Volume fractions were subsequently calculated from the mass fractions using densities of 1.8 and 0.92 g/cm^3 for the carbon black and PIB, respectively.

Resistances of each of the chemiresistor sensors were measured using an Agilent 34970A datalogger. The thickness of the conductive polymer covering each spiral electrode was measured using an Alphastep 200 profilometer (Tencor Inc., San Jose, CA). The profilometer data showed that the surface of all dried composite spots was very rough. Therefore, for each drop, the 6 profile scans were in general self-consistent in terms of average thickness and general roughness.

The software FEMLAB (COMSOL, Stockholm, Sweden), running as a subprogram in MATLAB (MathWorks Inc., Natick, MA), was used to solve the LaPlace equation for the simplified 2-D model shown in Figure 2D. The profilometer measurements showed that the conductive polymer deposited on the spiral electrodes had a very rough surface. Therefore, FEMLAB models of rectangles with various types of rough surfaces were constructed and the LaPlace equation was solved to examine the sensitivity of the resistance to surface roughness.

4. Results

Two of the sensors had resistances too high to measure (> 1 x10^8 Ohms), and both these sensors were coated with a composite of 8% carbon. One of the sensors with 20% carbon had only about 40% of its spiral electrode area covered with the composite, so it was disqualified from further analysis. Thus, only data of 61 sensors were valuable.

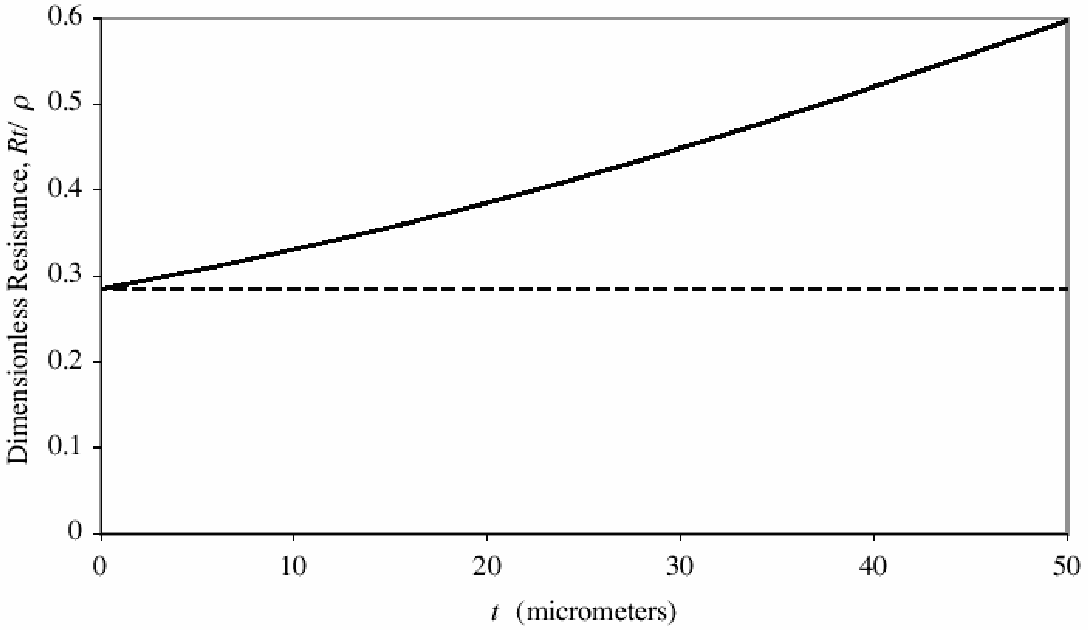

Figure 2. Dimensionless resistance, Rt/ρ, as a function of the thickness of the composite on the chemiresistor electrode. The solid line is predicted by the 2-D finite element model shown in Figure 1, with electrodes of 15 µm width separated by 50 µm. The dotted line is calculated for a model with electrodes on opposite sides of the composite.

Figure 2 shows the dimensionless resistance (Rt/ρ) as a function of the composite thickness calculated by FEMLAB using the 2-D model of the spiral sensor with electrodes of 15 μm separate by 50 μm (see Fig. 1D). This dimensionless resistance would be constant (independent of thickness) if the electrodes were placed on opposite sides of the composite, but placing both electrodes on the bottom of the composite causes the dimensionless resistance to increase at large thicknesses. Note however that when the thickness is much less than the electrode separation (50 μm), the dimensionless resistance is not significantly different than if the electrodes were on opposite sides; for example for a 2 μm thickness, the difference in dimensionless resistance is only about 1.5%. In this range the resistivity can be calculated very accurately using Eqn. (2) and assuming that the measured resistance arises between electrodes on opposite ends of a 50-μm rectangular composite. All of the average thicknesses measured in this work were less than 1.5 μm, so this correction, although important for thick sensors, has negligible impact on the present data.

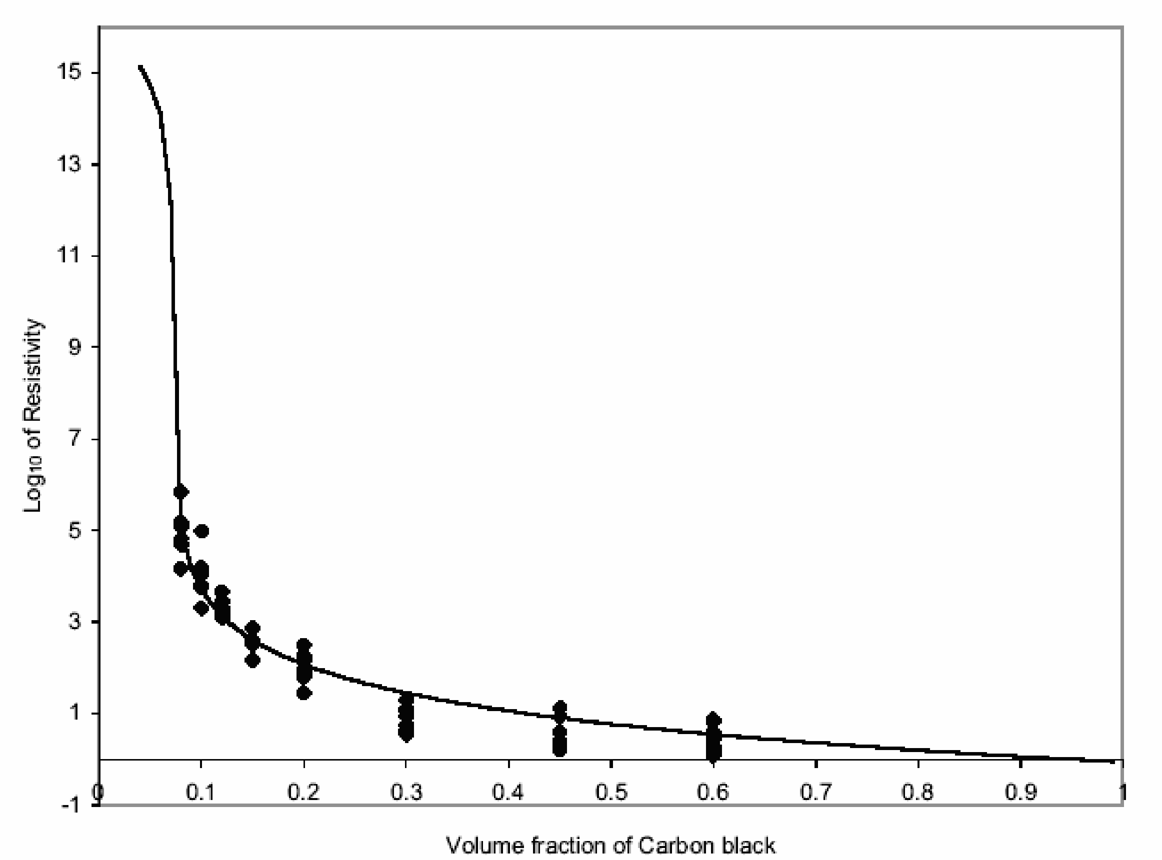

Figure 3. Resistivity values for PIB-carbon composites. The data points represent the individual values of resistivity calculated for each sensor using the resistance and thickness values. The continuous line represents the resistivity modeled by the GEM model using parameters estimated by a least squared fitting technique.

The GEM equation (see Eqn. 1) was used to model the relationship between the volumetric fraction of conductive carbon and dielectric components of the composite material and its resulting resistivity. The parameters of the GEM equation were simultaneously optimized to provide a least-squares fit to the 61 individual data points using an Excel spreadsheet. The value of PIB resistivity was held constant at 10^{16} Ω-cm during the optimization. The resultant fit is shown in Figure 3. The predicted resistivity value of the pure carbon black is 0.87 ohm-cm, and the parameters f_c and k are $f_c = 0.072$ and $k = 2.5$. These values are consistent with other reports in the literature [9].

5. Discussion

The technique used in this paper has advantages over common methods to measure resistivity of block composites because the geometry of the composite is the same as in the sensor application. Thus there will be similarity in the physical properties of the material from which the resistivity is measured and the properties of the material in its designed state of application.

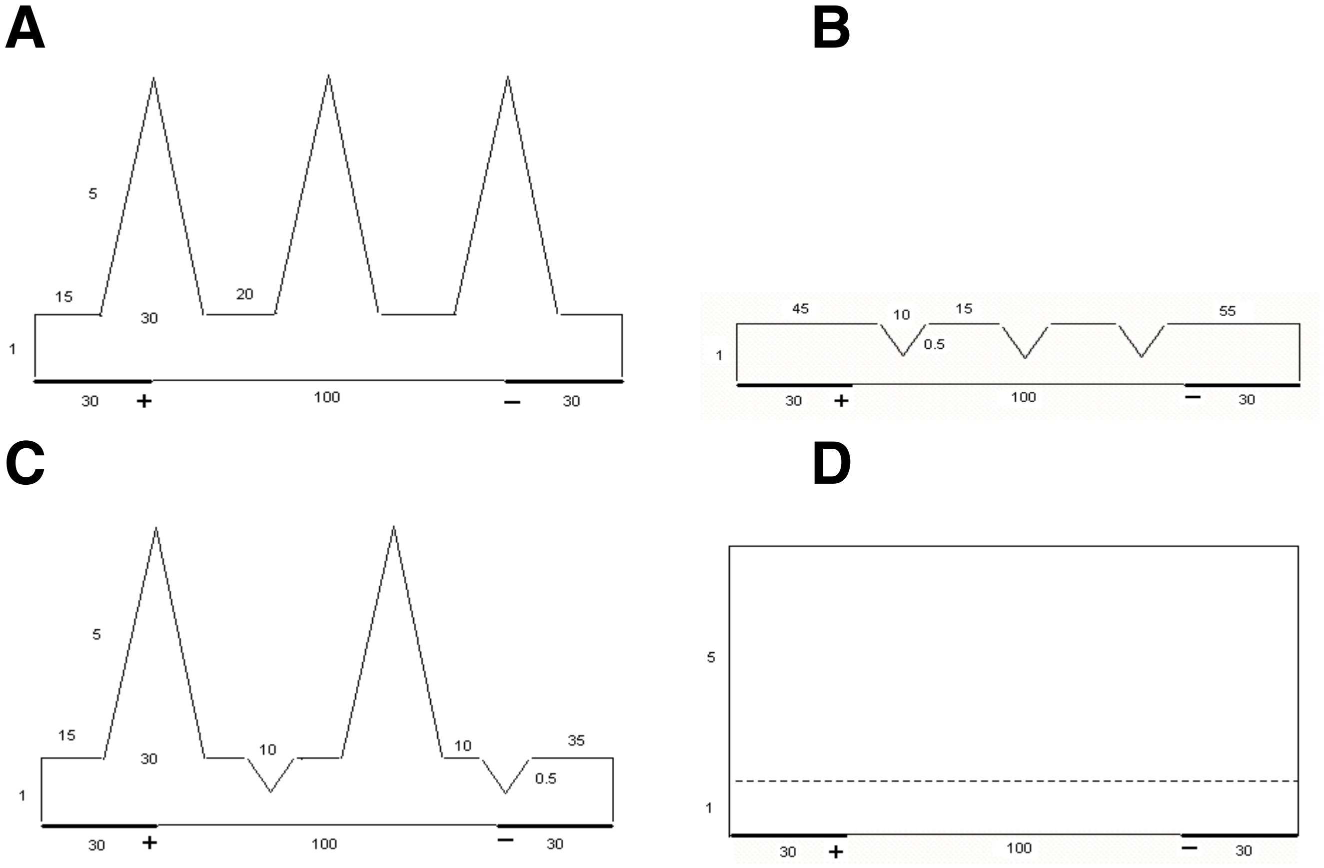

Figure 4. Four models of a rough surface between electrodes. The boundaries are all insulating except for the two electrodes on the bottom right and bottom left that are at constant potential.

The roughness of the surface of the composite inks was a large concern and therefore additional modeling with FEMLAB was done to examine the sensitivity of the calculated resistivity to roughness. Figure 4 shows some examples of the 2-D roughness models that we examined to assess sensitivity of the calculated thickness to roughness. Figures 4A-4C show 2-dimensional cross sections in which positive or negative roughness between electrodes has been added to the simple rectangular cross section of Figure 1D. The numerals on the figures indicate the relative sizes used in the model. In our model, we placed a composite with the irregular profile over 20% of the length of the spiral electrodes, and a flat profile (1 unit thick) over the other 80%. In our observations of the profilometer scans, major deviations in surface roughness covered at most 10 to 20% of the surface. Next we calculated the resistance from the resulting current distribution in the irregular model. Then using the dimensionless resistance correlation shown in Figure 4, we calculated an average thickness that would correspond to a flat rectangular profile and compared it to the average geometrical thickness of the irregular model. Adding peaks or valleys changed the average geometrical thickness of these irregular models; therefore the average geometrical thicknesses of these irregular models were calculated the same way that the profilometer calculates average thickness, by numerical integration of the area under the profile. The sensitivity to roughness was calculated by the %difference in the calculated thickness compared to the average geometrical thickness of the irregular model.

The results of simulations using irregular models showed that adding peaks to the surface decreased the calculated thickness compared to the geometrical because not much current flows up into the peaks. For example, the thickness calculated from the resistance of model A in Figure 4 is only 12% less than the geometrical average thickness of the model. On the other hand, depressions in the surface constrict the current flowing between the electrodes, thus increasing the current density at the restriction and decreasing it slightly in the thick regions. The overall effect produces a slight decrease in calculated thickness; for example, the calculated thickness of model B in Figure 4 is only 0.2% less than the average geometrical thickness. The actual profilometry data from these sensors showed a mixture of peaks and depressions, whose individual effects both cause an underestimation of thickness. For example the irregular model of Figure 4C has a calculated thickness of 10% less than the average geometrical thickness.

The irregular model of Figure 4D represents some observations of large “chunks” of deposited ink that have length scales larger than the spacing between the electrodes, and thus they span the electrodes with constant thickness. As with the others, this model places 6-fold thick material over 20% of the electrodes, and 1-fold thick material over the other 80%. In this model, the difference in calculated thickness is only 0.6% less than the geometrical thickness. Thus large length-scale roughness appears to cause less error in calculating thickness than small scale roughness.

The irregular models used in this sensitivity analysis represent the extremes in height, depth and width (20% surface coverage) observed from the profilometry data, and thus they predict maximum errors expected in calculating the composite thickness from the resistance of the sensors. The actual errors are probably much less than these “worst-case” extremes. Therefore surface roughness produces an underestimation of composite thickness by only a few percent, and the large length-scale roughness of “chunks” of material spanning electrodes produces negligible error in calculation of average composite thickness. This analysis also shows that the resistance in the chemiresistor is much more sensitive to the carbon concentration and to the average thickness than to the surface roughness of the conductive composite.

6. Conclusion

In this work, we constructed sensors of carbon black dispersed in PIB. As expected, the measured resistance changes widely with carbon composition, decreasing by 5 orders of magnitude as composition increased from 8 to 60 vol% carbon black. At all compositions the upper surface of the composite was not smooth.

Finite element modeling was successfully employed to obtain a correlation between the measured resistance across the spiral electrode, the composite thickness, and the resistivity of the composite. This correlation was used to calculate the resistivity of each composite from its measured resistance and average thickness. A model involving surface roughness showed that the resistance is much more sensitive to the carbon content and the thickness of the composite than to the surface roughness. The GEM equation fits the resistivity data adequately, and the regressed values of carbon resistivity and percolation threshold are consistent with other literature, giving credibility to this method of measuring resistivity.

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