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Modeling Carbon-Black/Polymer Composite Sensors

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Abstract

Conductive polymer composite sensors have shown great potential in identifying gaseous analytes. To more thoroughly understand the physical and chemical mechanisms of this type of sensor, a mathematical model was developed by combining two sub-models: a conductivity model and a thermodynamic model, which gives a relationship between the vapor concentration of analyte(s) and the change of the sensor signals. In this work, 64 chemiresistors representing eight different carbon concentrations (8–60 vol% carbon) were constructed by depositing thin films of a carbon-black/polyisobutylene composite onto concentric spiral platinum electrodes on a silicon chip. The responses of the sensors were measured in dry air and at various vapor pressures of toluene and trichloroethylene. Three parameters in the conductivity model were determined by fitting the experimental data. It was shown that by applying this model, the sensor responses can be adequately predicted for given vapor pressures; furthermore the analyte vapor concentrations can be estimated based on the sensor responses. This model will guide the improvement of the design and fabrication of conductive polymer composite sensors for detecting and identifying mixtures of organic vapors.

Keywords

Chemiresistor; Sensor array; Carbon black-polymer composite; Model; General effective media equation

1. Introduction

Chemical sensor arrays have been studied extensively for application in an “electronic nose” which simulates the mammalian olfactory system. Unlike the traditional chemical sensors that use a “lock-and-key” approach, wherein a specific receptor is synthesized to bind an analyte strongly and selectively, an array of chemical sensors, with each sensor chosen to respond differently to given analytes, allows a detector to respond to and distinguish a large number of analytes [1]. In such a system, identification of an analyte cannot be accomplished from the response of a single chemical sensor; but a distinct pattern of responses in the array of sensors can provide a fingerprint from which the analyte can be

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classified and identified. Once the sensor array is calibrated, it can provide both quantitative and qualitative information regarding the composition of a mixture.

Conductive polymer composite sensor arrays made from carbon black dispersed in various insulating polymers have been explored actively by Lewis and co-workers [1-3], Ho and co-workers [4-6] and others [7-12]. Since the response of this type of device is the change of resistance of the sensor, it is called a “chemiresistor”. Upon exposure to an analyte, the analyte diffuses into the polymer composite and the polymer swells, which causes the dispersed conductive carbon particles to move further apart from each other. As the result, the resistance of the sensor increases. The diversity of the responses of sensors is achieved by selecting polymers with various thermodynamic properties. For example, poly(N-vinylpyrrolidone) is hydrophilic, so it swells substantially (and increases the sensor resistance) in water vapor, but not in toluene vapor; whereas polyisobutylene is hydrophobic, so it swells (and increases the sensor resistance) in toluene vapor, but not water vapor. Given the various responses of a sensor array to various analyte vapors, samples can be classified, identified and quantified by using statistical methods, such as linear discriminate analysis (LDA), principle component analysis (PCA), partial least squares (PLS), neural networks, and more [13].

The response mechanism of the individual carbon-black/polymer composite sensors is qualitatively explained by percolation theory, which describes the relationship between the resistivity of the composite and carbon black content [1, 3, 14, 15]. When the concentration of carbon black is very high, the carbon black particles pack very close in the composite and form conductive pathways, which imparts a low resistance response of the sensor. As the concentration of carbon black decreases (e.g., in a swollen polymer), the distances between carbon black particles increase, and the resistance of the composite increases gradually. When the concentration of carbon black decreases to a point at which the conductive pathways are disrupted, the resistance of the composite increases sharply (by many orders of magnitude). This point is called the percolation threshold. In carbon-black/polymer composite sensors, the carbon black concentration is usually only slightly higher than the percolation threshold. Therefore, a small amount of swelling may cause a dramatic change in the sensor resistance. Lewis and co-workers demonstrated the correlation of their sensor responses with percolation theory [3]. However, percolation theory can not describe the complete sensor performance. The relationships among composite resistance, resistivity, carbon black concentration, polymer swelling, and vapor concentration are not well known. Thus, it is difficult to design sensors and to optimize polymer selection for an anticipated sample or set of samples.

In our previous work, we proposed that an individual carbon-black/polymer composite sensor can be modeled by combining two sub-models: a conductivity model and a thermodynamic model [16]. The conductivity model was well described; the geometry of the sensor was modeled and analyzed. In this work, we combine that previous conductivity model with a thermodynamic model and demonstrate that the responses of sensor arrays can be estimated from the analyte vapor pressures; conversely, and more importantly, the vapor pressure of analytes can be predicted from the resistance of sensors in the array. In the conductivity model, three key parameters of the polyisobutylene (PIB)-carbon black composite model were optimized by fitting the experimental data. These same model parameters were then used to successfully estimate the responses of chemiresistors in various vapor pressures of trichloroethylene (TCE). Finally, we discuss how to improve the fabrication of this type of sensor.

2. Theory

To date, little work has been done to model the carbon-black/polymer composite sensor theoretically. Two sub-models are used to describe such sensors: a conductivity model and a thermodynamic model (Fig. 1).

The conductivity model establishes the relationship between the concentration of carbon black in the composite and the resistance of the composite in the sensor. The thermodynamic model relates the sum of volume fractions of the polymer and analytes in the composite to the vapor pressure of analytes. By combining these two models, we can estimate the vapor pressure (and thus the concentration) of analytes based on the change of resistance of sensors in the array, or predict responses (resistance) of sensors as a function of the vapor pressures or concentrations of analytes.

2.1 Conductivity model

In the conductivity model, the resistance of the composite is related to the sum of volume fraction of polymer and analytes by two steps as shown in Fig. 2. The resistivity was calculated from experimental measurements of resistance by modeling the circuit and applying the definition of resistivity. The general effective media (GEM) equation further related the resistivity to the volume fraction of the high resistivity phase.

In the first step, the responses (the change of the sensor resistance) must be converted to resistivity. This can be done by using the definition of resistivity, as shown in Eq. 1:

$$\rho = \frac{RA}{L} \quad (1)$$

where R is the resistance, A is the cross section of the material perpendicular to the current flow, and L is the length between source electrodes. Eq. 1 shows that resistivity of the composite can be obtained if the geometry of the composite and electrodes are available.

In this research, actual chemiresistors made at Sandia National Laboratories were used. In these chemiresistors, both electrodes are adjacent 2-turn spirals (Fig. 3A). This design makes it complicated to define the cross section A in Eq. 1. A symmetrical model was made by simplifying the adjacent spiral electrodes into a model of two adjacent straightened electrodes (Fig. 3B-3D). We previously showed, using finite element software, that the estimated error generated by this simplification was only about 1.5% for the composite of 2 micron thickness. Thus, this is a fairly good model with which to simulate the current flow in the sensor. The details of this resistivity model have been published [16].

In the second step, as in our previous work, the GEM equation was used to relate the resistivity to the concentration of the various components in the composite [8, 16]. This equation was developed by combining effective media theory and percolation theory, and can be applied to the entire range of carbon black content [17-19]. The GEM equation is formulated as

$$\frac{f(\rho_c^{-1/k} - \rho_m^{-1/k})}{\rho_c^{-1/k} + B\rho_m^{-1/k}} + \frac{(1-f)(\rho_p^{-1/k} - \rho_m^{-1/k})}{\rho_p^{-1/k} + B\rho_m^{-1/k}} = 0 \quad (2)$$

where

$$B = \frac{1 - f_c}{f_c};$$

f_c is the critical volume fraction of the carbon black or percolation threshold, ρ_c is the resistivity of the carbon black, ρ_m is the resistivity of the composite mixture, ρ_p is resistivity of the polymer, k is an exponent, and f is the volume fraction of the carbon black. When the sensor is in the dry air, $1-f$ is the volume fraction of the polymer; however, when the sensor is in the analyte vapor, $1-f$ is the sum of volume fraction of polymer and absorbed analyte. Section 2.3 shows how the volume fraction of polymer and analyte can be obtained for an analyte/polymer binary system.

Our physical model of the chemiresistor sensor satisfies the assumptions upon which the GEM equation is based, with perhaps two minor exceptions. One is that carbon black particles are distributed uniformly in the composite; another one is that the resistivities of analytes and polymers applied in chemiresistors are sufficiently high. With proper experimental preparation, even these assumptions can be adequately met.

2.2 Thermodynamic model

In this study, only the simplest case, that of an analyte/polymer binary system, is considered. There are two steps in the thermodynamic model (see Fig. 4). First, the volume fraction of solvent in the polymer phase is calculated based on the sum of the volume fractions of polymer and of solvent, and the volume fraction of polymer in the dry composite. (The details of this calculation are presented in Appendix A.) Then the solvent vapor concentration is estimated.

The theory used in the binary system was derived from the Flory-Huggins theory for polymer solutions and was further developed by Tompa who derived the following equations [20]:

$$\frac{\Delta\mu_1}{RT} = \ln\phi_1 + \left(1 - \frac{1}{m}\right)\phi_2 + \chi\phi_2^2 \quad (3)$$

$$\frac{\Delta\mu_2}{RT} = \ln\phi_2 - (m-1)\phi_1 + m\chi\phi_1^2 \quad (4)$$

where

$$m = \frac{v_2}{v_1}$$

The subscripts refer to analyte (1) and polymer (2). The R is the gas constant, T is the absolute temperature, μ_i and ϕ_i represent the chemical potential and the volume fraction of component i , respectively, χ is the analyte/polymer interaction parameter and v_i is molar volume of species i . At equilibrium, the concentration of the polymer and analyte in the polymer phase and the vapor phase can be computed by applying Eq. 5:

$$\Delta\mu_{1,g} = \Delta\mu_{1,p} \quad (5)$$

with the constraints:

$$\sum_i \phi_{i,g}=1 \text{ and } \sum_i \phi_{i,p}=1$$

where g and p represent the vapor phase and the polymer phase, respectively. This equation can be further simplified by setting $\phi_{2g}=0$, because the concentration of the polymer in the vapor phase is negligible. Combination of Eqs. 3 - 5 with the constraints and the simplification gives [21, 22]:

$$\ln(a_1)=\ln\phi_1+\left(1-\frac{1}{m}\right) \cdot (1-\phi_1)+\chi \cdot (1-\phi_1)^2 \quad (6)$$

where a_1 is the activity of the analyte.

Since the experiments in our research were done at very low analyte vapor pressures (< 1 atm), the vapor phase can be considered an ideal vapor phase. Thus, the vapor-liquid equilibrium equation can be simplified as

$$y_1 P=a_1 P_1^{sat} \quad (7)$$

where P_1^{sat} is the saturated vapor pressure of the analyte at temperature T . Since air or any non-interactive carrier gas is excluded from the system, only one analyte vapor exists in the vapor phase, y_1 equals to 1, and P is the vapor pressure of the analyte in the system. Eq. 7 can be rewritten as

$$a_1=\frac{P}{P_1^{sat}} \quad (8)$$

Substituting Eq. 8 into Eq. 6, the vapor pressure of the analyte can be related to the volume fraction of the analyte in the composite and the interaction parameter by

$$\ln\left(\frac{P}{P_1^{sat}}\right)=\ln\phi_1+\left(1-\frac{1}{m}\right)\phi_2+\chi\phi_2^2 \quad (9)$$

Similar thermodynamic equations for systems with more than two components can be derived based on Flory theory [20]. For example, the equation of the analyte1/analyte2/polymer ternary system has been derived and widely used [20, 23-25].

This thermodynamic model incorporates three assumptions: (1) air absorbed or adsorbed by the carbon black does not change the resistivity of the carbon black; (2) air (or non-reactive carrier gas) has negligible solubility in polymer (compared to analytes) and has no effect on polymer swelling in the composite; and (3) polymer swelling reaches equilibrium, which is easily observed and verified during the experiments.

2.3 Calculation Procedure for Optimizing Parameters

In order to apply the GEM equation, three key GEM parameters – the percolation threshold f_c , the resistivity of the carbon black ρ_c and the exponent k – need to be determined. Using these values, the resistivities of the dry and swollen polymer composites in the sensors were calculated. Then, the three parameters were optimized by fitting the resistivity data to the GEM equation. In this work, the three GEM parameters of the polyisobutylene (PIB)–toluene system were optimized by the following steps:

Step 1. Convert resistance signal to resistivity. The resistance measured in the dry air environment was converted based on the sensor geometry. The resistance measured in toluene vapor was converted following the procedure shown in Appendix B.

Step 2. Estimate the volume fraction of toluene (ϕ_1) in the swollen phase in Eq. 9 based on the activity data published in literature [26].

Step 3. Calculate the volume fraction of carbon black (f) in term of the results in Step 2. The $1-f$ is the sum of toluene and PIB in the composites and was computed as shown in Appendix A; then the theoretical resistivity was derived by solving the GEM equation.

Step 4. Optimize the percolation threshold f_c , the resistivity of the carbon black ρ_c and the exponent k by minimizing the squared difference between the experimental and corresponding theoretically calculated resistivity data.

2.4 Calculation Procedure for Model Validation

To validate the model, the resistance response was calculated for each individual PIB chemiresistor that was used in the experimental measurements of the swelling response in TCE. The calculation procedure included the following steps:

Step 1. The interaction parameters of TCE in PIB derived from the activity data measured by Lei et al. [27] were applied in Eq. 9, which produced the volume fractions of TCE at various TCE vapor pressures.

Step 2. The resistivities of the PIB chemiresistors were calculated by applying Eq. 2 for the values of various volume fractions of TCE.

Step 3. The thicknesses of the swollen composites in the sensors were calculated based on the relationship between activities and weight fractions of the TCE-PIB system measured by Lei et al. [27].

Step 4. The responses (which were resistances of the various composites in the sensors) were calculated by using Eq. 1 and the circuit model introduced in Section 2.1.

Step 5. The theoretically calculated responses were compared to the experimental responses.

3. Methods and Materials

The toluene (Fisher Scientific, FairLawn, NJ) was used as received. The sensors and other materials (polyisobutylene, carbon black and trichloroethylene) were the same as those described in our previous work [16].

When measuring resistance, the sensors were placed inside a customized Nalgene bottle to expose the sensors to a variety of controlled environments. The chemiresistors were placed inside the bottle, and dry air was passed through the bottle. When the resistances became stable, the resistances of the chemiresistors in dry air were measured. The same drying procedure was repeated before the chemiresistors were exposed to other environments. To expose the device to toluene vapor, toluene was poured into a glass gas bubbler (Corning, PN 170-220 EC) and clean dry air was passed through the toluene to produce 100% saturated toluene vapor. Various concentrations of the toluene vapor were generated by mixing the 100% saturated toluene vapor with dry air. Since only eight chips could be held in the Nalgene bottle, 16 chips were equally divided into two groups: A and B. The exposure environment for each group is summarized in Table 1. Concentrations were verified using a M200 Micro Gas Chromatograph (MTI Analytical Instruments, Fremont CA).

The exposure procedure was different for the TCE. Bubblers were not used during the TCE exposure runs. Certified gas cylinders from Matheson/Tri-Gas with 10,000 ppm of TCE were used for this exposure. A mixture of dry air and TCE were exposed to the sensors to yield exposures at approximately 5,000 and 10,000 ppm TCE. Concentrations of TCE were also verified by the M200 Micro Gas Chromatograph. The M200 Micro Gas Chromatograph was calibrated prior to the experiment by exposing known concentrations of toluene and TCE separately and generating linear regressions of the resulting peaks.

The experiments were conducted at temperatures between 22.6 °C and 23.6 °C. The PIB-toluene activity data (previously published in the literature) was measured at 25°C [25]. The group contribution activity coefficient method developed by Chen et al. [28] showed that the difference between the PIB-toluene activity coefficient at 25°C and at 23°C was less than 0.2%. Thus, the interaction parameter measured at 25°C was applied in this work.

4. Results

4.1 Resistance and Resistivity of Sensors

Eight carbon black concentrations in the dry sensors were formulated (8.0, 10.0, 12.0, 15.0, 20.0, 30.0, 45.0 and 60.0 vol%). Eight sensors were made for each carbon black concentration for a total of sixty-four. However, one sensor failed prior to testing, and others generated resistances too high to measure, particularly those sensors with low carbon content in high vapor concentration. Data from these sensors were not used. Tables 2 and 3 present the mean values of resistance and resistivity for the sensors after exposure to toluene vapor. The data of the sensors exposed to dry air were published previously [16].

4.2 Parameter optimization

The GEM equation was used to model the relationship between the volume fraction of carbon black in the polymer composite and its resistivity. The GEM parameters for the PIB-carbon black composite were simultaneously optimized by minimizing the following function

$$\sum_n (y - y')^2 \quad (10)$$

where y and y' are the $\text{Log}_{10}(\text{resistivity})$ based on the experimental data and the resistivity estimated by the GEM equation with the three GEM parameters, respectively, and n is the number of data points.

During the optimization, the resistivity of PIB was set to $1.0 \times 10^{16} \Omega\text{-cm}$, and the resistivity of carbon black was set to $0.87 \Omega\text{-cm}$ which is the same as the value optimized using dry-air data as described in our previous work [16]. Two toluene vapor concentrations and dry air were applied for the optimization. The results of the optimizations are shown in Fig. 5. The best-fit values for the parameters f_c , and k are $f_c = 0.069$ and $k = 2.38$.

4.3 Model Validation

In previous sections, a theoretical model of chemiresistors was constructed and the values of f_c and k were determined by measuring swelling in toluene. Thus this model should be able to estimate the responses of chemiresistors or predict the vapor concentrations of analytes. Therefore, the model was validated by applying the sensors to detect known concentrations of TCE vapor, and comparing the experimental responses and the model estimated responses. The comparison results are shown in Table 4 for each individual sensor.

In Table 4 and Figs. 6 and 7, the model predicted responses and their corresponding experimental data are in the same order of magnitude. The model predicted that responses increase with an increase of the vapor pressure of TCE and with a decrease in the carbon concentration in the composites. This observation indicates that our hypothesized model agrees qualitatively with the experimental data. Although the model (without experimental calibration) can not predict exactly the experimental responses of chemiresistors accurately, it is sufficiently accurate to provide a theoretical method from which to estimate the responses of chemiresistors and to help investigators select polymers from which to construct a chemiresistor array for the anticipated samples.

4.4 Sensitivity Analysis

From the experiments employing toluene swelling of PIB, the three parameters in the GEM equation were obtained, and further modeling of the chemiresistors was performed. However, errors in experiment and measurement always exist. These errors may come from the measurements of responses of sensors, the thicknesses of the composites, and any simplification of the model. To estimate how much these errors impact the accuracy of the model, a sensitivity analysis was performed. In this sensitivity analysis, the resistivities of PIB-carbon composites with 10 and 20 vol% carbon in toluene vapor at 30% of its saturation were derived. Since resistivity is a linear function of resistance, resistivities were used as the sensor responses in this analysis. Then errors in the range from 10% to -10% of the responses were added to these resistivities. Finally vapor pressures corresponding to these “noisy resistivities” were calculated. The differences between the predicted vapor pressure and the actual vapor pressure are shown in Fig. 8.

The results in Fig. 8 show that a 10% error in the response of the chemiresistor with 10 vol% carbon generates about 17% deviation from the true vapor pressure, which indicates that errors in the responses of chemiresistors have only small effect upon the estimation of the vapor pressure. Fig. 8 also shows that the estimation of vapor pressure using the chemiresistors with a higher volume fraction of carbon, for example 20 vol% carbon, is more sensitive to the error in sensor responses. This suggests that one should develop the chemiresistors using composites with lower volume fractions of conductive particles.

5. Discussion

We have developed a theoretical model of the physics and thermodynamics of chemiresistors, and have shown that even without calibration of the sensors with TCE, the model was able to predict (fairly accurately) the resistivity responses of the sensors to two vapor pressures of TCE. There are some simplifications and assumptions that went into the development of this model. Most of these have negligible impact on the accuracy. But some simplifications may have an impact as discussed below.

The conductivity model assumes that polymers have no swelling in dry air. Fig. 9 shows that the resistance of a sensor with the PIB composite decreased very slightly with time as the sensors were put into dry air and residual water was removed. Then the resistance became stable when helium and dry air passed in turn through the chamber. Other experiments employing sensors with polyethylene-vinyl acetate copolymer (PEVA), poly(N-vinylpyrrolidone) (PNVP) and poly(epichlorohydrin) (PECH) composites showed similar results (data not shown). Therefore dry air has as little interaction as helium has with polymers. During the experimental measurements, dry air flowed across the sensors until the resistances became stable in the dry-air environment, which means that the responses of the sensors to the dry air can be used as the baseline for the dry state of each sensor. The analyte vapors with various concentrations are the mixtures of dry air and vapor of pure analytes. Usually, the concentration of air is very high, even when the analytes are at their saturated

concentration in water. For example, at 25°C and 1 atm, the volume fraction of dry air in the saturated toluene vapor is about 97%. Thus, we assume that the swelling interaction between dry air and most polymers is negligible.

In these experiments, the resistance data of the sensors with the same carbon black concentration varied within a range of one order of magnitude. The sensors are made by carefully placing a drop of the TCE solution of the polymer-carbon black mixture onto the surface of the spiral electrodes. When the solvent vaporizes, some carbon black particles migrate with evaporating solvent and cluster unevenly. This phenomenon was also observed by Lewis [3]. In these experiments, the resistance data of the dry sensors with the same carbon black concentration varied within a range of one order of magnitude. Some of the error in the predicted concentration is believed to have come from the agglomeration of the carbon black, which makes the surface of the composite very rough and generates some variation in the resistance [16]. Our previous work has demonstrated that the rough surface can cause errors of up to 12%. Thus, another source of error comes from the non-uniform thickness and the non-uniform distribution of the carbon black inside the composite. If the carbon black clusters are right above the electrodes, a negative deviation in resistance is generated; if not, they cause a positive deviation. Therefore, producing a uniform distribution of the carbon black uniform is the key point to improve the consistency and quality of conductive polymer composite sensors.

In the conductivity model, it is assumed that the resistivities of the analytes and polymers applied in chemiresistors are sufficiently high such that the shape of the curve above the percolation threshold is negligibly affected. This is a good assumption if analytes are organic solvents, because the resistivities of organic solvents are usually very high. For example, the resistivity of toluene is above $1.0 \times 10^{12} \Omega\text{-cm}$ and the resistivity of PIB is $1.0 \times 10^{16} \Omega\text{-cm}$. If we used the GEM equation as the conductivity model, when the given samples are aqueous solutions which have high ion concentration, the resistivity of the polymer ρ_p would decrease, the percolation threshold f_c would deviate, and the exponent k would increase. All three parameters would be functions of the polymer swelling. Thus direct contact of this type of sensor with ground water would be problematic. In the situation of sensing organic vapor in equilibrium with ground water, the ion concentration is extremely low (if not zero) in the vapor phase; thus, the conductivity model can be used for conductive polymer composite sensors to measure analyte concentrations in vapors of ground water.

In designing a conductive polymer composite sensor for a given sample, one wants to choose a polymer material and carbon black concentration to give the sensor a large range of capacity and very high resolution. An excellent ohmmeter can accurately detect resistance up to $1 \times 10^9 \Omega$, which corresponds to a resistivity of $1 \times 10^7 \Omega\text{-cm}$ in this design. For example, in the experimental data of this work, the resistivities of the chemiresistor with 10 vol% carbon change much more than the chemiresistors with a higher volume fraction of carbon (Fig. 10) because its 10 vol% carbon is very close to the percolation threshold and imparts a very high sensitivity to any change of vapor pressure.

Fig. 11 shows the desired range (shade box) of the sensor response and carbon concentration. By analyzing the relationship between the resistivity of the composite and the carbon black concentration described by the GEM equation, a very sensitive polymer-carbon black pair can be selected. If the carbon concentration is too close to the percolation threshold, some data points will be lost because their resistivity is off scale, as can be seen by comparing the left-hand-most data of Fig. 5. As the toluene swelled the polymer, more sensors read “off-scale”, and did not contribute to the data set.

In addition to the three fitted parameters of the GEM equation, there is a fourth parameter that was assumed to be constant: ρ_p , the resistivity of the polymer. This value, along with the other three constants, affects the shape of the curve generated by the GEM equation independently as follows. Fig. 12 shows that the resistivity of the polymer and carbon black determine the upper bound and the low bound of the curve. Because of the capacity limitation of ohmmeters, the resistivity of polymers does not need to be extremely high. A resistivity $1 \times 10^7 \Omega\text{-cm}$ is sufficient for sensors. However, it is desirable to keep the resistivity of carbon black as low as possible, because the same swelling can generate more change of the resistance for the composite when the carbon black has lower resistivity. In other words, using a carbon black of lower resistivity increases the sensor sensitivity.

Fig. 13 shows how the percolation threshold (f_c) determines the transition point of the composite. Theoretically, the position of the transition point does not affect the performance of sensors. But a very low percolation threshold could make a sensor very sensitive to the distribution of the carbon black in the composite. When the percolation threshold is very low, such as 6.9 vol% in this study, only a few conductive pathways can be constructed in the region near the percolation threshold if the carbon black is not distributed uniformly during sensor construction. Minimal swelling may break some of these pathways and cause a dramatic and perhaps unreliable change of resistance. This is why the experimental data points of sensors having carbon black concentrations near 8 and 10 vo.% are very scattered.

The slope of the line near the transition region is controlled by the exponent k as shown in Fig. 14. The lower k value makes the transition sharper. Since the transition goes across several orders of magnitude, sensors usually have sufficient sensitivity even when the exponent value is high. Meanwhile, a large value of exponent k increases the range of the sensor performance significantly. Therefore, composites with higher exponent values make better sensors. Unfortunately, the value of k is a function of the type of carbon and type of polymer used, so the sensor designer may have less option in selecting the value of k .

Traditionally, one would always choose the polymer which swells the most for the given analyte concentration. However, if the polymer swelled too much, its carbon concentration may decrease out of the best performance range shown in Fig. 11, and the performance of the sensor would be inadequate. To design a good sensor, its required measurement capacity (the range of the vapor concentration) should be determined first, and then the polymer type and carbon black concentration should be estimated according to its required capacity. The range of the change of the carbon concentration (carbon black dilution upon swelling) should be located within the best performance range. Thus, it is very beneficial if the species and concentrations in the anticipated samples are known, so that the sensor(s) can be designed optimally.

The composite formulations used herein were not uniformly distributed over the entire range of carbon concentration, but instead were distributed with more samples near the percolation threshold (8, 10, 12, 15, 20, 30, 45 and 60 vol%). As explained previously, the resistivity of the composite changes significantly around its percolation threshold, and the volume fraction of the carbon black in most sensors is designed to be close to the percolation threshold to obtain high sensitivity; that is why we designed the experiment to force the optimization to emphasize the sensitivity near the percolation threshold. However, because of this non-uniformly distributed data, small deviations in experimental data around percolation thresholds generate an apparent large change in the optimized resistivity of carbon black when the three parameters are optimized simultaneously. For example, if the data of the toluene vapor at 500 Pa were used to optimize the three parameters, the fitted resistivity of carbon black was $0.44 \Omega\text{-cm}$, which obviously deviates below the experimental data points at high carbon concentrations (see Fig. 15). Therefore, to obviate this problem,

the resistivity of carbon black was fixed at 0.87 Ω -cm during the optimization, since this value was obtained for dry carbon black and this value is not inconsistent with other published values of carbon black [29].

The common logarithm values of resistivity instead of absolute resistivity values were used in the optimization procedure because the common logarithm values appear to be randomly distributed around a mean value (see Fig. 5); whereas the absolute values are not randomly distributed. This allows for more equitable weighting of the data during the optimization procedure.

6. Conclusions

The conductive polymer composite sensor (chemiresistor) was modeled by combining a conductivity model and a thermodynamic model. In the conductivity model, the resistance values of the composites in the sensors were converted to resistivity by measuring the geometry of the electrodes and the thickness of the composite film in the sensor; then the GEM equation was applied to relate the resistivity of the composite to the volume fraction of the polymer and analyte in the composite. The thermodynamic model, which is a thermodynamic equation of a polymer/analyte binary system in this work, further related the volume fraction of the polymer and analyte in the composite to the vapor concentration of the solvent. Using this model, we could estimate the responses of chemiresistors based on the vapor concentration of the solvent, or predict the vapor concentration in term of the sensor responses.

Conductive polymer composite sensors can be tailored by proper selection of the polymer matrix such that the sensor array responds differentially to various analytes. In this work, to test the model, we constructed sensors of carbon black dispersed in polyisobutylene, which was deposited on platinum spiral electrodes. These sensors were exposed to dry air and various vapor concentration of toluene and trichloroethylene. A large number of responses of sensors were obtained. As expected, the measured resistance changed widely with carbon composition, decreasing by 5 orders of magnitude as the composition increased from 8 to 60 vol% carbon black. The GEM equation was able to adequately fit the resistivity data of the sensors in dry air and toluene vapor, and the regressed values of carbon resistivity and percolation threshold were consistent with other literature values, giving credibility to this model. The whole model was verified by successfully and without prior calibration estimating the responses of the sensors to the various vapor concentrations of trichloroethylene.

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Appendix A: Calculating the Sum of the Volume Fraction of the Toluene and PIB in the Wet Composite

Since the volume of the polymer and the carbon black are constant during swelling, the volume fractions of the polymer and the analyte can be derived as

$$f_p = \frac{t_{dry} \cdot (1 - f_{0c})}{t_{wet}} = \frac{t_{dry} \cdot (1 - f_{0c})}{\frac{t_{dry} \cdot f_{0c}}{f}} = \frac{(1 - f_{0c}) \cdot f}{f_{0c}} \quad (\text{A-1})$$

$$f_s = \frac{t_{wet} - t_{dry}}{t_{wet}} = 1 - \frac{t_{dry}}{t_{wet}} = 1 - \frac{t_{dry}}{\frac{t_{dry} \cdot f_{0c}}{f}} = 1 - \frac{f}{f_{0c}} \quad (\text{A-2})$$

where f is the volume fraction of the carbon black, f_p and f_s are the volume fractions of the polymer and the analyte in the swollen composite, respectively, f_{0c} is the volume fraction of the carbon black in the dry composite, and t_{wet} and t_{dry} are the thickness of the swollen composite and the dry composite, respectively. Then, it is simple to obtain the volume fraction of the sum of the toluene and PIB by solving the following equation

$$\phi_1 = \frac{f_s}{f_s + f_p} = \frac{f_{0c} - f}{(1 - f) \cdot f_{0c}} \quad (\text{A-3})$$

where ϕ_1 is the volume fraction of toluene. By combining Eqs. A-1 through A-3, the sum of volume fractions of the toluene and PIB can be computed.

Appendix B. Converting Resistance of Swollen Composite to Resistivity

According to the definition of resistivity, the resistivity of the swollen rectangular composite is given by

$$\rho_{wet} = R_{wet} \cdot \frac{w \cdot t_{wet}}{L} \quad (\text{B-1})$$

and

$$t_{wet} = t_{dry} \cdot \left(\frac{f_{0c}}{f} \right) \quad (\text{B-2})$$

where ρ_{wet} is the resistivity of the swollen composite. L and w are the length and width of the dry composite, respectively. L and w are constants. R_{wet} is the resistivity of the swollen composite. $1-f$ is the sum of the volume fraction of the polymer and the analyte in the swollen composite. By combining Eqs. B-1 and B-2, the resistivity of the swollen composite can be calculated as

$$\rho_{wet} = R_{wet} \cdot \frac{w \cdot k_{dry}}{L} \left(\frac{f_{0c}}{f} \right) \quad (\text{B-3})$$

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Biographies

Biographies

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Fig. 1. Modeling the chemiresistor by combining the conductivity model and the thermodynamic model.

Fig. 2.
The conductivity model.

Fig. 3.

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 Pt spiral electrodes used to measure resistance in the conductive polymer. B: Expanded top view of a section of spiral electrodes having 30- μm line widths with 50 μm spacing. C: Cutaway view of a section of adjacent electrodes covered with a layer of conductive polymer of thickness t . These electrodes of 15- μm widths are the half width of the full Pt line width. D: 2-dimensional representation of lines of current flow in a section of polymer of thickness t above the electrodes.

Fig. 4.
The thermodynamic model.

Fig. 5. Optimization results in various environments at 23°C. A: resistivity in dry air; B: resistivity in toluene vapor around 500 Pa; C: resistivity in toluene vapor around 1700 Pa.

Fig. 6.
Resistance values for PIB-carbon composites at 416 Pa of TCE vapor.

Fig. 7.
Resistance values for PIB-carbon composites at 833 Pa of TCE vapor.

Fig. 8.

Errors in the responses of chemiresistors vs. errors of the predicted vapor pressures. The data of 10 and 20 vol% carbon are represented by (◆) and (◇), respectively.

Fig. 9. Preliminary experiment of PIB composite sensor responding to dry helium and dry air. The jump around 1800 s came from some air trapped in the tubing connecting to the helium tank.

Fig. 10.

Resistivity vs. vapor pressure of toluene for various volume percent of carbon in chemiresistors. The resistivity data in the chemiresistors with 10, 15 and 20 %carbon are represented at ($\blacklozenge$), ($\diamond$) and (*), respectively.

Fig. 11.

The shaded range is the desired range of the sensor response and polymer swelling.

Fig. 12. GEM equation with various values of resistivity of polymer and carbon black ρ_c/ρ_p at constants $k = 1.5$ and $f_c = 0.2$.

Fig. 13. GEM equation with percolation threshold f_c at constants $k = 1.5$, $\log(\rho_c) = 1$ and $\log(\rho_p) = 14$.

Fig. 14.
GEM equation with various exponents k at constants $f_c = 0.2$, $\log(\rho_c) = 1$ and $\log(\rho_p) = 14$.

Fig. 15.
Optimization of the three parameters using the data in the toluene vapor around 500 Pa.

Table 1

Vapor pressures of analytes applied in this work

	Vapor pressure (Pa)			
Group	A	B	A	B
Toluene	506	561	1738	1768
TCE	416	416	833	833

Table 2

Chemiresistor data in toluene vapor around 500 Pa

Carbon %	# of samples tested	Toluene vapor pressure (Pa)	Mean resistance (Ω)	$\text{Log}_{10}(\text{mean resistivity}) (\Omega\text{-cm})$
8	2	506	6.62E+06	4.677
10	4	506	1.73E+06	3.471
	4	561	7.09E+05	3.627
12	3	506	3.88E+05	2.924
	4	561	8.69E+05	3.383
15	4	506	8.95E+04	2.481
	4	561	7.22E+04	2.526
20	3	506	2.81E+04	2.089
	4	561	2.81E+04	2.058
30	4	506	9.74E+02	1.036
	4	561	1.89E+03	0.847
45	4	506	3.60E+02	0.692
	4	561	5.05E+02	0.565
60	4	506	3.20E+02	0.637
	4	561	2.93E+02	0.385

Table 3

Chemiresistor data in toluene vapor around 1700 Pa

Carbon %	# of samples tested	Toluene vapor pressure (Pa)	Mean resistance (Ω)	Log ₁₀ (mean resistivity) (Ω -cm)
8	1	1738	7.25E+06	4.834
10	4	1738	3.01E+06	3.884
	4	1768	1.09E+06	3.690
12	3	1738	5.51E+05	3.116
	4	1768	8.81E+05	3.433
15	4	1738	1.39E+05	2.701
20	3	1738	3.86E+04	2.263
30	4	1738	2.23E+03	1.183
	4	1768	1.27E+03	0.960
45	4	1738	5.15E+02	0.720
	4	1768	3.64E+02	0.598
60	4	1738	3.21E+02	0.656
	4	1768	2.94E+02	0.405

Table 4

Comparison model predicted data with experimental data in various TCE vapor pressures

Volume % carbon in dry sensors	Resistance (Q) at 416 Pa (model)	Resistance (Q) at 416 Pa (Exptl.)	Resistance (Q) at 833 Pa (model)	Resistance (Q) at 833 Pa (Exptl.)	Resistance (Q) in dry air (Exptl.)
10	2.36E+05	9.89E+05	2.44E+05	1.13E+06	9.40E+05
	8.39E+05	4.30E+06	8.67E+05	5.11E+06	4.03E+06
	8.32E+05	6.63E+05	8.60E+05	7.43E+05	6.29E+05
	9.19E+05	1.49E+05	9.50E+05	1.64E+05	1.43E+05
12	3.47E+05	5.85E+05	3.55E+05	6.44E+05	5.63E+05
	3.77E+05	1.30E+05	3.86E+05	1.46E+05	1.24E+05
	4.63E+05	4.01E+05	4.74E+05	4.43E+05	3.84E+05
	2.91E+05	3.37E+05	2.98E+05	3.77E+05	3.22E+05
15	6.00E+04	1.32E+05	6.11E+04	1.58E+05	1.17E+05
	9.56E+04	7.31E+04	9.73E+04	8.71E+04	6.53E+04
	9.00E+04	9.24E+04	9.16E+04	1.10E+05	8.33E+04
	7.34E+04	3.37E+04	7.47E+04	3.96E+04	2.98E+04
20	2.01E+04	1.38E+04	2.04E+04	1.63E+04	1.21E+04
	2.62E+04	2.50E+04	2.65E+04	2.94E+04	2.22E+04
	1.48E+04	3.91E+04	1.50E+04	4.39E+04	3.64E+04