Freestanding Chemiresistive Polymer Composite Ribbons as High-Flux Sensors

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ABSTRACT: Chemiresistive polymer composite ribbons that function as chemical detectors were produced from solution-cast films of polymers and carbon composites. An array with multiple polymer sensor threads was exposed to dimethyl methyl phosphonate, a nerve agent simulant, and different interferents in the vapor phase. Principal component analysis was used to differentiate between the analytes. The response of the ribbon sensors as a function of the carbon composite and the host polymer source was investigated. The freestanding threads/sensors were mounted into a cell perpendicular to the gas flow to provide little pressure drop and were imbedded into fabrics to provide an example of a small, low-cost, wearable chemical sensor. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: composites; conducting polymers; fibers; sensors

INTRODUCTION

Polymer-based transducers have received much attention in recent years as chemical detectors and environmental monitors. In particular, polymer-based chemiresistors are a promising platform for small, light-weight, low-power sensors.[1,2] Unlike most other volatile organic compound (VOC) sensors, they do not require heating, mechanical excitation, or a light source to detect target chemicals. Ideally, a chemiresistive sensor uses an analyte-selective polymer or polymer composite that alters its conductance upon absorption or adsorption of the analyte. There are two main types of electronically conducting polymers: materials that are conductive because of their electronic structure (doped polyaniline, polypyrrole, polythiophene, and polyacetylene)[3] or composite materials[4] prepared from insulating polymers mixed with conductive particles, such as carbon particulates or metal nanoparticles, at sufficiently high levels to form continuous conductive pathways through the matrix. Films prepared from these materials allow direct-current resistance measurements without large power requirements or complex circuits.

Polymer composite-based chemiresistors[2] are inexpensive, easily fabricated matrices for sensor arrays. The conductive particles form electron percolating pathways through polymer films. Films can be made from a range of polymer/conductive particle ratios with the resistance of the composite film dependent on the concentration of the conductive materials and the temperature.[5–7] When a polymer/conductive particle composite physically swells from thermal expansion or from chemical sorption, the electrical resistance increases as the conductive pathways are disrupted. These changes can be large if the composite film is close to the percolation threshold.[6,7] These composite films respond to different solvents, depending on the particular solvent–polymer interaction, whereas for the conductive particles, typically only the degree of swelling is reported (Fig. 1).[5,6]

Polymers matrices in chemiresistors are selected on the basis of their ability to form stronger reversible chemical bonds (hydrogen bonds, van der Waals bonds, and dipole–dipole interactions) with the analyte rather than with interferents.[8] The amount of VOC that sorbs into the polymer depends on certain chemical properties of the polymer; for example, nonpolar polymers tend to absorb nonpolar analytes, whereas polar polymers tend to absorb polar analytes.[9–12] It is possible to distinguish different VOCs from each other by the comparison of the responses of several sensors;[1,13] each constructed with a different polymer. Using pattern recognition algorithms in conjunction with multiple sensors in the array, one can mitigate the remaining cross-sensitivities. Hansen solubility parameters[11,14] (HSPs) are one semi-empirical method of modeling and predicting the
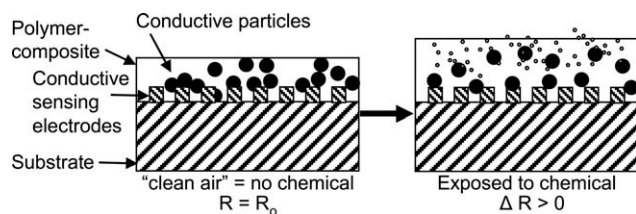
Figure 1 Simplified schematic of a conventional polymer composite chemiresistor that contains conductive particles and sorbent polymer materials. In clean air (left), electricity is conducted by a percolation path between electrodes, and when a chemical is absorbed into the polymer (right), the polymer swells, separating the particles and disturbing the percolation pathways.

strength of the interactions between polymers and chemicals. When the solubility parameter of two liquids or a liquid and a polymer match, they are miscible and likely absorb each other. The more chemical is sorbed, the greater the measurable change in that material's chemical, physical, or electrical properties will be.

Among portable sensor devices, wearable sensors embedded in textiles have been developed as a form of minimally interfering chemical monitors.[15–17] However, the types of fabric-integrated sensors and the sensitivity and selectivity that have been achieved thus far are limited.

EXPERIMENTAL

Materials

The sensor polymers with their stated melting points or molecular weights (MWs) upon availability were as follows. Poly(ethylene-*co*-vinyl acetate) (PEVA; 18%, melting point = 87°C), polyepichlorohydrin (PECH; MW = 700,000),[18,19] polyisobutylene (PIB; MW = 1350), and polycaprolactone (PCP; MW = 70,000–90,000)[20] were purchased from Sigma Aldrich Corp. (St. Louis, MO). Poly(vinyl acetate) (PVAC; 260,000)[21] and polydimethylsiloxane (PDMS; Sylgard 184) were obtained from Scientific Polymer Products, Inc. (Ontario, NY) and Dow Corning Corp. (Midland, MI), respectively. PDMS was a two-component mixture that was crosslinked at elevated temperatures. All of the polymers were used as received without further purification. The reagents used in the syntheses of hyperbranched poly(\{bis[(Z/E)-1,1,1-trifluoro-2-(trifluoromethyl)-pent-4-en-2-ol]silylene\}-\{2-[1,1,1-trifluoro-2-(trifluoromethyl)-propan-2-ol]\}propyne) (STH157C)[22] and poly[(Z/E)-1,1,1-trifluoro-2-(trifluoro-methyl)-pent-4-en-2-ol]methylsiloxane (SXFA)[9,22] were received from Sigma Aldrich or Gelest, Inc. (Morrisville, PA).

The target analytes, dimethyl methylphosphonate (DMMP), 2-nitrotoluene (2-NT), methanol, ethanol, acetone, isooctane, toluene, and trichloroethylene (TCE), were purchased from Sigma Aldrich and were used as received.

The conductive carbons are described as follows. Graphitized carbon nanopowder (CB) with an average particle size of less than 200 nm was obtained from Supelco (Bellefonte, PA). Single-walled carbon nanotubes (SWNTs) with dimensions of 1.2–1.5 nm × 2–5 μm (Diameter × Length), multiwalled carbon nanotubes (MWNTs) with dimensions of 6–9 nm × 5 μm, and carbon nanofibers (NFs) with dimensions of 100 nm × 20–200 μm were purchased from Sigma Aldrich. Graphene (GR) with dimensions of less than 1 nm × less than 5 μm was purchased from Angstron Materials (Dayton, OH). All carbon materials were used as received.

Sensor preparation

Typical methods for polymer threads preparation include extrusion, spinning, and drawing. We used solution casting onto silicon wafers to produce a polymer film that was subsequently dissected to best mimic a polymer thread/ribbon. Solutions of the structural polymers were made in concentrations ranging from 2 to 5 wt % with the added conductive particles being homogeneously dispersed by ultrasonication for several hours. The ratio of carbon particles to host polymer particles ranged from 30 to 50 wt %. In the following figures, the number after the dopant abbreviation is the weight percentage of that dopant. Solution-cast polymer composite films were dried at an elevated temperature of up to 80°C under atmospheric pressure. We created the freestanding ribbons by cutting off narrow strips from the cast polymer composite films with a razor blade of suitable dimensions. The polymer composite films and the composite ribbons were stored under ambient conditions before use. No change in the baseline resistance was observed over the duration of this study, and a shelf life of several years is expected to be realistic for the polymer composite materials employed in this study. The thickness of the individual polymer composite ribbons was not constant; this contributed to the diversity of the sensor array. Spin casting or microextrusion will lead to improved thickness uniformity of the ribbons in future sensor composite preparations.

Measurements

All testing of the chemiresistive polymer composite ribbons was performed in a temperature- and humidity-controlled test system.[23] Target analytes were delivered by the passage of a known flow of dry air through a bubbler filled with the analyte. Flow-control meters regulated the dilution with dry air to produce different analyte concentrations. Two-probe resistance measurements were made with a Hewlett–Packard 34970A data acquisition

switch unit (Hewlett-Packard, Palo Alto, CA). Electrical metal leads were attached to the ends of the polymer ribbons with silver epoxy glue or silver paste and were so connected to the measurement equipment. Likewise, we made the connection by tying a knot at the ribbon ends with a thin metal wire or a conductive thread (Lame Lifesaver, Victoria, Canada). Many figures in this paper are shown as normalized plots, representing the measured resistance R divided by the baseline resistance R_0 (measured resistance without chemical exposure).

The mathematical regression calculations of the test system data were analyzed with the software package ProStat (Poly Software International, Inc, Pearl River, NY). This package had some rudimentary functions for statistical data analysis and simple pattern recognition.

RESULTS AND DISCUSSION

Individual polymer composite ribbon response

The overall objective of this project was to build low-cost chemical sensors that could be embedded in fabrics to detect and distinguish between a toxic agent and common VOC interferents. Polymer-based chemiresisitors best fit these size and cost requirements. However, most chemiresistors described in the literature use a substrate as a support, which limits the required sensor flexibility and size. The few descriptions of chemiresistive thread sensors[24,25] use the same concept, where the polymer composite solution is deposited on an inert support thread, for example, a polyester fiber that holds the active sensor material. These dip-coated thread sensors show limited mechanical stability and sensitivity. The ribbon sensors described herein were freestanding, unsupported, and produced only from the active chemisorbent polymer/carbon composite. The benefit of a freestanding chemiresistor ribbon lies in its three-dimensional structure; this allows it to have access to air and, thus, chemical analytes from all sides. As a result, the thread or ribbon can swell in all directions; this allows for faster absorption and desorption (recovery) and faster sensor response. Furthermore, the small dimensions of the thread sensors allow placement of the ribbon normal to sample air flow to provide little pressure drop and allow high flow.

Ribbons from the solution-cast polymer composite films were place in the temperature- and humidity-controlled stainless steel chamber and exposed to pre-programmed sequences of chemical vapors. As an example, Figure 2 shows the response of a PCP–GR composite ribbon subjected to a sequence of water vapor and four chemicals (toluene, isooctane, ethanol, and DMMP, a chemical warfare simulant). Limits of detection (LODs) for the ribbon sensors were calculated with three times the short-term electrical noise
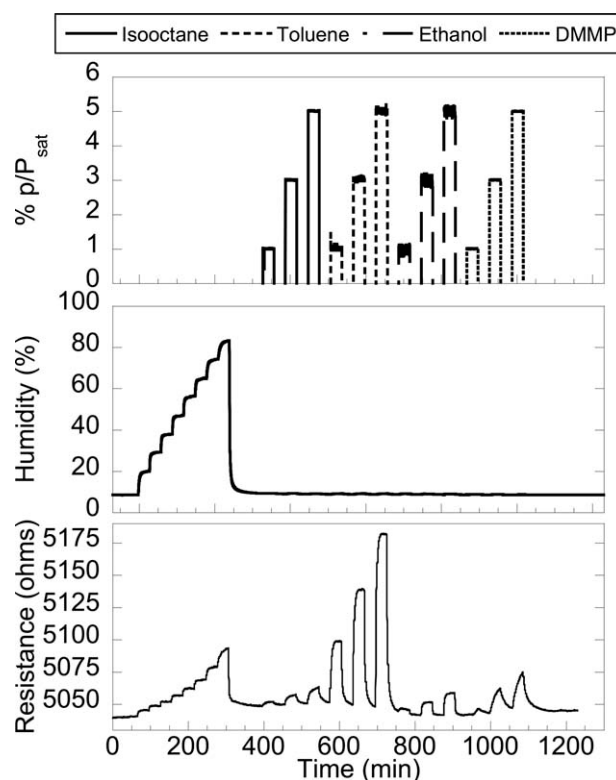

Figure 2 Chemiresistive polymer composite ribbon of PCP with GR (PCP–GR) tested against four chemicals and water vapor at 20°C. The concentrations of the chemicals are shown in the upper graph followed by the humidity concentration measured with a Hycal sensor (Honeywell, Golden Valley, MN), and the ribbon sensor response is shown in the lower graph.

to peak signal and extrapolated from the response to a given concentration exposure. The vapor concentrations were calculated via the Antione equation or from the reported vapor pressure of the analytes and are reported on a volume basis.[26] The vapor-phase concentrations are presented as a percentage of the saturation vapor pressure (Psat), usually denoted p/Psat, at the temperature of the vapor source (p is the partial pressure of the chemical). For the particular PCP–GR ribbon sensor, the response shown in Figure 2 with an LOD of 2.2 ppmV was calculated for DMMP.

To selectively discriminate the interfering VOCs from the nerve agent simulant, an array of multiple sensor threads were necessary. Different polymers provide sensors with varied relative sensitivities to a given set of chemicals, depending on their chemical structure. Polymers were chosen from previous experiments at Seacoast Science or from the literature on the basis of predicted interactions with the target chemical vapors. The polymers investigated were PEVA (18%), PECH, PIB, PVAC, PCP, PDMS, STH157C, and SXFA. The other variable in the production of diversified chemiresistor ribbons is the nature of the conductive additive. The tested conductive materials included graphitized carbon,
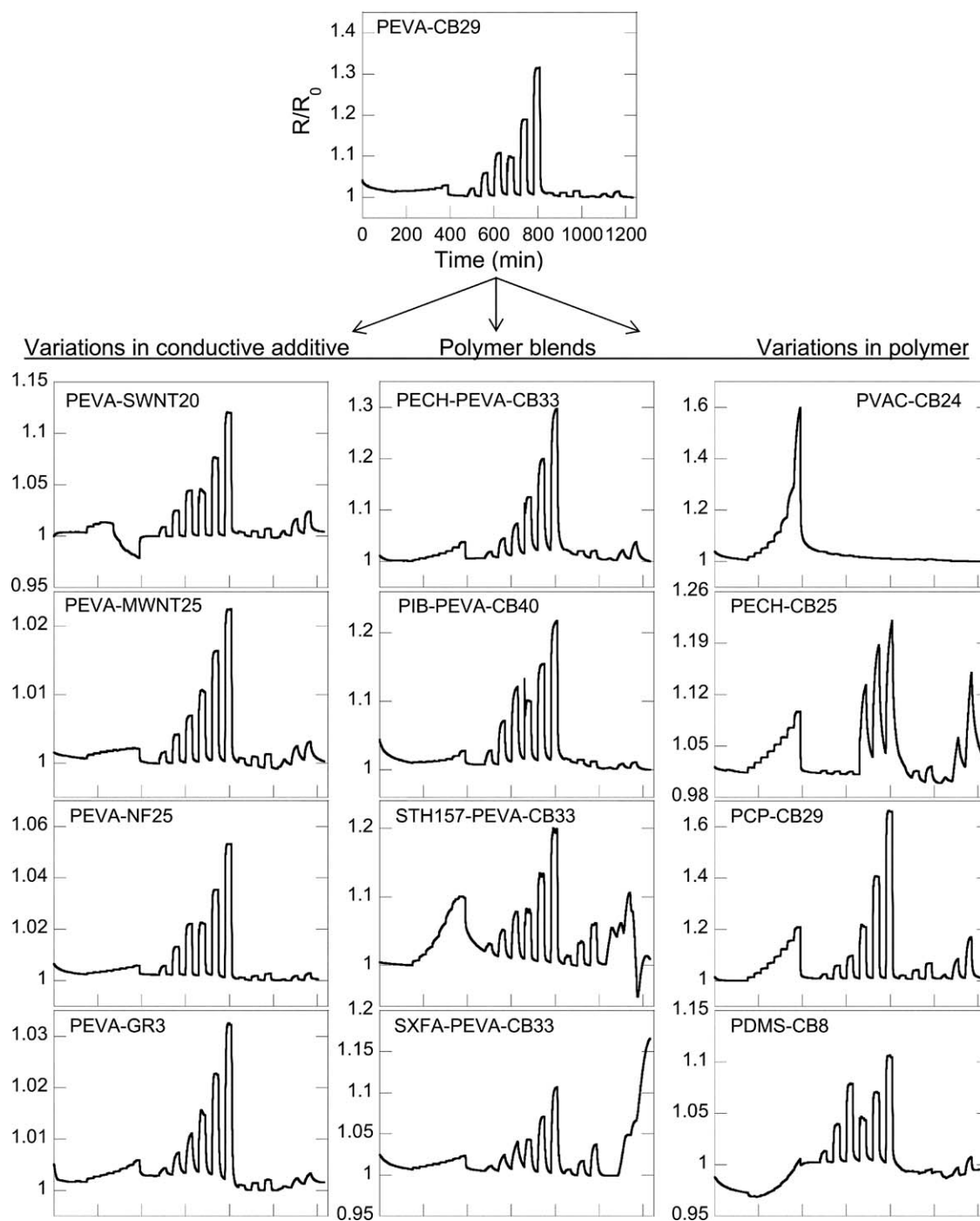
Figure 3 Matrix of the ribbon sensor responses (normalized by R_0) to the same test exposure set shown in Figure 2 (water vapor, isooctane, toluene, ethanol, DMMP). The first column shows variations in the conductive additive, the second column shows the PEVA polymer blends, and the third column illustrates the alterations of the host polymer. The relative conductive particle weight percentage is given in the legend. All sense element responses (resistance vs time) were acquired at a constant temperature of 20°C.

SWNTs and/or MWNTs, NFs, and GR. Another option to vary the composition of the chemiresistive composites is to use polymer blends mixed with a conductive dopant. The latter approach is often a necessity when one deals with polymers that have a low glass-transition point or may be liquid at room temperature. Such polymers alone would lack

the mechanical stability to form freestanding ribbons. Blending polymers with a solid polymer can overcome this problem. For instance, low-molecular-weight PIB, a viscous liquid at room temperature, can be mixed with a supporting polymer, such as PEVA, with a mass content of up to 60% PIB to form a freestanding film. The physical and chemical
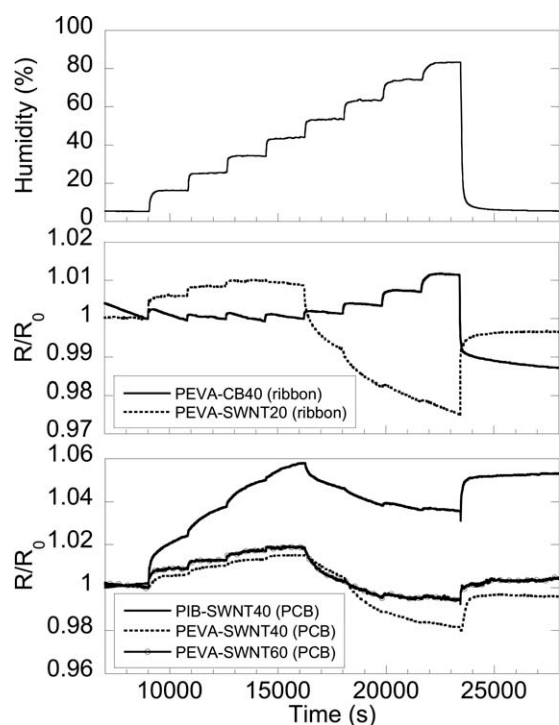
Figure 4 Close-up view of the humidity response at 20°C (normalized by R_0) of the PEVA–SWNT and PEVA–CB ribbon sensor (middle). The relative conductive particle weight percentage is given in the legend. The SWNT composite showed an increase in conductance in the mid-range of the water vapor exposure. For comparison, similar composites on a printed circuit board (PCB) substrate are shown (bottom).

properties of the polymer blend are different from either constituent; therefore, these films are a valuable addition to a sensor array.

Figure 3 shows the matrix of chemiresistive polymer composite ribbon sensors that were exposed to the same test system sequence used in the previous experiments (water vapor, isooctane, toluene, ethanol, DMMP). The variation of compositions described previously is illustrated in the three columns of the matrix. The first column shows the effect of different carbon dopants.

Unexpectedly, the SWNT devices showed a trend reversal when the humidity was increased stepwise (Fig. 4, middle). Traditional carbon–polymer composites always showed a continuously increasing resistance with increased humidity, similar to the PEVA-CB40 ribbon shown in the same figure. The resistance-reversal behavior of the PEVA–SWNT chemiresistor was confirmed by the coating of similar composites on a silicon nitride passivated substrate and a printed circuit board (PCB). This verified that the observed humidity effect was independent of the sensor platform and the carbon loading ratio (Fig. 4 bottom). Furthermore, similar behavior was observed when the SWNTs were mixed with PECH or PIB; this showed that the SWNT humidity effect was independent of the host polymer (Fig. 4

bottom). These experiments clearly showed that the resistance reversal with increasing humidity exposure was due to the nature of the SWNTs. Finally, we found that the same humidity behavior was observed without the addition of the polymer, that is, SWNTs only, deposited onto a PCB and an alumina substrate. The interaction of SWNTs with humidity has been studied by others,[27,28] and some have reported similar observations. Zahab et al.[29] attributed the conductivity change of SWNTs upon the exposure of H_2O to a transition from *p*-type to *n*-type behavior at higher humidity levels. The unusual humidity behavior with SWNT additives may also have been due to the water loading inside the carbon nanotubes. This phenomenon of a sudden increase in the sensor's conductance, despite the increased composite swelling, was never observed for any of the other carbon additives that were tested, including the MWNTs. Additionally, we found that this SWNT chemiresistor behavior was humidity-specific. The same stepwise analyte addition was tested with toluene and ethanol up to at least 50% p/P_{sat}; it resulted in a constantly increasing ribbon resistance. This humidity effect with SWNTs is the subject of further research in our group. Among other things, we will establish whether the observed behavior is characteristic to the specific type and size of SWNTs used in this study or whether it is common for other SWNTs also.

GR as the conductive additive did not show any obvious advantages compared to the other conductive carbons. However, the weight fraction needed to achieve similar resistances of the single-layered carbon in the composite was much lower compared to the other carbon additives. Because of the large surface area, as little as 3% GR compared to about 30% of the other carbon allotropes was present in the composite mixture for obtaining a similar resistance of the cast film (kΩ range).

Figure 5 shows a plot of the calculated LODs of the PEVA ribbon composites with different carbon additives. Because of the variation in the polymer/carbon ratio, a difference in the analyte sensitivity was expected. However, the disparity in the response levels of these ribbon sensors for DMMP relative to toluene was also due to the variation in the conductive additive. Figure 5 also shows the ratio of the two LODs (DMMP/ toluene). Both, the SWNT and the MWNT composites showed higher relative sensitivities to DMMP compared to the ribbon sensors made with the other carbon dopants. These data demonstrated that the relative selectivity of the sensor could be tuned with the choice of carbon additive in the chemiresistor composite.

The second column in Figure 3 shows the variation in sensor responses from different polymer blends. All of the blend-sensor responses had distinct features, but the addition of STH157C, a hydrogen-bond acidic polycarbosilane, to the PEVA
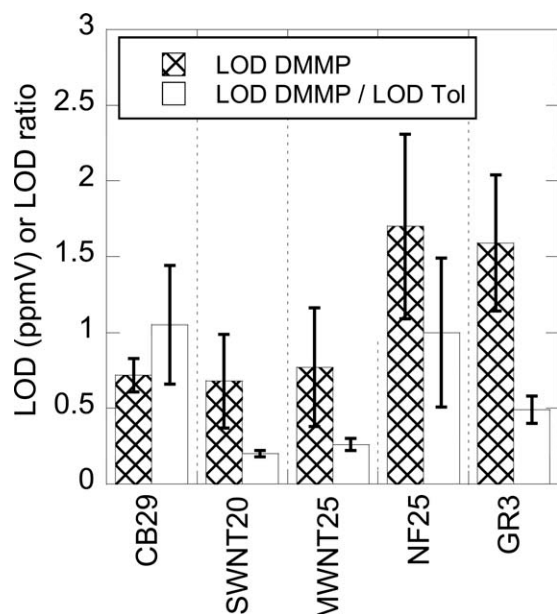
Figure 5 PEVA–chemiresistor composites produced with different carbon conductive additives. LOD of DMMP and the LOD ratio of DMMP to toluene are shown as an average of six measurements. The error bars represent ±1 standard deviations. The relative conductive particle weight percentage is stated after the abbreviated carbon description.

polymer modified the signal the most. This combination rendered the blend more polar and increased the sorption; this emphasized the response toward water, ethanol, and DMMP. In contrast, the addition of PIB to the PEVA matrix improved the sorption of isooctane by reducing the polarity of the mixture, as would be predicted by HSP models.

Finally, the last column in Figure 3 shows the response of different host polymers all mixed with carbon-black nanopowder, from the most polar and strongest hydrogen-bonding characteristics at the top to least polar and weakest hydrogen-bonding strength at the bottom. The PVAC chemiresistor provided a highly selective humidity sensor, whereas the PECH sensor showed a strong affinity toward toluene and DMMP. The nonpolar crosslinked PDMS composite had no response to the water vapor, whereas the PCP chemiresistor sensed all analytes and showed similar behavior to that of the GR composite shown in Figure 2. These results were consistent with supported chemiresistive devices reported in the literature[30] and with expectations from HSP theory. It is worth noting that the PCP–CB ribbon sensor showed better sensitivity compared to the PCP–GR chemiresistor. An LOD for DMMP of 0.1 ppmV was calculated for the PCP–CB sensor. Variations in the ribbon thickness, dopant dispersion uniformity, concentration of the dopants, and overall resistivity also contributed to the different sensitivity observations.

A sensor response matrix, such as the one shown, allows the identification of sensor redundancies and points out the chemiresistors that are most useful for algorithmic compensations in a diversified sensor array.

Ribbon sensors embedded in textiles

Most of the ribbons from the solution-cast polymer composite films showed good mechanical stability, such that the threads could be manually sewn into textiles. As an example, Figure 6 displays a chemical sensor ribbon in a fabric containing metal fibers, which could be used as electrodes or electrical contact points to a signal-measuring circuit. The conductive fabric[31] allowed the measurement of the ribbon's resistance at various points along its length for averaging purposes (reduction of noise) or sections of different polymer ribbons in line.

Likewise, the freestanding polymer ribbon sensor was woven into a fairly densely woven fabric patch (Fig. 7) that could be integrated with other circuitry to provide a functional chemical sensor on a uniform. The terminals of the chemical sensor element ribbon could be removably connected to the circuitry of a chemical sensor to allow the patches to be disposable. Both the polymer ribbons in the conductive fabric and in the patch resulted in a sensor response almost identical to that of the freestanding polymer sensor ribbon.

Compensation algorithms and principal component analysis (PCA)

A set of four different polymer composite ribbons from the matrix shown in Figure 3 was used to study the effectiveness of the sensor array. The four chemiresistor ribbons chosen for the array were PEVA–CB, PECH–CB, PCP–CB, and PVAC–CB. This set of polymer composite sensors was exposed to a pattern of different test system conditions to collect training data for the data-processing task. The test
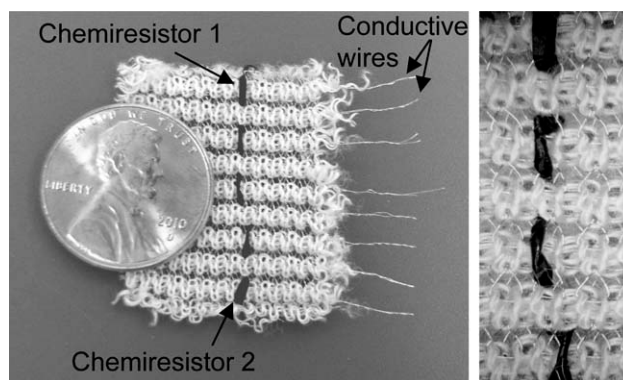

Figure 6 Photographs of a ribbon chemiresistor threaded through conductive fabric (left) with wires for electrical connection to readout and close-up view of the chemiresistor (right). A U.S. penny is shown for scale.
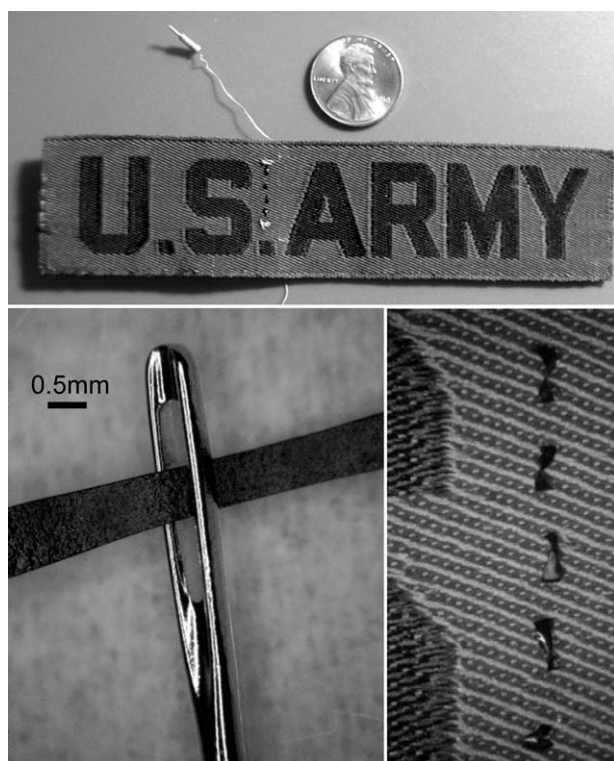
Figure 7 Close-up view of a chemical sense element ribbon chemiresistor threaded through the eye of a needle (lower left). A chemical sense element ribbon was woven into a fabric patch (upper, and enlarged view, lower right) and is shown with metal threads connecting to wires for resistance measurement. A U.S. penny is shown for purposes of scale.
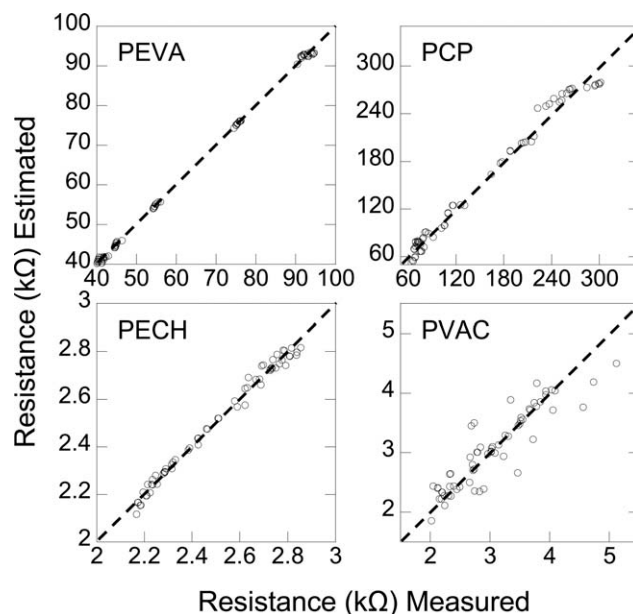

Figure 8 Regression model results of each of the four chemiresistors based on a temperature and humidity training set (abscissa: test data; ordinate: modeled data). The diagonal lines (ideal slope = 1) are meant to guide the eye.

environment variables included the temperature, humidity, and chemical vapor concentration of methanol, ethanol, acetone, isooctane, toluene, trichloroethylene, 2-nitrotoluene, and DMMP.

The Pearson correlation results from all of the training data collected (1023 instances), in Table I, show that these four sensors were not highly correlated[32] and, thus, were well suited to form a diverse array. Correlation analysis was performed with the auto-scaled responses (ΔR) from each sensor. The strongest correlation appeared to be between PEVA and PCP, whereas the PVAC was not similar to any of the other sensors.

At first, a mathematical algorithm was established to demonstrate the temperature and humidity compensation of the individual polymer-based thread sensors. Generally, regression techniques can be

implemented to provide a mathematical model of a sensor's behavior, to actively correct baseline variations, or to model a particular behavior for quantification or to improve classification results. Using the aforementioned training data from the four polymer chemiresistor ribbons, we set up a multiple linear regression model to take into account the expected environmental field variations in temperature and humidity. The goal was to accurately model R_0 under any condition where no chemical was present (within the limits tested). Figure 8 shows the results of the regression of the training data from the four chemiresistors in the form of the following equation:

$$R_{sensor_j} = a_j T + b_j T^2 + c_j/T + d_j/T^2 + e_j RH + f_j RH^2 + g_j/RH + h_j/RH^2 + i_j$$

where the measured humidity (H) and temperature (T) are the independent variables, the measured resistances (R's) are the dependent variables, a to i are constants that the modeling software determines, and j represents each sensor (polymer) in the array. R_{sensor} is the resistance of the modeled chemiresistive sensor. The regression terms were selected from previous work, where the behavior of a number of sensors was modeled with respect to chemical concentration.[33] The linear and nonlinear terms were based on observations of the raw data. The training data for these models included data collected at various temperatures (10–40°C) and relative humidity (0–80%) conditions (63 points), where each point was the average of the last five resistance
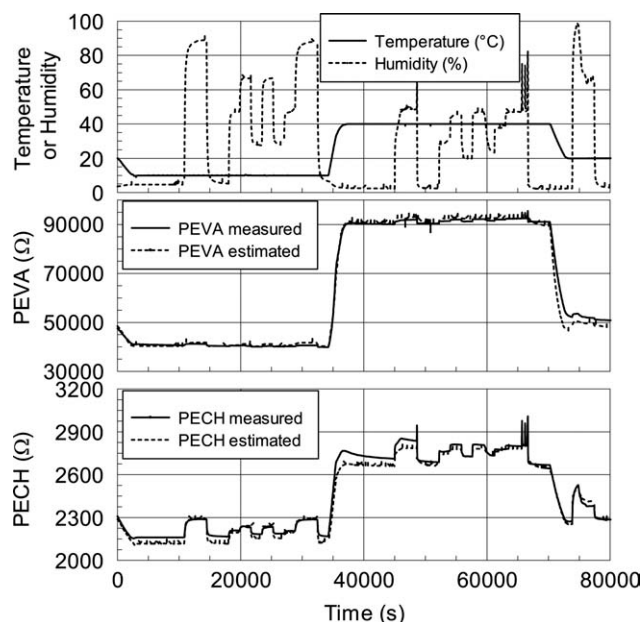
TABLE I
Pearson Correlation Results from Training Data

	PEVA	PECH	PCP	PVAC
PEVA	1			
PECH	0.28	1		
PCP	0.57	0.41	1	
PVAC	−0.09	−0.08	−0.04	1

Figure 9 Temperature and humidity (top) compensation of the PEVA–CB (middle) and PECH–CB (bottom) polymer composite chemiresistor ribbons demonstrated with multiple linear regression of the training data.

levels. Although these models were successful in compensating for the extremes in the training data, it would still possible for one to improve them by taking into account further nonlinearity (requiring more training data). Any deviations from the raw and modeled data in the sensors will lead to errors in any qualification and quantification algorithms that can be developed later. Because those calculations use the relative sensor response or change in response to determine a chemical exposure, it is important to reduce any errors in these early compensation models.

The next step in the modeling of the four polymer composite chemiresistors was to take into account all the chemical vapor exposures. Table II lists the host polymers used in the chemiresistors and the chemicals selected for this study. The HSPs[11] helped to predict the strength of interaction between the host polymer and the target chemical. The eight chemicals were measured at three temperatures (15, 25, and 35°C) and four humidities (0, 20, 50, and 80% RH) and twice at a total of four vapor concentrations (1, 3, 5, and 10% p/P_{sat}). Principal component analysis[34] (PCA) was used to model the chemical exposure data.

In Figure 10, the first three principal components (PCs), with the data sets at 25°C, showed that this simple array provided some discriminating power at higher chemical concentrations. In this figure, each point represents an individual chemical in dry and humid conditions. To aid viewing, each sensor's responses (ΔR) were scaled by the standard deviation of that sensor's data set. Even though the percentage of total variance described by the PCs was well distributed in these data set, ethanol and isooctane were still not distinguishable from the central cluster; however, chemicals such as DMMP and 2-

measurements (over about 1 min) at a given equilibrated condition. It should be noted that some sensors were better modeled than others. PEVA's low humidity sensitivity made it easier to model versus PVAC, which had a high humidity sensitivity and a lower temperature sensitivity. In the plots in Figure 8, the deviations from the diagonal are representative of the error from ideal.

Figure 9 shows the same regression models applied to the raw data set from two of the chemiresistor ribbons at three temperatures and a range of humidity

TABLE II
Host Polymers in Ribbon Sensors and Selected Target Analytes

| Polymer/chemical	Solubility parameter (MPa$^{1/2}$)	Description
PVAC	20[12]	High polarity, strong hydrogen bonding, interacts with water alcohols[21]
PEVA	16–22[12]	Low-polarity polymer with the highest sensitivity to low- to medium-polarity chemicals
PCP	21–21.85[20]	Medium polarity, low hydrogen bonding, demonstrated sensitivity to DMMP[29]
PECH	17–20[12]	Medium polarity, hydrogen-bond base, good response to toxic industrial chemicals[18,19]
Water	47.8	Most common interferent
Methanol	29.6	Common solvent, used in de-icing operations
Ethanol	26.5	Common solvent
Acetone	19.9	VOC, common solvent
Isooctane	14.1	VOC, simulant for fuels
Toluene	18.2	VOC, common solvent, simulant for fuels
Trichloroethylene	18.7	Chlorinated common solvent
Nitrotoluene	22.6	Explosive simulant
DMMP	22	Nerve agent simulant
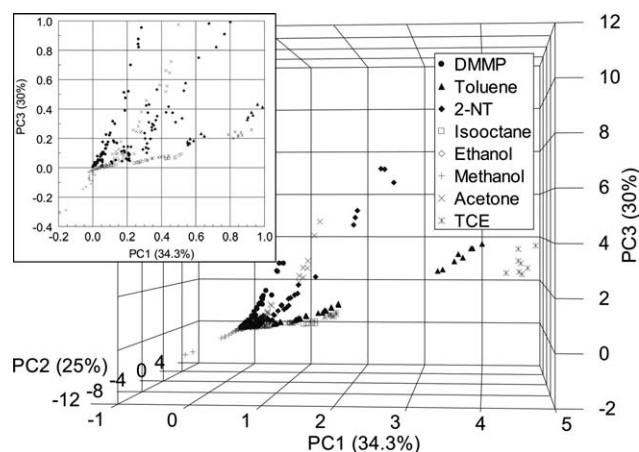
Figure 10 PCA results from the training data for four polymer/carbon chemiresistor ribbons. The percentage total variance is given with each PC axis title. The chemical concentrations ranged from 0 to 10% p/P_{sat}, the temperature ranged from 10 to 40°C, and the relative humidity ranged from 0 to 80%. The inset graph shows a close-up view of the central region.

nitrotoluene extended away from the middle. Clearly, a more diverse array or more sophisticated set of algorithms would be required to further discriminate these compounds.

CONCLUSIONS

We have described polymer-based chemiresistive sensors that were built in the form of unsupported, free-standing polymer composite ribbons. The small, threadlike transducers required only a simple readout circuitry. The ribbons were integrated into textiles, as illustrated with a sensor sewn into an insignia patch that responded to DMMP and other interferences.

A four-polymer composite ribbon sensor was exposed to different chemicals at various temperatures and humidities to demonstrate a selectivity concept with a mathematical model. The collected training data could be modeled well with linear regressions to compensate for temperature and humidity data. The PCA of the sensor array demonstrated that certain compounds could be distinguished with the four-polymer array; however, further improvements could be made to advance the chemical classification. Also, more complex mixtures of chemicals should be considered to model the sensor behavior in expected operational environments.

Comparisons of the absolute sensitivities of the polymer chemiresistors were avoided because of the differences in the composites' carbon mass fractions and the thicknesses of the ribbons. The sensor composite uniformity will be improved with more advanced manufacturing techniques to produce conductive ribbons.

Compared to substrate-supported sensors, the freestanding polymer composite ribbons had faster

response and recovery times because of swelling and diffusion from all sides. Low-cost polymer composite sensors could be produced in volume by traditional thread manufacturing techniques, such as extrusion or electrospinning. Potential applications for the sensor ribbon array include environmental high-flux monitors, electronic noses for threat agents, and chemical-sensing fabrics.

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