Use of Compatible Polymer Blends To Fabricate Arrays of Carbon Black−Polymer Composite Vapor Detectors

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Compatible blends of poly(vinyl acetate) and poly(methyl methacrylate) have been used to produce a series of electrically conducting carbon black composites whose resistance is sensitive to the nature and concentration of an analyte in the vapor phase. The dc electrical resistance response of the composites was found to be a nonlinear function of the mole fraction of poly(vinyl acetate) in the blend. These compatible blend composite detectors provided additional analyte discrimination information relative to a reference detector array that only contained composites formed using the pure polymer phases. The added discrimination power provided by the compatible blend detectors, and thus the added diversity of the enhanced detector array, was quantified through use of a statistical metric to assess the performance of detector arrays in various vapor classification tasks.

Recent work has shown that arrays of chemically sensitive resistors, formed from composites of carbon black with a collection of swellable insulating organic polymers, are broadly responsive to a variety of odors yet allow classification and identification of organic vapors through application of pattern recognition methods.[1] To date, these array elements have been fabricated from a relatively small number of approximately 10−20 organic polymers, with a distinct polymer backbone composition in each detector.[1] Detectors having on the order of 3−10 different polymer backbones have also formed the basis for vapor detector arrays based on bulk conducting polymer films,[2,3] surface acoustic wave devices,[4−6] fiber-optic micromirrors,[7] quartz crystal microbalances,[8] and dye-containing coatings on optical fibers.[9] Although a limited number of polymeric detector compositions might be chosen to perform optimally for a specific application,[4,10] attempts to mimic the sense of olfaction or attempts to address applications in which the sensing task is time dependent or is not defined in advance of the detector array construction will almost certainly require use of extensive, compositionally diverse polymeric detector libraries. Since it is likely to be nontrivial to prepare arrays that contain thousands of chemically distinct polymers using thousands of individual polymer-containing feedstock solutions, combinatorial and/or gradient methods seem appropriate to address this problem. Herein we describe an approach to the construction of detector arrays in which compatible blends of two base polymers are used to create compositionally varying chemically sensitive resistor films. The resolving power of such an array is shown to be superior, in several test tasks, to that of arrays containing an identical number of detectors but composed of only the base polymeric materials.

Nonlinearity of the gas−solid partition coefficient with respect to the mole fraction of the polymers that comprise the compatible blend is crucial to increasing the diversity of a broadly responsive detector array that is fabricated through gradient or combinatorial methods. Otherwise, the response of the blended chemiresistor elements can be predicted precisely from the responses of the base polymeric detector materials. Two polymers, poly(vinyl acetate) (PVA) and poly(methyl methacrylate) (PMMA), were selected to form the compositionally varied chemiresistor composites studied in this work. These materials were chosen because a similar binary polymer blend system, formed from poly-(vinyl acetate) and poly(methyl acrylate), has previously been reported to exhibit gas−solid partition coefficients for benzene that are not linearly related to the mole fraction of PVA in the polymer blend.[11]

EXPERIMENTAL SECTION

Eight different PVA/PMMA blend compositions were investigated as carbon black composite chemiresistor vapor detectors. The compatible blend detector fabrication was achieved by combining the two initial base polymer feedstocks to produce solutions of PVA/PMMA having PVA mole fractions (by monomer) of 0.00, 0.11, 0.28, 0.44, 0.64, 0.78, 0.91, and 1.00, respectively. Each stock solution contained 20 mL of tetrahydrofuran, 200 mg of total dissolved polymer, and 86 mg of suspended carbon black.

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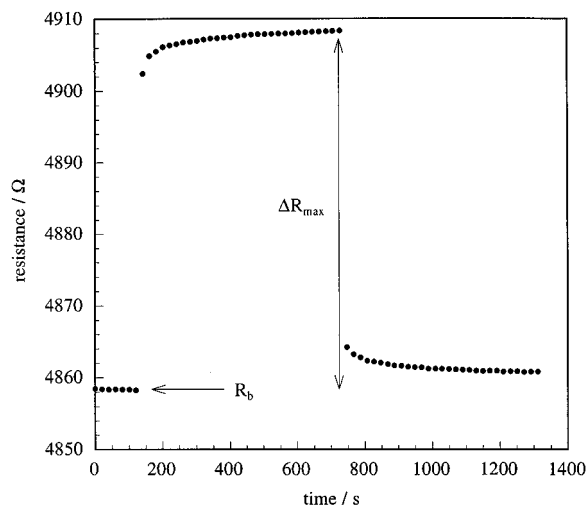
Figure 1. Temporal resistance response of a typical polymer composite chemiresistor detector. This particular carbon black composite detector contained 64% PVA and 36% PMMA by monomer mole fraction. The detector was exposed to 11.3 ppth of methanol in air for 600 s starting at $t = 120$ s. The baseline resistance before the exposure, R_b, and the maximum resistance change during the exposure, ΔR_{max}, were 4858 and 50 Ω, respectively.

Standard glass microscope slides, cut to a size of approximately 2 cm $\times$ 2.5 cm, were modified for use as the substrate for each polymer blend detector. Two parallel bands of 20 nm thick chromium ($\approx$2 cm $\times$ 1 cm), spaced 0.5 cm apart, were evaporated onto each slide. The chromium bands were then coated with 30 nm of evaporated gold, thus forming robust electrical contacts. Each carbon black–polymer suspension was sonicated for 10 min and was then spin-coated, at 1000 rpm, onto a modified glass slide such that the gap between the slide electrical contacts was spanned by the polymer composite film. The detectors were allowed to dry in ambient air for 12 h before use.

To obtain response data, the detectors were placed into a 1.2 L sampling chamber and electrical leads were attached to the two chromium–gold bands of each detector. The dc resistance of each detector was recorded as a function of time using a Keithley model 7001 channel switcher connected to a Keithley model 2002 multimeter that was interfaced to a personal computer. An automated flow system consisting of LabVIEW software, a personal computer, and electronically controlled solenoid valves and mass flow controllers was used to produce and deliver controlled concentrations of solvent vapors to the detectors in the sampling chamber. The desired vapor concentrations were obtained by passing a stream of carrier gas through a bubbler that had been filled with the solvent of choice and then diluting this flow into a stream of air maintained at a controlled flow rate. The time protocol for each exposure was 120 s of air, followed by 600 s of test vapor in air, ending with another 600 s of air.

Figure 1 displays the resistance response of a typical detector. Upon exposure to a test vapor, the resistance of the composite film increased, and the response then decreased after the vapor exposure was terminated. This behavior has been discussed in detail for a series of pure polymeric compositions that have been used as either carbon black or polypyrrole composites to provide

arrays of electrically conductive vapor detectors.[1,12] To assess the performance of the compatible blend composites, all of the detectors were exposed 10 times each, in random order, to five different analytes, with the vapor concentrations chosen to be 11.3 parts per thousand (ppth) of methanol, 5.2 ppth of ethanol, 20.7 ppth of acetone, 8.3 ppth of ethyl acetate, and 8.2 ppth of acetonitrile in air at 21 °C. These concentrations all correspond to 7.1% of the solvent-saturated concentration of each analyte in 21 °C air, under a total atmospheric pressure of 753 Torr. The maximum differential resistance response relative to the baseline resistance ($\Delta R_{max}/R_b$) was used in the analysis of the array performance carried out in this work.

RESULTS AND DISCUSSION

Figure 2 depicts plots of $\Delta R_{max}/R_b$ for the polymer blend chemiresistors upon exposure to ethyl acetate, ethanol, acetonitrile, acetone, and methanol. For each analyte, a statistically significant nonlinearity was observed for the detector response vs the mole fraction of the base polymer feedstocks. Since the nonlinearity is not the same for all solvents, this indicates that useful information is available through use of such compatible blend materials in a detector array for vapor classification.

The ability of a specific detector array to resolve pairs of solvent vapors can be quantified statistically through reference to a generalized resolution factor, rf. This quantity is equivalent to that proposed by Müller[13] and recently used by Gardner and Bartlett[14] and is a multidimensional analogue of the separation factors used in gas chromatography. Resistance responses, $\Delta R_{max}/R_b$, of carbon black–polymer composite detectors, containing $\geq$20 wt % carbon black, have been shown to vary linearly over at least an order of magnitude in the concentration of the analyte in the vapor phase.[1] Hence, detector arrays which can resolve analytes at one concentration can also be used to resolve analytes at other concentrations. The detector responses were autoscaled to account for the different dynamic ranges of different detectors. The autoscaled response of the jth detector to the ith exposure, A_{ij}, was thus

$$A_{ij} = \frac{(\Delta R_{ij,max}/R_b) - \alpha_j}{\beta_j} \qquad (1)$$

where α_j and β_j are the mean and standard deviations, respectively, in the responses of the jth detector to all analytes. The mean response vector, $\bar{x}_a$, of an n-detector array to analyte a is taken as the n-dimensional vector containing the mean autoscaled response of each detector, $\bar{A}_{aj}$, to the ath analyte such that

$$\bar{x}_a = (\bar{A}_{a1}, \bar{A}_{a2}, ..., \bar{A}_{an}) \qquad (2)$$

The average separation, $|\vec{d}|$, between two analytes, a and b, in the Euclidean detector response space is then simply the magnitude of the difference between $\bar{x}_a$ and $\bar{x}_b$. The reproducibility of the array responses to the analytes is also important in quantifying the resolving power of the array. A measure of array response reproducibility to analyte a, $\sigma_{a,\vec{d}}$, is obtained by projecting

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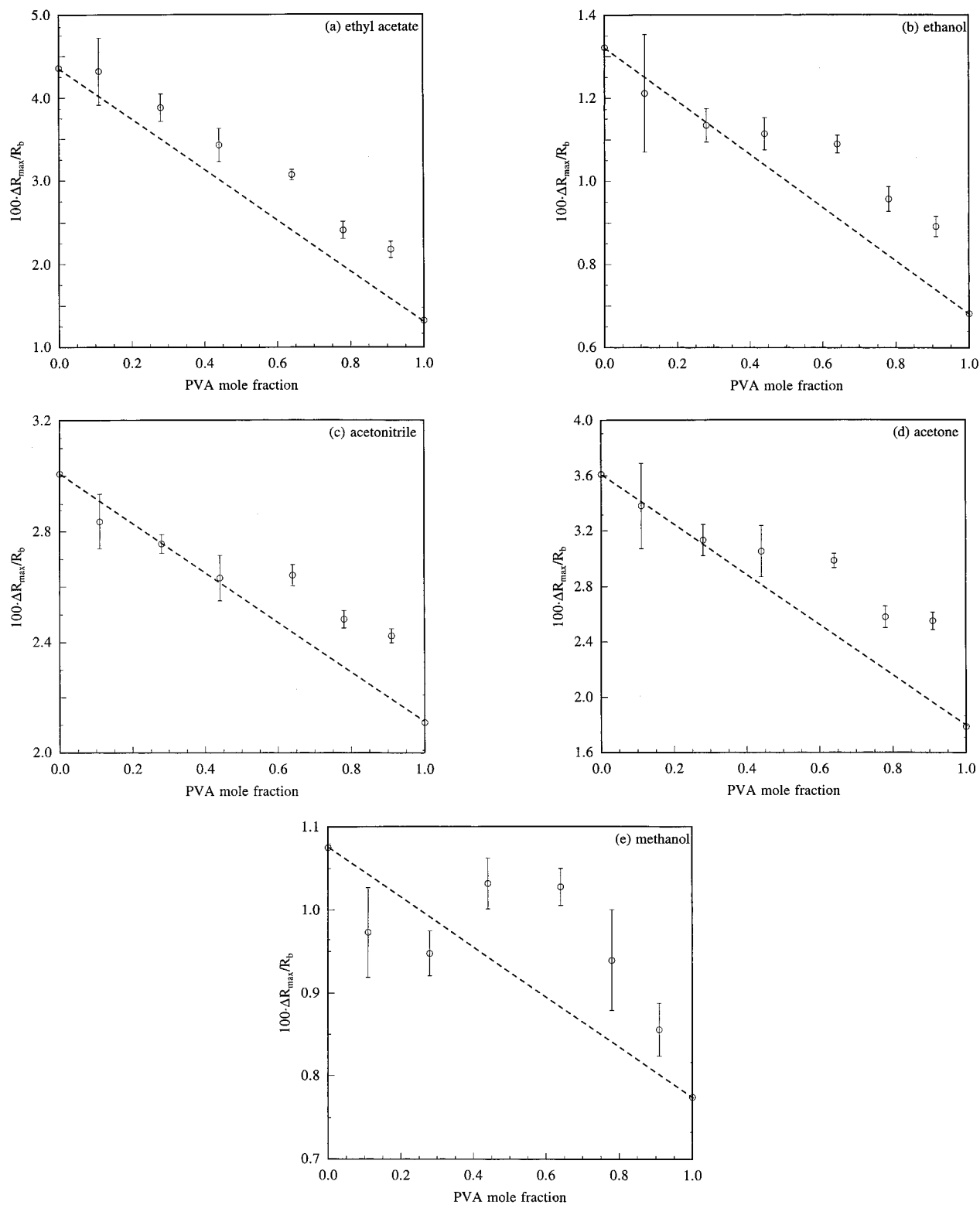(14) Gardner, J. W.; Bartlett, P. N. *Sens. Actuators B* **1996**, *33*, 60.

Figure 2. Maximum relative differential resistance response, $\Delta R_{max}/R_b$, of a series of polymer blend−carbon black composite chemiresistors upon exposure to (a) 8.3 ppth of ethyl acetate, (b) 5.2 ppth of ethanol, (c) 8.2 ppth of acetonitrile, (d) 20.7 ppth of acetone, and (e) 11.3 ppth of methanol in air. The plots depict data obtained from 14 detectors of pure PMMA, 10 with 11% (by monomer mole fraction) PVA, 10 with 28% PVA, 15 with 44% PVA, 10 with 64% PVA, 15 with 78% PVA, 10 with 91% PVA, and 15 of pure PVA. The responses plotted for each mole fraction are the mean $\Delta R_{max}/R_b$ values for 10 exposures to each set of detectors containing the specified mole fraction of PVA, while the error bars represent one standard deviation unit. Dashed lines were drawn, joining the end points, as a guide to the eye indicating a linear response relationship.

the array response vectors for each exposure to analyte a onto the vector $\vec{d}$, and calculating the standard deviation in these scalar

projections about the projection of the mean response vector, $\vec{x}_a$ onto $\vec{d}$. The same procedure is repeated for analyte b of the a,b

Table 1. Resolution Factors Quantifying the Average Ability of 8-Detector Arrays, Composed from Four Different Detector Sets, To Resolve Pairwise the Collection of Test Analytes[a]

sensors used	overall av rf	methanol vs ethanol	methanol vs ethyl acetate	methanol vs acetonitrile	methanol vs acetone	ethanol vs ethyl acetate	ethanol vs acetonitrile	ethanol vs acetone	ethyl acetate vs acetonitrile	ethyl acetate vs acetone	acetonitrile vs acetone
set A	52	25	61	90	44	58	93	42	58	20	27
set B	60	19	67	104	81	67	110	81	31	17	26
set C	81	4.6	122	102	181	103	93	148	17	31	8.7
set D	60	23	84	93	60	82	96	58	55	22	26

[a] The overall average rf represents the average resolution factor across all analyte pairs for random combinations of detectors from a given detector set. The results for set A, set B, and set D were obtained by averaging over 500 randomly selected 8-detector arrays composed of only the detectors within each respective set. The results for set C were obtained by averaging over all 45 possible 8-detector combinations of the detectors within the set. Set A contained all 14 of the 0% PVA detectors and all 15 of the 100% PVA detectors (i.e., all the base polymer detectors). Set B contained all 99 of the prepared detectors ranging from 0% to 100% PVA Content. Set C contained only the 10 detectors with 91% PVA. Set D contained all 14 of the 0% PVA detectors, all 10 of the 91% PVA detectors, and all 15 of the 100% PVA detectors.

analyte pair, allowing a pairwise resolution factor to be defined as

$$\mathrm{rf} = \frac{|\vec{d}|}{\sqrt{\sigma_{a,\vec{d}}^{2} + \sigma_{b,\vec{d}}^{2}}} \quad (3)$$

This metric allows quantification of the ability to resolve pairwise the vapors of concern in the test analyte set based on the response patterns that they produce on the detector array. Because the functional form of the response of the various polymer composite chemiresistors was very similar, this procedure can be used to provide an objective measure of array performance, as opposed to performing a subjective assessment of the performance of task-specific neural network classifiers on functionally dissimilar responses of various array elements.[15] It is important to realize, however, that the results are nevertheless coupled to the metric used to evaluate the responses and that different algorithms, such as, for example, Fisher linear discriminants, which are linear data analysis methods that are not confined to pass through the mean response values of the analytes of concern,[16] may well yield different conclusions from the same response data.

The responses produced by a set of 99 detectors, 14 detectors with pure PMMA, 10 with 11% PVA, 10 with 28% PVA, 15 with 44% PVA, 10 with 64% PVA, 15 with 78% PVA, 10 with 91% PVA, and 15 with pure PVA, were investigated using this approach. The performances of 8-detector combinations from different sets of detectors were evaluated to determine if arrays containing some of the compatible blend polymer detectors would perform better than arrays containing only detectors made from the base polymers, for certain test tasks. The performance of each studied array was measured by its ability to resolve the solvents pairwise, as given by the calculated rf values obtained using the simple linear data analysis method described above.

Results are presented for four sets of detectors. Set A contained all 14 detectors with 0% PVA and all 15 detectors with 100% PVA (i.e., all the base polymer detectors). Set B contained all 99 of the prepared detectors ranging from 0% through to 100% PVA content. Set C contained only the 10 detectors with 91% PVA.

Set D contained all 14 of the 0% PVA detectors, all 10 of the 91% PVA detectors, and all 15 of the 100% PVA detectors. Since there are extremely large numbers of possible 8-detector combinations from within sets A, B, and D ($\approx 10^{11}$ unique 8-detector combinations out of 99 set B detectors), 500-member subsets of the total number of 8-detector array combinations were selected randomly and their corresponding rf values were calculated. For set C, rf values for all 45 possible 8-detector combinations out of 10 detectors were calculated. The results of the calculated resolution factors for arrays of 8-detectors within each set were averaged and are presented in Table 1.

Clearly, the inclusion of compatible blend detectors produced a statistically significant improvement in maximizing the overall average rf, which is the average ability of all calculated 8-detector array combinations within a set of detectors to resolve all analyte pairs using the metric defined above. For example, sets B, C, and D, which contained compatible blend detectors, had overall average rf's of 60, 81, and 60, respectively, whereas the base polymer detector arrays (set A) had an overall average rf of 52. The array performance in separating the pair of solvents, ethyl acetate vs acetone, that was worst resolved by set A (base polymer detectors) could also be improved by using 8-detector arrays containing only 91% PVA detectors (set C) or by including these detectors in arrays that contained the base polymer detectors (set D). Set D arrays, containing blended polymers, exhibit a larger overall average rf, a larger rf for the worst resolved analyte pair, and resolved 7 of the 10 analyte pairs better than did the base polymer arrays of set A.

The results presented in Table 1 show that each of the four detector sets produces arrays with at least one advantage over the others, such as the ability to resolve at least one analyte pair better than the other selected arrays. This reinforces the concept that more detector diversity is desirable, since it provides a larger basis of chemically unique detectors from which to tailor arrays for specific tasks.

Another significant conclusion arising from the data is that the classification of these various vapors, at fixed concentrations, is statistically robust from the array response even though the individual detectors themselves were not designed to possess high selectivity toward a specific analyte. For example, a pairwise resolution factor of 4.5 implies that, in a single presentation of the challenge vapors to the detector array, a given vapor can be

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distinguished from the other member of the test pair with >99.9% confidence level using the simple statistical pairwise method of data analysis described herein. This level of performance was met or exceeded by all of the eight-element detector arrays of Table 1 for all of the test vapor pairs used in this work, even though the array elements were not chosen in advance specifically to perform any particular set of vapor classification tasks.

Utilization of a nonlinear response of binary, tertiary, and quarternary blend composite chemiresistors to various solvent vapors should offer the opportunity to increase significantly the diversity of a polymer composite detector array and therefore to increase its classification performance relative to an array that contains chemiresistors fabricated from the pure polymeric phases alone. The binary polymer blend advantages reported herein are in agreement with those recently published using a different detector modality, polymer−dye optical detectors.[17] The exact performance gain of any specific array will likely be task dependent and must be evaluated for each application of concern. We note, however, that the olfactory bulb of canines has approximately 100 million receptor cells and that humans have over 1000 different olfactory receptor proteins.[18] Thus, attempts to mimic functionally the olfactory sense are unlikely to be realizable without exploitation of methodologies capable of incorporating extensive diversity into a polymer-based vapor-sensing array.[18] Extension of the approach described herein to other blends and a comparison of the detector diversity that can be achieved through the use of block and random copolymers as a complement to the use of compatible blends in detector arrays will be reported separately.

ACKNOWLEDGMENT

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