Chapter 2

Effects of Film Composition and Structure on the Response of Small Molecule- and Polymer-Based Carbon Black Composite Chemiresistor Vapor Sensors

2.1 Abstract

A series of polymer-based and small molecule (SM)-based carbon black composite vapor sensors has been prepared to understand why the SM-based sensors exhibit higher signalto-noise ratios at a much higher carbon black loading (75% by weight) than their polymerbased counterparts (40% by weight). Quartz crystal microbalance (QCM), powder X-ray diffraction (XRD), and ellipsometric measurements indicated that the decreased relative differential resistance response of SM-carbon black composite films at low loadings of carbon black is related to the increased rigidity that results from the crystallinity of these films. The SM-based sensors thus require greater carbon black loadings to break the film

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crystallinity and hence allow such films to swell by sorption of analyte vapor. In contrast, the polymer/carbon black composite films that were fabricated using low glass transition temperature materials were amorphous, and exhibited good vapor responses over a wide range of carbon black loadings.

2.2 Introduction

Broadly responsive arrays of vapor sensors have attracted significant interest for the detection and quantification of analytes. Systems studied include surface acoustic wave devices, ^{1–3} metal oxide sensors, ^{4–6} polymer-coated quartz crystal microbalances (QCMs), ^{7,8} and polymer-conductor composite chemiresistors ^{9–11} In such arrays, each sensor displays a distinct but non-selective response towards each analyte. The collective response fingerprint produced by the array provides the information needed to detect and quantify analytes. Chemiresistive sensors made from mixtures of insulating organic polymer with conducting carbon black (CB) sorb vapor into the polymer phase, causing the polymer to swell and thereby changing the overall resistance of the film. ^{9,12–18} Such sensors are low power, ^{19,20} can be created using a variety of methods and in a variety of form factors, ^{21–23} and can be cast onto a variety of substrates. ^{23–25}

Instead of organic polymers, a variety of low volatility small organic molecules (SM) have recently been used in carbon black composite chemiresistive vapor sensors. In performance tests, such SM-CB chemiresistors exhibited vapor detection performance that was comparable to that of polymer-based CB composites.²⁶ However the SM-CB composite sensors displayed their highest signal-to-noise ratios (SNR) at 60–75 weight percent of

CB,²⁶ whereas the polymer-CB (P-CB) sensors yielded best results at 20–40 weight percent of CB.

In the P-CB systems, the resistivity of the film, and the relative differential resistance response of the films to vapors, decreases as the fraction of CB is increased in the mixture.¹⁸ The ability of SM-CB sensors to operate with increased levels of CB allows the use of smaller quantities of potentially expensive materials in the production of such sensors, compared to P-CB sensors. SM-CB sensors also offer potential increases in sensing ability compared to P-CB composites, due to the larger variety of small molecules that are available to broaden the responsive ability of an array of SM-CB sensors.

The SM-CB sensors also have the potential to exhibit increased performance relative to P-CB sensors. The greater density of functional groups in the SM-CB composite films, and the random arrangement of the small molecules within the films, has been suggested to allow high vapor permeability, enhanced vapor-sensor interactions, and potentially increased sensitivity for such materials relative to P-CB films.²⁶

In this work, we have investigated and compared the properties of these two different types of sensors, to gain insight into why the SM-CB composite sensor films exhibit optimal performance at higher CB loadings than the P-CB composites. A library of polymers and a library of small molecule analogs that are structurally similar to the polymers were employed to compare and contrast the features of the two types of sensor formulations, and assess if chemical similarity would result in similar behavior. Sets of paired molecules were chosen on the basis of commercial availability (Figure 2.1). Hence, the relative differential resistance responses of these sensors, as well as quartz crystal microbalance (QCM),



Figure 2.1: All compounds used as sensors in this study. Displayed in matched pairs of small molecule/polymer.

powder X-ray diffraction (XRD), microscopy, and ellipsometric data, were collected for a series of films and analyte vapors.

2.3 Experimental

2.3.1 Materials

Polyethylene (PE, low density), poly(n-vinyl carbazole) (PnVC, molecular weight $[M_w]$ = 1.1 M), poly(caprolactone) (PCL, M_w = 14k), docosane, ethyl stearate (ES), dioctyl phthalate (DOP), gold wire (0.25 mm diam., 99.9+%), 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), and p-xylene were acquired from Aldrich. 2,4-dimethyl glutaric acid (DGA) and 9-isopropyl carbazole (iC) were acquired from Acros Organics, whereas lauramide was obtained from TCI America and Nylon 12 (polylauryllactam) was obtained from Poly-

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sciences, Inc. Hydroxypropylcellulose (HPC, $M_w = 60$ k), poly(acrylic acid) (PAA, $M_w = 450$ k), and poly(vinyl stearate) (PVS, $M_w = 90$ k) were purchased from Scientific Polymer Products, and 6-hydroxy hexanoic acid (HHA) and β -d-Lactose (β dL, 80% β , 20% α) were purchased from Alfa Aesar. Reagent grade hexane, heptane, chloroform, ethanol, isopropanol, ethyl acetate, acetone, and tetrahydrofuran were acquired from VWR. Chromium metal was purchased from RD Matthes. Black Pearls 2000, a carbon black (CB) material, was donated by Cabot Co. (Billerica, MA). All materials were used as received.

2.3.2 Sample Preparation

To make sensors, microscope slides (Corning or VWR) were cleaned with methanol and then with hexanes. The long, center axis of each cleaned glass slide was then masked with 1.0 mm wide drafting tape, and two leads were formed on each slide by evaporative deposition of 300 Å of chromium followed by deposition of 600 Å of gold. The tape was then removed and the slide was cut into 0.5 cm x 2.5 cm samples to produce substrates for subsequent deposition of a sensor film.

All sensors were formed from varying ratios of the sensor material, DOP (a plasticizer), and a suspension of CB. Prior to sensor fabrication, the organic material and the plasticizer were dissolved in the solvent, carbon black was added, and the solution was sonicated for >30 min to disperse the CB particles. In this process, the materials were added to 20 mL of solvent (Nylon 12 mixtures in HFIP, PAA mixtures in MeOH, PE mixtures in p-xylene, β dL mixtures in 50/50 acetone/water; all of the other materials in THF) in amounts sufficient to produce a total of 200 mg of solid material (Table 2.1). SM-CB mixtures were

Label	Sensor (mg)	Plasticizer (mg)	Carbon Black (mg)	Used
А	90	30	80	Δ R/R, QCM, XRD, SEM, DLS
A/noCB	90	30	0	QCM, XRD, ellipsometry
A/noCB/noDOP	90	0	0	XRD, ellipsometry
В	50	0	150	Δ R/R, QCM, XRD, SEM, DLS
B/noCB	50	0	0	QCM
СВ	0	0	80	QCM, SEM
CB/DOP	0	30	80	QCM, SEM

Table 2.1: Composition of all mixtures used to make sensor films. The first column lists the abbreviation used in the manuscript to denote each type of film composition. The last column lists the analyses that were performed on each type of sensor film.

formulated to produce either type A (40 wt% CB) and or type B (75 wt% CB) sensor films, whereas P-CB films were prepared solely in the type A compositional regime (Table 2.1). Dilutions of these mixtures were examined via dynamic light scattering (DLS).

Samples for QCM, XRD, scanning electron microscopy (SEM), and optical microscopy were prepared from these same SM- and P-CB mixtures. QCM, XRD, optical microscopy, and ellipsometric data were also collected on films that were prepared from nominally identical solutions that did not, however, contain carbon black. QCM measurements were additionally performed on films that were made from suspensions of carbon black both with and without plasticizer, but that contained no polymer or small molecule sensor material (Table 2.1).

Using an airbrush (Iwata, Inc), the chemiresistive sensor films were sprayed onto the

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sensor substrates until the resistance of the deposited film was between 5 and 1000 k Ω , a level shown to provide consistent responses, with film thicknesses of several hundred nanometers.^{26–28} Two sensors were made from each suspension. The substrates for QCM measurements were 10 MHz polished quartz crystals (International Crystal Manufacturing). Each substrate contained a 0.201" diameter electrode that was formed by deposition of 100 Å of Cr followed by 1000 Å of Au. For QCM measurements, the baseline frequency of the crystal was recorded, and a thin film of sensor material was then sprayed onto the crystal using an airbrush. Each film-coated QCM crystal was placed in a vacuum desiccator for at least 2 h. The frequency shift effected by deposition of the sensor film was then recorded, after which QCM response data were collected.

For XRD measurements, samples were sprayed onto cleaned pieces of a microscope slide. SEM samples were sprayed onto both pieces of silicon wafer and pieces of sensor substrate. Samples for ellipsometry were spin-coated onto pieces of silicon wafers, to obtain the surface smoothness necessary for the laser-based ellipsometric measurements.

2.3.3 Measurements and Data Analysis

2.3.3.1 Chemiresistive Sensors

Automated, LabVIEW-controlled, vapor generation and delivery systems were used to deliver the background and analyte vapors to the chemiresistive detectors.^{13,14} The DC resistances of the sensors were monitored using a Keithley 2002 multimeter and a Keithley 7001 multiplexer. All data were recorded to the computer that controlled the analyte exposures.

The sensor array was placed in a chamber made from PTFE and stainless steel that

was connected via Teflon tubing to the vapor delivery system. The sensors were initially exposed to a 2.5 L min⁻¹ flow of air for a period of time sufficient to stabilize the baseline resistance of the sensors. A single exposure to an analyte vapor consisted of 100 s of baseline oil-free air with a water content of 12 ppth, followed by 100 s of analyte, followed by a further 100 s purge of air.

The analytes were *n*-hexane, *n*-heptane, chloroform, ethanol, isopropanol, ethyl acetate, and toluene, spanning a range of chemical functionality. The seven analytes were presented in random order 25 times each to the detector array. All exposures were made at an analyte partial pressure in air of $P/P^0 = 0.01$ (where *P* is the partial pressure and P^0 is the vapor pressure of the analyte at room temperature). All data collection runs were performed at least twice. The first complete run was treated as preconditioning,²⁹ and data analysis was performed only using the data obtained on later runs.

The resistance of each sensor was measured approximately every 5 s. The sensor response to each analyte exposure was expressed as $\Delta R_{\text{max}}/R_{\text{b}}$, where R_{b} is the steady-state baseline resistance of the sensor and ΔR_{max} is the maximum resistance change observed during exposure to the analyte. ΔR data were calculated by subtracting from all data points a straight line fit to the exposure baseline. From these data, R_{b} was calculated by taking the average of at least five data points recorded immediately before the exposure of analyte was initiated. The value of ΔR_{max} was computed as R_{max} - R_{b} , where R_{max} is the maximum resistance during the exposure. The value of R_{max} was calculated as the average of at least three consecutive resistance measurements that were obtained after the sensor exhibited a steady-state response. The $\Delta R_{\text{max}}/R_{\text{b}}$ value for such chemiresistive sensors has been shown to be insensitive to the technique used to deliver the analyte vapor, and additionally has been shown to increase linearly with the concentration of the analyte vapor.^{27,30} Signalto-noise ratios (SNR) were also calculated for each exposure, with the SNR value defined as ΔR_{max} divided by the standard deviation of the data points used to calculate R_{b} .

2.3.3.2 QCM Measurements

Crystals for QCM measurements were mounted in a housing made from stainless steel and PTFE, and were exposed to analytes via the same software-controlled vapor delivery and data collection system that was used to collect data on the responses of the chemiresistive vapor sensors. The frequencies of the QCM crystals were measured with an HP53181A frequency counter and were recorded by the controlling computer.

Each QCM crystal was exposed to analytes using a protocol that was similar to that used for the chemiresistors. The time periods for the baseline, analyte exposure, and purge steps for the QCM crystals were 70, 80, and 60 s, respectively. Hexane and ethyl acetate were used as analytes for QCM data collection, and were exposed to the sensors in random order 10 times each. All exposures were performed at a partial pressure of $P/P^0 = 0.01$. Two or more data runs were recorded from each crystal, and the data were analyzed only from the final run.

For small frequency shifts of quartz crystals coated with thin films, the frequency change is primarily determined by the change in mass of the film. Under such conditions, the changes in frequency and mass are related by the Sauerbrey equation, Eq. (2.1):³¹

$$\Delta f = \frac{-2f_0^2}{A\sqrt{\rho_q \mu_q}} \Delta m \tag{2.1}$$

where Δf is the change in resonant frequency (Hz) upon exposure to the analyte of interest, f_0 is the initial resonant frequency of the crystal (Hz), Δm is the change in mass (g), Ais the piezoelectrically active area of the crystal (cm²), ρ_q is the density of quartz (g/cm³), and μ_q is the shear modulus of quartz (GPa). For a given crystal, all of the values except for Δf and Δm are constants, allowing simplification of Eq. (2.1) to Eq. (2.2):

$$\Delta f = C\Delta m \tag{2.2}$$

Several frequency values were recorded for each crystal. Before film deposition, the baseline frequency (f_0) was recorded. After drying the film, but prior to analyte exposure, a new baseline (f_f) was recorded, yielding $\Delta f_f = f_f \cdot f_0$. The largest frequency shift during exposure, Δf_a , was obtained from $f_a \cdot f_f$, where f_a is the average of at least three frequency readings collected during the steady-state response portion of the analyte exposure.

The change in frequency, $\Delta f_{\rm f}$, caused by deposition of the film allowed determination of $Cm_{\rm f}$, while measurement of the frequency change during analyte exposure, $\Delta f_{\rm a}$, yielded $C\Delta m_{\rm a}$. These two measurements thus allowed determination of a unitless quantity, the mass absorbed per mass of the deposited film, as represented by Eq. (2.3):

$$\frac{\Delta f_{\rm a}}{\Delta f_{\rm f}} = \frac{\Delta m_{\rm a}}{m_{\rm f}} \tag{2.3}$$

The $\Delta m_{\rm a}/m_{\rm f}$ values for all exposures were then calculated and used for further QCM

analysis.

2.3.3.3 DLS

All DLS data was gathered with a Precision Detectors PDExpert multi-angle light scattering platform. Samples in the A regime were examined at a 1:64 dilution, and B regime samples were diluted 1:128. All samples were examined at 90° and 110°.

2.3.3.4 Imaging (SEM and Optical Microscopy)

SEM images were taken on a LEO 1550 VP system, and optical microscopy was performed using a Nikon TE2000S.

2.3.3.5 XRD Data

XRD measurements were performed with a Phillips XPert PRO xray diffractometer (Cu K α radiation). XRD data were collected from 5–85°, at 10 s step⁻¹, to determine the locations of the peaks. All further exposures were from 5–40° at a rate of 35 s step⁻¹.

2.3.3.6 Ellipsometry

Ellipsometry was performed with a Gaertner L116C system. Samples for ellipsometry were placed in a plastic container that had an opening at each end, which allowed the laser beam to reach the sample and detector in an unobstructed fashion. The baseline thickness readings were collected under a steady stream of air, at 65 mL min⁻¹, with an adjacent ventilation tube used to flush the chamber. Exposures to saturated vapor of ethyl acetate, EtOAc, were performed at a flow rate of 65 mL min⁻¹. During these exposures, the



Figure 2.2: Representative responses for different types of sensors. From top to bottom, Nylon 12 A, lauramide A, and docosane B show good, marginal, and no significant response to analyte, respectively. All traces are on the same time scale from the same set of exposures; the y-axes are different on each. Analyte exposure is at $P/P^0 = 0.01$.

ventilation tube was removed, to encourage maximum retention of EtOAc in the chamber. The purge and exposure times were each ≥ 2 min. Each sample was exposed a minimum of five times, and at least five data points were taken during and between each exposure. These data points were averaged to yield the relative thickness change of the film for each analyte exposure.

2.4 Results

2.4.1 Sensor Responses

Table 2.2 presents the SNR values for all of the sensors investigated in this work. (Table 2.3 summarizes this information, Figure 2.2 provides a qualitative overview). The sensors shown in bold (docosane B, DGA A, β dL A, HHA, and PAA) did not produce responses with SNR values above 3, whereas all of other sensors exhibited good SNR values for the analytes of interest. Films of lauramide or iC that contained CB exhibited higher responses in the B regime (75% CB), while ES-containing CB sensors produced higher responses in the A regime. In most cases, the P-CB sensors produced slightly higher SNR values than the SM-CB sensors. No specific correlations in responses between matched pairs were seen.

2.4.2 QCM Data

All of the CB-containing sensor films exhibited clear mass sorption and high SNR values when used as QCM-based sensors (Figure 2.3a). In general, the different SM-CB type B (75% CB) films exhibited higher $\Delta m_a/m_f$ values, but less variation between film materials, than either the P-CB films or the type A films (40% CB) of SM-CB. Films that contained CB exhibited easily differentiable mass uptakes to hexane and ethyl acetate (Figures 2.3, 2.4).

The QCM responses of the films that contained either SM or polymer were also examined in the absence of carbon black (Figure 2.3b). In all cases except one, the $\Delta m_a/m_f$

compounds	CB %	hexane	heptane	toluene	chloroform	EtOH	iPrOH	EtOAc
docosane docosane	40 75	$egin{array}{c} 16 \pm 5 \ 1 \pm 4 \end{array}$	$egin{array}{ccccccc} 14 \pm 4 \ 0.8 \pm 2 \end{array}$	$\begin{array}{c} 24 \pm 7 \\ 1 \pm 2 \end{array}$	$\begin{array}{c} 28 \pm 7 \\ 1 \pm 3 \end{array}$	$\begin{array}{c} 6 \ \pm \ 2 \\ 0.2 \ \pm \ 2 \end{array}$	7 ± 2 0.5 ± 2	6 ± 1 0.4 \pm 1
ES ES	40 75	$\begin{array}{c} 6 \pm 2 \\ 5 \pm 2 \end{array}$	$\begin{array}{c} 5 \pm 2 \\ 4 \pm 1 \end{array}$	$\begin{array}{c} 10 \pm 3 \\ 6 \pm 2 \end{array}$	$\begin{array}{c} 24 \pm 6 \\ 13 \pm 5 \end{array}$	$\begin{array}{c} 4 \\ 2 \\ \pm \\ 2 \\ 1 \\ 1 \end{array}$	4 ± 2 1 ± 1	5 ± 1 3 ± 2
lauramide lauramide	40 75	7 ± 3 29 ± 7	$\begin{array}{c} 7 \pm 2 \\ 32 \pm 9 \end{array}$	$\begin{array}{c} 10 \ \pm \ 6 \\ 40 \ \pm \ 10 \end{array}$	$\begin{array}{c} 15 \ \pm \ 6 \\ 80 \ \pm \ 20 \end{array}$	$\begin{array}{c} 4 \\ 12 \\ \pm 3 \\ 3 \end{array}$	$\begin{array}{c} 4 \pm 2 \\ 13 \pm 3 \end{array}$	$\begin{array}{c} 5 \pm 2 \\ 14 \pm 4 \end{array}$
ic ic	40 75	$\begin{array}{c} 11 \pm 2 \\ 22 \pm 5 \end{array}$	2 ± 1 16 ± 3	149 ± 4 41 ± 12	$\begin{array}{c} 12 \pm 3 \\ 21 \pm 7 \end{array}$	$\begin{array}{c} 11 \pm 3 \\ 27 \pm \end{array}$	$\begin{array}{c} 2 \pm 1 \\ 14 \pm 3 \end{array}$	$\begin{array}{c} 2 \pm 1 \\ 16 \pm 4 \end{array}$
DGA DGA	40 75	3 ± 2 94 ± 100	$\begin{array}{c}1 \ \pm \ 1\\26 \ \pm \ 9\end{array}$	$\begin{array}{c} 4 \pm 2 \\ 110 \pm 23 \end{array}$	$\begin{array}{c} 3 \ \pm \ 1 \\ 70 \ \pm \ 20 \end{array}$	$\begin{array}{c} 3 \pm 2 \\ 90 \pm 23 \end{array}$	$\begin{array}{c}1 \ \pm \ 1\\28 \ \pm \ 6\end{array}$	2 ± 1 40 ± 50
HHA HHA	40 75	$\begin{array}{c} 2 \pm 1 \\ \pm 1 \end{array}$	$\begin{array}{c} 0.5 \ \pm \ 1 \\ 1 \ \pm \ 0.9 \end{array}$	$\begin{array}{c} 4 \\ 4 \\ \pm 2 \\ 2 \\ 2 \end{array}$	$\begin{array}{c} 2 \ \pm \ 0.8 \\ 4 \ \pm \ 2 \end{array}$	$\begin{array}{c} 2 \ \pm \ 1 \\ 3 \ \pm \ 2 \end{array}$	$\begin{array}{c} 0.7 \pm 1 \\ 2 \pm 1 \end{array}$	1 ± 1 ± 1
β dL βdL median	40 75	$\begin{array}{c} 0.2 \ \pm \ 1 \ 5 \ \pm \ 2 \ 9(2.5) \end{array}$	$\begin{array}{c} 0.4 \ \pm \ 1 \\ 2 \ \pm \ 0.9 \\ 9.2(2.5) \end{array}$	$\begin{array}{c} 1 \ \pm \ 1 \\ 5 \ \pm \ 3 \\ 10.5(4.5) \end{array}$	$\begin{array}{c} 0.6 \pm 1 \\ 6 \pm 2 \\ 26(6) \end{array}$	$\begin{array}{c} 0.3 \pm 1 \ 5 \pm 2 \ 4(2) \end{array}$	$\begin{array}{c} 0 \ \pm \ 1 \ 1 \ \pm \ 1 \ 4(2) \ \end{array}$	$\begin{array}{ccc} 0.2 \ \pm \ 2 \\ 2 \ \pm \ 1 \\ 5(1.5) \end{array}$
PE PVS	40 40	$\begin{array}{c} 15 \pm 6 \\ 120 \pm 45 \end{array}$	$\begin{array}{c} 14 \pm 4 \\ 110 \pm 30 \end{array}$	$\begin{array}{c} 17 \pm 6 \\ 160 \pm 50 \end{array}$	$\begin{array}{c} 35 \pm 13 \\ 270 \pm 70 \end{array}$	$\begin{array}{c} 4 \pm 1 \\ 38 \pm 9 \end{array}$	5 ± 2 50 ± 17	$\begin{array}{c} 3 \pm 2 \\ 40 \pm 12 \end{array}$
Nylon 12 HPC	40 40	$\begin{array}{c} 32 \pm 12 \\ 28 \pm 8 \end{array}$	$\begin{array}{c} 26 \pm 10 \\ 23 \pm 6 \end{array}$	50 ± 30 50 ± 15	$\begin{array}{c} 120 \pm 30 \\ 150 \pm 60 \end{array}$	$\begin{array}{c} 73 \pm 30\\ 35 \pm 8\end{array}$	$\begin{array}{c} 50 \pm 20 \\ 50 \pm 18 \end{array}$	$\begin{array}{c} 70 \pm 30 \\ 43 \pm 9 \end{array}$
PnVC	40	36 ± 10	25 ± 8	$\begin{array}{c} 47 \pm 10 \\ 2.0 \pm 10 \end{array}$	96 ± 20	18 ± 5	15 ± 6	19 ± 7
PCL	40 40	$\begin{array}{c} 0.3 \pm 1 \\ 13 \pm 3 \end{array}$	$\begin{array}{c} 0.3 \pm 1 \\ 13 \pm 4 \end{array}$	$\begin{array}{c} 0.8 \pm 1 \\ 23 \pm 6 \end{array}$	2 ± 1 50 ± 9	5 ± 3 6 ± 2	$\begin{array}{c} 0.3 \pm 1 \\ 7 \pm 3 \end{array}$	2 ± 1 ± 4
median		28(8)	23(8)	47(10)	96(20)	18(5)	15(6)	19(7)
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Table 2.2: SNR values for all sensors measured in this study. Data are means obtained from 25 exposures to a given analyte. Values above 3 demonstrate an acceptable response. The reported error is one standard deviation.



Figure 2.3: QCM responses of a) SM and P films with CB and b) without CB. From left to right: Nylon 12, PE, PAA, PnVC, HPC, PVS, PCL, lauramide A, docosane A, DGA A, iC A, β dL A, ES A, lauramide B, docosane B, DGA B, iC B, β dL B, ES B.

	A/LP (40%)	B/LP (75%)	A/P (40%)	B/P (75%)	Linear chain atoms	MW (g/mol)
Docosane	>20	<3	6	<3	22	310
ES	8	6	4	<3	22	312
Lauramide	9	>30	4	>10	13	199
iC	>10	> 20	<3	>10	-	209
DGA	3	>90	<3	>20	7	160
x HHA	<3	3	<3	<3	8	132
βdL	<3	5	<3	<3	-	342

Table 2.3: Median values of the SNR values for SM A and B type sensors for less polar (LP) analytes (hexane, heptane, toluene, and chloroform) and polar (P) analytes (EtOH, iPrOH, EtOAc)

values of such films were lower than the responses observed for films that contained CB. The films that did not contain CB also exhibited much larger exposure-to-exposure variation (Figure 2.3b). Films made from ES only exhibited high noise values, and the two SMs that failed to yield CB composite chemiresistive sensors (βdL and HHA) did not show significant mass uptake in the QCM measurements.

The QCM response was also investigated for films that were formed from either pure CB or from CB/DOP (Table 2.1, Figure 2.4). The pure CB film showed a high sorbancy, with $\Delta m_a/m_f$ values exceeding by >30% those of almost all of the other films studied. The CB/DOP film showed reduced sorbancy compared to that of pure CB, displaying $\Delta m_a/m_f$ values ~40% of those of pure CB. Films that contained polymers or small molecules in addition to CB exhibited a variety of QCM responses, with values in some cases larger and in some cases smaller than that of the CB/DOP film. The sorbency of the CB and of the CB/DOP films to hexane was double that to ethyl acetate.

Every SM-CB film that functioned as a sensor sorbed more hexane than EtOAc, in a



Figure 2.4: QCM responses of CB and CB/DOP films

pattern similar to that observed for the CB and CB/DOP films. This was not the case for the P-CB films (Table 2.4)

2.4.2.1 DLS

At the dilutions necessary to allow the DLS laser to traverse the solution, all CB mixtures were uniformly suspended. No significant CB particle size differences were apparent between all samples tested, except for those clearly explained by solvent variation — β dL in 50/50 acetone/water and PAA in MeOH showed significantly larger particle aggregates (Figure 2.5). PE yielded no information.

		With CB		Without CB	
Compound		hexane	EtOAc	hexane	EtOAc
docosane	А	$2.88 \hspace{0.1cm} \pm 0.2 \hspace{0.1cm}$	1.59 ±0.1	3.73 ± 0.5	1.96 ±0.4
docosane	В	2.74 ± 0.3	1.39 ± 0.06	0.88 ± 0.2	0.58 ± 0.3
ES	А	$2.79\ \pm 0.2$	$1.58\ \pm 0.09$	$0.73 \hspace{0.1in} \pm 3.7 \hspace{0.1in}$	$1.36 \ \pm 0.4$
ES	В	4.10 ± 0.2	$2.06 \hspace{0.1 cm} \pm 0.07$	4.98 ± 13.7	-0.94 ± 12.5
lauramide	А	1.11 ± 0.04	$0.88 \hspace{0.1 cm} \pm 0.05$	$0.56 \ \pm 0.05$	$0.65 \ \pm 0.07$
lauramide	В	$2.15 \hspace{0.1 cm} \pm 0.08$	$1.45 \hspace{0.1 cm} \pm 0.07$	$0.19 \hspace{0.1cm} \pm 0.04$	$0.14\ \pm 0.09$
βdL	А	$0.89\ \pm 0.05$	$0.75 \hspace{0.1 cm} \pm 0.04$	$0.28 \hspace{0.1 cm} \pm 0.6 \hspace{0.1 cm}$	$-0.07 \ \pm 0.8$
βdL	В	$4.28\ \pm 0.2$	$2.34 \hspace{0.1cm} \pm 0.1 \hspace{0.1cm}$	$0.07 \hspace{0.1 cm} \pm 0.09$	$0.10\ \pm 0.07$
iC	А	$7.22\ \pm 0.4$	$4.70\ \pm 0.2$	$0.49 \hspace{0.1 cm} \pm 0.09$	$0.44 \hspace{0.1cm} \pm 0.03$
iC	В	$4.13 \hspace{0.1 cm} \pm 0.2 \hspace{0.1 cm}$	1.72 ± 0.1	3.14 ± 13.3	$4.35 \hspace{0.1 in} \pm 2.7$
DGA	А	$4.40\ \pm 0.09$	$2.11 \hspace{0.1 cm} \pm 0.03$	$1.94 \hspace{0.1in} \pm 0.1 \hspace{0.1in}$	$0.98\ \pm 0.1$
DGA	В	$4.42 \hspace{0.1 cm} \pm 0.2 \hspace{0.1 cm}$	$2.06 \ \pm 0.1$	3.22 ± 1.0	$2.02 \hspace{.1in} \pm 0.8$
HHA	А	$1.14 \hspace{0.1 in} \pm 0.05$	$1.42 \hspace{0.1 cm} \pm 0.05$	$-0.82\ \pm 0.5$	$-2.37 \ \pm 0.5$
HHA	В	$3.56 \ \pm 0.2$	$2.04 \hspace{0.1in} \pm 0.08$	$0.13 \hspace{0.1cm} \pm 0.2 \hspace{0.1cm}$	$-0.52 \ \pm 0.2$
median		3.22(0.16)	1.65(0.07)	0.64(0.36)	0.51(0.32)
PE	А	$1.15 \ \pm 0.05$	$0.71 \hspace{0.1 cm} \pm 0.04$	$-0.21 \ \pm 1.3$	$0.48 \hspace{0.1in} \pm 1.1$
PVS	А	$1.16\ \pm 0.03$	$0.91 \ \pm 0.04$	$0.25 \hspace{0.1 cm} \pm 0.02$	$0.17\ \pm 0.01$
Nylon 12	А	$1.04 \ \pm 0.07$	$1.10\ \pm 0.05$	$1.29 \hspace{0.1in} \pm 0.07$	1.11 ± 0.06
HPC	А	$1.18 \hspace{0.1 cm} \pm 0.05$	$1.90\ \pm 0.1$	$0.03 \hspace{0.1 cm} \pm 0.06$	$0.17 \ \pm 0.05$
PnVC	А	13.56 ± 0.7	17.69 ± 1.0	1.35 ± 0.1	$1.73\ \pm 0.1$
PAA	А	1.27 ± 0.1	$5.15 \hspace{0.1 cm} \pm 0.2 \hspace{0.1 cm}$	$0.16 \ \pm 1.8$	-0.41 ± 1.8
PCL	А	$0.88 \hspace{0.1in} \pm 0.06$	$1.20\ \pm 0.07$	-195.1 ± 620.9	$1.10\ \pm 0.3$
median		1.16(0.06)	1.20(0.07)	0.16(0.13)	0.48(0.13)

Table 2.4: $\Delta m_{\rm a}/m_{\rm f} \ge 10^3$ values for all compounds, from QCM. Reported error is one standard deviation.



Figure 2.5: DLS CB particle size information. β dL in 50/50 acetone/water, PAA in MeOH, PE in p-xylene, Nylon 12 in HFIP, and all other materials in THF. 40 wt% samples were at 1:64 dilution, and 75 wt% samples were at 1:128 dilution

2.4.3 Imaging

Optical microscopy of the films showed no differences among the films that contained CB. SM films without CB showed highly crystalline growths, whereas the pure polymer films were amorphous (Figure 2.6).

SEM images of SM-CB A or B and P-CB A films showed no clear differences in the structures of the visible CB aggregates. The only difference in the SEM images was that pure carbon black dispersed cleanly, whereas mixtures of CB with SM, polymer, or DOP exhibited droplet formations that were presumably a result of the airbrush deposition process (Figure 2.7). No differences were seen between SEM samples deposited on silicon wafers and samples deposited onto sensor substrates.

2.4.4 XRD

XRD was used to evaluate the crystallinity of the various types of sensor films. Clean microscope slide substrates showed a broad peak at $2\theta \sim 25^{\circ}$ that appeared in all spectra. All pure SM films (A/noCB/noDOP) exhibited sharp peaks indicative of crystallinity, whereas none of the polymer films showed any sharp XRD features. SM films with (SM A/noCB) and without DOP plasticizer (SM A/noCB/noDOP) (Figure 2.8) showed similar XRD patterns, although the count numbers varied for different films, due to a lack of control over the film thickness. The XRD spectra of SM-CB A (40% CB) films exhibited small peaks, but these peaks were undetectable for SM-CB B (75% CB) films (Figure 2.9).

Docosane peaks were assigned according to the literature.³² The lauramide spectrum does not match the literature pattern precisely.³³ However, such *n*-alkylamides are known



2.6(a) 2,4-dimethyl glutaric acid film, 40x.



2.6(b) 9-iPr-carbazole/DOP film, 40x.



2.6(c) Poly(vinyl stearate)/DOP film, 40x.

Figure 2.6: Optical microscope images of a) 2,4-dimethyl glutaric acid, b) 9-iPr-carbazole/DOP, and c) PVS/DOP films sprayed onto cleaned microscope slides. All images are at 40x and scale bars are 20 μ m.



Figure 2.7: SEM images of a) pure carbon black on a silicon substrate and b) lauramide with 75% by mass carbon black on a silicon substrate. Both images are at a magnification of 1,000x.



Figure 2.8: XRD spectra of pure docosane (A/noCB/noDOP) and docosane/DOP (A/noCB). The crystalline peaks are in the same locations on each sample. Note the amorphous peak from the glass slide centered around 25° .

to be polymorphic,³⁴ and the molecular structure of the compound has been confirmed by proton NMR in both *d*-chloroform and *d*-THF. Given the range of long spacings reported for lauramide,³⁴ the peak in the reported spectrum has been tentatively assigned as the (003) reflection.

2.4.5 Ellipsometry

Ellipsometry was used to probe the thickness changes of the films upon exposure to analyte. Ellipsometric measurements were not performed on films that contained carbon black, because such films were black to the eye and additionally were optically inhomogenous.



Figure 2.9: XRD of lauramide-CB type A and lauramide-CB type B composite films.

	No DOP Plasticizer		With Plasticizer		
	$\Delta h/h$	Δh (Å)	$\Delta h/h$	$\Delta h({ m \AA})$	
Blank Silicon		4.5			
Docosane	1.2(0.3)	3.8(0.8)	12.9(0.6)	50.9(1.9)	
Lauramide	1.4(0.1)	8.5(0.8)	12.8(1.0)	105.1(9.2)	
iC	-0.6(0.1)	-0.9(0.2)	n/a		
DGA	2.0(0.3)	4.0(0.5)	16.4(2.6)	16.9(2.9)	
PVS	3.0(0.1)	16.6(0.5)	15.9(2.0)	114.3(14.1)	
N12	3.7(0.5)	12.3(1.6)	20.2(3.3)	62.6(10.3)	
PnVC	12.2(0.6)	37.7(1.8)	7.5(0.8)	39.6(4.3)	
HPC	10.0(0.3)	45.6(1.6)	77.3(7.5)	771.8(77.2)	

Table 2.5: Ellipsometry data. Averaged percent swelling and thickness change of each film, with and without DOP plasticizer, in response to a saturated flow of ethyl acetate. A blank Si sample showed an ellipsometric signal change equivalent to a film swelling response of \sim 4 Å. Reported error is one standard deviation

Ellipsometric data were therefore collected only for pure films (A/noCB/noDOP) as well as for films that included plasticizer (A/noCB).

Under a saturated stream of ethyl acetate, the SM films that did not contain added plasticizer swelled $\leq 2\%$ of their original thickness (-1% to +2%), while polymer films swelled $\geq 3\%$ (3–12%). The change in thickness of the SM films was 3–10 Å, while polymer films exhibited thickness changes of 10–45 Å(Table 2.5). Under a saturated stream of EtOAc, a piece of silicon substrate used as a control sample showed a change in ellipsometric signal equivalent to a film swelling response of 4 Å, similar to the change recorded for two of the SM films. Docosane, iC, DGA, and lauramide all showed a decrease in film thickness over the course of the vapor exposures, whereas the polymer films yielded stable responses. The films that contained plasticizer almost uniformly exhibited increased swelling responses, in several cases almost an order of magnitude (Table 2.5) larger than that of unplasticized films.

2.5 Discussion

Small molecule-CB sensors have been determined previously to exhibit the highest SNR values at high carbon black loadings, with concomitantly reduced quantities of organic phase in the sensor film as compared to P-CB sensors. The SM-CB sensors thus form an attractive class of sensor films due to this lowered required mass of organic phase, and also due to the very large number of potential sensing materials that are available as small organic molecules.

Except for docosane, the SM-CB sensors performed better in the 75% CB regime (B) than in the 40% CB regime (A), with all sensors exhibiting higher SNRs for less polar analytes (Table 2.2). Lauramide, ES, and iC performed well in both the A and B regimes, whereas docosane yielded measurable responses only in the A regime, and DGA yielded measurable responses only in the B regime.

2.5.1 Film Composition

SEM images and optical inspection revealed clear crystalline regions in the SM films that did not contain CB. The SM films exhibited a variety of crystalline growths, although docosane exhibited mostly smooth, undifferentiated planes, with occasional small ordered areas. In contrast, all of the polymer films exhibited no long range order visible by microscopy.

No crystalline domains were observed in either SEM or optical microscopy images of the films that contained CB. The P- and SM-CB films showed clear droplet formations that were not observed for the pure CB films. When the airbrush deposition method is used, the formation of such aggregates has been reported,³⁰ and their failure to appear in the pure CB films presumably reflects the influence of the mixture composition on the morphology of the films (Figure 2.7).

Carbon black is often understood to simply provide a conductive structure in composite chemiresistive vapor sensors, but its role is more complicated than that simple picture. The QCM data show that CB sorbs solvent vapor and provides a differentiable mass uptake to various analytes. Yet despite the high $\Delta m_a/m_f$ values exhibited by such films, neither pure CB nor CB/DOP function as chemiresistive vapor sensors.²⁶ Addition of other components almost uniformly effected decreases in the $\Delta m_a/m_f$ values, but such reductions did not follow any clear pattern. Weight averaging the QCM responses of the pure CB film with that of the A/noCB films did not yield the response of the A films (PnVC/CB and iC/CB notably have higher $\Delta m_a/m_f$ values than pure CB). Furthermore, the QCM responses of the SM-CB films exhibited a pattern of responses that was similar to the QCM responses of the pure CB or CB/DOP films, regardless of the QCM responses of their pure films. Thus, from the deposition images and QCM responses of the composite films, certain film features are not the sum of the individual components.

2.5.2 Small Molecule Crystallinity

The pure SM films (including docosane) showed clear, sharp Bragg peaks in the XRD spectra, while pure polymer films showed no such features. The polymer films that contained added plasticizer showed no notable differences from those that did not contain plasticizer. Addition of plasticizer to the SM films did not affect the formation of crystalline structures in the XRD data, and although the peak amplitudes varied with film thickness, the peak positions did not shift.

Peaks ascribable to residual crystallinity were observed for the SM-CB A films (40% CB), but all such peaks disappeared when the CB content was increased to 75% in the type B films. Hence, 75 wt% CB was sufficient to prevent crystal formation in the SM type B films.

Previous work has explored the nature and effects of crystallinity in selected polymer-CB composites. In one study, at a given level of CB, the more crystalline the polyolefin used, the higher the overall resistivity.³⁵ In a separate study, triblock polystyrene poly(ethylene glycol) - polystyrene polymer sensors showed a crystalline region that effectively forced the CB to segregate into the more amorphous region, which was determined to be the region that was primarily responsive to the analyte when such films were used as chemiresistive vapor sensors.³⁶ Both of these studies dealt strictly with polymers, and used dissimilar methods of sensor preparation from those used in this work, but nevertheless provide evidence consistent with the expectation that the crystallinity of the film can affect the response characteristics of CB composite vapor sensors.

2.5.3 Variations in Swelling Response

Films of the SMs that did not contain DOP showed only very slight swelling responses, both as a percent of the film thickness and on an absolute scale. Some of the small molecules displayed a net decrease in thickness upon exposure to analyte vapor. The crystalline films would not be expected to swell as much as non-crystalline films, in accord with the observed responses.

The presence of plasticizer aids the sensor response of polymer films, decreasing the response time and increasing the magnitude of the relative differential resistance response by increasing the ability of the polymer chains to slide past one another. This behavior suggests that increased rigidity decreases the swelling of the film upon exposure to analyte vapor. However, the addition of plasticizer markedly increased the recorded thickness changes of ellipsometric films that contained either the small molecules or the polymers. For polymers, plasticizer disperses within the polymer film and aids the movement of the polymer chains, thus increasing the swelling response. The XRD data, however, indicated that the addition of the plasticizer (DOP) did not disrupt the crystallinity of the small molecule films. As the SMs retain their crystalline structure, and do not noticeably swell in pure films, the SMs and DOP appear to be segregated in SM-DOP films, with the observed swelling response attributable to the plasticizer portion of the film.

2.5.4 Small Molecule Structure

All of the small molecules are crystalline, and none swell appreciably, yet their formulation requirements varied significantly to produce optimal chemiresistive vapor sensors. If the SMs did not swell when locked into rigid crystalline films, some other aspect of the composite film must break up their crystalline structure.

A distinct trend was observed in the responses of the five functional SMs (Table 2.2). As the molecules became larger and less polar, the resulting sensors switched from working best in the B regime to working best in the A regime. One potential explanation of this behavior is that the strength of the crystalline interactions in each film is a function of the size and polarity of each small molecule. As the size increases and the polarity decreases the crystalline interactions decrease and less CB is needed to prevent crystal formation.

Docosane, the least polar, and one of the largest, SMs investigated in this work, functioned only with low CB, regime A. No large-scale crystalline features were observed in optical microscopy images of this film. This large, hydrophobic molecule has no structural features to aid crystallization, and less CB should then be needed to disrupt the crystallinity.

The majority of the SMs (ES, lauramide, and iC) exhibited good chemiresistive vapor responses in both regimes of carbon black loading. However, while ES worked about equally well in both regimes, both lauramide and iC yielded significantly better SNR values in the B regime (Table 2.2). ES and lauramide are generally linear in shape, whereas iC is not. These molecules have functional groups that can aid crystallization. ES, which is as large as docosane, contains an ester, but lacks H-bonding protons. Lauramide, half this size, is an amide with H-bonding protons, and iC, much more bulky, has a multi-ring structure that can facilitate π -stacking interactions. Both higher and lower CB regimes break up the crystallinity of such films. ES, the longest of these three and lacking Hbonding protons, was most responsive in the 40% CB regime, containing plasticizer, while the smaller lauramide and iC exhibited better vapor sensor performance at 75% CB, with no plasticizer included.

Finally, DGA, both compact and with excellent H-bonding ability, only functioned well as a vapor sensor at 75% CB, the B regime. The compactness and high self-affinity of DGA made this film harder to disrupt, necessitating a high proportion of CB to make functional

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composite sensors.

2.6 Conclusions

Small molecule/carbon black composite sensors have been studied and compared to P-CB composites, to better understand the required composition of this family of sensors. The small molecule sensors had been shown previously to offer an increased density of functional groups, and to have comparable overall performance to their polymeric predecessors. We have shown that the rigid crystalline thin film structure of the small molecule films requires a film composition that can break up the crystallinity to have the film swell and therefore provide a functional relative differential resistance response to analyte vapors. This disruption of the film structure could be produced by either an increased ratio of carbon black to molecule or by the addition of plasticizer/carbon black. A framework for the specific requirements of each film has been proposed, depending on the size and polarity of the small molecule involved.

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