Use of Compatible Blends To Fabricate Carbon Black Composite Vapor Detectors

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ABSTRACT: The aim of this work was the development of materials to be used in the field of gas sensing for the detection of organic vapors. Conductive sensors were prepared with carbon black filled blends of poly(vinyl chloride) and diol-terminated poly(ϵ-caprolactone), an oligomeric plasticizer. For comparison, blends with di(2-ethylhexyl)-phthalate, a traditional low-molecular-weight plasticizer, were also prepared. All sensors were tested upon exposure to different organic vapors. In general, the plasticizer content affected the response rates of the sensors, and a linear variation of the relative resistance with the analyte concentration was observed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1816–1821, 2004

Key words: sensors; composites; blends; poly(vinyl chloride) (PVC); polyesters

INTRODUCTION

The increased demand for odor analysis for the quality assurance of foodstuffs, fragrances, and so forth and for environmental control has been the driving force behind the development of electronic noses.[1–3] An electronic nose is an instrument that consists of an array of electronic chemical sensors with partial specificity and an appropriate pattern-recognition system capable of recognizing simple or complex odors. This definition restricts the term to those types of intelligent chemical sensor arrays that are specifically used to sense odorant molecules on the analogy of the human nose. However, the architecture of an electronic nose also applies in the field of gas sensing to the detection of individual components or mixtures of gases and vapors.

For the construction of chemical sensors, considerable efforts have been directed toward the use of inorganic materials such as semiconducting oxides. In oxide materials, the odorant molecules react with chemisorbed oxygen species, thus modulating the conductivity. These devices operate at elevated temperatures (100–600°C) and are quite sensitive to combustible materials (0.1–100 ppm).[4]

Organic materials are the other choice. In this case, most devices are based on the detection of physical or chemical changes occurring in a polymer film upon its exposure to a gaseous analyte.[5] For instance, the electrical resistance of a conductive polymer[6,7] or a conductive composite film[8–12] can be measured. A single detector does not respond with high specificity toward a single analyte, but the pattern of responses provides a characteristic fingerprint that is used to classify and, in some cases, to quantify the analyte.

Intrinsically conductive polymers constitute an attractive class of materials for realizing chemiresistive detectors in such sensor arrays;[13,14] however, obtaining chemical diversity involves significant synthetic effort, and the polymers commonly used, such as polypyrrole and polythiophene, are sensitive to oxidative processes and show long-term stability problems.

Nevertheless, a variety of composites formed from conducting materials dispersed in different insulating polymers can be used, and this results in a chemically diverse set of resistive detectors.[8] The properties of these composite systems can be understood in terms of percolation theory.[15] When a sufficient volume of a conductive filler is loaded into an insulating matrix, the composite transforms from an insulator into a conductor. This is known as the *percolation threshold* and coincides with the formation of the first continuous conducting network through the polymer matrix. The exposure of a polymer film to organic vapors increases its electric resistance because of the variation of the matrix volume fraction with respect to the conductive phase. Carbon black (CB), Ag, Cu, and con-

ductive organic polymers have all been used as conductive phases.[9–12]

Another approach toward obtaining sensor diversity involves the modification of the properties of a base polymer vapor detector through the addition of plasticizers. Several polymeric matrices and traditional low-molecular-weight plasticizers have been used.[16] However, an interesting alternative might be represented by polymeric blends containing a polymer that has a low glass-transition temperature (T_g) and high miscibility with the matrix.[17,18] The main advantage of such systems would be that drifting phenomena typical of low-molecular-weight plasticizers could be avoided.[19] In addition, the properties of these sensors might be tuned through the variation of the plasticizer molecular weight.

Poly(vinyl chloride) (PVC)/poly(ϵ-caprolactone) (PCL) binary blends appear to be promising systems in this respect because partial miscibility exists between PVC and high-molecular-weight PCL,[20,21] and it is well known that miscibility can be increased if an oligomeric PCL, such as diol-terminated poly(ϵ-caprolactone) (PCDT), is used.[22] Furthermore, PCDT has a low T_g value (−80 to −60°C, depending on the molecular weight), and so it can be considered an interesting oligomeric plasticizer for PVC.[23]

The aim of this work was to prepare conducting CB–polymer composites based on compatible blends of PVC, used as a base polymer, and PCDT. In addition, films made from these blends were used to prepare conductive gas sensors. A comparison with analogous composites containing di(2-ethylhexyl)phthalate (DOP), a typical low-molecular-weight plasticizer, was also considered.

EXPERIMENTAL

Materials

CB (Printex XE2B) was a kind gift from Degussa-Hüls Chimica S.p.A. Rho (Milan, Italy) PVC (weight-average molecular weight = 95,000), PCDT (number-average molecular weight = 1250), and DOP were purchased from Aldrich Co. (Milan, Italy). Acetone, benzene, 1-butylamine, and tetrahydrofuran (THF) were reagent-grade solvents from Aldrich. All the materials were used as received.

Preparation of the substrates

Alumina A-493 (0.3 × 3 × 3 mm), from SPEC.TEC S.r.l. (Milan, Italy), was used to provide physical support to the composite films of each sensor. Two parallel gold pads (0.2 mm) were deposited via sputtering over each support, and two gold wires were bonded. After film deposition, each support was mounted on a commercial electrical case.

TABLE I
Sensor Composition and Electrical and Thermal Properties

Sensor	Plasticizer (wt%)[a]	ρ (Ω cm)[b]	T_g (°C)[c]	T_g (°C)[d]
DOP10	10	1.65	60.2	43.0
DOP25	25	1.87	25.3	17.8
DOP40	40	12.10	−20.1	−34.9
PCDT10	10	2.75	68.4	45.3
PCDT25	25	6.60	nd	16.2
PCDT40	40	1.10	nd	−23.0

nd = not determined.
[a] In the matrix. The filler content was 20 wt % for all composites.
[b] Film resistivity (average thickness = 11 μm).
[c] For CB-filled films.
[d] For unfilled films.

Instruments

The calorimetric analyses were carried out with a Mettler TC11 thermal analyzer processor equipped with a DSC30 low-temperature cell (Perkin Elmer, Norwalk, CT).

The electric measurements were performed with a Hewlett–Packard 34401 A multimeter (Palo Alto, CA) and a LabView 5.0.1 acquisition system running on a Pentium III personal computer. Standard laboratory glassware was used to assemble the sensing chamber.

The measurements of film vapor sorption were carried out with a dedicated system based on arrays of variable-mass (i.e., microbalance) sensors, which were resonant piezolayer (RPL) elements of lead zirconate titanate screen-printed on an alumina substrate, as previously described.[24,25] The system consisted of a stainless steel sensor test chamber; electronic mass-flow regulator for controlled vapor introduction in the test chamber; and an electronic board containing sensor oscillators and circuitry for interfacing with a personal computer, which supervised the whole system.

Preparation of the composite films and individual sensors

The composite films were obtained via casting from a suspension prepared as follows. An organic matrix (PVC and a plasticizer in the proper ratio; 80 mg) was dissolved in 10 mL of THF, and 20 mg of CB was added. The mixture was sonicated for 5 min and was diluted with 10 mL of THF. An alumina support was dipped into this suspension, and the solvent was allowed to evaporate at room temperature and atmospheric pressure. The films were finally dried in air for 24 h before use. The remaining stock solutions were used to prepare films for thermal analysis. The same procedure was followed to prepare films without CB. The composition, resistivity, and calorimetric data of the obtained films are reported in Table I.

Resistance measurements

The resistance response of each sensor was measured as a function of the time or organic vapor concentration. In both cases, each sensor was first placed into the sensing chamber (volume = 0.517 L), and then it was kept under a nitrogen stream (1 L/min) until its resistance was stabilized ($\Delta R = \pm0.002$ kΩ, where ΔR is the resistance change of the detector upon exposure to organic vapors). Finally, the resistance was sampled for 20 min more under static conditions to obtain a baseline. All measurements were run in nitrogen, at 22°C, under static conditions. Three types of experiments were carried out:

- Short-time experiments. The resistance values were collected for 3 min at intervals of 1.5 s. The analyte concentration was 12.5 parts per thousands on a volume basis (12.5 v/v ppth).
- Long-time experiments. The resistance values were sampled every 60 s, for 120 min, at an analyte concentration of 32 v/v ppth. The sensor response was then followed for 120 min more, while a nitrogen stream (1 L/min) removed the analyte vapors from the sensing chamber.
- Variable-concentration experiments. The analyte concentration was increased in steps of 3.5 ppth from 3.2 to 32 ppth. For every concentration, the resistance values were sampled after 15 min of exposure.

In each set of experiments, the resistance change percentage [$\Delta R/R$ (%)] was used to analyze the data (R is the baseline resistance).

RESULTS AND DISCUSSION

The possibility of using PCDT as an oligomeric plasticizer in PVC blends was discussed previously.[22] In this work, these materials were used as matrices to prepare conductive sensors for the detection of organic vapors.

Conductive composite films were prepared via casting from PVC solutions containing a dispersion of CB. For comparison, films without CB were also produced. The calorimetric data of the films plasticized with PCDT and DOP are summarized in Table I. The unfilled DOP and PCDT blends had comparable T_g values, with the exception of DOP40 and PCDT40, for which a higher difference can be observed ($T_g = -34.9$ or -23.0°C, respectively). In general, the addition of CB increased T_g, making the films stiffer. Our data suggest that complete miscibility existed in samples PCDT10 and PCDT25, but not in PCDT40. In fact, the unfilled blends were transparent, except for PCDT40, in which some crystallinity was found, as in its CB-filled counterpart. For instance, unfilled PCDT40
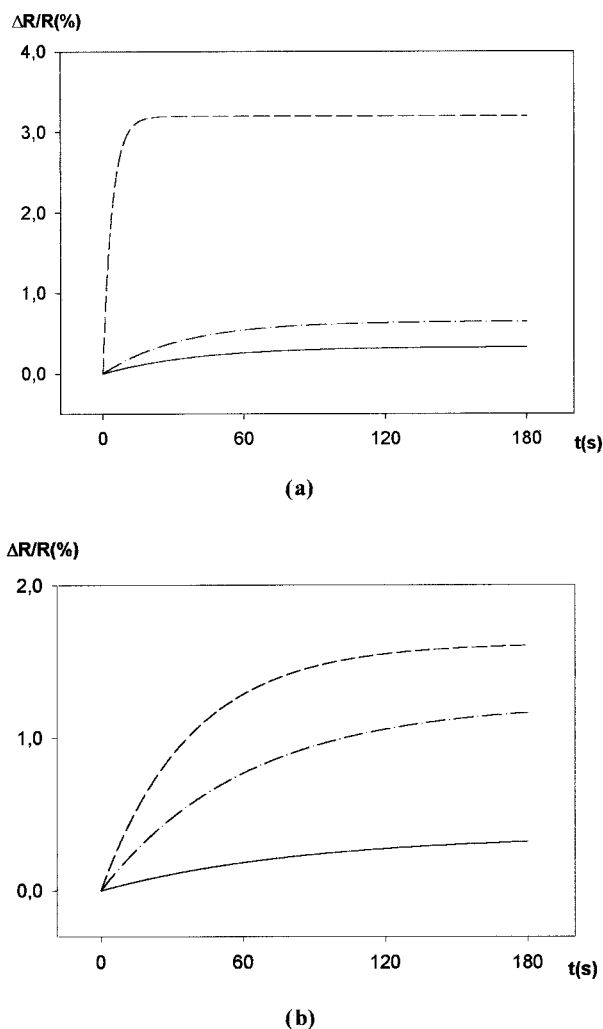

Figure 1 $\Delta R/R$ (%) versus time for CB/PVC composites with (a) DOP and (b) PCDT upon exposure to 12.5 ppth acetone: (——) DOP10 and PCDT10, (– · –) DOP25 and PCDT25, and (——) DOP40 and PCDT40. The measurements were carried out at 22°C.

showed a fusion peak at 40.9°C with a fusion enthalpy of 0.3 J/g.

The resistivity values reported in Table I show that all the materials produced were conductive because a polymer film is generally considered a conducting material if its resistivity is in the range of $1–10^2$ Ω cm.[26]

The composite films cast on alumina were first tested as sensors in short-time experiments under static conditions. Figure 1 displays $\Delta R/R$ (%) upon exposure to 12.5 ppth acetone for 3 min (the test was performed under nitrogen; the data were sampled every 1.5 s). The resulting response rates, defined as the slopes of the curves for $t \to 0$, are reported in Table II. As expected, they increased with the amount of the plasticizer in both types of sensors. The increase was two orders of magnitude from DOP10 to DOP40 and one order from PCDT10 to PCDT40. These results are consistent with the T_g values of the corresponding

TABLE II
Response Rates on Exposure to 12.5 ppth Analyte at 22°C

	Acetone	Benzene	1-Butylamine
DOP10	8.215×10^{-3}	—	—
DOP25	1.954×10^{-2}	6.555×10^{-1}	1.099×10^{-1}
DOP40	8.154×10^{-1}	—	—
PCDT10	4.226×10^{-3}	—	—
PCDT25	2.003×10^{-2}	2.700×10^{-1}	3.128×10^{-1}
PCDT40	4.268×10^{-2}	—	—

films because it is well known that diffusion processes occur rapidly above T_g.[27] It is clear, however, that only qualitative information on such processes can be obtained from these data.

Although the short-time response of sensors is more interesting for practical applications, we also studied their equilibrium response to obtain a better understanding of the penetrant–composite interactions. Long-time tests were run under analogous conditions, but with a contact time of 3 h. A desorption step under a controlled stream of nitrogen (1 L/min) was performed. Figure 2 shows $\Delta R/R$ (%) versus time for all sensors upon exposure to 32 ppth acetone. After 2 h, only DOP40, PCDT40, and PCDT25 seemed to reach an equilibrium value and exhibit a negligible baseline drift at the end of the desorption step [Fig. 2(a,b)]. On the contrary, DOP25 and PCDT10 were quite far from equilibrium and showed incomplete desorption. DOP10 [Fig. 2(c)] exhibited the highest response but an anomalous trace, which might be a result of an inhomogeneous distribution of CB particles in the film, even if the preparation conditions were the same for all samples.

In principle, $\Delta R/R$ (%) at equilibrium can be related to parameters such as the partition coefficient, the percolation conditions, and possibly the occurrence of a glassy–rubbery transition during the penetrant absorption. The higher the analyte solubility is in the polymeric matrix, the higher the resistance change should be, and so the Hildebrand solubility parameters can be used to predict qualitatively the variation of the equilibrium $\Delta R/R$ (%) value with the plasticizer content. If δ_m and δ_a are the Hildebrand parameters of the matrix and analyte, respectively, their mutual solubility is expected to increase as $(\delta_m - \delta_a)^2$ decreases.[28] Therefore, because δ for acetone is 19.9 $J^{1/2}/cm^{3/2}$, whereas its values are 19.2 and 16.2 $J^{1/2}/cm^{3/2}$ for PVC and DOP, respectively, a decrease in $\Delta R/R$ (%) should be expected for increasing DOP contents. The same trend should be also observed in PCDT sensors ($\delta = 18.7$ $J^{1/2}/cm^{3/2}$).[23,29] All samples except PCDT10 followed the expected trend. This suggests that chemical affinity is the most important factor determining the resistance variation of films under equilibrium conditions.

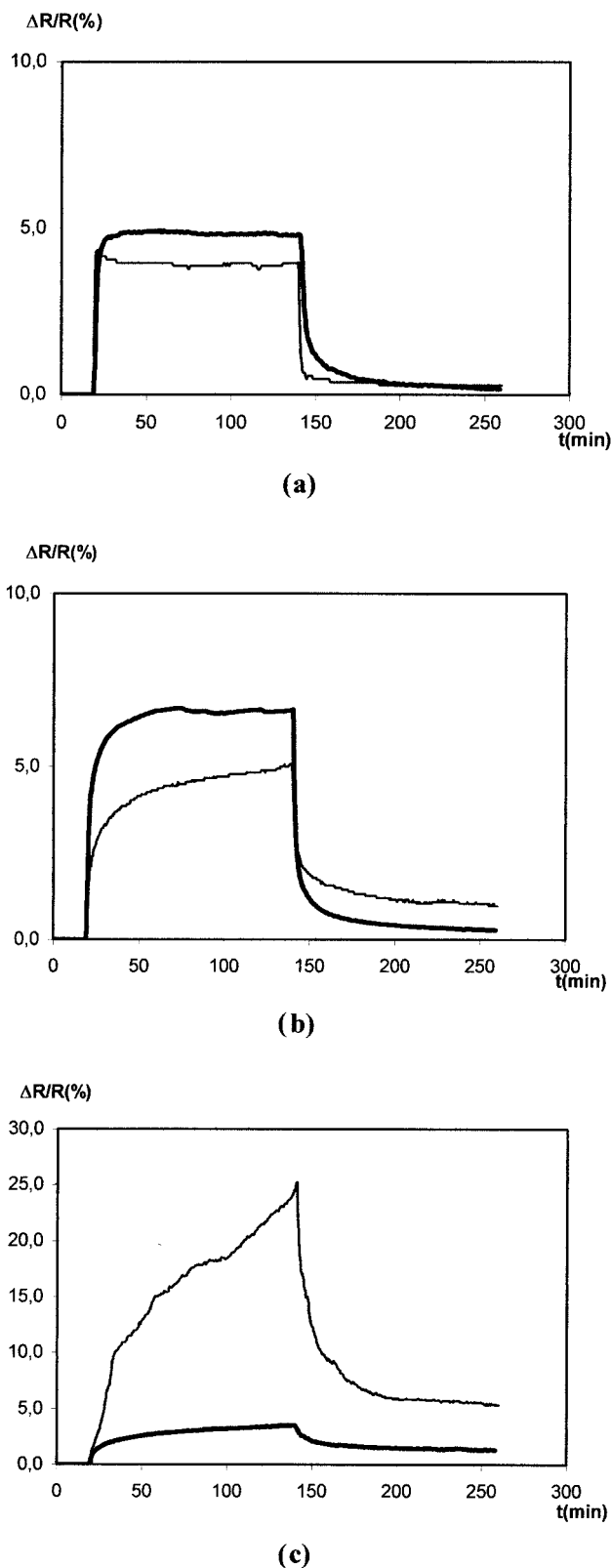The same trend was obtained by mass-variation measurements made on unfilled PVC/DOP films cast

(a)

(b)

(c)

Figure 2 $\Delta R/R$ (%) versus time for CB/PVC composites with the same plasticizer content upon exposure to 32 ppth acetone: (a) DOP40 and PDCT40, (b) DOP25 and PCDT25, and (c) DOP10 and PCDT10. The thin lines represent DOP, and the thick lines represent PCDT. The measurements were carried out at 22°C.
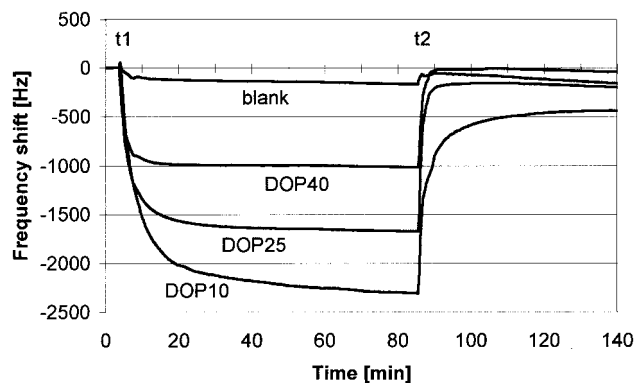
Figure 3 Frequency shift versus time for three RPL microbalance sensors coated with PVC films containing different amounts of the plasticizers plus one blank sensor under step exposure to 32 ppth acetone.

on 7-MHz RPL microbalance sensors. Figure 3 shows the frequency shift versus time measured simultaneously for four sensors, that is, one for each amount of the plasticizer in the film plus an uncoated RPL element (blank), under exposure to acetone. We took the measurements by keeping the flow in the sensor chamber constant at 500 mL/min. Up to time t_1, the flow was made entirely by nitrogen; at time t_1, a nitrogen stream containing 32 ppth acetone was introduced, and at time t_2, the acetone flow was turned off. The lower the frequency shift was (which was proportional to the mass uptake in the film), the higher the amount was of the plasticizer in the film.

The sensor response under a range of analyte concentrations was studied too. The behavior upon exposure to acetone concentrations increasing by 3.5 ppth from 3.2 to 32 ppth is shown in Figure 4. The resistance values were sampled after 15 min from each step, and the experiments were carried out in nitrogen, at 22°C, under static conditions. The least-squares method was applied to evaluate the linearity of the response. The resulting parameters and correlation coefficients are listed in Table III. It is evident that, apart from DOP10, a good linear fitting was generally obtained.

DOP25 and PCDT25 were also tested in the presence of benzene and 1-butylamine. The response rate to these vapors was one order of magnitude higher than to acetone (see Table II). However, the response of DOP25 to benzene was six times faster than to 1-butylamine, whereas PCDT25 showed nearly the same behavior with both analytes.

The long-time experiments (data not shown) pointed out that $\Delta R/R$ (%) equilibrium values were reached within 30–40 min. For both sensors, these values were higher with 1-butylamine than with benzene. In fact, the equilibrium $\Delta R/R$ (%) value of DOP25 was about 27 when it was exposed to 1-butylamine, whereas it was only 14 upon exposure to
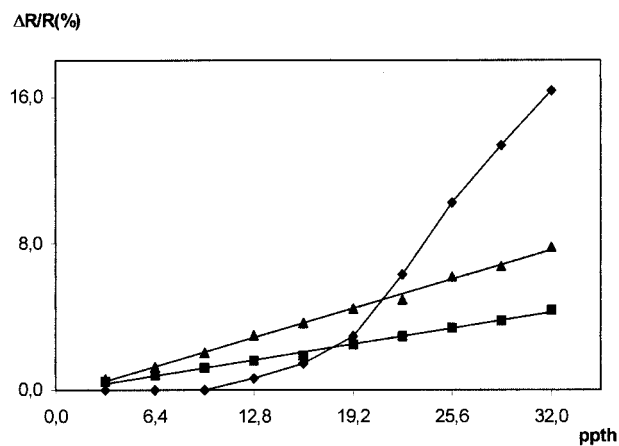
(a)
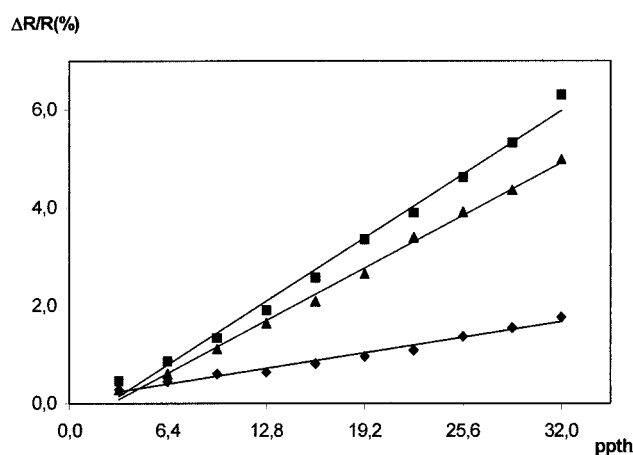
(b)

Figure 4 $\Delta R/R$ (%) versus the acetone concentration for CB/PVC composites with (a) DOP and (b) PCDT at 22°C: (♦) DOP10 and PDCT10, (■) DOP25 and PCDT25, and (▲) DOP40 and PCDT40.

benzene. For PCDT25, the $\Delta R/R$ (%) values were 43 and 23, respectively. In both cases, incomplete desorption was observed with 1-butylamine [residual $\Delta R/R$

TABLE III
Statistics of Variable-Concentration Experiments at 22°C for Sensors Exposed to Acetone Vapors (3.2–32 ppth)

	R^{2a}	Intercept	Slope
DOP10	0.8199	−3.5542	0.5133
DOP25	0.9958	−0.0919	0.1354
DOP40	0.9963	−0.3022	0.2478
PCDT10	0.9804	0.0807	0.0498
PCDT25	0.9913	−0.4975	0.2026
PCDT40	0.9960	−0.4413	0.1675

[a] Correlation coefficient.

TABLE IV
Statistics of Variable-Concentration Experiments at 22°C for DOP25 and PCDT25 Sensors (3.2–32 ppth)

	DOP25			PCDT25		
	R^{2} [a]	Intercept	Slope	R^{2} [a]	Intercept	Slope
Acetone	0.9958	−0.0919	0.1354	0.9913	−0.4975	0.2026
Benzene	0.9657	−4.6406	0.7669	0.9931	−1.6995	0.6575
1-Butylamine	0.9951	2.8387	0.5171	0.9984	0.6632	0.8833

[a] Correlation coefficient.

(%) ≈ 5]. The high response to 1-butylamine was probably due to hydrogen bonding between the basic amino groups of the analyte and the acidic hydrogens of PVC.[30]

Variable-concentration experiments were performed to assess the response of DOP25 and PCDT25 in the presence of increasing concentrations of benzene and 1-butylamine. As observed with acetone, an excellent linear trend was generally noticed with these vapors, with the sole exception of DOP25 exposed to benzene (see Table IV).

CONCLUSIONS

The high miscibility of PVC/PCDT blends coupled with the low T_g of PCDT makes the latter a useful oligomeric plasticizer for preparing conductive composites for sensor applications, even if lower response rates, in comparison with those of blends containing a typical low-molecular-weight plasticizer (DOP), are obtained in some cases. Although not investigated in this work, a potential benefit deriving from the macromolecular nature of PCDT would be a higher sensor stability with respect to conventional plasticizers as a result of reduced plasticizer leaching. Studies are in progress to investigate this point.

The plasticizer concentration affects both the response rate and the amount of the adsorbed penetrant at equilibrium. The former effect is related to the changes in the analyte diffusivity induced by the presence of different amounts of the plasticizer, whereas the latter effect can be explained on the basis of thermodynamic considerations. In general, a linear response versus the analyte concentration is observed.

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