Conductive Polymer Foams as Sensors for Volatile Amines

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Intrinsically conductive polymers (ICPs) represent an attractive class of materials for sensor applications.[1−6] ICPs can be easily prepared from various inexpensive monomers[7] and possess long-term stability in electrical conductivity.[8,9] Chemical sensing by ICPs may occur either by changes in the extrinsic conductivity due to swelling of polymers by analytes or by changes in the intrinsic conductivity due to charge-transfer interactions between polymers and analytes,[10−13] and can be easily measured using inexpensive instrumentation. Furthermore, ICPs have been incorporated into composite structures with insulating polymers for sensor applications and the wide choice of insulating polymers available provides a chemically diverse array of resistive detectors having good chemical vapor classification properties.[14,15]

ICP-loaded polymeric foams may represent an ideal structure for chemical vapor sensors in that ICP−foam sensors may have kinetic and sensitivity advantages over conventional ICP thin-film sensors due to their flow-through capability and greater surface area provided by a highly porous, open-cell structure.[16,17] Another potential advantage of foam sensors is that the dielectric, organic polymer from which the foam is derived can interact with various chemicals which should also contribute to the changes in the resistance of the ICP−foam composite.[14] Therefore, a broad range of chemical discrimination may be possible for sensing by simply varying the foam matrix, as well as the nature of the ICP and the dopant used.

We have previously reported on the development of conductive polymer foams based on an in situ polymerization of pyrrole within preformed polyurethane foams.[18−21] Most recently, we described a solvent-free process to prepare these foams.[21] In this communication, we report the preparation of intrinsically conductive polymer open-cell foams of lower densities than those we have previously reported using our solvent-free process and the electrical resistance response of the resultant polypyrrole(PPy)/polyetherurethane composite foams when exposed to two different volatile amines, triethylamine and butylamine.

Polyetherurethane (PEU) open-cell foams with a density of 0.045 g/cm^3 were obtained from McMaster-Carr Supply Company. Foam samples (2.54 × 2.54 × 1.27 cm) were impregnated with I_2 by placing the foams in a desiccator containing I_2. The diffusion rate of I_2 into the foams was controlled by placing a desiccator into a convection oven and by varying the temperature for impregnation. After a specified soak time, the foams were removed from the desiccator, weighed, and transferred to another desiccator saturated with pyrrole vapor at 40 °C. The in situ polymerization of pyrrole by I_2 occurred when the foams containing I_2 were exposed to pyrrole vapor and the time for polymerization was fixed at 48 h. The resultant PEU/PPy composite foams were then placed in a fume hood for a minimum of 96 h to allow for any unreacted I_2 and pyrrole to desorb from the foam. The in situ polymerization process did not affect the structure of PEU foams, as was indicated by optical microscopy, and the resulting composite foams were black due to the PPy as shown in Figure 1. Electrical conductivities of the foams were measured with a four-probe technique.

As depicted in Figure 2, I_2 was the oxidant used for the polymerization of pyrrole and later provided the charge-compensating dopant ions for the conductive PPy, which were principally in the form of triiodide.[22−24] Because the charge-compensating dopant ions for conductive PPy were derived from iodine, a direct gravimetric measurement of the amount of PPy formed was not possible. Instead, the amount of conductive PPy formed including dopants derived from I_2, that is, what has been termed the PPy−I_2 charge-transfer com-

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(1) Slater, J. M.; Paynter, J.; Watt, E. J. *Analyst* **1993**, *118*, 379.
(2) Hatfield, J. V.; Neaves, P.; Hicks, P. J.; Persaud, K.; Travers, P. *Sens. Actuators B* **1994**, *18*, 221.
(3) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.
(4) Albert, K. J.; Lewis, N. S.; Schauer, C. L.; Sotzing, G. A.; Stitzel, S. E.; Vaid, T. P.; Walt, D. R. *Chem. Rev.* **2000**, *100*, 2595.
(5) Barisci, J. N.; Conn, C.; Wallace, G. G. *Trends Polym. Sci.* **1996**, *4*, 307.
(6) Feng, J.; MacDiarmid, A. G. *Synth. Met.* **1999**, *102*, 1304.
(7) Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers, Second Edition, Revised and Expanded*; Marcel Dekker: New York, 1998.
(8) Kang, E. T.; Neoh, G.; Tan, T. C.; Ong, Y. K. *J. Macromol. Sci., Chem.* **1987**, *A24*, 631.
(9) Wang, Y.; Rubner, M. F. *Synth. Met.* **1990**, *39*, 153.
(10) Slater, J. M.; Watt, E. J. *Analyst* **1991**, *116*, 1125.
(11) Slater, J. M.; Watt, E. J.; Freeman, N. J.; May, I. P.; Weir, D. J. *Analyst* **1992**, *117*, 265.
(12) Slater, J. M.; Watt, E. J. *Anal. Proc.* **1992**, *29*, 53.
(13) Jahnke, S. A.; Niemann, J.; Kautek, W.; Bischoff, R.; Pfeiffer, C.; Kossmehl, G. *Int. J. Environ. Anal. Chem.* **1997**, *67*, 223.
(14) Lonergan, M. C.; Severin, E. J.; Doleman, B. J.; Beaber, S. A.; Grubbs, R. H.; Lewis, N. S. *Chem. Mater.* **1996**, *8*, 2298.
(15) Sotzing, G. A.; Briglin, S. M.; Grubbs, R. H.; Lewis, N. S. *Anal. Chem.* **2000**, *72*, 3181.
(16) Lee, W. M. *J. Cell. Plast.* **1973**, *9*, 125.
(17) Patterson, J. *Annu. Techn. Conf.*—*Soc. Plast. Eng.* **1997**, *55*, 3560.
(18) Fu, Y.; Palo, D. R.; Erkey, C.; Weiss, R. A. *Macromolecules* **1997**, *30*, 7611.
(19) Fu, Y.; Weiss, R. A.; Gan, P. P.; Bessette, M. D. *Polym. Eng. Sci.* **1998**, *38*, 857.
(20) Shenoy, S. L.; Kaya, I.; Erkey, C.; Weiss, R. A. *Synth. Met.* **2001**, *123*, 509.
(21) Shenoy, S. L.; Cohen, D.; Erkey, C.; Weiss, R. A. *Ind. Eng. Chem. Res.* **2002**, *41*, 1484.
(22) Hsu, S. L.; Signorelli, A. J.; Pez, G. P.; Baughman, R. H. *J. Chem. Phys.* **1978**, *69*, 106.
(23) Kang, E. T.; Tan, K. L.; Neoh, K. G.; Chan, H. S. O.; Tan, B. T. G. *Polym. Bull.* **1989**, *21*, 53.
(24) Czerwinski, W.; Wrzeszcz, G.; Kania, K.; Rabek, J. F.; Linden, L. A. *J. Mater. Sci.* **2000**, *35*, 2305.

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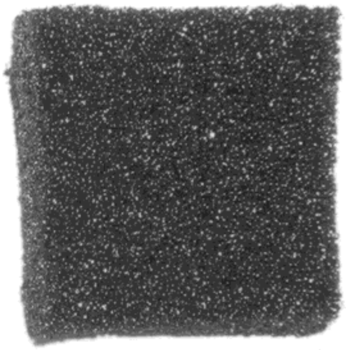

Figure 1. Graphic of the conductive polypyrrole/polyetherurethane composite foam.

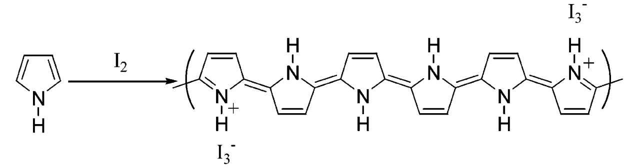

Figure 2. Chemical oxidative polymerization of pyrrole using iodine.

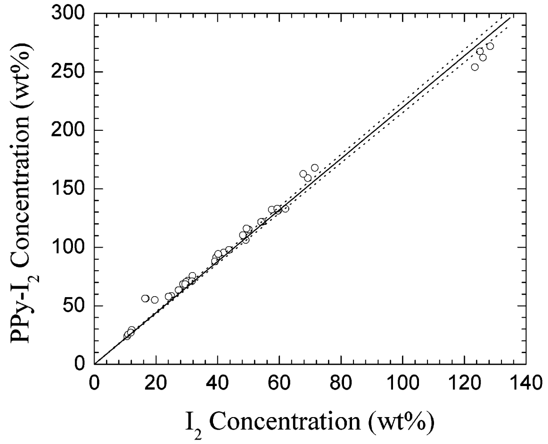

Figure 3. Amount of conductive polypyrrole (i.e., $PPy-I_2$ complex) formed at 40 °C versus amount of I_2 impregnated into the foams at 40 °C before the polymerization. The concentrations of I_2 and $PPy-I_2$ complex in the foams were defined as weight percentage (wt %) based on the mass of the original neat foams. The solid line is a linear regression fit of the data, and the dashed lines represent the 95% confidence limits.

plex,[25,26] was measured and this was found to be linearly dependent upon the concentration of I_2 in the PEU foams following the I_2-impregnation step as shown in Figure 3. The concentrations of I_2 and $PPy-I_2$ complex in the foams were defined as weight percentage (wt %) based on the mass of the original neat foams: wt % $PPy-I_2 =$ (mass of $PPy-I_2$ complex/mass of foam before iodine loading) × 100%.

The electrical conductivity of the PEU/$PPy-I_2$ composite foams is plotted against the $PPy-I_2$ complex concentration in Figure 4. The neat PEU foam is a dielectric material and the conductivity is developed due to percolation as the $PPy-I_2$ concentration increased above a critical threshold value.[19] The conductivity increased from $\approx 5 \times 10^{-6}$ to $\approx 3 \times 10^{-4}$ S/cm as the $PPy-I_2$ concentration increased from ≈25 wt % to ≈270 wt %; within that concentration range, the conductivity followed a power law relationship,

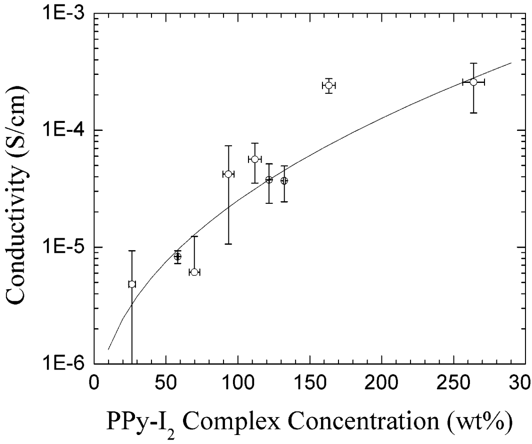

Figure 4. Electrical conductivity of conductive polypyrrole/polyetherurethane composite foams versus the concentration of the $PPy-I_2$ complex. The solid line is the least-squares fit of eq 1, and the standard deviations (error bars) were calculated from 3 to 6 data points.

$$\mathrm{Log}(\sigma) = -6.63 + 0.28c^{0.43} \qquad (1)$$

where σ is the conductivity in S/cm and c is the $PPy-I_2$ in wt %. The conductivity achieved with these foams was considerably lower than that achieved for higher density foams with similar $PPy-I_2$ concentrations,[18-21] which is believed to be related to the effect of the density on the integrity of the percolation network.

To evaluate the polypyrrole-impregnated foams as chemical sensors, an automated flow system was used to deliver diluted amine vapor to the foams and at the same time the dc resistance of the sensors was measured as a function of time. The sensor was placed into a poly(tetrafluoroethylene) chamber and a background flow of compressed air (5 L/min) was introduced through the foam sensor throughout the experiments. To obtain the desired concentration of amine in the gas phase, a stream of carrier gas (N_2) was passed through a bubbler containing amine at low flow rate (<0.5 L/min) to ensure that the vapor was saturated with amine prior to dilution with the background air. The addition of the saturated amine/N_2 stream into background air was controlled using a solenoid valve and the flow rates were monitored using Gilmont gas flowmeters with the lower and upper limits of the gas flowmeters being either 0.0230 and 13.4 L/min for background air or 11.3 and 656 mL/min for the carrier gas, respectively. Two one-way valves were used to prevent backflow in the system and resistance measurements were performed using a simple two-point configuration using a Keithley 2700 multimeter.

Figure 5 shows the resistance response of a PPy/PEU foam sensor (24% $PPy-I_2$ complex) during the first fifteen 300-s exposures to triethylamine vapor at 5% of its saturated vapor pressure. The trend in these data is representative for three tested foams. These exposures were separated by 300-s recovery periods in which only background air was allowed to pass through the

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[25] Kang, E. T.; Ti, H. C.; Neoh, K. G.; Tan, T. C. *Polym. J.* **1988**, *20*, 399.

[26] Chan, H. S. O.; Munro, H. S.; Davies, C.; Kang, E. T. *Synth. Met.* **1988**, *22*, 365.

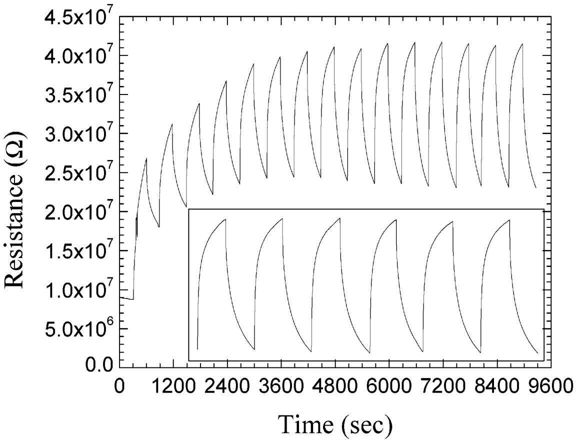

Figure 5. Resistance response of PPy/PEU foam upon 15 exposures to 5 L/min flow rate of air containing triethylamine at 5% of its saturated vapor pressure. The PPy/PEU foam used contained 24% PPy$-$I$_2$ complex. The exposure periods were 300 s. These exposures were separated by recovery periods (300 s) in which only the background air stream was used. The inlet shows a magnification of the last six exposures.

sensor. Air-induced changes in contact resistance were minimal compared to the vapor-induced resistance changes of the foam sensors. When the amine vapor was introduced through the foam sensor at the beginning of a 300-s amine exposure or removed from the foam sensor at the end of a 300-s amine exposure, the sensor responded immediately to the change in the composition of triethylamine in the flow stream. The response was reversible in that the resistance recovered when the exposure to the amine was terminated, but for the initial exposures of the foam to amine there was a distinct hysteresis in the steady-state resistance values before and after amine exposure. This may represent retention of solvent by complexation with either the foam or the conductive PPy, or it may be a result of some permanent change, for example, a permanent set due to swelling in the foam. After 10 exposures, the hysteresis disappeared and the response was completely reversible. The last 6 exposures (magnified in the inset) demonstrate that good reproducibility and stability can be achieved with the PPy/PEU foam sensors. For these exposures, the minimum resistance before analyte exposure was defined as the baseline response of the steady-state condition, R_b, which was 23.3 MΩ. The difference between the maximum and the minimum, ΔR (18.3 MΩ), was the resistance change due to exposure to the analyte for 300 s. The steady-state relative percent differential resistance response, defined as $\Delta R/R_b \times 100\%$, was about 78%.

Figure 6 is a plot of the relative differential resistance response versus analyte concentration for the foam sensor exposed to triethylamine vapor. The response was linear, which is an ideal property for a sensor since it removes concentration dependency on pattern generation for sensor arrays, thereby simplifying mathematics for odorant discrimination.[14,15,27,28] The PPy/PEU foam was very sensitive to triethylamine, displaying a sensitivity value of $(\Delta R/R_b)/(P/P^0)$ (where P is the partial pressure of the analyte in the carrier gas and P^0 is the vapor pressure of the analyte) of 16.4, which is almost an order of magnitude greater than response values reported for composite thin film sensors comprised of carbon black as a filler (usually <2.5).[15,27,28] A foam sensor containing 29% PPy$-$I$_2$ complex was also tested with butylamine at 5% of its vapor pressure, and $\Delta R/R_b$ was 68%, which is on the same order of magnitude as the response to triethylamine. Polyetherurethane foams containing 29% PPy$-$I$_2$ complex were also tested with methanol vapor at 5% of its saturated vapor pressure, and $\Delta R/R_b$ was found to be 2.9%. These results indicate that our conductive polymer loaded foams are an order of magnitude more sensitive to amines than to alcohols.

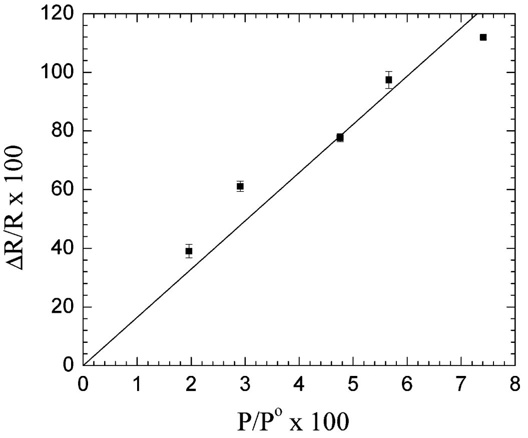

Figure 6. Relative differentiate resistance response, $\Delta R/R_b$, for a PPy/PEU foam containing 24% PPy$-$I$_2$ complex as a function of the concentration of triethylamine in the gas phase. The triethylamine (having a vapor pressure P^0) was maintained at a partial pressure P in a stream of air flowing through the foam sensor. The solid line is a linear regression fit of the data, and the standard deviations (error bars) were calculated from four to six exposures.

This preliminary data demonstrates that conductive foams have potential as chemical sensors. Polymeric foam sensors and sensor arrays could also have the potential to be multifunctional in that they can simultaneously serve as filtering devices and a means by which to detect and identify volatile organic compounds. Applications of these sensors for various analytes, as well as fabrication of sensor arrays to obtain discriminating ability for different analytes, are currently in progress in our laboratory.

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(27) Severin, E. J.; Lewis, N. S. *Anal. Chem.* **2000**, *72*, 2008.

(28) Severin, E. J.; Doleman, B. J.; Lewis, N. S. *Anal. Chem.* **2000**, *72*, 658.