

A Novel Approach for Evaluation of Polymeric Interface Materials for Chemical Sensors Using Alternate Indirect Methods

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ABSTRACT: The heart of a chemical sensor based on bulk or surface acoustic wave devices is a polymer-coated piezoelectric substrate that selectively sorbs and concentrates the target analyte vapors. The development of such sensors often necessitates the screening and evaluation of suitable polymeric interface materials meeting the specified sensitivity and selectivity toward the analytes of interest. The magnitude and dynamics of sorption–desorption of the vapors in the polymer and the extent of polymer–vapor interactions largely determine the performance of a sensor. The standard protocol used for the purpose is rather tedious, involving the generation and calibration of individual analyte vapors, with stringent control on temperature, humidity, and test parameters. This article outlines four different alternative

techniques based on mass uptake of the analyte vapors, on its partitioning in polymers, or both, which in combination can determine the characteristics of an interface material used for coating a piezoelectric substrate in acoustic wave-based chemical sensors. These methods were applied to poly(ethylene maleate), a representative interface material. The analytes ranged from volatile organic chemicals to sarin—a chemical warfare agent—and its simulant, dimethyl methylphosphonate. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3428–3432, 2004

Key words: sensor; interface; sorption; poly(ethylene maleate); coating

INTRODUCTION

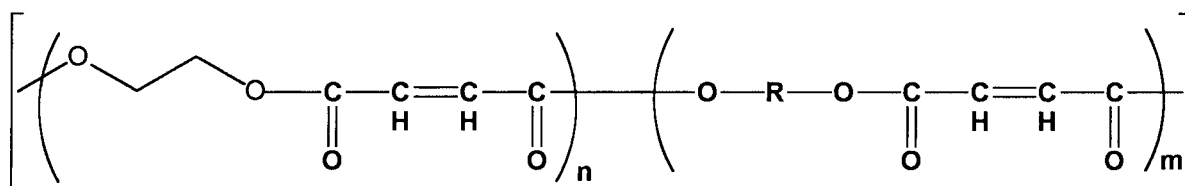
Over the last decade, attempts at the development of acoustic wave-based chemical sensors for the detection of environmental pollutants, explosives, toxic chemicals, and chemical warfare agents have been made worldwide.^{1–4} A polymer-coated piezoelectric quartz or gold crystal constitutes the interface between the analyte vapors and the transducer in such surface or bulk acoustic wave sensors.^{1–4} The performance of the sensor is defined in terms of sensitivity, selectivity, response time, reversibility, and reproducibility. These parameters in turn are dependent largely on the magnitude and dynamics of sorption–desorption of analyte (or the challenge) vapors in the polymer.^{1–4} If a polymer exhibits a high sorption of analyte, it is deemed to be sensitive; the reversibility is attained if the analyte is only physisorbed, so that the desorption occurs with ease. A large hysteresis in the sorption–desorption isotherms adversely affects the reversibility.⁴ Faster kinetics of sorption help in achieving the desired low response time. Additionally, an ideal interface material should possess chem-

ical and thermal stability besides to good adherence to the piezoelectric substrate.¹

Several chemically diverse polymers often need to be screened to develop a suitable interface for a challenge vapor. The test protocol adopted for the purpose is rather tedious, involving an acoustically thin coating of the polymer on the piezoelectric crystal, generation and calibration of individual challenge vapors, stringent control on temperature, relative humidity and test parameters, and defining pattern-recognition algorithms. To validate the results obtained from the sensor in the preliminary stages of development and to limit the number of polymers to be evaluated, alternative prescreening techniques for the selection of potential interface materials must be developed. These techniques are not aimed at replacing the existing test protocols using the sensor, but are meant to complement and support such methods in defining the characteristics of the interface.

We propose the following simple and reliable alternative methods for screening suitable interface materials for the detection of volatile organic chemicals, chemical warfare (CW) agents, and their simulants: (1) static sorption monitored gravimetrically to determine the sensitivity of the polymer toward the vapor on the basis of its equilibrium mass uptake; (2) dynamic sorption followed by liquid-stripping and gas chromatographic analysis to evaluate the sensitivity and selec-

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Polymer Code

R

PEM

-CH₂CH₂-

PEM-6H

-Ph-C(CH₃)₂-Ph-

PEM-6F

-Ph-C(CF₃)₂-Ph-

Figure 1 Sensor-coating material poly(ethylene maleate) (PEM) and its derivatives.

tivity of the coatings; (3) inverse gas chromatography for obtaining partition coefficients of various vapors into the coated polymer; and (4) sorption-desorption isotherms obtained using an automated sorption analyzer based on the principle of mass relaxation in the polymer, characterizing the magnitude and dynamics of sorption-desorption and the reversibility of the coating material.

These methods were applied to the evaluation of poly(ethylene maleate) (PEM), a well-known interface material.¹⁻⁴ The results were compared with the values of frequency shift (δF) observed using a PEM-coated quartz crystal microbalance (QCM) based bulk acoustic wave chemical sensor. Thermodynamic interaction and solvatochromic parameters were used in the interpretation of the results, thereby providing an understanding of polymer-vapor interactions, thus facilitating designing of the sensitive interface materials for chemical sensors.

EXPERIMENTAL

Materials

PEM and its derivatives, namely PEM-6H and PEM-6F (Figure 1), were synthesized as reported.^{2,5,6} The solvents were of HPLC grade. The CW agents {sarin O=P(F)(CH₃)[CH(CH₃)₂] and chloropicrin CCl₃NO₂} and the simulant dimethyl methylphosphonate (DMMP) were obtained from Process Technology Division of the Defence Research and Development Establishment.

Static sorption method

The method based on change in weight (δW) of the bulk polymer was used to determine the %mass-up-

take (Q_e) of the analyte DMMP. Microcups containing 20 to 25 mg (W_d) of the polymers were placed in a closed, saturated atmosphere of DMMP vapors at $35 \pm 2^\circ\text{C}$. δW of the polymer was monitored after regular intervals up to 20 hours using a weighing balance (accuracy $\pm 1 \times 10^{-4}$ g). Q_e was calculated from the formula in eq. (1)^{4,7,8}:

$$Q_e = (\Delta W / W_d) \times 100 \quad (1)$$

An average value of three replicates was taken to report Q_e . The samples then were desorbed at ambient temperature, and the time taken for attaining initial weight W_d was noted. An average value of three replicates was reported.

Dynamic sorption method

Five to 30% (w/w) of the polymer was impregnated on chromosorb (Analabs, US, 80-100 mesh) and packed in 3-inch long glass capillary tubes. The weight of the packing was 250 to 260 mg, containing 33 to 39 mg of the polymer. Two such tubes were connected in series to enable the determination of breakthrough and safe sampling time. 1.25 mg/m³ of DMMP vapor generated⁶ at 50°C was passed over the chromosorb-impregnated polymer at 400 mL/minute for 30 minutes. The tubes then were emptied and desorbed in 1 mL MeOH. The concentration of DMMP in the solution (y) was determined by gas chromatography (GC). The actual amount of DMMP sorbed (Q) was obtained from the desorption efficiency (DE) using the formula in eq. (2):

$$Q = DE / y \quad (2)$$

TABLE I
Static DMMP Sorption–Desorption and QCM Response

Polymer code	W_d (mg)	Q_e (%)	Desorption Time (h)	ΔF (Hz)
PEM	18.6	86	31	1549
PEM-6H	28.4	146	28	3567
PEM-6F	23.5	153	24	2985

DE in turn was determined by spiking the loaded capillary tube, using a syringe, with 20 mg DMMP at $35 \pm 1^\circ\text{C}$, stripping with MeOH after 8 hours and subsequent GC analysis.

Inverse GC

Fifteen percent PEM immobilized on chromosorb was packed into a column, fitted onto the GC, and maintained at 40°C . The injector was kept at 60°C , whereas the flame ionization detector was at 80°C . The flow rate of the carrier gas (nitrogen) was 55 mL/minute. The retention volume and partition coefficients of various solvents, CW agents, and simulants were determined from the retention times using standard formulae.^{9,10}

Automated sorption–desorption analysis

A microprocessor-controlled intelligent gravimetric analyzer (Hiden Analytical, UK) was used to obtain the sorption–desorption kinetics and isotherms of various vapors on the polymers, as reported recently.⁴

δF determination using a QCM-based sensor

PEM and its derivatives were coated on the 10-MHz piezoelectric quartz crystal by dropping 20 μL of the polymer solution using a ten microliter syringe according to the reported method,^{5,6} the δF values (Hz) were determined on exposure of the coated crystal to predetermined concentration of DMMP vapors.

RESULTS AND DISCUSSION

As observed from Table I, QCM and the static method are in complete concurrence with respect to the ranking of PEM and its derivatives, based on their sensitivity for DMMP sorption. PEM sorbs 86% of DMMP, which is enhanced further by approximately 1.6 times on incorporation of polarizable aromatic moieties in the backbone (*cf.* PEM-6H, PEM-6F). A similar trend is observed in δF values. Under ambient conditions, the time taken to restore the initial weight (*viz.*, desorption time) varied from 24 hours in PEM-6F to 31 hours in PEM. The desorption was highest in PEM and lowest in PEM-6F, as manifest in the desorption efficiency (DE) values in Table II. It was also observed that the DE was compar-

TABLE II
Desorption Efficiency and Dynamic Sorption of DMMP

Polymer (% loading)	DE	Q ($\mu\text{g/g}$)
PEM		
(5)	0.91	182
(10)	0.82	1197
(15)	0.80	225
(30)	0.77	218
PEM-6H		
(5)	0.69	327
(10)	0.64	1402
(15)	0.60	250
(30)	0.58	242
PEM-6F		
(5)	0.85	386
(10)	0.73	1514
(15)	0.65	256
(30)	0.63	254

atively higher at lower loading of the polymer. Probably, chemisorption comes into play at higher polymer loading.^{9,10} Thus, the lower uptake of DMMP by 30% loaded polymers may be attributed to the reduced DE . Maximum sorption and fairly high DE was obtained at 15% loading of the polymers. For inverse GC experiments, we therefore chose 15% PEM on chromosorb.

The interaction between vapor and polymer coating in acoustic wave-based sensors is considered similar to gas–liquid thermodynamic equilibrium in gas chromatography.^{1,9,10} A higher retention volume or partition coefficient K on a GC column implies a higher vapor–polymer interaction for PEM. As observed from Table III, the K values range from 23 (for the nonpolar compound hexane) to 417 (for Sarin). PEM thus is the potential interface material for sensing CW agents such as sarin and chloropicrin. The lowest detection limit for sarin was found to be 25 μg . PEM also has a high affinity for polar compounds such as methanol, acetone, acetonitrile, chlorobenzene, and so forth. These compounds

TABLE III
Retention Volume (RV) and Partition Coefficient K for PEM

Analyte	RV (ml)	K
Sarin	91	416.86
Chloropicrin	48	223.87
Chlorobenzene	72	335.73
Methanol	67	312.60
Acetone	32	149.62
Acetonitrile	61	284.44
Chloroform	14	65.31
Benzene	15	69.98
Toluene	26	121.33
Cyclohexane	06	27.98
Hexane	05	23.33
Nonane	10	46.55
Decane	18	50.00

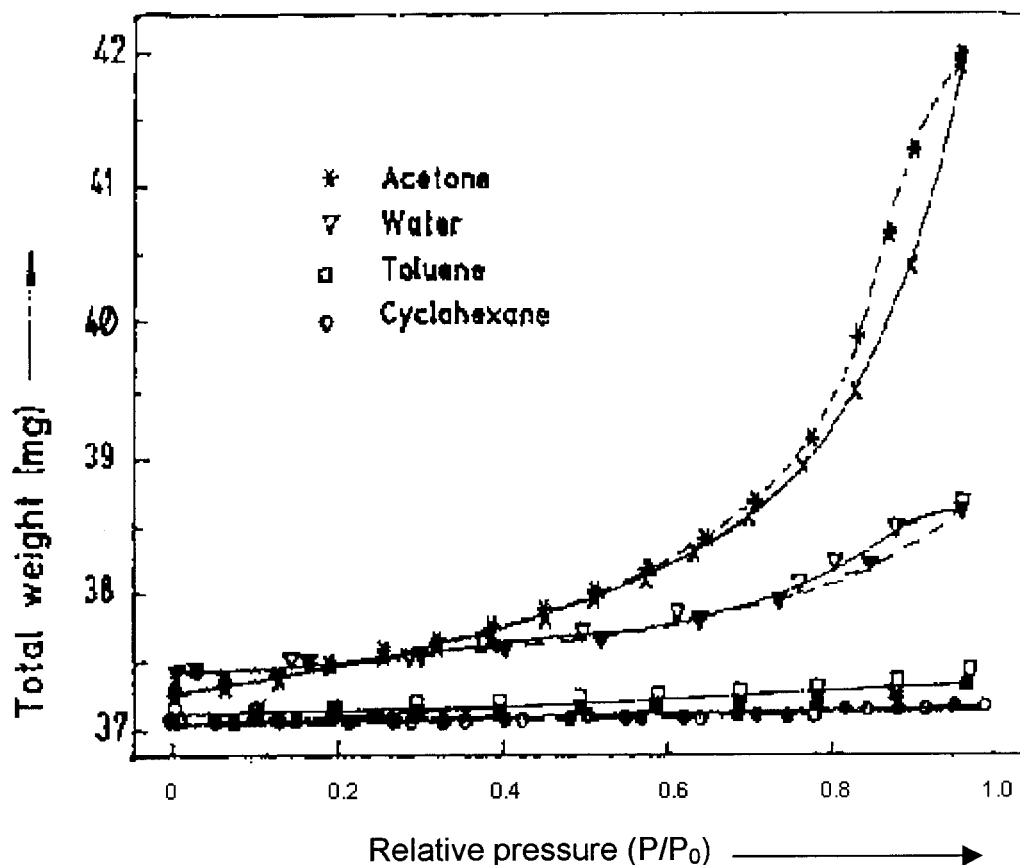


Figure 2 Vapor sorption-desorption isotherms for water and organic vapors on PEM.

therefore are the likely interferents in the selectivity offered by PEM on a chemical sensor for CW agents. A high value of K for chlorobenzene also indicates the potential of PEM for monitoring the presence of such aromatic chlorinated hydrocarbons in the environment. The affinity of PEM toward aliphatic hydrocarbons, such as hexane, nonane, or decane, is comparatively poor.

The extent of polymer-vapor interaction can also be determined from the sorption isotherms and kinetics, as explained in our earlier work.⁴ A representative isotherm for the sorption of water and organic vapors on PEM is depicted in Figure 2. It is observed that with a polar vapor such as acetone, the interaction is high, the isotherm has higher convexity, and it approaches the y-axis. A hysteresis in sorption-desorption is observed at higher concentration (P/P_0), implying slow reversibility of baseline in a PEM-coated sensor when a substantial amount of polar organic vapors are present in the environment. Similar results have been reported by Snow et al² using a PEM-coated surface acoustic wave device. As inferred from a low partition coefficient (refer to Table 3), the interaction of PEM with cyclohexane is poor, and so its sorption isotherm is observed to be closer to the abscissa. Because of the π electron cloud, toluene shows a comparatively higher interaction than cyclohexane with PEM. The

magnitude and dynamics of sorption obtained from such isotherms for PEM and its derivatives was reported recently⁴ in our earlier work.

The convexity in the sorption isotherms can also be related to the thermodynamic interaction parameter χ , which is a measure of energy change that occurs when a mole of organic vapor molecules is removed from the pure solvent and is immersed in an infinite amount of pure polymer.^{7,8} $\chi \geq 1$ represents limited sorption, whereas $\chi < 0.5$ implies a high sorption; namely, a lower value of χ implies a higher vapor-polymer interaction, leading to a higher partition coefficient K , and thus a higher convexity of the sorption isotherm. χ was calculated, as reported earlier,⁴⁻⁶ using the standard equations. As seen from Figure 3 for the sorption of organic vapors on PEM, the trend in the experimentally determined values of K is in good agreement with the calculated values of χ .

The solvatochromic parameter (SP) derived from linear solvation energy relationship also is used frequently to estimate the extent of polymer-vapor interaction.^{4,9,10} SP is a summation of various kinds of interactions resulting from n or π electrons, a hydrogen bond, dispersive forces, polarizability, dipolarity, and so forth. In general, SP values are supposed to increase with the value of K .^{4,9,10} However, as observed from Figure 3, we

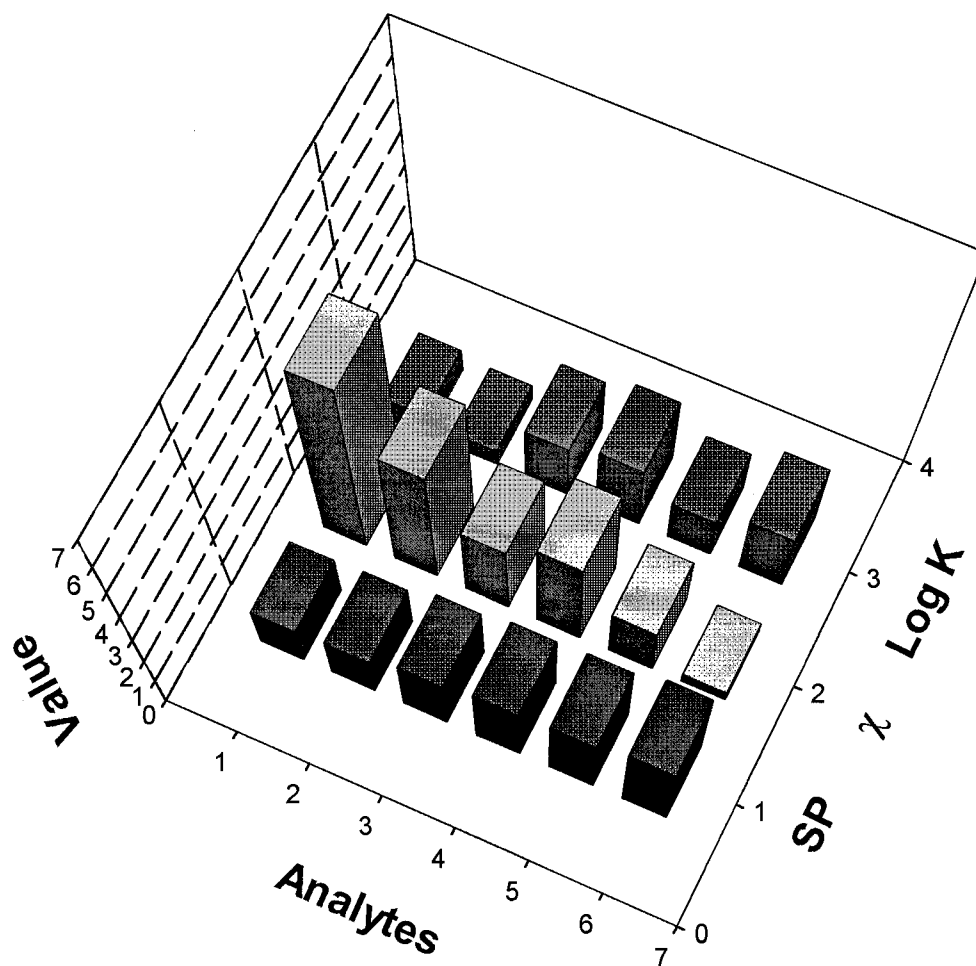


Figure 3 Correlation of partition coefficient K , solvatochromic parameter (SP), and thermodynamic interaction parameter χ for organic vapors on PEM. (Analytes—1: Hexane; 2: Cyclohexane; 3: Benzene; 4: Toluene; 5: Acetone; 6: Methanol).

did not find a satisfactory correlation of K with SP. This may be because SP is a summation of various kinds of interactions, all of which may not be applicable during the partitioning of vapors in GC.

CONCLUSIONS

The sorption characteristics of PEM, a potential interface material for chemical sensors for CW agents, were determined successfully using simple methods based on mass uptake, partitioning of organic vapors in polymers, or both. The results obtained were in good agreement with the response (frequency shift) observed using a QCM-based sensor and could be interpreted in terms of various semiempirical models for polymer–vapor interactions.

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References

- Nieuwenhuizen, M. S.; Venema, A. *Sensors*, Vol. 2; Gopel, W., et al., Eds.; VCH Publ.: Germany, 1991; p 647.
- Snow, A. W.; Wohltjen, H. *Anal Chem* 1984, 56, 1411.
- Grate, J. W.; Kaganove, S. N.; Patrash, S. J.; Graid, R.; Bliss, M. *Chem Mater* 1997, 9, 1201.
- Dubey, V.; Kuthe, S.; Saxena, C.; Jaiswal, D. K. *J Appl Polym Sci* 2003, 88, 1760.
- Dubey, V.; Saxena, C.; Asrey, R.; Gupta, D. C.; Vyas, K. D. *Proc Macro 2000; Natl. Symp. Recent Trends in Polymers and Composites*, 1–2 Dec., 2000; DMSRDE: Kanpur, India, 2000; p 222.
- Gupta, D. C.; Gutch, P. K.; Saxena, C.; Dubey, V.; Asrey, R.; Vyas, K. D. *Proc Macro 2000; Natl. Symp. Recent Trends in Polymers and Composites*, 1–2 Dec., 2000; DMSRDE: Kanpur, India; p 217.
- Dubey, V.; Gupta, A. K.; Maiti, S. N.; Rao, N. B. S. N.; *J Appl Polym Sci* 2000, 77, 2472.
- Dubey, V.; Rao, N. B. S. N.; Maiti, S. N.; Gupta, A. K. *J Appl Polym Sci* 1998, 69, 503.
- Abraham, M. H.; Whiting, G. S.; Doheaty, R. M.; Shuely, W. J. *J Chem Soc Perkin Trans* 1990, 2, 451.
- Abraham, M. H.; Hamerton, I.; Rose, J. B.; Grate, J. W. *J Chem Soc Perkin Trans* 1991, 2, 1417.