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Vapor sorption in plasma polymerized vinyl acetate and methyl methacrylate thin films

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Abstract

Vapor sorption isotherms of vinyl acetate (VAc) and methyl methacrylate (MMA) plasma polymer thin films are measured and compared with those for cast films of the conventionally polymerized analogs. Sorption isotherms are collected for methanol, acetone, hexane, and water at 30°C using a Quartz Crystal Microbalance (QCM). The isotherms are analyzed using both Dual-Mode and Flory–Huggins sorption models. In general, plasma polymer sorption isotherms approximate those of the conventional polymer analogs, but exhibit an enhanced Langmuir-type sorption component at low activity. Accordingly, Dual-Mode model parameters show roughly equivalent Henry's Law solubility coefficients with the Langmuir-type capacity parameters (C_H') being 5–20-fold higher than those for the conventional polymer materials. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Plasma polymerization; Sorption isotherms; Microsensors

1. Introduction

The use of plasma polymerization to synthesize new materials for membrane separations has been proposed and investigated over the past several decades [1–3]. More recently, microsensor technology has driven interest in the use of plasma polymer thin films to selectively absorb chemical compounds from flowing gas and liquid streams [4–10]. Plasma polymers can be synthesized from an extremely broad range of chemical structures while being directly deposited as thin selective layers on the order of 100 nm or less [11,12]. To realize the full potential of this thin film technology for use in either sensor or membrane applications, a fundamental understanding of the structure–property relationships that govern both sorption and diffusion of small penetrants in plasma polymers is necessary. As a step toward deeper understanding of these unconventional materials, this paper provides a characterization of the vapor sorption isotherms for plasma-polymerized thin films prepared from vinyl monomers.

Unlike conventional polymers, plasma polymers are highly crosslinked materials with an irregular chemical composition [1,2]. Therefore, the structure–property relationships commonly used to control the diffusion and sorption processes in these materials may not be as straightforward as with conventional polymers. At the same time, however, spectroscopic evidence of low-wattage plasma polymers from vinyl monomers suggests that the chemical structure is "polymer-like" [13]. Thus, a central question emerges as to the applicability of conventional polymer transport models to the case of plasma polymers.

At present, a definitive mechanism for small penetrant transport in plasma polymers has not been established. Permeability coefficients and gas pair selectivities of plasma polymer separating layers are, in most cases, in line with those reported for conventional polymers [11]. This observation suggests that the mechanism governing sorption of small gas molecules in plasma polymers is in accord with that established for conventional polymers. Additionally, a few authors have probed the sorption isotherms of plasma polymer thin films while investigating sorbent layers in microsensor applications [6–10]. In a direct comparison of plasma-polymerized styrene with cast poly(styrene) films, CO_2 sorption levels in the plasma material were on the same order of magnitude as those for conventional poly(styrene) [10]. In this case, however, the plasma polymer exhibited a significant increase in the Langmuir-type sorption component at low activity. Above this Langmuir-type sorption regime, the incremental capacity of the plasma polymer to absorb CO_2 with increasing activity was virtually equivalent to that of conventional poly(styrene).

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Table 1
Henry's law solubility coefficients (k_D) and sorption capacity parameters (C'_H) from Dual-Mode model (Dual-Mode model affinity parameters: $b = 0.1\ \mathrm{mmHg}^{-1}$ except for water, $b = 0.5\ \mathrm{mmHg}^{-1}$. Saturated vapor pressure at 30°C (mmHg): acetone (284), hexane (187), methanol (163), water (32)) analysis of conventional and plasma polymers at 30°C

Polymer	Vapor	$k_{D\ lit}$[a] (cm^3 (STP)/(cm^3 (poly) atm))	$k_{D\ conv}$ (cm^3 (STP)/(cm^3 (poly) atm))	$k_{D\ plasma}$	$C'_{H\ conv}$ (cm^3(STP)/(cm^3 (poly))	$C'_{H\ plasma}$ (cm^3(STP)/(cm^3 (poly))
MMA	Acetone	190	110	100	1	11
	Hexane	70	80	80	1	8
	Methanol	100	150	170	1	5
	Water	710	760	330	5	6
VAc	Acetone	210	240	100	1	13
	Hexane	40	70	40	2	12
	Methanol	140	260	180	1	22
	Water	860	840	460	5	13

[a] Derived from Flory–Huggins analysis using χ_{lit} parameters from Table 2.

In this work, the sorption isotherms of plasma polymers prepared from vinyl acetate (VAc) and methyl methacrylate (MMA) are compared with those for conventionally polymerized analogs. The sorption isotherms are obtained for thin films using a quartz crystal microbalance (QCM) apparatus. As a means of assessing the mechanistic nature of sorption, the plasma polymer sorption model parameters are compared with those generally accepted for conventional polymers. The work suggests that vapor sorption in low-wattage plasma polymers can largely be justified by sorption mechanisms and theory accepted for conventional polymer systems. Establishing such predictive models for plasma polymers will be critical in developing appropriate algorithms for chemical detection and separation applications.

2. Background

2.1. Sorption models for glassy and rubbery polymers

The sorption of vapors and other small penetrants in polymeric materials is well documented and the subject of even current developments in the literature [14–25]. With regard to sorption in plasma polymers, linear solvation energy relationships (LSER) have been used in a predictive capacity [5,8]. The subject of this study is to use sorption models established for conventional polymers (e.g. Henry's Law, Dual-Mode and Flory–Huggins) as probes to characterize the phenomenological process of sorption in plasma-polymerized materials.

In the low solubility limit, Henry's Law accounts for the concentration of sorbed vapor in rubbery polymers and is simply a linear relation between vapor concentration and partial pressure written as

$$C_D = k_D p_i \qquad (1)$$

where C_D is the sorbed vapor concentration (cm^3(STP)/cm^3(poly)), k_D the Henry's Law solubility coefficient (cm^3(STP)/(cm^3(poly) atm)), and p_i the vapor partial pressure (atm) [14].

For glassy polymers, in addition to a Henry's Law component, a Langmuir-type adsorption component is also observed [14,15]. The predominance of this type of behavior in glassy polymers is referred to as "hole-filling" and is generally attributed to sorption in the excess free volume associated with the glassy state. The hole-filling contributions to the sorption isotherm have a modified Langmuir form:

$$C_H = C'_H b p_i/(1 + b p_i) \qquad (2)$$

where the terms C'_H and b are the Langmuir-type parameters reflecting the capacity and affinity, respectively, of the polymer for the particular sorbent. Here p_i is again the vapor partial pressure (atm), C'_H is a molar concentration term (cm^3(STP)/cm^3(poly)), and b has units of inverse pressure.

The combination of both Henry's Law and Langmuir-type hole-filling modes creates the Dual-Mode model [14,15], the isotherm for which is described by the summation of contributions from Eqs. (1) and (2):

$$C = k_D p_i + C'_H b p_i/(1 + b p_i) \qquad (3)$$

Rubbery polymers and glassy polymers in the range of high vapor activities often demonstrate non-ideal behavior leading to positive curvature of the sorption isotherm. This mode has been successfully characterized by the Flory–Huggins equation:

$$\ln(p_i/p^0) = \ln v_S + (1 - v_S) + \chi(1 - v_S)^2 \qquad (4)$$

where p^0 is the saturated vapor pressure, v_S the volume fraction of sorbed vapor in the polymer–sorbent matrix and χ the Flory interaction parameter. The term χ empirically defines the polymer–sorbent interaction energy [16–19]. For crosslinked systems, the Flory–Rehner equation has been used to describe the effect of crosslinking

Table 2
Flory–Huggins interaction parameters (molar volumes at 25°C (cm^3/mol): acetone (74); hexane (132); methanol (41); water (18)) for plasma and conventional polymers at 30°C

Polymer	Vapor	χ_{conv}	r^2	χ_{plasma}	r^2	χ_{lit}	Reference
MMA	Acetone	0.9	0.982	0.7	0.992	0.5	[17]
	Hexane	1.7	0.997	1.1	0.945	1.2[a]	[17]
	Methanol	1.9	1.000	1.8	0.988	2.2[a]	[17]
	Water	2.6	0.996	3.2	0.976	2.7	[9]
VAc	Acetone	0.4	0.997	0.7	0.958	0.4	[17,18]
	Hexane	1.5	0.965	1.3	0.922	1.7[a]	[17]
	Methanol	1.5	0.991	1.5	0.949	1.4	[19]
	Water	2.6	0.982	2.7	0.954	2.5	[18]

[a] Calculated using Eq. (5).

on the overall sorption behavior [20]. Aside from deriving χ from experimental sorption isotherms, χ can also be calculated using the van Laar–Hildebrand equation:

$$\chi = 0.35 + V_S/RT(\delta_S - \delta_P)^2 \tag{5}$$

where V_S is the sorbent molar volume, and δ_S and δ_P are Hildebrand solubility parameters for the sorbent and polymer, respectively [17,18].

In the low-activity region (say 0–10%), the Flory–Huggins relationship generates a near-linear isotherm allowing the prediction of Henry's Law solubility coefficient k_D from the single parameter χ [17–19]. Using χ parameters from experimental data or from the solubility parameter calculation (Eq. (5)) in conjunction with Eq. (4), the Henry's Law solubility coefficient can be calculated from the initial slope of the Flory–Huggins isotherm. Estimated Henry's Law solubility coefficients for the polymer–sorbent pairs used in this work are shown in Table 1 (k_{Dlit}). To outline such a calculation, the Henry's Law solubility parameter for PMMA–methanol is determined to be 100 cm^3 (STP)/(cm^3 (poly) atm) using an estimated χ parameter of 2.2. Here, the PMMA–methanol χ parameter is obtained using Eq. (5) with the "preferred" solubility parameters ($\delta_{PMMA} = 19\ MPa^{1/2}$, $\delta_{MeOH} = 29.6\ MPa^{1/2}$) and solvent molar volume ($V_{MeOH} = 41\ cm^3/mol$) from the literature [17,18]. For the literature-derived Henry's Law solubility coefficients in Table 1, χ parameters from experimental sorption isotherms are preferred, while the van Laar–Hildebrand estimates are used when no isotherm data is available (See Table 2).

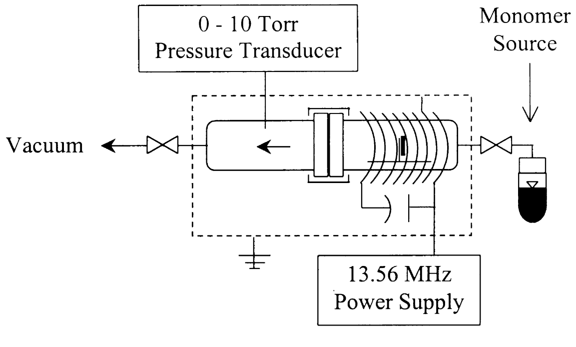

Fig. 1. Inductively coupled RF plasma reactor for synthesis and deposition of polymer films.

It is noteworthy that the presence of all three sorption mechanisms is commonly observed for vapor sorption in conventional glassy polymer materials [21–25]. In these cases, Dual-Mode modeling is used to analyze the lower activity regions of the isotherms. When the sorption levels are high enough to plasticize the polymer matrix, the characteristically Dual-Mode isotherms yield to a Flory–Huggins type isotherm in the higher activity regions [21–23].

3. Experimental

3.1. Materials

The materials used in this study have been purchased from Sigma Aldrich Chemical Company including plasma polymer monomers (vinyl acetate (VAc) and methyl methacrylate (MMA)), conventional polymer analogs (poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA)), and the vapor sources: methanol, acetone, and hexane. Each material is used either as purchased or after a specific conditioning protocol described below. Distilled water is also used as a vapor source.

3.2. Film formation

3.2.1. Plasma polymerization

Thin polymer films are prepared by both plasma polymerization of vinyl monomers and solution casting of conventional polymer analogs. Plasma polymerization is conducted with the inductively coupled RF plasma (ICP) reactor schematically shown in Fig. 1. For all depositions in this work, the ICP reactor operated at 13.56 MHz, 30 W coupled power, and 80 mTorr system pressure. The ICP apparatus is electrically configured in a serial arrangement of tunable capacitor and auto-transforming solenoid achieving 0.7 A and nearly 2500 Ω impedance. The entire apparatus is enclosed in a Faraday cage to prevent RF escape.

The method of plasma polymerization follows a standard protocol. Prior to each run, a 1-h 60 W oxygen plasma is used to clean the reactor. Following the cleaning procedure, 5 ml of monomer is poured into a sample vessel and attached to the ICP reactor for conditioning with a freeze–thaw–freeze procedure. Here, the monomer is repetitively frozen with liquid nitrogen and thawed under vacuum to remove moisture and other possible contaminants. The conditioned monomer is then closed off from the reaction chamber while the substrates (quartz crystals and silicon wafer fragments) are positioned inside the vessel. The quartz crystal devices are mounted orthogonal to monomer flow in the radial center of the ICP reactor and a silicon wafer placed near the quartz crystal. After the reactor is again sealed, the reactor volume and substrates are exposed to vacuum for 15 min to allow for complete removal of captured atmospheric gases. Introduction of monomer vapor to the evacuated reactor results in a system pressure increase proportional to monomer flow rate. The plasma is then ignited with 30 W coupled power and the chamber pressure is adjusted to 80 mTorr for the duration of the polymerization. For this system and specified operating conditions, a deposition time of 20 min yields an approximate film thickness of 200 nm, which has been verified by both SEM and mass deposition measurements. Following deposition, the monomer flow is terminated and the system is degassed for 10 min ensuring complete removal of organic vapor and a consistent plasma polymer quench.

3.2.2. *Conventional polymer casting*

To provide a comparison with conventional polymer materials, poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) were solution cast onto the quartz crystal devices. Dilute PMMA–acetone and PVAc–methanol solutions were prepared for the casting procedure. The quartz crystals were placed on the bottom of a Petrie dish, which was then filled with the polymer solution. The solvent was allowed to evaporate leaving a cast film on the quartz crystal surface. The total mass of polymer deposited was then determined from the difference in oscillation frequency measured before and after deposition in a manner described below. The cast and plasma polymer films used this work exhibited roughly equivalent mass as demonstrated by the similar frequency shifts following deposition. Since diffusion experiments are not performed in this work, uniform film coverage from the casting technique is not necessarily required.

3.3. *Isotherm testing*

3.3.1. *QCM apparatus*

The quartz crystal microbalance (QCM) is becoming a common tool used in measuring sorption in thin films (see Fig. 2). The QCM apparatus consists of a vapor-conditioning manifold, a quartz crystal mounted in a flow cell, a temperature-controlled chamber, an oscillator, and a data acquisition system. The apparatus configuration is similar to that used by previous workers [10,26–28]. The flow cell and oscillator were purchased from International Crystal Manufacturing (Oklahoma City, OK). The data acquisition hardware and software were purchased from National Instruments (Austin, TX). The configuration allows continuous data collection of the crystal oscillation frequency at a resolution of 1 Hz per 10 MHz (or 0.1 ppm). The quartz crystals used in this work are disc-shaped 10 MHz AT cut quartz with gold sputter-coated electrodes on each face (ICM Model #131227). The oscillator (ICM model #PD-25) is designed to operate in the 1–25 MHz frequency range and the 10 V supply voltage is regulated with a DC power supply.

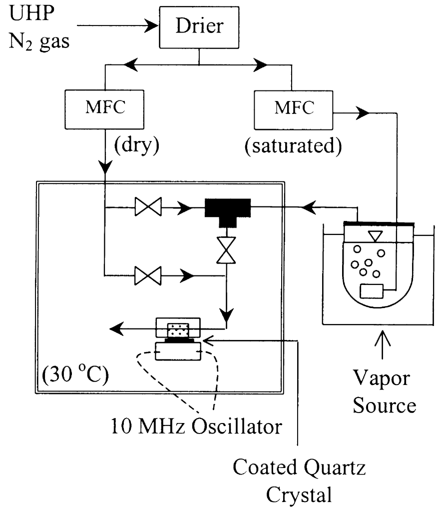

Fig. 2. Quartz Crystal Microbalance (QCM) with vapor conditioning manifold, environmental chamber, flow cell, and coated quartz crystal.

The crystal is mounted in an acrylic flow cell and held by two O-rings. The coated side of the crystal is exposed to a 70 μl flow chamber volume. As shown in Fig. 2, the quartz crystal, flow cell, and crystal oscillator are all enclosed in an environmental chamber with a proportional control system set at 30°C (±0.1°C). The entire environmental chamber and QCM device is isolated from laboratory vibrations using an isolation pad placed on an inflated rubber bladder.

The vapor feed system is also shown in Fig. 2 and is designed to deliver vapor flows over a range of activities from 0 to 80%. Ultra-High Purity (UHP) nitrogen gas is dried and then split into two streams. One stream remains dry and the other is saturated in a gas/liquid contacting vessel. The gas/liquid contacting vessel consists of an aspirating stone (10 μm pore size) bubbling the dry gas through a standing liquid column. The liquid vapor source is controlled at 25 or 5°C below the temperature of the QCM device to limit condensation in the system. The vapor exiting the column is assumed to be saturated and has been verified by significantly lowering the liquid level height with no changes in sorption in the QCM device. The flow rates of the dry and saturated streams are controlled using mass flow controllers (MFC) operating at 0–50 sccm and 0–10 sccm gas, respectively. The dry and saturated streams are recombined within the confines of the environmental chamber and mixed in an oversized tee fitting. Prior to contact with the crystal, the combined gas/vapor stream flows through a long piece of coiled tubing to ensure temperature equilibration. Adjusting the ratio of the wet and dry flow streams controls the flowing vapor activity. For example, 10 sccm of saturated vapor combined with 10 sccm dry gas results in a chemical vapor activity of 0.5.

3.3.2. Mass measurements

Changes in mass, either as deposited polymer films or absorbed vapor within the film, are measured by monitoring frequency damping (Δf) of the oscillating quartz crystal. The frequency shift is related to mass uptake on the QCM device by the Sauerbery equation [29]:

$$\Delta m = \Delta f(\rho v / f_0^2) \tag{6}$$

where Δm is the mass loading per unit area of crystal surface, Δf the measured frequency shift, f_0 the fundamental oscillation frequency of approximately 10 MHz, ρ the quartz density of 2650 kg/m^3 and, v the 3340 m/s speed of sound propagation in quartz [30]. The Sauerbery relationship is used extensively with quartz crystal sorption studies [26–28]. In this work, two frequency shift measurements are performed: (1) the frequency shift associated with polymer deposition (Δf_{poly}) and (2) the frequency shift associated with vapor sorption (Δf_{vap}). Since Δf_{vap} is proportional to vapor mass sorbed and Δf_{poly} is proportional to polymer mass, the ratio $\Delta f_{\mathrm{vap}}/\Delta f_{\mathrm{poly}}$ is equivalent to the concentration of sorbed vapor on a dry polymer film basis. For Flory–Huggins analysis, these mass concentration terms are converted to the analogous volume ratios (v_S/v_{poly}) by incorporating the molecular weight and molar volumes of the condensed vapors (see Table 2) and densities of the conventional polymer analogs (1.19 g/cm^3 for ppMMA/PMMA, 1.19 g/cm^3 for ppVAc/PVAc [19]).

3.3.3. Polymer mass deposition measurements (Δf_{poly})

A protocol has been established to determine the total frequency shift associated with polymer mass deposited on the crystals Δf_{poly}. Each blank crystal is first mounted in the isothermal QCM chamber and dried using the standard protocol of 50 sccm dry UHP nitrogen at 30°C for 8 h. The resulting, or zeroed, frequency is taken as the fundamental frequency f_0. The zeroed crystal is then removed for polymer deposition. Following either the plasma-polymerization or casting procedures described above, the coated crystal is remounted in the QCM cell and again dried for 8 h under flowing dry nitrogen. At this point, the baseline frequency is recorded. The difference between the zeroed and baseline frequencies corresponds to the polymer mass frequency shift Δf_{poly} and is related to the polymer mass using the Sauerbery relationship (Eq. (6)). In this study, Δf_{poly} is on the order of 2.0 kHz for both the plasma polymer and conventional polymer analog films. Utilizing the conventional polymer amorphous density and area of mass loading (0.2 cm^2 QCM electrode area), these frequency shifts correspond to an equivalent film thickness on the order of 200 nm.

3.3.4. Conditioning and isotherm protocol (Δf_{vap})

Prior to measurement of the sorption isotherms, both the plasma and conventional polymer films are conditioned with exposure to 80% activity acetone for a period of 8 h. The conditioned film is again dried using the standard drying protocol, allowing the crystal to return to the original baseline frequency. Following this conditioning and drying protocol, isotherms for the coated crystals are measured for the various vapors in a fixed order: methanol, acetone, *n*-hexane, and water. The sorption protocol involves step increases in vapor activity of 5% covering the range of 0–80%. The time allotted for mass loading and stabilization at each activity is 10 min, well above the equilibrium sorption times expected for Fickian diffusion in 200-nm thick films. The difference between the measured equilibrium sorption frequency at any given vapor activity and the baseline frequency yields the frequency shift for mass uptake associated with vapor sorption, Δf_{vap}. Between each isotherm, the crystal is dried and the vapor source replaced and allowed to equilibrate at the controlled temperature. When not in use, the quartz crystals, both coated and uncoated, are stored at ambient conditions.

3.4. FTIR spectroscopy

Infrared spectroscopy measurements were conducted using a Mattson Instruments 2020 Galaxy Series FTIR with a 4 cm^{-1} resolution. For both cast and plasma polymer samples, FTIR spectra were obtained under a nitrogen purge in the transmission mode using polymer samples coated on silicon wafers. Background signals from the relatively transparent silicon wafers are subtracted from the polymer spectra.

4. Results and discussion

4.1. FTIR spectroscopy

The FTIR spectra for both the plasma polymers and the cast polymer analogs are shown in Figs. 3 and 4. The similarity of the conventional and plasma polymer spectra clearly indicate that the chemistry of the plasma polymer

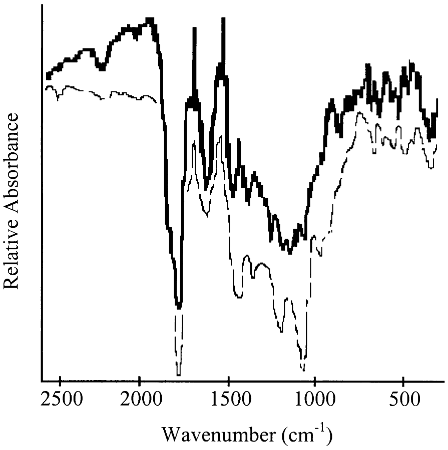

Fig. 3. FTIR spectra of plasma polymerized MMA (solid line) and cast poly(methyl methacrylate) (PMMA) (dashed line).

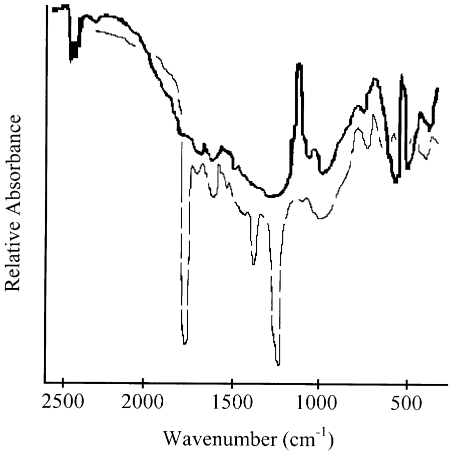

Fig. 4. FTIR spectra of plasma polymerized VAc (solid line) and cast poly(vinyl acetate) (PVAc) (dashed line).

can be "polymer-like". This is particularly true in the case of the plasma-polymerized MMA materials (Fig. 3) where the carbonyl peaks associated with the ester moieties near 1735 cm^{-1} are preserved. Similar spectroscopic evidence has been observed for other plasma-polymerized MMA materials [13]. With the plasma-polymerized VAc monomer (Fig. 4), the FTIR spectrum is considerably more distorted from the PVAc analog. In the case of VAc, the dominant carbonyl peak at 1740 cm^{-1} found in PVAc is virtually absent in the plasma polymerized coating.

4.2. Vapor sorption isotherms

The vapor sorption isotherms for the MMA and VAc polymers are shown in Figs. 5 and 6, respectively. As described previously, the ratio of $\Delta f_{vap}/\Delta f_{poly}$ is equivalent to the concentration of sorbed vapor in the polymer films. As a first approximation, the sorption isotherms observed for the plasma polymers are in accord with those for the conventional polymer analogs. Both the sorption levels and the relative affinity of the plasma polymers for the various vapors are similar to those of the conventional polymer analogs. One observable difference between the two types of polymers is that the plasma polymers have a significantly enhanced Langmuir-type sorption component at low analyte activity. For example, conventional PVAc (Fig. 6) exhibits approximately 1 wt.% sorption at 5% hexane and acetone activities, whereas the plasma materials exhibit nearly 2–3 times this sorption level.

The plasma polymer sorption isotherms in the higher vapor activity regions appear to be in agreement with those for the conventional polymers. As seen in Figs. 5 and 6, for vapor activities in excess of 10%, plasma polymers exhibit similar incremental increases in sorption level with increasing activity. At very high activities, the sorption levels observed for the conventional polymers often exceed those of the plasma polymers. This reversal of sorption levels with increased activity suggests that crosslinking inherent in plasma polymers limits the swelling of the polymer matrix and reduces total sorption capacity. The acetone

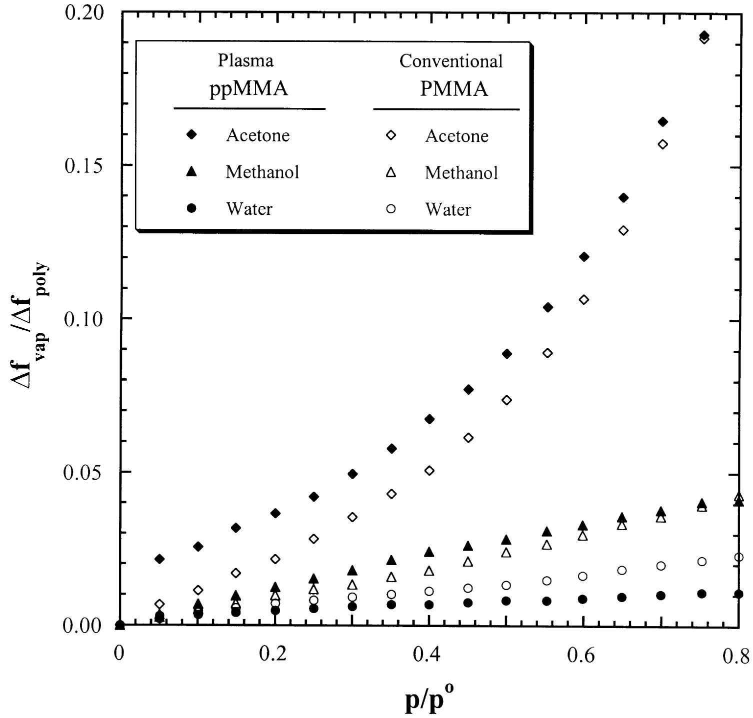

Fig. 5. Vapor sorption isotherms of conventional PMMA (open symbols) and plasma polymerized MMA (filled symbols) at 30°C. (Note: Hexane isotherms are removed for clarity.)

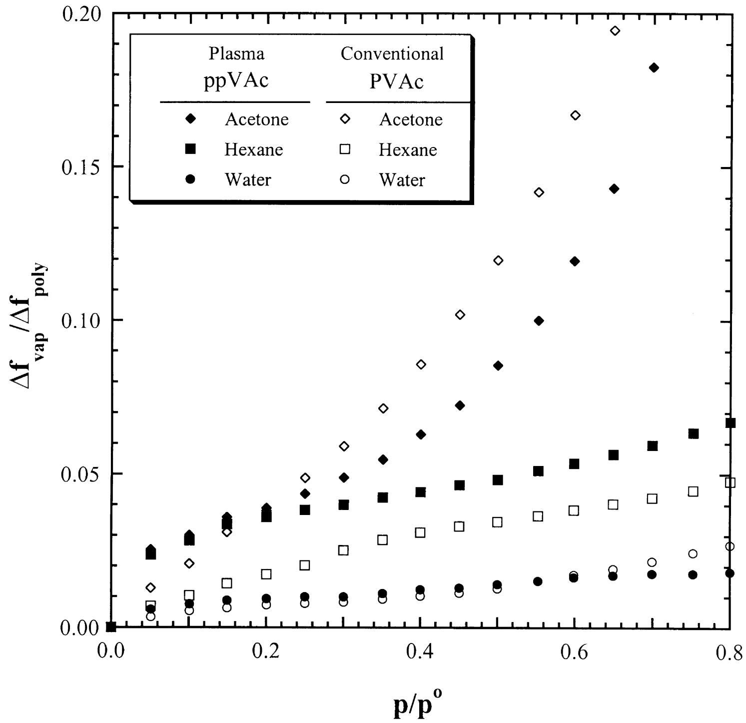

Fig. 6. Vapor sorption isotherms of conventional PVAc (open symbols) and plasma polymerized VAc (filled symbols) at 30°C. (Note: Methanol isotherms are removed for clarity.)

isotherms for both conventional and plasma polymer materials exhibit significant upswing in sorption level, characteristic of Flory–Huggins-type sorption or penetrant clustering in the plasma polymer matrix.

4.3. Sorption modeling in plasma polymers

In this section, the Dual-Mode and Flory–Huggins models are applied to the vapor sorption isotherms to assess two main points: (1) whether the model parameters observed for the conventional polymer systems using the QCM technique agree with those expected from the literature and (2) whether reasonable model parameters noted for conventional polymers can account for the observed sorption behavior of the plasma polymer systems.

4.3.1. Dual-mode analysis

Table 1 contains the parameters for fitting the Dual-Mode sorption model (Eq. (3)) to the polymer sorption isotherms presented in Figs. 5 and 6. Typical Dual-Mode modeling results are shown in Fig. 7 for plasma-polymerized MMA (ppMMA). The model accounts for the Langmuir-type component at low activity and the linear increase in sorption with increasing activity. The upward curvature observed with acetone sorption will be addressed with Flory–Huggins analysis later.

The application of the three-parameter Dual-Mode model to such limited data sets has some obvious limitations. Since the isotherms shown in Figs. 5 and 6 contain very little data regarding the approach to saturation, insight into the Dual-Mode affinity term b is obscured. For this work, k_D and $C_H{}'$ are derived from regression analysis after constraining the Langmuir affinity term b to reasonable values expected for sorption in glassy polymers. Values employed for b are 0.5 mmHg^{-1} for the water isotherms and 0.1 mmHg^{-1} for the three other vapor systems. With unconstrained non-linear regression analysis, several isotherms yield affinity parameters (b values) near those adopted as the constraints. However, non-convergence is encountered with some isotherms, thus the constraint of the affinity term b to a reasonable value is necessary. The affinity term has been shown to correlate well with the Lennard-Jones potential and/or critical temperature of the sorbent [14,25]. Affinity parameters of 0.05 mmHg^{-1} for methanol in PMMA [23], 0.1 mmHg^{-1} for acetone in PET [25], and 0.2 mmHg^{-1} for benzene in PET [24], suggest that values for b near 0.1 mmHg^{-1} are reasonable estimates for modeling vapor sorption in glassy polymer systems. Adjusting the constrained b term through the range of 0.05–0.5 mmHg^{-1} leads to changes in the estimates for k_D and C'_H on the order of ±25%, which does not appear to influence the general trends noted in Table 1. The higher affinity parameter required for a reasonable fit of the water sorption isotherms points to a potential source of error, which will be discussed below.

As shown in Table 1, the Henry's Law solubility

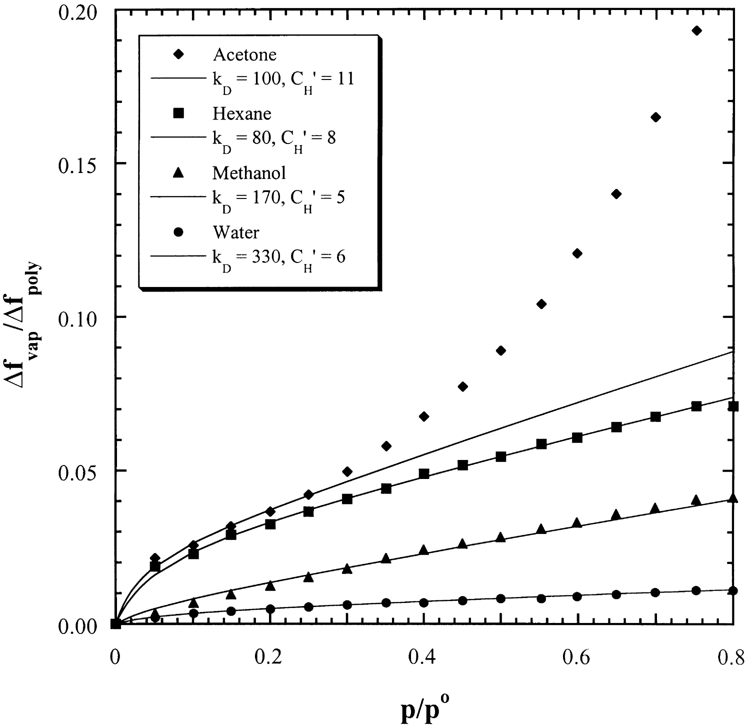

Fig. 7. Dual-Mode modeling of vapor sorption isotherms of plasma polymerized methyl methacrylate (MMA) at 30°C. (Note: $b = 0.5\ \mathrm{mmHg}^{-1}$ for the water isotherms and $0.1\ \mathrm{mmHg}^{-1}$ for acetone, methanol and hexane).

coefficients of the plasma polymers ($k_{\mathrm{D\ plasma}}$) agree quite well with those measured for the conventional polymer analogs ($k_{\mathrm{D\ conv}}$). The Henry's Law solubility coefficients for virtually every conventional/plasma polymer pairing differ by less than a factor of two with several being essentially equivalent. At the same time, the k_{D} values derived from the conventional polymer sorption isotherms also show good agreement with those expected from the literature ($k_{\mathrm{D\ lit}}$). The $k_{\mathrm{D\ lit}}$ values differ from those measured for the conventional polymers by less than a factor of two, which is notably in good agreement between these different sources. From Dual-Mode analysis, Connelly et al. measured a k_{D} value of 130 (cm^3 (STP)/cm^3(poly)atm) for methanol in PMMA; however, the apparent solubility coefficient increased by roughly a factor of two when full relaxation was allowed to occur [23]. These results are in accord with the MMA–methanol solubility coefficients reported in Table 1 and demonstrate the range of values, which can be encountered with such measurements.

In Table 1, the Langmuir-type capacity parameters (C'_{H}) for the plasma polymerized materials range between 5 and 22 cm^3 (STP)/cm^3 (poly). With the exception of the polymer–water isotherms, the Langmuir-type model parameters for the plasma polymers are 5–20-fold higher than those measured for the conventional polymer analogs. Similar differences have been observed previously in a comparison of plasma polymerized and conventional poly(styrene) [10]. By graphical analysis of the data in Ref. [10], the C'_{H} parameter for CO_2 in plasma-polymerized styrene is 11 cm^3(STP)/cm^3(poly) and that for conventional poly(styrene) is 5 cm^3(STP)/cm^3(poly).

Although higher than the capacity parameters measured for the conventional polymer analogs, the range of C'_{H} parameters for plasma polymer materials are within the range of values reported for vapor sorption in other glassy polymers. For example, C'_{H} capacity parameters for carbon dioxide sorption in glassy polymers range from 0 to 30 cm^3(STP)/cm^3(poly) [14]. Since the condensed molar volumes of the vapors used in this study are similar to that of CO_2 (46 cm^3/mol [15]), similar magnitudes of C_{H}' parameters would be expected if indeed the hole-filling mechanism governs the sorption process. Additionally, a C'_{H} of 7.0 cm^3(STP)/cm^3(poly) has been reported for methanol in PMMA [23]. While this value is substantially higher than that reported for methanol–PMMA in this work, the authors observed that the Langmuir component diminished significantly when equilibrium relaxation was allowed to occur at each activity [23]. In comparison, the small Langmuir component observed following relaxation is in very good agreement with the small values observed for the PMMA films studied in this work. Other Dual-Mode analysis for vapor sorption in glassy poly(ethylene terephthalate) (PET) has yielded C'_{H} parameters of 1.7 and 7.2 cm^3(STP)/cm^3(poly) for benzene and acetone, respectively [24,25].

In all cases, both for this work and that of previous authors [10], plasma polymer films exhibit an enhanced Langmuir-type sorption capacity over that observed for

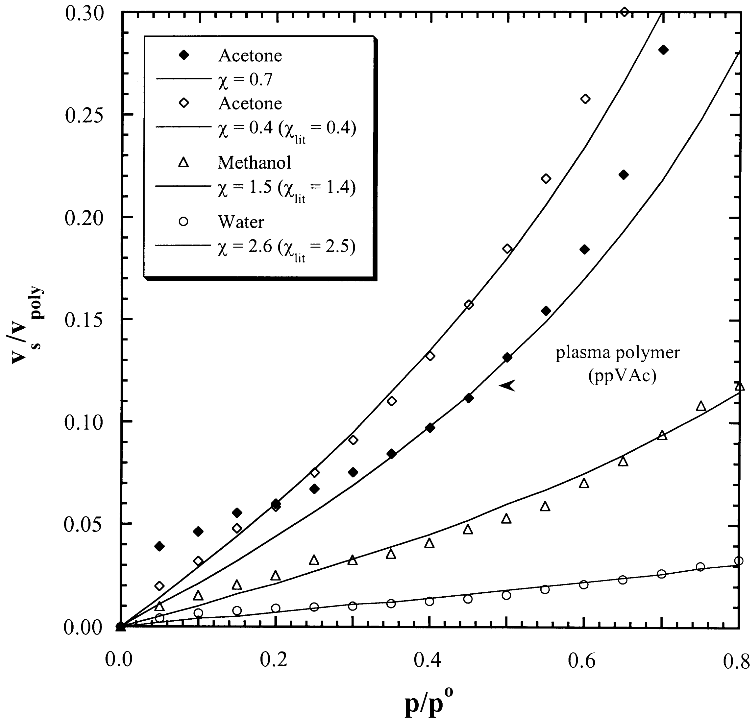

Fig. 8. Flory–Huggins modeling of vapor sorption isotherms for poly(vinyl acetate) (PVAc) (open symbols) and plasma polymerized vinyl acetate (ppVAc) (filled symbols).

conventional polymer analogs. At the same time, the enhancement of fixed-site sorption capacity is still within the range of values expected for glassy polymers. The enhancement is also consistent with observed trend of increasing C'_{H} values with increasing glass transition temperature, which may accompany the highly crosslinked nature of these materials [14]. These observations, combined with the close agreement of the observed Henry's Law parameters for both conventional and plasma polymers, suggest that low wattage plasma polymers may be viewed as more "glassy" versions of the conventional polymer analogs. At this point, systematic analysis of the hysteretic sorption phenomena typically associated with glassy polymers has not been performed [15]. However, it can be stated that over the course of this work, the plasma polymer sorption isotherms and attendant Langmuir component have been highly reproducible and stable with time.

The fact that the analysis leads to relatively small Langmuir-type hole-filling contributions in a rubbery material such as conventional PVAc suggests that there are distinct errors with this methodology. A small amount of surface adsorption is observed on uncoated quartz crystal surfaces, which likely persists on uncoated areas following the coating procedure. These apparent surface adsorption contributions are more pronounced in low sorption level isotherms such as water and lead to larger b and C_{H}' Dual-Mode model parameters. However, the magnitude of this error does not detract from the general trends noted in this work.

4.3.2. Flory–Huggins analysis

Flory–Huggins analysis of the conventional and plasma polymer sorption isotherms is summarized in Table 2. Fig. 8 contains the typical result of Flory–Huggins modeling of several isotherms for conventional PVAc and plasma-polymerized VAc. Analysis of the three PVAc isotherms in Fig. 8 yields best-fit χ values of 0.4, 1.5 and 2.6 for acetone, methanol and water. As shown in Table 2, these values are in excellent agreement with the literature χ values of 0.4, 1.4 and 2.5 [17–19]. In fact, for both the PMMA and PVAc materials, the χ parameters derived from the conventional polymer sorption isotherms fall near the expected values obtained from the literature [9,17–19]. This agreement is generally true for the plasma-polymerized materials; however, the regression coefficients suffer markedly due to the dominant Langmuir character at low vapor activity. Like the analysis of Barens [21,22], χ has been adjusted such that the predicted sorbent volume fraction most nearly approximates the high activity regime, thus avoiding the Langmuir contribution at low activity. The failure to capture the Langmuir component is clearly evident in the modeling of ppVAc–acetone isotherm in Fig. 8. By removing the Langmuir-type contributions quantified by Dual-Mode analysis from the sorption isotherms, Flory–Huggins modeling of the plasma polymers yields near-perfect fits.

For the acetone isotherms, it is difficult to capture the high activity regime using the simple Flory–Huggins analysis. This underestimate of sorption level may be due to changes in the visco-elastic nature of the films at these high loadings resulting in a non-linear frequency damping with mass uptake [26].

5. Conclusions

Sorption models routinely used with conventional glassy polymers appear to loosely predict sorption behavior of low-power plasma polymer materials. Although the sorption isotherms for both conventional and plasma polymers are similar in magnitude, there exist observable differences. Specifically, the isotherms measured for plasma polymers exhibit an enhanced Langmuir-type sorption component at low activities. When Dual-Mode analysis is employed, both plasma polymers and conventional analogs exhibit similar Henry's Law solubility coefficients (k_D). However, the corresponding Langmuir-type fixed-site sorption capacity ($C_H{}'$) parameters in plasma polymers are 5–20-fold higher than those for the conventional polymer analogs. The enhanced fixed-site sorption contributions observed for the plasma polymers are within the range of those reported for Dual-Mode modeling of vapor sorption in other glassy polymers. From the work to date, analysis of the sorption isotherms suggests that the plasma polymer materials may be regarded as more "glassy" versions of the conventional polymer analogs.

Future work will focus on the hysteretic behavior of these isotherms to elucidate any aging phenomena typically associated with glassy polymer systems. Following such analysis, more definitive statements can be made about whether the observed Langmuir-type component is indeed that normally ascribed to vapor sorption in conventional glassy polymer materials. Establishing definitive sorption models and elucidating any hysteresis associated with aging and dilation are two critical steps for integrating plasma polymer films into microsensor technologies. In addition to the findings described above, the validity of the QCM technique has been demonstrated through general agreement of the measured conventional polymer sorption isotherms with those expected from the literature.

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