

Moisture Diffusion Properties of HFPE-II-52 Polyimide

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Received 9 August 2005; accepted 27 March 2006

DOI 10.1002/app.24549

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Moisture diffusion properties of the polyimide HFPE-II-52 were determined using weight gain, weight loss, and swelling experiments over a temperature range of 25–200°C. Below 100°C, diffusivity was measured using standard weight loss and weight gain methods. Above 100°C, diffusivity is found by weight loss experiments performed by placing moisture saturated samples in an oven and recording weight loss dynamically. The diffusivity of the polyimide was found to obey the Arrhenius relation over the entire range of

temperature. Weight gain experiments were performed to determine the equilibrium level of moisture absorbed by the polyimide as a function of relative humidity. Swelling experiments were performed to measure swelling strain as a function of moisture absorption. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3471–3479, 2006

Key words: polyimides; diffusion; swelling; glass transition; activation energy

INTRODUCTION

Polyimides are an important class of polymers due to their high glass transition temperatures and outstanding thermal stability. These properties make them ideal for use in high temperature applications, either as a pure polymer or as the matrix in high temperature polymer matrix composites (PMC). Proposed applications of high temperature PMCs include components of rocket engines^{1–6} and advanced turbine engines.^{7,8} For modeling and design of polyimide-based parts, it is important to know the moisture diffusion properties, since absorbed moisture can affect mechanical properties, cause swelling, and lead to popcorning^{9,10} or delamination¹ under conditions of rapid heating.

Diffusivity and equilibrium weight gain as a function of temperature and relative humidity are measured for the polyimide HFPE-II-52, a material developed at NASA Glenn Research Center for high temperature PMCs.¹¹ HFPE-II-52 has a glass transition temperature of $\sim 350^\circ\text{C}$.¹² The moisture diffusion properties were found by performing weight gain and weight loss experiments over a wide range of temperature and relative humidity conditions. Diffusivity below 100°C was found by performing weight gain

and weight loss experiments using standard methods.^{13,14} Above 100°C, diffusivity is found using weight loss experiments performed by placing moisture saturated samples in an oven and recording weight loss dynamically. In this manner, diffusivity was determined over the temperature range of 25–200°C and an Arrhenius relation was obtained by fitting $\ln D$ versus T^{-1} , as is typical for polymers.^{1,15,16} Weight gain as a function of relative humidity was found by performing equilibrium weight gain experiments at different relative humidities. The Guggenheim-Anderson-de-Boer (GAB) equation was used to model the relation weight gain and relative humidity.

Swelling experiments were performed to determine swelling strain as a function of water absorption. Swelling due to moisture absorption in the matrix of a composite can lead to detrimental residual stresses^{17,18} and to bending and twisting of laminates.¹⁹ Swelling strain was found to be linear with mass gain. The percentage change in the polymer volume because of swelling was plotted against the volume of moisture absorbed and an estimate of the free volume was obtained.

THEORY AND DATA REDUCTION

Diffusivity, D is generally measured by exposing a dry sample to a humid environment and measuring the mass of water absorbed, i.e., the weight gain, as a function of time. The measured weight gain is then fit to the solution to the diffusion equation (Fick's law) to determine D . One can also start with a sample that has already been saturated with moisture

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Contract grant sponsor: NASA; contract grant number: NCC3-994.

Contract grant sponsor: National Science Foundation Materials Research Science and Engineering Center Program; contract grant number: DMR-0520404.

and allow it to dry out, measuring the weight loss as a function of time.

In either case, for an isotropic, homogenous material with a concentration independent diffusivity, the three dimensional Fick's law takes the form:²⁰

$$\frac{\partial \psi}{\partial t} = D \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) \quad (1)$$

where x , y , and z are rectangular spatial coordinates, t is the time, and $\psi(x, y, z, t)$ is the concentration of water inside the polymer.

The standard method¹⁴ for determining D is based on the solution to the one-dimensional diffusion problem. This solution is applicable only when the test sample is very thin; the ASTM standard requires that the in-plane dimension to thickness ratio be 100 : 1. The sample size required by the ASTM standard to determine D is not always possible because of material cost and production issues. In addition, the standard bases the determination of D only on the initial slope of the weight gain or weight loss measurements.

These requirements can be relaxed if one interprets the data in the context of the fully 3D solution to eq. (1). The 3D solution presented here is available in standard texts²⁰⁻²² and mentioned here for review purposes only.

For the initial conditions,

$$\psi = \psi_0 \quad \text{at } t = 0 \quad \text{for } 0 < x < l, 0 < y < w, 0 < z < h \quad (2)$$

and the boundary conditions,

$$\psi = \psi_\infty \quad \text{at } t > 0 \quad \text{for } x = 0, l; y = 0, w; z = 0, h \quad (3)$$

where l and w are in-plane dimensions, and h is the thickness as shown in Figure 1, the solution to eq. (1) can be written as,^{21,22}

$$\psi(x, y, z, t) = \psi_0 + g(x, y, z, t)(\psi_\infty - \psi_0)$$

$$\begin{aligned} g(x, y, z, t) &\equiv \frac{\psi(x, y, z, t) - \psi_0}{\psi_\infty - \psi_0} \\ &= 1 - \left(\frac{4}{\pi} \sum_{n=1,3}^{\infty} \frac{1}{n} \sin \left[\frac{n\pi x}{h} \right] \exp \left[\frac{-Dn^2\pi^2 t}{h^2} \right] \right) \\ &\quad \left(\frac{4}{\pi} \sum_{n=1,3}^{\infty} \frac{1}{n} \sin \left[\frac{n\pi y}{w} \right] \exp \left[\frac{-Dn^2\pi^2 t}{w^2} \right] \right) \\ &\quad \left(\frac{4}{\pi} \sum_{n=1,3}^{\infty} \frac{1}{n} \sin \left[\frac{n\pi z}{l} \right] \exp \left[\frac{-Dn^2\pi^2 t}{l^2} \right] \right) \quad (4) \end{aligned}$$

Integration of eq. (4) over the plate volume gives weight gain in the form,

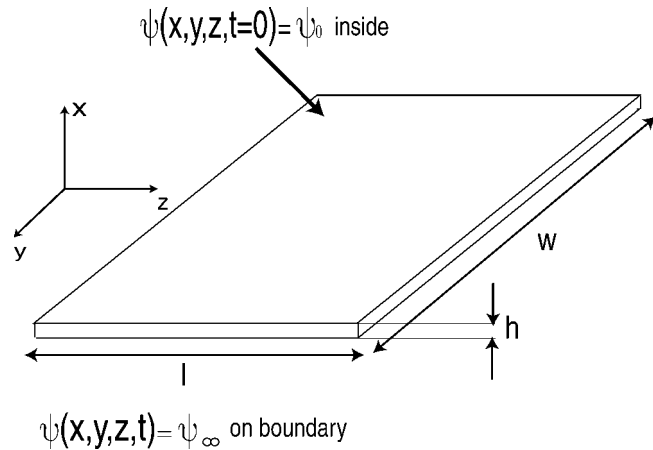


Figure 1 Sketch of 3D moisture diffusion problem for a plane sheet. For weight gain and weight loss experiments, $l = 20$ mm, $w = 20$ mm, and $h = 1$ mm.

$$M(t) = M_0 + G(t)(M_\infty - M_0) \quad (5)$$

where

$$\begin{aligned} G(t) &\equiv \frac{M(t) - M_0}{M_\infty - M_0} \\ &= 1 - \left(\frac{8}{\pi^2} \sum_{n=1,3}^{\infty} \frac{1}{n^2} \exp \left[\frac{-Dn^2\pi^2 t}{h^2} \right] \right) \\ &\quad \left(\frac{8}{\pi^2} \sum_{n=1,3}^{\infty} \frac{1}{n^2} \exp \left[\frac{-Dn^2\pi^2 t}{l^2} \right] \right) \\ &\quad \left(\frac{8}{\pi^2} \sum_{n=1,3}^{\infty} \frac{1}{n^2} \exp \left[\frac{-Dn^2\pi^2 t}{w^2} \right] \right) \quad (6) \end{aligned}$$

In the case that (h/l) and (h/w) are less than ~ 0.25 , eq. (6) can be approximated by¹⁶

$$G(t) = 1 - \frac{8}{\pi^2} \left(1 - 4\sqrt{\frac{t^* h^2}{\pi l^2}} \right) \frac{8}{\pi^2} \left(1 - 4\sqrt{\frac{t^* h^2}{\pi w^2}} \right) \sum_{n=1,3}^{\infty} \frac{1}{n^2} \exp[n^2\pi^2 t^*] \quad (7)$$

where $t^* = Dt/h^2$. A nonlinear least squares fit of eq. (7) using six terms in the summation was fit to the experimentally measured $G(t)$ to determine D . The diffusivity obtained by using more than six terms in eq. (7) does not show any significant change.

EXPERIMENTAL SETUP AND PROCEDURE

The test samples were cut from HFPE-II-52 polyimide resin plates fabricated by compression molding for 2 h at 172 atm part pressure and 377°C. Details of the fabrication can be found in Refs. 23 and 24. Five plates were

prepared with the exact same procedure and are labeled as Plate 1–Plate 5 in this text. The test samples used for the weight gain and weight loss experiments have dimensions 20 mm × 20 mm × 1 mm.

Weight gain and weight loss experiments below 100°C

For the weight gain experiments, samples were first dried in a vacuum chamber at 25°C until an equilibrium weight was reached. The dry specimens were then placed in a temperature and relative humidity controlled environmental chamber. Specimens were removed at intervals of 20–360 min and weighed using a Mettler-Toledo, AG-280, 10 µg resolution microbalance.

For the weight loss experiments, samples were first saturated at 25°C and 95% RH using an environmental chamber. The saturated samples were then placed in a vacuum oven for drying. Specimens were removed at intervals of 20–360 min to measure weight using the microbalance.

Weight loss at temperatures above 100°C

For weight loss at higher temperatures, the samples were first saturated at 25°C; 95% RH using an environmental chamber. The saturated specimens were then placed in an oven and weight loss was recorded dynamically using the microbalance. The experimental set up is shown in Figure 2. Three fin-type air heaters in the oven ensure that the sample, placed in the center in a sample basket (Fig. 2), is heated uniformly. The dimensions and shape of the sample basket are

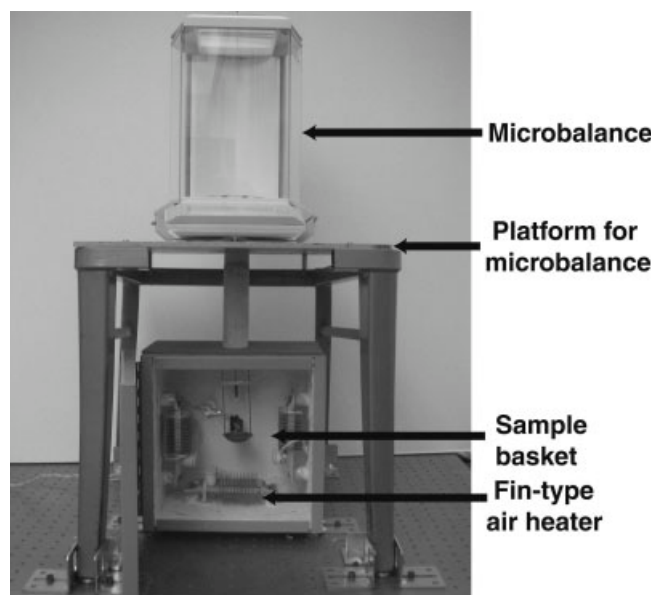


Figure 2 Experimental setup for measuring weight loss at higher temperatures.

such that only the corners of the sample touch the sample basket. This ensures that the sample loses weight evenly from all the sides during the experiment. A steel wire connecting the sample basket to the microbalance passes through a small hole on the top of the oven. The microbalance is interfaced with a computer to acquire data at rates up to 1 datapoint/s. Hot air escaping from the hole at the top of the oven pushes up against the sample basket and causes buoyancy effects such that the sample appears to weigh less at higher temperatures. To account for buoyancy, the oven was brought up to the test temperature and the reading of the microbalance was zeroed just before the sample was installed for weight loss measurements. Although placing the sample inside the basket changes the surface area over which buoyancy is acting and thus changes the buoyant force, this difference was measured to be less than 0.1% of the sample weight. The escaping hot air also creates currents inside the oven causing fluctuations in the microbalance readings. These were smoothed using a simple, 20-point moving average algorithm.

Swelling measurements

For the swelling experiments, six 65 mm × 2.5 mm × 4.0 mm samples were cut from the same plate to provide data on the variability on swelling within the plate. Samples were first dried in a vacuum oven at 70°C and their dry lengths at room temperature were recorded. The samples were then saturated at different relative humidities and the change in length was measured along the maximum dimension. A digital indicator with a resolution of 2×10^{-3} mm was used to measure the dry and moist sample lengths. Five different relative humidities of RH (20, 40, 60, 80, 100%) were selected to perform the experiment. The temperature of conditioning at RH of 20, 40, 60, and 80% was 85°C and was 65°C at RH of 100%. Samples were allowed to cool down to room temperature before measuring the swelling strain. Since it was found through weight gain experiments that equilibrium weight gain was not a function of temperature, it is expected that the temperature at which the samples are conditioned is not significant in contrast to systems where temperature of conditioning can be important.^{25,26}

RESULTS

Weight gain experiments

Effect of removing sample from environmental chamber on results

We first investigate whether the periodic interruption in moisture absorption caused by removing the samples from the environmental chamber for weighing affects the results to a measurable degree. To do so,

TABLE I
Percentage Weight Gained by Samples
for Given Number of Hours

Sample number	Weight gain (in %)				
	2 (h)	6 (h)	20 (h)	24 (h)	50 (h)
1a	0.49	0.92	1.27	1.31	1.39
1b	–	0.88	1.26	1.28	1.36
1c	–	–	1.27	1.36	1.41
1d	–	–	–	1.35	1.41

Data shows that the effect of removing samples from environmental chamber is negligible.

four samples were saturated at 25°C, 50% RH, and were removed for weighing at various intervals. The results are tabulated in Table I. While samples 1a, 1b, and 1c were taken out at different intervals of time for weight measurement, sample 1d was not disturbed at all. Comparing percentage weight gain at 24 and 50 h shows that the effect of removing the samples 1a, 1b, and 1c from the environmental chamber is negligible.

This is reasonable since the total duration of removal is small, ~ 1 min per measurement, compared to the time taken by the sample to saturate, ~ 3–4 days at 25°C and 1/2 day at 85°C. The number of readings taken during the entire saturation period is about 20. Similar observations have been made in previous experiments.¹⁶

Diffusivity versus temperature

Diffusivity was measured at four temperatures (25, 50, 75, and 85°C). Data from four weight gain experiments performed at $T = 25^\circ\text{C}$, $\text{RH} = 95\%$ are shown in Figure 3 where normalized weight gain, $G(t)$, is plotted against $t^{1/2}/h$. Diffusivity for each sample was determined by fitting the data to eq. (7). Also shown in Figure 3 is the

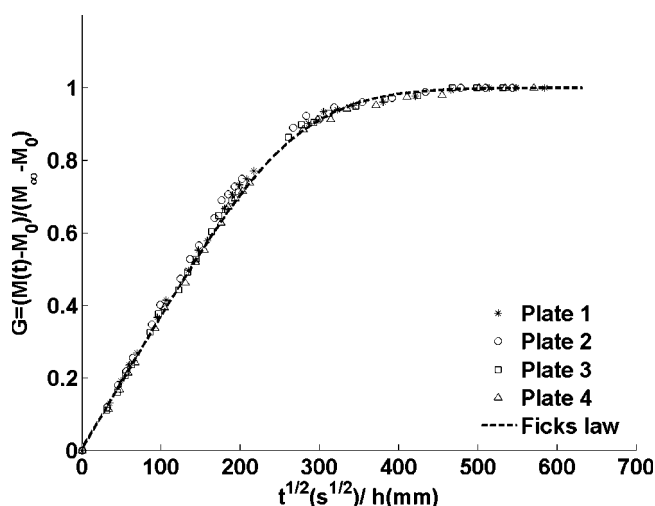


Figure 3 Weight gain data for four different plates at $T = 25^\circ\text{C}$, $\text{RH} = 95\%$. Fick's law is a good fit to experimental data.

TABLE II
Diffusivity Values for Different Temperatures
Determined by Weight Gain Experiments

T (°C)	D (mm^2/s)					SD
	Plate 1	Plate 2	Plate 3	Plate 4	Average	
25	2.55e-6	2.70e-6	2.46e-6	2.36e-5	2.51e-6	1.44e-7
50	7.81e-6	7.46e-6	7.22e-6	8.01e-6	7.62e-6	3.53e-7
75	2.33e-5	1.89e-5	1.98e-5	2.00e-5	2.05e-5	1.96e-6
85	2.88e-5	2.98e-5	2.86e-5	3.13e-5	2.96e-5	1.21e-6

Fick's law fit to the data with $D = 2.55 \times 10^{-6} \text{ mm}^2/\text{s}$. Good agreement is found between the experimental and theoretical (Fick's law) results.

To estimate the variability in diffusivity, tests were performed with samples cut from four different plates. Table II shows the diffusivity values obtained from each experiment along with the average values and standard deviations. The data can be collapsed to a single curve, or master plot, by plotting $G(t)$ versus \sqrt{Dt}/h^2 as in Figure 4. That the experimental data collapse to a single curve shows that Fick's law is a good model for diffusion over the 25–85°C temperature range.

Equilibrium weight gain versus temperature

The dependence of equilibrium weight gain on temperature was investigated using the data from the diffusivity experiments. Table III shows the data for

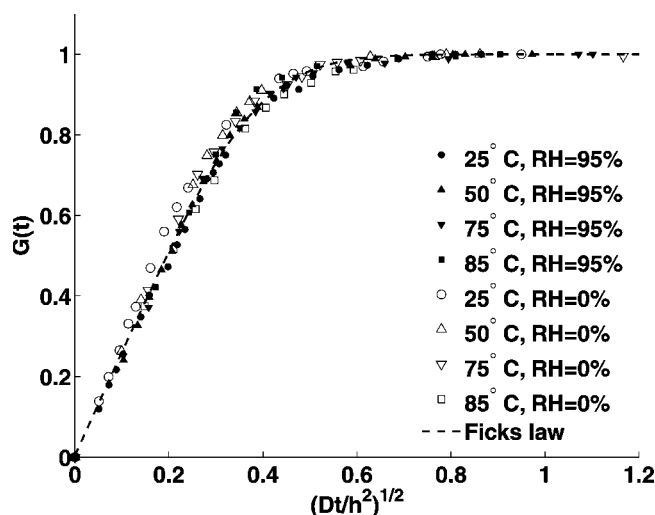


Figure 4 Master plot for weight gain and weight loss experiments. For weight gain experiments, closed symbols, $G(t) = \text{normalized weight gain} \equiv (M(t) - M_0) / (M_\infty - M_0)$ where $M(t) = \text{weight at time } t$, $M_0 = \text{weight when sample is fully dry}$, $M_\infty = \text{weight when sample is fully saturated}$. For weight loss experiments, open symbols, $G(t) = \text{normalized weight loss} \equiv (M_0 - M(t)) / (M_0 - M_\infty)$ where $M(t) = \text{weight at time } t$, $M_0 = \text{weight when sample is fully saturated}$, $M_\infty = \text{weight when sample is fully dry}$.

TABLE III
Percentage Weight Gain and Temperature at RH = 95%

T (°C)	Plate 1	Plate 2	Plate 3	Plate 4	Average	SD
25	3.03	3.09	2.99	3.04	3.04	0.039
50	3.13	3.05	3.05	3.11	3.08	0.045
75	3.07	2.96	2.99	3.07	3.02	0.059
85	3.05	3.05	3.03	3.05	3.05	0.008

Results show that equilibrium weight gain is independent of temperature.

percentage weight gain at RH = 95% at different temperatures. The results show that equilibrium weight gain is independent of temperature.

Equilibrium weight gain versus relative humidity

The sorption behavior of the polyimide was investigated at 25°C, under different relative humidities. Six RH conditions (20, 40, 60, 80, 95, and 100%) were selected and equilibrium weight gain was obtained as a function of RH. To estimate the variability, the tests were performed with samples cut from four different plates. The equilibrium weight gain of the samples versus relative humidity is plotted in Figure 5. Note that the maximum weight gain is 3.2% and the curve is concave upwards. Several models were investigated to interpret the data.

If the absorption of water in the polymer followed Henry's law,²⁷ a behavior that some authors argue must occur,²⁸ then equilibrium weight gain and relative humidity would be related linearly though the equation:

$$M_{\infty} = a \left(\frac{\text{RH}}{100} \right) \quad (8)$$

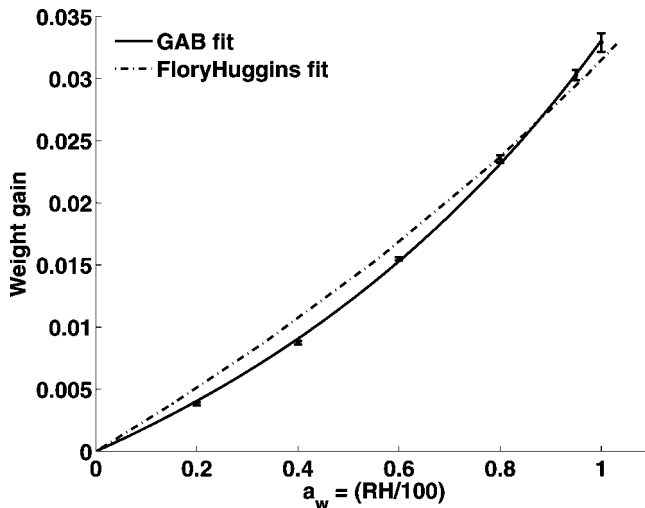


Figure 5 Weight gain and relative humidity, for GAB fit: $M_m = 0.352$ (kg water)/(kg dry basis), $A = 0.28$ and $C = 0.18$. For Flory-Huggins fit: $\chi = 2.36$.

where M_{∞} is the weight gain and α is a constant. Since the weight gain was found to be independent of temperature, the constant α would be independent of temperature. However, it is clear from Figure 5 that a simple linear relation between equilibrium weight gain and RH, as predicted by Henry's law is insufficient to model the data. Deviation from Henry's law indicates a concentration dependent interaction of water molecules with the polymer chains potentially leading to a concentration dependent diffusivity.²⁹

The sorption isotherm of small molecules in many glassy polymers including various polyimides³⁰ is concave down at low RH and is generally described by the dual absorption model.^{30–32} The upward curvature seen in Figure 5 for HFPE-II-52 indicates that the water sorption did not go through a distinguishable Langmuir or Henry's sorption phase. Such upward curvature is sometimes attributed to swelling of the polymer which may cause exposure of more sites for increased water sorption³³ or cluster formation of water molecules inside the polymer.^{34,35}

The Flory-Huggins equation³⁶ was also investigated to model the isotherm at 25°C:

$$\ln a_w = \ln \phi_w + (1 - \phi_w) + \chi(1 - \phi_w)^2 \quad (9)$$

where a_w and ϕ_w are the water activity and volume fraction of water in the polymer, respectively, and χ is the polymer-solvent interaction parameter. In calculating ϕ_w , the additivity of the volumes is assumed. A best fit to the data based on eq. (9) with $\chi = 2.36$ is shown in Figure 5. It is clear that the Flory-Huggins model does not fit the data well. It is based on the assumption of random mixing and does not take into account the presence of specific interactions between the sorbate (water) and the sorbant (polymer).

The sorption isotherm of water is also modeled using the GAB equation,³⁷

$$M_{\infty} = \frac{M_m A C a_w}{(1 - A a_w)(1 - A a_w + A C a_w)} \quad (10)$$

where M_{∞} is the weight gain, a_w is the water activity, M_m is the monolayer moisture content, and A and C

TABLE IV
Diffusivity and Relative Humidity at $T = 25^\circ\text{C}$

RH	D (mm ² /s)					
	Plate 1	Plate 2	Plate 3	Plate 4	Average	SD
35	2.88e-6	2.94e-6	2.52e-6	2.44e-6	2.69e-6	2.18e-7
50	2.66e-6	2.54e-6	2.79e-6	2.55e-6	2.64e-6	1.01e-7
75	2.88e-6	2.94e-6	2.52e-6	2.44e-6	2.69e-6	2.18e-7
85	2.75e-6	2.43e-6	2.92e-6	2.69e-6	2.69e-6	1.75e-7
95	2.55e-6	2.70e-6	2.46e-6	2.36e-6	2.51e-6	1.25e-7

Results show that diffusivity is independent of relative humidity.

TABLE V
Diffusivity Values for Different Temperatures Determined by Weight Loss Experiments at Lower Temperatures

T (°C)	D (mm ² /s)				Average	SD
	Plate 1	Plate 2	Plate 3	Plate 4		
25	2.86e-6	2.61e-6	2.83e-6	2.75e-5	2.76e-6	1.10e-7
50	8.26e-6	7.87e-6	8.73e-6	9.71e-6	8.64e-6	7.93e-7
75	2.17e-5	2.04e-5	2.01e-5	1.96e-5	2.05e-5	8.89e-7
85	2.31e-5	2.34e-5	2.57e-5	2.96e-5	2.55e-5	2.29e-6

are constants related to heat of sorption.³⁷ Since the weight gain was found to be independent of temperature, the constants A and C are independent of temperature. Fitting the data to eq. (10), the coefficients were found to be $M_m = 0.352$ (kg water)/(kg dry basis), $A = 0.28$ and $C = 0.18$. The GAB equation, as seen in Figure 5, fits the data well.

Diffusivity versus relative humidity

Because of the non-Henrian behavior shown by HFPE-II-52 in water sorption, the dependence of the diffusivity on relative humidity was also investigated. Dry samples were moisture saturated at constant temperature and different relative humidities. Table IV shows the data for diffusivity at $T = 25^\circ\text{C}$ at different relative humidities. The results show that the diffusivity is independent of RH.

Weight loss below 100°C

To check that diffusivity from weight loss and weight gain are the same, weight loss measurements were performed at 25, 50, 75, and 85°C. To estimate variability, the tests were performed with samples cut from four different plates. Diffusivity was determined by fitting the solution given by eq. (7) to the experimental data. Table V shows the diffusivity values obtained from experiments along with the average values and standard deviations. As with the

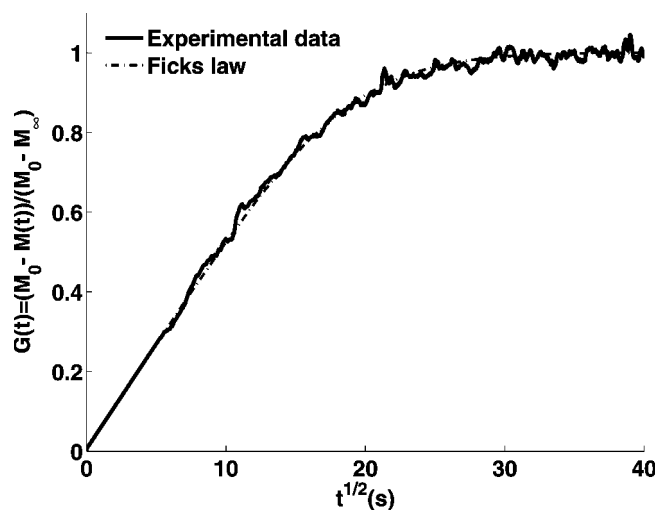


Figure 6 Typical data for weight loss experiment using the oven. Normalized weight loss versus $t^{1/2}$ at $T = 200^\circ\text{C}$.

weight gain results, the data can be collapsed onto a single curve by plotting $G(t)$ versus $\sqrt{Dt/h^2}$ (Fig. 4). Good agreement is seen between the experimental data and Fick's law.

Equivalence of weight gain and weight loss experiments

The diffusivities obtained from weight gain (Table II) and weight loss experiments (Table IV) for the same temperatures are close to each other. In addition, Figure 4 shows that both experiments show good agreement with each other and with Fick's law. Hence weight gain and weight loss experiments were considered to be equivalent. Similar observations have been made for several other polymer systems where diffusivity obtained through weight gain and weight loss experiments were found to be same.¹³ Deviations from Fick's law are observed in hydrophilic polymers during sorption of water and in most polymers during sorption of organic vapors.^{38,39}

TABLE VI
Diffusivity Values for Different Temperatures Obtained by Performing Weight Loss Experiments Using the Oven

T (°C)	D (mm ² /s)					Average	SD
	Plate 1	Plate 2	Plate 3	Plate 4	Plate 5		
95	–	7.78e-05	6.10e-05	7.13e-05	–	7.00e-05	8.50e-06
100	–	7.83e-05	–	7.26e-05	9.85e-06	5.36e-05	3.80e-05
105	1.09e-04	9.84e-05	8.72e-05	–	–	9.81e-05	1.07e-05
110	–	1.55e-04	–	1.46e-04	1.63e-04	1.55e-04	8.78e-06
125	1.25e-04	1.15e-04	1.37e-04	1.49e-04	–	1.32e-04	1.50e-05
150	1.94e-04	1.97e-04	2.20e-04	2.11e-04	–	2.06e-04	1.19e-05
175	3.52e-04	2.99e-04	3.50e-04	3.30e-04	3.56e-04	3.37e-04	2.35e-05
200	4.60e-04	7.02e-04	4.40e-04	5.92e-04	5.95e-04	5.58e-04	1.08e-04

Weight loss at temperatures near and above 100°C

As discussed earlier, over the temperature range of 95–200°C, diffusivity was measured by drying samples in an oven and recording the weight loss dynamically. When the sample is first placed in the preheated oven, during the time it takes the sample to equilibrate to the oven temperature, D is varying. Hence to determine D for a fixed temperature, the data from the first 30 s were discarded. The remaining data are initially linear with respect to $t^{1/2}$. The linear portion of the data was extrapolated back to zero weight loss and then all the data were shifted in time so that the extrapolated curve starts at $t = 0$. An example is shown in Figure 6 where normalized weight loss is plotted against shifted time, $t^{1/2}$. As discussed previously, the resulting $G(t)$ data were fit to eq. (7) to determine D . Table VI shows the diffusivity values obtained using the oven along with the average values and standard deviations.

Diffusivity over 25–200°C

The entire set of diffusivity values, determined from weight gain and weight loss experiments below 100°C and from dynamic weight loss experiments above 100°C, were used to determine $D(T)$. Diffusivity follows the Arrhenius equation,

$$D = D_0 e^{[-E_a/RT]} \quad (11)$$

where E_a is the activation energy, R is the Universal gas constant, and D_0 is a constant. Plotting all of the data as $\ln D$ versus T^{-1} in Figure 7 and fitting a straight line, the parameters $D_0 = 9.0 \pm 2.4 \text{ mm}^2/\text{s}$ and $E_a = 37.0 \pm 2.8 \text{ kJ/mol}$ were found.

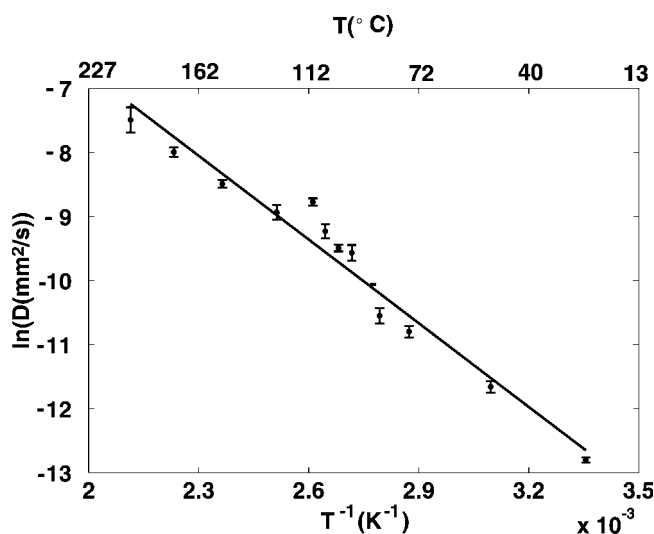


Figure 7 $\ln D$ versus T^{-1} from weight loss experiments. $D_0 = 9.0 \pm 2.4 \text{ mm}^2/\text{s}$, $E_a = 37.0 \pm 2.8 \text{ kJ/mol}$.

TABLE VII
Results for Swelling Experiments

RH (%)	Percentage swelling						Average	SD
	1	2	3	4	5	6		
20	0.028	0.047	0.054	0.028	0.042	0.047	0.041	0.011
40	0.075	0.108	0.111	0.090	0.099	0.088	0.095	0.014
60	0.147	0.181	0.164	0.158	0.175	0.166	0.165	0.012
80	0.221	0.229	0.231	0.249	0.225	0.229	0.231	0.010
100	0.334	0.341	0.317	0.333	0.324	0.325	0.329	0.008

Numbers 1–6 indicate sample number.

Swelling experiments

The equilibrium swelling strains for six different samples exposed to relative humidities of RH (20, 40, 60, 80, and 100%) are given in Table VII. Plotting all of the data in Figure 8, the figure shows that the swelling strain is linear with respect to moisture gain and hence can be expressed as $\varepsilon = cM$, with swelling strain coefficient $c = 0.0935 \pm 0.0037$.

To place this swelling in context, Figure 9 plots the percent change in polymer volume $\Delta V/V_0$, (where V_0 is the polymer volume) as a function of $V_m/V_0 = (\Delta m/\rho)/V_0$, where V_m is the volume of absorbed water, ρ is the density of water, and Δm is the mass of water absorbed calculated from the change in specimen weight. The dashed line (unity slope) represents the swelling that would be expected if the volumes of the dry polymer and absorbed moisture were additive, referred to as free swelling in polymers. The actual data has a slope of 0.60. This deviation results from a combination of water occupying free volume in the polymer, and modification of the polymer chain conformation resulting from hydrogen bonding between water molecules and polymer chains. An esti-

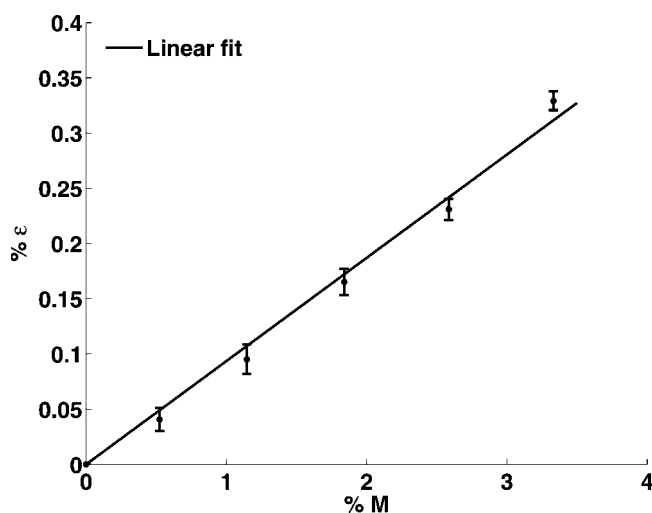


Figure 8 Percentage swelling strain and percentage mass gain. For linear fit, $\varepsilon = cM$, where $c = 0.0935 \pm 0.0037$.

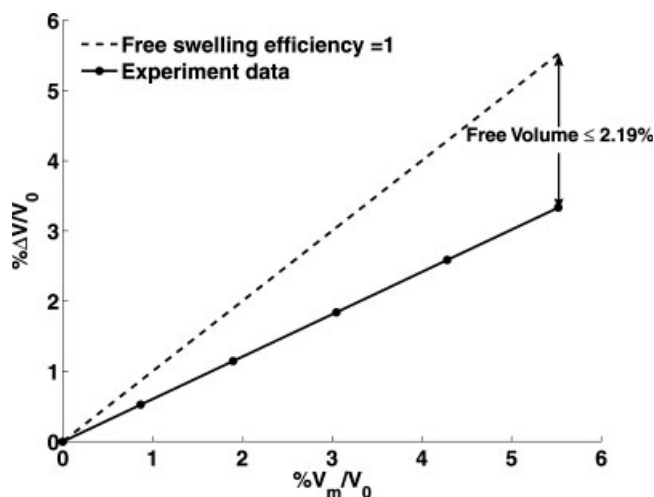


Figure 9 Swelling efficiency of polyimide HFPE-II-52, slope for linear fit is 0.604.

mate for the free volume occupied by water at 100% RH is given by the final deviation of 2.19% from the free swelling curve, consistent with measurements in other resin systems^{25,26} and theoretical predictions for polymers.^{36,40,41}

CONCLUSIONS

Motivated by potential applications of the polyimide HFPE-II-52 to high temperature composite materials, the moisture diffusivity, equilibrium moisture absorption and swelling strains, were measured for this polymer. To cover a wide range of temperatures and to minimize sample size requirements, novel experimental and data reduction methods were developed. Diffusivity was determined by fitting weight gain or loss data to the 3D solution to the diffusion equation. This nonlinear least squares fitting method eliminates the need for very large aspect ratio samples as allows weight gain to be fit over the entire experiment, rather than just for short times as with the standard method. A small oven in which samples hang from a microbalance and hence can be weighed dynamically was developed and used to determine D above 100°C.

The results show that diffusivity, D , is well represented by the Arrhenius law, $D = D_0 e^{[-E_a/RT]}$ with $D_0 = 9.0 \pm 2.4 \text{ mm}^2/\text{s}$ and $E_a = 37.0 \pm 2.8 \text{ kJ/mol}$ over a wide range of temperatures. Diffusivity was found to be independent of relative humidity. Equilibrium moisture absorption is nonlinear with respect to relative humidity and can be modeled using the GAB equation, $M_\infty = M_m A C a_w / (1 - A a_w) (1 - A a_w + A C a_w)$, with $M_m = 0.352 \text{ (kg water)/(kg dry basis)}$, $A = 0.28$ and $C = 0.18$. Equilibrium moisture absorption was independent of temperature. Swelling was found to

be linear with moisture absorption and can be expressed as $\varepsilon = cM$ with $c = 0.0935 \pm 0.0037$.

Kenway Chen was supported through the Cornell Center for Materials Research (CCMR) Research Experience for Undergraduates (REU) program. The authors thank Prof. Michael Thompson of Cornell for discussion of this article.

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