# Characterization of Temperature-Dependent Moisture Diffusivity in PMR-15 Resin

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**ABSTRACT:** The temperature-dependent moisture diffusion behavior of high-temperature polyimide resin, PMR-15, is presented. Adsorption and high temperature desorption tests are used to experimentally determine moisture diffusivity at several temperatures. Diffusivity is determined from the weight change based on the initial slope and using a nonlinear regression technique with Fickian diffusion assumption. The basic test procedures and diffusivity values are presented in this study. The results also include the relative humidity (RH) dependent equilibrium moisture concentration and a relationship between the RH and equilibrium moisture concentration. As direct measurement at typical operating temperature may be precluded by blistering, an Arrhenius-type temperature-diffusivity relationship is used to estimate the temperature-dependent moisture diffusivity for the PMR-15 resin. The moisture diffusivity of PMR-15 tested is estimated to be 6.64 E $-10$ m$^2$/s at 288°C. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1281–1290, 2007

**Key words:** PMR-15; moisture diffusivity; adsorption; desorption; Fickian

## INTRODUCTION

Composite materials are susceptible to humidity in the environment during both the processing phase and in service. These changes compromise the resin mechanical stiffness and strength performance and durability of composite structures. Moisture adsorption causes weight gain, hygroscopic dimensional changes, and can cause material degradation. When exposed to the humid and elevated temperature environments, polymer composite materials adsorb moisture from the exposed surfaces and may irreversibly change its load carrying properties. The rate and the equilibrium concentration of moisture in the material is affected by several factors, such as temperature, relative humidity (RH), the area of the exposed surface, and the behavior of constituent material (fiber, matrix) behavior. To this end, characterization of the moisture uptake behavior of the resin is significant.

Shen and Springer[1] described the basic test procedures for determining the moisture adsorption properties and moisture diffusivity from the weight gain experiments. A more specific test procedure can be found in the international standard BS EN ISO 62[2] in which the conditioning environment and specimen geometrics are defined for obtaining the diffusivities in the ''through-the-thickness'' direction. BS EN ISO 62 is suitable for polymers and composites and can be applied to both water vapor exposure and liquid immersion. ASTM standards[3] define the RH and temperature conditions and the tolerance for reliable determination of diffusivity. High temperature desorption tests can be used to accelerate the testing. However, when high temperature desorption test uses saturated samples under rapid heating, it can lead to plasticization, hydrolysis and blistering of the samples. Rice and Lee[4] determined safe heating rates that reduce blistering of high temperature polymer composites (HTPMC). In their study, the safe temperature for PMR-15 composites was to be in the viscinity of 288–300°C, the heating rates from ambient to working temperature may be constrained to allow moisture egress from the material.[5] On the basis of Fickian diffusion assumption, Newill et al.[6] presented a one-dimensional analytical solution of multi-domain structures and correlated with the experiment results of the coated composite substrates. Their work shows that most experiment results match the analytical solutions very well. But some cases with faster moisture uptake may imply that the moisture diffusion is non-Fickian.

Bond[7] considered the effects of non-Fickian adsorption and fiber spatial distribution on moisture diffusion using a predictive model for moisture

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transport in laminated composite materials. Roy[8] developed a non-Fickian model for moisture diffusion in visco-elastic polymers. He compared model predictions with published experimental data for the special case of isothermal diffusion in an unstressed graphite/epoxy symmetric angle-ply laminate. Loh et al[9] studied non-Fickian diffusion in rubber toughened epoxies. Their model uses several saturation levels and a diffusion constant for each saturation level. These constants are obtained using iterative regression fits to moisture uptake curves.

The objective of this study is to obtain the diffusivity versus temperature relationship for PMR-15 using both moisture adsorption test and high temperature desorption test. Those PMR-15 samples are made with preimidized powders. As PMR-15 processing involves handling of known carcinogens and due to export control limits on information sharing, further details of the process are not known. The results from the high temperature desorption test are correlated to the adsorption test and the simulation results. While fibers are less susceptible to moisture induced degradation, matrix, and the interphase/interface regions are affected. As the moisture diffusivity response of the resin is of particular interest, we focus on characterizing the high temperature moisture diffusivity of the resin. PMR-15 is chosen for this study. Fick's law assumes a concentration independent diffusivity for the material. When the rate of diffusion is comparable to that of the polymer segment mobility, or when the diffusion and the polymer segment mobility is greater compared with other relaxation process, the classical Fickian diffusion is not sufficient to describe these anomalous cases. In practice, both Fickian and non-Fickian diffusion mechanisms coexist in several polymers.[10,11]

### Theory

The moisture concentration and transport in polymer and composite materials are modeled using Fick's second law with temperature-dependent diffusivity for the material.[1]

$$\frac{\partial c}{\partial t} = D_1 \frac{\partial^2 c}{\partial x^2} + D_2 \frac{\partial^2 c}{\partial y^2} + D_3 \frac{\partial^3 c}{\partial z^3} \qquad (1)$$

Where, $t$ is time, $c$ is the moisture concentration in the material. $D_1$, $D_2$, and $D_3$ are the orthotropic moisture diffusivities in $x$, $y$, and $z$ directions. Diffusivity typically exhibits Arrhenius type relationship as a function of temperature.[12]

$$D_i = D_i^0 \exp\left(-\frac{E_a^i}{RT}\right) \qquad (2)$$

$D_i^0$ are material constants, $E_a^i$ are activation energies and $R$ is the universal gas constant.

The boundary conditions for eq. (1) are divided into moisture specified and concentration flux specified. Equation (3) depicts the boundaries where moisture is specified. Equation (4) is for vanishing concentration flux or impermeable boundaries.

$$c(x, y, z, t) = c_b(t) \quad \text{on} \quad \Gamma_m \qquad (3)$$

$$-D_i \nabla_i c = 0 \text{ on symmetry surfaces} \qquad (4)$$

$c_b$ is the specified moisture concentration on $\Gamma_m$ (moisture specified) boundary.
The initial moisture concentration is defined everywhere on the domain Q as in eq. (5):

$$\begin{cases} c(x, y, z, 0) = c_i \\ \text{on } \Gamma_m \ c(\Gamma_m, 0) = c_b(0) \end{cases} \qquad (5)$$

A measure of the total weight of the moisture in the domain Q is proportional to the total moisture concentration ($M$), which is obtained by integrating the moisture concentration field:

$$M(t) = \int \int_Q \int c(x, y, z, t) dV \qquad (6)$$

The extent of moisture adsorption or desorption can be correlated to the weight gain or weight loss in the specimen as:[1]

$$M(t)$$
$$= \frac{\text{Weight of moist material} - \text{Weight of dry material}}{\text{Weight of dry material}}$$
$$\times 100 \quad (7)$$

The total moisture concentration for a completely saturated sample is termed as the equilibrium moisture concentration, $M_\infty$. The value of $M_\infty$ is RH-dependent and not temperature-dependent. However, the time required to reach the saturation state is temperature-dependent. The relation between $M_\infty$ and the surrounding RH is typically given by eq. (8).

$$M_\infty = a(\text{RH})^b \qquad (8)$$

Where $a$ and $b$ are empirically determined material constants. When the material is immersed in water, $M_\infty$ is a constant, but differs from that obtained when exposed to environment with a RH of 100%. Next, we can consider the methods for obtaining diffusivity.

### Initial slope method

To obtain the diffusivity of the material from the weight change data, correlations are made with predictions from Fickian diffusion analysis. Concentra-

tion profiles $c(x, t)$ for one-dimensional (Fig. 1) moisture diffusion are given by solving eq. (9) with boundary conditions specified in eq. (10).

$$\frac{\partial c}{\partial t} = D_1 \frac{\partial^2 c}{\partial x^2} \tag{9}$$

Where $D_1$ is the moisture diffusivity in $x$ (thickness) direction.

For the semi-infinite solid ($h \to \infty$), the boundary conditions:

$$\begin{array}{ll} c = c_i & 0 < x < \infty \quad t \leq 0 \\ c = c_\infty & x = 0 \quad\quad t > 0 \end{array} \tag{10}$$

where $c_i$ is the uniform initial moisture concentration, $c_\infty$ is moisture concentration due to boundary sorption. The moisture concentration as a function of position and time in the plate for this case is given by eq. (11)

$$\frac{c - c_i}{c_\infty - c_i} = 1 - \operatorname{erf} \frac{x}{2\sqrt{D_1 t}} \tag{11}$$

Integrating the concentration field for the 1D problem, we get the total moisture concentration in the specimen (which is proportional to the weight gain) is given by eqs. (12) and (13).

$$M \propto \int_0^h c(x, t) dx \tag{12}$$

$$M(t) = 4(M_\infty - M_i) \sqrt{\frac{D_1 t}{\pi h^2}} \tag{13}$$

Where $M_i$ is proportional to the instantaneous moisture concentration in the whole specimen. In practice, moisture enters or leaves the specimen from all the surfaces and the infinite boundary assumption as in eq. 10 is typically not valid. Therefore, a correction factor needs to be applied for a fi-
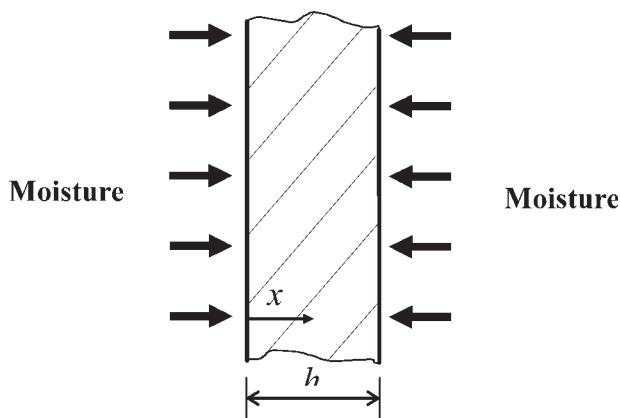


**Figure 1** Description of the problem.

nite sized specimen. For a rectangular specimen, the total moisture adsorption from the six sides can be summed as:

$$M(t) = \frac{4(M_\infty - M_i)}{h\sqrt{\pi}} \left( \sqrt{D_1} + \frac{h}{l} \sqrt{D_2} + \frac{h}{b} \sqrt{D_3} \right) \sqrt{t} \tag{14}$$

where $D_2$ and $D_3$ are the moisture diffusivities in $y$ and $z$ directions.

From eq. (14), an apparent diffusion coefficient can be defined for the specimen as:

$$D_c = \left( \sqrt{D_1} + \frac{h}{l} \sqrt{D_2} + \frac{h}{b} \sqrt{D_3} \right)^2 \tag{15}$$

For a homogeneous material, $D_1 = D_2 = D_3 = D$,

$$D = D_c \left( 1 + \frac{h}{l} + \frac{h}{b} \right)^{-2} \tag{16}$$

$D$ is defined as the one-dimensional diffusivity normal to the surface. Equation (16) has specimen dimensions correcting for the edge effects.

An apparent diffusion coefficient $D_c$ can be determined by relating the total moisture concentration to the observed weight loss or weight gain data. The initial slope method[1] uses the initial slope of the curve and the diffusivity can be determined by eq. (17).

$$D_c = \pi \left( \frac{h}{4(M_\infty - M_i)} \right)^2 \left( \frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \tag{17}$$

When a predried composite specimen placed in an environment under given temperature and RH level, the total moisture concentration function $M(t)$ is plotted versus square root of time $\sqrt{t}$ as shown in Figure 2. $M_1$ and $M_2$ are the instantaneous total moisture concentration at time $t_1$ and $t_2$, $h$ is the thickness, $M_i$ is the initial moisture concentration and $M_\infty$ is the equilibrium moisture concentration. $D_c$ is obtained from the slope of linear part of the total moisture concentration change curve. A set of moisture diffusivities obtained under different exposure temperatures can be used in determining temperature and diffusivity relationship.

In practice, all the surfaces of the specimen are exposed to the test environment. Because of the one-dimensional nature of the analysis, this initial slope method determines the components of the diffusivity tensor oriented normal to the largest surface of the material accurately. Finite sample dimensions cause errors in the diffusivity estimates. To reduce the errors due to edge effects, the square plate speci-
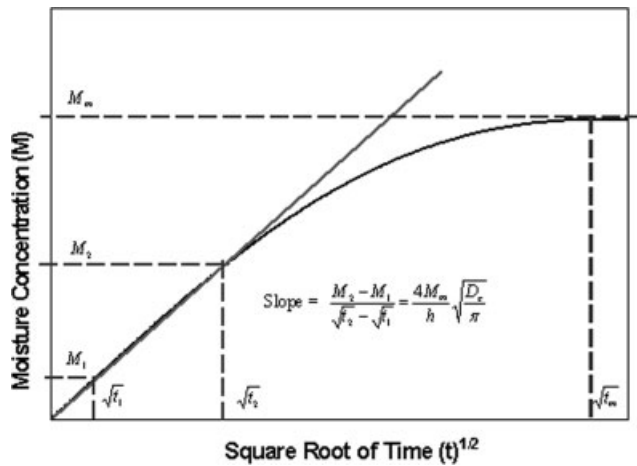
**Figure 2** The moisture concentration versus the square root of time.

mens with a width ≤100 thickness are typically recommonded to be used.[2]

## Optimization method

Aktas et al.[13] indicate that the primary reason for the inaccuracy of the initial slope method based on aforementioned solution is the arbitrary determination of the initial slope of the weight gain curve from discrete weight change data points. A method based on the least square curve fitting of all the experimental data points is used to obtain the moisture diffusivity more accurately. The demonstration of the method is presented by using the model developed by Li et al.[14] The combined effects of multidimensional geometry and anisotropy can be analyzed by considering all points of the discrete weight change measurements. The concentration profile model with anisotropic diffusivity is given by Carslaw and Jaeger[15] as in eq. (18).

$$\frac{M(D_i, t)}{M_\infty} = 1$$

$$- \frac{512}{\pi^6} \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \sum_{r=0}^{\infty} \frac{e^{-\pi^2 t \left( D_1 (2p+1)^2 / h^2 + D_2 (2q+1)^2 / b^2 + D_3 (2r+1)^2 / l^2 \right)}}{(2p+1)^2 (2q+1)^2 (2r+1)^2}$$

$$(18)$$

As the predicted concentration is a function of the assumed material diffusivity, an inverse problem is solved by correlating the experimental and predicted weight changes. The diffusivity parameters, $D_i$, are obtained by minimizing the predicted concentration value $M(D_i,t)$ and experimental values $M_{exp}(t)$ for all discrete time measurements $t_i$ as in eq. (19). Find $D_i$, such that:

$$\min[E(D_i)] = \sum [M(D_i, t_j) - M_{exp}(t_j)] \qquad (19)$$

## EXPERIMENTAL METHODS

### Adsorption test

The moisture adsorption properties and diffusivity in the thickness direction of the test samples are measured. The test procedure is shown in the flow chart illustrated in Figure 3. The specimen is pre-dried in a environmental chamber maintained at 50 ± 2°C until the specimen weight reaches a constant value. The temperatures of the drying oven are set to ensure that the polymer is chemically (and thermo-oxidatively) stable at that temperature. The specimen is then exposed to a conditioning environment with given temperature and RH. The specimen is periodically removed and weighed. After weighing, the specimen is returned to the test environment
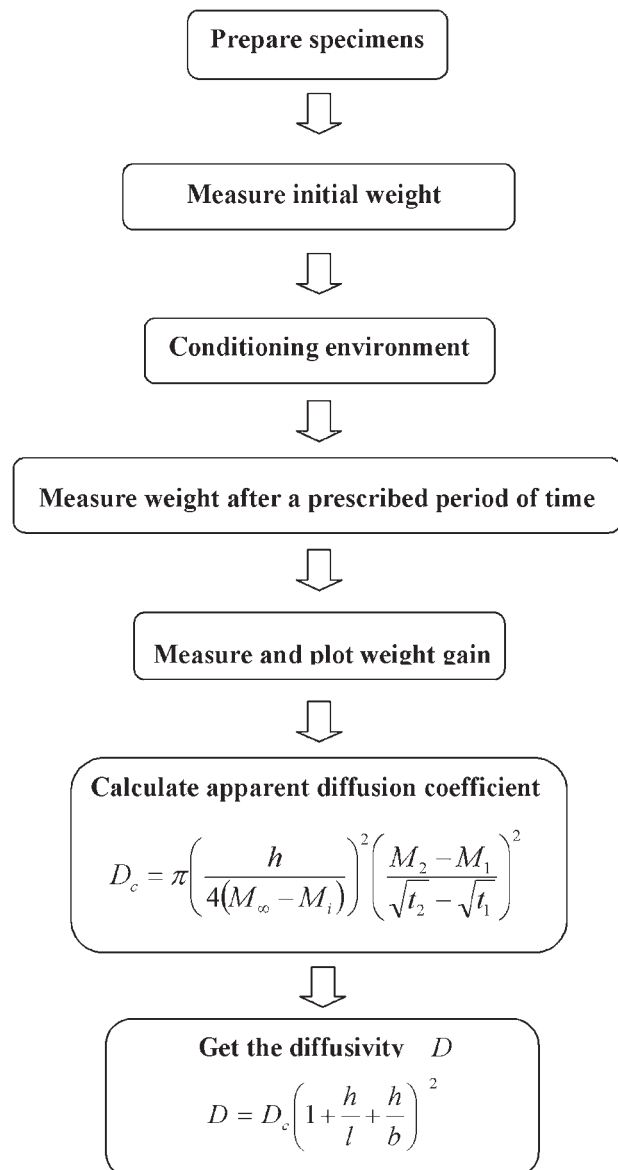


**Figure 3** Adsorption test procedure flow chart.

Pre-dry specimens at 50 °C

⬇

Measure initial weight

⬇

Condition the samples in the elevated humidity environment until $M$ reaches $M_\infty$

⬇

Heat the specimens

⬇

Get the weight loss curve

⬇

Calculate apparent diffusion coefficient

$$D_c = \pi \left( \frac{h}{4(M_\infty - M_i)} \right)^2 \left( \frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2$$

⬇

Get the diffusivity $D$

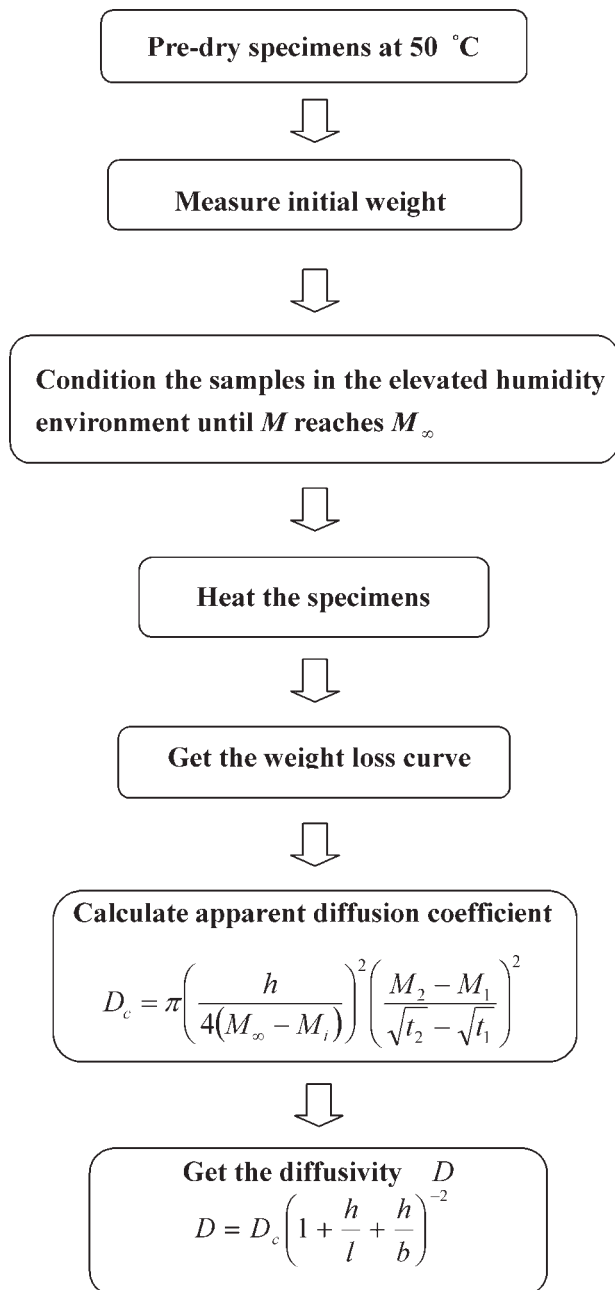$$D = D_c \left( 1 + \frac{h}{l} + \frac{h}{b} \right)^{-2}$$

**Figure 4** High temperature desorption test procedure flow chart.

and the process is repeated until the weight of the specimen reach equilibrium.

The methods described in previous section are used to determine the apparent diffusion coefficient $D_c$ from the experimental data. The one-dimensional diffusivity normal to the largest surface, $D$, is obtained by eq. (16). Considering the edge effects, the adsorption tests typically require a considerably long period of time and a great deal of attention to perform. It is very common for testing samples to take weeks, month or several years to reach their equilibrium state at room temperature.

## High temperature desorption test

The high temperature desorption test uses weight loss due to water evaporated from the sample. A moisture analyzer[16] with heat chamber and online weight measuring capability is used to measure the weight loss of specimen continuously. The specimen is also heated at a precisely controlled temperature. The complete test procedure flow chart is shown in Figure 4. The moisture diffusivities are the same for both moisture adsorption and desorption under the same temperature, the moisture diffusivity obtained by high temperature desorption test must correlate with the moisture diffusivity obtained by adsorption test at the same temperature.

The apparent diffusion coefficient, $D_c$, for the samples is determined by using the initial slope methods. With high temperature desorption test, for the same RH only one thorough test is required to obtain the $M_\infty$. In same RH but different temperature environment, rest of the tests can stop at where a satisfied linear region of Fickian diffusion curve obtained. One can do online measurement with adsorption tests also online weight measurement reduces the measurement effort. In the adsorption test method, test samples have to be removed from the conditioning environment at predescribed intervals and weighed, which requires great attention. Tests can be performed at high temperatures (below blistering temperature), which reduces test time.

The dimensions of the specimens are parameterized by l, length, b, width, and h, thickness. Figure 5 shows the relative orientation of the coordinate system with the specimen geometry. A group of speci-
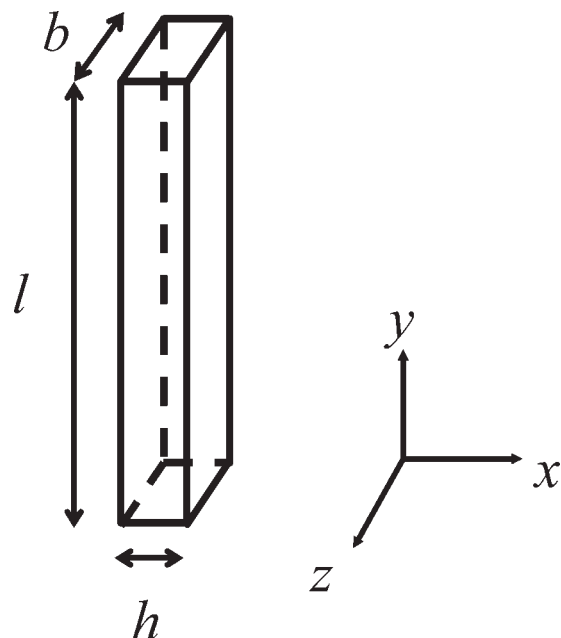


**Figure 5** Geometry of the test specimen.

**TABLE I**
**Specimen dimensions and test conditions**

| Sample | Dimensions - l × b × h (mm) | Immersed time (h) | Dry time | Dry temperature (°C) |
|---|---|---|---|---|
| 1 | 36.65 × 24.64 × 3.87 | 203 | 6 h 29 min | 200 |
| 2 | 36.27 × 23.90 × 3.99 | 273 | 21 h 38 min | 140 |
| 3 | 36.09 × 23.93 × 3.96 | 218 | 14 h 54 min | 160 |
| 4 | 36.47 × 23.37 × 3.99 | 199 | 3 h 30 min | 200 |
| 5 | 24.13 × 22.78 × 4.00 | 1540 | 24 h 15 min | 93 |
| 6 | 36.70 × 24.11 × 3.86 | 500 | 36 h 19 min | 70 |
| 7 | 36.65 × 36.60 × 3.89 | 669 | 38 h 41 min | 100 |
| 8 | 24.28 × 17.42 × 3.86 | 1396 | 10 h 27 min | 160 |
| 9 | 19.89 × 19.36 × 4.00 | 0 | 5 h 44 min | 200 |

mens with dimensions listed in Table I are used for testing. The thickness variation is measured to be <5%. The thickness variation is because samples cut from different plates. All specimens were predried by the moisture analyzer at 50 ± 2°C until the specimen weight reaches a constant value. First, adsorption tests are preformed as described in Figure 3. The predried specimens are fully immersed in water at the room temperature for different durations of time. Since the immersion duration for each speci-

men is different, the final moisture concentration will also be different. Some of them will reach the equilibrium state from which $M_\infty$ can be obtained and for rest of them only get the initial portion of the Fickian diffusion curve. The consistency of final diffusivity results, the mean and standard deviation values, will be examined among these specimens.

The moisture analyzer is used to dry the saturated samples at desired temperatures until the weight becomes a constant. The apparent diffusion coefficient, $D_c$, is determined from the high temperature desorption tests. The one-dimensional diffusivity normal to the largest surface, $D$, is obtained by eq. (16), which corrects for the edge effects. It should be pointed out that some samples prepared for adsorption test were not dried completely to zero moisture concentration in the preparation period. To find out the initial moisture concentration $M_1$ and the moisture equilibrium $M_\infty$ value, one prepared specimen, sample 9, was dried with the temperature of 200°C directly without immersion. The result shows there was 1% moisture concentration in the stored samples. After high temperature desorption test, sample 1 was fully immersed in water to do the adsorption test. Their moisture concentration increased 3.96%.
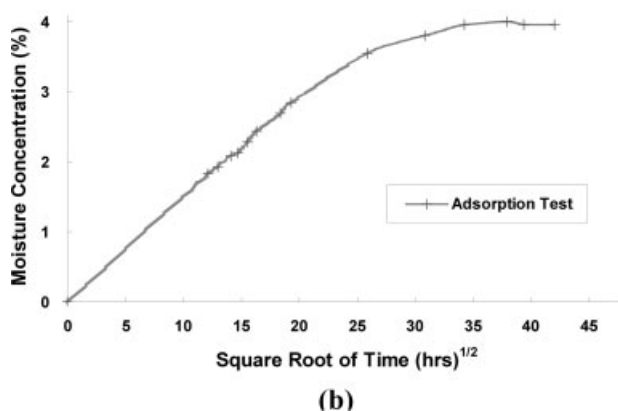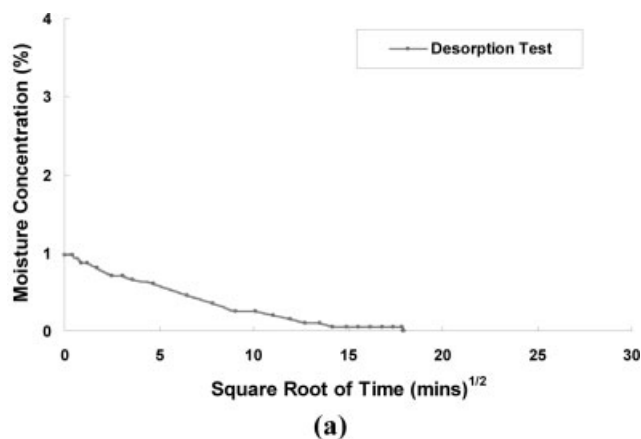


**(a)**



**(b)**

**Figure 6** The moisture equilibrium test for sample 9.



**Figure 7** Weight gain with moisture adsorption.

**TABLE II**
**Apparent diffusion coefficient ($D_c$) test results**

| Sample | Edge effect factor | Apparent diffusion coefficient (m²/sec) | |
| | | Adsorption test (25°C) | High temperature desorption test (Temperature ref. to TABLE I) |
|---|---|---|---|
| 1 | 0.627 | 1.39 E −12 | 9.75 E −10 |
| 2 | 0.613 | 1.45 E −12 | 2.44 E −10 |
| 3 | 0.615 | 1.48 E −12 | 4.28 E −10 |
| 4 | 0.610 | 1.33 E −12 | – |
| 5 | 0.556 | 1.44 E −12 | 2.09 E −11 |
| 6 | 0.622 | 1.39 E −12 | 1.58 E −11 |
| 7 | 0.680 | 1.26 E −12 | 5.48 E −11 |
| 8 | 0.579 | 1.50 E −12 | 1.11 E −10 |
| 9 | 0.556 | – | 3.04 E −10 |



**Figure 8** Weight loss behavior at various desorption temperatures.

Therefore, $M_\infty$ for the sample is 3.96%. Figure 6 shows the weight loss and weight gain curve for this sample. All other weight gain curves for the adsorption tests are shown in Figure 7. Not all samples have reached the equilibrium state during tests. Sample 5 and 8 reached their equilibrium state after 1400 h. Their moisture concentration increased 2.98%. Since an initial average concentration of 1% exists in the samples. $M_\infty$ is a constant when composites are fully immersed in water, $M_\infty = 3.98\%$ was used for moisture diffusivity calculation for the adsorption test.

## RESULTS AND DISCUSSION

The apparent diffusion coefficients obtained from both adsorption and high temperature desorption tests are shown in Table II. The moisture diffusivities obtained after correcting for the edge effects using eq. (16) from the tests are shown in Table III. The average moisture diffusivity is calculated to be $D = 8.58$ E −13 m²/s at room temperature (25°C). The standard deviation is 3.95 E −14, which is 4.6% of the average diffusivity. The curves for high tempera-

ture desorption tests with different heating temperatures are shown in Figure 8.

The Fickian diffusion assumption requires that the initial diffusion curve be linear and the slope determines the diffusivity of the material. In this study, the slope is obtained from the experimental data using the least square regression fits when using the initial slope method. The cutoff point for the linear curve is set at 65% of $M_\infty$. If the moisture concentration did not reach 65% of $M_\infty$ in the test, then all the available test data are used for the fitting of the slope.

Since the models used for determining the diffusivity with the high temperature desorption test assume a uniform initial concentration profile in the test specimen, it is important to ensure that the samples have the uniform initial moisture distribution ($c = c_i$ $0 < x < \infty$ $t = 0$). Before heating a sample, the sample need to reach the equilibrium moisture concentration ($M_\infty$) in an elevated humidity environment. Sample 4 shows the case for which the high

**TABLE III**
**Moisture diffusivity ($D$) results**

| Sample | Diffusivity (m²/s) | |
| | Adsorption test (25°C) | High temperature desorption test (Temperature ref. to TABLE I) |
|---|---|---|
| 1 | 8.74 E −13 | 6.11 E −10 |
| 2 | 8.87 E −13 | 1.50 E −10 |
| 3 | 9.10 E −13 | 2.63 E −10 |
| 4 | 8.09 E −13 | – |
| 5 | 8.03 E −13 | 1.16 E −11 |
| 6 | 8.66 E −13 | 9.86 E −12 |
| 7 | 8.56 E −13 | 3.73 E −11 |
| 8 | 8.66 E −13 | 6.45 E −11 |
| 9 | – | 1.69 E −10 |


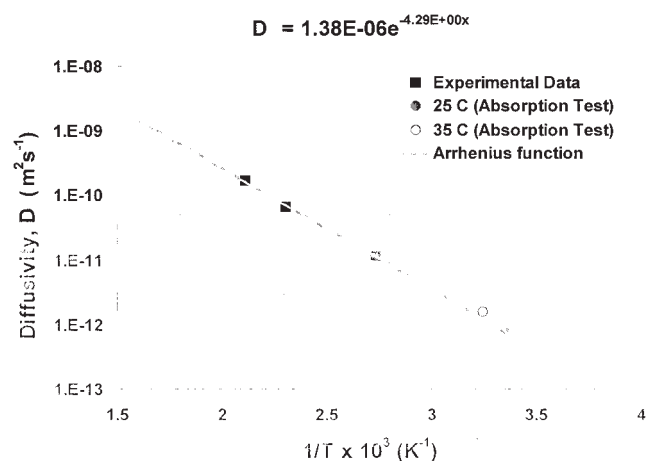
$$D = 1.38E\text{-}06 e^{-4.29E+00x}$$

**Figure 9** Moisture diffusivity versus temperature relation for PMR-15.
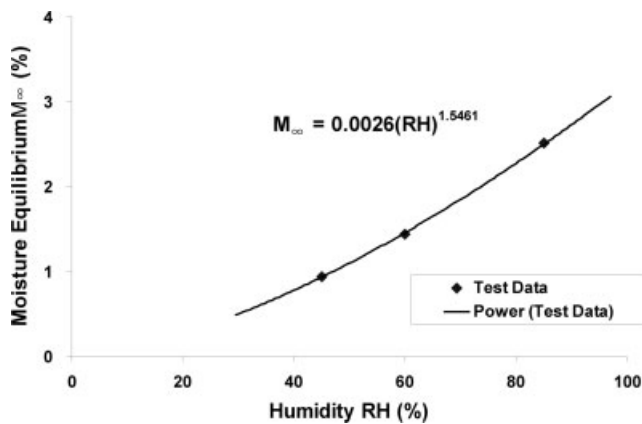
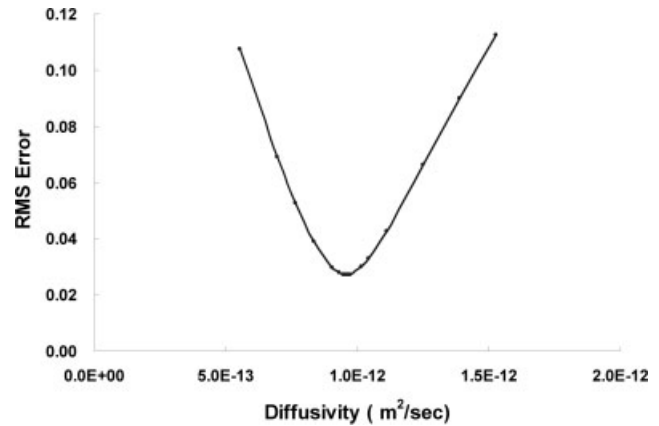**Figure 10** RH and equilibrium moisture concentration relationship.



**Figure 11** Diffusivity value and RMS error in the fit (eq. 19).

temperature desorption test was interrupted can still be used for moisture diffusivity and $M_\infty$ determination. Sample 5 and sample 8 were immersed in water long enough to reach the moisture equilibrium state. Sample 9 was not immersed in water and is considered in its moisture equilibrium state under room temperature in open air. Their dry temperatures and weight loss curves are shown in Figure 8. The high temperature desorption results show that the diffusivity values obtained from specimen are sensitive to the initial concentration profiles and accurate results can only be obtained from specimens that have saturated or have reached an equilibrium moisture state. To find out how important it is for a specimen to reach its equilibrium status of moisture content prior to heating in a high temperature desorption test, two samples are studied. Sample 1 and Sample 2 were immersed in water for a short time (203 and 273 h) before the high temperature desorption test and did not reach its equilibrium moisture state. From weight loss curves in Figure 8, one can tell that those curves from samples that reached their moisture equilibrium status fit better to the standard Fickian diffusion curve shown as in Figure 1. The initial linear region of the Fickian diffusion curve for samples with longer immersion time is straighter then that of samples with shorter immersion time. They are more likely to yield accurate and reliable results when calculating moisture diffusivity. For those samples which did not reach

their moisture equilibrium status, the moisture concentration within the materials were not uniform from outer-layers to cores. Therefore, it is important when using heat and try method to obtain diffusion curve that the test sample has to be in its moisture equilibrium status prior to heating.

On the basis of the above discussion, three samples 5, 8, and 9, are identified to have long enough immersion times to have reached the equilibrium (saturation) state. The high temperature desorption test results from these three samples are used to draw the Arrhenius function of diffusivity with temperature as shown in Figure 9. A trend line has been fitted with these 3 points. The fitting result gives the Arrhenius relation as eq. (20)

$$D = 1.38 \times 10^{-6} e^{-4.29(1000/T)} \qquad (20)$$

where the moisture diffusivity, $D$, is in m²/s and temperature, $T$, in Kelvin.

From this fitting result, the best estimate diffusivity for 25°C is 7.84 E −13 m²/s. As a comparison, the estimated value is 9% less than that obtained from the adsorption test.

**TABLE IV**
**Influence of relative humidity (RH) of the environment on $M_\infty$**

| | Saturation (%) | | |
|---|---|---|---|
| RH | 45% | 60% | 85% |
| $M_\infty$ test1 | 0.95 | 1.46 | 2.55 |
| $M_\infty$ test2 | 0.92 | 1.42 | 2.47 |
| Average | 0.94 | 1.44 | 2.51 |

**TABLE V**
**Moisture diffusivity results from the two methods**

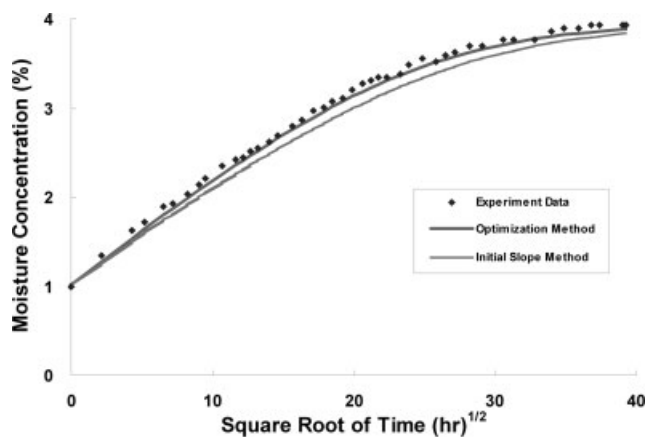| | Moisture Diffusivity (m²/s) | |
|---|---|---|
| Sample | Initial slope method | Optimization method |
| 1 | 8.74 E −13 | 1.03 E −12 |
| 2 | 8.87 E −13 | 1.07 E −12 |
| 3 | 9.10 E −13 | 1.09 E −12 |
| 4 | 8.09 E −13 | 9.22 E −13 |
| 5 | 8.03 E −13 | 9.58 E −13 |
| 6 | 8.66 E −13 | 1.08 E −12 |
| 7 | 8.56 E −13 | 9.25 E −13 |
| Average | 8.58 E −13 | 1.01 E −12 |
| STD | 3.94 E −14 | 7.41 E −14 |

**Figure 12** Simulation of moisture uptake for the diffusivity predicted by initial slope method and with diffusivity predicted by the optimization method.

The relationship of the equilibrium moisture concentration and RH is investigated. Two samples were exposed to three humidity levels with constant temperature 35°C. A VersaTenn environmental chamber[17] was used to provide the different humidity environments. The average moisture diffusivity is found to be $D = 1.57$ E $-12$ m$^2$/s at temperature 35°C and RH (RH = 85%). The estimated diffusivity at 35°C from eq. (20) is 1.25 E $-12$ m$^2$/s. The estimated value is 20% less than the one from the adsorption test. The parameters of eq. (8) can also be determined by test results. Figure 10 shows the data for various RH and corresponding equilibrium moisture concentrations, $M_\infty$. Table IV shows the results for three sets of data. The values of parameter $a$ and $b$ in eq. (8) are found to be 0.0026 and 1.5461 respectively.

The results from the initial slope method are used to correlate with results from optimization method. The goal is to minimize the objective function given by the standard deviation equation as follows:

$$E = \left[ \frac{1}{n} \sum_{i=1}^{n} \left( M_t(i) - M_{\exp}(i) \right) \right]^{1/2} \tag{21}$$

The convergence result of curve fitting of sample 5 is shown in Figure 11. The diffusivity calculation result comparison is shown in Table V. The calculated diffusivity results of sample 5 obtained by eq. (18) from both slope method (8.03 E $-13$ m$^2$/s) and optimization method (9.58 E $-13$ m$^2$/s) are used to reconstruct the adsorption curves and compared to measurement curve, as shown in Figure 12. The standard deviations to the measurement are 0.0448 and 0.0272 for initial slope method and optimization method respectively, which shows that the diffusivity result from optimization method is less variable.

## Concluding remarks

The objective of this work is to characterize the moisture diffusivity of a high temperature resin, PMR-15, by two different test methods, the adsorption test and high temperature desorption test. The test results are processed using two different analytical methods, initial slope method and optimization method to obtain the diffusivity of the samples. The temperature-diffusivity relationship for PMR-15 and the relationship between the RH and equilibrium moisture concentration are been obtained from the experimental results.

When using eq. (17) to determine the moisture diffusivity from experiments, a long linear region is preferred for obtaining a stable fit from the scattered measurement points by the initial slope method. The equilibrium moisture concentration $M_\infty$ is RH dependent only. Therefore, the saturation state can be reached by using high temperature exposure of the specimens to humid environments and determining $M_\infty$ from selected but few samples. Determination of $M_\infty$ allows diffusivity estimates from samples that are not completely saturated by using $M_\infty$ in eq. (17).

Using the initial slope method obtains the apparent diffusion coefficient, $D_c$, is obtained from experimental data and then the moisture diffusivity $D$ is determined after correcting for the edge effects. The initial slope method involves an artificial initial region in which the linearity of the diffusion curve is assumed. When such a linear region is not obvious in experimental data, the optimization method is better suited to extract the diffusion values as it considers the entire weight gain curve till saturation. However, the initial slope method is simpler to estimate the diffusivity when an initial linear region can be clearly identified.

The high temperature desorption test is effective as an alternative approach to the adsorption test. The diffusivity results from high temperature desorption test show good agreement with that obtained from adsorption tests. By extending the Arrhenius curve fit, the diffusivities at temperatures beyond testing temperature range can be estimated. The moisture diffusivity for estimates for a typical 288°C (550°F) operation temperature is estimated to be 6.64 E $-10$ m$^2$/s.

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