A Dual Stage Model of Anomalous Moisture Diffusion and Desorption in Epoxy Mold Compounds

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Abstract
Absorption and desorption tests were conducted on five distinct commercial epoxy mold compounds (EMCs) used in electronic packaging. For absorption, the samples were subjected to 85°C /85% relative humidity and 60°C /85% relative humidity soaking. Desorption conditions were above glass transition temperature at 140°C and 160°C. A dual stage model is developed in this paper for both absorption and desorption processes. Both stages in moisture absorption and desorption, i.e., Fickian diffusion and relaxation process, are described mathematically using a combination of Fickian terms. The models generated reasonable results for the diffusive properties and displayed outstanding experimental fits. All five compounds have shown strong non-Fickian diffusion behaviors, which were further demonstrated by experiments with different thicknesses. For absorption, results show Fickian diffusion is significantly faster than non-Fickian diffusion. Saturated moisture concentration associated with Fickian-stage diffusion is independent of temperature if it is below glass transition temperature. Sample thickness played a major role in diffusive behavior in the second stage where non-Fickian diffusion occurs. For desorption, higher temperature corresponds to less percentage of the permanent residual moisture content. At 160°C, 90% of the initial moisture for all samples could be desorbed out within 24 hours, following a modified Fickian diffusion process. The dual stage model developed in this paper provides a foundation for modeling anomalous moisture diffusion behavior using commercial finite elemental method software.

1. Introduction
Epoxy mold compounds are an essential subject in microelectronics reliability. While these compounds have advantages that make them ideal in electronic packaging such as molding ability and thermal properties, their behavior is limited by the moisture gain from the environment [1]. After moisture has entered the compounds, the water molecules can induce stresses which are even higher than the thermal stresses. One result is hygroscopic swelling which can lead to cracking. In other cases, the water molecules are vaporized during soldering reflow producing the infamous “popcorn” effect [1-4]. Moisture may also change the mechanical properties of the compound itself such as lowering the glass transition temperature or elastic modulus, limiting the operating temperature [1,3]. EMCs have varied chemical makeup as well as additives for enhancing performance which gives every EMC distinct characteristics. It is therefore pertinent to study the properties of moisture diffusion of these compounds.

The moisture mass obtained by a polymer occurs in two states, mobile or bound [3,5]. The first state is sometimes called physical absorption. Water molecules from the environment migrate to the microscopic pores or voids in the compound to achieve concentration equilibrium. The process was illustrated in great detail by Crank in which he developed a model for polymers in diffusion based on Fick’s laws [6,2]. This model is now known as classic Fickian diffusion. The second state is when the water molecules become chemically bonded to the polymer chains’ hydroxyl groups [3,7]. This chemical absorption process can be irreversible and causes non-Fickian behavior. These states are essential to understanding the mechanisms of absorption and desorption in EMCs [8].

The moisture mechanisms can be categorized in three groups: Case I, Case II, and anomalous uptake. Case I refers to classic Fickian absorption. In this case, the diffusion rate is assumed to be constant and governs the uptake [8]. Although Fickian diffusion has been used for decades, it has a very limited window of accuracy. Class II refers to moisture uptake governed by relaxation rate. In relaxation, the pressure of the absorbed water molecules causes the compound to swell, and then settle to equilibrium. This causes irregular, discontinuous behavior, and the moisture is known to increase linearly with time. The third category is anomalous uptake and arises when both relaxation and diffusion rate govern the moisture absorption. The relaxation rate and chances of chemical binding are negligibly at the beginning of the absorption process [5]. The behavior is mostly Fickian and the mass gain is in the “free” state. However, as more moisture is collected in the compound, the diffusion rate is slowed. This can be explained by two phenomena. As moisture is gained, more molecules are bonded to the polymer chains. This reduces the amount of moisture which can be absorbed in classic diffusion by limiting the space in the nanopores. Secondly, the relaxation rate becomes larger than the diffusion rate and governs the rest of the absorption process [3,9]. Consequently, anomalous uptake has been frequently modeled as a dual stage sorption [8-12]. This concept has been applied to several different diffusion processes of many artificial
materials [10]. The Fickian behavior is superpositioned with a function of the relaxation and/or chemical sorption such as Carter and Kibler’s Langmuir-Type Model or Gurtin and Chikayoshi’s “free” and “trapped” phase model [5,11].

In this paper, a dual-stage mathematical model is developed with both stages being described by Fickian terms. The model applies to both absorption and desorption processes. Experiments were conducted on testing five EMCs in both moisture uptake and loss processes. The dual stage model was used to analyze the experimental data, quality of data fittings, thickness effects, and diffusion mechanics were also investigated.

2. Mathematical Models

2.1 Fickian Diffusion

Moisture uptake with constant diffusivity can be modeled with an application of Fick’s Second Law of diffusion with diffusivity, \( D \), and concentration, \( C \) [3,6].

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{1}
\]

\( C \) is taken as a function of the distance from the center of the plate, \( x \), and time, \( t \). If the body is taken to be one-dimensional with an infinite plate thickness, the boundary and initial conditions are

\[
C = C_0, \quad -l < x < l, \quad t = 0
\]

\[
C = C_b, \quad x = \pm l, \quad t \geq 0
\]

where \( C_0 \) is the initial moisture concentration in the plate and \( C_b \) is the moisture concentration of the boundary. \( l \) is half the thickness of the plate. Fig. 1 illustrates an infinite plate and the coordinate system used in this work.

![Fig. 1: An infinite plate with the thickness 2l](image)

Using the separation of variables technique and assuming the fundamental solutions of \( C \) can be written as the product of two independent functions of time and thickness

\[
C(x, t) = F(x)G(t) \tag{3}
\]

The differential equation of the fundamental solutions of Equation (1) becomes

\[
F \frac{dG}{dt} = DG \frac{d^2F}{dx^2} \tag{4}
\]

The ordinary differential equations for Equation (4) has the following form of solution

\[
C = (A \sin \lambda x + B \cos \lambda x) \exp(-\lambda^2Dt) \tag{5}
\]

The solution of Equation (1) is the linear combination of all possible solutions of Equation (4). The most general solution of Equation (1) takes the following form

\[
C = \sum_{m=1}^{\infty} (A_m \sin \lambda_m x + B_m \cos \lambda_m x) \exp(-\lambda_m^2Dt) \tag{6}
\]

where \( A_m, B_m, \) and \( \lambda_m \) are determined by initial boundary conditions specified in Equation (2).

Solving for constants \( A_m, B_m, \) and substituting the boundary and initial conditions into Equation (6) yield the general solution for Fickian diffusion [6],

\[
\frac{C(x, t) - C_b}{C_0 - C_b} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n + 1)} \exp \left[ \frac{-(2n + 1)^2 \pi^2 Dt}{4l^2} \right] \times \cos \left( \frac{(2n + 1) \pi x}{2l} \right) \tag{7}
\]

If the plate is assumed to have no moisture content at \( t = 0 \) when it is placed into a humidity chamber then \( C_0 = 0 \) and \( C_b = C_{sat} \), the saturated moisture content at given temperature and humidity. The absorption solution based on Equation (6) becomes

\[
\frac{C(x, t) - C_b}{C_{sat} - C_b} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n + 1)} \exp \left[ \frac{-(2n + 1)^2 \pi^2 Dt}{4l^2} \right] \times \cos \left( \frac{(2n + 1) \pi x}{2l} \right) \tag{8}
\]

If the plate has initial content \( C_0 \) and is then desorbed in an environment with no relative humidity, this desorption process can be described as

\[
\frac{C(x, t) - C_b}{C_0} = -\frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n + 1)} \exp \left[ \frac{-(2n + 1)^2 \pi^2 Dt}{4l^2} \right] \times \cos \left( \frac{(2n + 1) \pi x}{2l} \right) \tag{9}
\]

Integrating over the thickness \( 2l \) makes Equation (7) and Equation (8) independent of location, \( x \). The equations become

\[
\frac{M_t}{M_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n + 1)^2} \exp \left[ \frac{-(2n + 1)^2 \pi^2 Dt}{4l^2} \right] \tag{10}
\]

for absorption and

\[
\frac{M_t}{M_0} = -\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n + 1)^2} \exp \left[ \frac{-(2n + 1)^2 \pi^2 Dt}{4l^2} \right] \tag{11}
\]
for desorption [1,6]. \( M_t \) is the total mass of moisture at time \( t \), and \( M_{\infty} \) is the saturated mass of moisture. \( M_0 \) is the initial moisture mass in the plate. The relation of concentration and moisture mass is easily given by dividing the mass by volume, \( V \).

\[
C_{\text{sat}} = \frac{M_{\infty}}{V}, \quad C_0 = \frac{M_0}{V}
\]

(1)

2.2 Dual Stage Diffusion: Absorption

The dual stage model applies the notion that Fickian and non-Fickian diffusion occur simultaneously throughout the process. The stages are distinguished by which behavior is most dominant. In the first stage, Fickian behavior is dominant. As the relaxation rate increases and diffusion rate slows, the non-Fickian behavior appears signaling the start of the second stage. If \( C_1 \) is the function of concentration due to Fickian behavior and \( C_2 \) represents the concentration due to non-Fickian behavior, superpositioning these two functions gives the total concentration of the sample as seen in Fig. 2. \( C_1 \) is very fast at the beginning of absorption while \( C_2 \) is very slow. Where the functions meet is the transition point between the first and second stage as no moisture is gained from Fickian behavior.

\[
C(x, t) = C_1(x, t) + C_2(x, t)
\]

(12)

![Diagram](image_url)

Fig. 2: Representation of superpositioned diffusion functions for a dual stage model

\( C_1 \) will use Fick’s law, but the second stage is an irreversible, Non-Fickian process. However, it is modeled in Fickian terms for mathematical simplicity and comparability. Both functions therefore have Fickian diffusivity coefficients and saturation. Equation (12) becomes

\[
C(x, t) = C_1(D_1, C_{\text{sat},1} x, t) + C_2(D_2, C_{\text{sat},2} x, t)
\]

(13)

\( C_{\text{sat},1} \) and \( D_1 \) and \( C_{\text{sat},2} \) and \( D_2 \) are the respective first and second stage diffusion coefficients and concentrations. The total concentration, \( C \), becomes a function of diffusivity, saturation, time and location. Since both functions use the Fickian terms to describe uptake, they can be represented like Equation (1),

\[
\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2},
\]

with boundary conditions

\[
C_1 = 0, \quad -l < x < l, \quad t = 0
\]

\[
C_1 = C_{\text{sat},1}, \quad x = l, x = -l, \quad t \geq 0
\]

and

\[
\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2},
\]

with boundary conditions

\[
C_2 = 0, \quad -l < x < l, \quad t = 0
\]

\[
C_2 = C_{\infty} - C_{\text{sat},1}, \quad x = l, x = -l, \quad t \geq 0
\]

Equation (14) and Equation (15) are solved by the separation of variables technique. Both become similar to Equation (3). After solving, applying boundary conditions, and integrating over thickness, Equation (15) resembles Equation (9) with the addition of the second stage:

\[
M_t = M_{\infty,1} \left[ 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^2} \exp \left( \frac{-4l^2}{(2n+1)^2} \right) \right] + M_{\infty,2} \left[ 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^2} \exp \left( \frac{-4l^2}{(2n+1)^2} \right) \right]
\]

(16)

with

\[
M_{\infty,1} = C_{\text{sat},1} V, \quad M_{\infty,2} = M_{\infty} - M_{\infty,1} = (C_{\infty} - C_{\text{sat},1}) V
\]

\( M_t \) is the sum of the moisture mass for both stages at time, \( t \), and \( M_{\infty,1} \) and \( M_{\infty,2} \) are the total moisture mass gained by each stage. It is expected that \( D_1 \) is significantly larger than \( D_2 \) because the chemical bonding and relaxation of the sample is negligible in the beginning of absorption.

2.3 Dual Stage Diffusion: Desorption

For the desorption model the process may be described by a dual stage model similar to Equation (16), the desorption equation is

\[
M_t = M_{\infty,1} \left[ -\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^2} \exp \left( \frac{-4l^2}{(2n+1)^2} \right) \right] + M_{\infty,2} \left[ \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^2} \exp \left( \frac{-4l^2}{(2n+1)^2} \right) \right]
\]

(18)
where, $D_1$ and $M_{0.1}$ are the diffusivity and initial moisture content for Fickian diffusion, $M_{0.2}$, is equal to $M_{in} - M_{0.1}$, and $D_2$ is the diffusivity of the non-Fickian behavior. Given the fact that the sample will never lose all the moisture gained by absorption at certain temperature due to the irreversible processes, $D_2$ is taken to be zero in Equation (18). As a result, the second stage term in Equation (18) becomes $M_{0.2}$, representing the amount of residual moisture in the sample after it has reached equilibrium. Fig. 3 visually displays this idea. Equation (18) becomes:

$$\frac{M_t}{M_0} = \frac{M_{0.1}}{M_0} \left[ -\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^2} \right] \times \exp \left[ -\frac{(2n+1)^2 \pi^2 D_1 t}{4n^2} \right] + \frac{M_{0.2}}{M_0} \tag{19}$$

$M_0$ is the total amount of initial moisture in the sample. By dividing each term by this value, the percent of moisture is found for $M_t$, $M_{0.1}$, and $M_{0.2}$.

![Fig. 3: Representation of dual stage desorption concept](image)

3. Experimental Procedure

Four distinct weight gain/loss tests were conducted using a humidity-temperature chamber. A total of twelve samples went into the chamber for each test, two of each compound and geometry. Compounds A, B, C, and D were 1 mm thick with a 50 mm diameter disks. Compound E had two geometries, a square with 1.4 mm thickness and a 50 mm diameter disk with 3 mm thickness. Table 1 and Table 2 summarize the experiment details. Testing included absorption at 85°C/85% RH and 60°C/85% RH and desorption tests at 140°C and 160°C. At the beginning of the absorption test, the samples were baked for 72 hours at 125°C to drain the ambient moisture content. After recording the dry weight of each sample, the chamber was set to the desired environmental conditions. The samples were periodically taken out of the chamber and weighed manually with a balance scale. For desorption, the wet samples used in the absorption tests were baked at the respective temperatures. The samples were allowed to cool for approximately 30-60 seconds before weighing due to the high temperature of some of the tests.

<table>
<thead>
<tr>
<th>Test</th>
<th>Process</th>
<th>Condition</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Absorption</td>
<td>85°C/85% RH</td>
<td>650 hrs.</td>
</tr>
<tr>
<td>2</td>
<td>Desorption</td>
<td>140°C</td>
<td>25 hrs.</td>
</tr>
<tr>
<td>3</td>
<td>Absorption</td>
<td>60°C/85% RH</td>
<td>1233 hrs.</td>
</tr>
<tr>
<td>4</td>
<td>Desorption</td>
<td>160°C</td>
<td>48 hrs.</td>
</tr>
</tbody>
</table>

The errors associated with the absorption experiments can be contributed to several factors. One is the thermal expansion of the samples affecting the weight read-out, though this was minimized by the cooling period. The amount of time the samples were out of the chamber was no greater than 8 minutes. This error can be considered negligible because the samples were exposed to room temperature for a short period relative to the whole duration of the test. For desorption, errors come primarily from the samples being exposed to high temperatures in the chamber then quickly being removed to room temperature. These samples were always allowed to cool for a short period, but the rapid change in environmental conditions may have affected the readings. Some moisture may have also re-entered the compounds upon cooling and weighing. It is difficult to have an extremely accurate desorption test at high temperatures using manual weighing. Other, more accurate methods include using electrical moisture sensors and analyzers.

4. Fickian Absorption and Desorption

First, a classic Fickian model, Equation (9), was applied to the data for the entire duration of each test. The values of diffusivity and $C_{sat}$ were found using the least-square method. This method takes the value of diffusivity and $C_{sat}$ only when the sum of the error in calculated and experimental values is minimized [4]. This is represented by

$$E = \sum_{n=1}^{K} [M_n - \hat{M}(t_n)]^2 \tag{20}$$

$E$ is the total error found by subtracting the calculated values of moisture content $\hat{M}(t_n)$ from the measured experimental value $M_n$ at data point $n$ at time $t$. The Fickian model produced very unsatisfactory fits for both absorption and desorption as seen in Fig. 4 and Fig. 5, making the values found very unreliable.
5. Dual-Stage Absorption

5.1 Dual-stage Fit

The dual stage model proposed by Equation (16) was developed with the least square-method solving for values of $C_{\text{sat},1}$ and $D_1$ and $C_{\text{sat},2}$ and $D_2$ simultaneously. This generated excellent fits for all samples for conditions at 85°C /85% RH and 60°C /85% RH as shown in Fig. 6 and Fig. 7, respectively. Given the fact that the saturated Fickian moisture concentration is independent of temperature, Table 3 summarizes the results of the dual stage fits with “forced” same values of $C_{\text{sat},1}$, which were obtained by the average at two different temperatures for each compound. The values of $D_1$, $C_{\text{sat},2}$, and $D_2$ were then solved simultaneously with Equation (20). This procedure still generated excellent curve fits that are almost indistinguishable from Fig. 6 and Fig. 7. From Table 3, it can be seen that the diffusivity of the second stage is two orders lower than the first stage at 85°C /85% RH. At 60°C /85% RH, the difference in $D_1$ and $D_2$ is less, but it is still greater than one order. This indicates that the relaxation process is very slow in the beginning of absorption. The diffusivity at both stages increases with temperature as expected. In addition, $C_{\text{sat},2}$ is always comparable, or greater than $C_{\text{sat},1}$, meaning that the non-Fickian behavior plays a major role in moisture uptake.

### Table 3: Dual stage model parameters at 85°C/85 %RH and 60°C/85 %RH

<table>
<thead>
<tr>
<th>Compound</th>
<th>$D_1$ (mm²/hr)</th>
<th>$C_{\text{sat},1}$ (mg/cm³)</th>
<th>$D_2$ (mm²/hr)</th>
<th>$C_{\text{sat},2}$ (mg/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.23E-02</td>
<td>2.29E+00</td>
<td>5.61E-04</td>
<td>3.59E+00</td>
</tr>
<tr>
<td>B</td>
<td>1.39E-02</td>
<td>2.90E+00</td>
<td>5.30E-04</td>
<td>2.86E+00</td>
</tr>
<tr>
<td>C</td>
<td>1.80E-02</td>
<td>3.26E+00</td>
<td>5.54E-04</td>
<td>3.22E+00</td>
</tr>
<tr>
<td>D</td>
<td>1.92E-02</td>
<td>3.34E+00</td>
<td>5.04E-04</td>
<td>2.22E+00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>$D_1$ (mm²/hr)</th>
<th>$C_{\text{sat},1}$ (mg/cm³)</th>
<th>$D_2$ (mm²/hr)</th>
<th>$C_{\text{sat},2}$ (mg/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4.28E-03</td>
<td>2.29E+00</td>
<td>2.80E-04</td>
<td>2.42E+00</td>
</tr>
<tr>
<td>B</td>
<td>5.01E-03</td>
<td>2.90E+00</td>
<td>2.72E-04</td>
<td>2.22E+00</td>
</tr>
<tr>
<td>C</td>
<td>5.93E-03</td>
<td>3.26E+00</td>
<td>2.02E-04</td>
<td>1.95E+00</td>
</tr>
<tr>
<td>D</td>
<td>6.14E-03</td>
<td>3.34E+00</td>
<td>2.06E-04</td>
<td>1.28E+00</td>
</tr>
</tbody>
</table>

5.2 Absorption Thickness Effects

Compound E had two thicknesses of 1.4mm and 3.0mm, respectively. The fitted results are displayed in Table 4, and in Fig. 8 and Fig. 9, respectively. The figures use normalized time and thickness, $(t/t_0)^{1/2}$, for comparison. The two curves overlap at the beginning of the processes then deviate at a particular point.
According to Fick’s law, the diffusivity and \( C_{\text{sat}} \) are material properties independent of geometry. The smooth and overlapping portion of the curves in Figs. 8 and 9 represent Fickian behavior. However, the thinner sample’s absorption profile deviates from the thicker sample even in an early stage of moisture uptake, indicating the non-Fickian diffusion process. Moreover, the data points for the thinner samples have more erratic trends, which reflect discontinuous relaxation behavior. These observations indicate that relaxation rate has more of an effect on thinner samples, making it a thickness dependent property. The compound clearly demonstrates the two mechanisms of anomalous moisture uptake, Fickian diffusion and relaxation.

### Table 4: Dual stage model parameters for Compound E

<table>
<thead>
<tr>
<th>Thickness</th>
<th>( D_1 ) (mm²/hr)</th>
<th>( C_{\text{sat,1}} ) (mg/cm³)</th>
<th>( D_2 ) (mm²/hr)</th>
<th>( C_{\text{sat,2}} ) (mg/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 mm</td>
<td>1.52E-02</td>
<td>2.17E+00</td>
<td>1.95E-03</td>
<td>3.38E+00</td>
</tr>
<tr>
<td>1.4 mm</td>
<td>1.52E-02</td>
<td>2.17E+00</td>
<td>6.61E-04</td>
<td>2.99E+00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thickness</th>
<th>( D_1 ) (mm²/hr)</th>
<th>( C_{\text{sat,1}} ) (mg/cm³)</th>
<th>( D_2 ) (mm²/hr)</th>
<th>( C_{\text{sat,2}} ) (mg/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 mm</td>
<td>6.57E-03</td>
<td>2.17E+00</td>
<td>1.15E-03</td>
<td>1.52E+00</td>
</tr>
<tr>
<td>1.4 mm</td>
<td>6.57E-03</td>
<td>2.17E+00</td>
<td>3.31E-04</td>
<td>1.60E+00</td>
</tr>
</tbody>
</table>

### Table 5: Desorption model parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>( D ) (mm²/hr)</th>
<th>( C_0,1/C_0 ) (%)</th>
<th>( C_0,2/C_0 ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>7.65E-02</td>
<td>10.05E-01</td>
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</tr>
<tr>
<td>B</td>
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<td>1.12E-01</td>
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<td>C</td>
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<td>1.10E-01</td>
<td>76.8</td>
</tr>
<tr>
<td>D</td>
<td>8.56E-02</td>
<td>1.10E-01</td>
<td>86.5</td>
</tr>
</tbody>
</table>

6. Dual Stage Desorption

#### 6.1 Dual-Stage Fit

The dual stage model for desorption considers a residual moisture \( (M_{0,2}) \) parameter in a Fickian model as shown in Equation (19) to fit the data curve. This can be considered as a “modified” Fickian model. Since desorption depends on the initial moisture content, which can vary, depending on prior absorption content, the absolute value of \( M_{0,1} \) and \( M_{0,2} \) are not of interest. For example, in the 140°C test there was much more initial moisture because these were the same samples used in 85°C /85% RH absorption test. Correspondingly, the 160°C test had less moisture because these were the same samples used in the 60°C /85% RH absorption test. Instead, the percent moisture, \( M_{0,1}/M_0 \) and \( M_{0,2}/M_0 \), is used in the following analysis. As mentioned above, \( M_{0,2} \) was set to the final data point found experimentally. \( M_{0,1} \) and \( D_1 \) were solved using the least square method in conjunction with Equation (19). The resulting values from this method are displayed in Table 5 with the curve fits shown in Fig. 10 and Fig 11, respectively. For 160°C test, which was actually conducted for 48 hours, Fig. 11 shows the shortened graph up to 25 hours, since there was little change in residual moisture content. Table 5 clearly shows that the 140°C test has much greater residual moisture (around 25%) than 140°C (less than 10%). This is due primarily from the higher temperature allowing more moisture to be released. The higher energy at higher temperature may break more of the hydroxyl bonds that bind the water molecules to the polymer. Surprisingly, the diffusivities for each of the 1 mm samples at 140°C and 160°C are very close to each other. The diffusivities at 140°C are significantly smaller than 160°C. The difference in the dual stage and Fickian models becomes less noticeable as duration and temperature increases. With so little moisture left in the samples after the test is completed, the subtraction of the residual moisture left in the samples is also less mathematically significant at a higher temperature.

### Table 5: Desorption model parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>( D ) (mm²/hr)</th>
<th>( C_0,1/C_0 ) (%)</th>
<th>( C_0,2/C_0 ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>7.65E-02</td>
<td>10.05E-01</td>
<td>77.3</td>
</tr>
<tr>
<td>B</td>
<td>7.65E-02</td>
<td>1.12E-01</td>
<td>88.3</td>
</tr>
<tr>
<td>C</td>
<td>7.21E-02</td>
<td>1.10E-01</td>
<td>76.8</td>
</tr>
<tr>
<td>D</td>
<td>8.56E-02</td>
<td>1.10E-01</td>
<td>86.5</td>
</tr>
</tbody>
</table>

Fig. 8: Dual stage fits of Compound E at 85°C /85% RH

Fig. 9: Dual stage fits of Compound E at 60°C /85% RH
6.2 Desorption Thickness Effects

For Compound E with two thicknesses, the initial diffusivities, and \( C_{0,1}/C_0 \), were fitted with Equation (19). Then the averaged values for two thicknesses were forced back into Equation (19) to solve the residual moisture content \( C_{0,2}/C_0 \). The results are displayed in Table 6, and the fitted curves are plotted in Fig. 12 and Fig. 13 for two temperatures, respectively. These two fitted curves are essentially parallel each other with a small shift due to the difference in initial moisture content. This indicates that the dual-stage desorption model of Equation (19) is independent of sample thickness. The variations in Figs. 12 and 13 are more likely due to the lower accuracy of the test more than the desorption mechanisms. All data shows the thickness seemed to matter very little in the final residual moisture percentage.

Table 6: Desorption model parameters for Compound E

<table>
<thead>
<tr>
<th>Thickness</th>
<th>D (mm(^2/hr))</th>
<th>( C_{0,1}/C_0 ) (%)</th>
<th>( C_{0,2}/C_0 ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140°C</td>
<td>160°C</td>
<td>140°C</td>
<td>160°C</td>
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<tr>
<td>3 mm</td>
<td>1.69E-01</td>
<td>2.21E-01</td>
<td>72.4</td>
</tr>
<tr>
<td>1.4 mm</td>
<td>1.69E-01</td>
<td>2.21E-01</td>
<td>72.4</td>
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</tbody>
</table>

7. Concluding Remarks

Several epoxy mold compounds in absorption and desorption were studied. When the Fickian model produced insufficient results, the anomalous moisture uptake was described with a dual stage model using two Fickian models superpositioned. This idea was extended to the desorption process to account for residual moisture content. These models can describe both Fickian and non-Fickian behavior with Fickian parameters. They can be used to compare the two different mechanisms and produce consistent, fairly accurate results that correlate well with the actual physical processes. The models produced good curve-fits with the experimental data for all five samples. For absorption, non-Fickian behavior was proven to be a great influence on the amount moisture uptake though Fickian diffusion rates were quite larger. Thickness also has a significant role in absorption, indicating the role of anomalous uptake. Relaxation appeared more readily in thinner samples of the same compound which slowed the diffusion rate. In desorption, thickness of the samples does not have nearly as much influence on the amount of residual moisture as the temperature. Residual moisture content decreases significantly as temperature rises. Not only was the desorption model able to generate better curve fits to the
data, but it was also able to predict the proper residual moisture content.

For anomalous moisture diffusion, there has been a lack of simulation tools to model the diffusion process in actual packaging systems. In this paper, a dual-stage model is developed to describe both Fickian and non-Fickian diffusions using two sets of Fickian parameters. This work provides a theoretical foundation with experimental validation for a feasible finite element model of anomalous moisture diffusion using currently available finite element software. The results will be reported separately in the future.

Acknowledgement
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References