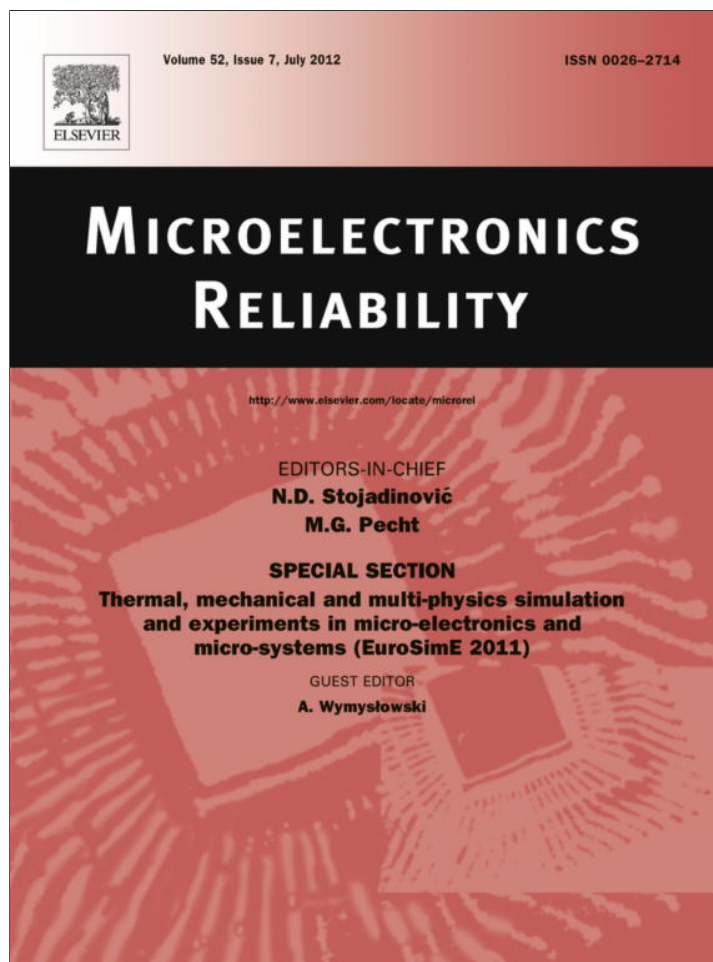


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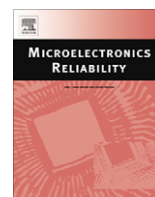
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Dual stage modeling of moisture absorption and desorption in epoxy mold compounds

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ABSTRACT

A dual stage diffusion model is developed in this paper for both absorption and desorption processes. Both stages in moisture absorption and desorption, i.e., Fickian and non-Fickian process, are described mathematically using a combination of Fickian terms. Absorption and desorption tests are also conducted on six distinct commercial epoxy mold compounds (EMCs) used in electronic packaging. For absorption, the samples are subjected to 85 °C/85% relative humidity and 60 °C/85% relative humidity soaking, respectively. Desorption conditions are above glass transition temperature at 140 °C and 160 °C. The dual stage models generate reasonable results for the diffusive properties and display outstanding experimental fits. All six compounds show strong non-Fickian diffusion behaviors, which are further verified by the experiments with different thicknesses. For absorption, while Fickian diffusion is dominant in the beginning of process, non-Fickian mechanism plays a large role with time increasing. Saturated moisture concentration associated with Fickian-stage diffusion appears to be independent of temperature under the tested conditions. For desorption, higher temperature leads to less percentage of the permanent residual moisture content in most compounds. At 160 °C, 90% of the initial moisture for all samples is diffused out within 24 h, following an approximate modified Fickian diffusion process. The dual stage model developed in this paper provides a mathematical formulation for modeling anomalous moisture diffusion behavior using commercial finite element analysis software.

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1. Introduction

Epoxy mold compounds (EMCs) are an essential subject in microelectronics reliability. While these compounds have advantages that make them applicable in electronic packaging such as molding ability and thermal properties, their behavior is limited by the moisture absorption from the environment [1]. After moisture has entered the compounds, the water molecules can induce stresses which may be 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. Moisture may also change the mechanical properties of the compound itself such as lowering the glass transition temperature or elastic modulus, and 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 absorbed by a polymer occurs in two states, mobile or bound [2–14]. 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 is similar to a typical mass concentration gradient driven diffusion process, and can be described well by Fick's laws [15]. 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. This chemical absorption process can be irreversible and causes non-Fickian behavior. These states are crucial to understanding the mechanisms of absorption and desorption in EMCs.

The moisture mechanisms can be categorized in three groups: Case I, Case II, and anomalous uptake, as illustrated in Refs. [7,8]. Case I refers to classic Fickian absorption. In this case, the diffusion rate is assumed to be constant and governs the uptake. Although Fickian diffusion has been used for decades, it has a very limited window of accuracy for describing long-term moisture absorption in EMCs and desorption at elevated temperatures [16–18]. Case II refers to moisture uptake governed by relaxation rate. In relaxation, the pressure of the absorbed water molecules causes the com-

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pound 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 negligible at the beginning of the absorption process. 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. Consequently, anomalous uptake has been frequently modeled as a dual stage sorption [5–7,9–11]. This concept has been applied to several different diffusion processes of many artificial materials. The Fickian behavior is superpositioned with a function of the relaxation and/or chemical sorption such as Carter and Kibler’s Langmuir-Type Model [5] or Gurtin and Yatomi’s “free” and “trapped” phase model [10]. For moisture desorption at elevated temperatures in a short time scale such as in a reflow process, the diffusion mechanism becomes more complicated. Higher activation energy of material at higher temperature certainly increases the diffusivity exponentially, and therefore the diffusion process is much faster. In addition, some of the hydrogen bonds that bind the water molecules to the polymer will be broken to release some of bound water. Few models in literature have been developed to describe the desorption process at high temperature [13].

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 six EMCs in both moisture uptake and loss. The dual stage model is then used to analyze the experimental data, quality of data fittings, thickness effects, and diffusion mechanics. The paper is organized as follows: Section 2 discusses the mathematical dual stage models for absorption and desorption process. Section 3 describes the experimental procedure and testing conditions. The Fickian absorption and desorption models are demonstrated in Section 4. The dual stage absorption model is introduced in Section 5 to analyze the experimental data, and the dual stage desorption model is shown in Section 6. Finally, Section 7 gives the concluding remarks.

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 [15].

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where 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, the boundary and initial conditions are

$$\begin{aligned} C &= C_0, & -l < x < l, & & t = 0 \\ C &= C_b, & x = l, & x = -l, & t \geq 0 \end{aligned} \quad (2)$$

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.

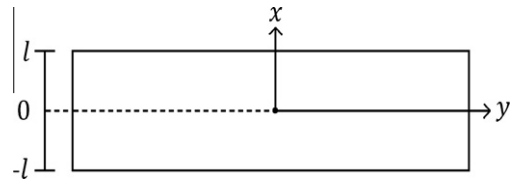


Fig. 1. An infinite plate with the thickness $2l$.

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

$$C(x, t) = F(x)G(t) \quad (3)$$

The differential equation of the fundamental solutions of Eq. (1) becomes

$$F \frac{dG}{dt} = DG \frac{d^2 F}{dx^2} \quad (4)$$

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

$$C = (A \sin \lambda x + B \cos \lambda x) \exp(-\lambda^2 Dt) \quad (5)$$

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

$$C = \sum_{m=1}^{\infty} (A_m \sin \lambda_m x + B_m \cos \lambda_m x) \exp(-\lambda_m^2 Dt) \quad (5a)$$

where A_m , B_m , and λ_m are determined by initial boundary conditions specified in Eq. (2).

Solving for constants A_m , B_m , and λ_m and substituting the boundary and initial conditions into Eq. (5a) yield the general solution for Fickian diffusion of an infinite plate,

$$\begin{aligned} \frac{C(x, t) - C_0}{C_b - C_0} &= 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \exp\left[\frac{-(2n+1)^2 \pi^2 Dt}{4l^2}\right] \\ &\times \cos\left(\frac{(2n+1)\pi x}{2l}\right) \end{aligned} \quad (6)$$

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 Eq. (6) becomes

$$\begin{aligned} \frac{C(x, t)}{C_{sat}} &= 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \exp\left[\frac{-(2n+1)^2 \pi^2 Dt}{4l^2}\right] \\ &\times \cos\left(\frac{(2n+1)\pi x}{2l}\right) \end{aligned} \quad (7)$$

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

$$\begin{aligned} \frac{C(x, t)}{C_0} &= \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \exp\left[\frac{-(2n+1)^2 \pi^2 Dt}{4l^2}\right] \\ &\times \cos\left(\frac{(2n+1)\pi x}{2l}\right) \end{aligned} \quad (8)$$

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

$$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{-(2n+1)^2 \pi^2 Dt}{4l^2}\right] \quad (9)$$

for absorption and

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

for desorption. M_t is the total mass of moisture at time t , and M_{∞} 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 .

$$C_{sat} = \frac{M_{\infty}}{V}, \quad C_0 = \frac{M_0}{V} \quad (11)$$

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 follows,

$$C(x, t) = C_1(x, t) + C_2(x, t) \quad (12)$$

which is illustrated in Fig. 2. C_1 represents the moisture concentration due to Fickian diffusion while C_2 is non-Fickian contribution to moisture concentration. Eventually the total saturation will be reached after the relaxation process is complete. The concept of dual stage model has been applied to several different diffusion processes, such as Carter and Kibler's Langmuir-Type Model [5] or Gurtin and Yatomi's "free" and "trapped" phase model [10]. Those models provide good agreement with experimental data, but introduces additional parameters and mathematical complexity.

In this paper, the second stage is also modeled in Fickian terms for mathematical simplicity and comparability. It should be noted that the second stage (C_2) is an irreversible, non-Fickian process. Eq. (12) becomes

$$C(x, t) = C_1(x, t, D_1, C_{sat,1}) + C_2(x, t, D_2, C_{sat,2}) \quad (13)$$

where $C_{sat,1}$ and D_1 and $C_{sat,2}$ 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 as follows,

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2}, \quad (14)$$

with boundary conditions

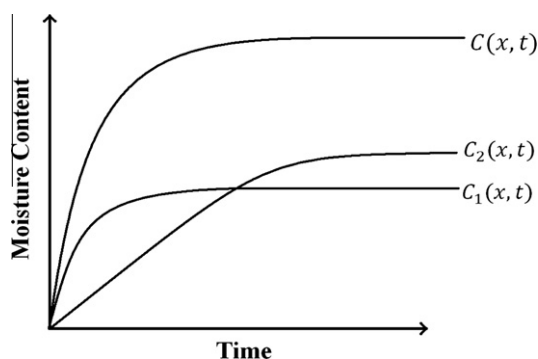


Fig. 2. Representation of superpositioned diffusion functions for a dual stage model.

$$C_1 = 0, \quad -l < x < l, \quad t = 0$$

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

and

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2}, \quad (15)$$

with boundary conditions

$$C_2 = 0, \quad -l < x < l, \quad t = 0$$

$$C_2 = C_{sat,2} = C_{\infty} - C_{sat,1}, \quad x = l, \quad x = -l, \quad t \geq 0$$

Superpositioning Eqs. (14) and (15) yield Eq. (12). Eqs. (14) and (15) are solved by the separation of variables technique, similar to Eq. (3). The solution for Eq. (12) resembles Eq. (9) with the addition of the second stage:

$$M_t = M_{\infty,1} \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[\frac{-(2n+1)^2 \pi^2 D_1 t}{4l^2} \right] \right] + M_{\infty,2} \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[\frac{-(2n+1)^2 \pi^2 D_2 t}{4l^2} \right] \right] \quad (16)$$

with

$$M_{\infty,1} = C_{sat,1} V, \quad M_{\infty,2} = C_{sat,2} V = M_{\infty} - M_{\infty,1} = (C_{\infty} - C_{sat,1}) V \quad (17)$$

M_t is the sum of the moisture mass for both stages at time, t . $M_{\infty,1}$ and $M_{\infty,2}$ represent the total moisture mass gained by each respective stage. It is expected that D_1 is significantly larger than D_2 because the chemical bonding and relaxation of the sample is negligible at the beginning of absorption. Both functions therefore have Fickian diffusivity coefficients and saturation. While $C_{sat,1}$ and D_1 are actual material properties, $C_{sat,2}$ and D_2 are mathematical simplifications solely for modeling and comparison purposes. In the other words, D_2 and $C_{sat,2}$ are not considered as material properties.

2.3. Dual-stage diffusion: desorption

The desorption model may be obtained using the same method to find Eq. (16). The desorption equation is

$$M_t = M_{0,1} \left[\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[\frac{-(2n+1)^2 \pi^2 D_1 t}{4l^2} \right] \right] + M_{0,2} \left[\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[\frac{-(2n+1)^2 \pi^2 D_2 t}{4l^2} \right] \right] \quad (18)$$

where D_1 and $M_{0,1}$ are the diffusivity and the maximum moisture content that can be escaped at desorption temperature, and $M_{0,2}$ is equal to $M_{\infty} - M_{0,1}$, the residual moisture content, and D_2 is the diffusivity of the second stage. During desorption at elevated temperatures, not only those "free-state" moisture can be diffused out, but also some water molecules with relatively weak bonding can be broken to escape. However, the rest of the bound water molecules will remain in a reasonable time period. Therefore, in the dual stage model described by Eq. (18), the first term describes the moisture diffusion for a combination of free and bound water, and second term describes the trapped moisture. In this sense, D_2 may be taken to be zero to approximately model a "permanent" moisture state in material. As a result, the second stage term in Eq. (18) becomes a constant term $M_{0,2}$, representing the amount of residual moisture in the sample after it has reached equilibrium. Fig. 3 visually displays this idea. Eq. (18) becomes:

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

where 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

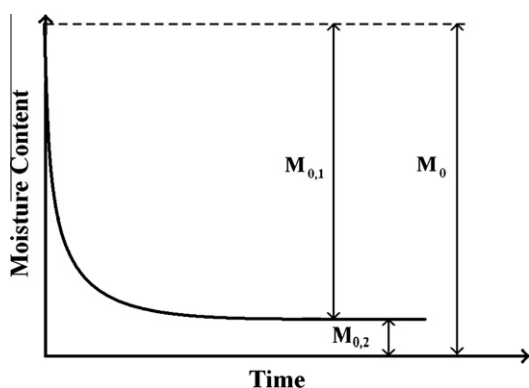


Fig. 3. Representation of dual stage desorption concept.

for M_t , $M_{0,1}$, and $M_{0,2}$. Since Eq. (19) involves only one diffusivity (D_1), it is called “modified” Fickian model in this paper. From Eq. (19), if the normalized time scale t/l^2 (or $t^{1/2}/l$) is used, different sample thickness should generate the same results.

3. Experimental procedure

Four distinct weight gain/loss tests were conducted using a humidity-temperature chamber. Two samples of each compound and geometry were placed in the chamber for each test. Compounds A, B, C, D, and F 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. Compound F was tested separately than the other compounds, and the order and duration of the tests changed. Table 1 displays the compound geometry details, and Tables 2 and 3 show the testing details. Testing included absorption at 85 °C/85% RH and 60 °C/85% RH and desorption tests at 140 °C and 160 °C. Compounds A–E were first soaked at 85 °C/85% RH and then baked at 140 °C for desorption. New samples were then soaked at 60 °C/85% RH and baked at 160 °C. Conversely, Compound F was first soaked at 85 °C/85% RH and then baked at 160 °C. Fresh samples were then soaked at 60 °C/85% RH and baked at 140 °C. Other than the order of desorption tests, no experimental procedure changed. At the beginning of each absorption test, the samples were baked for 72 h 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 dried at the respective temperatures. The samples were allowed to cool for approximately 30–60 s before weighing due to the high temperature of some of the tests.

The errors associated with these experiments can be contributed to several factors. One is the change in the environmental conditions while the samples were being weighed. The amount of time the samples were out of the chamber was no greater than

Table 1
Details of EMCs used in each test.

Compound	Geometry	Thickness (mm)
A	Circular	50 mm dia. 1
B	Circular	50 mm dia. 1
C	Circular	50 mm dia. 1
D	Circular	50 mm dia. 1
E	Circular	50 mm dia. 3
E	Square	2.4 mm side 1.4
F	Circular	50 mm dia. 1

Table 2
Test conditions and durations for Compounds A–E.

Test	Process	Condition	Duration (h)
1	Absorption	85 °C/85%RH	650
2	Desorption	140 °C	25
3	Absorption	60 °C/85%RH	1233
4	Desorption	160 °C	48

Table 3
Test conditions and durations for Compounds F.

Test	Process	Condition	Duration (h)
1	Absorption	85 °C/85%RH	316
2	Desorption	160 °C	27
3	Absorption	60 °C/85%RH	500
4	Desorption	140 °C	25

8 min. 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 moisture sensors are being studied [19].

The glass transition temperatures of these six compounds are in between 100 °C and 120 °C. Since the diffusivity follows two sets of Arrhenius equation constants below and above glass transition temperatures, respectively [2], the desorption temperatures were chosen as 140 °C and 160 °C. It is desirable to test moisture desorption properties at even higher temperatures as the peak reflow temperature is around 270 °C. However, due to the difficulty of manually measuring moisture mass, the data at higher temperature become very unreliable.

4. Fickian absorption and desorption

First, a classic Fickian model, Eq. (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. This is represented by

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

where E is the total error found by subtracting the calculated values of moisture content $M(t_n)$ 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 Figs. 4 and 5, making the values found very unreliable.

5. Dual-stage absorption

5.1. Dual-stage fit

The dual stage model proposed by Eq. (16) was developed with the least square-method solving for values of $C_{sat,1}$ and D_1 and $C_{sat,2}$ 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 Figs. 6

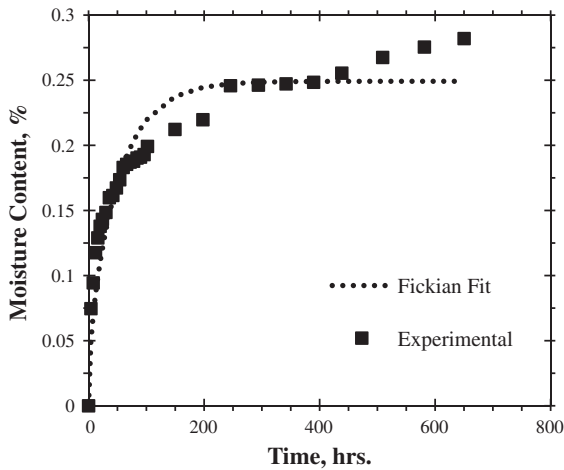


Fig. 4. Fickian fit of Compound A at 85 °C/85%RH.

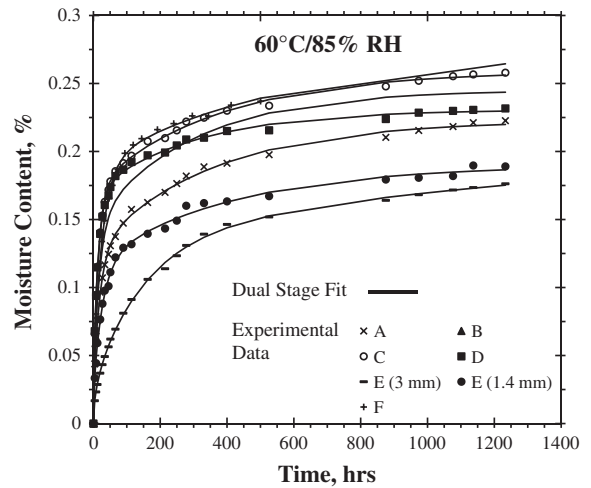


Fig. 7. Dual stage fits at 60 °C/85%RH.

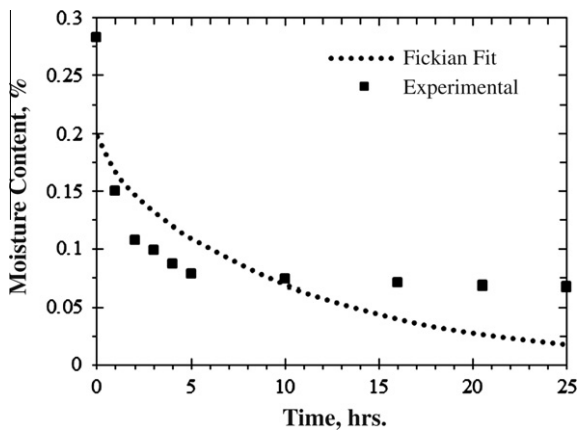


Fig. 5. Fickian fit of Compound A at 140 °C/0%RH.

Table 4
Dual stage parameters.

Compound	D_1 (mm ² /h)	$C_{sat,1}$ (mg/cm ³)	D_2 (mm ² /h)	$C_{sat,2}$ (mg/cm ³)
<i>85 °C/85%RH</i>				
A	1.23E-02	2.29E + 00	5.61E-04	3.59E + 00
B	1.39E-02	2.90E + 00	5.30E-04	2.86E + 00
C	1.80E-02	3.26E + 00	5.54E-04	3.22E + 00
D	1.92E-02	3.34E + 00	5.04E-04	2.22E + 00
E (3 mm)	1.52E-02	2.17E + 00	1.95E-03	3.38E + 00
E (1.4 mm)	1.52E-02	2.17E + 00	6.61E-04	2.99E + 00
F	1.16E-02	3.85E + 00	1.17E-03	2.27E + 00
<i>60 °C/85%RH</i>				
A	4.28E-03	2.29E + 00	2.80E-04	2.42E + 00
B	5.01E-03	2.90E + 00	2.72E-04	2.22E + 00
C	5.93E-03	3.26E + 00	2.02E-04	1.95E + 00
D	6.14E-03	3.34E + 00	2.06E-04	1.28E + 00
E (3 mm)	6.57E-03	2.17E + 00	1.15E-03	1.52E + 00
E (1.4 mm)	6.57E-03	2.17E + 00	3.31E-04	1.60E + 00
F	3.72E-03	3.85E + 00	1.29E-04	2.57E + 00

and 7, respectively. Table 4 summarize the results of the dual stage fits with “forced” same values of $C_{sat,1}$, which were obtained by the average at two different temperatures for each compound. The values of D_1 , $C_{sat,2}$, and D_2 were then solved simultaneously with Eq. (20). This procedure still generated excellent curve fits that are almost indistinguishable from Figs. 6 and 7. This indicates that saturated moisture concentration associated with Fickian-stage

diffusion is relatively independent of temperature under the tested conditions. From Table 4, it can be seen that the diffusivity of the second stage is one or two orders lower than the first stage at both 85 °C/85% RH and 60 °C/85% RH conditions. This shows that the Fickian behavior is dominant in the beginning of absorption process. It is interesting to note that $C_{sat,2}$ is comparable, or greater than $C_{sat,1}$, meaning that the non-Fickian behavior plays a major role in moisture uptake when time increases.

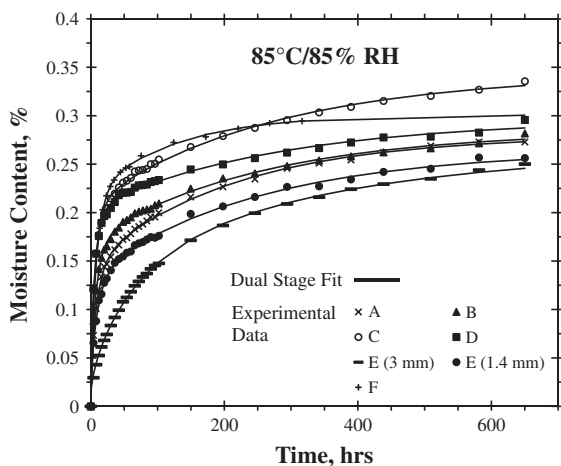


Fig. 6. Dual stage fits at 85 °C/85%RH.

5.2. Thickness effects on absorption

$C_{sat,1}$ and D_1 are material properties that are independent of specimen geometry. But $C_{sat,2}$ and D_2 are mathematical simplifications solely for modeling and comparison purposes. To verify this, compound E, with two thicknesses of 1.4 mm and 3.0 mm, was tested. The fitted results are shown in Figs. 8 and 9, respectively. The figures use normalized time and thickness, $(t/l^2)^{1/2}$, based on a typical Fickian diffusion from Eq. (6), to reveal the deviation of moisture diffusion behavior from Fickian behavior due to different thicknesses. Figs. 8 and 9 presented the excellent fits using the dual stage model for both thicknesses under two soaking conditions. The two curves overlap at the beginning of the processes. According to Fick’s law, the diffusivity and C_{sat} are material properties independent of geometry. The smooth and overlapping portion of the curves in Figs. 8 and 9 represent Fickian behavior. However,

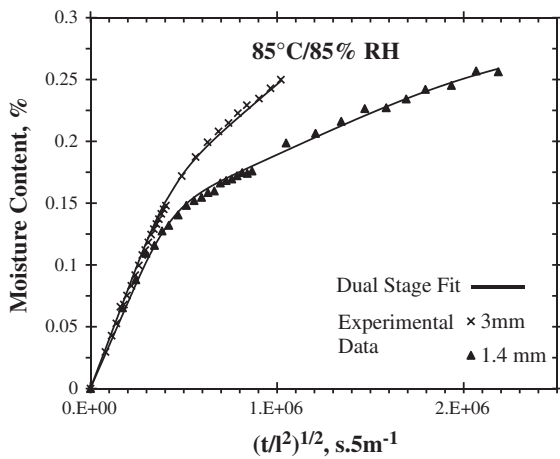


Fig. 8. Dual stage fits of Compound E at 85 °C/85%RH.

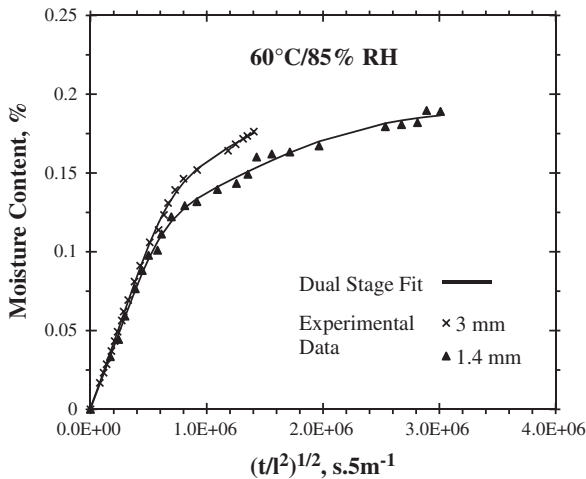


Fig. 9. Dual stage fits of Compound E at 60 °C/85%RH.

the thinner sample's absorption profile deviates from the thicker sample after a period of time, indicating the non-Fickian diffusion process. These results clearly demonstrate the two mechanisms of anomalous moisture uptake, Fickian diffusion and relaxation. From Table 4, it can be seen that two samples with different thicknesses generated the same values of $C_{sat,1}$ and D_1 , but geometry-dependent $C_{sat,2}$ and D_2 .

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 modified Fickian model as shown in Eq. (19) to fit the data curve. It is noted that $M_0 = M_{0,1} + M_{0,2}$, is the saturated moisture mass at the temperature and humidity of preconditioning. In actual experimental testing, since the final saturation may never be reached, M_0 is considered as initial moisture mass measured for each desorption test. Since desorption depends on the initial moisture content, which can vary, the absolute value of $M_{0,1}$ and $M_{0,2}$ are not of interest. For example, in the 140 °C test for Compounds A–E 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.

Therefore, instead of absolute moisture content, the percent moisture, $M_{0,1}/M_0$ and $M_{0,2}/M_0$, is used in the following analysis. $M_{0,2}/M_0$ is obtained from the final data point when the equilibrium is reached (no further significant moisture loss in a reasonable time period). $M_{0,1}$ and D_1 were then solved using the least square method in conjunction with Eq. (19). The curve fits are shown in Figs. 10 and 11, respectively, and the resulting values from this method are displayed in Table 5. The dual stage desorption model generated excellent fits for all samples for conditions at 160 °C/0% RH and 140 °C/0% RH. 160 °C test was actually conducted for 48 h, Fig. 11 shows the shortened graph up to 25 h, since there was little change in residual moisture content. Figs. 10 and 11 show that when the residual moisture is considered in the model in Eq. (19), the “modified” Fickian diffusion can describe the desorption process well. However, it is noted that during desorption at elevated temperature greater than 100 °C, moisture diffusion is not only driven by the concentration gradient, but also by vapor pressure. In addition, the higher energy at elevated temperature breaks more of the hydrogen bonds that bind the water molecules to the polymer to release moisture. The moisture diffusion due to these combined effects somehow follows a Fickian diffusion characteristics well, according to Figs. 10 and 11. Table 5 also shows that for Compounds A–E the 160 °C test has much greater residual moisture (around 25%) than 140 °C (less than 10%). The higher energy at higher temperature may break more of the hydrogen bonds that bind the water molecules to the polymer, resulting in a less percentage of residual moisture. However, Compound F showed little difference in the amount of residual moisture for the higher temperature. In fact, the residual moisture content is nearly identical. The change in procedure, order of absorption/desorption test conditions, may be to blame. Another explanation may be that longer absorption exposure time, which was double for Compounds A–E, could lead to higher irreversible bonding behavior and would lead to more residual moisture in these compounds [16,17].

6.2. Thickness effects on desorption

For Compound E with two thicknesses, the initial diffusivities, and $C_{0,1}/C_0$, were fitted with Eq. (19). The fitted curves in normalized scale are plotted in Figs. 12 and 13 for two temperatures, respectively. These two fitted curves are essentially parallel to each other with a small shift due to the difference in initial moisture content. This indicates that both geometries provide the same diffusive properties, as predicted by Eq. (19). The variations in Figs. 12 and 13 are more likely due to the lower accuracy of the test more

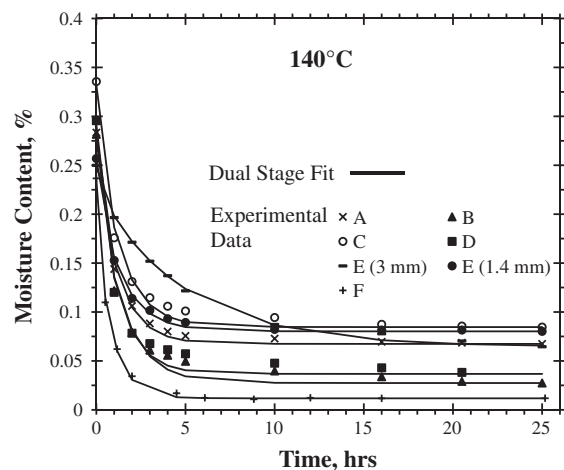


Fig. 10. Dual stage fit of desorption at 140 °C.

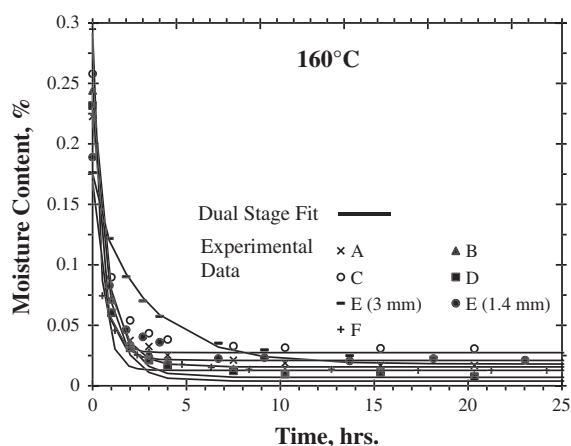


Fig. 11. Dual stage fit of desorption at 160 °C.

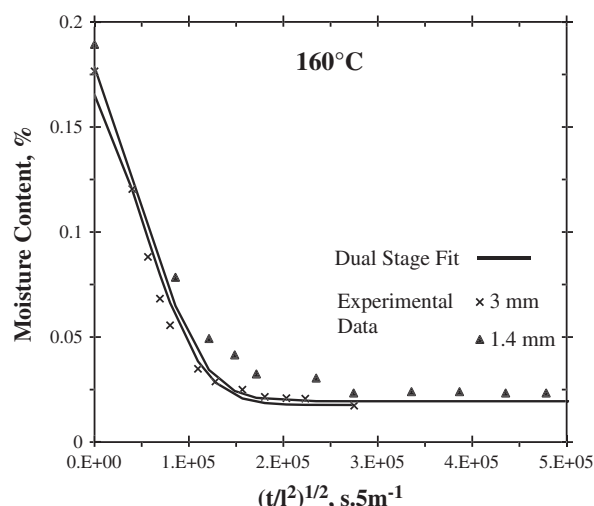


Fig. 13. 'Modified' Fickian fit of Compound E at 160 °C.

Table 5
Desorption model parameters.

Compound	D (mm ² /h)		$C_{0,1}/C_0$ (%)		$C_{0,2}/C_0$ (%)	
	140°C	160°C	140°C	160°C	140°C	160°C
A	7.65E-02	1.05E-01	77.3	95.5	22.7	4.5
B	7.65E-02	1.12E-01	88.3	97.7	11.7	2.3
C	7.21E-02	1.10E-01	76.8	90.1	23.2	9.9
D	8.56E-02	1.10E-01	86.5	98.9	13.5	1.1
E (3 mm)	1.69E-01	2.21E-01	72.4	90.0	27.6	10.0
E (1.4 mm)	1.69E-01	2.21E-01	72.4	90.0	27.6	10.0
F	1.21E-01	2.06E-01	94.3	94.2	5.7	5.8

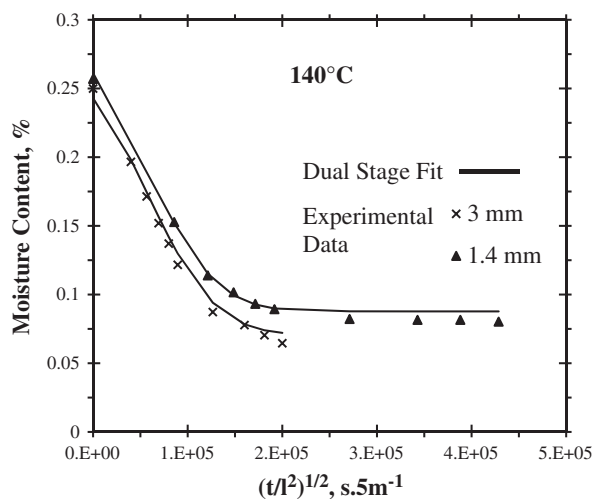


Fig. 12. 'Modified' Fickian fit of Compound E at 140 °C.

than the desorption mechanisms. Since the D_2 is approximately assumed to be zero in the model, and effect of the non-Fickian effect appears only in terms of the residual moisture content, and is thickness-independent. Further verification of these observations has been made with the in situ moisture analyzer measurement [19].

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 also 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 six samples with different chemical makeups. For absorption under the tested conditions, non-Fickian behavior was proven to be a great influence on the amount moisture uptake with time increasing. The model parameters for the first Fickian stage, $C_{sat,1}$ and D_1 , are material properties, but $C_{sat,2}$ and D_2 are not considered as material properties. These have been further verified experimentally with different thicknesses. Saturated moisture concentration associated with Fickian-stage diffusion appears independent of temperature under the tested conditions. In desorption at elevated temperatures, the moisture diffusion follows a Fickian characteristic well when the residual moisture content is included in the modified Fickian model. Higher temperature corresponds to less percentage of the permanent residual moisture content in most compounds. At 160 °C, 90% of the initial moisture for all samples is diffused out within 24 h. Residual moisture content decreases significantly as temperature rises in most cases. Reversing the order of absorption/desorption tests and lowering the initial uptake exposure time showed to have much significance in the amount of 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 mathematical formulation framework 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 [20].

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