

In-situ Moisture Desorption Characterization of Epoxy Mold Compound

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Abstract

Moisture desorption characteristics of an epoxy mold compound (EMC) at 100°C, 120°C, 140°C, 160°C, 180°C, 200°C, 220°C, 240°C, and 260°C, respectively, is studied in this paper. A high resolution moisture analyzer is used to measure *in-situ* moisture weight loss as a function of time at different temperatures. The specimens are preconditioned (e.g. 85°C /85%RH) before they are placed in the analyzer for desorption process. The material can be heated to the desired temperature in a contained septum bottle that connects to a dry air flow system and a moisture sensor. The moisture sensor detects water in the gas stream to generate an accurate measurement of the moisture content released from the specimen. Manual moisture weight gain tests at 85°C/85% RH and 60°C/85% RH are also performed for comparison analysis. It is found that while dual stage model describes the anomalous moisture absorption and desorption well at temperatures below 100°C, a single-phase Fickian diffusion model fit the desorption curves reasonably above 100°C. This means that the initial moisture content, which includes both free and bound water, can be released completely at higher temperatures in reflow process. Arrhenius constants, i.e. pre-factor and activation energy, are obtained for an entire temperature range both below and above the glass transition temperature.

Introduction

Moisture diffusion in epoxy molding compounds (EMCs) is one of the most important factors that determine the shelf life and reliability performance of semiconductor packages. The most dramatic moisture-induced failure mechanism would be so-called popcorning, which involves catastrophic crack growth during a solder reflow process [1, 2]. Diffusion properties of the EMC at high temperatures are essential to prediction of the moisture-related behavior of plastically encapsulated microcircuits (PEMs) subjected to the reflow process. From a predictive modeling point of view, the diffusivity of desorption is more critical than the diffusivity of absorption because the package loses moisture during the reflow process. On the other hand, the diffusivity of absorption is required for modeling the package subjected to moisture soaking at low temperatures such as JEDEC moisture standards [3].

The properties reported in the literature [1, 4-7] were obtained at relatively low temperature range, i.e., below the boiling point of water (100°C). Although some data above 100°C can be found in the literature [6, 7, 8-10],

the data do not cover a sufficiently wide range of high temperature diffusion behavior. As a result, properties at higher temperatures are usually approximated by extrapolating the Arrhenius equation for the diffusivity of absorption obtained at low temperatures. This extrapolation can lead to a large prediction error when the diffusion model is applied to the solder reflow process because the Arrhenius relationship may not be valid above the glass transition temperature (T_g) of polymeric materials [11-14] and the diffusivity of absorption can be substantially different from the diffusivity of desorption. Recently diffusion properties of EMCs in both absorption and desorption modes at a wide range of temperatures were obtained by moisture weight gain and loss measurements [10]. However, moisture weight gain test is not practical at high temperatures above 100°C because pressurization of a chamber with water vapor is required at above 100°C (e.g., 2 atm at 121°C/100%RH). It takes a significant amount of time for the chamber to reach a targeted condition (stabilization time). This causes a significant error in the measurement of moisture weight gain, not only due to an inaccurate time history but also due to undesirable and hard-to-predict moisture transport during stabilization.

Although the procedure of the weight loss test is described in detail in the JEDEC standard [15], it is also difficult to achieve a high level of accuracy at high temperatures above 100°C due to extremely fast moisture diffusion. The thermo-gravimetric analysis (TGA) has been often utilized to measure the diffusivity of desorption [16]. Although it works well for transient weight change measurement at low temperatures, the use of TGA at high temperatures poses numerous technical challenges. Shi et al. [5] have reported that the high temperature diffusivity data produced by a TGA differed significantly from those by a titrator. Recently the moisture absorption-desorption behavior of thin polymer film was characterized *in-situ* using a TA Instruments Q5000 SA Thermogravimetric Analyzer (TGA) [17]. This instrument is a high sensitivity thermogravimetric analyzer which enables sorption/desorption analysis of materials under controlled temperature and humidity conditions. However, such a TGA with humidity control is still not suitable for obtaining desorption properties above 100°C. For the above reasons, the standard weight loss test was implemented for measurements at high temperatures but the thickness of a specimen was carefully determined so as to minimize the measurement uncertainty [10].

In this paper, a high resolution moisture analyzer, Computrac Vapro Pro Moisture Analyzer, is used to measure *in-situ* moisture loss as a function of time at a wide range of temperatures from 100°C to 260°C. Such a temperature range covers well the reflow process temperature range. Based on the experimental data, the diffusion constant and the saturated moisture concentration can be determined by Fickian constants or dual stage models. We will demonstrate that how a Fickian diffusion model might fit well the high temperature desorption characteristics. The Arrhenius constants are obtained for entire temperature range in reflow process below and above glass transition temperature.

Instrument

The Computrac Vapro Pro (Figure 1) is a moisture analyzer with a detection limit of 10 parts per million (ppm), and uses a sensor-based technology and correlates to the Karl Fischer coulometric titration method (with an oven attachment) in precision and accuracy. The principles of operation can be illustrated in Figure 2. The analyzer utilizes a cylinder shaped bottle heater, a dry air flow system and a moisture sensor. The instrument heats a sample of test material contained in a 25 ml (milliliter) septum bottle. Moisture masses released from the sample are carried by the air system through the sensor block containing the relative humidity (RH) sensor. The RH sensor used to detect water in the gas stream is a polymer capacitor relative humidity sensor. The reading from this sensor is combined with sensor block temperature and carrier gas flow rate in a microprocessor to generate an accurate measurement of the moisture content in the sample. The instrument then displays the result in terms of parts per million, percent moisture, or total micrograms of water. The heating range of the analyzer is 25°C to 275°C. Test parameters such as sample size, heater temperature and test ending criteria can be altered to optimize speed and accuracy.



Figure 1 Computrac Vapro Pro moisture analyzer

Material and Test Procedures

In this study, both manual moisture weight gain test at 85°C /85% RH and 60°C /85% RH, and *in-situ* moisture weight loss test using Vapor Pro analyzer are conducted. One commercial epoxy mold compound is selected. For moisture weight gain test, the sample dimension is 1 mm thick with a 50 mm diameter disk. For desorption test, the sample dimension is 14mm by 14mm with 1mm thickness.

For moisture weight gain test, at the beginning of each test, the samples are baked for 72 hours at 125°C to drain the ambient moisture content. After recording the dry weight of each sample, the chamber is set to the desired environmental conditions. The samples are periodically taken out of the chamber and weighed manually with a balance scale. As a baseline study, a manual weight loss test at 85°C is also conducted.

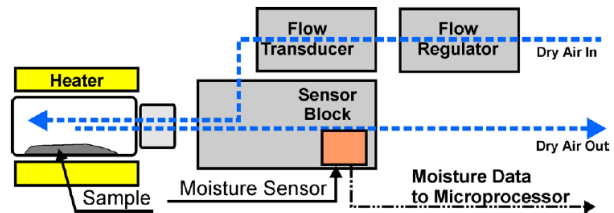


Figure 2 Illustration of the operation principle of moisture analyzer

For the *in-situ* moisture weight loss test, the tests are performed at 100°C, 120°C, 140°C, 160°C, 180°C, 200°C, 220°C, 240°C, and 260°C, respectively. The test procedures are as follows. The samples are baked for 72 hours. The dry weight of the sample is recorded. The samples are then preconditioned (e.g. 85°C/85%RH for at least 7 days). Before using the analyzer, an empty vial for each measured temperature is used to run the test to record the ambient moisture content in the vial, and determine the purge time needed. The sample is weighted manually in the balance before the test. Then the sample is placed in the vial to run the test with the preset purge time at desired temperature. The analyzer will record the *in-situ* escaped moisture from the sample in terms of parts per million (ppm), percent moisture, or total micrograms of water, as function of time. We usually set the test time between 15 minutes and 30 minutes since desorption at higher temperature is very fast. In addition, since the reflow process is within 5 to 10 minutes, we are interested in the desorption characteristics in a short time period only. After the test is done, the sample is taken out to weigh manually again in the balance. The data will be used to double check the readings from the analyzer.

Test Results

Moisture Absorption at 85°C /85% RH and Desorption at 85°C /0%RH

Figure 3 shows the moisture weigh gain curve subjected to 85°C/85%RH for 10 days, followed a desorption at the same temperature for 12 days, together with a dual stage model fits [8,9]. Table 1 gives the values of diffusivity and saturated moisture concentration for both absorption and desorption. Several important findings are observed,

- 1) During absorption, both Fickian and non-Fickian diffusions appear. A dual stage model describes the experimental data well. The Fickian diffusivity D_1 is one order greater than the non-Fickian diffusivity D_2 .
- 2) The non-Fickian moisture diffusion contributes to about 25% of the Fickian saturated moisture

concentration ($C_{sat,2}/C_{sat,1}$). The moisture content due to non-Fickian diffusion is expected to be nonreversible since it forms as bound water in material.

- 3) From desorption curve, the ‘permanent’ residual moisture content can be obtained from experiment. It is well aligned with as $C_{sat,2}$, predicted and obtained by the dual stage model in absorption. This demonstrates the validity of the dual stage model applicability.
- 4) Fickian diffusivity at desorption by fitting the experimental data is obtained the same as the Fickian diffusivity at absorption. Two parameters are obtained independently from experimental data. Such results confirm that Fickian part of diffusion predicted by the dual stage model is sound.
- 5) That the Fickian diffusion is a reversible process is also supported by the consistency of the Fickian saturated moisture concentrations obtained both from absorption and desorption, separately.

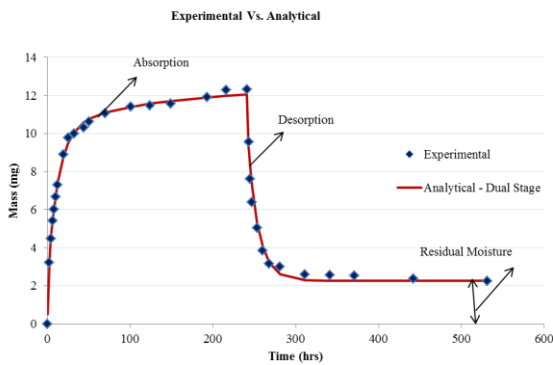


Figure 3 Moisture weigh gain and loss curve at 85°C/85%RH and 85°C/0%RH with dual stage model fit

Table 1 Dual stage model fit parameters at 85°C/85%RH and 85°C/0%RH

	Absorption	Desorption
D_1 (mm ² /hr)	8.00E-03	8.00E-03
$C_{sat,1}$ (mg/mm ³)	5.00E-03	5.00E-03
D_2 (mm ² /hr)	8.50E-04	0
$C_{sat,2}$ (mg/mm ³)	1.27E-03	1.15E-03

Moisture Absorption at 85°C /85% RH and Desorption at 60°C /85%RH

Figure 4 plots the moisture weigh gain curve subjected to 85°C/85%RH and 60°C/85%RH, respectively, with the dual stage model fits. Table 2 gives the values of diffusivity and saturated moisture concentration at both temperatures. It is seen that non-Fickian moisture diffusion contribution at 60°C is significantly smaller than that at 85°C ($C_{sat,2}/C_{sat,1}$, 3%

versus 25%). This implies that at lower temperature, non-Fickian diffusion may not be as significant as at a higher temperature. It is also seen that the Fickian saturated moisture concentration at both temperatures stay the same. This is consistent with the findings previously, i.e., the Fickian saturated moisture concentration may be independent of temperature [11].

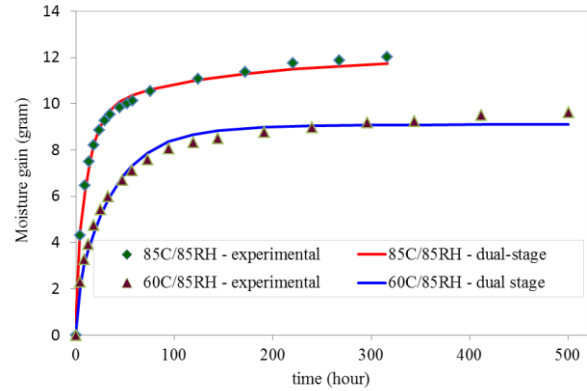


Figure 4 Moisture weigh gain curves at 85°C/85%RH and 60°C/85%RH with dual stage model fits

Table 2 Dual stage model fit parameters at 85°C/85%RH and 60°C/85%RH

	85°C/85%RH	60°C/85%RH
D_1 (mm ² /hr)	8.00E-03	2.50E-03
$C_{sat,1}$ (mg/mm ³)	5.00E-03	5.00E-03
D_2 (mm ² /hr)	8.50E-04	3.31E-04
$C_{sat,2}$ (mg/mm ³)	1.27E-03	1.52E-04

In-situ Desorption Test above 100°C

Figure 5 plots the moisture weight loss curves at 100°C, 120°C, 140°C, 160°C, 180°C, 200°C, 220°C, 240°C, and 260°C, respectively, along with weight loss data at 85°C by the manual method. As expected, moisture loss is much faster due to the elevated temperature range. At 260°C, almost all moisture content, which include free and bound water, are released from the material. As studied by Zhou et al. [18], two types of bound water are found in epoxy resins, which are classified as Type I or Type II bonding. They depend on the difference in the bond nature and activation energy. Type I bonding corresponds to a water molecule which forms a single hydrogen bond with the epoxy resin network. This water molecule possesses a lower activation energy and is easier to remove from the resin. Type II bonding is a result of a water molecule forming multiple hydrogen bonds with the resin network. This water molecule, therefore, possesses a higher activation energy and is correspondingly harder to remove. Higher temperature and longer exposure time is required to remove the Type II bond water molecules. The test data presented here support Zhou et al.’s theory.

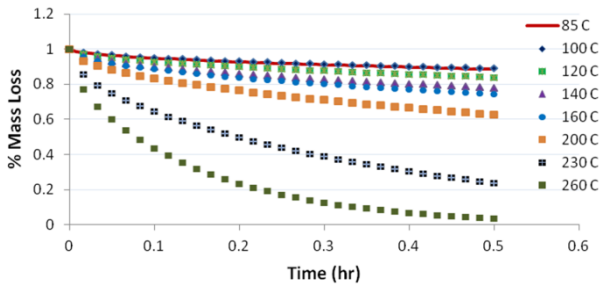


Figure 5 Desorption curves at various elevated temperatures by *in-situ* method

Table 3 presents the test data of the total mass loss during desorption from the moisture analyzer and the manual balance readings, respectively. It can be seen that the differences between the two readings are very small. It is very important to verify the data of the moisture analyzer by the external balance readings. There are two major sources of errors that could be possible in using the moisture analyzer. The first one is the incorrect setting of the purge time to remove the ambient moisture in vial before the test. Another source of error is the inability to have a complete seal by the septum. At higher temperature, the septum tends to warp and therefore it is possible that moisture from ambient will enter into the vial continuously.

Table 3 Comparison of moisture mass loss between moisture analyzer and balance

Temperature	Vapro Pro	Balance
°C	µg	µg
100	69	65
120	99.5	95
140	168.5	170
160	181	180
180	333.5	315
200	327	320
230	625.5	610
260	797.5	800

Moisture diffusion mechanism at elevated temperatures becomes much more complicated. It involves with not only the concentration gradient driven diffusion, i.e. Fickian diffusion, but also the diffusion of bound water due to higher energy that can break the hydrogen bonds. In addition, material becomes much more compliant and vapor pressure is very high inside material. A vapor pressure driven or steam flow mechanism may also play a role in diffusion. Nonetheless, it turns out that a single-phase ‘Fickian’ diffusion model, a simple phenomenal model, fit the experimental data

well. The fitted curves are shown in Figure 6 with the extrapolated time duration up to 10 hours. This implies that at the elevated temperature, all moisture eventually will be released out completely from the material. Table 4 gives the fitted diffusive parameters.

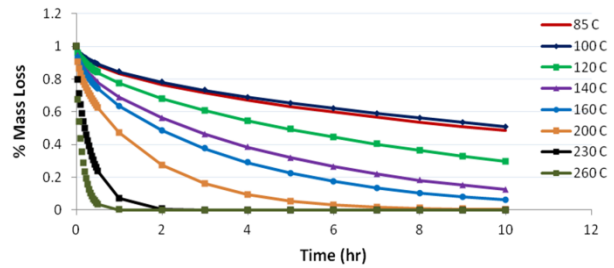


Figure 6 Fitted desorption curves using Fickian diffusion model

Table 4 Fickian parameters for desorption

Temperature (°C)	D (mm ² /hr)	Csat (mg/mm ³)
100	5.78E-03	6.27E-03
120	1.24E-02	
140	2.31E-02	
160	3.18E-02	
200	6.71E-02	
230	3.11E-01	
260	7.32E-01	

Previously manual moisture weight loss test conducted at 140°C and 160°C show a ‘permanent residual moisture content’ at least up to 48 hours [8,9]. Such results seem contradictory to the fitted data from Figure 6. Indeed, the desorption tests using the moisture analyzer run only 30 minutes, and within this time period, we obtained good experimental fit using Fickian diffusion model. Such fitted material parameters are very useful for predictive modeling of reflow process since the reflow process completes within 10 minutes, but may not be valid for a longer duration period. Nonetheless, the fitted data are accurate and adequate for modeling purpose.

Arrhenius Equations

The temperature dependence of the diffusion constants is described by the following Arrhenius equation:

$$D = D_o \exp\left(-\frac{E_d}{RT}\right), \quad (1)$$

where D_o is a ‘pre-factor’ (diffusion constant for zero activation energy), and E_d is the activation energy. If the activation energy is defined with the unit eV, the R is taken as Boltzman’s constant (8.83×10^{-5} eV/K), and T is the absolute temperature. It has been pointed out that the Arrhenius constants may be different for the temperature range below and above T_g [11], but few data have been available to test an Arrhenius fit in an entire reflow

temperature range. Figure 7 displays the Arrhenius fits based on the results of Table 2 and 3, respectively. The fitted parameters are summarized in Table 5. It seems the two lines are distinct, but relatively close. For the tested material, the extrapolation using the Arrhenius equation obtained at low temperatures may provide a reasonable approximation to high temperature range. More data need to be collected to verify if such a trend is valid for other materials, and we will report those data in the future.

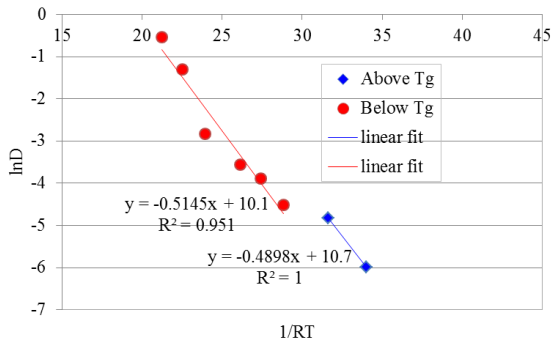


Figure 7 Arrhenius fits for the entire reflow temperature range below and above glass transition temperature

Table 5 Arrhenius constants for the entire reflow temperature range below and above glass transition temperature

	D_0 (mm ² /h)	E_d (eV)
Below T_g	4.4E+04	0.49
Above T_g	2.4E+04	0.51

Summary

Few experimental data of moisture desorption at elevated temperatures across the entire reflow temperature range are available in literature. This is probably due to the difficulty of manually measuring moisture mass, as moisture diffuses very fast at high temperature. This paper uses a high resolution moisture sensor to obtain the *in-situ* moisture desorption characteristics up to 260°C. For the first time, desorption diffusivity for the entire reflow temperature range is obtained. The results obtained from the moisture analyzer are verified by the manual reading of mass loss method. Manual moisture weight gain and loss test at the temperatures below 100°C are also conducted for comparison analysis. Arrhenius constants for diffusivity, for the entire reflow temperature range below and above the glass transition temperature, are obtained. Some important findings are summarized as follows,

1. Desorption above 100°C follows a Fickian diffusion model very well, despite the complicated diffusion mechanisms.
2. On the contrary, a dual stage model is needed to describe moisture absorption and desorption when the temperature is below 100°C for the relative long period of time.

3. For the tested material, two sets of Arrhenius constants below and above the glass transition temperature range are distinct, but relatively close. This means that the extrapolation using the Arrhenius equation obtained at low temperatures may provide a reasonable approximation for high temperature range.

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