

Mechanism of Moisture Diffusion, Hygroscopic Swelling and Adhesion Degradation in Epoxy Molding Compounds

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Abstract

Epoxy Molding Compounds (EMCs) are widely used as encapsulation materials in semiconductor industry for protecting the IC's/MEMS against the environment. Despite their advantages like low-cost and good mechanical behavior, an important disadvantage of these materials is moisture absorption from the environment. This causes many reliability problems, including interface delamination and 'popcorn' effect during soldering reflow process. In this paper a systematic approach was conducted to investigate the mechanisms of Fickian and non-Fickian moisture absorption in EMCs. Different sample geometries were produced and their mass uptake/loss due to moisture absorption/desorption were investigated. Results reveal a dual-stage moisture uptake during absorption and irreversible residual moisture content upon complete desorption, indicating that some EMCs retain moisture for long time even at elevated temperatures. This residual content is a complex function of sample geometry, baking temperature and sample sorption history.

The hygroscopic swelling was investigated by the means of warpage measurement of Cu/EMC bimaterial beams. A significant permanent change of the dimension of EMCs due to irreversible residual moisture content was observed. This indicates that not all the swelling of samples can be recovered when they are baked in dry conditions.

The adhesion of Cu/EMC was also measured for dry and moist samples. The interfacial fracture toughness was obtained using the end-notched flexure (ENF) tests based on interface fracture mechanics. Two mechanisms of adhesion losses were observed. Some of the adhesion loss due to small amount of moisture content was recovered via a proper annealing. However, upon activation of the second saturation phase, none of the adhesion loss was recovered after baking the moist samples.

Key words

Moisture, Absorption and Desorption, swelling, Adhesion, Epoxy Molding Compound (EMC)

1. Introduction

In spite of many advantages like smaller size, lower weight, good performance, and lower-cost of Plastic Encapsulated Microcircuits (PEMs), an important disadvantage is that the molding compound absorbs moisture when exposed to a humid environment [1-8].

Epoxy molding compounds (EMC) compose of a polymer matrix, silica fillers and other additives. Moisture behavior of EMC is mainly dominated by the diffusion of water through epoxy resin. However, the amount of filler and its shape can influence the moisture diffusivity [9].

Diffusion of water in polymers has been widely investigated and for most cases the rate of diffusion has been assumed to be constant (Fickian diffusion) [1-4]. However, the diffusion at high temperature and high humidity level for an extended period of time can show a

dependency to the time exposed to moisture [6]. Moisture content in a material can be analyzed using the so-called thermal-moisture analogy [2-4]. The method can be also developed to overcome the discontinuity problem of moisture concentration across the bi-material interfaces [3]. More recently, a direct concentration approach (DCA) has been developed to study the moisture diffusion with varying temperature and humidity conditions such as in soldering reflow [10].

Water molecules in polymeric materials have been identified to have two distinct states. "Free" or "unbound" state of water is attributed to water molecules that are present in voids and nanopores of the material [11-13], while "bounded" water molecules react with the polymer chains via hydrogen bonding or some chemical reactions. This identification is further supported by measurement of the ratio of hygroscopic volume expansion to the volume of

absorbed water which is less than unity, indicating that some of the absorbed water does not contribute to swelling. Interfacial adhesion is of important concern for multilayered structures such as microelectronic packages [14-17, 25]. Moisture can influence the interfacial adhesion through three mechanisms. The first mechanism is the intrinsic aggregating effect of water molecules upon direct presence at the interfaces and degrading the interfacial adhesion by bonding to the polymer chains [14]. The second mechanism is that the absorbed moisture changes the mechanical properties of polymeric materials [15-17, 22]. For example moisture can change the elastic modulus and shift the glass transition temperature of polymers to lower values. This mechanism leads normally to a slight difference in the mode mixity of the measured fracture toughness of moist sample when compared to that of dry sample [16]. The third mechanism is the swelling of polymeric materials upon exposure to moist environments and causing an additional mismatch between volumetric expansions of substrate and adhesives [6, 18, and 19]. This is even more pronounced when the joint between a polymer and metal is investigated. Since the metallic substrate is impermeable to moisture, only the polymeric adhesive absorbs moisture and causes mismatch in hygroscopic strains. In order to measure the intrinsic fracture toughness of a moisture preconditioned sample, the influence of hygroscopic swelling which induces an apparent change in the measured fracture toughness should be isolated. In this work, we first investigated the non-Fickian behavior of moisture absorption and desorption. The residual moisture content upon the desorption of the EMC was investigated by comparing the results of moisture desorption of different sample geometries at different baking temperatures. In addition, the first run of moisture absorption was compared to the second run after baking in different conditions. Secondly, the hygroscopic swelling of the molding compound was investigated by a bimaterial beam which was exposed to humid environment and its warpage was documented periodically. Finally, the influence of aging in humid conditions on the adhesion between EMC and copper was studied.

2. Moisture Diffusion

2.1 Fickian Moisture Diffusion

Fick's second law can be applied to describe the moisture diffusion process in polymeric materials [1-4]:

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C), \quad (1)$$

where D [mm^2/s] is the diffusion coefficient, C [g/mm^3] is the moisture concentration, t [s] is the time and x [mm] refers to Cartesian coordinates. For isotropic materials, Fick's second law can be simplified as:

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

If the one-dimensional case of an infinite plate of thickness l with appropriate boundary conditions is considered, the analytical solution, giving the temporal and spatial moisture concentration, C , at time t and distance x from the mid-plane, is given by [1]:

$$\frac{C_t - C_0}{C_\infty - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left(\frac{-D(2n+1)^2 \pi^2}{4l^2} t\right) \times \cos\left(\frac{(2n+1)\pi}{2l} x\right) \quad (3)$$

Here C_∞ is the maximum equilibrium moisture concentration, C_0 is the initial moisture content, D is the Fickian diffusion coefficient and l is the half-thickness of the bulk film.

Since it is not possible to measure the moisture concentration at a point experimentally, the above expression is integrated over the thickness of the bulk film and the fractional mass uptake of the specimen as a function of time is [1]:

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

where M_t is the mass of moisture after absorption time t and M_∞ is the mass of saturated sample.

In order to determine the Fickian coefficient of diffusion, the initial stage of moisture absorption ($M_t/M_\infty < 0.5$) is simplified as [1]:

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{\pi l^2} \right)^{1/2} \quad (5)$$

Equation (5) shows that in the initial stage of moisture absorption, the mass uptake has a linear relationship with the square root of the time if the Fickian law is followed. The Fickian diffusion coefficient, D , depends on an initial diffusion constant, D_0 , temperature, T , and activation energy, ΔE , and is independent of relative humidity (RH) according to [7]:

$$D = D_0 \exp\left(-\frac{\Delta E}{kT}\right) \quad (6)$$

where k is Boltzmann's constant.

2.2 Non-Fickian Moisture Diffusion

It is important to note that in Eq. (2) the diffusivity D in Fickian diffusion is assumed to be independent of moisture concentration C . This assumption may not hold true for many polymers and, consequently, equations (2)-(6) cannot be used directly for the case of non-Fickian diffusion [6].

The moisture absorption in some molding compounds can be characterized by linearly decreasing diffusivity as a function of average moisture content [4], while for highly non-Fickian diffusion of some organic substrates a power-law relation between the diffusivity and moisture content has been observed. Non-Fickian behavior may be the consequence of a relaxation process in polymer molecules and/or the result of an irreversible reaction between polymer and moisture such as formation of hydrogen bonds and chemical reactions. It has been found that non-Fickian diffusion can take diverse forms [26]. Two-stage or dual-uptake diffusion has been observed in many polymeric materials and is referred as *anomalous* moisture uptake in literature [6, 26].

3. Experimental Results

3.1 Moisture Absorption

The weight gain measurements were performed to evaluate the moisture uptake of a conventional molding compound. Two different sample geometries both from the same material in the form of molded disks were produced by the manufacturer. Samples with the thickness of 1 mm (MC1) have a diameter of 50 mm and the samples with the thickness 2 mm (MC2) have a diameter of 100 mm, respectively. The aspect ratio (diameter/thickness) of both samples is the same, meaning that for both samples one-dimensional moisture diffusion can be assumed. In order to determine the dry weights, the samples were dried initially at 125°C for 24 hours. They were then exposed to the 85°C/85%RH conditions in a humidity chamber. An electronic balance scale (0.01 mg) was used for the weight gain measurements. The samples were periodically removed and weighed and returned to the chamber for further soaking. The *Weight Gain* of the samples at the time t can be determined from:

$$\text{Weight Gain (\%)} = \frac{M(t) - M_{\text{Dry}}}{M_{\text{Dry}}} \times 100, \quad (7)$$

where $M(t)$ is the weight of the sample at time t and M_{Dry} is the dry weight before moisture preconditioning.

The results of moisture absorption at 85°C/85%RH using the gravimetric measurements described in reference [6] is shown in Fig. 1.

The moisture absorption of both samples show a dual-stage non-Fickian behavior. A rapid initial moisture uptake to quasi-equilibrium (virtual saturation) is followed by a slower linear moisture uptake. The virtual saturation was selected to be the start of second linear absorption phase and is marked with point A in Fig.1. The thicker samples (MC2) which were investigated in our previous study [6] were exposed in humid environment for 8 months. Although for semiconductor industry such long term moisture aging is not normal and the aging is within some weeks, it was aimed to know if there is a saturation point.

The experimental data showed that the moisture weight gain reached about 0.3 % after 8 months compared to the 0.2% at the virtual saturation point. No final saturation was achieved for that sample suggesting that at least two different mechanisms are available in the moisture absorption of polymeric materials. The first mechanism is the absorption of water molecules in the free volumes or nano-voids. The second mechanism is the hydrogen bonding between the water molecules and polymer chains due to their molecular polarity. The former mechanism reaches a saturation point and is a reversible phenomenon in nature. The latter seems to be linear without a clear saturation, at least for the time scales of this study. At low desorption temperatures this mechanism is not fully recoverable (see section 3.2 for more details).

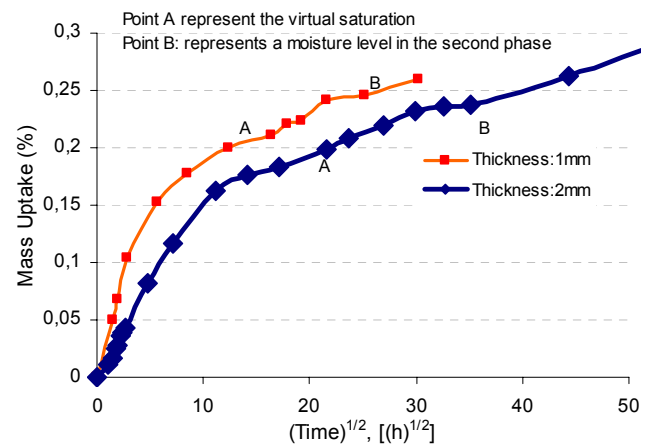


Fig.1 Experiments on moisture uptake of EMC samples with different thicknesses at 85°C/85%R.H.

Fickian model fails to predict the exact moisture content of such materials with dual-stage moisture content. A suitable method for the prediction of exact moisture concentration by FEA may be a curve fitting [6].

3.2 Moisture Desorption

Polymers lose their moisture content when are exposed to dry environments at high temperatures. The temperature-dependent desorption coefficient of the EMC studied in this work was previously investigated [6 and 12] and it was observed that the desorption coefficient fulfills Eq. (6) and the activation energy of the material can be estimated as 0.55 eV. However, not all the moisture may escape from the polymeric materials even upon exposure to high temperature. In this work a systematic approach was conducted to find out at which state of the moisture absorption the formation of the *residual moisture content* may take place. Samples of both geometries were placed in the humid conditions (85°C/85%RH) and removed for the

desorption process. Two points from moisture absorption diagram were selected. Point A represents a virtual saturation state which was 2 weeks for sample MC-1 and 4 weeks for sample MC-2. The samples were placed later in an infrared oven at two different temperatures. Since the glass transition temperature of the studied molding compound is 120°C, a temperature below that (110°C) and a temperature above that (160°C) were selected. The desorption process after a longer period of moisture absorption was also investigated. Point B represents a point at which the sample is in its second phase of saturation (second linear stage of the absorption curve). Figures 2 and 3 illustrate the weight loss of both samples at 110°C and 160°C respectively.

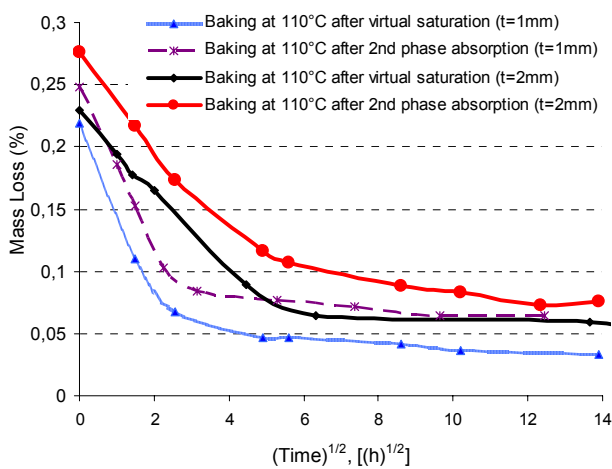


Fig.2 Experimental results of moisture desorption at 110°C.

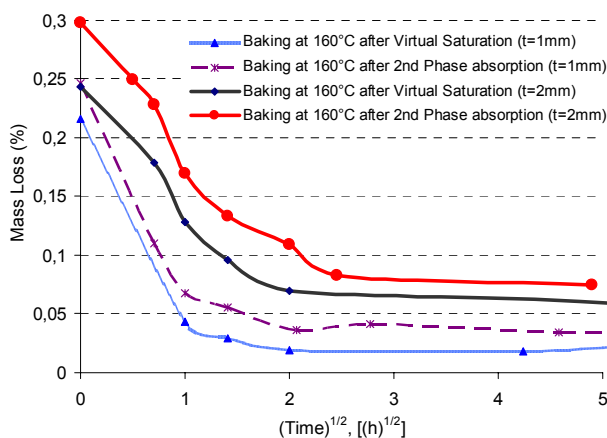


Fig.3 Experimental results of moisture desorption at 160°C.

From the desorption curves the following results can be postulated:

- The dry condition is not achieved for any of the samples within the time period investigated. Samples with higher initial moisture content show a higher final residual

content, suggesting that a longer time of exposure to moisture leads to a higher amount of 'non-reversible' moisture content at a certain temperature. Desorption at elevated temperatures (e.g. 160°C) leads to more moisture release and a lower amount of residual moisture content. This means that for the debonding of hydrogen bonds a certain amount of energy is needed, which is apparently not available at lower temperature (e.g. 110°C).

- The thicker samples (MC-2) show to retain a higher amount of residual moisture content when compared to the thinner samples (MC-1). This is obvious, because thicker samples need normally more time to reach a certain amount of moisture content (see Fig. 1). A longer exposure to moisture results in a higher amount of non-reversible hydrogen bonds and consequently higher amount of residual moisture contents. This suggests that the hydrogen bonding is active from the early stages of exposure to moisture; however, its influence is more dominant when the Fickian mechanism decelerates upon reaching a virtual saturation.
- An interesting observation is the parallel initial linear part of the desorption curves. For a certain geometry at a constant temperature, the desorption curves of samples with different histories are in parallel. It is an important result, which suggests that the desorption rate is mainly dominated by the amount of moisture was previously absorbed by reversible mechanisms (e.g. water molecules reside in the nano-voids for which a Fickian behavior is assumed). The longer exposure to moisture results in a higher amount of nonreversible absorption mechanism (e.g. bonding of water molecules to polymer chains via hydrogen bonding). No matter how long the samples were previously kept in humid environment, the initial desorption rate at a constant temperature remains unchanged.

It must be noted, that not all the polymeric materials retain moisture upon long term baking at high temperatures. For example for some cross linked amorphous polymers [22] and thin Bismaleimide-triazine resin/glass fiber laminates [23] repeatable moisture absorption-desorption was observed. It is possible that only the first phase of moisture absorption was activated within the time period of the recycled test.

Prediction of moisture content by commercial FEM tools may not be possible, because most of the simulation tools use Fickian model to predict the moisture content. However, Fickian model fails to predict the moisture content, because it essentially assumes a final dry state. To solve this problem, a method based on two parallel moisture diffusions may be used [6].

3.3 Second Run of Absorption (Re-sorption)

The complex mechanism of moisture absorption suggests that a second run of moisture absorption after an

absorption/desorption cycle would be even more complicated. Samples were initially placed in a humid chamber to reach a virtual saturation (two weeks for thin samples and four weeks for the thick samples). They were then removed from humid chamber and placed in an infrared dry oven at two temperatures of 110°C and 160°C to release their moisture at a constant temperature. After reaching a 'virtual dry state' (the plateau value in Fig.2 and Fig.3) the samples were again placed in humid chamber for the second run of moisture absorption. Since the samples had undergone an absorption/desorption cycle, they had an initial moisture content (residual moisture content at the end of desorption) as described in previous section. This initial content was low, because the absorption was stopped as far as the samples reached the virtual saturation. Fig. 4 and Fig. 5 show the comparisons between the first run of moisture absorption with the second run after baking at 110°C and 160°C for two different geometries, respectively. The initial moisture content for the re-sorption curves was assumed to be zero (although an initial content due to non-reversibility exists), to make the comparison easier.

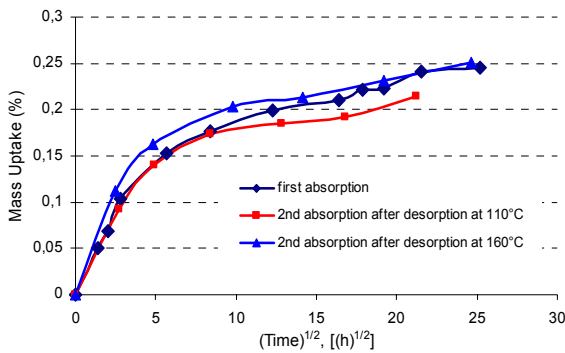


Fig.4 Comparison between first run of moisture absorption of samples with thickness 1mm and second run after baking at 110°C and 160°C.

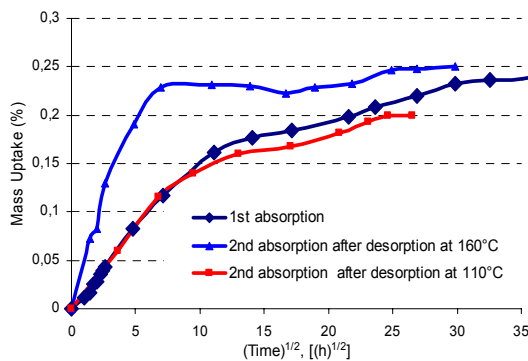


Fig.5 Comparison between first run of moisture absorption of samples with thickness 2mm and second run after baking at 110°C and 160°C.

From these curves the following results can be postulated:

- In spite of the initial 'non-reversible' moisture existing in the material after the desorption at 110°C, the new moisture weight gain curve before 'virtual saturation point' during re-sorption was found to be almost same to the first run for both 1mm and 2mm samples. This means the moisture absorption due to the first phase of moisture diffusion is mostly repeatable. The moisture desorption at 110°C happens below the glass transition temperature, at which the relaxation of polymer chains and the change of free volumes are not significant;
- However, the desorption at 160°C affected the second run of moisture absorption significantly. The rate of moisture absorption at the second run was found to be higher than that at the first run. The increase in the rate of moisture uptake can be attributed to the expansion of free volumes in the polymeric materials due to the storage of the material, which was baked at 160°C, well above the glass transition temperature. For the thin samples (Fig.4) the difference between the first and second runs of moisture absorption is much less than the thicker sample (Fig.5), because of less exposure to elevated temperature. Consequently, the formation of new free volumes which is dependent on the time exposure to temperature is less.

3.4 Hygroscopic Swelling

An important aspect of reliability concerns in plastic packages is the swelling or volumetric expansion of polymeric materials due to moisture absorption, which is referred as hygroscopic swelling. Hygroscopic Swelling of EMCs has been usually investigated by performing two parallel analyses. In one analysis the weight loss of a saturated sample during desorption at a constant temperature is measured. This can be done via a TGA (Thermal Mechanical Analyzer) or running a finite element simulation of the desorption process of the sample [6]. In other analysis, the dimensional change of the sample during the desorption is measured. A TMA (Thermal Mechanical Analyzer) [6, 13, 17, 18,] or shadow Moiré Interferometry [19] is used for the in-situ measurement of the hygroscopic strains. The amount of hygroscopic strain found from dimensional change is normally assumed to be linearly proportional to the moisture concentration as [17-20]:

$$\varepsilon_h = \beta C \quad (8)$$

where ε_h is the hygroscopic strain, β [mm^3/g] is the coefficient of hygroscopic swelling (CHS) and C [g/mm^3] is the moisture concentration. However, there are lots of possible errors [24, 27], when the above methods are used for the calculation of CHS in epoxy molding compounds. In all these methods the dimensional changes of the sample during the isothermal desorption is considered and it is assumed that the behavior of the polymeric materials in terms of swelling and shrinkage during the absorption and

desorption is the same. However, similar to the residual moisture content upon desorption of the molding compounds a residual hygroscopic strain may also exist. In other words, not all the swelling during the moisture uptake may be recovered after the desorption. In this work the swelling of the EMC's was investigated by measuring the deflection of a bi-material beam during the moisture absorption. A bi-material beam of Copper/EMC was designed and manufactured. The samples were used later for the characterization of interfacial fracture toughness between EMC and copper leadframe [16 and 25]. Copper substrates were machined into $50 \times 10 \times 0.4 \text{ mm}^3$ strips. After cleaning with acetone the substrates were placed in the cavity of a molding machine. Pellets of the same EMC were introduced into the cavity of a pre-heated mold at about 175°C and kept under a pressure of 60-80 MPa for 120 s; the molding compound was dispensed automatically on the copper surface at 175°C . After molding, the samples were placed in an environmental chamber for post-mold curing at 175°C for six hours to complete the polymerization process of the epoxy molding compound. Fig.6 shows the dimension of the bimaterial beam.

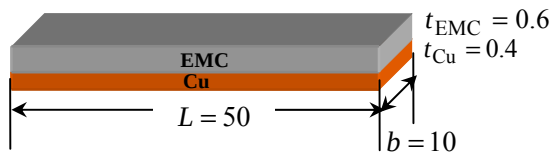


Fig.6 Bi-material beam designed for the measurement of hygroscopic swelling of EMC and its adhesion to Cu.

The initial warpage of the sample due to chemical cure shrinkage and mismatch between coefficients of thermal expansions (CTEs) was measured at room temperature by a chromatic sensor. Some samples were later placed in a humid chamber and were removed periodically from the moisture chamber and their warpage was measured at room temperature. During the moisture absorption, the warpage changed from concave to the convex shape (see Fig.7). The convex shape increased and reached a constant value of approximately 150 micrometers after 3 weeks. Further exposure to moisture did not affect the warpage. Some samples were removed from moisture chamber after the saturation and were placed in a dry infrared oven at 110°C . The Warpage of the samples was measured at room temperature after 10 Days desorption. This was done to investigate, if the hygroscopic swelling of the sample is reversible. As it was expected, not all the moisture-induced warpage due to moisture absorption was recovered. This suggests that the measurement of the hygroscopic swelling by any method that deals with the dimensional change during the desorption of the sample should be avoided, at

least for the polymeric materials which show such nonreversible hygroscopic swelling. Since during the desorption of the bimaterial beam at 110°C some stress relaxation takes place, the amount of residual hygroscopic swelling cannot be exactly measured.

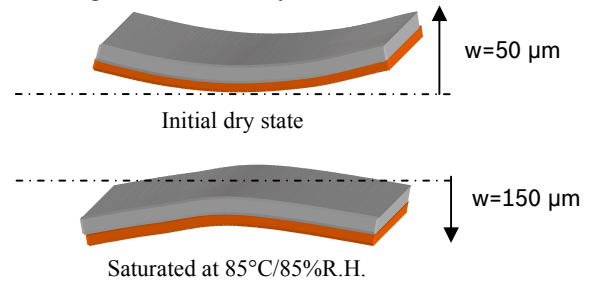


Fig.7 Effect of hygroscopic swelling on the warpage of the bimaterial beam.

3.5 Adhesion Measurement

The end-notched flexure (ENF) test [16, 21] has been widely used to characterize the mode II fracture toughness. A schematic picture of the test setup is illustrated in Fig.8.

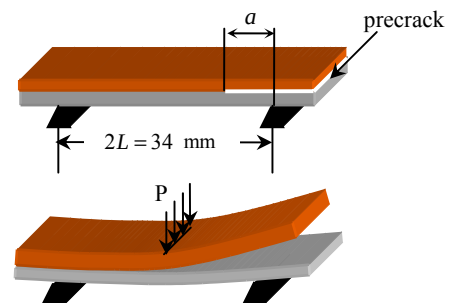


Fig.8 ENF for the Measurement of interfacial adhesion.

Finite element analysis using the virtual crack closure technique (VCCT) was performed to calculate the intrinsic interfacial fracture toughness of moisture preconditioned samples based on the experimental data. More details about the adhesion test, precracking technique and test conditions can be found in reference [6 and 16].

Fig.9 shows the effect of aging in humid environment on the interfacial fracture toughness of Cu/EMC interface. All fracture tests were conducted at room temperature with the displacement-controlled rate of 0.1 mm/min. In addition, the effect of moisture on the elastic modulus of EMC was investigated using the three-point bending of bulk EMC bars. It was found that moisture does not affect the elastic modulus significantly. Hence, all the fracture toughness measurement can be assumed to be at a constant mode angle [16]. Using the diffusion coefficient from the experimental results [6], the time to virtual saturation of the samples was found numerically to be almost two weeks (0.21 % weight gain of the whole sample). Results show that the interfacial fracture toughness initially being 58.7

J/m² in dry condition reduced to 26.3 J/m² when the virtual saturation level was achieved at interface.

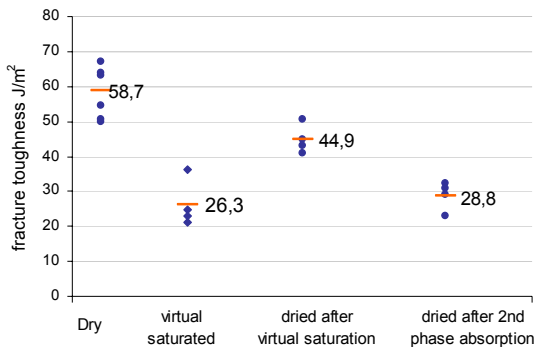


Fig.9 Effect of Moisture absorption and desorption on the adhesion of Cu/EMC interface.

In order to study the effect of an absorption/desorption cycle on the adhesion, moist samples were baked for 24 h at 125°C to reach a virtual dry state. A longer exposure to moisture was also investigated by 4 weeks aging in humid condition (0.25% weight gain of the sample) and then drying for 24 h at 125°C. The fracture toughness of these samples was measured again at room temperatures. Some of adhesion loss due to moisture absorption up to virtual saturation was recovered after drying (44.9 J/m²). However, samples which remained longer in humid conditions (4 weeks) showed almost no recoverability upon the same annealing condition (28.8 J/m²). This is an important result, which shows the extreme degrading effect of second phase of moisture absorption. The moisture absorption during the first phase degrades the adhesion due to intrinsic effect of the presence of water molecules at the interface, which is partially reversible if a proper annealing is performed. However, the second phase of moisture absorption seems to destroy the adhesion bonds permanently, and none of the adhesion loss may be recovered if the moisture level at the interface reaches this critical content.

The reversibility of the adhesion was reported for organosilicate glass (OSG) film [20]. However nonreversible adhesion loss was also reported [14] for an epoxy based underfill adhesive. This implies that the reversibility of the adhesion after a moisture absorption/desorption cycle differs for different materials due to different mechanism of moisture absorption.

4. Conclusion

In this study a systematic investigation of absorption and desorption of moisture in epoxy molding compounds was conducted. Absorption of moisture was found to show a dual-stage non-Fickian behavior. The exposure of sample upon a virtual saturation (end of the first absorption phase) to dry environment was found to lead to an almost dry state with slight residual moisture content at the end. However, a

dry state was not achieved when the samples with higher initial moisture content (which were kept in humid environment for a longer time) were exposed to dry environments. A residual moisture content was present which was a complex function of time exposed to moisture, sample geometry and temperature at which the desorption process takes place. The schematic picture of the influence of sample history may be depicted in Fig. 10. Samples which reached point A (virtual saturation) show a lower residual moisture content when compared to the samples reached point B (second absorption phase). However, the rate of desorption for both cases were the same, indicating that at least two mechanism are active in desorption of moisture. One is a reversible mechanism that dominated the diffusion rate. The other is a non-reversible mechanism that is a function of time, temperature and sample geometry.

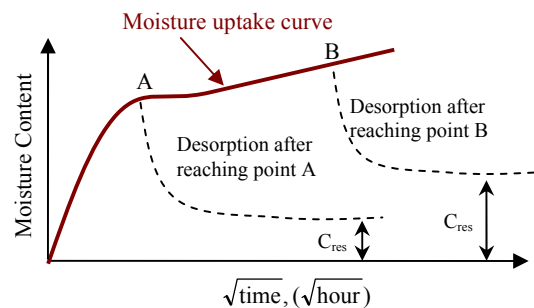


Fig.10 Schematic model for the residual moisture content upon desorption of moisture.

The second run of moisture absorption showed also some differences with the first run. The sample sorption history was found to be the dominating factor. The rate of moisture absorption at the second run was found to be higher than that at the first run. The increase in the rate of moisture uptake can be attributed to the formation of new voids in the polymeric materials, which facilitates the transformation of water molecules in the sample. A higher temperature leads to formation of more new free volumes. A schematic picture of the effect of sample history on the rate of second run of moisture absorption may be depicted like the one in Fig. 11.

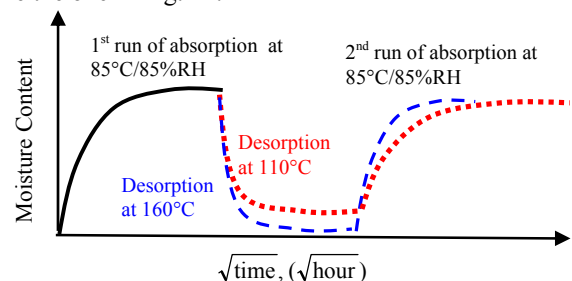


Fig.11 Schematic model of the second run of the moisture absorption after an absorption/desorption cycle.

Coefficient of hygroscopic swelling is normally found by relating the dimensional change of a saturated sample to its mass loss during the isothermal desorption. However, not all the moisture absorbed is released upon baking a specimen. Moreover, swelling of EMC upon moisture uptake was not recovered completely after its moisture desorption. Consequently, other methods based on the absorption process should be used for the estimation of the coefficient of hygroscopic swelling. Warpage measurement of a bi-material beam could be a possible approach; however it is not also free of errors. Significant stress relaxation may occur, when the sample is aged for long times. A detailed analysis of the warpage via FEA which considers the effect of cure shrinkage, stress relaxation due to viscoelasticity and moisture-induced swelling should be investigated in future.

Adhesion between copper and EMC was also investigated under moisture. It was found, that some of adhesion loss upon moisture absorption up to virtual saturation may be recovered, when a proper annealing condition is used. However, if the samples were exposed for a longer time to humid environment, none of the adhesion loss can be recovered, because the second stage of moisture absorption has a permanent degrading effect.

References

- [1] Shen, C.H., and Springer, G.S., "Moisture Absorption and Desorption of Composite Materials," *J. Composite Materials*, Vol. 10, No. 2, pp. 2-20, 1976.
- [2] Teverovsky, A., "A Rapid Technique for Moisture Diffusion Characterization of Molding Compounds in PEM," NASA Technical Report, 2002.
- [3] Wong, E. H., Teo, Y. C., and Lim, T. B., "Moisture diffusion and vapor pressure modeling of IC packaging," *Proc. 48th Electron. Comp. Technol. Conf.*, 1998, pp. 1372-1378.
- [4] Chen, X., Zhao, S., "Moisture Absorption and Diffusion Characterization of Molding Compound," *Journal of Electronic Packaging*, Vol. 127, (2005), pp. 460-465.
- [5] Pecht, M. G., Nguyen, L. T., and Hakim, E. B., *Plastic Encapsulated Microelectronics*, Wiley (New York, 1995).
- [6] Shirangi M.H., Auersperg J., Koyuncu M., Walter H., Müller W.H., and Michel B. "Characterization of dual-stage moisture absorption, residual moisture content and hygroscopic swelling of epoxy molding compounds" *proc. o. 9th EuroSime2008, Freiburg, Germany*, pp. 455-462.
- [7] Loh, W.K., Crocombe, A.D., et al., "Modeling anomalous moisture uptake, swelling and thermal characteristics of a rubber toughened epoxy adhesive," *Int. J. of Adhesion and Adhesives*, Vol. 25, (2005), pp. 1-12.
- [8] Dudek, R., Walter, H., and Michel, B., "Studies on Moisture Diffusion and Popcorn Cracking," *proc. of 3rd EuroSime, 2002*. pp. 225-232.
- [9] Braun T. et al. "Nano-Particle-Enhanced Encapsulants for Improved Humidity Resistance," *Proc. 58th Electron. Comp. Technol. Conf., ECTC2008*.
- [10] Fan X.J., et al, "Direct concentration approach of moisture diffusion and whole field vapor pressure modeling for reflow process: part I: theory," *ASME Journal of Electronic Packaging*, 2008, (accepted)
- [11] Dermitzaki E., Wunderle B., Bauer J., Walter H., and Michel B., "Molecular Dynamics Simulation for the diffusion of water in amorphous polymers examined at different Temperatures," *IEEE 8th EuroSime*, 2007.
- [12] Shirangi M.H., Müller W.H., and Michel B. "Study of Moisture Diffusion of Epoxy Molding Compound for Reliability Assessment of Plastic IC Packages" *proc. of 3rd Microcar 2008*, Leipzig, Germany.
- [13] Fan, X. J., "Moisture Related Reliability Issues in Electronic Packaging," *ECTC short course*, 2006, 2007 and 2008.
- [14] Ferguson, T., and Qu, J., "Predictive Model for Adhesion Loss of Molding Compounds from Exposure to Humid Environment," *Proc of ECT2006*, pp. 1408-1414.
- [15] Ferguson, T., and Qu, J., "Elastic Modulus Variation due to Moisture Absorption and Permanent Changes Upon Redrying in an Epoxy Based Underfill," *IEEE Trans. Comp. Package. Technol.*, (2005).
- [16] Shirangi M.H., Müller W.H., and Michel B. "Contribution of moisture diffusion, thermal aging and viscoelasticity to the adhesion change of polymer/metal interface" *proc. of 5th international conference on fracture of polymers, composites and adhesives*, Les Diablerets, Switzerland (In Press).
- [17] Fan X.J., "Mechanics of moisture for polymers: fundamental concepts and model study", *proc. of 9th EuroSime2008, Freiburg, Germany*, pp. 159-172.
- [18] Ardebili, H., Wong, E. H., and Pecht, M., "Hygroscopic swelling and sorption characteristics of epoxy molding compounds used in electronic packaging," *IEEE Trans. Comp. Package. Technol.*, Vol. 26, No. 1 (2003), pp. 206-214.
- [19] Stellrecht, E., Han, B., and Pecht, M.G., "Characterization of Hygroscopic Swelling of Mold Compounds and Plastic Packages," *IEEE Transactions on components and Packaging Technologies*, Vol. 27, No. 3, pp. 499-506.
- [20] Lin Y., Tsui T.Y. and Vlassak J.J., "Water diffusion and fracture in organosilicate glass film stacks" *Acta Materialia* 55(2007), pp. 2455-2464.
- [21] P.G. Charalambides, J. Lund, A.G. Evans and R.M. McMeeking, "A test specimen for determining the fracture resistance of bimaterial interfaces" *J. of Appl Mech* 56 (1989), pp. 77-82.
- [22] Dermitzaki, E., Wunderle B., Bauer J., Walter H., and Michel B. "Structure Property Correlation of epoxy resins under the influence of moisture and temperature; and comparison of Diffusion coefficient with MD-simulations," *IEEE 2nd int. conf. ESTC*, London 2008 (in Press).
- [23] He Y., and Fan X.J., "In-situ characterization of moisture absorption and desorption in a thin BT core substrate", *proc of Electronic Components and Technology Conference*, pp. 1375-1383, 2007
- [24] Fan X.J., Zhou J., and Chandra A. "Package structural integrity analysis considering moisture", *Proc. Of Electron. Comp. Technol. Conf. ECTC 2008*, pp. 1054-1066
- [25] Shirangi M.H., Gollhardt A., Auersperg J., Walter H., Fischer A., Müller W.H., Michel B. "Investigation of Fracture Toughness and Displacement Fields of Copper/Polymer Interface Using Image Correlation Technique" *proc. of 41st International Symposium on Microelectronics (IMAPS2008)*, Providence, USA (In Press).
- [26] Weitsman, Y.J., "Anomalous fluid sorption in polymeric composites and its relation to fluid-induced damage," *J. of Composites: Part A* 37 (2006), pp. 617-623.
- [27] Zhou J. et al, "Effect of Non-uniform moisture distribution on the hygroscopic swelling coefficient", *IEEE Transactions on Components and Packaging Technologies*, 31(2), 2008, 269-276.
- [28] Shi X., Zhang Y., Zhou W., and Fan X.J. "Effect of hygrothermal aging on interfacial reliability of silicon/underfill/FR-4 assembly", *IEEE Transactions on Components and Packaging Technologies*, 31(1), 2008, 94-103.