

Environmentally Induced Swelling and Shrinkage of Molding Compounds in PEMs

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Abstract

This work analyzes swelling and shrinkage of plastic packages of PEMs caused by various environmental conditions. These conditions include moisture sorption during normal storage in laboratory conditions, accelerated environmental stress testing in humidity chambers, bake-outs at 125 °C and 150 °C, and short-term high temperature exposure at temperatures above 200 °C simulating soldering processes. The volume deviations in molding compounds and plastic packages of microcircuits were measured using a simple hygrostatic weighting technique.

Several types of plastic encapsulated microcircuits (PEMs) and encapsulating materials have been evaluated. The coefficients of moisture expansion (CME) were found to depend on moisturizing conditions, increasing with temperature and relative humidity above 60% RH. Saturation with moisture at 85 °C/85% RH resulted in the CME varying for different molding compounds from 0.1 to 0.49. The extent of deformations caused by moisture removal (baking out) in the samples stored for a long time at normal conditions ($T \approx 22$ °C, $RH \approx 50\%$) was comparable with the deformation caused by swelling in high humidity environments. Depending on the type of molding compound used, initial moisture content, and temperature of bake, baking of PEMs can result either in increase or in decrease of the volume of the package. Exposure to high temperatures causes significant reduction of the volume of plastic packages. Different physical mechanisms of environmental effects causing swelling and shrinkage of plastic packages in PEMs are discussed.

1. Introduction

It is known that moisture sorption at high humidity conditions might degrade mechanical characteristics and cause swelling or hygrothermal expansion of molding compounds (MC) in PEMs. These effects can significantly increase mechanical stresses in plastic packages and degrade performance and reliability of sensitive microcircuits operating in humid environments.

Several researchers have observed a significant decrease (tens of °C) of glass transition temperature in MC due to moisture sorption [1, 2]. The thermal expansion of cured epoxy resin that had been saturated with water was found in [3] to be more than twice that of the dry resin.

Moisture caused reduction in tensile strength and adhesion of epoxy underfill materials, used in the flip-chip technology [2]. Hygroscopic swelling of the underfill in flip chip PBGA packages was found to be the main failure driver during autoclave test (121 °C, 100% RH) [4] and the prime reason of the warpage of large PBGA packages [5].

Moisture induced mechanical stresses were found to be significant compared to thermal stress during the solder reflow process [4]. Calculations showed that the moisture expansion coefficients of MCs and polymer die attach materials have a significant impact on delamination failures during soldering of PEMs [6].

Until recently, moisture-induced stresses have been largely ignored in the analysis of packaging stresses. E.H.Wong and co-authors [4] attributed this to the lack of characterization techniques, lack of material hygroscopic swelling characteristics, and under-assessment of the magnitude of hygroscopic stress.

In spite of their importance for reliability evaluation of PEMs in moisture environments, hygrothermal expansion characteristics for epoxy compositions and MCs are rarely found even in special technical literature. Table 1 shows some reported characteristics and the techniques used for their measurements. Here the coefficients of moisture expansion (CME) is defined as the ratio of the hygro-swelling strain and the moisture absorption (both measured in %).

Table 1. Reported value of the coefficient of moisture expansion in epoxy compounds.

Study	Material	Technique	CME, %/%
H. S. Choi et al. '01 [7]	epoxy/carbon composite	Size measurements	0.2 – 0.53
K. Ogi et al., '99 [8]	epoxy/carbon composite		0.47
L.Nguyen et al., '95 [9]	MC	Size measurements	0.24 – 0.26
Wong, E.H et al., '00 [4]	MC	TMA + TGA	0.45 – 1.53
VanLandingham., '99 [10]	Unfilled epoxy	Size measurements	0.22
E. Stellrecht et al., '02 [11]	MC	Moire interferometry	0.16 – 0.27

The available data show that the CME values vary from 0.2 to 1.5 for different epoxy materials.

To estimate the significance of the hygro-swelling effect in developing mechanical stresses in plastic packages let us consider thermo- and moisture-related strains in encapsulating materials. Deformation of MC due to temperature expansion is $\varepsilon_T = \alpha \times \Delta T$, where α is the coefficient of thermal expansion (CTE) and ΔT is the increase in temperature. For a typical MC $\alpha = 1.6E-5$ 1/°C. At $\Delta T = 100$ °C, $\varepsilon_T = 0.16\%$. The strain caused by moisture swelling is $\varepsilon_{sw} = CME \times \delta_{MC}^m$, where δ_{MC}^m is the moisture uptake. At 85% RH the δ_{MC}^m typically varies from 0.3% to 0.5%. At CME in the range from 0.2 to 1.5, the moisture induced strain ε_{sw} varies from 0.06% to 0.75%.

These estimations show that the strain in MC at high humidity conditions might be comparable and even much larger than the deformation caused by the temperature expansion. The

mechanical stress in a plastic package of PEM is the sum of stresses caused by moisture swelling and by the CTE mismatch between MC, α_{MC} , and the lead frame, α_{LF} :

$$\sigma \propto E \times [(\alpha_{LF} - \alpha_{MC}) \times \Delta T + CME \times \delta_{MC}^m],$$

where E is the Young's modulus.

The portion of this stress caused by the CTE mismatch will be negligible when $\alpha_{MC} \approx \alpha_{LF}$. In this case the stress will be due to only hygroscopic swelling of the packaging material.

Opposite to the hygrothermal expansion of encapsulating materials in humid environments, shrinkage of MCs can be expected in space, where parts are operating in vacuum. In these environments moisture will gradually desorb from polymers causing reduction of the volume of plastic packages, changing mechanical characteristics of encapsulating materials, and thus imposing additional stress to the active elements of the circuits. The effect of these variations on performance and reliability of PEMs intended for space applications has not been properly addressed in the literature so far. Understanding of the physical mechanisms of the environmentally induced deformations and stresses in encapsulating polymer materials is important to develop an adequate qualification strategy, evaluate results of reliability testing, and predict behavior of parts during operation in space.

A purpose of this work is to develop a simple measurement technique, evaluate expansion and shrinkage of molding compounds due to moisture absorption and desorption processes, and discuss physical mechanisms of the environmental hysteresis in volume deviations of PEMs.

2. Technique

2.1. Measurements of volume deviations and hygroscopic swelling.

Several techniques are available for measurement of the hygroscopic swelling characteristics of epoxy composites and molding compounds (see Table 1). The simplest method is direct measurement of the dimensions of samples before and after moisturizing. However, due to the small size of plastic packages, this technique has poor accuracy when applied to PEMs. Moire interferometry has been used at the CALCE center [11]. This technique requires special optical equipment and corrosion-resistant gratings. Combined thermal mechanical analysis (TMA) and thermal gravitational analysis (TGA) measurements, performed simultaneously on two identical samples, has been used by E. H. Wong et al. [4]. The samples were subjected to isothermal high temperature bake, during which their mass loss and linear dimension were monitored with time. The high temperature baking, as shown below, might itself cause non-moisture-related deformations of polymer samples with time. This effect, in particular, could be responsible for anomal large values of the CMEs measured by this technique.

In this work, the hygrothermal expansion coefficient was calculated based on volume measurements of PEMs using the Archimedes principle. According to this technique, the weight measurements of a plastic package, P, were first performed in air and then after immersion into a fluid, P_{im}. The volume of the sample was calculated using the density of the liquid, ρ_{liquid} :

$$V = \frac{P - P_{im}}{\rho_{liquid}}$$

To calculate the coefficient of moisture expansion, CME, the volume and mass of the sample was measured two times: after saturation in moisture environments and after baking-out at high temperatures:

$$CME = \frac{1}{3} \times \frac{V_{moist} - V_{bake}}{M_{moist} - M_{bake}} \times \frac{M_{bake}}{V_{bake}}$$

Galden D02 was used as media for the immersion measurements. It is a low molecular weight perfluoropolyether (PFPE) liquid having extreme chemical inertness, boiling point of 175 °C, density at 25 °C of 1.77 g/cm³, kinematic viscosity at 25 °C of 1.8 cSt, and vapor pressure at 25 °C <1 torr. This liquid used widely for electronic reliability testing, including thermal shock and hermetic seal testing.

The weight measurements were performed using a digital scale with 0.1 mg accuracy, which gives an error in the volume measurements of 0.1% to 0.004% for the packages with volume ranging from 0.1 cm³ to 3 cm³, respectively.

2.2. Effect of lead frame

Measurements of moisture uptake and volume deviations on PEMs would give different results compared to the measurements on samples of MCs due to the presence of the lead frames. Assuming the volume of the lead frame is V_{LF} , and the specific density ρ_{LF} , the relationship between the hygroscopic volume swelling, β , moisture uptake, δ^m , and volume deviation, δ^v , measured on a package and on encapsulating material can be written as follows:

$$\delta_{MC}^m = \delta_{pac}^m \times \left(1 + \frac{\rho_{LF} V_{LF}}{\rho_{MC} V_{MC}} \right)$$

$$\delta_{MC}^v = \delta_{pac}^v \times \left(1 + \frac{V_{LF}}{V_{MC}} \right)$$

$$\beta_{MC} = \beta_{pac} \frac{1 + \frac{V_{LF}}{V_{MC}}}{1 + \frac{\rho_{LF} V_{LF}}{\rho_{MC} V_{MC}}}$$

Here $\delta_{MC}^m = m_w/M_{MC}$ and $\delta_{MC}^v = v_w/V_{MC}$, where m_w and v_w are the mass and volume of absorbed moisture. The subscripts v and m refer to volume and mass; LF, pac, and MC refer to the lead frame, package, and molding compound, respectively.

For a typical case of a QFP144 package with a thickness of 3.4 mm and a copper lead frame of 0.18 mm of thickness, $V_{LF}/V_{MC} \approx 0.036$. Considering that the specific densities of copper and

MC are 9 g/cc and 1.8 g/cc, calculations give $\delta_{MC}^m \approx 1.275 \times \delta_{pac}^m$, $\delta_{MC}^v \approx 1.055 \times \delta_{pac}^v$, and $\beta_{MC} \approx 0.87 \times \beta_{pac}$.

To estimate the accuracy of assessments of CME for MCs based on measurements of moisture uptake and swelling of PEMs, experiments were performed with QFP144 plastic packages and samples of MC used in these packages. Three samples of MC with a thickness of ~1 mm were prepared by grinding off a part of the package with a die and lead frame. Masses and volumes of the three packages and three samples of MC were measured two times: first after baking at 125 °C for 48 hours and then after saturation with moisture in 85 °C/85% RH chamber for one week. Average values of the moisture characteristics and their standard deviations are shown in Table 2.

Table 2. Moisture uptake and swelling of QFP-144 packages and molding compound.

Sample	dM, %	stdev._M	dV, %	stdev._V	β_{MC}	CME
Package	0.329	0.011	0.266	0.034	0.81	0.23
MC	0.426	0.011	0.281	0.077	0.66	0.22

The results show that the CME calculations based on direct measurements on samples of MCs and on plastic packages agree within 5%. The accuracy of moisture swelling measurements depends on the initial volume of the sample, V_o , and was 12.7% for packages ($V_o \sim 2.5 \text{ cm}^3$) and 27.4% for MC samples ($V_o \sim 0.75 \text{ cm}^3$). This gave overall accuracy of CME measurements of 16% and 29% for the packages and MC samples, respectively.

Characteristics of plastic packages used in this study, including the thickness of packages and lead frame-to-package volume ratios, are displayed in Table 3.

Table 3. A list of studied PEMs.

Mfr	PN	DC	Package	L, mm	t, mm	V_{LF}/V_p
Harris	HA3-5217A-5	9827	DIP-8	3.3	0.25	0.038
Harris	HA3-5104-5	9810	DIP-14A	3.3	0.24	0.035
Harris	HA3-5330-5	9732	DIP-14B	3.3	0.24	0.035
Ramtron	1808	9907	DIP28	3.82	0.25	0.032
Ramtron	1608	0045	DIP28	3.82	0.25	0.032
Dallas	DS80C320	9536	QFP44	2.0		
IDT	49C465PQF	9832	QFP144	3.4	0.18	0.036
AMD	LT1014IS	9617	PLCC32	2.84	0.24	0.05
XILINX	XC4005H-5	9608	QFP240	3.29	0.16	0.024
V3 Semi	H7MG00104B	9652	QFP160	3.75	0.19	0.025
ACTEL	A1240A - 1	9505	QFP144	3.36	0.19	0.028

3. Swelling characteristics of different MCs and encapsulating materials

The swelling characteristics were measured on packages listed in Table 3 and also on two Hysol liquid epoxy compositions and on Struers Epofix epoxy compound. All measurements were performed on three packages or three samples of materials.

3.1. Testing in 85 °C/85% RH chamber

For this testing the parts were measured after baking at 125 °C/48 hours and then after one week of storage at 85 °C/85% RH conditions. Averaged moisture characteristics of the packages and encapsulating materials and standard deviations of the moisture uptake and swelling are displayed in Tables 4 and 5. Also, the calculated errors of the β_{pac} measurements are shown.

Table 4. Moisture characteristics of different PEMs after 85 °C /85% RH/186 hrs.

Package	dM, %	stdev._M	dV, %	stdev _V	β_{pac}	error, %	CME MC
DIP-8	0.296	0.016	0.252	0.074	0.85	34.9	0.25
DIP-14A	0.310	0.012	0.527	0.106	1.70	24.0	0.49
DIP-14B	0.319	0.002	0.395	0.045	1.24	12.1	0.36
DIP28	0.184	0.002	0.200	0.015	1.09	8.7	0.32
QFP144/IDT	0.329	0.011	0.266	0.034	0.81	16.1	0.24
PLCC32	0.266	0.013	0.168	0.07	0.63	46.5	0.18
QFP240	0.315		0.116		0.37		0.11
QFP160	0.278	0.012	0.092	0.02	0.33	26.0	0.10
QFP144/Actel	0.318	0.011	0.122	0.023	0.38	22.3	0.11

Table 5. Moisture characteristics of different encapsulating materials after 85 °C /85% RH/186 hrs.

Material	dM, %	stdev._M	dV, %	stdev _V	β	error, %	CME MC
QFP144 MC	0.426	0.011	0.281	0.077	0.661	29.8	0.22
Hysol FP4450	0.348	0.014	0.268	0.055	0.770	24.5	0.25
Hysol EO1016	2.026	0.007	1.976	0.024	0.975	1.56	0.32
Struers Epofix	2.020	0.012	1.542	0.010	0.764	1.23	0.25

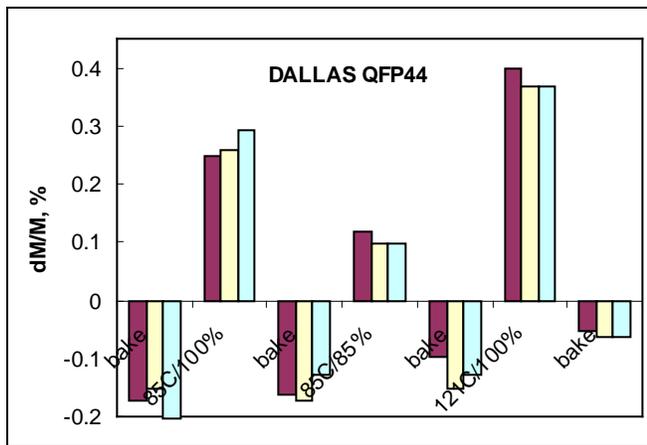
The results show that the CME for different molding compounds varies from 0.1 to 0.49. In spite of different level of filling, variation of the CME for encapsulating materials was relatively

small: $0.22 < CME < 0.32$. These data are in agreement with the results reported in literature (see Table 1).

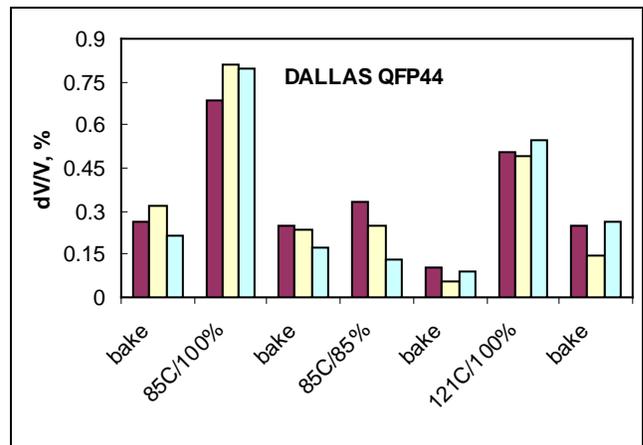
Sample-to-sample variations were in the range from 1% to 5% and from 10% to 25% for the moisture uptake and volume deviation measurements, respectively. This gives an error of the hygroscopic expansion coefficients below 30%.

3.2. Effect of temperature and humidity

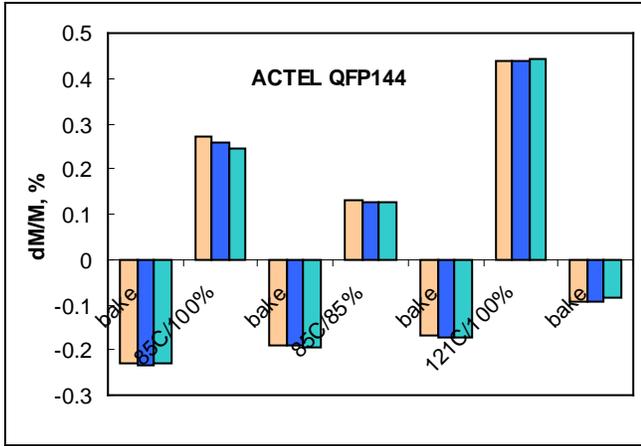
Swelling in several types of PEMs was measured after storing in humidity chamber at 85 °C /100% RH for 168 hrs and after pressure cooker testing (PCT) at 121 °C /100% for 140 hrs. As a reference, a standard testing at 85 °C /85% RH for 168 hrs was also performed. Before each environmental stress the parts were baked at 150 °C for 17 hours. Typical test results are shown in Figure 1. The data (masses and volumes) measured after each bake were used as a baseline for calculations of the hygrothermal volume expansion coefficients. Figure 2 shows results of these calculations plotted against the moisture uptake as it increased during storage at higher humidity and/or temperature conditions.



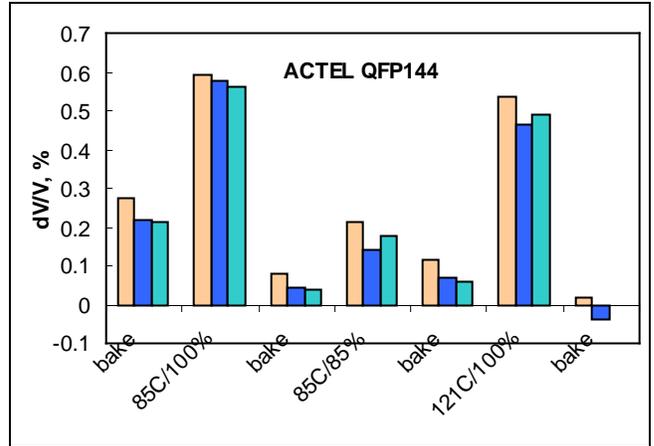
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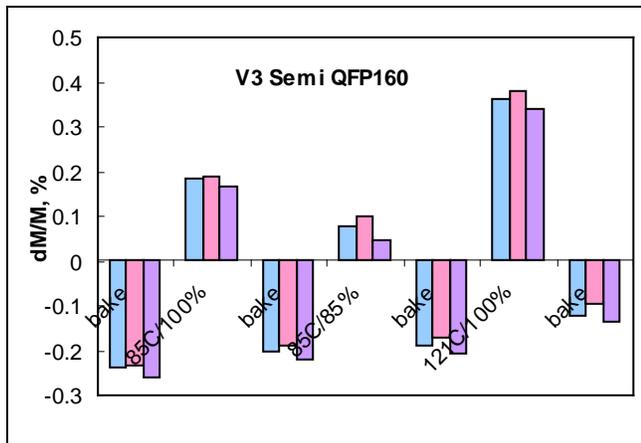
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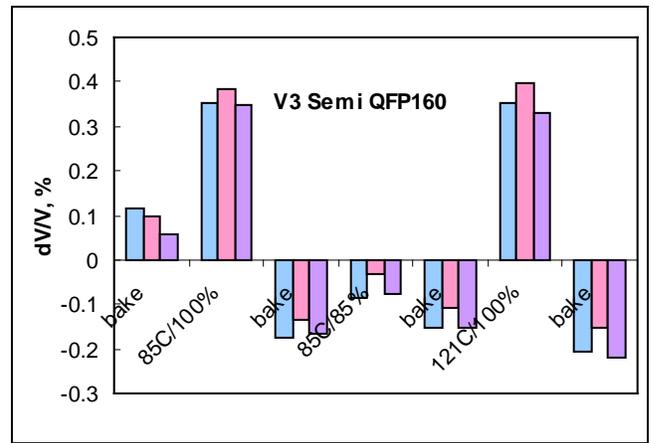
c)



d)



e)



f)

Figure 1. Moisture uptake (a, c, e) and volume deviations (b, d, f) of three types of PEMs during bakes and different moisturizing conditions. Three samples were tested for each package type.

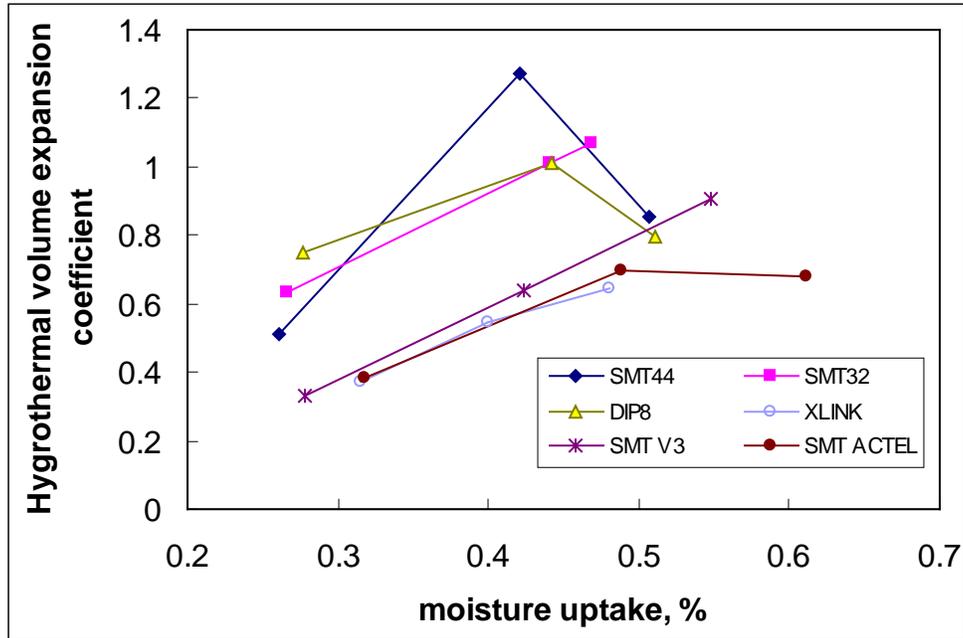
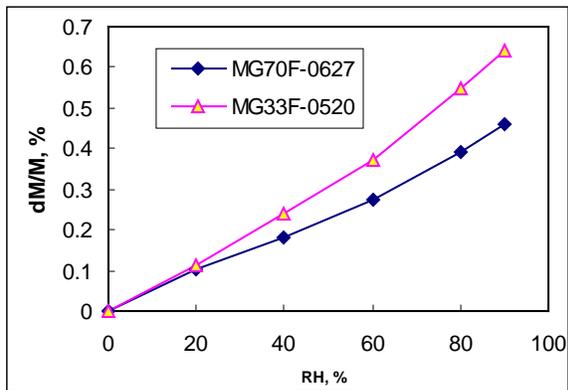


Figure 2. Hygroscopic volume expansion coefficients for different PEMs plotted against the moisture uptake, which varied with moisturizing conditions: 85 °C /85% RH, 85 °C /100% RH, and 121 °C /100% RH.

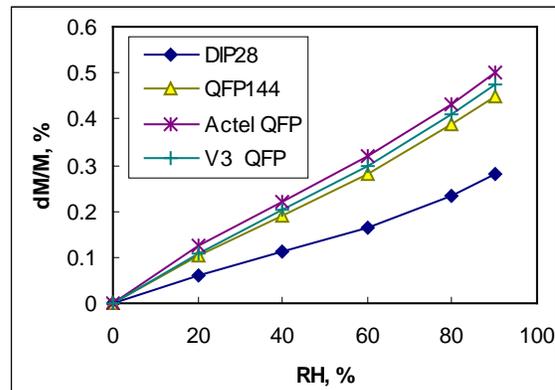
The results show that the coefficient of hygrothermal expansion is not a constant, but depends on moisturizing conditions and has a trend of increasing with moisture uptake.

3.3. Sorption isotherms

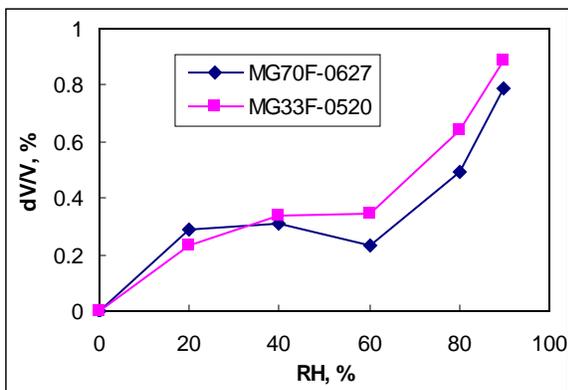
To evaluate the effect of relative humidity on moisture uptake and swelling of molding compounds, several types of PEMs and two types of epoxy molding compounds were subjected to environmental stresses at 85 °C and relative humidity varying from 20% to 90%. The epoxy molding compounds used, MG33F-0520 and MG70F-0627, were manufactured by DEXTER/HYSOL for encapsulation of solid chip tantalum capacitors. Three samples of each type of package and MCs were stored consequently at humidity of 20%, 40%, 60%, 80%, and 90% for 168 hrs. Before storing at 20% RH the parts were baked at 150 °C for 24 hours and the MC samples were post mold cured at 177 °C for 2 hours. Masses and volumes of all samples were measured after bake (baseline data) and after each RH run. Average values of moisture uptake, volume swelling, and CME are shown in Figure 3.



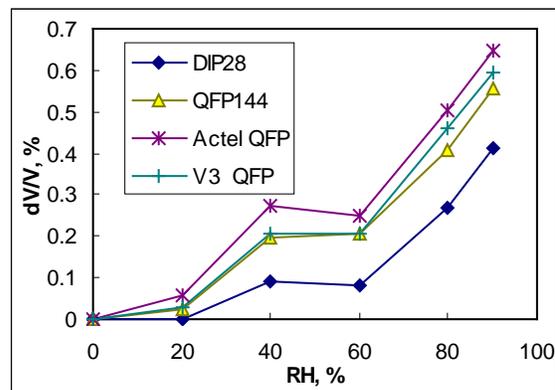
a)



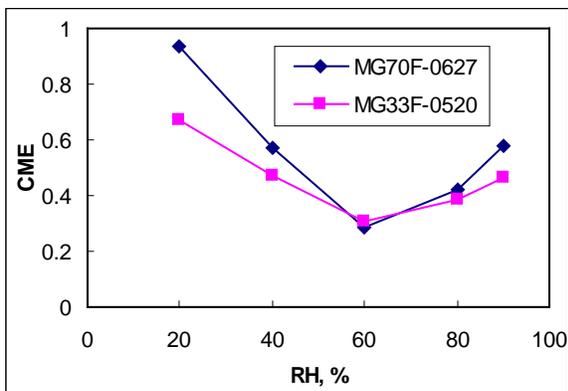
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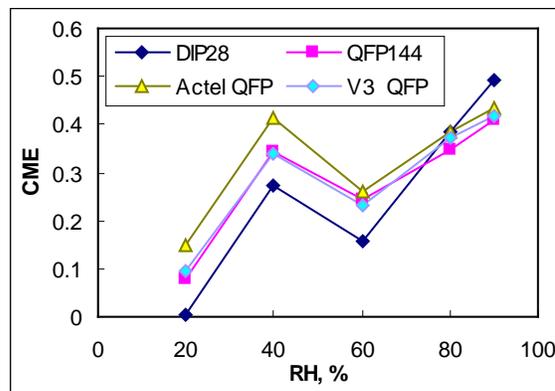
c)



d)



e)



f)

Figure 3. Isotherms of the equilibrium moisture uptake (a, b), volume swelling (c, d), and coefficient of moisture expansion (e, f) at 85 °C for different PEMs (b, d, f) and epoxy molding compounds (a, c, e).

The results show that the moisture uptake is virtually a linear function of the relative humidity (see Figures 3a, b) for all tested MCs and plastic packages. This confirms that at equilibrium conditions, the concentration of moisture in epoxy polymers follows Henry's law, and the moisture uptake increases linearly with the pressure of moisture vapor (P):

$$dM_{\infty} = \eta \times P = \eta \times P_s \times f$$

where P_s is the pressure of saturated water vapor, f is the relative humidity, and η is the sorption coefficient, which varies exponentially with temperature.

Figure 3c and 3d show that the moisture swelling isotherms for all samples had a sigmoidal shape. The volume did not change significantly when moisture soaking was performed between 20% and 60% of relative humidity for molding compounds and between 40% and 60% RH for PEMs and then increased at $RH > 60\%$. Similar to what was observed before, the CME increased 2.5 to 5 times when RH increased from 60% to 90%. Minimal CME values for MCs and PEMs were observed at 60% RH and at lower RH the CMEs for molding compounds increased up to 0.67 to 0.93. All PEMs had anomaly low swelling at 20% RH, which resulted in the CMEs below 0.15.

4. Effect of bake-out and high temperature exposure

Bake-out of epoxy polymers was expected to remove moisture from the samples and, opposite to moisture-induced swelling, cause shrinkage of molding compounds. To evaluate this shrinkage experiments were performed with several types of PEMs stored in laboratory conditions (22 °C, ~50% RH) for time varying from one to more than 4 months. Masses and volumes of these parts were measured before and after 125 °C/48 hours bake. The results of these tests are displayed in Table 6.

Table 6. Effect of bake at 125 °C for 48 hrs

Package/material	dM avr, %	dV avr, %	β_{pack}
QFP44	-0.18	0.27	-1.51
SMT32	-0.16	-0.03	0.17
SMT16	-0.15	0.01	-0.07
DIP8	-0.13	-0.02	0.13
QFP144	-0.22	-0.1	0.47
QFP260	-0.21	0.28	-1.32
QFP160	-0.24	0.09	-0.37
ACTEL QFP144	-0.23	0.23	-1.01
DIP28	-0.06	0.15	-2.48

Baking resulted in mass losses varying from 0.1% to 0.24%, thus indicating that the moisture uptake at room temperature conditions is comparable with the moisture uptake at 85 °C/ 85% RH

conditions. This suggests that the moisture uptake virtually does not depend on temperature and can be explained assuming that the heat of moisture solution in polymer and the heat of water vaporization have close absolute values. As it was shown above, the moisture uptake varies linearly with RH and the dM_{RT} values measured after saturation at 50% RH and room temperature are approximately 59% of the $dM_{85/85}$ measured after quenching at 85 °C/85% RH conditions. Using data from Table 4, the $dM_{85/85}$ varies from 0.2% to 0.3%. This gives dM_{RT} estimations of 0.12% to 0.18%, which is close to data presented in Table 6.

Much to our surprise, after baking the volume of some PEMs increased 0.06% to 0.27%, resulting in negative values of the hygroscopic volume expansion coefficients.

To evaluate how bake temperature affects results of the measurements, IDT QFP144 packages, which manifested normal volume-reduction-at-bake behavior, were baked at different conditions: 125 °C during 96 hrs, 165 °C during 24 hrs, and 205 °C during 2 hrs. Nine samples were split in three groups, with 3 samples each. Each group was subjected to baking at one of the three conditions, then to moisturizing at 85 °C, 100% RH for 168 hours, and then baking was repeated at the same temperature as before. The results of these measurements are shown in Figure 4.

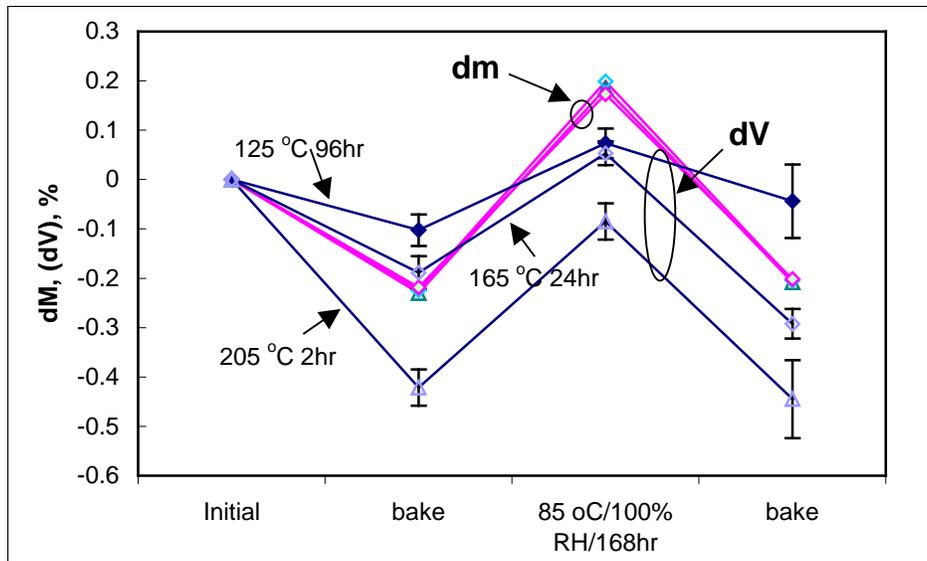


Figure 4. Effect of baking conditions on moisture uptake and volume deviation in IDT QFP144 packages.

It is seen that different baking conditions and moisturizing resulted in the same variations of the mass of the samples, suggesting that in all cases baking resulted in virtually complete removal of moisture. However, the volume variations increased with the bake temperature. The two-hour bake at 205 °C caused more than 0.4% decrease in the volume compared to only ~ 0.1% after 125 °C bake. The decrease in volume after high temperature bake was not restored after one week of saturation of the samples with moisture at 85 °C.

Note that the decrease in the mass after baking was more significant (~ 0.106%) compared to the moisture uptake due to saturation at 85 °C, 85% RH (~0.07%). This also confirms the fact that the equilibrium moisture uptake does not depend on temperature.

Based on the data in Figure 4, the hygroscopic expansion volume coefficients, β_{pac} , had been calculated for different bake/moisture saturation conditions. Results of these calculations are displayed in Table 7. An increase in the bake-out temperature from 125 °C to 205 °C more than 3 times increased swelling effectiveness of moisture absorption. Analysis of the data presented in Table 7 shows that moisture, which was absorbed by the plastic packages during the long-term storage at room conditions, has higher swelling efficiency compared to the moisture absorbed at 85 °C, 100% RH conditions.

Table 7. Effect of bake temperature on the hygroscopic expansion volume coefficient.

Bake temperature	Calculations	
	Initial-to-bake	Moisture-to-bake
125 °C	0.47	0.31
165 °C	0.87	0.83
205 °C	1.83	0.92

During assembly of PEMs, which are designed for surface mounting technology (SMT), the parts undergo baking (to remove moisture and thus reduce the probability of popcorning) and then soldering reflow when they are experiencing a high temperature shock. To simulate these conditions, several PEMs were baked at 125 °C for 96 hours and then exposed to 230 °C for 15 minutes. Figure 5 shows mass and volume variations in these parts during the bake, high temperature exposure, and then after 6 month of storing at room conditions (RH ~ 50%). In all cases most of the mass losses, ~ 80%, occur during the 125 °C bake, and only ~20% were lost during HT exposure. It is possible that much more than 80% of moisture was removed during the bake, and the losses at high temperature exposure were due to some volatile organic molecules in the molding compound. The long-term storage of the samples at RT conditions in all cases, except for DIP 28 packages, resulted in moisture uptake, which overshoots the initial level of moisture; however, the initial level of volume was restored only partially.

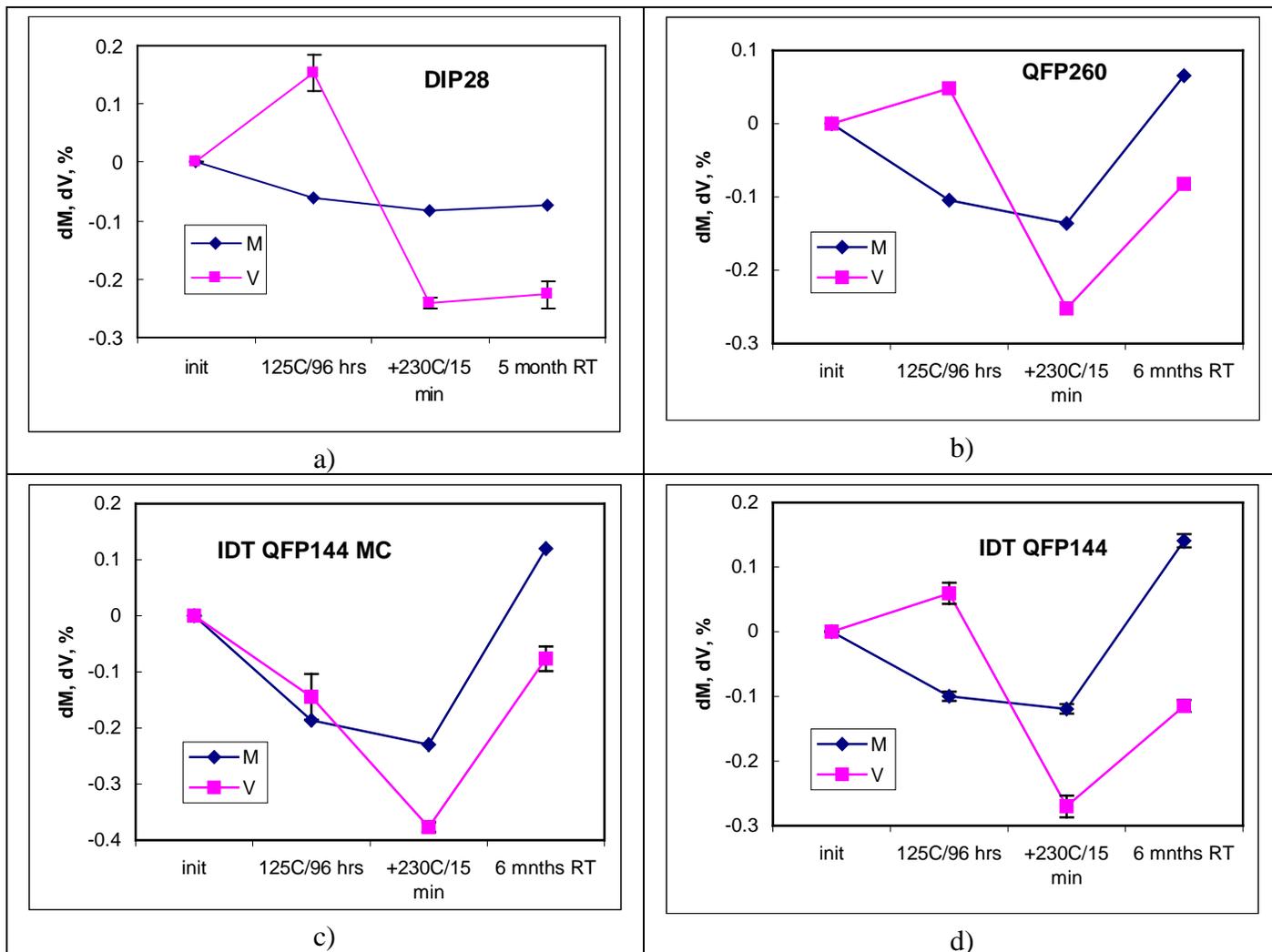


Figure 5. Effect of 125 °C bake and exposure to 230 °C on the mass and volume deviations in different PEMs (a, b, d) and MC (c). All samples have been stored initially for several months at laboratory conditions ($T \sim 22$ °C, $RH \sim 50\%$).

Baking 0.05% to 0.15% increased the volume of packages, but the high temperature exposure resulted in a significant decrease (from 0.3% to 0.5%) of the volume. Assuming that mass losses during the high temperature exposure were due to a release of some remnant moisture from the packages, calculations of the hygroscopic volume coefficient yield anomaly high values of β_{pack} varying from 5 to 17.

5. Discussion

The performed experiments show that the coefficient of moisture expansion is not a constant, but strongly depends on both conditions: moisturizing and baking. Possible physical mechanisms of deviation of moisture induced swelling from a simple linear relationship with the moisture content are discussed below.

5.1. Mechanism of hygroscopic swelling

The universally adopted mechanism of hygroscopic expansion is based on the concept of two states of the absorbed water in epoxy polymers [1, 3, 10, 12]. Unbonded or free water molecules, which exist as clusters, reside in micropores or nanovoids, and can easily move through the free volume of polymer, are forming one state. In this state water does not cause swelling. Another state is formed by water molecules, which are disrupting interchain polymer ties, causing swelling and plasticizing the polymer. It should be noted that so-called “unbonded” water molecules in reality are attached to the polymer by weak hydrogen bonds, which causes their condensation in the micropores. The “bonded” molecules are attached to polar sites of the polymer forming stronger bonds, which secure molecules in states with lower energy compared to the “unbonded” molecules.

To evaluate maximum swelling of molding compound, let us consider a polymer as a liquid without free volume. In this case an increase in the volume of the sample will be equal to the volume of absorbed water and a simple relationship between the relative moisture uptake, $\delta^m = m_w/M_p$, and moisture swelling, $\delta^v = v_w/V_p$, can be obtained:

$$\delta^v = \frac{\rho_p}{\rho_w} \times \delta^m$$

where m_w , v_w , and ρ_w are the mass, volume, and specific density of water; m_p , v_p , and ρ_p are the mass, volume, and specific density of polymer.

It can be shown that a similar equation is valid also for filled polymers, and in particular for molding compounds:

$$\delta_{MC}^v = \frac{\rho_{MC}}{\rho_w} \times \delta_{MC}^m$$

where $\delta_{MC}^m = m_w/M_{MC}$ and $\delta_{MC}^v = v_w/V_{MC}$.

The volume hygroscopic expansion coefficient, β_{MC} , is defined as a ratio of moisture swelling and moisture uptake: $\beta_{MC} = \delta_{MC}^v/\delta_{MC}^m$ and indicates the “efficiency” of the adsorbed moisture to cause swelling of the polymer. The coefficient of moisture expansion, CME, is defined as the ratio of the strain to the moisture uptake and is one-third of the volume coefficient:

$$CME = \frac{\Delta l/l}{\delta_{MC}^m} = \frac{1}{3} \beta_{MC} = \frac{1}{3} \frac{\delta_{MC}^v}{\delta_{MC}^m} = \frac{1}{3} \frac{\rho_{MC}}{\rho_w}$$

where l is the initial dimension of a dry MC and Δl is the change due to moisture absorption at saturation.

For a typical molding compound $\rho_{MC} \approx 1.8 \text{ g/cm}^3$, which gives maximum value of the $\beta_{MC} \approx 1.8$ and maximum CME ≈ 0.6 . All CME values, calculated for the standard moisturizing conditions of 85 °C/85% RH, were below 0.6. A deviation from the maximum CME level indicates a

proportion of water, which exists in the free volume and does not mix intimately with the polymer chain:

$$1 - \frac{CME}{CME_{\max}} = \frac{v_u}{v_b + v_u}$$

where v_u and v_b are the volumes of the bonded and unbonded water.

Based on the obtained data, the proportion of the free, or unbonded, water after saturation at 85 °C/85% RH conditions varied for different materials from 20% to 80%.

It is reasonable to assume that the filler does not absorb moisture and the moisture sorption and swelling of MC are due to the polymer binder. In this case the relationship between moisture characteristics of MC and polymer binder can be written in the following form:

$$\delta_{PB}^m = \frac{\delta_{MC}^m}{1 - \gamma_f^m},$$

$$\delta_{PB}^v = \frac{\delta_{MC}^v}{1 - \gamma_f^v},$$

$$\beta_{PB} = \beta_{MC} \frac{1 - \gamma_f^m}{1 - \gamma_f^v}$$

where γ_f^m and γ_f^v are respectively mass and volume fractions of filler in the molding compound.

In a typical case $\gamma_f^m \sim 0.75$ and $\gamma_f^v \sim 0.5$, which gives the following approximations: $\delta_{PB}^m \approx 4\delta_{MC}^m$ and $\delta_{PB}^v \approx 2\delta_{MC}^v$; hence $CME_{PB} = \delta_{PB}^v / \delta_{PB}^m = 0.5 CME_{MC}$. This means, that the CME for molding compounds are approximately two times larger than for the epoxy binder resin.

To estimate maximum moisture uptake, which might be due to the free volume of an epoxy binder in a molding compound, let us assume that φ is the proportion of the free volume in the epoxy resin. In this case maximum possible moisture uptake, which will not cause swelling, can be calculated as:

$$\delta_{MC}^m = \varphi \times \frac{\rho_w}{\rho_{MC}} \times (1 - \gamma_f^v)$$

For most polymer materials the fractional free volume α is approximately 2.5%. This gives the moisture uptake for a molding compound with free volume completely filled up with water molecules of $\sim 0.69\%$. Note that this value does not consider water molecules possibly residing in micropores at the MC – filler interface. Accounting for this amount of absorbed water would further increase the possible capacity of MC to absorb moisture without swelling. Typical moisture uptakes for MCs are below 0.5%. Considering that from 20% to 80% of this water causes swelling, the free volume is filled with water molecules to less than 15% to 60%.

This estimation shows that calculations of the free volume by the difference between the volume of adsorbed water and actual swelling of a polymer, which has been suggested in [3], are not correct. The relatively low swelling efficiency of water observed in [3], which is absorbed at the first stages of the sorption kinetic, can be explained by a swelling delay. Most likely, first absorbed molecules reside in a free volume, but their transfer to a bonded state with a lower energy level requires overcoming some energy barriers and occurs relatively slowly. It is quite possible that most of the bonded water is the water, which causes non-Fickian diffusion behavior, that typically manifests as a gradual increase of moisture uptake with time and might be considered as a swelling creep.

Sorption isotherms and experiments with baking showed that the swelling efficiency is larger at low RH and after high temperature bakes. This can be explained assuming that at the steady-state conditions with a low moisture concentration, most water molecules will occupy the low energy sites at disrupted polymer chains, thus causing swelling of the material. As humidity increases, most of the available low-energy sites became occupied and the dynamic equilibrium between the concentration of bonded and unbonded molecules shifts towards increasing the proportion of unbonded molecules. This means that a larger proportion of water will be clustering in free volume of the polymer without swelling. This explains saturation of the swelling isotherm at $20\% < RH < 60\%$ (see Figure 3c). It is possible, that swelling enhances the access of water molecules residing in the free volume to new low-energy interchain sites in the polymer resin, thus causing the swelling creep. This might explain an increase in the volume of samples as swelling progresses at humidity higher than 60%.

5.2. Mechanisms of the bake-induced volume deviations

Experiments showed that the hygroscopic coefficients depend on the baseline state of MCs, which are formed as a result of a high temperature baking. Moisture removal during baking-out at relatively mild conditions (125 °C to 150 °C) increased volume in some MCs. Exposure to temperatures above approximately 200 °C caused significant negative deviations in volume of the packages resulting in anomaly high coefficients of the hygroscopic expansion.

The observed anomalies with the baking-induced volume deviations strongly indicate that moisture is not the only factor affecting swelling and shrinkage of molding compounds and that the exposure to high temperature might cause significant deformations in plastic packages. Superposition of volume deviations caused by variations of moisture content and by exposure to high temperatures complicates swelling/shrinkage processes in PEMs.

The thermal hysteresis is a well-established effect in glassy polymers [13, 14]. It results, in particular, in gradual decrease in the volume of a sample heated above the glass transition temperature (T_g) and then cooled down below T_g . For MCs with a relatively high T_g , above 125 °C, this effect is negligible at room temperatures (the relaxation time exceeds several years), but occurs with a noticeable rate at temperatures close to T_g ($T_g > T > T_g - 20$ °C). Using the free volume concept and the kinetic theory [14], this process can be explained as a volume relaxation to the stationary state. When a sample is quenched at temperatures above T_g , a significant amount of the free volume is introduced. Normally (unless cooled extremely slowly, with the rate $\gg 1$ C/min), cooling to temperatures below T_g results in the non-equilibrium state of the glassy polymer with excessive free volume. Aging of such a sample at $T < T_g$ will result in

squeezing out of this excessive volume with time, resulting in gradual decrease in the size of the sample. According to this mechanism, baking would cause a decrease in the volume of a sample, which is not related to the moisture content, resulting in an apparent increase of the swelling efficiency.

In cases when MC was not cured fully during manufacturing of PEMs, high temperature storage might provide additional post-mold curing of the encapsulating material, which also affects the volume of PEMs. In a separate set of our experiments with molding compounds MG33F-0520 and MG70F-0627, it was shown that additional curing decreased the specific density of the molding compounds and increased their volume on approximately 0.35%. These results agree with the results reported by Ko and Kim [15]. The post-mold curing effect is also not related to the moisture content, and opposite to the physical aging would result in an apparent decrease the CME.

Gonon and co-workers [16] observed drastic decrease in the dielectric constant of MCs subjected to preconditioning in humidity chamber at 85% RH and 85°C during 168 h and then to reflow soldering simulations at 240°C per standard JEDEC procedures. The results were explained by the building of micro-porosity within the material, which should proceed with an increase in the volume of the molding compounds. This micro-popping effect was not observed in our experiments, where high temperature exposure always decreased the volume of the parts.

To evaluate the effect of high temperature exposure, deformations in QFP144 packages and molding compounds were monitored using a thermo-mechanical analyzer TMA2904. Experiments were performed on samples “naturally” moisturized during a long-term storage at laboratory conditions and after highly accelerated testing (HAST) at 130 °C, 85% RH for 72 hours. During these experiments the temperature was raised from 125 °C to 200 °C with 15 °C increments and 15 minutes bake at each step. After exposure to 200 °C for 15 minutes the samples were cooled down to room temperature with the rate of 3 °C /min. The deformation and temperature of the sample were monitored and recorded. The thermo-mechanical analysis performed using the cooling curve gave the glass transition temperature for the molding compound of 153 ±3 °C.

Figure 6 a shows variations of dimension and temperature with time during testing of molding compound, which had been “moisturized” at room conditions. A reduction in size was observed during each 15-minutes step. The total deformation during this test was 0.26% and the mass loss was 0.47%. This gives CME of ~ 0.55, which is in agreement with our previous results presented in Table 7.

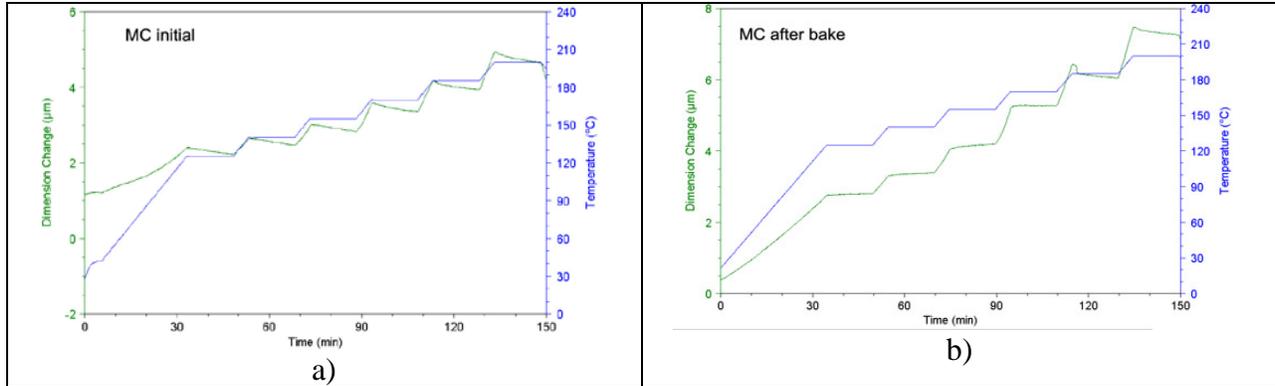


Figure 6. Results of thermo-mechanical analysis carried out twice on a sample of MC. First test was performed after moisturizing at “normal” conditions, when a sample has been stored for a few months at laboratory conditions (~22 °C and ~50% RH). The second test (b) was performed right after the first one, which resulted in moisture removal from the sample.

The repeat testing was performed right after the first one, so this time the sample is considered as being baked and containing no moisture. This time (see Figure 6b) an increase in the size at temperature steps below 175 °C was observed. Similar results were obtained during measurements performed with the plastic package. Figure 7 displays deformations measured during the 15-minute bakes in the MC and QFP144 package versus the temperature of baking for different conditions of the samples.

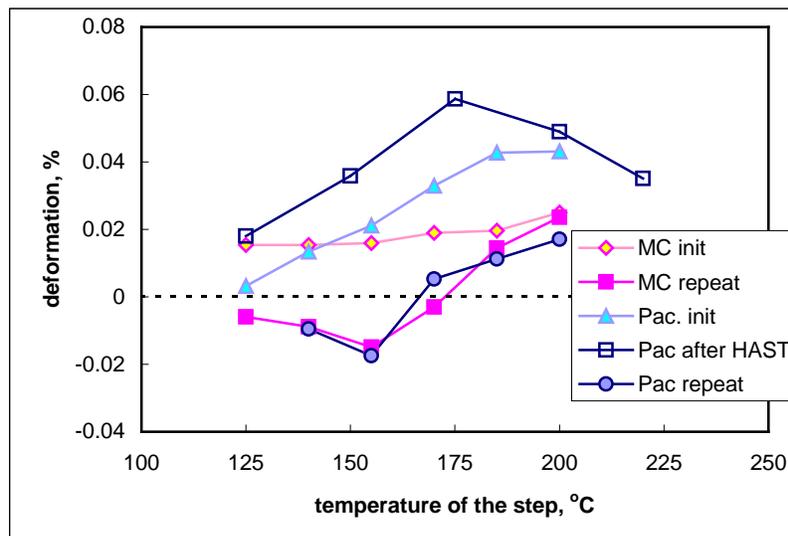


Figure 7. Decrease in size of the package (QFP144) and the sample of MC during 15-min bake at different temperatures calculated from the thermo-mechanical tests. The tests of the package were performed after normalizing at laboratory conditions (initial measurements), after HAST at 130 °C/85% RH for 72 hours and then repeated after 15-minuted step baking in the range from 125 °C to 200 °C.

The results show that the MC and the package manifested similar behavior. In both cases samples containing moisture reduced in size during the each baking step, while for the dry (baked) samples the size increased with time at temperatures below approximately 170 °C. This behavior is opposite to the one expected during physical aging of epoxy resins, when the free volume supposedly squeezes out from the sample.

This anomaly most likely can be explained if mechanical stresses in the resin of molding compound are taken into account. In highly filled molding compounds typically used in PEMs, the resin at normal conditions is under significant tensile stresses due to the difference between CTE of the epoxy resin and the filler. Most glassy materials dilate under the tensile stress by the amount proportional to the applied tensile strain [13]. This dilation is mostly suppressed at low temperatures, but will manifest as a creep when the temperature approaches T_g , thus resulting in a gradual increase of the volume of the package with time. Depending on moisture content and moisture swelling efficiency, the creep, which is due to baking conditions, will change the value and even the sign of the hygroscopic moisture swelling coefficient.

Anomaly low increase in the volume of plastic packages during sorption isotherm measurements at 85 °C and 20% RH (see Figure 3d) could be explained considering that along with the moisture-related swelling, aging processes resulting in volume reduction of MCs occur. One such process could be physical aging taking place at 85 °C during 168 hours storing in the humidity chamber. However, the storing temperature was far below the glass transition temperatures for the used MCs ($T_g > 130$ °C). At these conditions the rate of the volume reduction should be extremely small. Another possibility is the baking-induced creep during the 150 °C bake before storing the parts in a humidity chamber. As it was shown above, similar bake might increase the volume of plastic packages. As creep in polymers at low strains (<1%) is essentially recoverable [17], it is possible that this recovery occurred in the humidity chamber during the first testing (20% RH), causing reduction of the volume and thus decreasing the effect of moisture-induced swelling. Note also that additional thermo-mechanical analysis performed on MG33F-0520 and MG70F-0627 MCs did not reveal any significant creep during 125 °C / 150 °C bakes.

High temperature exposure, at $T > 200$ °C, caused considerable reduction of the volume of PEMs and relatively small losses of the mass. This resulted in values of β varying from 5 to 17, which significantly exceeded the calculated maximum value of ~ 1.8 . The higher efficiency of water to cause reduction of the volume during desorption at higher temperatures is most likely due to a lower energy level of the bonded water molecules. Obviously, more energy is necessary to activate and remove bonded water molecules compared to the molecules in the free volume. However, to explain the fact that this efficiency exceeds the maximum level, calculated by a simple, volume-added model, we have to assume that the high temperature exposure causes some chemical and structural changes in the resin, which are partially reversible during long-term aging at normal room temperature and humidity conditions.

6. Conclusions

1. A simple, hygrostatic weighting technique has been suggested to assess deviations in volume of plastic packages caused by environmentally induced swelling and shrinkage of molding compounds in PEMs.
2. Measurements of 11 different types of plastic packages and 3 types of liquid epoxy encapsulants showed that the coefficient of moisture expansion varies from 0.1 to 0.49 when the samples are moisturized at 85 °C/85% RH conditions.
3. The coefficient of moisture expansion is not a constant, but depends on moisturizing and baking conditions increasing with the moisture uptake at RH > 60%. The efficiency of moisture to cause swelling has a trend to increase at low humidities and after high temperature bakes (at T > 200 °C).
4. All tested molding compounds manifested virtually linear sorption isotherm at 85 °C. However, the swelling isotherms had a sigmoidal shape, indicating higher swelling efficiency of water molecules absorbed at low humidity (<60 % RH).
5. Depending on moisture content in a plastic package, baking at relatively low temperatures (125 °C to 150 °C) might result in positive or negative variations in the volume of PEMs. Baking of samples with even relatively low moisture content at temperatures above 200 °C significantly reduces the volume of molding compounds.
6. Physical mechanisms of environmentally induced volume deviations in PEMs are discussed. The observed anomalies in moisture-induced swelling and moisture desorption caused shrinkage of plastic packages are attributed to a creep in epoxy resins, which occurs at baking temperatures.
7. Moisture sorption in PEMs at normal laboratory conditions (~22 °C and ~50% RH) during ground phase integration period or moisture desorption in vacuum during space operations might cause significant (up to 0.35%) deviations in the volume of plastic packages. Similar deformations might affect characteristics of precision microcircuits and degrade performance of sensitive space instruments. Parametric sensitivity of PEMs intended for space applications due to environmentally induced swelling and shrinkage of molding compounds requires additional analysis.

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