# Effect of Environments on Degradation of Molding Compound and Wire Bonds in PEMs

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**Abstract**

Degradation of wire bonds (WBs) is one of the major factors limiting reliability of plastic encapsulated microcircuits (PEMs) at high temperatures. Use of PEMs in military and aerospace applications requires extended and thorough evaluation of encapsulating materials and reliability of packages in harsh environments. However, the effect of environmental conditions on characteristics of molding compounds (MCs) and reliability of wire bonds has not been studied sufficiently to date.

In this work, two types of PEMs in QFP-style packages have been stored in different environments at temperatures from 130 °C to 225 °C for up to 4,500 hours in some cases. To assess the effect of oxygen, the parts were aged at 198 °C in air and vacuum chambers. The effect of humidity was evaluated during long-term highly accelerated temperature and humidity stress testing (HAST) at temperatures of 130 °C and 150 °C.

Thermo-mechanical and thermo-gravimetrical analyses were used to evaluate the effect of environment on characteristics of molding compound used. Measurements of contact resistances of wire bonds and their mechanical strength were employed to monitor degradation of wire bonds throughout the testing. Correlation between degradation of MC and WB failures has been analyzed. The effect of environmental conditions on accelerating factors of WB failures has been assessed, and the mechanism of wire bond degradation due to the presence of moisture and oxygen is discussed.

## 1. Introduction

It is well known that characteristics of molding compounds used in PEMs affect reliability of gold/aluminum wire bonds and that temperature is the major accelerating factor of WB degradation. A generally accepted mechanism of WB failures includes formation of Au/Al intermetallics phases, their transformation with time into gold-rich compositions ($Au_4Al$ or $Al_5Au_2$), formation of micro-voids inside the bonds at the gold/intermetallic or intermetallic-1/intermetallic-2 interfaces (due to Kirkendall effect and/or volumetric changes of the Au/Al phases), and dry corrosion of the gold-rich intermetallics as a result of a chemical attack by products of thermal decomposition of the molding compound [1-3]. The most aggressive products of thermal decomposition are halogens or halogen-containing molecules cleaved from the epoxy resin or flame retardant, which are typically brominated epoxy and antimony oxide [4, 5]. Corrosive reaction of the halogen molecules (e.g., HBr, $CH_3BR$) with intermetallics weakens the bonds mechanically and increases their resistance to the point at which the part fails.

It is also known that environmental conditions during long-term storage at high temperatures might affect the rate of degradation of epoxy resins used in MCs. For example, the presence of oxygen results in thermo-oxidative decomposition and significantly accelerates degradation and failures of in epoxy composite materials [6]. Moisture absorbed in humid environments plasticizes epoxy resins, resulting in swelling and decreasing of glass transition temperature of MCs, thus facilitating transport of corrosive molecules to WB areas and increasing the rate of failures in PEMs [4].

Only a limited number of studies have reported on environmental effects of WB failures. Gallo [4, 7] has shown that the presence of moisture might significantly accelerate degradation of wire bonds in PEMs, and the parts stored in humid environments at 158 °C and 85% relative humidity (RH) failed faster than in dry environments at 200 °C. In our work [8] it has been shown that PEMs encapsulated in SOIC-8 packages had median times to failure three to eight times greater when stored at high temperatures in vacuum compared to air conditions. However, there is not much information on correlation between environment-induced degradation of MCs and on the effect of ambience on accelerating factors of WB failures in PEMs.

The purpose of this work was to gain more insight into the effect of oxygen and moisture on degradation of molding compounds and WBs in PEMs. For this purpose several groups of microcircuits encapsulated in QFP-style packages were stored at different temperatures in humidity, vacuum, and air chambers for up to 4,500 hours in some cases. Thermo-mechanical and gravimetrical characteristics of MCs and contact resistances of wire bonds were measured periodically throughout this testing. Accelerating factors of environments and the mechanism of WB degradation in PEMs are discussed.

## 2. Experiment

The parts used in this study were mixed-signal application-specific integrated circuits (ASICs) with dies manufactured by the same technology. The dies were bonded with 1-mil gold wires and encapsulated into QFP80 and QFP44 packages by the same assembly shop using a low-stress o-cresol novolac (OCN) epoxy resin molding compound (SUMITOMO EME6650RA). High-temperature storage (HTS) testing was performed on several groups of microcircuits stored in air chambers at temperatures of 175 °C, 200 °C, 210 °C, and 225 °C for up to 2,300 hours and in vacuum and air chambers at 198 °C for 800 hours. Humidity testing was carried out in a HAST chamber at 85% RH and temperatures of 130 °C for 4,400 hours and 150 °C for 3,400 hours.

To assure that the parts in air and vacuum conditions are stored at the same temperature, a small vacuum cell, where vacuum-stored parts were maintained at a pressure of ~0.1 torr, was placed in a regular temperature chamber next to the air-stored parts. The temperature during HTS was monitored directly in the area of the parts' location.

X-ray microanalysis of the molding compound has indicated the presence of bromine and antimony, thus suggesting a use of conventional brominated epoxies and antimony trioxide synergist as a flame retardant. Quantitative analysis has shown that both packages had similar concentration of Br (0.7 to 1.1 wt%) and of Sb (1.1 to 1.6 wt%).

### *2.1. TMA*

The glass transition temperature (Tg) and coefficients of thermal expansion in the glassy (CTE1) and rubbery (CTE2) states of the MC were measured using a thermo-mechanical analyzer, TMA2940, from TA Instruments. The thermo-mechanical characteristics were measured on pieces of molding compound cut from the plastic packages during heating up to 220 °C and cooling to room temperature at a rate of 3 °C/min. Calculations of Tg and CTEs were made using the cooling curves. This procedure allows for elimination of possible errors related to the presence of absorbed moisture and built-in mechanical stresses [9].

### *2.2. TGA and isothermal aging*

Thermal stability of the molding compound was characterized using thermo-gravimetrical analysis (TGA) and isothermal aging techniques. Plastic packages were used for isothermal aging, and samples cut from the edges of the packages with a size of approximately 2×3×6 $mm^3$ were used for TGA.

During TGA, mass losses were monitored as a function of time while temperature was increased linearly. TGA measurements were carried out using a TA2950 analyzer, TA Instruments, under standard nitrogen purging conditions and in air at two heating rates. At a heating rate of 1 °C/min. the temperature varied from room to 400 °C, and at a rate of 10 °C/min. the temperature varied from room to 700 °C.

Isothermal aging was carried out at temperatures of 175, 200, 210 and 225 °C for up to 2,300 hours. Masses of five packages at each aging condition were measured at room temperature periodically with time using a balance with an accuracy of 0.1 mg.

### *2.3. Contact resistance of WBs*

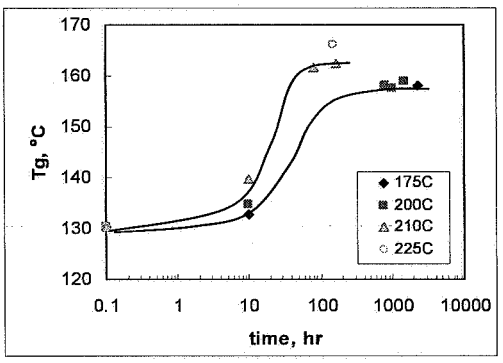
The variation of contact resistances ($R_c$) of wire bonds was calculated based on the forward voltage drop measurement technique described in [10]. The measurements were carried out at IF = 3 mA and room temperature periodically throughout the tests. The total number of wire bonds measured in each group of the parts varied from 105 to 175.

## 3. Degradation of MC in different environments

### *3.1. Effect of temperature in air chambers*

Figure 1 shows variations of thermo-mechanical characteristics of MC with time of HTS testing in air. The results indicate only a slight increase (~ 2 to 4 °C) in Tg and ~10% decrease in CTE2 after a relatively short-time storage (10 hours) at temperatures in the range from 175 °C to 225 °C. This indicates that the post-mold curing, which is typically carried out at 175 °C for ~5 hours, had been completed and characteristics of MC after encapsulation of ASICs were stable, so no significant changes with time are expected at storing temperatures below 175 °C.

Long-term high-temperature storage increased Tg from 130 °C initially to 160 °C to 165 °C after approximately 100 hours of aging at 210 °C and 225 °C. At temperatures of 175 °C and 200 °C, this level had been reached after ~1,000 hours of storage, and further storage did not increase Tg considerably.

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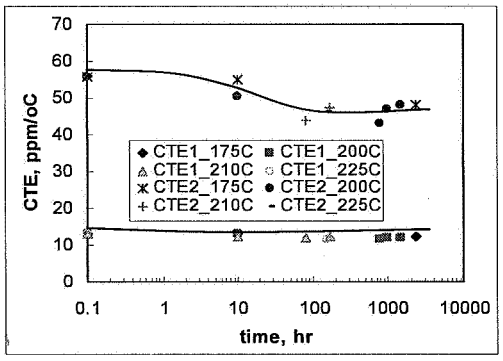



b)

Figure 1. Variations of glass transition temperature (a) and coefficients of thermal expansion with time of HTS testing in air at different temperatures.

No substantial variations of the coefficient of thermal expansion in the glassy state were observed: CTE1 decreased from 13 ppm/°C initially to ~12 ppm/°C after HTS. However, the values of CTE2 decreased approximately 20% from 55 ppm/°C initially to 43 to 48 ppm/°C after HTS. The increase in Tg and decrease in CTE indicate additional cross-linking in the epoxy matrix and is typical for high-temperature aging of MC used in PEMs [8, 11]. The results indicate that in the range from 175 °C to 225 °C the level, at which the characteristics are

stabilizing, does not depend significantly on the temperature; however, there is a trend of increasing the rate of variations of thermo-mechanical characteristics with temperature.

Results of TGA measurements in air at two temperature rates are shown in Figure 2, where mass variations of MC are plotted against the temperature. As expected, decomposition of MC starts at higher temperatures for higher temperature rates: a 0.1% mass loss has occurred at ~331 °C for the rate of 10 °C/min. and at ~298 °C for 1 °C/min., and both packages had similar TGA characteristics because the same MC was used in both part types.

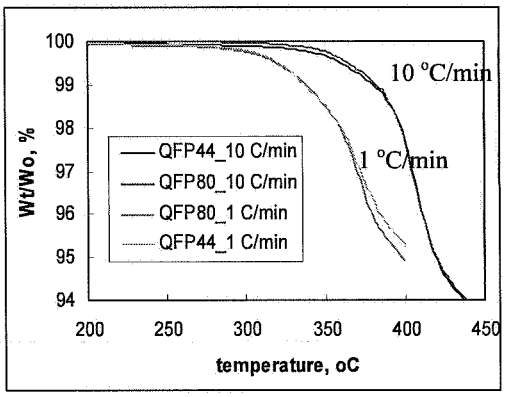



Figure 2. Results of thermo-gravimetrical analysis for QFP44 and QFP80 packages at different heating rates.

Average mass loss variations with time of isothermal aging at different temperatures are plotted in Figure 3. It is seen that in double logarithmic coordinates the data can be approximated with straight lines, suggesting that the mass losses follow a power law:

$$\frac{dM}{M} = A \times t^{\alpha},$$

where A is a constant, and $\alpha$ is the exponent, which according to the least-square fit calculations varied from 0.37 to 0.51. As the power exponent $\alpha$ is close to 0.5, a diffusion-controlled mechanism of thermal decomposition of the molding compound can be presumed.

Using the data in Figures 2 and 3, temperatures corresponding to different rates of decomposition of MC were calculated. For TGA data the decomposition rate was calculated based on the rate of temperature rise, *dT/dt*:

$$\frac{dM/M}{dt} = \frac{dM/M}{dT} \times \frac{dT}{dt}.$$

The corresponding temperatures were selected at the beginning of the decomposition when the rate varied from 0.01 to 0.05 %/°C. For the isothermal aging the decomposition rate was calculated at 175, 200, 210, and 225 °C for two levels of mass losses, *dM/M* = 0.15% and *dM/M* = 0.2% as a ratio of *dM/M* and time, which is necessary to reach these levels of mass losses. The results of these calculations are shown in Figure 4 and confirm that that the rate of decomposition of MC can be empirically fitted to Arrhenius law [12]:

$$\frac{dM/M}{dt} = B \times \exp\left(-\frac{E_a}{kT}\right),$$

where Ea is the activation energy, B is the constant, T is the temperature, and k = 1.38E-23 J/K is the Boltzmann's constant.

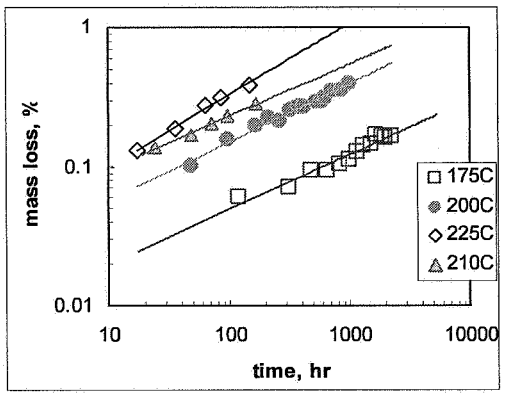



Figure 3. Results of isothermal aging at different temperatures in air chambers.

Calculations using the least-square fit approximation yielded Ea = 1.45 eV, which is within the range of values reported for epoxy resins (from ~0.5 to 1.9 eV) [13, 14] and close to the apparent activation energy for brominated epoxy resin FR4 (1.4 eV) [15].

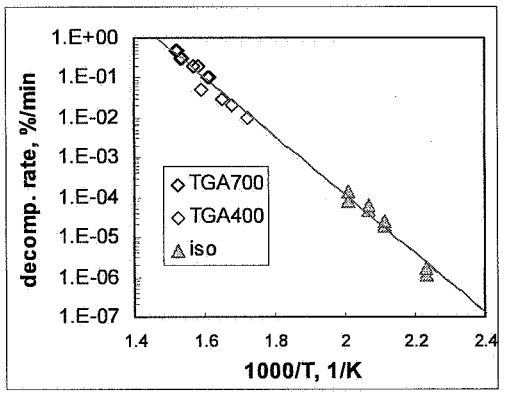


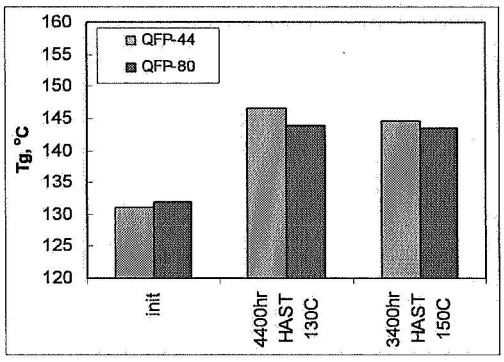

Figure 4. Arrhenius plot for the rate of mass losses obtained during TGA and isothermal measurements at different temperatures.

### 3.2. *Effect of humidity*

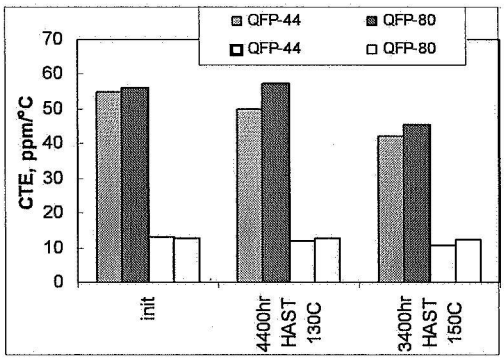
Thermo-mechanical characteristics of MC after long-term storage in the HAST chamber at a relative humidity of 85% and temperatures of 130 °C and 150 °C are shown in Figure 5. Both storage conditions resulted in similar effects: the glass transition temperature increased from 130 °C initially to ~145 °C after storage. The CTE in the glassy state did not change

significantly, and in the rubbery state approximately 15% decrease was observed only after HAST-150 storage.

Normally, a decrease of Tg is expected after humidity testing due to the plasticizing effect of moisture in polymers. Experiments have shown a 10 to 30 °C decrease in Tg after a standard humidity testing of PEMs (100 hours at 85% RH and 130 °C) [16]. An increase in Tg in our experiments probably is due to additional cross-linking as a result of the long-term effect of high temperature, which in the long run probably overrides the plasticizing effect of absorbed moisture. It is reasonable to assume that long-term storing of MC at 130 °C and/or 150 °C in dry conditions would have caused more significant cross-linking and increase of Tg to the level close to that reached during HTS testing at temperatures from 175 °C to 200 °C.




a)




b)

Figure 5. Variations of the glass transition temperature (a) and coefficients of thermal expansions in glassy (light bars) and rubbery (dark bars) states (b) during long-term testing in the humidity chamber.

Figure 6 shows moisture uptake in plastic packages with time during storing at 85% RH and temperatures of 130 °C and 150 °C. No saturation of the kinetics of moisture sorption was observed even after 4,400 hours of testing, and the experimental data can be approximated with a logarithmic law:

$$\frac{dM}{M} = C \times \ln(t) + D,$$

where C and D are constants. Calculations showed that the slope C is in the range from 0.084 to 0.088 for both temperature conditions. The value of moisture uptake at 150 °C was only slightly (~10%) greater than at 130 °C. This is likely due to a negative value of the heat of moisture solution in MC, which decreases the sorption coefficient, *h*, with temperature so that the moisture uptake, which is a product of *h* and the pressure of moisture vapor, only slightly varies with temperature [17].

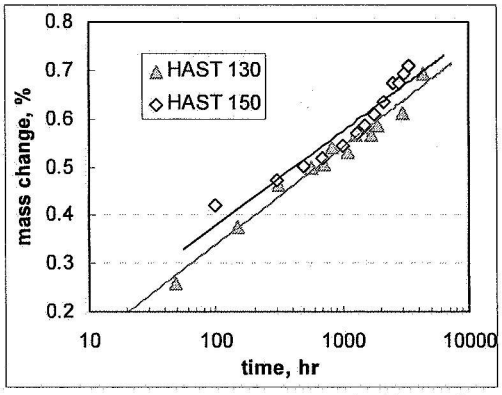



Figure 6. Mass gain of plastic packages during long-term testing in humidity chambers at 85% RH and temperatures of 130 °C and 150 °C.

A typical temperature dependence of moisture diffusion coefficient D follows Arrhenius law:

$$D = D_o \times \exp\left(-\frac{U}{kT}\right),$$

where $D_o = 7.3 \times 10^{-6}$ m$^2$/s is constant and U = 0.43 eV is the activation energy of moisture diffusion [18]. For a plastic package of a thickness H, the time necessary for moisture to saturate the package can be calculated as $\tau = H^2/4D$. Assuming H = 2 mm, $\tau$ = 9.3 hours and 5.2 hours for 130 °C and 150 °C respectively, which is more than two orders of magnitude less than the time at which moisture uptake still continues, thus clearly indicating a non-Fickian behavior of moisture sorption.

Similar deviations from the Fickian behavior have been observed in many studies of MCs typically at high-temperature and high-humidity conditions (more than 85% RH) during long-time exposure to moisture environments [19, 20]. The effect was explained by water condensation in micro-pores of the molding compound, swelling of the polymer matrix, and by chemical degradation of epoxy resins and/or epoxy/filler interface [21, 22].

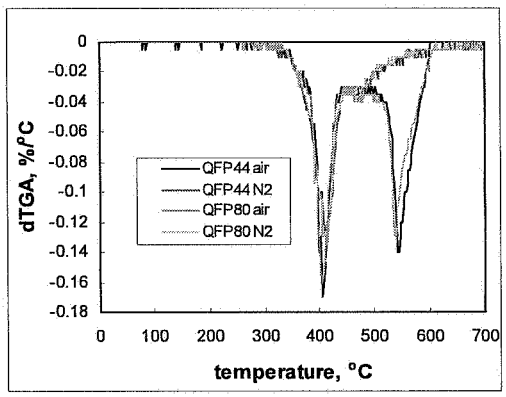
TMA measurements of moisture-induced deformations of the packages, ΔL, after HAST allowed for estimation of the coefficient of moisture expansion, $CME = (\Delta L/L)/(\Delta M/M)$, which sometimes is called as a hygroscopic swelling coefficient and is typically in the range from 0.3 to 0.6%/% [23]. Calculations based on ΔL measurements after HAST yielded CME in the range from 0.37 to 0.44, which is relatively

large and indicates significant swelling likely related to the observed non-Fickian behavior of the sorption process.

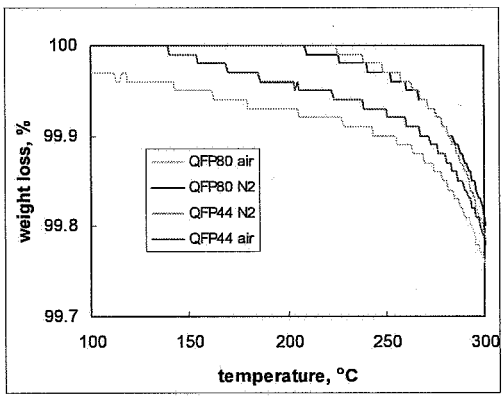
### 3.3. *Effect of oxygen*

Analysis of thermo-mechanical characteristics of plastic packages after 800 hours of HTS at 198 °C in air and vacuum chambers did not reveal any substantial differences. In both cases Tg was in the range from 155 °C to 160 °C, and CTE1 varied from 11 to 12 ppm/°C and CTE2 from 43 to 46 ppm/°C. These data confirm our previous results [8] where high-temperature storage of three different plastic packages in air and vacuum conditions caused similar variations of thermo-mechanical characteristics of molding compounds.

To evaluate the effect of oxygen on decomposition of MC, TGA measurements were carried out in two conditions: purging with dry nitrogen and with air. A comparison of the results of this testing is shown in Figure 7.




a) differential TGA




b) TGA

Figure 7. Thermo-gravimetrical analysis of molding compounds in air and dry nitrogen at a rate of 10 °C/min. (a) and 1 °C/min. (b).

Figure 7a clearly shows that decomposition of MC in air is a two-stage process. The first stage occurs at temperatures below ~410 °C and is similar for both N2-purged and air-purged samples. The second stage occurs at higher temperatures with a peak of DTGA at ~550 °C and is specific for air-purged samples only. A multi-stage decomposition of epoxy resins was also observed in [14], where the high-temperature stage of the process was also related to the presence of oxygen.

The data in Figure 7a, showing results of differential TGA at 10 °C/min., did not allow evaluating the effect of air at temperatures below 350 °C likely due to a poor resolution of the TGA technique at these conditions. However, when similar experiments were carried out at a rate of 1 °C/min. (see Figure 7b), the rate of decomposition in air was found to be greater than that in dry nitrogen. More significant difference in the rates of mass losses in air and vacuum conditions was obtained during isothermal aging as shown in Figure 8. A relatively large initial loss of mass, ~0.13%, which was similar in both cases, likely is due to absorbed water or residual low-molecular-weight species. However, after long-term storage the mass losses were on average ~30% less in vacuum compared to air storage: $dM/M_{vac}$ = 0.22% and $dM/M_{air}$ = 0.29%.

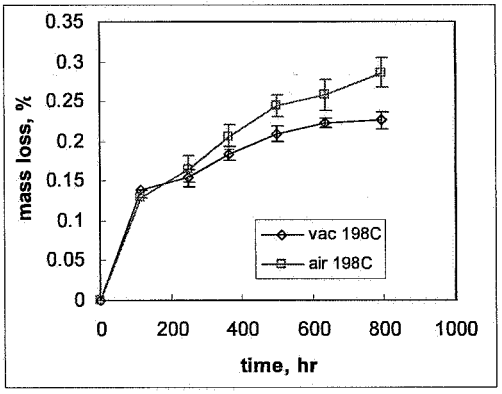



Figure 8. Decomposition of plastic packages in vacuum and air chambers at 198 °C.

## 4. Degradation of wire bonds

### 4.1. *Effect of temperature in air chambers*

Analysis of the $R_c$ measurements during HTS testing in air for these parts has been performed in our previous work [10] and showed that the times to wire bond failures (wire bonds with contact resistance exceeding 10 Ohms) can be described accurately enough with Weibull distributions. The mean life of WBs was calculated based on these distributions and is plotted versus the temperature in Figure 9. The results suggest that the mean time to WB failures is similar for both packages and closely follows Arrhenius law with activation energy of 1.52 eV.

### 4.2. *Effect of vacuum*

Weibull distributions of WB failures for two groups of parts stored at 198 °C in air and vacuum chambers are shown in Figure 10. These distributions were calculated based on testing of 270 WBs in air-stored parts and 305 WBs in vacuum-stored parts. The results show similar distribution for both groups, but

the mean time to failure was somewhat less for the air-stored microcircuits ($\tau_{50}$ = 255 hours) compared to the vacuum-stored parts ($\tau_{50}$ = 320 hours). The slope of the distributions, $\beta$, was virtually the same for both groups, $\beta$ = 5.4, and relatively large, suggesting wear-out mechanism of WB failures. The data indicate that oxygen accelerates WB failures in QFP-style packages on approximately 25% only, which is much less than the three to eight times observed earlier for SOIC-8 packages [8]. A possible reason for this is discussed in Section 5.

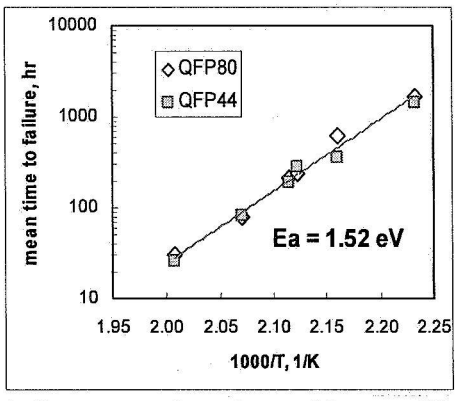



Figure 9. Temperature dependence of the mean life of wire bonds in ASICs encapsulated in QFP44 and QFP80 packages.

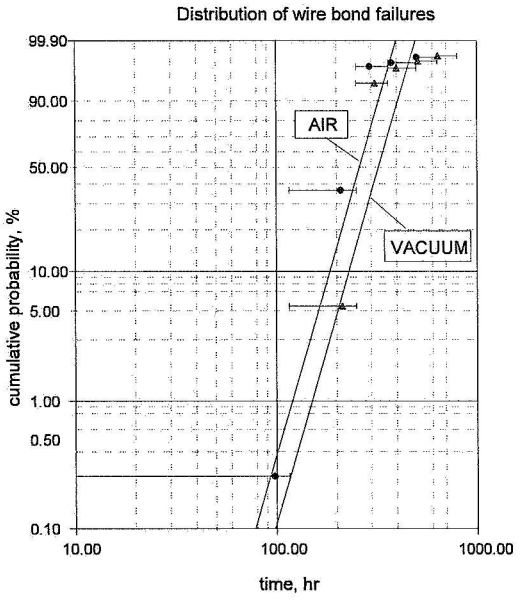



Figure 10. Effect of vacuum on wire bond failures.

Analysis of failed WBs in both groups of parts revealed excessive intermetallic growth in all cases (see Figure 11). Some bonds were found lifted after decapsulation, exposing porous intermetallics as shown in Figure 12. Wire pull testing of 40 bonds in each group showed that all bonds were easily lifted with a force of less than 1 g-f, indicating severe voiding and corrosion of intermetallics.

It is interesting to note that extensive intermetallics growth similar to that shown in Figure 11 was observed in a separate set of experiments where hermetically sealed microcircuits were subjected to long-term storage at high temperatures (175 °C to 200 °C). However, in this case no increase in $R_c$ and decrease in the pull force were observed even after 1,000 hours of HTS testing. This indicates that even significant intermetallic growth itself does not cause failures of WBs and that the decomposition of MCs plays a major role in WB failures in PEMs.

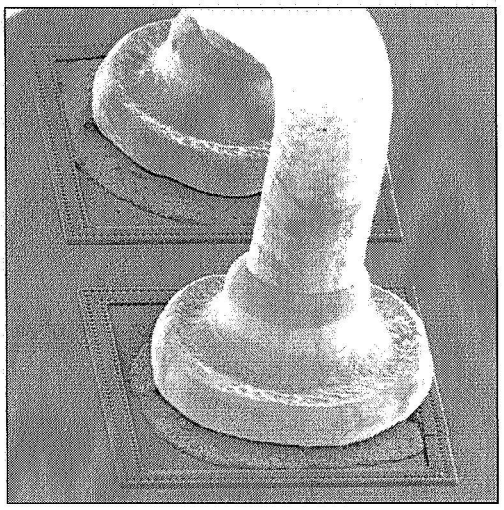
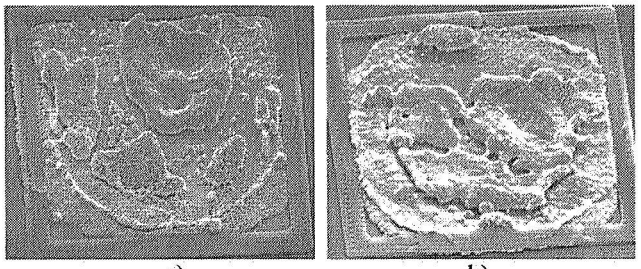


Figure 11. A typical view of degraded wire bonds with excessive intermetallics formed after 800 hours at 198 °C.



a) b)

Figure 12. Typical views of contact pads with lifted wire bonds in vacuum-stored (a) and air-stored (b) microcircuits. Note that intermetallic growth caused cracking and expanded through the passivation on the left side of contact pad in (a) and bottom side in (b).

*4.3. Effect of humidity*

Distributions of WB failures with time during HAST at 130 °C and 150 °C are shown in Figure 13. This figure shows also distributions calculated based on the experiments performed in the air chamber in the range of temperatures from 175 °C to 225 °C. For these calculations the temperature dependencies of the characteristic life, $\eta$, and slope, $\beta$, of Weibull distributions

were approximated with exponential and linear functions for $\eta$ and $\beta$ respectively to estimate parameters at 130 °C and 150 °C [10]: $\eta_{150}$ = 21,300 hours, $\eta_{130}$ = 181,300 hours, $\beta_{150} \approx \beta_{130}$ = 20.

The results show that the failures, which occur after ~1,500 hours for HAST-130 parts and after ~2,000 hours for HAST-150 parts, have rather large slopes of the distributions ($\beta$ ~5.1), indicating wear-out or intrinsic failures of WBs. However, failures that occurred earlier have much lower $\beta$ and most likely can be identified as infant mortality failures caused by some manufacturing defects, for example, contaminations on the contact pads or variations in bonding conditions.

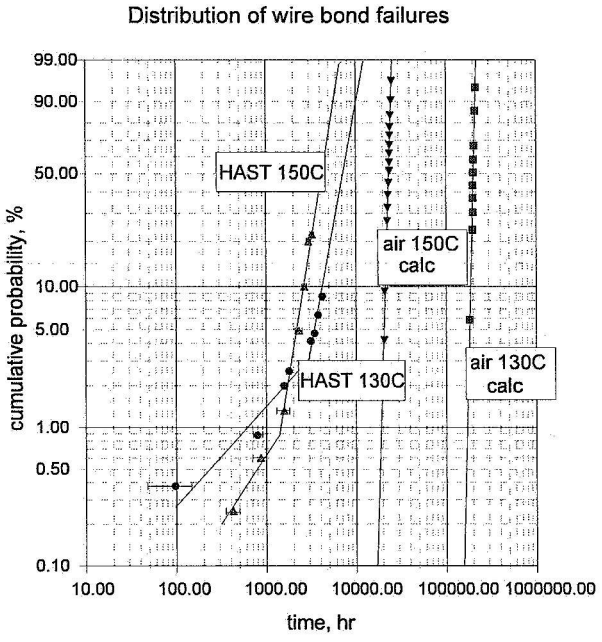



Figure 13. Weibull distributions of WB failures at 130 °C and 150 °C in air (calculations based on characteristic life and slope extrapolation to low temperatures) and in humidity chamber at 85% RH (experiment).

The mean life to failure calculated based on the data presented in Figure 13 is plotted against temperature in Arrhenius coordinates in Figure 14. The calculated data for dry air conditions are shown for comparison. The results indicate that activation energy of WB failures in humid environments is much lower than in dry air. Although the mean life data in humid environments are available only for two temperatures, the activation energy still can be estimated. Calculations yielded Ea ≈ 0.42 eV at 85% RH, which is far below 1.52 eV obtained for the dry air conditions.

An acceleration factor of moisture, AF, was calculated as a ratio of the mean life time in dry air environments and at 85% relative humidity. These calculations yielded AF = 4.6, 22, and 1,500 for temperatures of 150 °C, 130 °C, and 85 °C, respectively.

Internal examinations of the parts after HAST did not reveal any evidence of corrosion of aluminum metallization on contact pads and found relatively small (compared to results of HTS at 175 °C and 200 °C) growth of intermetallics outside the bond area (see Figure 15). However, some bonds were also lifted right after decapsulation, and all tested bonds had the wire-pull strength of less than 2 g-f. Only ~10% out of 40 WBs tested in each group had strength of more than 1 g-f. All lifted bonds revealed porous surfaces of intermetallic compounds and suggested severe corrosion at the gold-intermetallic interface, similar to what was observed after HTS testing.

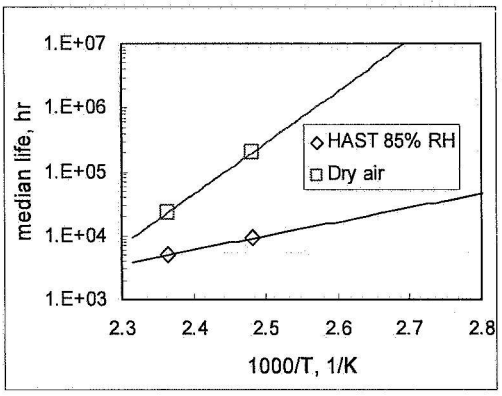
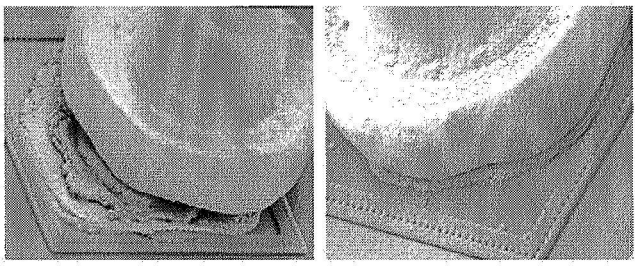



Figure 14. Temperature dependencies of mean life of wire bond failures in humid (85% RH) and dry air conditions.



a) b)

Figure 15. Typical SEM views of wire bonds after HAST at 150 °C for 3,400 hours (a) and after HAST at 130 °C for 4,400 hours (b).

## 5. Discussion

Several studies have shown that the rate of WB degradation in PEMs changes at a certain critical temperature, which is typically in the range of 175 °C to 225 °C [3, 8]. This effect was related to the changes in diffusion characteristics of molding compounds when the temperature exceeded the glass transition temperature of the encapsulant or to the formation of a gap between MC and the die at a critical temperature that exceeded Tg. It is assumed that in the presence of a gap oxygen reaches WBs; intensifies thermo-oxidative degradation

of MC in the bond vicinity; and increases generation of halogens, thus changing the rate of WB degradation at temperatures exceeding the critical one.

Contrary to what was observed in our previous study [8] for SOIC8 packages, in this study cross-sectioning of ASICs in QFP80/44 packages did not reveal discoloration in the molding compound along the internal areas of the assembly. This indicates that the mechanical integrity of the packages has not been compromised and that no gap between MC and assembly was formed at high temperatures during HTS testing. The absence of delaminations between the molding compound and die after HAST and/or HTS testing was also confirmed by the results of acoustic microscopy (C-SAM mode).

With limited access of oxygen, the rate of bromine generation is due mostly to thermal decomposition of the molding compound rather than to thermo-oxidative decomposition. This explains relatively high activation energy of wire bond failures, which did not change in the range from 175 °C to 225 °C, and a rather low difference in WB failures and in the rates of mass losses during air and vacuum testing. These results indicate also that WB degradation is related not only to the type of materials used for encapsulation, but also to the design of the package, which should be considered as an important factor affecting the rate of WB failures in PEMs.

An increase of WB time to failure in vacuum compared to air conditions might be argued to be a result of deficiency of oxygen at the bond area. This deficiency might retard oxidation of aluminum bromide, which is considered as a final stage of the intermetallic corrosion process [3, 24]:

$$2AlBr_3 + 3O \rightarrow Al_2O_3 + 6Br.$$

However, in [25] it has been shown that in the absence of halogen atoms oxygen does not accelerate high-temperature degradation of wire bonds, thus indicating that decomposition of MC is the major factor resulting in WB failures.

Pyrolysis of brominated epoxy resins starts earlier than for the non-brominated, results in HBr liberation, and has a relatively low activation energy of ~0.25 eV [26]. This allows the assumption that release of bromine molecules starts at the first stages of decomposition of MC. In this case, it is reasonable to presume that the higher the rate of decomposition of MC the higher concentration of corrosive molecules, and respectively the higher the rate of WB degradation. This means that factors accelerating decomposition of MCs accelerate also WB failures and explains the observed increase of WB failures in air compared to vacuum environments.

The rate of mass losses of epoxy MCs at high temperatures might be controlled by the in-diffusion of oxygen, by the rate of pyrolysis of macromolecules, or by the out-diffusion of the products of pyrolysis. Estimations have shown that oxygen has rather large diffusion coefficients in polymers at high temperatures, so its diffusion cannot be the limiting factor of the decomposition process [8].

If pyrolysis controls the rate of decomposition, the rate of mass losses would not depend on the thickness of samples. To evaluate the effect of thickness on decomposition of MCs, thin (~0.6 mm) and thick (~2 mm) samples cut from the packages were prepared and subjected to TGA. Results of this test are shown in Figure 16 and indicate that the rate of mass losses is significantly greater for thin samples. A simple diffusion model predicts that at the difference of thickness of samples used, mass losses in thin samples should be 11 to 13 times greater than in thick samples. Experimental data show that at 225 °C < T < 350 °C the ratio of mass losses varied from 20 to 5, which roughly agrees with the simplified estimations. This, together with the data on kinetics of mass losses during HTS testing (see Figure 3), suggests a diffusion-controlled mechanism of mass loses of MC when the rate of decomposition is limited by diffusion of low-molecular-weight fragments of the epoxy resin.

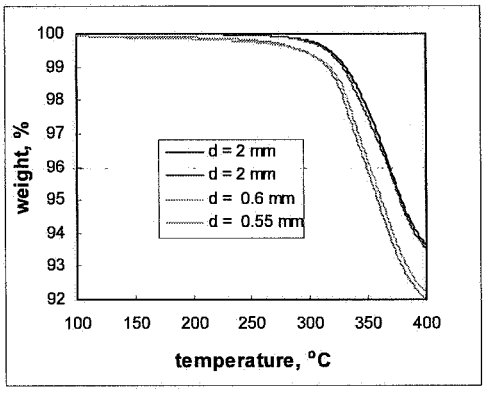



Figure 16. Effect of thickness, d, of samples of molding compound cut from the packages on the results of TGA (dark lines d ~ 2 mm; light lines d ~ 0.6 mm).

The estimated activation energy of decomposition of MC in air was 1.45 eV, which is close to activation energy of wire bond failures, 1.52 eV. This allows the assumption that the same mechanism, diffusion of corrosive low-molecular-weight molecules generated during high-temperature decomposition, controls both process and factors accelerating diffusion would also increase the rate of WB failures in PEMs.

Comparison of test results in humid environments (HAST) and in dry air conditions (HTS) shows that moisture accelerates failures and decreases substantially activation energy of WB degradation. This might be a result of enhanced diffusion of corrosive molecules caused by swelling and plasticization of epoxy resin in humid environments. A similar mechanism has been suggested by Khan et al. [27], who justified his hypothesis based on the fact that the activation energy for Br extraction in water (0.42 to 0.56 eV) was close to the activation energy of WB failures (~0.8 eV). Our data suggest that in dry conditions the activation energy of the diffusion and respectively WB failures is much larger (~1.52 eV) than in humid environments (~0.42 eV). It is interesting, that our data on $E_a$ of WB failures in humid environments are close to activation energy of Br

extraction obtained in [27]. This indicates that the rate of WB degradation in PEMs in humid environments as well as in dry conditions is controlled by the rate of diffusion of corrosive molecules.

The role of moisture in WB degradation in PEMs might not be limited to their effect on MCs. Moisture can also accelerate WB degradation working as an oxidant, and similar to the reaction with oxygen cause oxidation of aluminum bromide:

$$AlBr_3 + 3H_2O \rightarrow Al(OH)_3 + 3HBr.$$

It is also possible that moisture acts as a catalyst [1], degrading intermetallics even without corrosive effect of the products of MC decomposition. However, this contradicts to the results of [25], where addition of moisture (35 mbar) during baking of Au/Al bonds in air at 300 °C did not affect WB degradation. More data on WB degradation in humid environments are necessary and the role of moisture in the mechanism of corrosion of intermetallic compounds has yet to be investigated.

## 6. Conclusions

- Long-term high-temperature storage of OCN epoxy compound in air at temperatures from 175 to 225 °C resulted in increasing Tg from 130 °C initially to 160 to 165 °C and ~20% decreasing of CTE2, whereas CTE1 experienced only minor variations. Mass losses of MC increase with time according to a power law with an exponent close to 0.5, thus indicating a diffusion-controlled mechanism of thermal decomposition. The rate of decomposition increases with temperature according to Arrhenius law with activation energy of 1.42 eV.
- Storing in humid environments at 85% RH and temperatures of 130 °C and 150 °C for up to 4,400 hours resulted in increasing Tg on ~15 °C and decreasing CTE2 on ~15% (HAST at 150 °C only). Moisture uptake did not stabilize, but increased with time according to a logarithmic law, causing a significant swelling of MC.
- Thermo-mechanical characteristics of MC after vacuum and air storage at 198 °C for 800 hours were similar. However, results of TGA and isothermal gravimetric analysis showed that even at relatively low temperatures (< 300 °C) oxygen accelerates decomposition of MC by 30% to 50%.
- Moisture significantly decreases activation energy of WB failures from 1.52 eV for dry air condition to ~0.42 eV in 85% RH. Estimations showed that the acceleration factor of humidity testing at 85% RH increases with temperature from 4.6 at 150 °C to 1,500 at 85 °C.
- High-temperature storage testing at 198 °C in air and vacuum conditions resulted in similar WB failure distributions with the mean time to failure in vacuum being ~30% greater than in air, which correlates with the difference in the decomposition rates.
- Degradation of WBs in PEMs encapsulated with brominated OCN MC is controlled by the rate of decomposition of the MC and in particular by diffusion of low-molecular-weight halogenated products of the decomposition of epoxy resin. In dry air conditions the rates of MC decomposition and WB failures have relatively large and close activation energies (1.45 eV and 1.52 eV respectively). Moisture can significantly facilitate diffusion of the corrosive products and at high RH (85%) decreases activation energy of WB failures to ~0.42 eV.
- Oxygen increases the rate of pyrolysis of MC and WB failures; however, this effect depends significantly upon the package design. For a solid design in which no delaminations between the MC and die/lead-frame assembly at high temperatures occurs, the presence of oxygen only slightly (~30%) decreases the time to WB failures.

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