Influence of moisture on humidity sensitive material parameters of microelectronics relevant polymers

H. Walter[1,2], E. Dermitzaki[2], B. Wunderle[2,4], B. Michel[2,3]

[1]Angewandte Micro-Messtechnik GmbH, Volmerstr. 9B, D-12489 Berlin, Germany
[2]Micro Materials Center at Fraunhofer Institute for Reliability and Microintegration (IZM), Berlin, Gustav-Meyer-Allee 25, D-13355 Berlin, Germany
[3] Micro Materials Center at Fraunhofer Research Institution for Electronic Nano Systems (ENAS), Germany

Tel: +49 30 6392 3610; fax: +49 30 6392 3617; Email: hans.walter@izm.fraunhofer.de

ABSTRACT

It is well known that properties of polymer materials are highly dependent on temperature, time, curing conditions etc. The use of temperature and time dependent material parameters is state-of-the-art in microelectronic packaging. This paper presents various modified measurement methods for analysing the effect of moisture of thermo-mechanical properties of MEMS-relevant polymer systems. In the micro materials-lab, we developed an advanced measurement method - modified DMA multifrequency and hygroscopic swell analysis - for the determination of moisture dependent parameters for micro and nano scale samples. The time-moisture superposition principle has been introduced for some polymers where a humidity shift factor is used along the frequency axis at constant temperature. The relationship between the humidity shift factor and the equilibrium water content is analogically described by the WLF (Williams-Landel-Ferry)-type-equation on the time-temperature superposition. The main conclusions are that the water molecules seem to weaken the intermolecular forces for the polymers to prefer the state of entropy elasticity already to lower temperature, and the moisture shows influences on the visco elastic properties significantly. Furthermore, diffusion in highly filled epoxies does not follow the conventional Fickian diffusion of polymers. Modified non-Fickian absorption models provide an insight to the rate of initial (Fickian) moisture diffusion in the voids compared to the secondary non-Fickian diffusion, and show a very good agreement with experimental data. In combination with numerical methods, new strategies for life-time evaluation and fatigue of microelectronic packaging, MEMS and NEMS can be addressed.

Keywords: visco elastic, moisture polymers, small dimension, hygroscopic swelling paper layout

INTRODUCTION

In micro system technologies, a wide of range of materials with new property profiles are used to realize electronic components. This means that, alongside the enhancement of performance and multifunctionality, the demands on reliability for materials with new property profiles are used to realize electronic components. This means that, alongside the enhancement of performance and multifunctionality, the demands on reliability for higher operating temperatures proportionately increase. In materials compounds various thermo-mechanical materials properties exist, which under complex conditions influence the overall thermal-mechanical reliability (Fig.1). For the thermo-mechanical simulation and optimization of reliability aspects, particularly for the generation of lifetime models for products, a multitude of materials parameters are required. These materials data are determined under various environmental conditions and must be reproducible on real sample geometries.

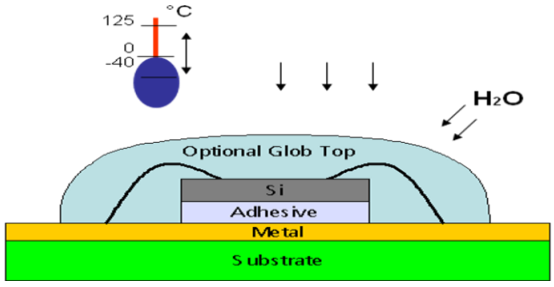

Fig. 1 Moisture and temperature contribute to failure of microelectronic packages

For electronic application many polymer systems such as thermoset and thermoplastic with different properties are widely used. Thermosetting polymers, e.g. epoxy resins, cause reliability problems when exposed to humid environments where phenomena such as moisture

absorption and diffusion take place. Consequently, moisture plays an important role in the reliability of microelectronic applications. Numerous assemblies with polymers fail, when exposed to elevated temperature and moisture or any combination of these parameters. All these alter the mechanical properties of the materials at the interfaces. This then may lead to adhesion loss, interface delamination and finally to crack propagation. Finite-Element-(FE) simulation tools have been used to calculate thermo-mechanical stresses and strains under thermal loading and moisture conditioning after material characterisation to compare the outcome to experimental results.

The modelling and prediction behaviour of these devices requires comprehensive knowledge of the thermo-mechanical properties of materials. For example the temperature in combination with environmental conditions leads to the alteration of the material properties of polymer systems. These properties could be visco- elastic relaxation over time under elevated temperature and moisture and/or moisture swelling due to (non-) Fickian moisture diffusion as a function of temperature and moisture concentration.

Moisture penetrating into polymers reduces the mechanical performance by its plasticization and degradation effect, as well as by decreasing the elastic modulus, fracture toughness and yield strength. Water molecules in polymers have been identified to have two distinct states: free- and unbound states of water that is present in voids or/and nanopores, and bound water molecules which form a hydrogen bond with the polar groups of the structure. Their diffusion in the structure is obtained via a hopping mechanism which is Brownian in nature. For the diffusion mechanism and the water concentration, the influence of the state of the polymers should be considered. Numerous diffusion models have been proposed for modelling of hygrothermal effects in different polymer systems. The rate of water diffusion has been assumed to be constant (Fickian diffusion). The diffusion at high temperature and humidity can show a dependency on the moisture exposure time. Diffusion in highly filled epoxies does not follow the conventional Fickian diffusion of polymers. Modified non-Fickian absorption models provide an insight to the rate of initial (Fickian) moisture diffusion in the voids compared to the secondary non-Fickian diffusion, and show a very good agreement with experimental data .
Another aspect for reliability is the swelling or volumetric expansion of polymer systems due to moisture absorption (hygroscopic swelling).
Characterization of the mechanical properties of wet polymer systems at elevated temperatures depends extremely on the duration of the experiments as well as sample geometry. The effects of moisture on the viscoelastic properties have been studied in the past. Absorbed water in polymers has an analogous effect on temperature (Tg) as well as on time dependent properties. The time-moisture superposition principle has been introduced for some thermoplastics where a humidity shift factor is used along the frequency axis as constant temperature was used. The relationship between the humidity shift factor and the equilibrium water content is analogically described by the WLF (Williams-Landel-Ferry)-type equation on the time-temperature superpostion [1-4].

EXPERIMENTAL METHODS

Most of used polymers show a visco-elastic behaviour. The significant change of the material properties is a function of time and temperature, and needs to be taken into consideration. Assuming thermo-rheological simple materials behaviour and invoking the principle of time-temperature superposition, the short-term and long-term visco-elastic behaviour in dependence on temperature can be theoretically described by the master curve and an appropriate temperature-time shift function. Linear visco elasticity, i.e. the relaxation modulus, does not depend on either stress or strain levels. If the material behaves linearly, the total stress response due to different load steps is the linear superposition of the response to each of the load steps. Mainly two experimental techniques are applied for that characterization: stress relaxation/creep tests with long testing times and dynamic mechanical experiments with sinusoidal, harmonic excitation, allowing significant shortening of testing. For visco-elastic characterization of polymers using DMA multifrequency analysis, the frequency dependence of the modulus can be determined. The master curve is constructed by shifting the curves on the logarithmic frequency scale by the shift factor $\log a_F$. The respective values for the shift function could be fitted to the so-called WLF-function by two coefficients C_1,C_2:

$$\log a_F = -\frac{C_1(T - T_{ref})}{C_2 + (T - T_{ref})} \quad (1)$$

Thereby, the thermo visco-elastic characterization is completed, when the obtained parameters can be used as for example in equation 2, 3:

For storage modulus

$$E'(t) = E_\infty + \sum_{i=1}^{N} E_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \quad (2)$$

Or for loss modulus

$$E''(t) = \sum_{i=1}^{N} E_i \frac{\omega\ \tau_i}{1 + \omega^2 \tau_i^2} \quad (3)$$

One way of interrelation of these data is to fit the measured curves E' (ω) and E'' (ω) and to use the approximation parameters (prony series) to describe the relaxation behaviour. This method has the advantage that the full dynamic modulus curve, including rubbery and glassy level, has to be transformed. The relation between time and frequency response of visco-elastic materials as appropriate

experimental frequency range is estimated. The experimental dynamic moduli data then often have to be converted from frequency into time domain and made comparable to the relaxation data (Fig. 2).

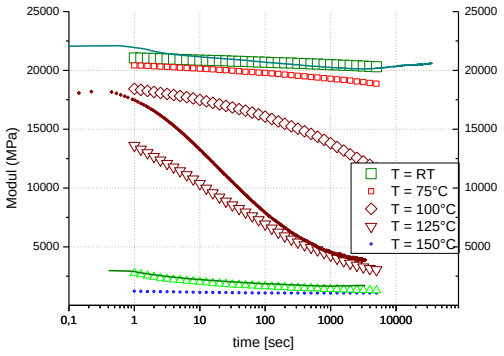

Fig. 2 Transformation from storage modulus (DMA) to relaxation modulus compared

EFFECTS OF MOISTURE

In the micro-materials-lab a measurement method for the determination of moisture dependent parameters for micro and nano scale samples was developed. The dependence of modulus and glass transition temperature Tg was measured by means of dynamic-mechanical analysis (DMA) (Eplexor 100N, Gabo Qualimeter with humidity chamber), see Fig. 4. Various experiments of dry and saturated samples were tested under dry and humid conditions. With this same equipment, it is also possible to measure standard relaxation properties under constant strain by means of mini-tensile testing.

The diffusion of moisture into the polymer was determined using an external environmental chamber with a constant temperature of 85°C and humidity 85 RH. The moisture absorption is a function of time. In the course of these measurements also the saturation concentration and the diffusion coefficient were determined by using a gravimetric method on thin samples. This is depicted in Fig. 3. As can be seen, the polymer shows perfect Fickian behaviour. After the initial fast diffusion, the uptake continues to increase slowly.

Fig. 3 DMA test set up with humidity chamber (Eplexor 100N, Gabo-Qualimeter)

The change of the mechanical properties of the modified polymer was studied. The result of the measurements can be seen in Fig. 4. It is shown that moisture also has a significant influence here on the multifrequency-dependent properties. Both the frequency-dependent storage modulus and the glass transition temperature of the saturated samples show lower values in comparison to the dry samples.

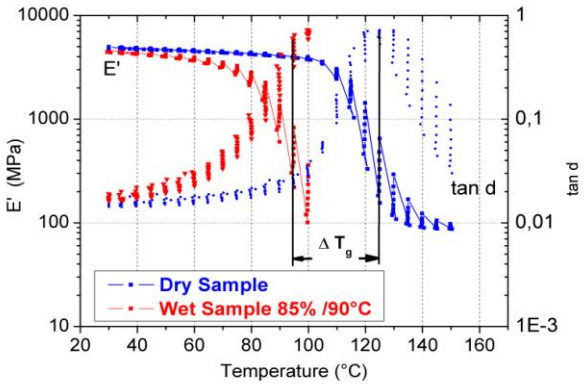

Fig. 4 Frequency dependent storage modulus versus temperature of dry and wet samples

The reason for these properties is that water molecules interfere increasingly with the intermolecular forces between the polymer chains. The water is assumed to act as a plasticizing agent which reduces the modulus and the glass transition temperature of these samples. Furthermore, it was assumed that the desorption rate was much lower during the temperature run from 25°C to 100°C, where the humidity conditions (85 RH) were used.

For a life-time model, the relaxation behaviour as a function of temperature over time is needed. Assuming thermo-rheological, simple materials behaviour and invoking the principle of time-temperature superposition, the short-term and long-term visco-elastic behaviour in dependence on temperature can be theoretically described by the master curve and an appropriate temperature-time shift function.

Here again, for visco-elastic characterization of polymers, the DMA was used to provide the frequency-dependent storage modulus, then transferred to the time domain and fitted to a master curve via the well-known WLF-function.

Fig. 5 shows shifted modulus and corresponding master curves of dry and saturated samples. The profile of these curves has different levels of moduli as well as different slopes.

The reference temperature T_{ref} for all curves was chosen to be 30°C. The data at each temperature were shifted to obtain the master curve by employing time-temperature superposition. This means that the modulus at the T_{ref} any time t can be defined relative to the modulus at other temperatures, where $\log a_f$ is a shift function. In Fig. 6 the horizontal shift factors $\log a_F$ for the corresponding master curves are given.

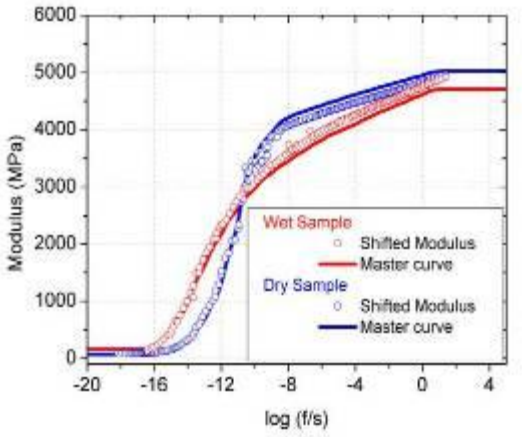

Fig. 5 Shifted storage modulus and corresponding master curve

The temperature dependence shift factor $\log a_F$ is represented by equation 1 (WLF-type).

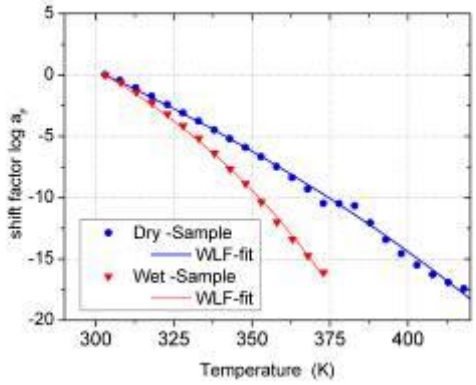

Fig. 6 Horizontal shift factor of dry and saturated samples

The moisture effect on the shift function is not negligible. The shift function should be defined as a function of temperature and moisture concentration. The relation-ship between the temperature dependent shift factor and moisture concentration can be written as:

$$\log a_F(T, MC) = -\frac{C_1[T - T_{ref}(MC)]}{C_2 + [T - T_{\mathrm{Re}f}(MC)]} \qquad (4)$$

By these experiments, the authors found empirical constants as given in Table 1. However, more experiments and investigations of internal moisture-dependent parameters are needed to make a conclusive statement.

SUMMARY

The influence of humidity on the materials behaviour shows that the humidity diffusion does not only effect a shift in the glass-transition temperature and a reduction in the modulus, but that it also influences the visco-elastic properties significantly. Multi-frequency dynamic analyses are suitable measuring techniques for the determination of temperature-dependent visco-elastic properties. Master curves for the moduli may be constructed by horizontal shifting along the log frequency axis. The used Prony series allowed a convenient master curve for comparing the two approaches to visco-elastic characterization. Furthermore, it was shown that moisture also has a significant influence here on the relaxation behaviour, which increases not only with temperature but also with moisture concentration.

Table 1: Moisture dependent parameters

Mat.	Condit	Dens. [g/cm³)	Tg [K]	Moist. Uptake [%-wt]	WLF C1	C2
Epoxy 2/1- 2	Dry	1,16	373		129	1912
	85°C/ 85% rh		349	4,78	25	121
Epoxy 2/1- 4	Dry	1,14	373		32	174
	85°C/ 85%rh		337	4,86	13	71
Epoxy 2/1- 6	Dry	1,12	363		34	157
	85°C/ 85%rh		333	3,97	12	66

Acknowledgement
Funding of the project NanoInterface by the European Commission (7th FWP) (Project No.: 214371) was gratefully appreciated.

REFERENCES

[1] E. Dermitzaki et al.:"Structure Property Correlation of epoxy resins under the influence of moisture and temperature; and comparison of Diffusion coefficient with MD-simulations**"**. *ESTC 2008, Greenwich, UK* : Proc. pp 897-902

[2] H.Shirangi et al.: "Characterization of Dual-Stage Moisture Diffusion, Residual Moisture Content and Hygroscopic Swelling of Epoxy Molding Compound"; *IEEE proc.9th, EuroSime 2008*, pp. 455-462

[3] B.Wunderle et al.: "Lifetime Model for Flip-Chip on Flex Using Anisotropic Conductive Adhesive under Moisture and Temperature Loading" *Proc. ITherm2008*, Orlando, Florida, USA, June 2008, pp 799-808

[4] H. Walter et al.:"Influence of moisture on the time and temperature dependent properties of polymer systems" *IEEE proc10th, EuroSime 2009*, pp. 481-485