Moisture Induced Swelling in Epoxy Moulding Compounds

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Abstract

Microelectronic components are introduced to an increasing number of applications as part of a controlling or monitoring device, as sensors or as means to tracking. Depending on the application, extreme loading profiles may need to be endured such as high temperatures, random vibrations or humid and even wet environments. Absorbed moisture has a plasticizing effect on the physical properties of polymers. Furthermore, moisture leads to corrosion of metallic parts of the devices and therefore molding compounds are used to protect sensible electronics.

However, the epoxy matrix of the molding compounds tends to absorb water molecules and subsequently exhibits a swelling behavior which is unique to the chemistry of the epoxy. Since most other materials involved do not swell when exposed to moisture, a stress between the materials is induced which is similar in origin (dimensional change in materials) and magnitude as the thermal mismatch induced stresses or chemical shrinkage. It is important to know both absorption and desorption properties of used epoxy systems. This paper represented results of moisture diffusion in different high filled epoxy molding compounds using two parallels analysis methods – Thermo Gravimetric Analyzer (TGA) and Thermal Mechanical Analyzer (TMA) at different loading conditions. TGA as a commonly measurement method for analysis of in-situ weight changing due to moisture absorption and desorption. Thermal Mechanical Analyzer was coupled with a conventional humidity generator to be able to in-situ measure the swelling strain of the sample. The enhanced TMA-technique can be used for measuring the dimensional changes of specimens as a function of variable temperature and humidity. The results can be used for integrated finite element analysis methodology, which couples the transient moisture diffusion and the hygroscopic swelling with temperature range.

Keywords: material characterization, epoxy molding compound, moisture, sorption, swelling (FE simulation)

Introduction

Absorption of moisture into molding compounds induces hygroscopic stresses within encapsulated packages due to hygroscopic swelling. Hygroscopic swelling is the expansion of a material due to the absorption of moisture. Similar to the thermal mismatch in a package, a hygroscopic swelling mismatch develops between materials that are prone to moisture absorption like polymers and those that are not (e.g. semiconductors and metals).

Furthermore, moisture poses a danger to the reliable performance of microelectronic devices due to corrosion when the diffusing water reaches the encapsulated electronics. In the literature different types of failure are observed, when electronic components are exposed to humidity conditions: Popcorn failure, swelling induced damage, electrochemical migration, degradation of mechanical properties [1]. In addition, the interfacial adhesion strength is strongly affected by the presence of moisture.

Consequently, moisture plays an important role in the reliability of microelectronic applications.

However, the swelling mechanism at a micro/nano-scale for highly filled polymers isn't fully understood. It was observed, that the ratio of hygroscopic volume expansion to volume of absorbed water is less then 1. This indicates, that not all of the absorbed water molecules contribute to swelling but instead is present inside voids of free volume of the polymer [2]–[4]. Free volume is the volume due to voids caused by molecular irregularity.

In order to characterize this influence for a simulation assisted reliability assessment the sorption and swelling characteristics, that is, kinetics and equilibrium level, need to be measured. While for sorption the weight change is commonly measured in a sorption balance, devices to measure in situ length changes at high resolution are not readily available. Instead, the contraction behavior of a desorbing sample is often observed entailing the following disadvantages in accuracy:

- Loss of moisture content between moisture chamber and start of measurement
- Often disagreement of the temperature conditions
- Usually observed disagreement of desorption and absorption properties

The objective of this study is to present an enhanced measurement technique for the analysis of the moisture induced volumetric expansion of polymers. This physical phenomenon is often addressed as hygroscopic swelling. The amount of hygroscopic strain found from the dimensional change is normally assumed to be linearly proportional to the moisture concentration. In the first one of investigation of swelling properties, the dimensional change of the fully saturated sample during desorption was measured by thermo-mechanical analysis (TMA). In this approach it is assumed that the behaviour of polymer materials is the same for swelling and shrinkage during absorption and desorption, respectively. In some literature data have been presented that show a difference between absorption and desorption properties. This can be caused by process induced residual

stresses or excess free volume within the epoxy matrix. That means, swelling of the polymer upon moisture uptake is not fully recovered (contracted) upon moisture desorption. Consequently, hygroscopic strain may not directly correlate to moisture mass and therefore a method based on the absorption process should be used for estimation of hygroscopic swelling properties.

If the moisture uptake and swelling curve show a Fickian diffusion characteristic, the model of Crank [5] can be used for analysis of the observed moisture uptake:

$$\Delta X(t) = \Delta X_f * f(t, D) \quad (1)$$

with

$$f(t,D) = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(-D(2n+1)^2 \pi^2 t / d^2\right) \quad (2)$$

where ΔX(t) is the time dependent change of mass or length. This equation contains D as a diffusion coefficient and the fraction of mass uptake $\Delta X_f = C_{sat}$ or length change $\Delta X_f = Q_{sat}$ as fit- parameters. It must be noted that this fit-function is only valid for samples in plane sheet geometry of thickness *d*.

Experimental measurements

Materials

For characterization of absorption and desorption behaviour 3 different highly filled epoxy resins were used. Samples were molded following the curing condition recommended by the manufacturer. The epoxy sheets used for this experiments were cut into samples with dimension of: 5 x 5 x 0,5 mm³. For pre conditioning the thin epoxy-samples are oven-dried for 12 h @ 105°C to ensure complete desorption of residual water. Thermomechanical material data as measured on the prepared samples are compiled in Table 1 along with the shift of the glass transition temperature (ΔT_g) induced by moisture saturation.

Table 1: Thermomechanical material data. T_g-shift refers to moisture-saturated samples.

Material	**E** [GPa]	**T_g** [°C]	**ΔT_g** [°C]	**CTE <T_g** [ppm/K]	**CTE >T_g** [ppm/K]
Henkel GR9810 1P	21	152	-8	16	41
Shin Etsu KMC 2280	13	186	-31	14	54
Sumitomo 6600 CS	19	138	-12	11	45

Swelling Analysis

For analysis of the swelling behaviour an enhanced thermo-mechanical Analyzer TMA/STDA840 (Mettler Toledo) shown in Figure 1 was coupled with a humidity generator VTI RH 200 (VTI). The resolution of the TMA length measurements is 10 nm. The length of samples could be up to 10 mm. A moisturized nitrogen (N_2) flow is led in through the top of the temperature chamber. The relative humidity inside the temperature chamber is controlled by the mass flow controllers.

The humidity generator provides a well defined moisturized nitrogen flow (10% to 60% rh) for use with analytical instruments such TMA and allows to select various environmental conditions within a temperature range of RT to 60°C. More technical details are described extensive in [6].

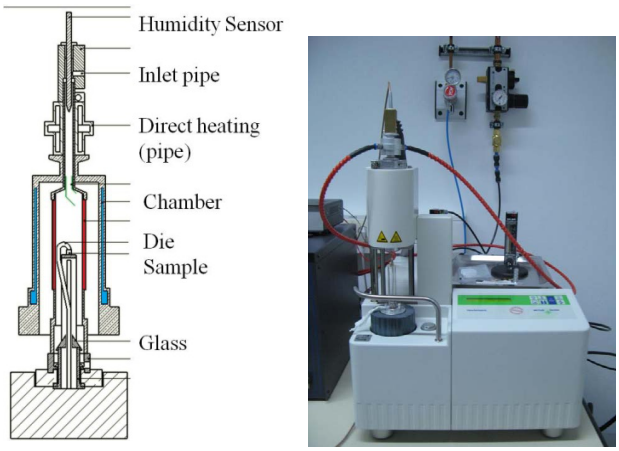

Figure 1: The TMA STDA840 Analyser is coupled with the humidity generator RH 200 (not shown). The schematics of the measurement chamber are depicted on the left side.

The samples are placed between a glass holder and a probe in expansion mode. Assuming isotropic swelling behaviour, the measured length change Δl can be to converted to volume change using

$$\frac{\Delta V}{V_0} = \left(\frac{1+\Delta l}{l_0}\right)^3 - 1 \quad (3)$$

where l_0 and V_0 denote the initial length and volume of the sample.

The test procedure for measuring the moisture uptake is as follows:

- Samples are preconditioned in an external temperature chamber at 105°C @ 12 h.
- Fully dried sample is placed in TMA-device.
- Measurement chamber with sample is heated to constant temperature; when TMA signal is stable, the humidity condition is set.
- Swelling is observed at constant temperature and humidity.

Desorption measurements can be programmed as well. Thermal gravimetric analysis (TGA) method is described in detail in [7].

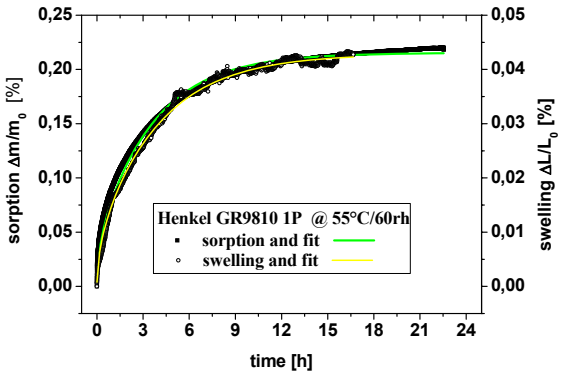

Figure 2: Sorption and swelling curves and corresponding fit of equation 1 for the Henkel material.

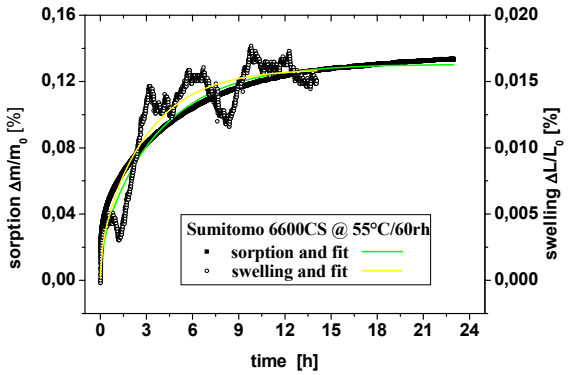

Figure 3: Sorption and swelling curves for the Sumitomo material.

Results and Discussion

Moisture absorption and swelling.

The swelling (TMA_QA) and sorption properties (TGA_SA) of three epoxy moulding compounds were measured and compared for conditions 55°C and 60%r.h. It was expected, that the moisture induced weight gain of the sample is rather low, because absorbed moisture is captured in the epoxy matrix and cannot be absorbed by the filler particles. For Henkel material, the mass changes and length changes due to moisture absorption show the same kinetics, as can be seen in the plot of mass and length change against time (Figure 2). It can be observed that a state of saturation in moisture absorption is reached within a period of 24h of exposure time to the humidity condition, when the moisture absorption curve reaches a plateau value. Furthermore, as can also be seen from Figure 2, the simple Fickian model (equation 1) can describe the moisture uptake correctly and shows a good agreement in kinetics for both, sorption and swelling behaviour.

In Figure 3 the same trend for Sumitomo materials was observed, showing a good agreement in the kinetics of sorption and swelling properties. Again, in a first approximation, the Fickian kinetic model can be used for the description of moisture uptake and moisture induced swelling behaviour. The reason for the scatter in the curve of length change is the limit of resolution of the TMA-analyser. The diffusion rate of water in this EMC is slightly faster than in the Henkel material.

Table 2: Fickian absorption parameters TGA-Sorption and TMA- Swelling.

Material	**TGA- SA**		**TMA-QA**	
55°C / 60%r.h.	**D^S [µm²/s]**	**C_{SAT} [%]**	**D^Q [µm²/s]**	**Q_{SAT} [%]**
Henkel GR9810 1P	**1,9**	**0,21**	**1,8**	**0,043**
Shin Etsu KMC 2280	**3,8**	**0,46**	**2,3**	**0,069**
Sumitomo 6600 CS	**1,8**	**0,13**	**2,6**	**0,016**

Furthermore, saturation level of swelling Q_{sat} exhibits the lowest value of all three investigated materials. Diffusion coefficients and saturation levels are shown in Table 2.The swelling behaviour of the Shin Etsu material shows a deviation from the Fickian model. It was observed after an exposure time of 12 h that the sorption process was finished, showing Fickian behaviour, but swelling continues as shown in on Figure 4. In comparison to the other molding compound materials, the moisture absorption was faster and reached higher saturation levels Q_{sat} and C_{sat}.

This may be attributed to the nature of the polymer matrix (e.g. polar groups) and/or different amount of free volume. Furthermore, saturated concentration values can be depend highly on the filler particles. Small particles can have a large amount of reactively surfaces.

Figure 5 shows the saturation levels of Q_{sat} (swelling) and C_{sat} (sorption) for all materials in comparison. The results illustrate that the Shin Etsu material absorbs moisture more quickly and at relatively high level of moisture uptake and subsequent swelling. The Fickian diffusion parameters (D^S and C_{sat}; D^Q and Q_{sat}) are compiled in Table 2.

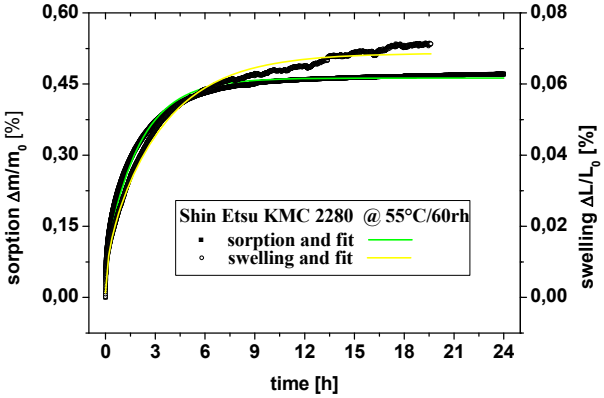

Figure 4: Sorption and swelling curves and corresponding fit of equation 1 for the Shin Etsu material.

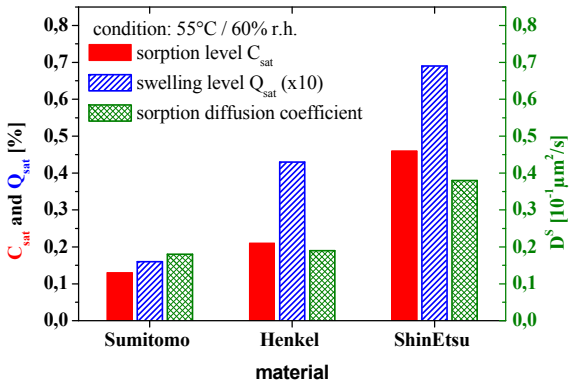

Figure 5: Sorption and swelling at 55°C and 60%r.h. for all materials as obtained from fit-curves.

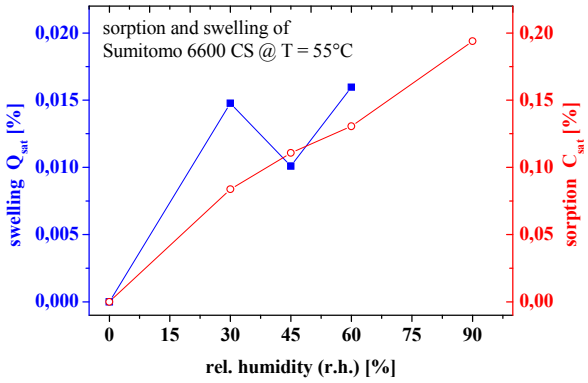

Figure 7: Saturated sorption and swelling for the Sumitomo material at different humidity levels.

Swelling and contraction.

Moisture desorption in epoxy molding compounds can occur during the reflow process, where temperatures beyond 100°C are reached. This often causes reliability problems and is therefore as much of interest as swelling due to moisture uptake is. Accordingly, mass and length decrease due to desorption at 60 °C are measured with the TMA and TGA equipment respectively. Desorption of penetrated moisture leads to a contraction (de-swelling) of the sample. To investigate de-swelling, a moisture absorption-desorption cycle was carried out for the Henkel material. The swelling-contraction cycle of the sample as a function of exposure time at 60°C is shown in Figure 6. For better time resolution, the contraction curve was shifted to start at t=0. Assuming Fickian properties, the contraction can be estimated from the experimental data by use of equation 1. A smaller value of desorption coefficient can be observed ($D^Q = 0.78$ µm^2/s). The slower de-swelling could be due to the reduction of the plasticising effect as the concentration level decreases, in contrast to the swelling process. A significant gap between initial length and desorbed sample is not observed.

Extrapolation of Swelling.

The TMA analyser in combination with the humidity generator as described above and shown in Figure 1 is limited to moisture levels of 60%r.h. for temperatures up to 60°C. However, common test conditions call for temperature/humidity levels of up to 85°C/85%r.h. or non-standard combinations. In such cases, results obtained from lower levels can be extrapolated to give an approximation for the desired conditions. This is shown in Figure 7 and Figure 8 for the Sumitomo material. Figure 7 shows the saturated mass uptake and length change for different humidity levels. From the sorption data which was possible to obtain for humidity levels up to 90%r.h., a linear relationship of the saturation level with increasing humidity level can be assumed. In a first approximation, this can be assumed for the swelling behaviour as well. The scatter in the data can be attributed to the low level of swelling near the resolution limit of the analyser. Figure 8 shows the extrapolation of the swelling data to a humidity level of 90%r.h. in a plot of saturated swelling against mass uptake.

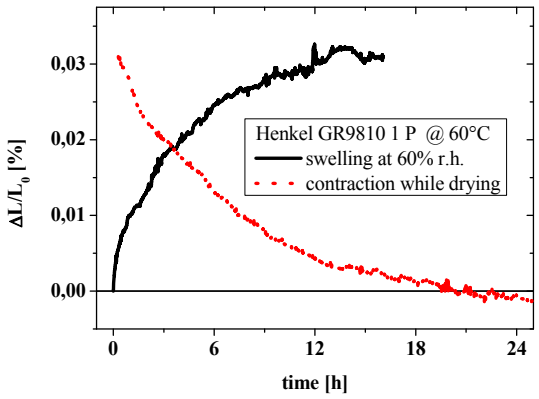

Figure 6: Swelling and de-swelling (contraction) curves for the Henkel material.

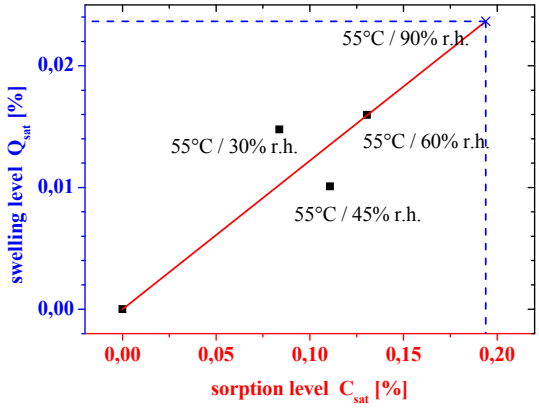

Figure 8: Extrapolation of swelling data to 55°C / 90%r.h. for the Henkel material using low humidity and sorption data.

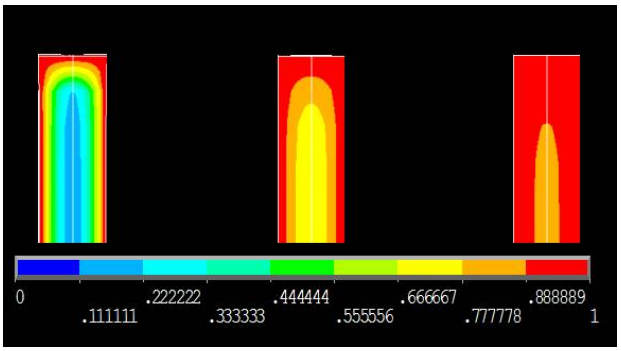

Figure 9: Normalized concentration profile in a cross sectioned sample. Diffusion was modeled using the diffusion feature of *solid226*-elements.

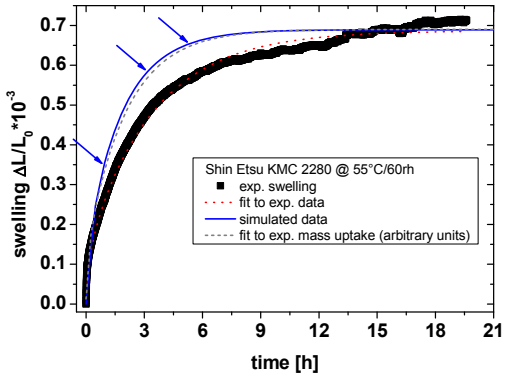

Figure 10: Simulation (blue, solid line) of swelling in comparison to measurement. Arrwos indicate the time of snapshots shown in Figure 9.

Outlook: Simulation of Swelling.

The obtained data for the kinetics of sorption, saturated concentration levels and swelling behaviour can now be used in finite element (FE-) simulations to obtain stresses within packages induced by the absorption of moisture. This is shown in Figure 9. For the FE-simulation, a simple $1/8^{th}$ model was set up in ANSYS using the material data of the Shin Etsu material (Table 1 and Table 2). In the past, often the temperature/diffusion analogy was used to model moisture diffusion in an FE-simulation [8]. Here, a relatively new feature of the ANSYS software (element type *solid226*) was used to incorporate the diffusion behaviour of moisture. This offers the advantage of simulating temperature changes and moisture uptake at the same time, coupling structural, thermal and diffusion behaviour.

The moisture uptake profile in a cross section at three time steps (1h, 3h and 5h, indicated by blue arrows in Figure 10) is shown in Figure 9. The normalized concentration $C(t,x)/C_{sat}$ is set to 1 at all open surfaces of the model as boundary condition. The diffusion of moisture and the displacement of the top nodes of the sample is observed under the same conditions as in the experiment.

The task definition in this case is very simple and could have been solved analytically. We present results here to show that this functionality opens new possibilities regarding complex geometries and coupling with thermal changes. Figure 10 shows the resulting displacement of the top node as a function of time along with the experimental data and fit shown in Figure 4. It can be seen that the simulation is in well agreement with the experiment regarding the saturation swelling level (input parameter Q_{sat}) and with sorption kinetics (input parameter D^S of the sorption measurement, dashed line). The small deviation of the simulation from experimental values at intermediate times results from the deviation of experimental sorption and swelling already shown in Figure 4. It can be debated if, for practical reasons, the kinetics of swelling (D^Q) should be used in the FE simulation since often not the moisture content but the induced swelling stresses are of interest.

Summary.

In this work the results of sorption and swelling measurements for three different molding compounds are presented. It could be shown that Fickian diffusion behaviour is observed for the mass uptake in all molding compounds, but the swelling behaviour deviated slightly in one case. A difference in uptake level (C_{sat}), kinetics (D^S) and swelling (Q_{sat}) was observed as Sumitomo < Henkel < Shin Etsu. An extrapolation of swelling behaviour was exercised for one material to describe humidity levels that are not accessible to the experimental equipment. Finally a simple simulation shows the feature of moisture diffusion and swelling that is now available for coupling thermal, structural and diffusion characteristics of materials used in microelectronic components.

It must be noted that in this study only the moisture uptake behavior of the three (commercially available) epoxy molding compounds was analyzed and compared. The results do not give information about the qualification of the material for a specific application; for that, other material properties need to be taken into account as well.

Acknowledgments

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References

[1] J. De Vreugd, „The effect of aging on molding compound properties - aging characterization of molding compounds and its modeling“, TU Eindhoven, Eindhoven, 2011.

[2] H. Ardebili, E. H. Wong, und M. Pecht, „Hygroscopic swelling and sorption characteristics of epoxy molding compounds used in electronic packaging“, *Components and Packaging Technologies, IEEE Transactions on*, Bd. 26, Nr. 1, S. 206 – 214, März 2003.

[3] M. H. Shirangi, X. J. Fan, und B. Michel, „Mechanism of moisture diffusion, hygroscopic swelling and adhesion degradation in epoxy molding compounds.“, *Proc. 41st*

International Symposium on Microelectronics (IMAPS), S. 917–923, 2008.

[4] O. Hölck, *Gas Sorption and Swelling in Glassy Polymers - Combining Experiment, Phenomenological Models and Detailed Atomistic Molecular Modeling*. Berlin: Federal Institute for Materials Research and Testing, 2008.

[5] J. Crank, *The Mathematics of Diffusion*, 2. Aufl. New York: Oxford Science Publications, 1975.

[6] H. Walter, J. Bauer, T. Braun, O. Hölck, B. Wunderle, und O. Wittler, „In-situ - characterization of moisture induced swelling behaviour of microelectronic relevant polymers“, in *2012 13th International Conference on Thermal, Mechanical and Multi-Physics Simulation and Experiments in Microelectronics and Microsystems (EuroSimE)*, 2012, S. 1/6 –6/6.

[7] T. Braun, J. Bauer, L. Georgi, K.-F. Becker, M. Koch, R. Aschenbrenner, und K.-D. Lang, „Enhancement of barrier properties of encapsulants for harsh environment applications“, in *Electronic Components and Technology Conference (ECTC), 2012 IEEE 62nd*, 2012, S. 1418 – 1425.

[8] F. Schindler-Saefkow, O. Wittler, T. Schreier-Alt, H. Kittel, und B. Michel, „Package Induced Stress Simulation and Experimental Verification“, *2008 2nd European Conference Exhibition on Integration Issues of Miniaturized Systems - MOMS, MOEMS, ICS and Electronic Components (SSI)*, S. 1 –4, Apr. 2008.