Georg Bogner[1], Alexandra Debray[1], Dr. Klaus Höhn[2]
[1]OSRAM Opto Semiconductor GmbH, Germany, [2]Siemens AG Corporate Technology ZT MF3, Germany

High Performance Epoxy Casting Resins for SMD-LED Packaging

Abstract

In order to come up with high volume SMD-LED production encompassing 1.9 billion devices for current fiscal year we did basic exploratory work to establish structure-processing-property relations for robust epoxy casting resin packages with identical ppm level of one.

Bisphenol A-based epoxy casting resins (DGEBA) with acidic ester modified Hexahydrophthalic anhydride (HHPA) hardeners using strictly controlled high-grade raw materials were formulated and thermally transferred to highly transparent polyester networks. For 1 mm thick samples transparency in the 400 to 800 nm region is above 90 %. Thermal aging tests for 6 weeks at 120 °C reveal only slight discoloration with a color distance of 2. To avoid significant light losses within the LED operating life of 100,000 hrs stress on mechanically sensitive light-emitting chips was reduced by matching glass transition temperature Tg and E-modulus to 115 °C and 2,800 MPa, respectively. Total chloride content below 1,000 ppm imply low corrosion potential.

Further, resin composition, epoxy-hardener mixing ratio as well as curing profile were adapted to materialize fast curing for demand quantities while introducing effective low stress moieties in the final structure. Low internal stress, superior thermal shock and crack resistance were derived from supreme fracture toughness: K_{IC} and G_{IC} values were 1.350 $MPam^{1/2}$ and 560 J/m^2. With favourable water absorption behaviour LED-packages withstand all soldering processes including TTW(through the wave) soldering. Thus, SMD-LEDs fulfill electronic industry standard JEDEC LEVEL 2.

Keywords: *SMD-Light-Emitting Diodes, Packaging, Epoxy Casting Resins, Moisture Uptake, Fracture Toughness*

In *Light-Emitting Diodes: Research, Manufacturing, and Applications IV*, H. Walter Yao, Ian T. Ferguson,
E. Fred Schubert, Editors, Proceedings of SPIE Vol. 3938 (2000) • 0277-786X/00/$15.00

1. Introduction

In the field of (opto-)electronics there is a general trend towards expanding functionality and performance including higher reliability in more adverse environments with increasing service temperatures and decreasing package size for demanding applications in automotive industries. Due to cost, processing, performance and reliability considerations, polymeric materials are of growing significance at a rapid pace for (opto-)electronic packaging.

Epoxy resin thermosets are currently the material of choice for optoelectronic packaging, because of their chemical resistance, mechanical and electrical strength associated with excellent thermal stability. Liquid state epoxy casting resins insure optical clarity and product uniformity. In addition to their unique processing and fabrication capabilities, epoxy resins are polymeric materials by design to suit desired applications by molecular engineering.

Besides high light transmission in the visible region, excellent colour stability upon long-term temperature exposure up to 120°C the whole package has to reach 100,000 hrs operation life time for light-emitting diodes (LED). Attachment of surface mount (SMD-)LEDs to a circuit board involves thermal soldering stress that mostly affects reliability regarding package cracking and delamination. Crack- and void-free epoxy thermosets comprising well-balanced mechanical properties, strong adhesion, especially, to the light-emitting chip as well as a robust design pave the way for reliable SMD-LEDs.

Reliability of the package depends mainly on two factors, namely, moisture uptake and mechanical stress developed during processing and operation attributed to the cure stress and cooling stress from the CTE (coefficient of thermal expansion) mismatch. Of major importance for SMD-packages is to withstand thermal stress profiles during soldering, particularly in TTW(through the wave)-processing. To this end the focus of our investigations was to improve fracture toughness features to render epoxy resin thermosets, which are inherently brittle owing to their high crossslink density suitable for SMD-LED packages. Noteworthy, from a polymeric materials view, it is not possible to change one property of the thermoset without altering another. For example glass transition Tg vs. E-modulus, CTE as well as network density and brittleness. Material science have to find out the optimum level of properties to accomodate all facets for the specific application.

This contribution reports the development of a two-component epoxy casting resin that possess outstanding properties for optoelectronic packaging. Thermal crosslinking of conventional-type Diglycidyl ether of bisphenol A (DGEBA) epoxy resin formulations are accomplished by acidic ester modified anhydride hardeners using specific accelerators. Another goal was to exclude HSE (health, safety, environmental) concerns for suitable formulations by the right choice of raw materials. Casting technology in conjunction with optimized reactivity for short curing cycles at reasonable temperatures allow successful high volume production for SMD-LEDs.

2. SMD-LED Assembly

In diagram 1 the flow chart for the SMD-LED manufacture is pictured. A stable automatic reel-to-reel process enables an efficient mass production for currently 1.9 billion units with a high output. Before mounting the chip the aromatic Polyphthalamide (PPA) housing is injection molded. Within the casting line the premixed epoxy casting resin is precisely brought upon the LED reflector using a multiple dosing system. After curing the resin, the galvanic bath treatment, splitting and testing, the LEDs are dry packed for transportation. The LEDs are suitable for automatic pick-and-place equipment in the field of SMT-technology.

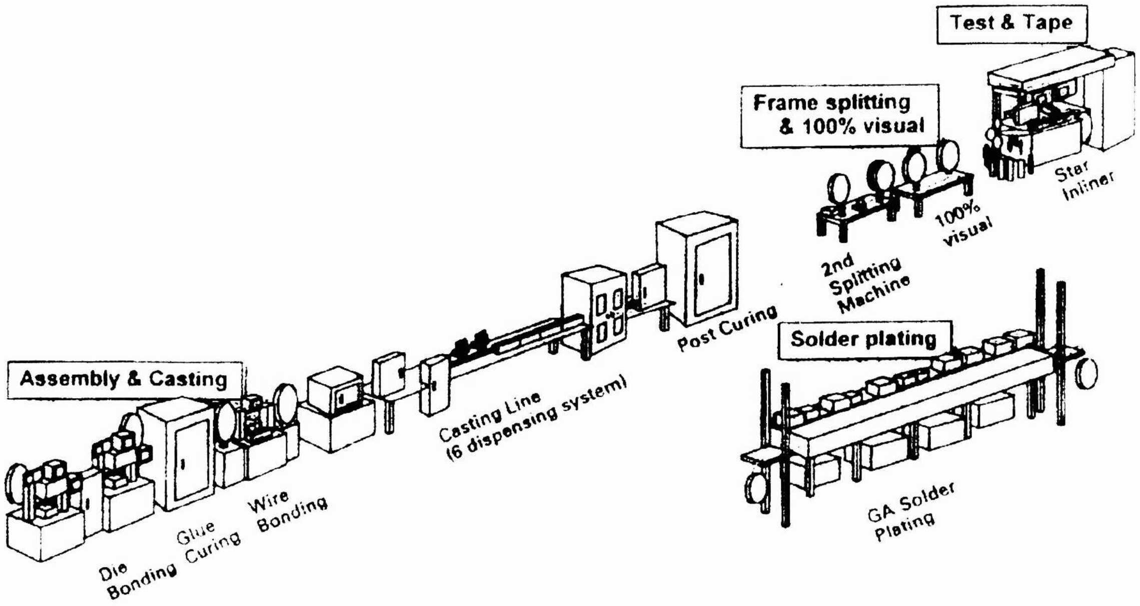


Diagram 1. Schematic set-up for SMD-LED manufacture.

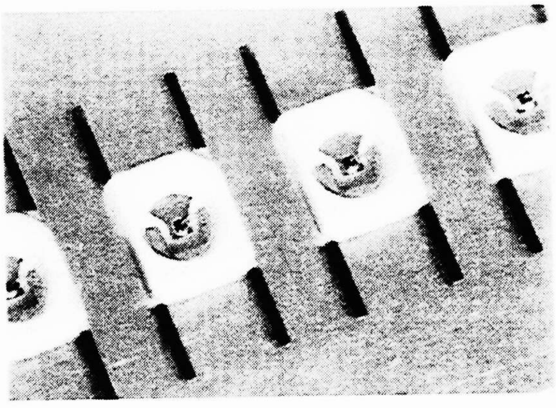


Figure 1. Premoulded SMD-LED upon reel after wire bonding.

3. Chemistry

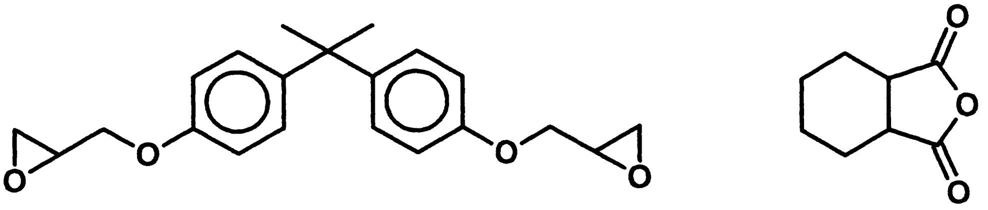
Epoxy resin chemistry and technology for a wide range of applications are outlined in the literature [1]. The specific requirements for transparent epoxy resins in safe mass production processes for optoelectronics comprise:

- a low viscosity of the bubble-free, homogeneous casting resin along with a pot life of at least four hours for trouble-free dosing

- and a specific cure chemistry to realize fast curing cycles at medium temperatures to overcome internal package stress caused by volatiles and thermal shrinkage.

Other desired critria are a broad formulation potential with an appropriate mixing ratio, shelf life of the components of at least 6 month as well as low cost. Additionally, the readily cured epoxy package has to protect the LED-device from mechanically and chemically extreme environments during the galvanic bath process and the entire service life.

The most widely utilized class of epoxy casting resins represent Bisphenol-A-based bifunctional prepolymers. Diglycidyl ether of bisphenol A (DGEBA) is the main constituent for the epoxy opto formulation with the chemical structure shown in diagram 2. The physical properties of the epoxy formulation are listed in table 1.



low molecular weight DGEBA

HHPA

Diagram 2. Chemical structure for the Diglycidyl ether of bisphenol A (DGEBA) and the Hexahydrophthalic anhydride (HHPA) hardener.

Table 1. Physical properties of the actual epoxy opto formulation.

Appearance	transparent, slightly blue
Viscosity (25 °C)	2,200 mPas
Epoxy value	0.56 mole epoxy/100 g resin
Specific gravity (20 °C)	1.20 g/ml
Refractive index n_D^{20}	1.569
Color number (gardner)	≤ 1
Shelf life (max. 30 °C)	15 months

In order to achieve high heat and chemical resistance along with low color drift during service life thermal curing is accomplished by a Hexahydrophthalic anhydride (HHPA) hardener (diagram 2.) formulation mediated by a specific accelerator agent. Besides a low viscosity of the hardener some Acidic ester modifications are introduced to match the reactivity and the mechanical features for the final Polyester-structured thermoset. The network formation is via an addition reaction mechanism without evolution of low molecular weight by-products accompanied by a small shrinkage of below 3 %. The key features for opto casting resins are exemplified in table 2.

Table 2. Key features of the LED casting resins.

Viscosity (25 °C)	600 – 800 mPas
A:B mixing ratio	100:(80-95)
Pot life	> 4 hrs
Chloride content:	
Total (DIN 53474)	800 ppm
Hydrolyseable (DIN 53188)	250 ppm
Free (DIN 53188)	< 5 ppm
Volume shrinkage	< 3 %

4. Reactivity

In DSC (differential scanning calorimetry) experiments changes of the heat capacity with temperature or with time in the isothermal mode are detected very precisely in the mg scale for versatile materials. Thus, DSC is ideally suited to study the reactivity and the extent of cure for epoxy thermosets. In a conventional DSC run the reactive formulation is subjected to a heat ramp of 10 K/min. The exothermic enthalpy for the chemical reaction of the crosslink process is indicated by the area under the curve. Further valuable features are the onset and the peak temperature. In addition to the reaction heat these data is vital to the process engineer to work out the curing profile in the assembly to accomodate short curing times on the one hand and to avoid too much overheating for stable packages on the other hand. Figure 2 shows the dsc line shape for epoxy anhydride opto formulations with increasing accelerator amounts. The lower the accelerator content the lower the reactivity and the higher the onset and peak temperatures. Obviously, network formation is more selective at higher accelerator amounts as the cure exotherm spans a smaller temperature range. For a given epoxy-hardener ratio (A:B) the cure exotherm was adjusted to an onset temperature of 140 °C that reveals a reasonable thermal budget necessary to compensate internal stress during network formation without posing time constraints in the production line.

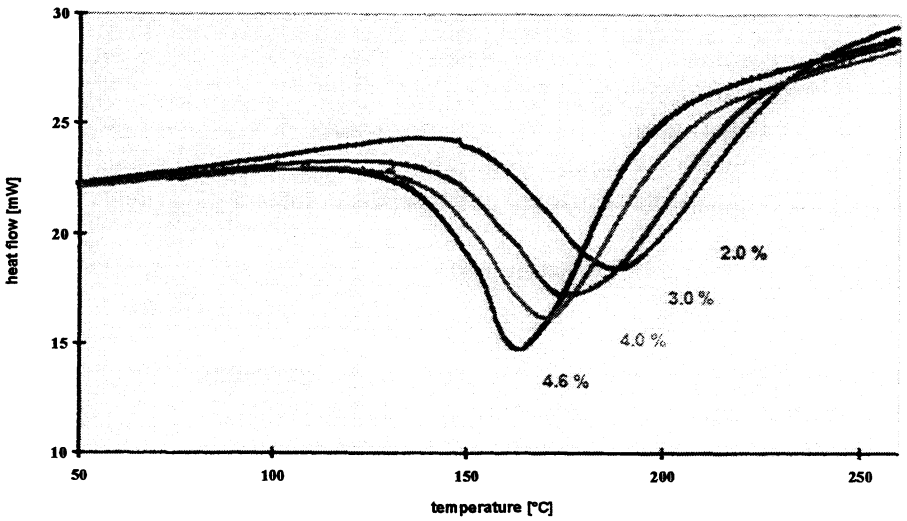


Figure 2. DSC cure exotherms for an epoxy opto resins with variable accelerator amounts (ramp: 10 K/min).

Another exploratory tool necessary to fine-tune the reactivity of the casting resin for specific line conditions is the gel time to transfer the liquid resin to a semi-solid state at the gel point. Gel times for an optimized A:B mixing ratio at a fixed accelerator content on a hot plate are summarized in table 3. Gel time vs. 1/T are pictured in diagram 3. The graph reveals a change of the reaction mechanism at around 140 °C with fast network formation at above this temperature. To come up with high volume demands precuring has to be performed at temperatures above 150 °C.

Table 3. Gel times for the actual epoxy opto resin (0.4 g).

T [°C]	1/T 10^{-3} [1/K]	Gel time [s]
100	2.68	2,000
120	2.54	1,200
130	2.48	750
140	2.42	360
150	2.36	240
160	2.31	160
170	2.26	100
180	2.21	60

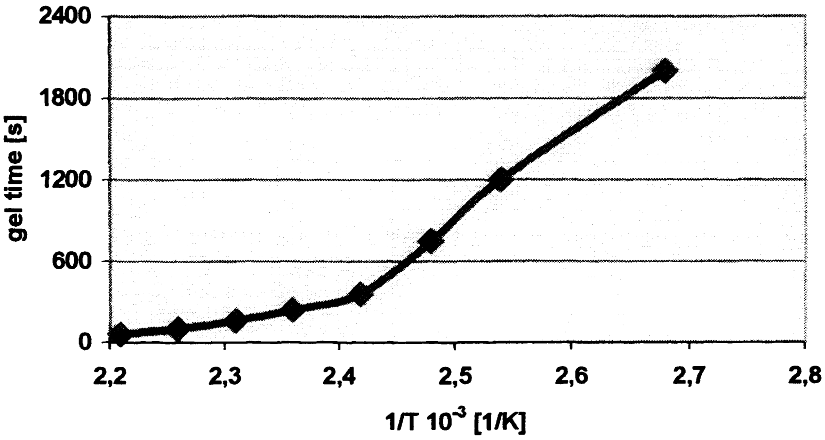


Diagram 3. Gel time vs. 1/T in Kelvin for the actual epoxy opto resin.

5. Transmission and cure stage properties

A strong performance feature of these LED epoxy resins is their clarity, their high light transmission in the visible range and their outstanding thermal stability. The transmission of a machined and polished 1 mm specimen is nearly 90 % in the visible range (diagram 4). Considering reflectance losses on the surface a total material transmission of roughly 98 % is reached. After 6 weeks thermal aging at 120 °C a color shift of 2.2 was observed. The high optical stability of the opto resin is further proved by a climate weathering test using Xe-radiation according to DIN 53387. After 1,000 hrs a color shift of 2.5 was found. Practically, there is no reduction of transmission after moisture saturation at 23 °C. Favourable LED light output is ensured by a reasonable refractive index n_D^{20} of 1.53. Further material characteristics are completed in table 4.

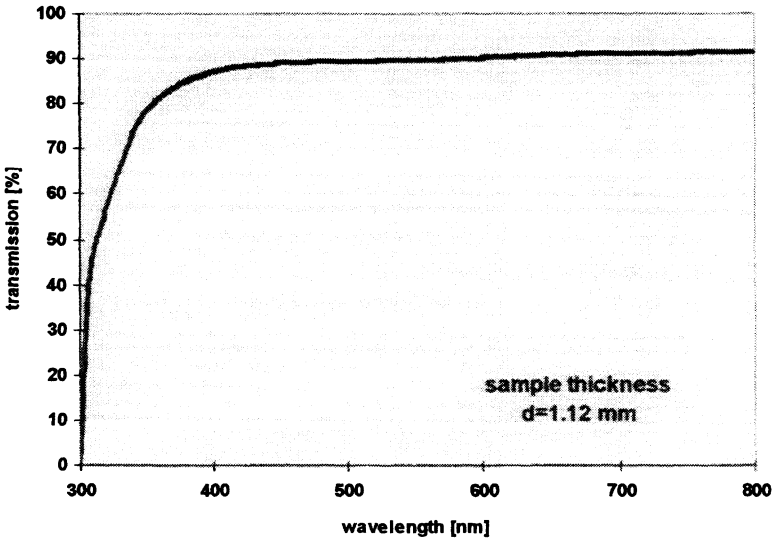


Diagram 4. Transmission characteristic for the actual epoxy opto resin.

Table 4. Complementary material characteristics for the actual epoxy opto thermoset.

Glass transition Tg (DSC: 10 K/min)	115 °C
Shore D hardness	87
CTE	
-50 to + 50 °C	65 ppm/K
> Tg	185 ppm/K
E-modulus (tensile, 1 Hz, 3 K/min)	
at 20 °C	3,100 MPa
at 100 °C	1,900 MPa
Bending modulus (DIN53452)	2,900 MPa
Flexural strength (DIN53452)	130 MPa
Tensile shear strength (DIN53283)	18.3 MPa

6. Moisture

The effect of environmental moisture absorption from the surrounding is critical as mechanical and electrical properties as well as functionality of moisture sensitive devices suffer. Under elevated temperatures in the presence of high humidity loadings, the package quality deteriorates and corrosion as well as chip degradation are likely. Potential humidity-related concerns imply formation of crazes, voids, microcracks along with moisture induced interfacial delamination and popcorning during reflow soldering. In order to understand the factors that control water absorption and to improve the hydrolytical durability in moist environments, investigations on moisture uptake behaviour for epoxy thermosets are an important technical objective.

Theoretical approaches on the sorption issue and moisture diffusion in glassy thermosets were cited in [2, 3]. Empirical thermodynamic models for accelerated humidity testing correlate sorption data at different temperatures successfully [4]. Water uptake in epoxy thermosets upon versatile temperature-humidity profiles were studied in detail [5]. General findings comprise:

- moisture saturation w_∞ is proportional to relative humidity (r. h.)
- log w_∞ is proportional to the reverse temperature 1/T in Kelvin units
- kinetically water absorption happens in two stages
- at low levels water absorption is diffusion controlled according to the Fickian model
- the diffusion coefficient D for polymers is in the order of 10^{-8} cm^2/s at ambient T
- Arrhenius approximation describes the T dependence for the diffusion coefficient D
- equilibrium data at higher water amounts support the hypothesis of penetrant water clustering

Extensive experimental reports point out the individual parameters for water absorption associated with the epoxy resin chemistry employed such as the type of the cure chemistry and the extent of cure for a given epoxy-hardener stoichiometry at specific temperature-time regimes [6, 7].

Voids and structural imperfections, free volume, polarity of the epoxy network and the nature of the polymer-water affinity involving the capability of H-bond formation control the amount of water absorbed. Besides optical grounds properly cured anhydride epoxy resins outperform amine curing systems by far in terms of moisture uptake behaviour and hydrolytical stability in wet conditions [8].

Material screenings on anhydride cured epoxy resins using accelerated water absorption tests at 85 °C/85 % r. h. reveal a considerable lower water uptake for an aromatic DGEBA-based formulation compared to a cycloaliphatic epoxy resin based on ERL4221 (3,4-Epoxy-cyclo-hexylmethyl-3',4'-epoxy-cyclo-hexanecarboxylate) (table 5). In line with an increasing free volume and the evolution of volatiles during high temperature cure the equilibrium water absorption for the cycloaliphatic epoxy resin with a Tg of 155 °C also increases.

Table 5. Gravimetrical water gain for fully anhydride cured epoxy casting resins at 85 °C/85 % r. h. (specimen: 50x6x4 mm).

Resin Base	Time [hrs]	Water gain [%]
DGEBA	4	0.21
	168	1.00
	336	1.09
ERL4221	4	0.49
	168	2.72
	336	3.22

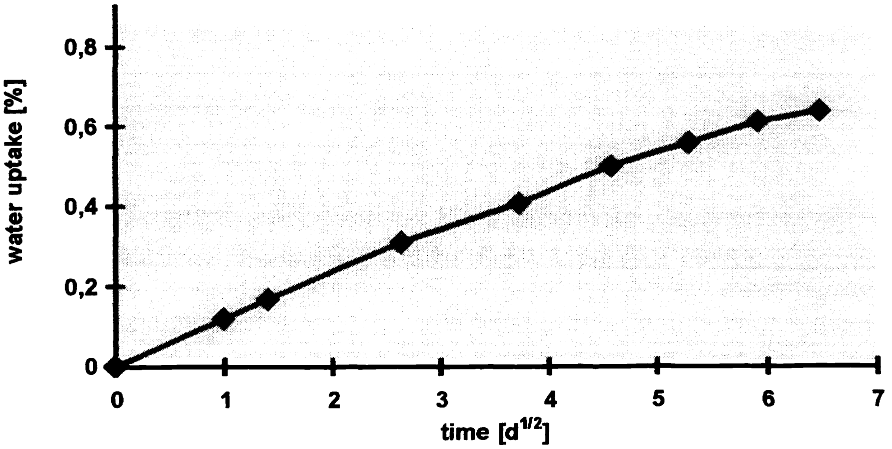
Comparative water immersion experiments at 23 °C on DGEBA-samples cured with HHPA-type and MHHPA-type opto hardeners yielding 0.64 % and 0.77 % ultimate water absorption after 1,000 hrs , respectively, show that the HHPA-type opto hardener system is more reasonable. As a result the actual epoxy casting resin is made up of a formulated DGEBA epoxy resin with a HHPA-based hardener.

The water absorption isotherm at 23 °C for the actual epoxy packaging material complies also with a two stage absorption mechanism including a diffusion controlled pickup within the first 7 days and penetrant clustering in the equilibrium region starting after 3 weeks immersion (table 6, diagram 5). Saturated water content w_∞ is extrapolated to 0.70 % with a mean diffusion coefficient D_∞(23 °C) in the order of 10^{-10} cm^2/s. The mean water absorption rate k_w at 23 °C is decreasing linearly with the square root of time (diagram 6). Unfortunately, from this graph no two-stage water absorption mechanism is evident.

Table 6. Moisture absorption characteristics for water immersion at 23 °C (DIN 53 495) for the actual LED epoxy resin (specimen: 50x6x4 mm).

Immersion time [d]	Immersion time [√d]	Uptake [%]	Rate k_W [%/√d]
1	1.00	0.12	0.120
2	1.41	0.17	0.121
7	2.65	0.31	0.117
14	3.74	0.41	0.110
21	4.58	0.50	0.109
28	5.29	0.56	0.106
35	5.92	0.61	0.103
42	6.48	0.64	0.099

Diagram 5. Water uptake for the actual opto resin with immersion time √d at 23 °C.



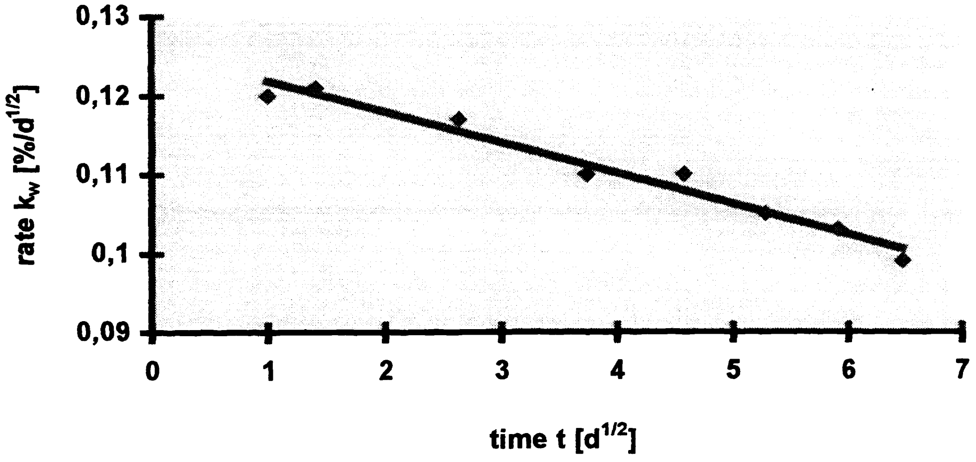


Diagram 6. Water absorption rate k_w(23 °C) for the actual opto resin with immersion time $\sqrt{d}$.

Moisture-related Tg drops due to matrix plasticization were largely reversible even after pc-testing (pressure cooker: 121 °C, 100 % r.h., 2.08 atm, 24 hrs). No acid was set free via hydrolytical decomposition nor a Tg decrease of the fully desiccated samples were observed after soaking in water for 3 d at 65 °C. In addition, sorbed water have not induced any further crosslinking of the anhydride cured epoxy thermoset. In this connection, it should only be stated here, that moisture concentration gradients will generate compressive and tensile force distributions within the epoxy package. For an E-modulus of 3,000 MPa the mean internal stress at 23 °C created by a 0.8 % load of water is calculated to 5 MPa.

7. Fracture toughness

Brittleness in epoxy thermosets arises from their highly crosslinked chemical architecture. Reliability of epoxy packages in a wide range of severe environments for different commercial applications encountering diverse mechanical stress situations depends mostly on the ability of the epoxy polymer to relieve stress peaks to overcome package cracking. Over the years a manifold of papers addresses the toughening issue for epoxies [9]. Improvement of the fracture strength is brought about by the incorporation of elastomer, rubber and core-shell particles. Intense studies on the size, size distribution, dispersability and hardness of the particles as well as on the nature of the particle-epoxy interaction along with demanding morphological investigations brought out controversial standpoints on toughening mechanisms [10]. Apart from that it is generally accepted, that fracture resistance is attributed to a series of energy-consuming events to take place in the stressed region of the resin, namely, shear yielding and crack propagation.

Because of restricted transparency of particle-modified epoxy resins attention was paid here on the question of how to toughen the neat epoxy matrix. Fracture resistance progressively decreases with increasing crosslink density and Tg. As for too low a Tg the fracture energy to dissipate stress also decreases, fracture toughness performs best at medium crosslink density. In order to build the ideal molecular lattice for ductile epoxy casting resins, selective raw material screenings for composing the optimum epoxy-hardener components were carried out. Further fine-tunig efforts were made to optimize the A:B mixing ratio and the cure process.

Fracture toughness experiments were performed at room temperature on single-edge-notched specimens in the three-point-bending mode (SENB) according to ASTM E399 D790 guidelines. Acidic ester modified acid anhydride-cured DGEBA-thermosets indicate unique fracture toughness characteristics. Applying linear elastic fracture mechanics the critical stress intensity factor K_{IC} and the fracture energy G_{IC} for the actual epoxy opto thermoset are 1.350 MPa√m and 560 J/m^2, respectively. For the epoxy thermoset matrix usually K_{IC} 0.55 to 0.65 MPa√m and G_{IC} 80 to 150 J/m^2 were reported. Actually, measurements on HHPA-cured DGEBA-resins without acidic ester modification show K_{IC} and G_{IC} 0.59 MPa√m and 110 J/m^2, respectively. To our knowledge the presented LED epoxy resin exhibit the highest fracture values for neat epoxy thermosets reported so far.

Specific acid ester modification of the HHPA-hardener for DGEBA-based thermosets allows outstanding fracture strength for crack-resistant, reliable SMD-LED packages. The hydrolytically resistant LED epoxy thermoset exhibit reasonable moisture absorption characteristics indicative for low deficiencies for SMD-LEDs during galvanic bath treatment and after reflow shock testing. Thus, LEDs are approved for all kinds of IR reflow soldering and TTW solderability for JEDEC level 2.

8. Conclusion

In packaging technology based on epoxy thermosets there is a strong structure-processing-property interdependence. In conclusion, the reliability of an epoxy package is strongly dependent on the chemical composition of the formulation and the time-temperature profile of the curing process. Systematical molecular engineering using the appropriate chemistry of epoxy resins and hardeners along with suitable accelerators cover the overall requirements for the fabrication of reliable SMD-LEDs in optimized mass production assemblies. Reliability has been verified in actual devices and systems by routine qualification tests that no critical failure is likely to occur during manufacturing, testing, transportation and operation. The robust LED design opens the door for widespread applications. Huge SMD-LED volumes for backlighting of dashboards and indicator panels are the stars in the automotive sector. Due to the low moisture uptake and attractive stress-relieving nature of the epoxy package encompassing superior fracture toughness characteristics humidity level JEDEC 2 was adopted. A low stress, high temperature epoxy casting resin for high power SMD-LEDs with a Tg of 135 °C is already in the channel and will supersede this standard opto resin in the very near future.

Acknowledgements:

The principal author would like to thank Siemens AG, Corporate Technology, for financial support to attend the symposium and colleagues from Osram OS for an open discussion and provision of test results from diverse qualification modes.

9. References

[1] C. A. May, in Epoxy Resins Chemistry and Technology, 2nd Edition, Marcel Dekker, Inc., New York, Basel, 1988

[2] J. S. Vrentas, C. M. Vrentas, J. Appl. Polym. Sci., 71, (1999) 1431

[3] M. R. Vanlandingham, R. F. Eduljee, J. W. Gillespie Jr., J. Appl. Polym. Sci., 71, (1999) 787

[4] J. E. Gunn, R. E. Camenga, S. K. Malik, Rapid Assessment of the Humidity Dependence of IC Failure Modes, Proc. Rel. Physics, 1983

[5] D. J. Belton, M. J. Molter, E. A. Sullivan, Coat. Appl. Polym. Sci. Proc., 59, (1988) 629

[6] M. T. Aronhime, X. Peng, and J. K. Gillham, J. Appl. Polym. Sci., 32, (1986) 3589

[7] J. B. Enns, and J. K. Gillham, J. Appl. Polym. Sci., 28, (1983) 2831

[8] B. H. Eckstein, Org. Coat. Plast. Chem., 38, (1978) 503

[9] G. Levita, S. De Petris, A. Marchetti, A. Lazzeri, J. Mat. Sci., 26, (1991) 2348

[10] J. Karger-Kocsis, and K. Friedrich, Colloid Polym. Sci., 270 (6), (1992) 549