Study on the Effect of Moisture and Elevated Temperature on the Fracture Properties of Visco Elastic Polymers

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Abstract

The universal applicability of polymer materials in microelectronics is based on the wide adaptability of their thermo-mechanical as well as fracture characteristics. These materials have strong time and temperature dependent mechanical properties and are sensitive to moisture. In this paper the effects of temperature and moisture on the thermo-mechanical and fracture properties of thermosetting polymers are studied. Moisture induces a reduction in glass transition temperature, changes the elastic stiffness slightly and degrades the fracture toughness of polymer determination. For the Analysis of fracture toughness, miniaturized CT specimens are initially pre-cracked. Strain fields around the crack-tip at the moment of crack-onset are later determined by gray scale correlation technique and mapped to finite-element analysis for the determination of energy release rate, considering the effect of moisture, temperature and visco elasticity. This work provides a unique method for the analysis of moisture-induced cracking in encapsulated devices.

Introduction

The rapid developments in microsystems technologies demand smaller structures with multiple layers made of different material with even higher reliability. Most electronic products are moving towards miniaturization and high performance leading to increased circuit density and extremely high reliability challenges. Microelectronic product failures in micro- and nano systems can be traced back to thermal, mechanical, chemical, electrical origins a combination of them. Typical failures are cracks, delamination, buckling, warpage, popcorning, stresses, voiding, fatigue, thermomigration and electromigration. In addition, along with the trend to miniaturization of components (microsystems), elevated temperatures have negative effect on overall component performances. Most materials are generally sensitive to moisture and temperature and their material parameters, although from wide range of data sheets, cannot be used for the required simulations. When exposed to humid environments, epoxy resins can absorb water up to a 10 weight -%, depending on the chemical nature and structure, stress state, exposure time, water concentration and temperature. The moisture

concentration leads to the reduction of interface adhesion and delamination. Due to the various thermo mechanical material properties in multi-layered structures (e.g. highly integrated components), very complex failure modes may develop that can impair overall mechanical-thermal reliability. In addition, it is known that physical properties of materials can change significantly, when the dimensions of specimens become very small ("size-effect"). Therefore, in many cases, the material properties cannot be deduced from data achieved from macro-specimens. Consequently, it is frequently required to determine mechanical and thermal properties of these materials in practical dimensions, and properties have to be measured directly on the components. For this purpose advanced deformation measurement methods are needed [1-3]. This paper deals with the development of some test methods for analysis of different materials behaviour on the micro scale level. The presented micro-scale level method is based on the standard test methods for the determination of fracture toughness by means of miniaturized CT-samples [4,5]. The measurement technique allows the determination of geometry-independent fracture mechanics values. This is a fundamental prerequisite for applying fracture mechanics materials parameters to evaluate the toughness of real structure. Some results show the influence of temperature and structural parameters on these properties

Moisture Uptake

The influences of moisture and temperature were investigated on modified epoxy resins without filler particles (Mat-2, Mat-4, Mat-6) and highly filled epoxy molding compounds (MC-A and MC-B). Since it is relatively difficult to determine the moisture concentration, the overall mass uptake of standard specimens was investigated. Considering a polymer which obeys the well known Fickian diffusion law, the moisture concentration equation can be integrated over the thicknesses of bulk material and the fractional moisture uptake of specimens can be expressed as :

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-D(2n+1)^2\pi^2}{4l^2}\right) \qquad (1)$$

Where M_t is mass of moisture after absorption time t and M_∞ is mass of saturated sample. In order to determine the Fickian coefficient of diffusion, the initial state of moisture absorption ($M_t/M_\infty < 0.5$) can be simplified as

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi l^2}\right)^{1/2} \qquad (2)$$

The Fickian diffusion coefficient D is dependent on an initial diffusion constant D_0 temperature T, and activation energy ΔE and is independent of relative humidity (RH) according to:

$$D = D_0 \exp\left(\frac{\Delta E}{kT}\right) \qquad (3)$$

where k is Boltzmann's constant [4,6]

For the characterisation of moisture absorption of epoxy resin without fillers the the structure was changed three times, by increasing the number of carbons in the hardener chain (increase of molecular weight) from 2 carbons (Mat-2) to 4 (Mat-4) and 6 (Mat-6) [7]. The moisture uptake was performed by gravimetric measurements. As the samples were placed in a humidity chamber under specific conditions and between certain time intervals, the weight of the samples was measured. Using the results of their mass-uptake measurements, the diffusion coefficient (D) and the maximum water concentration (C_{sat}) were obtained. Figure 1 shows the maximum of moisture concentration of the materials, under different loading conditions, and depends on polymer structures. The diffusion coefficient of their materials could be calculated by Fick's second law [7].

For each material the water concentration is increased as the humidity concentration in the chamber is increased as well. Furthermore, for each loading condition, when the molecular weight is increased, the concentration is decreased.

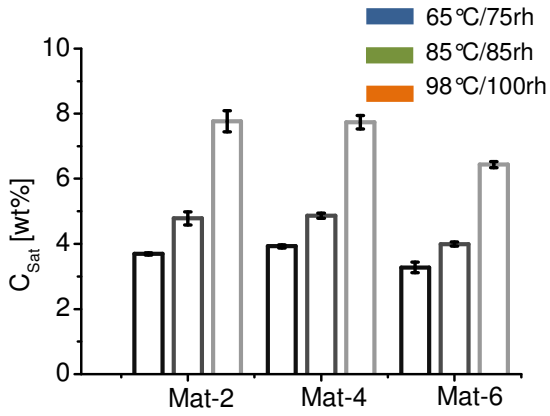
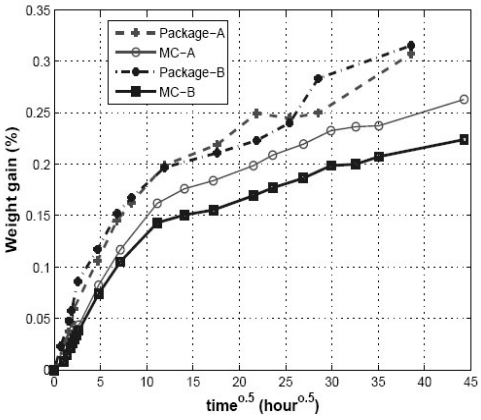


Fig. 1 Maximum of water concentration depends on structure and loading conditions.

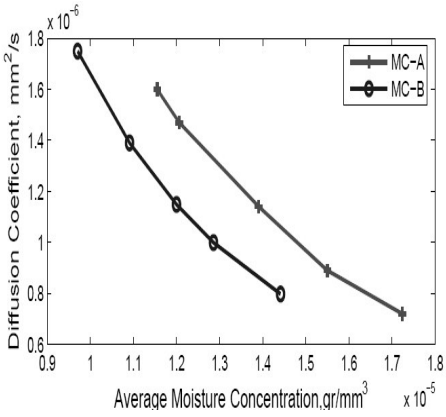
The diffusion of water molecules in epoxy resins is influenced by the structure, the atomic interactions and kinetics energy. The water molecules create a hydrogen bond with the polar groups and/or retreat into the nano-pores (non-bonding) of polymers. The diffusion of water in their structure is achieved via the hopping mechanism which is Brownian in nature. For the diffusion mechanism the state of the epoxy resin should be considered: In the glassy state (non-equilibrium) the molecular chains experience only local motions and vibrations. As a result the energetic barriers within the structure are stronger, thus prohibiting the diffusion and the frequency of hopping is considered to be controlled by these interactions. In the rubbery state, then the motions of the structure increase and the lifetime of the hydrogen bonds is decreased and/or weakened. The free volume is also linearly increased and therefore the diffusion is considered to be not that much controlled by the atomistic interactions. In this phenomenon the decrease of polarity and the increase of free volume may act in parallel.

The weight gain measurement was also performed to evaluate the moisture uptake of two commercial EMC with a filler content of 88 % SiO_2. These samples were also periodically removed and weighed and returned to the chamber (85°C/85% relative Humidity RH) for further soaking. The diffusion of moisture in EMCs (MC-A, MC-B) does not follow the conventional Fickian diffusion of polymers. Consequently, Fick's law fails to predict both moisture absorption and desorption behaviour of these materials. The reason of this behaviour is not fully understood. The first stage may involve physical sorption of moisture in the voids which is asymptotic in nature, while the second phase involves the chemical sorption of moisture along the resin-filler interface, which tends to be linear. The diffusion coefficient can be calculated from the slope of the initial linear part of the moisture uptake curve together with the sample weight at relatively fully saturated state [6], using longer time results and a smaller diffusion coefficient. The method of finite-element-analysis requires for determination a diffusion coefficient for each pair of data and the average moisture content in the sample. Figure 2 shows that the diffusion coefficient of two different EMCs (MC-A;MC-B) decreases with increasing moisture content.



a)

Fig. 2 Moisture uptake of samples vs. exposed time 85°C@85% RH



b)

Diffusion of High filled Epoxy resin as a function of average Moisture concentration

Furthermore, Figure 2 shows also the moisture uptake of two plastic IC_packages (package A and package B), which use MC-A and MC-B as molding compounds, respectively. In consequence, the diffusion of thin package material is faster than on their respective bulk materials. This can be attributed to the three dimensional nature of diffusion in the package application and also due to the higher diffusion rate along various interfaces.

Analysis of moisture induced visco elastic materials properties

For analysis of moisture sensitive and mechanical properties epoxy resins were used [1]. The mechanical properties of these polymers show a significant temperature and time dependence. Therefore, this material is examined by performing DMA tests to characterize the time and temperature dependent

modulus. The dependence of modulus and glass transition temperature T_g was measured by means of dynamical-mechanical analysis (DMA) (Eplexor 100N, Gabo Qualimeter with humidity chamber). Various experiments of dry and saturated samples were tested under dry and humid conditions. The shift of the glass transition region showed the same tendency with the water concentration. With the increase of moisture uptake the mobility of the polymer chains are enhanced and the T_g shifted to lower temperature (Fig. 3). This is the case because during the diffusion process the molecular interactions (mainly hydrogen bonds) are weakened and the chains are slightly separated. The storage modulus is also decreased with increasing the moisture concentration. The water molecules reduce the intermolecular forces between the polymer chains [1,2,7].

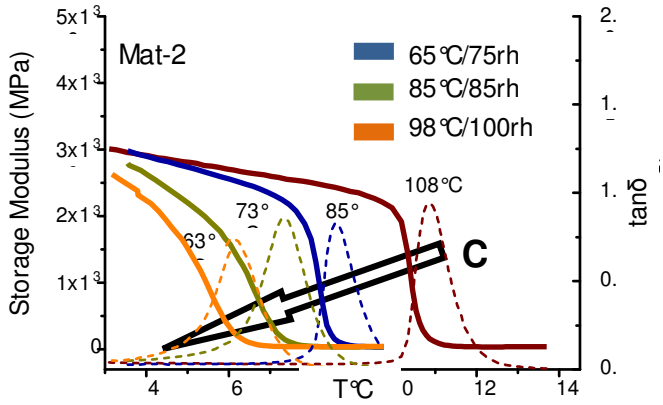


Fig. 3 Measured modulus and glass transition temperature as a function of moisture loading conditions

The theoretical analysis of stresses induced by environmental conditions, especially temperature changes, requires the characterization of complex material properties as well as materials interface properties. Thermosetting polymers undergo a dramatic property change at the so called glass transition temperature T_g, which divides the temperature range in the glassy state range below T_g, characterised by high stiffness and low CTE, and the rubbery state range above T_g characterised by a high CTE and low stiffness. For a lifetime 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 as a function of temperature can be theoretically described by the master curve and an appropriate temperature-time shift function [8]. 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. The result of the measurements can be seen in Figure 4. It is shown the moisture has also a significant influence on the relaxation behaviour, which increases not only on temperature but also with moisture concentration [4].

Determination of fracture properties of polymer systems

The fracture mechanics values of the cured resins were measured by mini-compact-tension-specimens with the dimensions length L = 25.4 mm, width W = 20.4 mm, and thickness of min 4 mm. For all specimens the ratio of the initial crack length to the width a/W was 0.55. Test conditions were described in [4, 5]

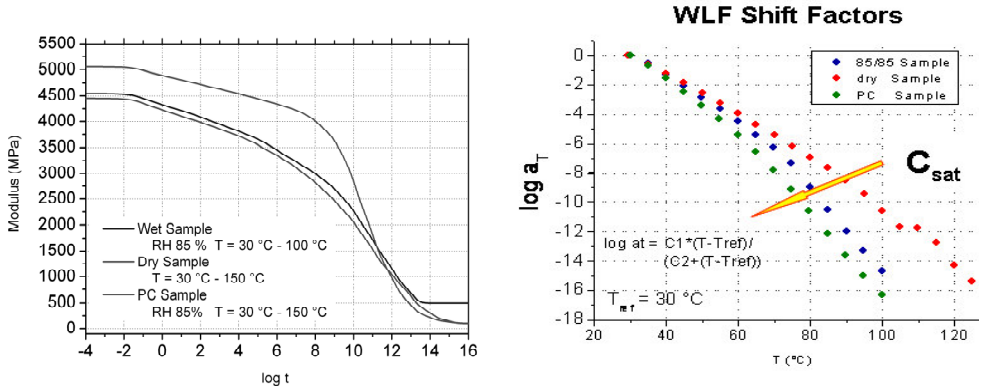


Fig. 4 Master curves and shift functions determined by frequency-temperature superposition of unfilled Epoxy resin

For the fracture mechanics test, a pre-crack ahead on the notch is required to measure reliable fracture toughness values even for minimized test samples. For the unfilled epoxy resin specimens a sharpened crack tip was notched with an industrial razor blade performed by in-house developed apparatus. For high filler epoxy resin it is rather difficult to introduce pre-cracks into small samples by this apparatus. Therefore, for materials with a high stiffness pre-cracks were introduced by cycling tensile method using a conventional mechanical testing machine (Tytron ^{TM}250, MTS). More than several thousands of cycles were necessary to make a defined pre-crack with a length of 0.2 mm (Figure 5). Both methods are allowed to measure accurate fracture toughness on minimized and pre-cracked samples.

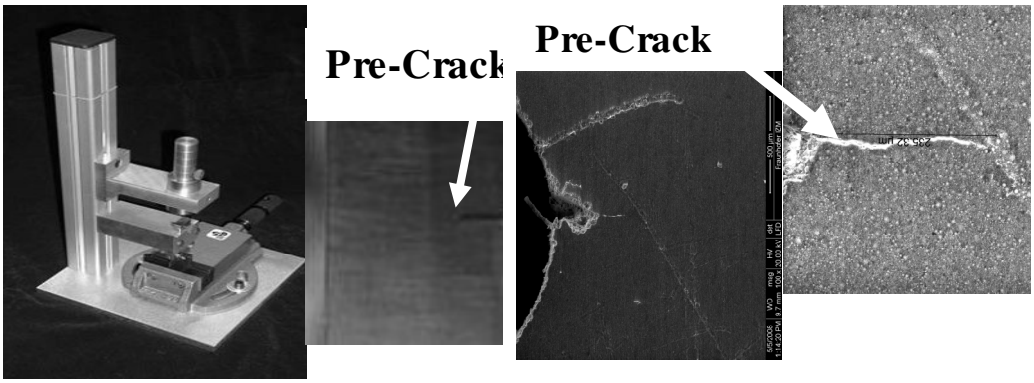


Fig. 5 Pre-crack introduced by apparatus (left) and by cyclic loading

From the viewpoint of the practisioner, the fixing of employment limits for epoxies is of a special significance and requires the description of the mechanical properties in dependence on temperature. Up to a temperature of 100°C the toughness behaviour changes insignificantly, but if the temperature rises further, the fracture toughness increases rapidly. The maximum load reaches the highest value in the vicinity of the glass transition temperature (T_g) (Figure 6).

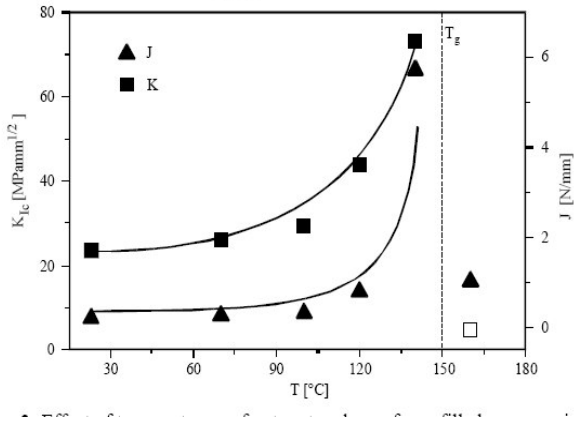


Fig. 6 Effect of temperature on fracture toughness for unfilled epoxy resin (dry samples)

This increase of fracture toughness at higher temperatures is caused by an increasing molecular mobility of the network chains. On the other hand, the temperature-induced decrease in the yield stress of the polymers leads to a larger plastic zone in front of the crack tip connected with a crack blunting (Figure 7) [4].

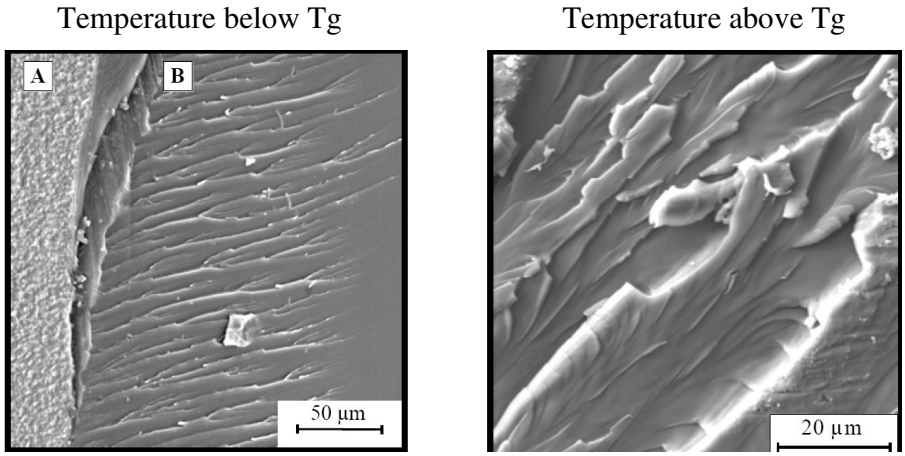


Fig. 7 SEM of crack surfaces depending on temperature, A) notch B) fracture area

The effect of moisture absorption on the performance of commercial highly filled epoxy formulations were studied on an example from the field of

microelectronics. After exposure at 85 °C by 85 % rel. humidity for 168 h, the specimen's moisture equilibrium was not reached for all epoxy formulations. At room temperature as well as at high temperature (215 °C), all composites show linear-elastic material behaviour. At room temperature, absorbed water acts as a light plasticiser for cured epoxy formulations. Above 215 °C, the absorbed moisture reduces the fracture toughness significantly and decreases the adhesion behaviour efficiently (Figure 8) [4, 9].

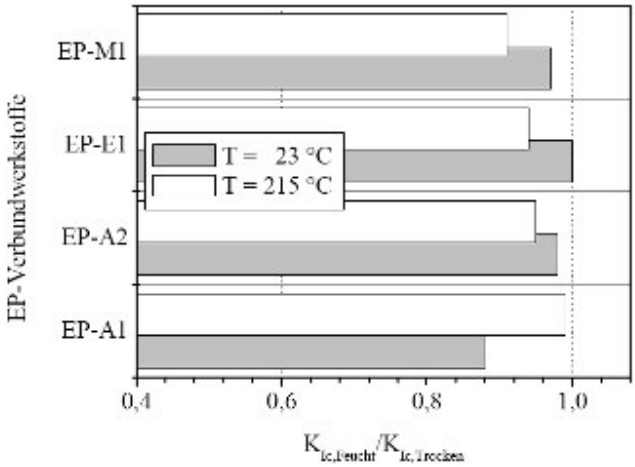


Fig. 8 Influence of moisture and temperature on fracture toughness of different epoxy molding compounds (EMCs)

Conclusion

Diffusion of moisture in unfilled epoxy resin follows the conventional Fickian diffusion of polymers, whereas the moisture uptake of highly filled epoxy resin (EMC) does not follow the Fickian diffusion. Consequently, for prediction of moisture absorption and desorption behaviour of these materials, a non-Fickian model is needed. It was shown that by changing the structure systematically, the water uptake, the Tg and the E' are influenced. The shift of the Tg showed water concentration and structure dependency. The modulus showed dependency on the structure, the water concentration and the state of the material (glassy or rubbery). Multi-frequency dynamic analyses are suitable measuring techniques for the determination of temperature-dependent visco-elastic properties. The influence of humidity on the materials behaviour shows that the moisture diffusion does not only affect a shift in the glass transition temperature and a reduction in the modulus, but also influences the visco-elastic properties significantly. The miniature specimens used allow the evaluation of the fracture toughness and the assessment of deformation behaviour. At higher temperatures, the fracture toughness increases and reaches the maximum near the glass-transition temperature. In the case of filled materials, the absorbed moisture reduces the fracture toughness significantly and decreases the adhesion behaviour efficiently.

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