

NOTE

Thermomechanical Characterization of Modified Duroplastic Low-Stress Materials

INTRODUCTION

Today's state-of-the-art duroplastic encapsulating materials for large-scale integrated circuits are based on filled epoxy-novolak-systems, which are characterized by high Young's moduli and glass transition temperatures and low thermal expansion coefficients; this triangle of macroscopic properties determines in a first approximation the internal stress in the molding material.¹

Especially in a microchip with its variety of different materials with different thermal and elastical properties, a temperature-dependent buildup of stresses is almost unavoidable and can lead to severe interferences in the chip function. Material development for further chip generations with increasing chip size and decreasing pattern size² has to take this into account.

The thermomechanical stress of any elastic body is given by Hooke's Law as a vectorial product of the body's strain and a material constant, which includes several anisotropic and temperature-dependent moduli, Poisson's ratio, and the thermal expansion coefficients. To approximate the stress of a chip-polymer sandwich, several simplifications lead to an expression, where only the temperature-dependent moduli and thermal expansion coefficients have to be known.^{1,3} Loss and storage moduli, which refer to the energy stored or dissipated in the sample, can be characterized with the dynamic mechanical thermoanalysis (DMTA), the glass transition temperature T_g , and the thermal expansion coefficients can be determined from thermomechanical analysis (TMA) measurements.

A different approach is to measure directly the bending of a polymer-substrate sandwich and to calculate the stress from the mechanical distortion. For a quantitative stress measurement of a polymer or a polymer-substrate sandwich several methods^{4,8} with expensive optic or electronic equipment are known. In this contribution we propose to determine thermomechanical stresses by simple mechanical measurements. Using a commercial TMA-device, a quick and cheap stress measurement over a wide temperature range can be realized.

EXPERIMENTAL

Thermoanalytical Measurements

TMA-measurements were carried out on a Perkin-Elmer TMA 7 equipped with a Perkin-Elmer 7700 computer in the temperature range from 0 to 270°C, with a heating respectively cooling rate of 5 K/min. Sample specimen of 4.5 mm height were cut from 1.6 mm thick plates of molding materials with a precision diamond-wire saw.

DMTA-measurements were carried out on a dynamic mechanical thermal analyzer MK-II (Polymer Laboratories) equipped with a Hewlett-Packard 9836C computer. Typical measurement conditions were 0.5N elongation force, 2 K/min heating rate, and 1 Hz oscillation frequency. Specimen for the DMTA-measurements of 29 mm length and 0.6 mm width were also cut from 1.6 mm thick plates.

Stress Measurements

The proposed method relies on measuring the changes in height caused by the bending of a coated silicon stripe as a function of temperature using the TMA device. The sample was prepared by coating a silicon wafer with the appropriate molding material; the thickness of the silicon should be about twice the thickness of the molding material. With a wire saw, stripes (10 mm long, 3.5 mm wide) were cut from the coated wafer. The specimen was then placed in the TMA device with the silicon side on top (see Fig. 1). In a first conditioning prerun it was heated to temperatures slightly above the glass transition temperature and cooled down to 0°C. This surface-conditioning procedure removes frozen stresses, curing artefacts, etc., and yields more reproducible results. The following measurement cycle, which was evaluated, was done in the temperature range from 0°C to 270°C. The differences in the measured heights for the second and all following measurement runs were less than 0.1%.

The temperature-dependent stress $\sigma(T)$ can then be calculated from the measured bending δT by Eq. (1):⁹

Table I Composition of Modified Duroplastic Low-Stress Materials

	EPA ₀	EPA ₅	EPA ₁₀
Epoxy component	74.4%	67.6%	60.9%
Siloxane-hardener	—	12.5%	25%
Novolak-hardener	25.6%	19.9%	14.1%
Total siloxane-content	0%	5%	10%
Filler content		70%	

$$\sigma(T) = \frac{4 \cdot E_1 \cdot h_1^3}{3 \cdot h_2} \cdot \frac{\delta(T)}{l^2 \cdot H} \cdot \left[1 + \frac{1}{3} \cdot \left(\frac{h_1}{H} \right)^2 \right]; \quad (1)$$

- E_1 : Young's modulus of silicon
 h_1 : thickness of silicon
 h_2 : thickness of molding material
 H : total thickness ($h_1 + h_2$)
 l : length of the specimen
 T : temperature

Effects of thermal expansion of the molding material and of the silicon wafer were corrected according to Eq. (2):

$$h = h_0 + [h_0 \cdot (T - T_0) \cdot \alpha]; \quad (2)$$

By variations of the applied force (from 5 to 100 mN) it could be proven that the mechanical contact between quartz rod and sample has no influence on the result of the measurement under these conditions.

Materials

The composition of the newly modified materials is shown in Table I. As siloxane component, a commercial preadduct of a siloxane and an alkylphenol-novolak (Albiflex, Hanse Chemie) was used. The filler consisted of powdered SiO₂ (FB 74, Denka). All components were intensely mixed and 1.6 mm thick plates were pressed in a transfer molding

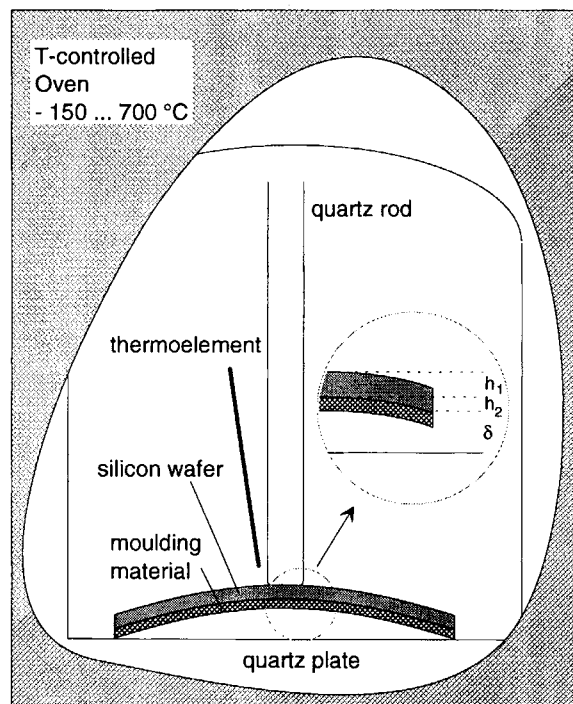


Figure 1 Schematics of TMA-method for temperature-dependent stress evaluation.

process. Typical processing parameters were a pressure of 100 bar and a reaction temperature of 175–190°C within a curing time of 60–120 s.

Additionally, two commercial materials, the standard molding material Nitto HC 10 (Nitto), and the low-stress material Aratronic 2180 VA (Ciba-Geigy), were included in the investigations.

RESULTS AND DISCUSSION

The results of the thermoanalytical investigations are summarized in Table II. The glass transition temperature

Table II Thermoanalytical Data of Molding Materials

Material	Glass Transition Temperature (°C) T_g (TMA)	Coefficient of Thermal Expansion (TMA)* [10^{-6} K^{-1}]		Storage Modulus [N/mm ²] at 50°C E' (DMTA)
		α_1	α_2	
EPA ₀	158	18	67	11050
EPA ₅	158	18	70	9660
EPA ₁₀	153	19	79	8170
Nitto	165	18	63	11420
Aratronic	162	13	64	12220

* α_1 : below T_g , α_2 : above T_g .

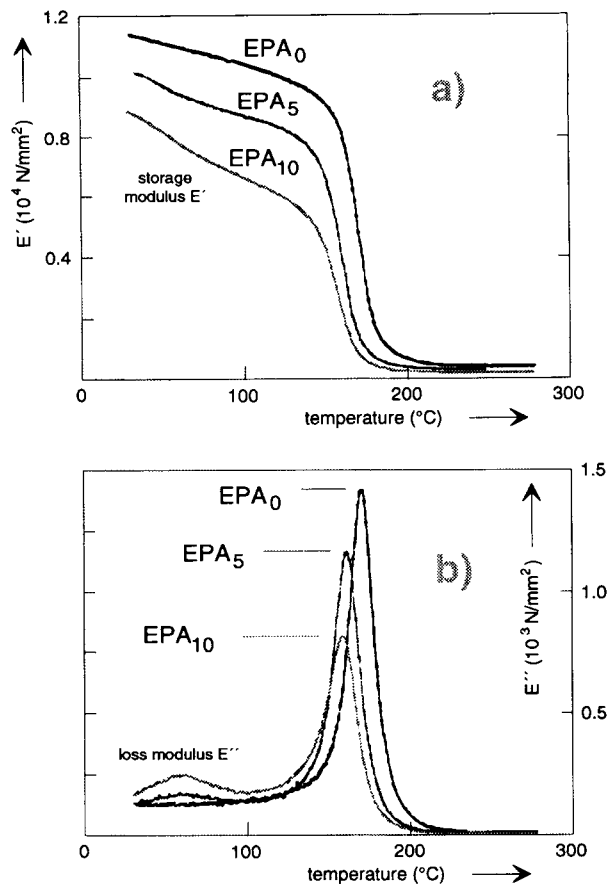


Figure 2 Dynamic-mechanical analysis of relaxations in modified duroplastic low-stress molding materials. (a) Young's modulus E' ; (b) loss modulus E'' .

T_g of the 5% siloxane-containing material EPA₅ is not significantly lowered, when compared to the siloxane-free EPA₀. Also, the coefficients of thermal expansion are al-

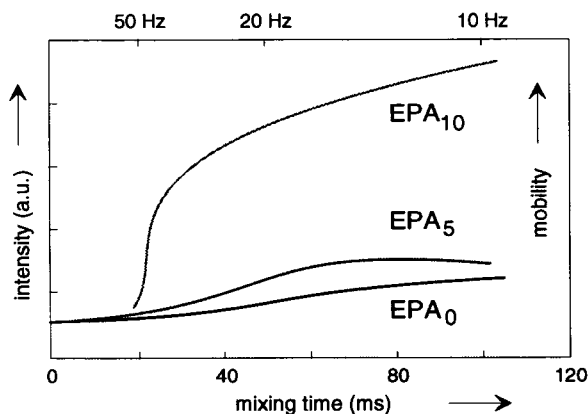


Figure 3 Mixing time dependence of solid-state NMR spinning sidebands intensities as a measure of the mobility of siloxane-epoxy-linkages.

most identical. Ten percent siloxane in EPA₁₀ cause a lowering of 5 K in T_g and a significant raise in the thermal expansion coefficient. The storage modulus (Young's modulus) of the modified systems decreases nearly proportional to the increasing siloxane content. Aratronic shows a significant lower coefficient of thermal expansion (below T_g), which is probably caused by its high filler content of about 80%.

DMTA measurements in the temperature range from 30°C to 250°C (Fig. 2) show two relaxations: the α -relaxation (glass transition) at 150–180°C and a β -relaxation at about 60°C. From the fact that the β -relaxation only appears in the siloxane (albiflex)-containing product, it is concluded that this relaxation is caused by structural elements of that modifying agent.

The level of the storage modulus E below the the glass transition temperature decreases almost proportional to the increasing siloxane content. The maximum of the loss modulus appears at higher temperatures compared to the glass transition temperatures evaluated with TMA because of the differences in the measurement frequencies. With increasing siloxane content this maximum is shifted to lower temperatures while the energy loss broadens and the loss maximum decreases. This is interpreted in terms of a broader frequency range of structural motions.

These assumption of additional motions at lower frequencies correlate with the results of solid-state NMR 1D-mixing time experiments (Fig. 3). This experiment allows to detect the rebuilding of previously suppressed spinning sidebands during a variable mixing time t_m and to correlate it to the structural mobility at a certain frequency of motion.¹⁰ While EPA₀ shows no significant effect, there is a small increase in mobility (sideband intensity) at mixing times from 40 to 60 ms for EPA₅ and an even stronger increase for EPA₁₀ from 20 to 30 ms. This corresponds to slow motions (50–20 Hz) of structural elements (C=O at 156 ppm) chemically attached to the siloxane chain.

The results of the thermomechanical stress determination are summarized in Table III. The total stress corresponds to a temperature interval from 265 to 0°C; the slope and the stress difference has been obtained in the

Table III Stress of Investigated Materials

Material	Stress at 0°C σ [MPa]	Stress Difference* $\Delta\sigma$ [MPa]	Slope* $\left(\frac{\Delta\sigma}{\Delta T}\right)$ [MPa/K]
EPA ₀	30	9.7	0.192
EPA ₅	16	5.9	0.120
EPA ₁₀	10	3.9	0.076
Nitto	30	7.5	0.150
Aratronic	18	4.7	0.096

* $\Delta T = 70-20^\circ\text{C}$.

temperature interval from 70 to 20°C. Figure 4 (a) depicts a typical measurement run for the commercial materials in the temperature range from 265 to 0°C; the measured heights have already been converted according to Eqs. (1) and (2). While cooling down from 265°C vs. the glass transition region, stress raises linearly with a very small slope until the temperature is approaching the glass transition region, then a gradual increase in slope is observed. Below the glass transition region, this slope is again approximately constant but at a significant higher value. Nitto shows the greater stress increase in both temperature regions, the inflection point is at temperatures significantly above the glass transition. While Nitto reaches an accumulated stress of 30 MPa at 0°C, Aratronic only yields a mean stress of 17.7 MPa at 0°C, with a standard deviation of 0.6 MPa.

EPA₀ shows qualitatively the same behavior as the commercial material Nitto [Fig. 4(b)], but the stress in-

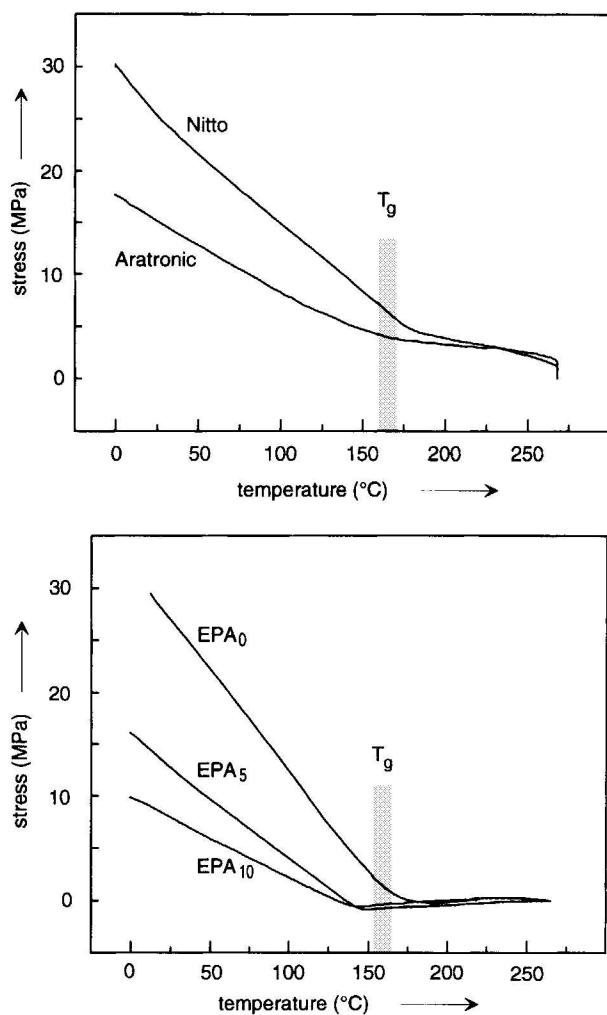


Figure 4 (a) Temperature dependence of stress in commercial molding materials. (b) Temperature dependence of stress in siloxane-modified molding materials.

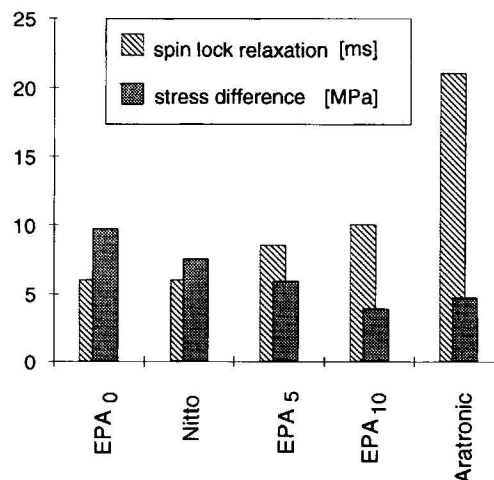


Figure 5 Correlation of stress measurements with solid-state NMR relaxation times.

crease in the glassy region is even larger. This stress increase in the siloxane-free material caused the silicon carrier to crack at temperatures below 20°C; here, the final stress value of approximately 30 MPa at 0°C was obtained by extrapolation.

In the siloxane-modified materials EPA₅ and EPA₁₀ stress even decreases slightly upon approaching the glass transition temperature. After a very distinct inflection point, which is significantly below T_g , stress increases with slopes comparable to Nitto (EPA₅) and Aratronic (EPA₁₀).

CONCLUSION

It is demonstrated that the modified TMA-method allows a quick, reproducible, and quantitative stress characterization with a readily available commercial device. The method is applicable not only for molding materials but also for all other sorts of chip encapsulations or polymer-silicon sandwiches.

Siloxane modification is very suited to reduce stress in filled epoxy novolak systems. The material containing 5% siloxane shows a drastic stress reduction without lowering the glass transition temperature. Ten percent siloxane addition reduces stress further, but at the expense of a lowered T_g . Stress reduction without lowering T_g is probably connected with the formation of biphasic microdispers systems,^{11,12} combining the advantages of both siloxane and epoxy-novolak matrices.

This hypothesis is supported by solid-state NMR measurements of the ¹H-relaxation time in the rotating frame $T_1(^1\text{H})$ ¹³. The siloxane-containing materials show different values for the signals originating from the siloxane structures and the signals of the matrix. A correlation can be established (Fig. 5) between the measured stress and the $T_1(^1\text{H})$ relaxation time within one class of molding

materials. The modified materials exhibit a stress at 0°C, which is the lower, the higher the siloxane content is. On the other hand, T_1 (^1H) relaxation time was found to decrease with increasing siloxane content. Probably because of the different composition of the matrix and the siloxane component, Aratricon deviates somewhat from the correlation found for the other samples.

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