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THE RATE DEPENDENCE AND COMPARABILITY OF GLASS TRANSITION TEMPERATURES

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INTRODUCTION

It is well known, that the glass transition temperature (Tg), measured by a TA method (e.g. DSC, TMA), depends on the heating rate (1). This transition, known to be of 2nd order, is a kinetically controlled physical process without a equilibrium between the glassy and the rubbery state.

Nevertheless all methods used to determine Tg need a certain rate of temperature change. And even worse, the methods use different evaluation procedures. Hence it results that Tg is rarely identical neither between methods (e.g. at same heating rates) nor within a method between different heating rates.

At the glass transition, which covers always a certain temperature range, specific heat, expansion coefficient, Young's modulus as well as dielectric constant change and it can be assumed, that all these physical properties change proportionally.

Consequently it can be deduced that all measuring methods, using the same heating rate, give the same characteristic temperature points when applying the same evaluation algorithms. It has to be observed, of course, that all signal destoring effects, e.g. temperature lags - also within the sample -, have to be corrected.

As a conclusion it is proposed, to apply the well known ICTA evaluation procedure for Tg determination not only to DSC but also to TMA and as many other measuring methods as possible. The rate dependence cannot be neglected and has to be measured for each method and for each substance.

EXPERIMENTAL

To prove the identity of Tg determination by DSC and TMA the following samples have been used:

i) Epoxy resin (printed circuit board)
approx. 38 mg
ii) 33 mg Epoxy resin
iii) 31 mg Polystyrene, high impact strength
for packaging purposes.

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The temperature reading and the thermal lag within the sample has been calibrated using the fusion of indium. Approx. 3 mg indium have been placed in the center of the sample (e.g. between two discs of sample). The corresponding temperature difference (internal lag) between crucible and middle of sample was approx. 1.5°C at 10°C/min heating (or cooling) rate.

The Mettler TA3000 system with DSC30, DSC20 and TMA40 measuring modules have been used. The TA processor TC10A enables data storage and retrieval by means of a connected personal computer.

Measuring of Tg at a certain heating rate was preceded by cooling the sample through the glass transition at the same rate.

RESULTS

The characteristic glass transition temperatures Tg (Tg1...Tg3) have been determined following the ICTA procedure (see Fig.1). The temperatures printed out by the instrument were corrected by the internal lag.
Fig.2 shows the comparison of a DSC curve and a TMA curve of the same sample. The DSC trace, which is approximately proportional to the cp curve coincides well with the curve of the local linear expansion coeffficient α measured by TMA:

$$\alpha = \frac{dL}{dt} \cdot \frac{1}{\beta} \cdot \frac{1}{Lo}$$

with dL/dt = derivative of TMA trace
β = heating rate
Lo = original length of sample

The mid temperature Tg2 (50% transition) is the same whereas the range Tg1...Tg3 depends on the filtering of the curve.
As it can be seen in Fig.3 the respective integral curves (enthalpy or length in function of temperature) do not correspond to the previous results due to different and more difficult evaluation (this evaluation procedure is normally applied for Tg determination by TMA measurements).
The dependence of Tg from positive and negative heating rates has been measured by DSC (Fig.4). Independent of the nature of the sample, Tg is a function of the heating rate (+β and -β) hence the change in cp is governed by the rate β. But at low rates (+β) Tg is governed by the rate law of the transition, leading to the appearence of a discontinuity near β = 0 (see Fig.4).

Consequently, the "real" Tg temperature is meaningless and is surely not the extrapolated one at $\beta = 0$. This fact can be considered to be similar to the determination of the "starting temperature" of a chemical reaction despite the fact, that a chemical reaction goes on even at low temperatures, but at a very low rate.

(1) B. Wunderlich in E.A.Turi Ed. "Thermal Analysis of Polymeric Materials", Academic Press, New York (1981) p. 169

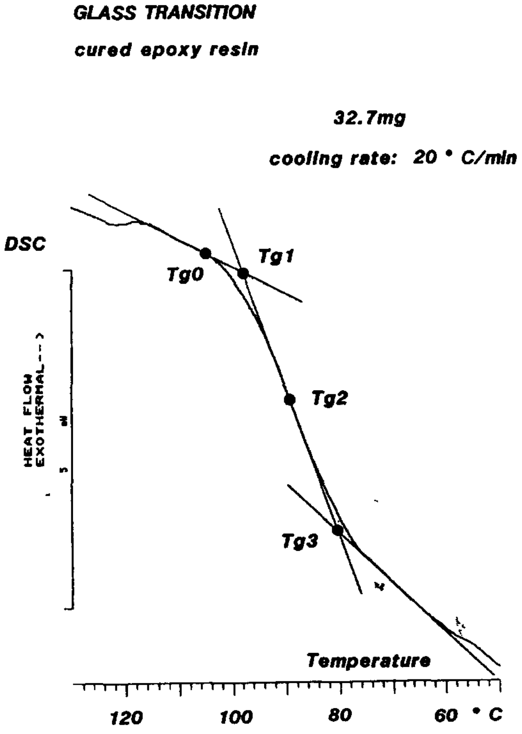

Fig.1:

DSC curve of an epoxy resin with construction lines for determination of characteristic glass transition temperatures Tg0...Tg4.

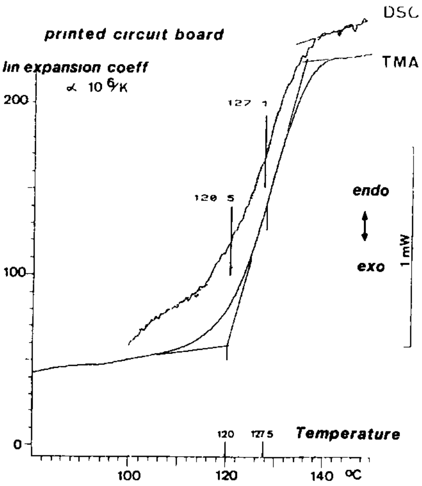

Fig.2: Glass transition of a printed circuit board (brominated bisphenol A resin) measured by DSC (heat flow curve) and TMA (curve of linear expansion coefficient) at a heating rate of 10 K/min.

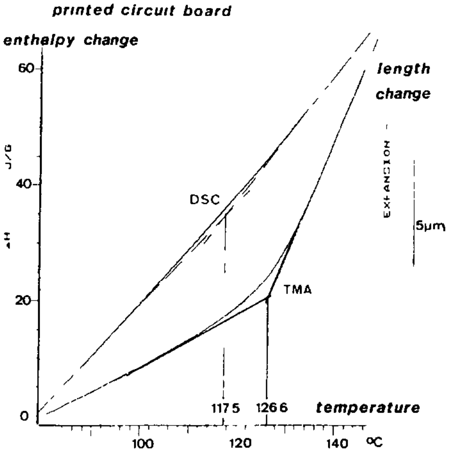

Fig.3: Same measurements as in Fig.2 but represented in form of integral curves: DSC (enthalpy change) and TMA (length change). Tg is defined by the intersection point of the two tangents at the curve.

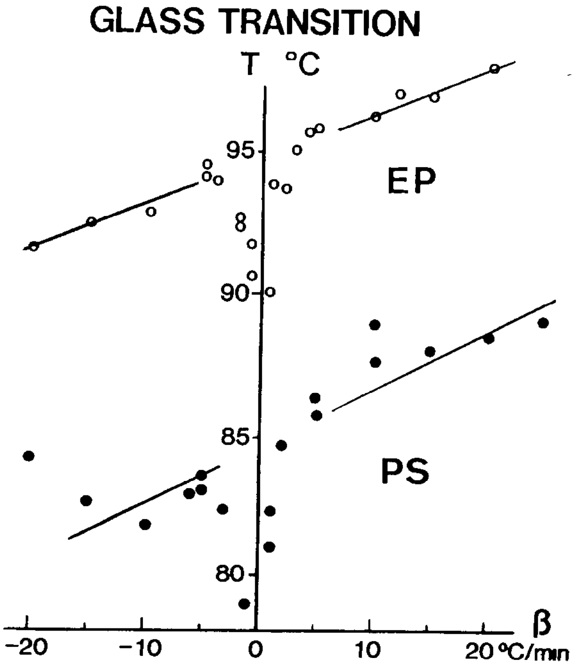

Fig.4: Glass transition temperature (Tg2) in function of heating rate β for an epoxy resin (EP) and a polystyrene (PS).