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DETERMINATION OF VISCOELASTIC PROPERTIES WITH TMA, DMTA AND DSC

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ABSTRACT

Viscoelastic properties mainly determine the application possibilities of polymers. Because of the generally high sensitivity required to see changes in the elastic properties, thermomechanical methods become increasingly important compared to calorimetric methods. On a sample of thermoplastic PU, and a unidirectional carbon fibre reinforced epoxy resin, a comparison is made between performance of TMA, DMTA and DSC to determine the viscoelastic properties.

INTRODUCTION

For organic macromolecules the internal mobility of molecular chains and regions influences greatly the thermal expansion, the elastic properties and heat capacity. Therefore, the TA methods TMA, DMTA and DTA/DSC are used to determine temperature dependent changes of elasticity.

The thermal expansion is characterised by the possible vibration amplitudes of the atoms and molecules in their equilibrium position. With additional mobility of molecules or molecule regions, e.g. at the glass transition, the expansion coefficient changes to a higher value. Therefore, the exact measurement of thermal expansion with dilatometry/TMA is a reliable means to determine transition temperatures. However, if an expansion measurement is made with compressive stress (or tensile stress) on the sample, the result is a deformation of the sample because of the energy dissipated for relative movements of molecules (viscoelastic behaviour) or because of the energy stored (and recovered when releasing stress) (fully elastic behaviour); the TMA measurement then shows an overlapping of both effects. The viscoelastic reaction of a sample, contrary to the fully elastic energy storage, is a time-dependent process. When applying a dynamic stress (alternating stress) a separation of both effects is possible. The description of this overlapping effect, dynamic Young's modulus (E) can be expressed: -

$$E = E' + i E''$$

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where E' describes the ideal elastic behaviour (stiffness, storage modulus) and E" the viscous behaviour (energy dissipation, loss modulus). The phase shift between E' and E", expressed as tanδ is a measure of the damping properties of a viscoelastic material.

To determine the dynamic E modulus, two methods are available:
TMA with defined load change at preselectable frequency and DMTA with dynamic bending stress at preselectable fixed frequency.

The principle difference between both methods:

The bending stress in the DMTA produces defined tension relations in the whole sample, the TMA produces a stress (compressive stress) only in part of the sample. Therefore the indication of viscoelastic transitions with DMTA measurements is clearer. A comparison with DTA/DSC for the determination of phase transitions of second and higher order shows the higher sensitivity of the dynamic mechanical TA methods in this field.

RESULTS AND DISCUSSION

On an unidirectional carbon fibre reinforced epoxy resin an exact determination of the glass transition temperature was carried out, dependent on the moisture of the sample. Here this T_g determination is compared on a dry sample with TMA, DMTA and DSC.

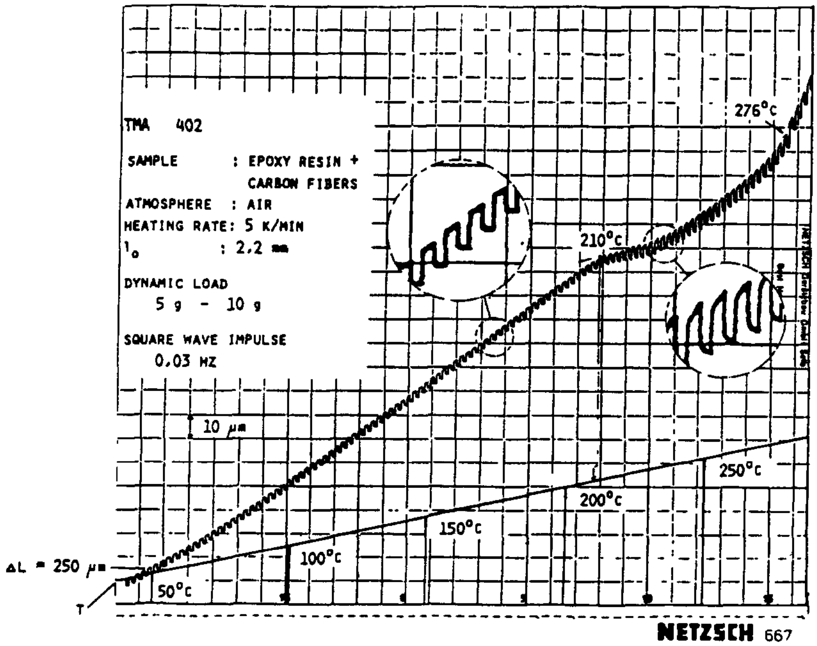

Fig. 1: Expansion of carbon fibre reinforced epoxy resin during dynamic TMA measurement

The measurement of the thermal expansion with constant and dynamically changing stress with TMA was made at right angle to the fiber direction. With dynamic load change between 5 and 10 g at a frequency of 0,03 Hz (square impulse) and a heating rate of 5 K/min, the sample shows linear expansion up to 200°C. At 210°C the glass transition can be determined from the point where the expansion curve (Fig. 1) deviates.

The impulse amplitude and shape above 210°C shows an increasing plastic behaviour of the sample. In this viscous range, above 210°C, considering single impulses (see segment enlargement Fig. 1) the shear modulus G (storage modulus and loss factor) can be determined from the impulse distortion, and this gives also a value for the energy dissipated in the sample. The sample deformation achieved by the changing load only applies to a limited part of the sample so that the quantitative result for the elastic constants is of restricted accuracy.

By the uniform stress which is induced by DMTA on the sample, the transition range of the epoxy resin sample can be better resolved. The glass transition starts with a decrease of stiffness in a first stage at 195°C, the main effect starts at 225°C. The stiffness, as well as the damping factor, show very constant values from ambient temperature to 190°C (log E' (Pa) = 10,1; tan δ = 0,02).

The calorimetric study of the viscoelastic transition of the epoxy resin sample with DSC shows only a relatively indistinct change of the base line at 180°C (endothermal) as well as exothermal curing or oxidation effects from 260°C. The glass transition at 210°C obtained from TMA and DMTA cannot be seen with DSC.

CONCLUSION

Dynamic thermomechanical analysis methods are well suited to determine viscoelastic properties on solids. The sensitivity for transition processes surpasses that of DSC. The calculation of the elastic constant (E or G) should only be made when exactly knowing the stress - deformation relationship of the sample used.