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Dedicated to Prof. Dr. H. J. Seifert on the occasion of his 60th birthday

THERMOMECHANICAL ANALYSIS OF QUARTZ, GLASSES AND WOODS

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The expansion and viscoelastic behavior of natural and synthetic materials changes during thermal treatment. Thermomechanical analysis (TMA) is the method to determine these mechanical properties directly as a function of time and temperature. Depending on the selected measuring mode either the expansivity (dilatometry), the viscous flow or the elastic behaviour can be investigated. Young's modulus is calculated from flexure and compression measurements.

To show some of these possibilities quartz, various glasses and woods have been analysed. The solid transition of $\alpha - \beta$ quartz revealed a minimum of the modulus of elasticity during the transition. Flexure measurements of wood samples during degradation show the different elastic regions.

Among many other physical or chemical properties, the elasticity and viscosity of natural and synthetic materials change during thermal treatment. DSC and TG measurements provide information on thermal effects such as uptake or release of heat and the loss of material which also influences the elastic behaviour. But TMA can determine these mechanical properties directly as a function of time and temperature. Knowledge of these properties is important because they influence the application range of the final products. Using TMA techniques, rapid measurements of even small-sized samples can be performed. One property to be determined is the elastic modulus, e.g. the measurement of the deformation (strain) produced by a force. The relation between these values is called the Young's modulus (E = stress / strain). Another, opposing physical characteristic is the viscosity of a substance, which describes the flow under shearing stress. Using a TMA with static or dynamic load, the combined influences of elasticity and of viscosity can be investigated even as a function of temperature.

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The range of materials to be investigated by the described TMA technique is very large and includes composite materials such as wood and inorganic materials such as glasses and single crystal quartz. In all these materials a pronounced change of elasticity or viscous flow could be observed as a function of temperature and time due to phase transitions, degradations or changes in plastic elastic behaviour.

Experimental

A Mettler TA4000 system with a TMA40 measuring cell (Fig. 1) has been used. The static or dynamic load is automatically applied by the TMA probe. Dynamic load TMA (DLTMA) is herein defined as the technique in which the deformation of a substance under changing load is measured as a function of the temperature while the substance is subjected to a controlled temperature program (dynamic or isothermal). The alternating load has a cycle time of 12 seconds and changes between two values. Hence, this technique simultaneously provides information on temperature and force. Depending on the sample arrangement, different probes have been used; their shapes are described in Fig. 2. The arrangement of the sample in the TMA for the measurement of the Young's modulus is shown as a cross-sec-

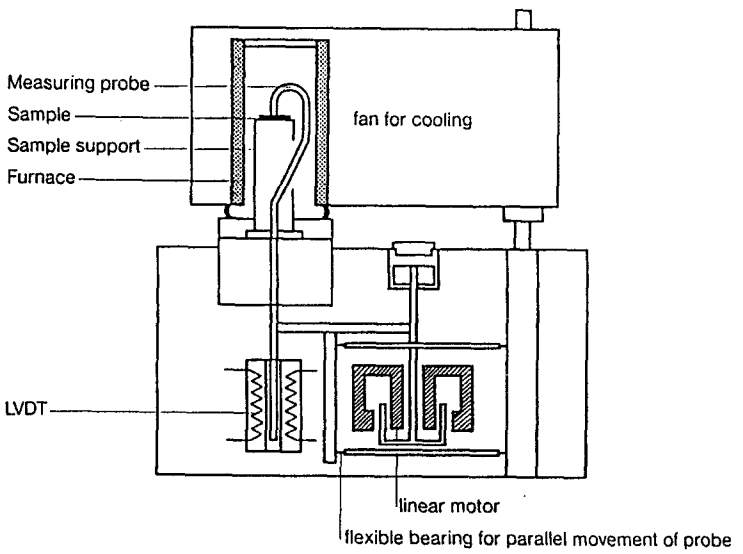

Fig. 1 Simplified cross section of the Mettler TMA40. The load to the sample is applied by the electromagnetic force in the linear motor. The size changes of the sample are detected by the LVDT

tion (Fig. 3a). Figure 3b indicates the specimen position and dimensions. An automatically alternating load in the range of 0 to 0.5 N can be applied when using all accessories.

The DSC measurement (Fig. 11) has been performed with the Mettler TA4000 system with DSC 20 module using standard aluminum crucibles in air.

The investigated materials are hydrothermally grown quartz, various technical glasses and bamboo, sequoia sempervirens, balsa and beech wood.

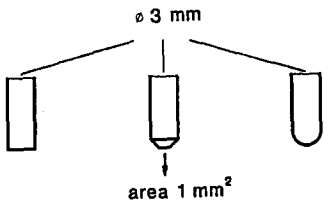

Fig. 2 Shapes of the three different probes used in the TMA40. The probes are made from fused silica

Results and discussions

Elasticity change of quartz during α - β phase transition

In thermal analysis, DSC–measurements of the heat of transformation of the $\alpha - \beta$ phase transition [2] are used for the identification of quartz. The phase transition at 573° is only due to a change of the bond angle of the linked SiO_4–tetrahedra. This change alters the symmetry from the trigonal-trapezoidal class to hexagonal. The corresponding space groups are D_3^4 – $P3_1\,21$ and D_3^6 – $P3_2\,21$, respectively [1].

The small forces applied in the TMA cell do not allow the measurement of high Young's moduli by compression. In this case the modulus of flexure may be measured.

The $\alpha - \beta$ quartz transition can also be observed by TMA measurements. [2]. The expansion stops immediately after the change in the bond angle of the linked SiO_4 tetrahedra. These results explain in an unorthodox way why quartz glass is temperature 'shock proof'. (It resists breakage, that means, that there is only a very small change of the expansion coefficient over a broad temperature range.) Reproducible curves of natural grown quartz can be obtained only after the samples have been heated and cooled two or three times.

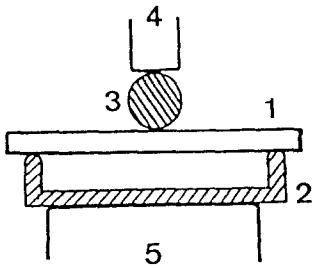

Fig. 3a Cross section of the bending accessory for the TMA40. The sample, in the shape of a thin bar (1), is supported by the U-shaped device (2) and stressed by the probe (4), centeredin the middle of the sample. Between probe and sample a cylindrical bar (3) is placed to apply an equally distributed force. The metal parts (support and bar) are made of Ni alloy. Sample support (5)

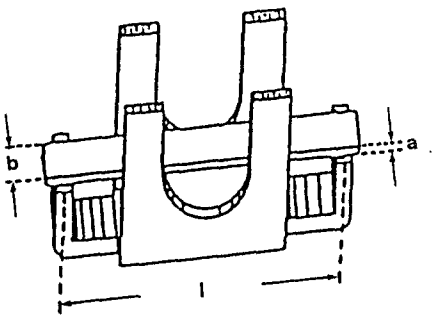

Fig. 3b Indication of specimen position and dimensions

The modulus of elasticity (flexure) of single crystal quartz has been determined using the accessory for bending measurements (Figs 3a and 3b). One cut was taken parallel, another perpendicular to the *c*–axis (Fig. 4). The dimensions of the samples were: length = 18 mm, thickness = 0.8 mm and width = 3 mm.

The bending measurements show in the region from 568 to 576°, where the $\alpha - \beta$ phase transition takes place, that the values of elasticity in the low temperature phase are larger than in the high temperature phase (see Fig. 5). The results of the heating and cooling of quartz crystal (1 deg/ min) in air are presented in Fig. 6. During the transition a strong change in elasticity takes place. Hence, during the phase change, the crystal becomes 'softer', i.e. the Young's modulus (by bending) shows the weakening of the interatomic links during the transition. Furthermore, a pronounced difference in the flexure behaviour was observed in quartz samples cut in dif-

ferent directions, parallel, perpendicular and at an angle of 45° to the hexagonal *c*–axis (see Fig. 6).

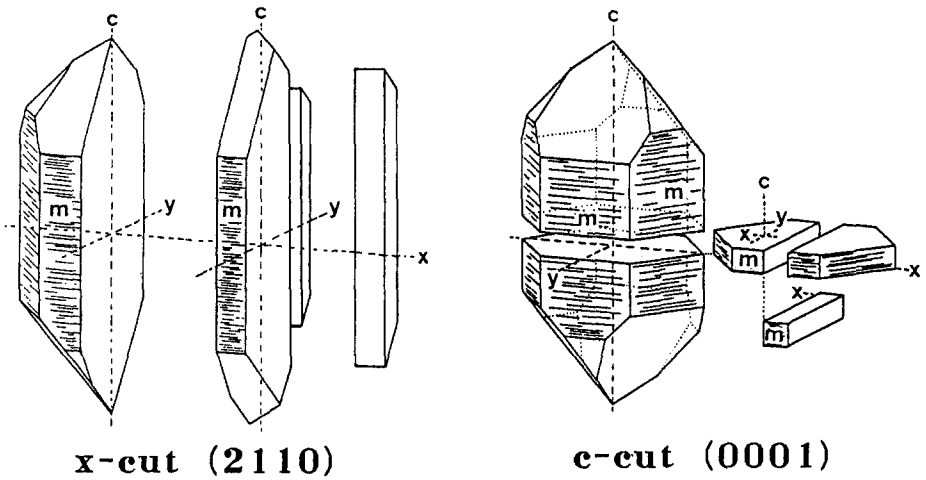

Fig. 4 Sample cut from the quartz crystal

The formula for the calculation of the Young modulus E (by bending) is, for rectangular bars:

$$E = (F \cdot l^3)/(4 \cdot s \cdot a^3 \cdot b)$$

Parameters:

E	MPa:	Young's modulus
F	N:	increase in force acting on the sample giving a flexure [s]
l	mm:	distance of supports (effective length of sample) = 17.0 mm
a	mm:	sample thickness (vertical)
s	mm:	flexure of the sample measured by TMA 40 – the blank has to be substracted
b	mm:	sample width (horizontal)

Transformation range and softening of glasses [3]

Rod shaped soda-lime glass and soda-titania-silicate glass samples of approx. 4 mm in diameter were used for TMA measurements under constant load (0.30 N). Both of these glass samples were prepared in the annealed state (slow cooling) and in a highly stressed state by rapid quenching. Owing to the different specific volumes which are 'frozen into' different zones of

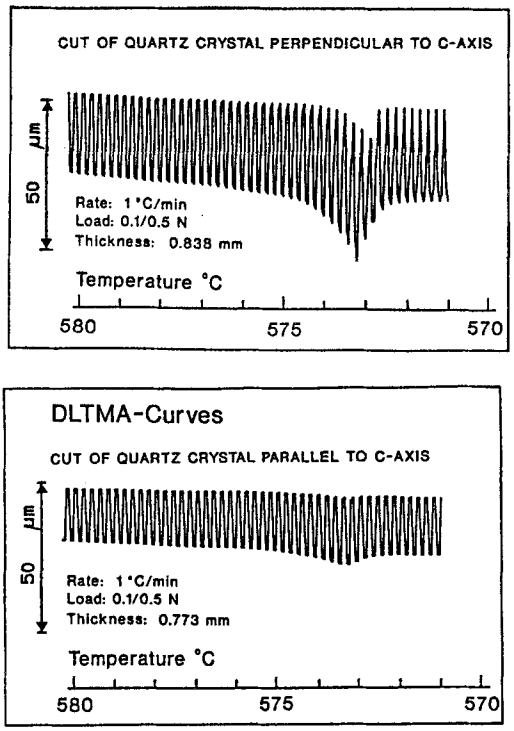

Fig. 5 Original tracings of a DLTMA cooling curve for quartz (flexure measurement during the phase transition)

the quenched glass, a broadening and shift of the glass transformation range should be observed.

This effect of quenching is not very pronounced for soda-lime glass, probably due to stress release during cutting of the sample and consequent heating of the sample (Fig. 7). However, there is a strong influence of the thermal history on the TMA curve of the higher softening soda-titania-silicate glass (Fig. 8). Further measurements on precisely quenched samples are necessary in order to explain the discontinuity in the expansion curves.

Elasticity changes of wood during the decomposition of cellulose

TG and DSC measurements showed that the main components of wood, i.e. cellulose and lignin, have different thermodynamic stabilities; cellulose decomposes in an oxidizing atmosphere at a temperature range from 250 to 350° and lignin from 350 to 450°. The limits of the temperature ranges

depend on the type of wood, on the structure and porosity and on many other factors [4].

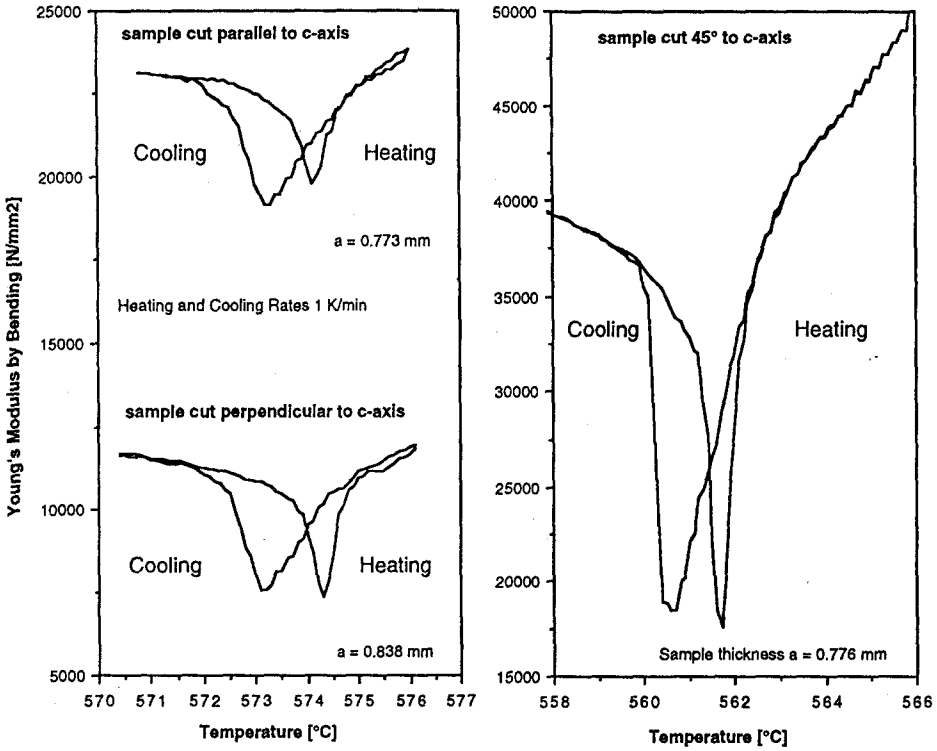

Fig. 6 Modulus of elasticity of quartz during phase transition (cooling and heating) calculated from the measurements as shown in Fig. 5. The accuracy of the temperature of $\alpha - \beta$ transition depends on heating rates, crystal cut, nature and sample size (These investigations are still being carried out.)

The elasticity and rigidity of wood, a natural composite material, has been investigated during the degradation of cellulose and lignin. In the first series of experiments the influence of sample thickness for optimal measurements was investigated. Figure 9 shows the flexure measurements of beech wood slices of different thicknesses (0.5 to 2 mm). The sample dimensions, length by width, were 17×3 mm respectively. The positioning of the samples in the measuring setup has been described in the previous chapter (see Figs 3a and 3b).

At the heating rate used, thick slices carbonize too slowly and break only at high temperatures. In addition, the measured flexure is very small. A very thin sample bends completely due to the applied mechanical load before

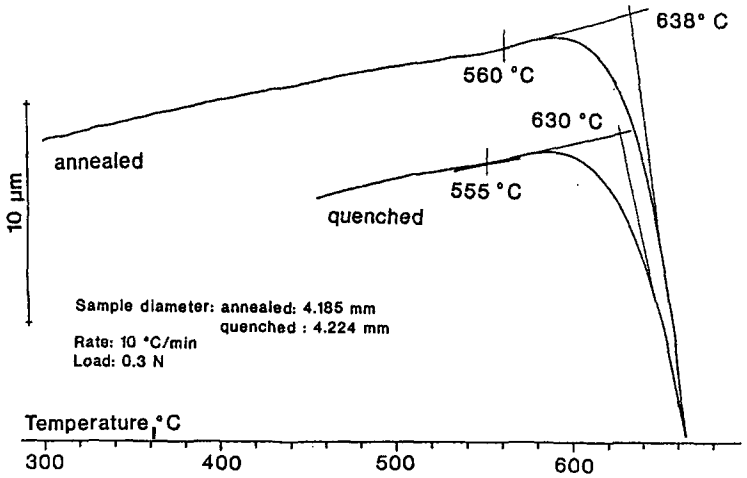

Fig. 7 TMA curves of annealed and quenched soda-lime glass

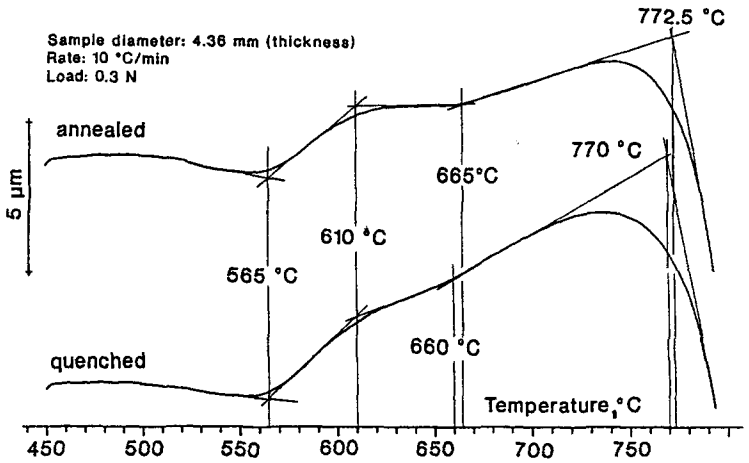

Fig. 8 TMA curves of annealed and quenched soda-titania-silicate glass

degradation. Using exactly the same sample size each DLTMA curve is highly reproducible. Even the breakdown of the structure takes place within a range of $\pm 3^{\circ}$. A thickness of 1 mm has been selected as optimal for the measurements, as seen from results from other types of wood. Figure 10 shows four different types of wood which have been investigated in the same way as the beech wood. After the oxidative decomposition of the cellulose, the breakdown of all the different woods can be detected in the range dif-

ference of approximately 60°. A comparison of such a TMA curve with a DSC curve confirmed that a breakdown takes place only after the cellulose component is completely decomposed (see Fig. 11).

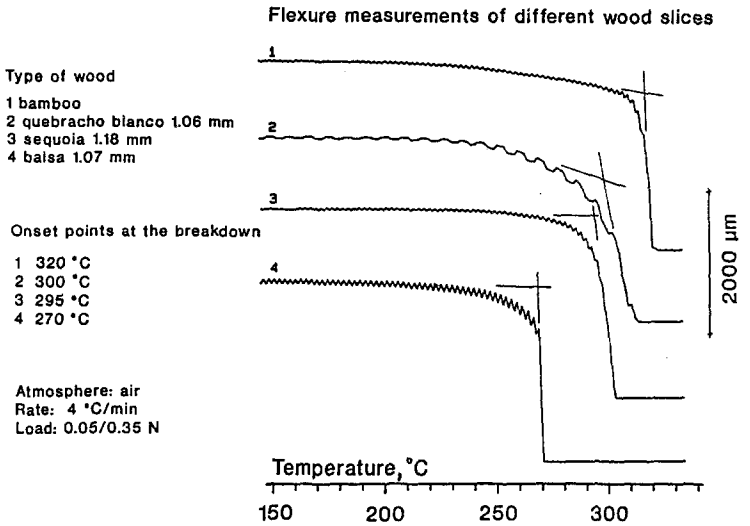

Fig. 9 Thermal stability of beech wood as shown by DLTMA curves

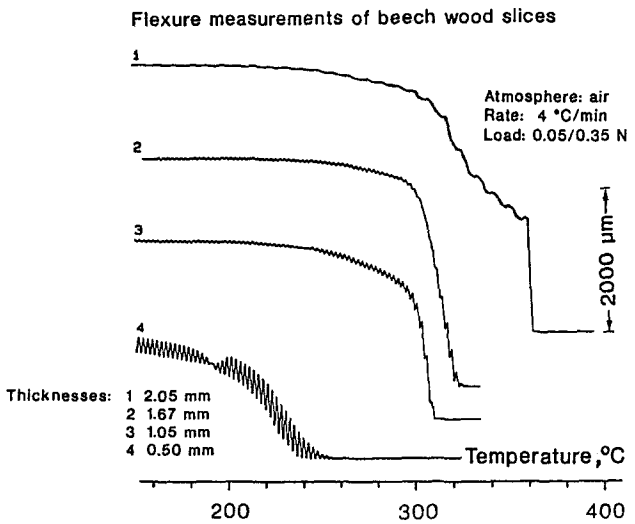

Fig. 10 Thermal stability of different kinds of wood as shown by DLTMA curves

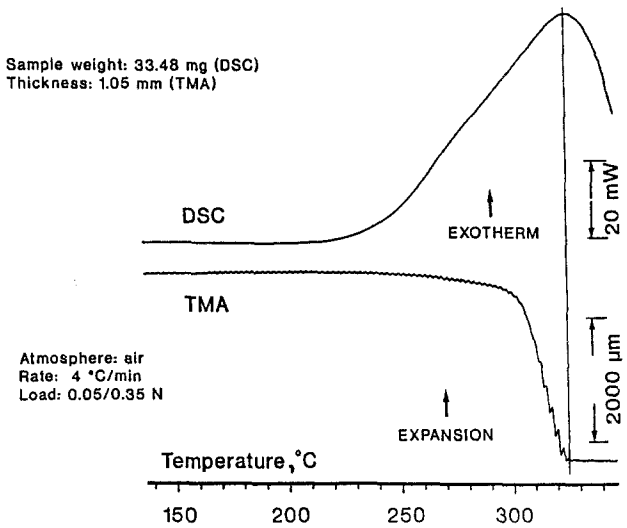

Fig. 11 Comparison of DSC and DLTMA curves for beech wood under identical thermal treatment

Conclusion

TMA methods proved to be very suitable for the investigation of the temperature influence on the viscoelastic behaviour of various materials. It provides a fast quantitative or qualitative method for screening the quality of industrial products such as hydrothermally grown highly pure crystalline quartz. Depending on the measuring mode, e.g. the applied probe-force, different information on the mechanical properties can be derived from TMA: dilatometry (linear expansion coefficient), penetrometry (viscous flow, soft ening), stress/strain-relation (Young's modulus of elasticity by DLTMA). The results on the flexure measurements by TMA and the related physical or chemical changes (cold crystallization, glass transition, polymorphic transition and degradation) coincide with findings from DSC studies.

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Zusammenfassung — Das Ausdehnungs- und viskoelastische Verhalten natürlicher und synthetischer Materialen verändert sich bei Wärmebehandlungen. Das Verfahren zur Bestimmung dieser mechanischen Eigenschaften als eine Funktion von Zeit und Temperatur ist die thermomechanische Analyse (TMA). In Abhängigkeit vom gewählten Meßverfahren können Ausdehnungsvermögen (Dilatometrie), Reibungsströmung oder das elastische Verhalten untersucht werden. Das Elastizitätsmodul wird aus Biegungs- und Kompressionsmessungen ermittelt.

Um einige dieser Möglichkeiten aufzuzeigen, wurden Quarz, verschiedene Gläser und Hölzer analysiert. Die Feststoffumwandlung -ß-Quarz zeigt während der Umwandlung ein minimales Elastizitätsmodul. Biegungsmessungen an Holzproben zeigen bei Zersetzung verschiedene elastische Regionen.