Expansion and shrinkage of fibers

Introduction

Fibers are produced worldwide in enormous quantities. More than 20 million tons of synthetic fibers and 20 million tons of natural fibers are manufactured each year. The total length of these fibers corresponds to about 10 000 times the distance from the earth to the sun.

A characteristic feature of a fiber is that its length is much greater than its diameter. The great anisotropy of the microstructure and the physical properties originating from spinning and stretching processes are two of the main reasons for the special properties and peculiarities of fibers [1, 2]. Spinning, stretching and annealing are in fact the most important steps in the manufacture of fibers. These processes determine properties such as the modulus of elasticity (Young's modulus, E) and toughness that are required for the application envisaged. Coloring properties, shrinkage (contraction of fibers) and thermal stability are determined by the size, number and orientation of the crystallites, as well as the molecular structure in the amorphous regions. Thermomechanical analysis (TMA) in particular, as well as DMA, DSC, TGA and TOA are all excellent techniques for the investigation of the effects of temperature and mechanical loading on fibers and yarns. They allow the relationship between structure, properties and the manufacturing process [3] to be investigated. Very often comparative measurements under identical conditions are sufficient to characterize transition temperatures, expansion and shrinking behavior. TMA measurements also yield numerical values such as the coefficient of linear expansion, Young's modulus, E, and the force of contraction as a function of temperature.

Terminology

Fiber strength is normally characterized by its linear density. The SI unit is the tex. The unit decitex (dtex) is often used, which is the weight in grams of a length of 10 000 m of fiber (or in other words: 1 dtex = 1 µg/cm). In order to compare fibers of different linear density with respect to their expansion behavior, the samples are usually heated under the same tensile force, e.g. 0.1 mN/dtex.

Example: a piece of silk thread has a length of 22 cm and a weight of 0.363 mg. The linear density is therefore 16.5 dtex. The thread was subjected to a load of 0.002 N in the TMA.

The average linear coefficient of expansion, α_l, in the temperature range T_1 to T_2 can be calculated from the change in length in this temperature range, ΔL, and the original length L_0 according to the equation:

$$\alpha_l = \frac{\Delta L}{L_0 (T_2 - T_1)}$$

The module of elasticity, E, is determined by the ratio of the tensile force to the expansion:

$$E = \frac{\Delta F / A}{\Delta L / L_0}$$

Here ΔF is the change in the tensile force, A is the cross-sectional area of the fiber and DL is the change in length as a result of the change in the tensile force. This assumes that the change in length, DL, is small compared with the total length, L_0.

In the TMA, the change in the tensile force is caused by a stepwise change in the load. During the heating measurement, the tensile force exerted on the sample is, for example, modulated with a constant value of 0.06 N with a period of 12 s and an amplitude of 0.01 N. This mode of operation is known as Dynamic Load TMA (DLTMA).

Experimental details

The measurements described in this article were performed with a METTLER TOLEDO STARe System and the TMA/SDTA840 module. The samples were prepared for measurement by mounting them in the fiber attachment accessory. The fibers were placed in copper clips and fixed in place by mechanically squeezing the clips together. The effective length of fiber between the two clips was always 13 mm. Samples prepared in this way were mounted between the hooks of the sample holder (see Fig. 1). During the heating measurement, the soft-

Sample	Description	Linear density [dtex]	Tensile force in the TMA [N]
Wool	Woll yarn	1157	0.116
Cotton	Cotton yarn, merceried	298	0.030
Silk	Silk thread	17	0.002
Hemp	Hemp fibers from a piece of string	57	0.006
Hair (horse tail)	Horse hair, black from a horse tail	324	0.033
Hair (human)	Human hair	47	0.005
PAN	Polyacrylnitril, yarn	219	0.022
PA 66 bulky	Nylon, crimped (Helanca)	252	0.025
PA 66	Nylon yarn	1400	0.144
PA 66	Nylon, 6 fibers (from yarn)	44	0.004
PA 66	1 fiber, 0.1 mm (Viscosuisse type 162)	90	various forces
PET	1 fiber 0.048 mm (Viscosuisse, type 200)	25	0.003
PET	1 fiber, 0.1 mm (Viscosuisse, type 260)	108	0.011
PE	1 fiber (Dyneema®)	13	0.002
Kevlar	Several fibers	85	0.009
Carbon	Several fibers	101	0.050
Aluminum	Aluminum wire, 0.3 mm	-	0.050
Copper	Copper wire, 0.2 mm	-	0.050
Fused Silica	Quartz fiber glass 0.1 mm	-	0.050

Table 1. List of the various fibers measured with details of their origin, linear density and the tensile force used in the experiment.

ware compensates for both the expansion of the clips (the effective length is 1 mm) and the expansion of the quartz sample holder.

The sample temperature was checked and adjusted using an indium melting point reference sample. To do this, two small pieces of indium with a total weight about 10 mg were squeezed together around a sample of fiber (see Fig. 1). This allowed the melting point of indium to be measured several times at different heating rates - the melting point of the fiber must of course be appreciably higher. The thermocouple for the measurement of the sample temperature was positioned about 3 mm away from the center of the fiber. As can be seen in Figure 2, the SDTA signal records the melting of the indium sample. The SDTA signal is the temperature difference between the measured temperature of the sample and the program temperature [4]. The SDTA curve in Figure 2 shows a small peak due to the melting of the indium standard. The onset temperature was evaluated in the same way as for DSC curves. The TMA curve also shows a small step in the same temperature range. The reason for this is that the temperature of the short section of fiber that is enclosed by the indium sample remains constant. This section of the fiber does not therefore expand while the indium melts.

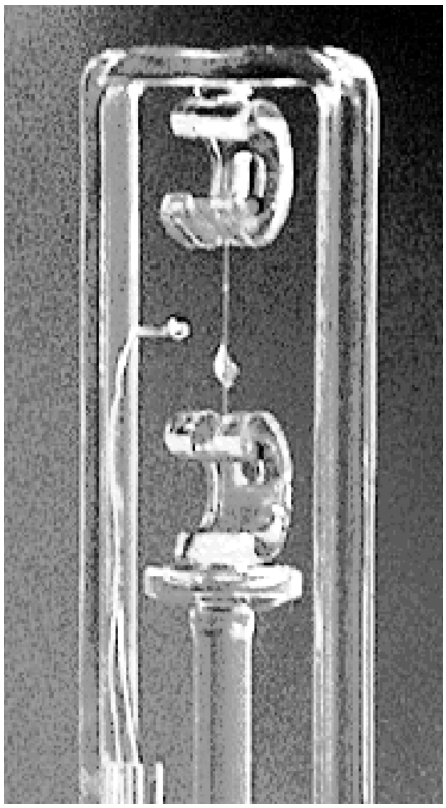

Fig. 1. Quartz glass sample holder with fiber sample mounted. A piece of indium is attached to the fiber.

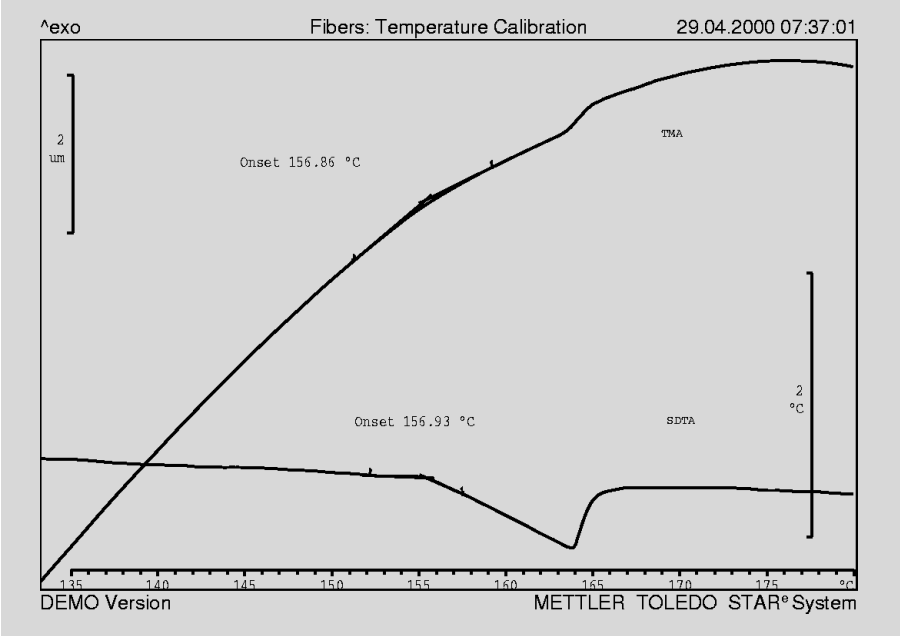

Fig. 2. TMA and SDTA curves showing the temperature check with indium on a PET fiber (see Fig.1). Heating rate: 10 K/min, stationary air atmosphere. SDTA curve: exothermic in the upward direction; TMA: expansion in the upward direction.

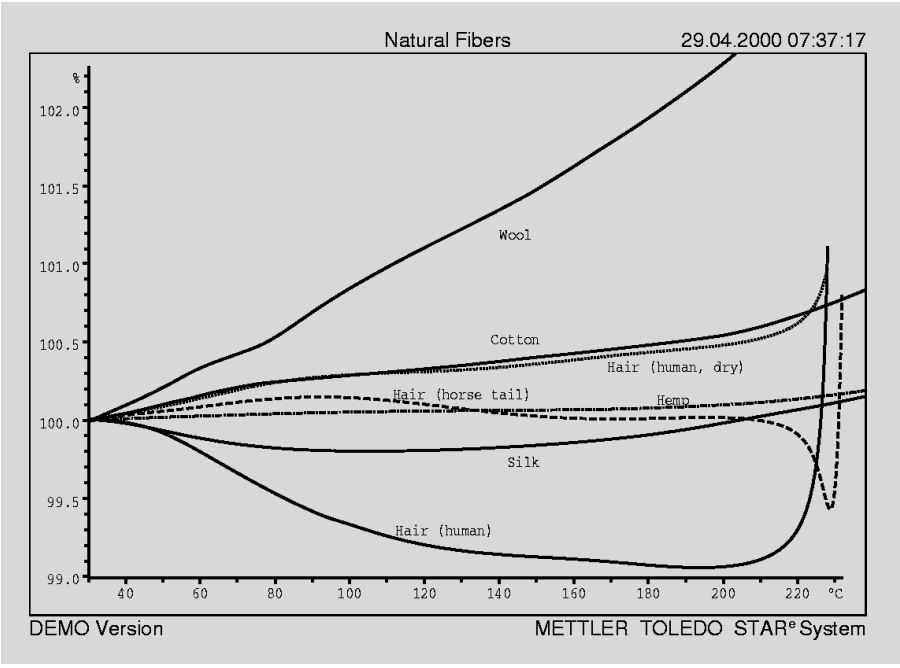

Fig. 3. Natural fibers (see Table 1). For clarity, dry hair is shown as a dotted curve and horsehair as a dashed curve.

The fiber samples were measured in the range 30 °C to 270 °C at a heating rate of 10 K/min in a stationary air atmosphere with a tensile force 0.1 mN/dtex. Table 1 shows a list of the fibers used for the measurements. Any deviations from the experimental conditions given above are noted together with the results of that particular sample.

Results

Shrinking behavior

Examples of TMA curves of natural fibers, synthetic fibers, and special fibers and wires are shown in three separate diagrams.
A detailed discussion of the thermoanalytical measurement of fibers is given in reference [2].

Natural fibers (Fig. 3)

Human hair and silk both shrink (i.e. contract) initially due to drying. Decomposition begins above 220 °C and the fibers rapidly tear. Horsehair and hemp show

relatively little change in length below 200 °C (< 0.1 %) under the tensile force used. Wool, however, expands in the same range by more that 2 %. Dry human hair shows a similar behavior. Cellulose fibers (e.g. cotton and hemp) show far greater thermal stability compared with fibers of human or animal origin and expand until they decompose and break at about 400 °C.

Synthetic fibers (Fig. 4)

Synthetic fibers, in contrast to fibers of natural origin, nearly always show a marked shrinkage that is very dependent on the manufacturing process, and also behave thermoplastically. With special extremely orientated fibers (e.g. Kevlar, Fig. 5), the degree of shrinking is low (< 0.5%) up to high temperatures (450 °C) and is also reversible from the second heating measurement onward. Normal, irreversible shrinkage begins above the glass transition temperature (e.g. PET: 80 °C; PA66: <50 °C depending on the moisture content; PAN: 90 °C) and increases shortly before melting. Melting is indicated by a very rapid increase in length of the fibers. The extremely rapid shrinkage of PE before melting is a result of the special manufacturing process, in which the fibers are stretched after the spinning process. Since the measurement force is normalized to a linear density (0.1 mN/dtex), the TMA curves of a yarn (with many fibers) are identical in form to those of an individual fiber taken from the same yarn. This comparison shows the excellent reproducibility of such measurements (see PA66 with 44 and 1400 dtex). The PET fibers used have different type designations and their curve forms also show somewhat larger differences. A comparison of the curve of PA66 (252 dtex) to the other PA66 curves shows how great the influence of processing on thermal expansion can be. Polyacrylonitrile, (PAN), is dimensionally very stable up to about 130 °C and shows only small changes in length of less than 0.5%. At higher temperatures, however, PAN expands more rapidly than wool for example.

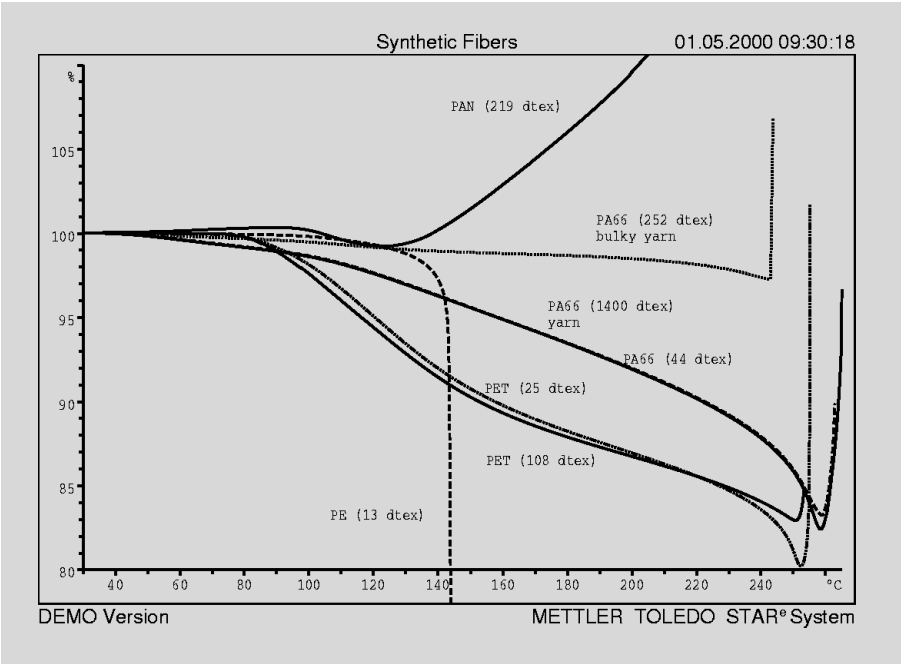

Fig.4: Synthetic fibers made from different polymers (see Table 1)

Special fibers and metal wires (Fig. 5)

Carbon fibers and quartz glass fibers show only a very low degree of expansion over a wide range of temperature. Quartz glass fibers are brittle and are therefore difficult to mount. They are, however, useful as "inert" material for the determination of the baseline (blank curve).

The fiber attachment can also be used to mount thin wires. The example shows the determination of the linear coefficient of expansion (α_l) of aluminum and copper wires. In contrast to polymer fibers, α_l for metals is only slightly temperature dependent and the values are much smaller (e.g. 25 ppm/K for aluminum compared to 125 ppm/K for wool). The mean values of α_l for aluminum and copper are entered in the diagram (calculated from the average slope over a range of 40 K). The literature values for the relevant temperature ranges are also given (upper left).

Effect of conditioning

TMA is not just a technique that can be used to measure a new sample of a fiber. It can also be used to condition samples thermally. Both the temperature and the applied tensile force have a large effect on the subsequent thermal behavior, which again can then be measured with TMA. This conditioning procedure allows process conditions to be simulated or understood, and their effect on the thermal behavior of the fibers to be investigated. To illustrate this, a polyamide fiber was cooled with different tensile forces and then heated again using a weak tensile force of 0.1 N (see Fig. 6a). Figure 6b shows the heating curves for different values of the tensile force, whereby the cooling beforehand was performed with a tensile force of 0.1 N. The larger the tensile force used on cooling, the greater was the shrinkage afterward on heating. If the tensile force used for cooling was lower that used for the subsequent heating, then the fiber expands until the force of contraction is sufficiently large to counteract the expansion.

Determination of the force of contraction

One would sometimes like to determine the force of contraction that develops when a fiber is heated but held at constant length. This type of measurement is only possible if the TMA is equipped with a suitable accessory (e.g. a converter). If, however, the heating curves of individual samples of the same fiber are measured with different tensile forces in the TMA, then the force of contraction can be determined directly as a function of temperature from the measurement curves (Fig. 7). The temperatures at which the length of the fiber after thermal expansion is the same as its initial length are read off from the array of curves. In Figure 8, the temperatures corresponding to the points of intersection of each TMA curve with the horizontal straight line through the starting point (at 30 °C) are plotted as a function of the force applied. The data points show a pronounced increase of the force of contraction above the glass transi-

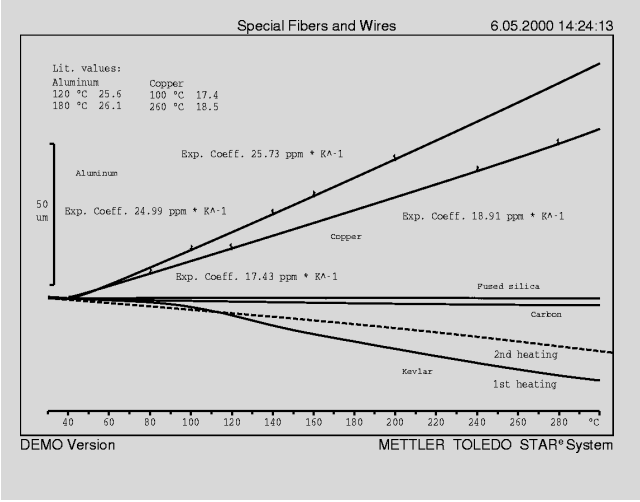

Fig. 5. Special fibers and metal wires

tion temperature of 80 °C. Recrystallization and relaxation processes [5] that take place above 100 °C are the cause of the slow decrease of the force of contraction at higher temperatures.

The great advantage of TMA measurements with different loads is that with relatively few measurements, the force of contraction and the shrinking behavior can be simultaneously measured without having to change the configuration of the instrument. A second heating measurement performed using the same measurement parameters does not show any force of contraction.

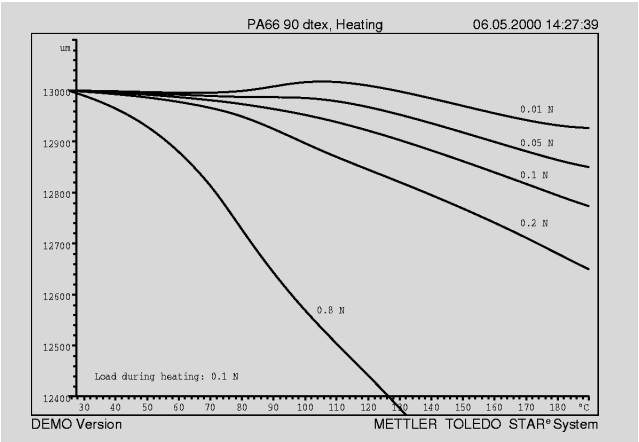

Fig. 6a. Thermal conditioning and measurement of the expansion/ shrinking behavior of a Nylon fiber (PA66, 90 dtex) using different tensile forces. The fibers were conditioned by cooling from 190 °C to 35 °C under a tensile force of 0.1 N. The subsequent measurements were performed with the tensile forces noted next to the curves.

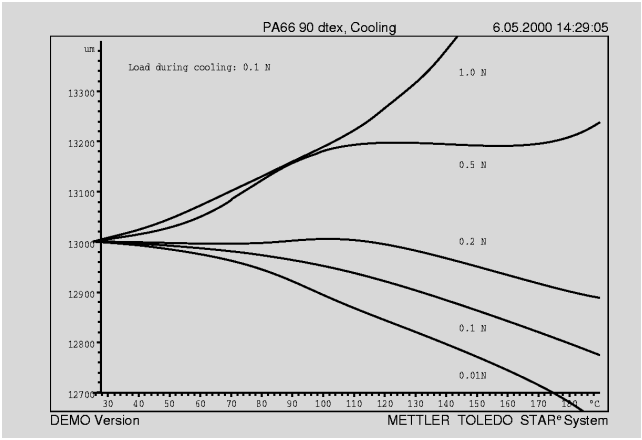

Fig. 6b. Measurement of the expansion and shrinking behavior of a Nylon fiber (PA66, 90 dtex) after conditioning the fiber by cooling from 190 °C to 35 °C under the tensile forces noted next to the curves. The subsequent measurements were performed with a tensile force of 0.1 N.

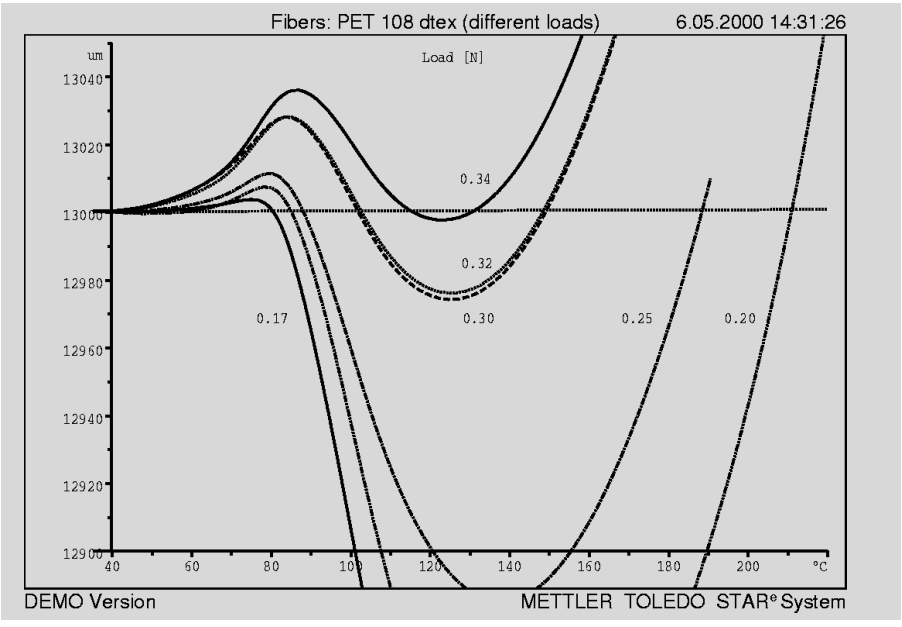

Fig. 7. TMA curves of PET fibers (108 dtex). A different constant tensile force was used for each sample for each heating run (30 °C to 220 °C at 10 K/min). This yields an array of shrinkage/expansion data curves.

Determination of Young's modulus

In addition to the investigation of shrinkage, one of the main applications of thermomechanical analysis for the characterization of fibers is the determination of Young's modulus, E, and its dependence on temperature. With the TMA/SDTA840, a periodically changing force is used instead of the constant force (DLTMA operating mode). The resulting expansion is used in the evaluation to calculate the value of Young's modulus. During heating, the sample is modulated with a periodic, stepwise change of force (period usually 12 s, amplitude typically 0.01 N). This also allows the temperature dependence of Young's modulus to be measured during shrinking. Figure 9 shows the DLTMA curves of a PET fiber. Young's modulus is calculated from the amplitude of the peri-

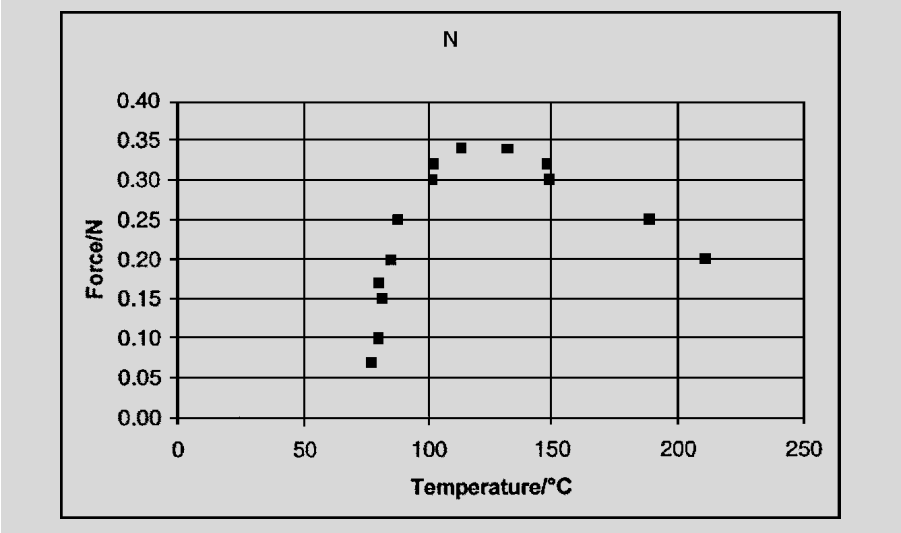

Fig. 8. The force of contraction of PET (108 dtex): the data points were determined from the curves in Figure 7 as described in the text.

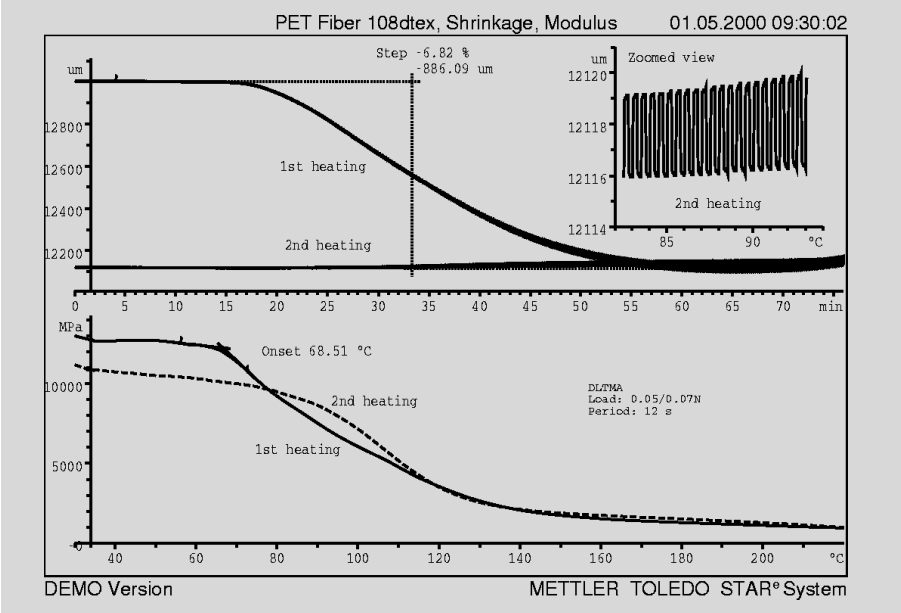

Fig. 9: DLTMA curves of a PET fiber (108 dtex) showing the first and second heating runs: heating to 220 °C at 10 K/min with a tensile force which changes every

odic change of length (storage modulus) using Fourier analysis (see lower diagram in Figure 9). The value of Young's modulus starts to decrease as soon as the glass transition begins (onset 68 °C). It in fact decreases by a factor of ten due to the glass transition. A comparison of the first and second heating curves shows that at low temperatures the value of the Young's modulus for the stretched fiber is somewhat larger than that of fiber after it has undergone shrinkage. Above 120 °C, i.e. above the glass transition, the values of Young's modulus are the same because the physical conditions are similar.

Conclusions

The TMA measurement technique and the evaluation the resulting curves is an excellent way to characterize the expansion and shrinking behavior of fibers. Effects originating in the manufacturing process and subsequent processing steps can be detected and described. The TMA curves allow properties such as the glass transition temperature, the degree of shrinking and the melting temperature to be determined. Values of the expansion coefficients, Young's modulus and the force of contraction can be calculated and displayed as a function of temperature. The copper clips allow very fine fibers and even thicker yarns and wires to be reproducibly mounted - this is of course absolutely essential for accurate results. The measuring system can also be used to condition fibers at different temperatures, or under different tensile forces or gas atmospheres. DMA, DSC, TGA and thermo-optical analysis are additional techniques that can be used to determine the properties of fibers.

Literature

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[2] *M. Jaffe, J. D. Menczel, W. E. Bessey, Chapter 7 in Thermal Characterization of Polymeric Materials, 2nd ed. (E. A. Turi, Ed.), Academic Press, New York (1997) 1767 - 1954.*

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