

THERMAL CHARACTERISTICS OF POLYMER FIBERS *

HANS G. WIEDEMANN and T. McKARNS

Mettler Instrumente AG, CH-8606 Greifensee (Switzerland)

G. BAYER

Institute of Crystallography, ETH, CH-8092 Zurich (Switzerland)

(Received 4 October 1989)

ABSTRACT

Thermal analysis (TG, DSC, TMA and TOA) allows the rapid characterization of fibers with respect to their processing, structure and properties. In order to derive the performance of a fiber directly from thermal analysis data, however, some experience and a large number of measurements are needed.

The present paper discusses and compares the thermal behavior of three industrially important polymer fibers, polypropylene, poly(ethylene terephthalate) and nylon. Besides the glass transition and melting temperatures, the recrystallization characteristics of these polymers were investigated by means of simultaneous DSC, thermomicroscopy and TMA. The absorption of water on synthetic and natural fibers was compared by TG and TMA measurements. The differences of the phase transitions, melting and crystallization behavior were demonstrated in the case of substituted PET. The sensitivity of thermal analytical methods towards fiber structure, crystallization and processing history suggests its use for quality control in various stages of fiber production. Also, for the purpose of comparison, the thermal characteristics of natural fibers (cotton, wool, silk) will be discussed briefly.

FIBERS

The uniqueness of fibers is based on their anisotropy: anisotropy of microstructure, of properties, and of geometry. Whether the fiber is natural or synthetic in origin, the fiber problems are related to the chemistry and physics of polymeric molecules.

The microstructure, and hence the specific properties, of any fiber depends on the conditions under which the filaments are produced. For fibers of plant (cotton, linen) or animal (wool, silk) origin these conditions are determined by species and environment. Natural fibers are partially crystalline and hydrophilic. For synthetic fibers a description of the principal

* Presented at the International Conference on Chemical Thermodynamics and Calorimetry, Beijing, P. R. China, 25–28 August 1989.

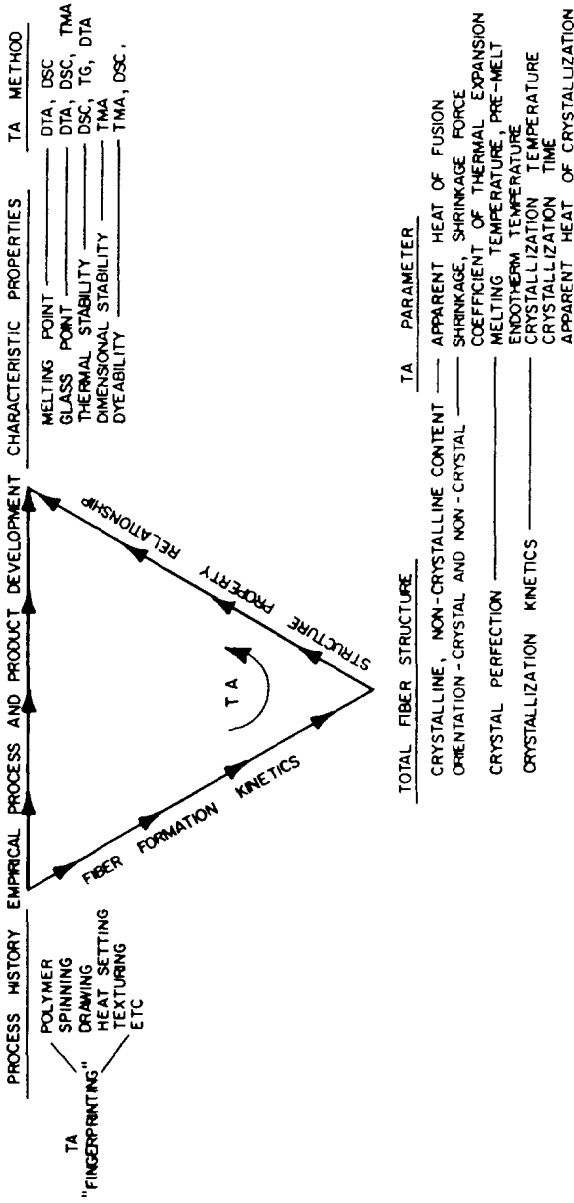


Fig. 1. Utility of thermal analytical method for providing information on the process-structure-property interrelation of polymer fibers [3].

TABLE 1
The common fibers

Common name ^a	Chemical name	Method of production		Nature of yarn
		Animal origin, sheep	Plant origin	
Wool	Keratin	Animal origin, sheep		Staple
Silk	Fibroin and sericin	Animal origin, silkworm		Filament, staple
Cotton	Cellulose	Plant origin		Staple
Cellulose acetate (CA)	15–92% acetylated cellulose	Dry spun		Filament, tow, staple
Cellulose triacetate (CTA)	> 92% acetylated cellulose	Dry spun		Filament, tow, staple
Rayon	< 15% acetylated cellulose	Wet spun		Filament, tow, staple
Acrylic (PAN)	Polyacrylonitrile \geq 85% by weight ^b	Wet or dry spun		Filament, tow, staple
ModAcrylic (PAN)	Polyacrylonitrile 35–85% by weight ^b	Wet or dry spun		Filament, tow, staple
Nylon 6	Polycaprolactam	Melt spun		Filament, tow, staple
Nylon 6,6	Poly(hexamethylene adipamide)	Melt spun		Filament, tow, staple
Polyester (PET)	Poly(ethylene terephthalate)	Melt spun		Filament, tow, staple
Polyolefin	Polypropylene	Melt spun		Filament, tow, staple

Common name ^a	Typical properties		Moisture level (%)	Safe ironing temperature (°C)	Major uses
	Tenacity (cN dtex ⁻¹)	T_m (°C)			
Wool	0.9–1.8	132 (degrades)	10–15	107	Wearing apparel, carpets
Silk	2.7–5.4	170 (degrades)	10–15	121	Wearing apparel
Cotton	2.7–5.4	240 (degrades)	6–10	182	Wearing apparel, home furnishings
Cellulose acetate (CA)	1.1–1.4	230	6	180	Wearing apparel, cigarette filters
Cellulose triacetate (CTA)	1.1–1.3	288	3.2	250	Wearing apparel
Rayon	0.6–5.4	205–240 (degrades)	13	215	Wearing apparel, home furnishings, industrials
Acrylic (PAN)	1.8–3.2	250–320	1.3–2.5	148–176	Wearing apparel, carpets
ModAcrylic (PAN)	1.8–3.2	188–250	0.4–4	130–148	Deep pile fabrics, carpets, wigs
Nylon 6	2.2–8.6	212	4.5	171	All fiber applications
Nylon 6,6	2.7–8.6	250	4–4.5	149	All fiber applications
Polyester (PET)	2.2–8.6	252	0.4–0.8	180	All fiber applications
Polyolefin	4.3–6.3	165	0	149 ^c	Carpet, home furnishings

^a For trade names, see, for example, ref. 1.

^b Co-polymerized with monomers such as vinyl acetate, vinyl chloride, styrene, etc.

^c For additional information see refs. 1 and 2.

fiber-spinning and modifying processes is necessary. Thermal analysis is an accurate and convenient tool for investigating the response of natural fibers and of polymers to temperature, stress and environment. It allows the chemical and structural “fingerprinting” of fibers, the specification of important end-use properties, the study of interactions of fibers with additives and coatings, and insight into the process–structure–property relations. The simplest fiber-forming process is the melt-spinning of thermoplastic polymers. The polymer melt is extruded through orifices (spinneret), and the resulting fibers are solidified in the spinning column and wound up on a bobbin. The principal parameters controlling the polymer fiber structure and properties are the applied stress and the rate of cooling. Non-thermoplastic polymers are spun from solution: if the solvent is volatile and removed in the spinning column, the process is called dry spinning; if the fibers must be coagulated in a non-solvent, the process is called wet spinning.

In most cases, as-spun synthetic fibers are unoriented and less crystalline than in the final product. They must be further processed to develop end-use properties, especially modulus and tenacity. This is achieved by stretching the fibers (drawing) so that significant molecular orientation is imparted. The principal variables are draw ratio (ratio of initial to final cross-sectional area), temperature, and strain rate.

Table 1 lists the common names, method of spinning, typical properties, and end-use applications of the major fibers. The range of properties achievable in most fibers is realized through control of the overall fiber formation process, which, in turn, specifies the fiber microstructure [3].

Figure 1 diagrammatically summarizes the utility of thermal analysis in providing the information for the process–structure–property triangle of fiber-forming polymers [3].

The biggest problem presented by fibers to the thermal analyst is the fiber geometry. Sample weights of even 5 mg can represent extremely long lengths. Care must be taken in the compaction of these samples to avoid introducing structural changes through deformation and to insure thermal equilibrium during heating.

When reporting TA data, as much sample information as possible should be included. Molecular weight, additive content, finishes, co-monomer levels, and moisture level can all significantly alter a fiber’s TA response. For meaningful data interpretation, some knowledge of the fiber processing history is vital. The use of appropriate supporting techniques to verify interpretations cannot be overemphasized.

EXPERIMENTAL

The simultaneous measurements are based on a commercial microscope and the hot stage of the Mettler Thermosystem FP 800 [4,5]. The schematic

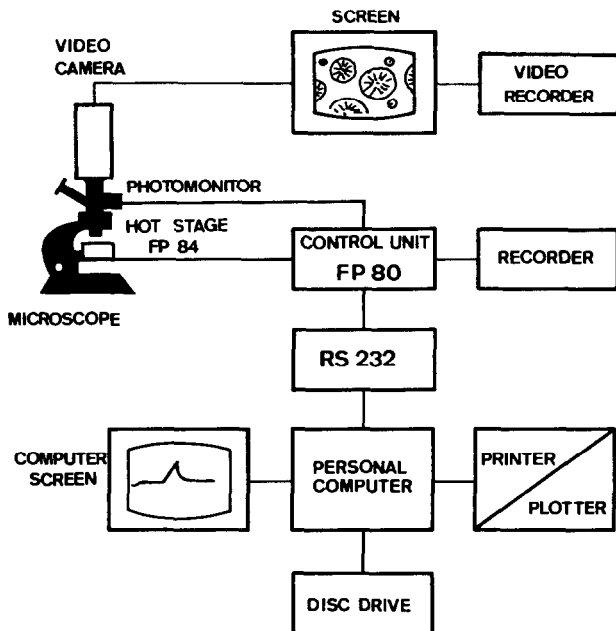


Fig. 2. Schematic set-up of the microscope with hot stage, control unit FP 80 and video recording system.

picture (Fig. 2) shows the microscope with the hot stage and the control unit FP 80, which can be connected via an RS 232C to a personal computer system, wherein the evaluation programs are accessible. The sample is filled directly into a sapphire crucible. In the case of low-viscosity substances and of liquid crystals, three sapphire balls act as spacers and help to maintain a uniform sample distribution and thickness during the measurement. The TG, DTG, DSC and TMA curves were recorded with the Mettler Thermo-system 4000 in air or nitrogen.

STRESS RELEASE IN POLYMERS (PS)

Microscopic investigations under polarized light are very suitable for the observation and photography of stresses in organic glasses. When polystyrene samples are heated linearly on a hot stage with a heat flow calorimeter, the disappearance of stresses (shown by interference colors) can be followed. Also, the specific heat of the samples changes during the heating process. The actual temperatures at which these interference color changes take place are indicated on the DSC curve (Fig. 3). A corresponds to the beginning of relaxation (86.0°C), B to the general disappearance of stresses (94.9°C), and C to the isotropic state (109.6°C).

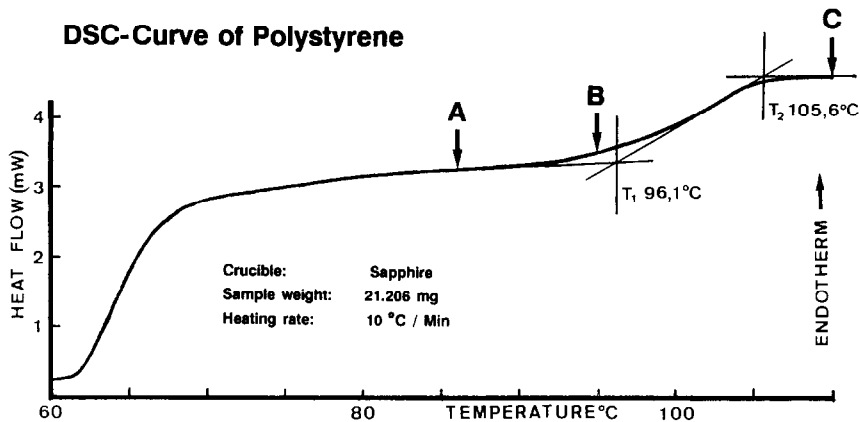


Fig. 3. DSC curve of polystyrene. A, The beginning of relaxation; B, the gradual disappearance of stresses; C, the isotropic state.

CRYSTALLIZATION OF POLYMERS (PETP)

The mobility of the macromolecules, of which polymers are composed, determines the tendency and degree of crystallinity. Depending on the side groups, various transitions are possible from amorphous (atactic) to crystalline (isotactic and syndiotactic). Polypropylene, polystyrene and poly(methyl acrylate) are examples of polymers which are known in atactic and isotactic forms [4].

Poly(ethylene terephthalate) samples for the measurement were prepared by melting and quenching a commercial granulate on the hot stage between microscopic slides. During heating the crystallization of PETP was recorded, by DSC and optically, from 50 to 275 °C. This could be correlated with simultaneously observed spherulitic crystallization on the hot stage, which started also at 130 °C and was complete at about 145 °C (Fig. 4). Therefore the recorded DSC peak corresponds to a 100% transformation from the glassy to the crystalline state. The heat of crystallization derived from this peak by integration was of the order of 115 J g⁻¹.

PHASE TRANSFORMATION AND MELTING OF SUBSTITUTED PETP

The photographs of single crystals of substituted PETP, dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate [6], were taken on the hot stage of a microscope (Fig. 5). Isothermal heat treatment at 118.9 °C, which is the temperature of the beginning of the phase transition, leads to a color change of the compound from yellow to white due to rotation of the molecules. This gives rise to the formation of cracks and fissures which can be seen in their growth state. The melting point of this substituted PET is strongly decreased to about 180 °C compared with 235 °C for non-substituted PETP.

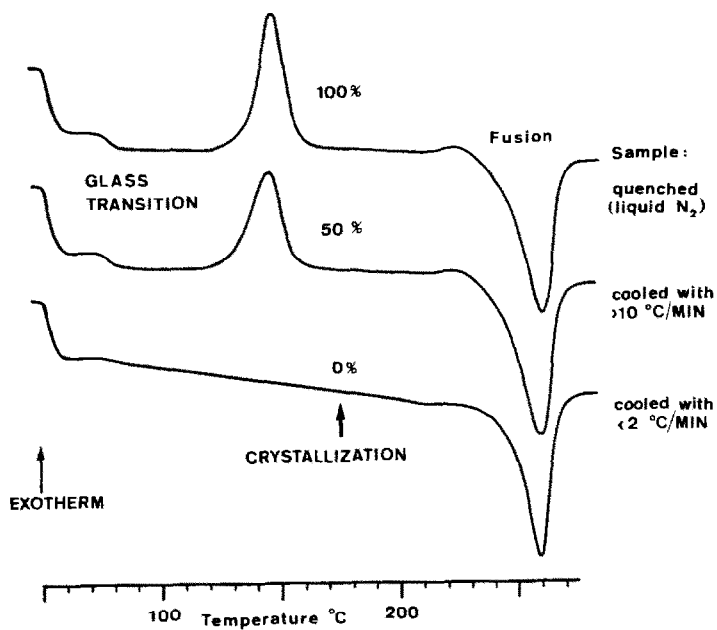


Fig. 4. DSC curves of the crystallization of poly(ethylene terephthalate). Sample weight, 5.25 mg; heating rate, $10^{\circ}\text{C min}^{-1}$.

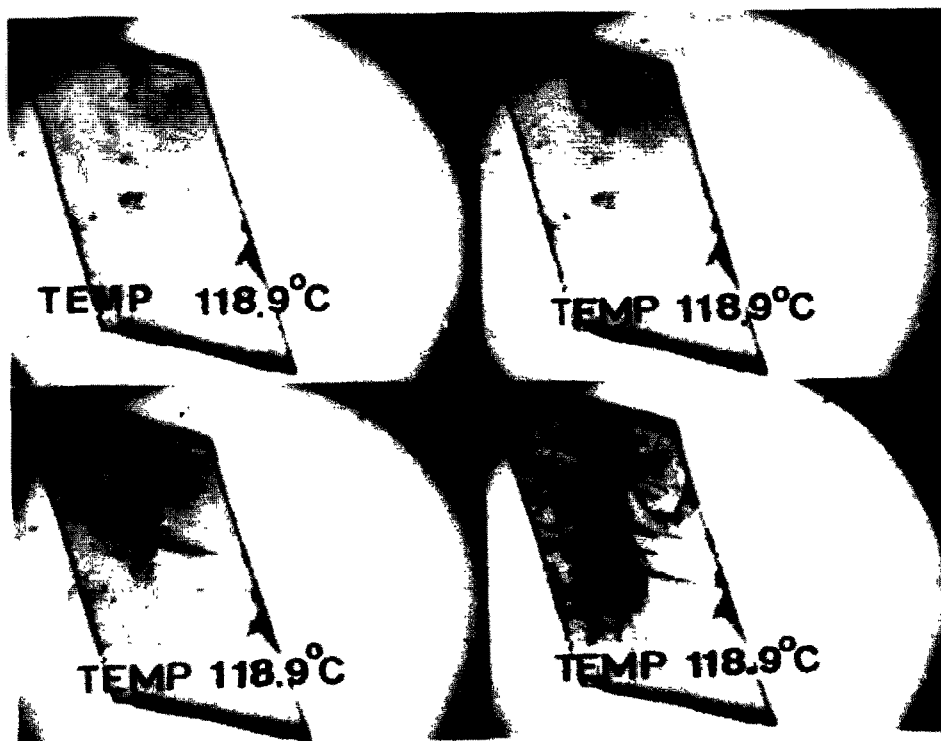


Fig. 5. Phase transformation of a substituted PETP (dimethyl 3,6-dichloro-2,5-dihydroxy-terephthalate) under isothermal treatment. $100\times$.

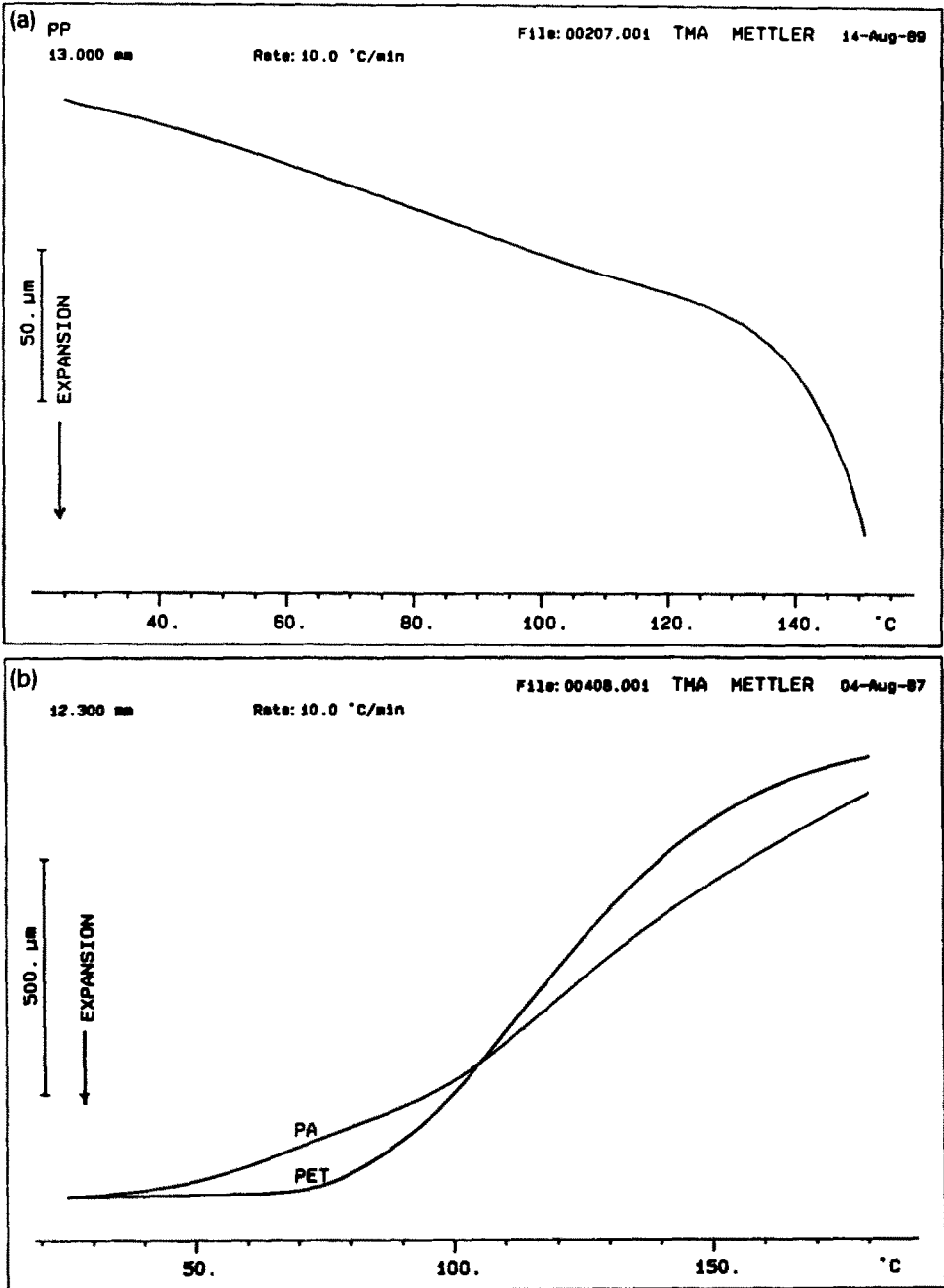


Fig. 6. TMA-curves of (a) polypropylene (PP) (b) polyamide (PA) and polyethylene terephthalate (PET) and (c) Kevlar.

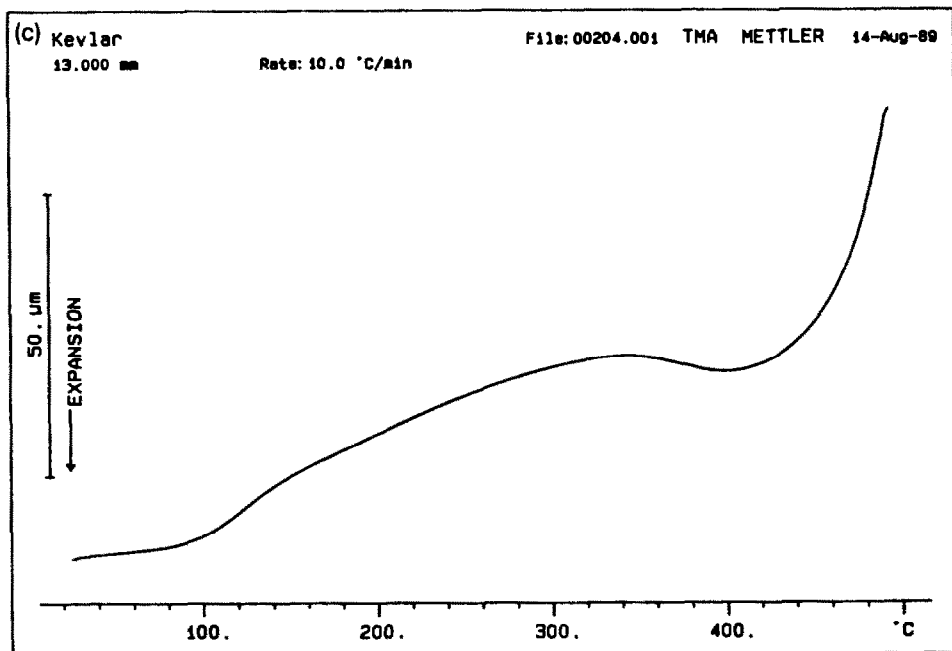


Fig. 6. (continued).

During cooling the recrystallization of the white modification starts at 164.9°C . Slow cooling rates ($0.1^{\circ}\text{C min}^{-1}$) lead to the formation of a single crystal, whereas rapid cooling ($10^{\circ}\text{C min}^{-1}$) results in a polycrystalline aggregate due to undercooling.

THERMOMECHANICAL ANALYSIS (TMA) OF POLYMER FIBERS

The expansion behavior of fibers of PP, PA, PET and Kevlar was investigated using a Mettler TMA 40, a thermal system with a TMA module. The polymer fibers (12.3 and 13 mm in diameter) were clamped between a fixed position and the mechanical sensor and heated at a rate of $10^{\circ}\text{C min}^{-1}$. The TMA curve for PP [Fig. 6(a)] shows a rather uniform expansion up to about 120°C . Above this temperature strong extension takes place due to plastic flow followed by melting of the fiber above 140°C . The PA and the PET fibers are characterized by a strong thermal shrinkage (one of the most important fiber properties) from about $50\text{--}70^{\circ}\text{C}$ up to the melting region at $200\text{--}230^{\circ}\text{C}$ [Fig. 6(b)]. If such fibers are preheated to about 150°C and reheated a second time, the thermal shrinkage is practically eliminated due to the release of stresses which were introduced in the fiber-drawing process. The high-strength Kevlar fiber showed moderate thermal shrinkage up to 300°C (glass transition) followed by extremely

strong thermal shrinkage above 400°C due to a re-orientation of the molecules [Fig. 6(c)]. Further TMA investigations on fibers will be useful because TMA is the thermal analysis technique which is most sensitive to molecular chain orientation and therefore gives information on the thermal history and on the fiber-forming process.

THERMOANALYTICAL INVESTIGATION OF CHINESE SILK [7]

Figure 7 shows the results of DSC measurements on two ancient silk materials. The differences between these curves are probably due to different environmental effects which have changed the composition of the silk.

The water absorption of silk and its reversibility is one of the characteristic features and is of importance for the quality. Silk feels moist only when it contains at least about 30% water. The supramolecular structure of silk contains protein polymers in crystalline regions, where properly aligned chains are linked by hydrogen bonding. It also contains oriented regions and amorphous regions. As the fiber absorbs water, the chains in the amorphous regions are pushed apart, but the crystalline tie points hold the chains together. This assumption of reversible swelling holds true only if the silk has not been desericinized. In other words, the moisturizing is proportional to the presence of sericine upon the silk fiber. This can be seen from Fig. 8 where the water absorption of a cocoon is compared with that of different kinds of silk weavings. The relatively low values and the slow rate of moisturizing are caused by the excessive drying temperature (150°C) which may already cause structural changes in the silk. The moisturizing behavior also shows differences caused by degradation of the sericine with time.

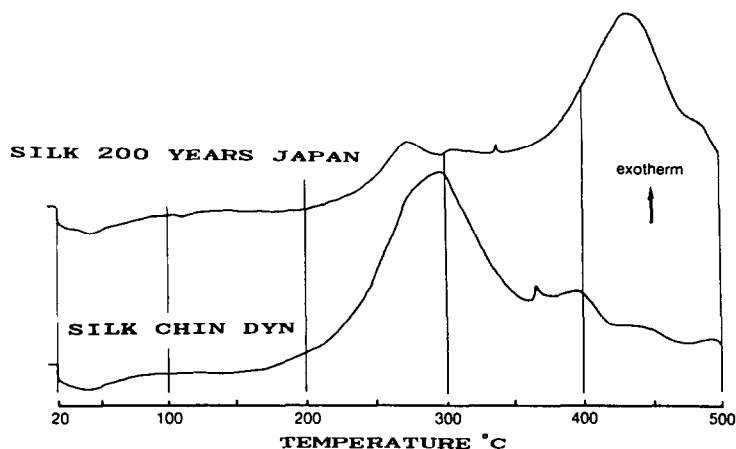


Fig. 7. DSC curves of ancient silk materials. Sample weight, 5 mg; rate, 2°C min⁻¹; atmosphere, air.

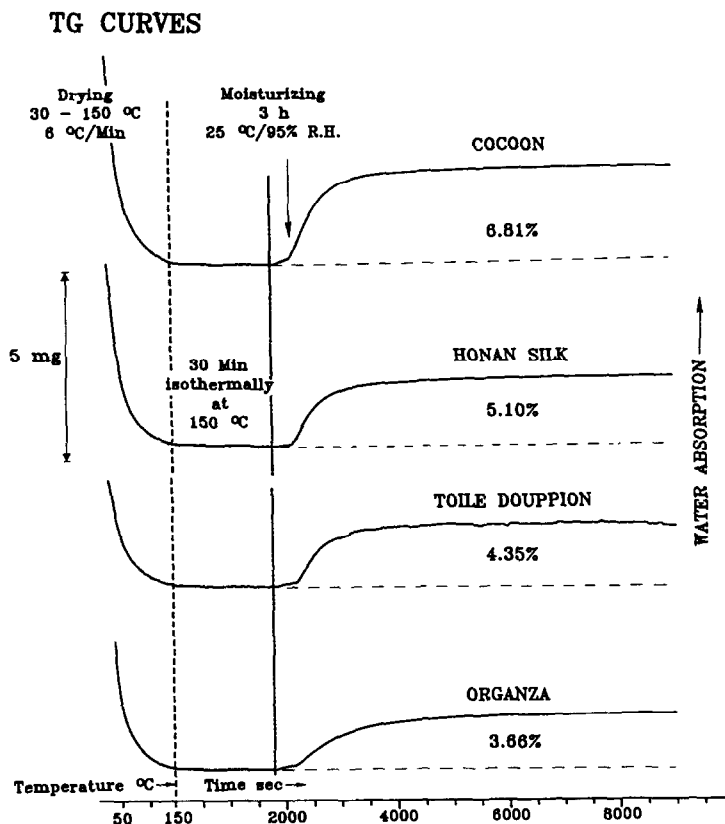


Fig. 8. Drying and moistening of different silks.

The thermal degradation of different silk materials (thread, raw silk) and sericine can also be derived from MS curves. There are obvious differences in the amounts of H_2O , CO , N_2 and CO_2 which are evolved during pyrolysis of such materials.

The decomposition of silk starts at about $260^\circ C$ and is complete at $310^\circ C$. These temperatures are shifted to lower values for the less stable sericine.

The double fiber of *Antheraea pernyi* is broader and less rounded as compared to the double fiber of *Bombyx mori*; the difference, however, is its covering with millions of whewellite crystals. This is characteristic for the spinnings of many Lepidopteres. Figure 9(a) shows DSC curves of these different silks (*Antheraea pernyi* and *Bombyx mori*). The DSC curve shows the drying at $20-100^\circ C$, followed by dehydration of the small whewellite crystals at $150^\circ C$, by the decomposition of the silk (up to $300^\circ C$) and by the combustion of the generated carbon. These reactions are clearly demonstrated by the DSC curves in the form of endothermic and exothermic peaks. The silk fiber of the *Antheraea pernyi* is thermally somewhat more

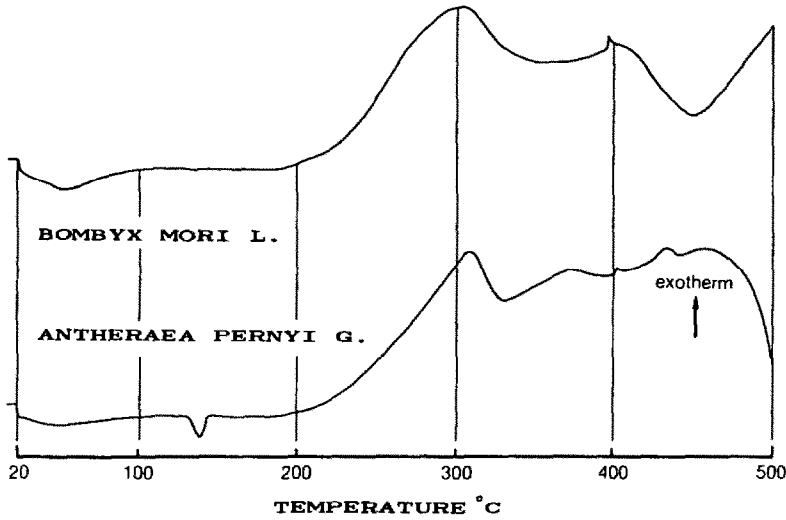


Fig. 9. DSC curves of two different silks. Sample weight, 5 mg; rate, $2^{\circ}\text{C min}^{-1}$; atmosphere, air.

stable and also has a higher strength. All these measurements were carried out in air. The difference from measurements in a nitrogen atmosphere is that here no combustion of the silk takes place but only structural degradation.

Figure 10 shows the application of thermomechanical analysis (TMA) for the determination of the expansion behavior of raw silk fibers. The silk

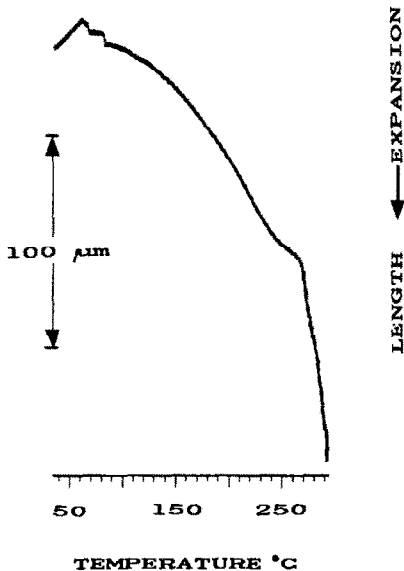


Fig. 10. TMA curve of silk thread (50 fibers). Rate, $6^{\circ}\text{C min}^{-1}$; atmosphere, N_2 .

thread (composed of 50 fibers) was clamped between a fixed position and the measuring sensor, and heated uniformly. Initially there is a contraction followed by elastic deformation up to 260°C. Above this temperature plastic deformation takes place simultaneously with the degradation of the silk. The slight ripples in the curve at the beginning of the measurement, are caused by sericin, which has a different expansion behavior from fibricin.

CONCLUSIONS

The results obtained prove that simultaneous thermomicroscopy/DSC in combination with thermoanalytical techniques (TG, DSC and TMA) is very useful for studies on the crystallization kinetics, stress release, thermal expansion and degradation of polymers and organic fibers.

ACKNOWLEDGEMENT

We thank Dr. E.A. Turi and Academic Press for permission to reproduce Fig. 1 and Table 1 from ref. 3.

REFERENCES

- 1 American Association for Textile Technology, 1977.
- 2 Encyclopaedia Britannica, 1966. Man-made Fiber Producers Association, 1970, 1971. Textile Institute, 1965. Mark et al., 1967, 1968. Moncrieff, 1975. Morton and Hearle, 1975. Stout, 1970.
- 3 E.A. Turi, Thermal Characterization of Polymeric Material, Academic Press, New York 1981.
- 4 H.G. Wiedemann and G. Bayer, *Thermochimica Acta*, 92 (1985) 399–402.
- 5 H.G. Wiedemann and B. Wunderlich, *Mol. Cryst. Liq. Cryst.*, 140, 219–241 (1986).
- 6 Quing-Chuang Yang, M.F. Richardson and J.D. Dunitz, *Acta Crystallogr., Section B*, 45 B, 312–232 (1989).
- 7 H.G. Wiedemann and G. Bayer, *Thermochimica Acta*, 100 (1986) 289–314.