ABSTRACT
The physical properties of synthetic fibers often need to be characterized in order to get an insight into end-use properties and processing options. An attempt is made throughout this presentation to show that thermal analysis is an accurate and convenient tool for monitoring the response of oriented polymer chains in fibers to temperature, stress and environment. Chemical and structural fingerprinting can be accomplished by this family of techniques by monitoring important end-use properties, studying the interactions of fibers with additives and coatings, thus ultimately getting an insight into the process-structure-property spectrum available to a given fiber forming material.

The techniques used include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), thermomechanical analysis (TMA), dynamic mechanical analysis (DMA) and other thermal analysis relaxation techniques. DSC, TMA and DMA allow characterization of orientation of fibers through various measurement techniques of their melting behavior and temperature dependence of dynamic mechanical behavior. For fibers important for the textile industry, such as nylons and acrylonitrile, the interaction of the oriented polymer chains with water can be characterized in various temperature regions often explaining their mechanical behavior. The measurement of various secondary transitions by DMA can be important for explaining drawing possibilities in fibers like poly(vinyl alcohol).

INTRODUCTION
Thermal analysis of synthetic fibers represents a special area of thermal analysis because fibers are oriented, most often semicrystalline polymers. The anisotropy of properties, microstructure and geometry of fibers can be followed by a number of physical characterization techniques. From structural point of view, X-ray diffraction and thermal analysis seem to be the two most important techniques. While X-ray (and sometimes neutron) diffraction is able to describe the microstructure of the fibers, various thermal analysis techniques characterize the physical properties of the fibers under controlled temperature programs. Since temperature, stress and environment are the three most important variables during the fiber formation, thermal analysis provides information about the setting of the process parameters. A detailed summary of thermal analysis of oriented systems (fibers and films) is given in Ref. 1 and 2. In this lectures it is attempted to show that thermal analysis is an excellent tool to establish the mentioned above parameters of fiber formation.

RESULTS and DISCUSSION
SPECIFIC FIBERS
1. Semicrystalline Fibers
a. Polyesters
Poly(ethylene terephthalate) is definitely the most important polyester in fiber production. Moreover, it is the largest-volume synthetic fiber (~30 million t worldwide production). PET
was the first fiber to be studied by thermal analysis in detail. Kawaguchi showed back in the 1950’s [3] by dynamic mechanical analysis (DMA) that the tensile storage modulus of PET fiber increases with increasing draw ratio. He also showed that the modulus of highly drawn PET fibers increases when they are heat-treated at various temperatures to increase their crystallinity. Kawaguchi and later Miller and Murayama [4] noticed that the glass transition temperature of PET fiber increases with increasing draw ration, and at the same time, the glass transition becomes broader.

Poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) is another polyester having improved modulus, better dimensional stability and improved retention of mechanical properties under conditions of outdoor exposure when compared with PET.

![Poly(ethylene-2,6-naphthalene dicarboxylate) (PEN)](image)

Figure 1 shows the DSC traces of as-spun and drawn PEN fibers. The as-spun fiber is largely amorphous as shown by the cold crystallization and a high heat capacity jump at the glass transition in the DSC curves. The drawn fibers are highly crystalline, the cold crystallization peak is absent, they exhibit a melting peak only. Moreover, there are differences in the melting response of drawn fibers held constrained (constant length during the measurement) and allowed to shrink during the heating in the DSC (unconstrained or free-to-shrink measurements). When the sample is constrained, the relaxation of the molecular orientation during the heating is retarded, and the orientation is preserved somewhat even in the melt. Finally, the decreased entropy change leads to a higher melting point. Thus, it is extremely important to properly prepare the samples before crimping. For running the samples in free-to-shrink state, the fiber needs to be chopped to very short pieces (length ~ 2-3 mm). Otherwise the crimping procedure may cause a number of monofilaments strained, and these pieces of the sample may give a higher melting point peak.

b. Nyans

Common properties of most Nyans are the high water pick-up and the possibility of having several crystal forms simultaneously in the sample. Thus, Nylon 6, Nylon 6.6 and Nylon 6.10 all have at least two (often three) crystal forms (these are monoclinic for Nylon 6 and triclinic for Nylon 6.6 and Nylon 6.10). Sometimes the traces of the simultaneous existence of the different crystal forms can be seen in the same sample. The DSC and DMA traces both depend on the water content and the specific crystal forms in the sample. A high temperature polyamide, poly(2-methylpentamethylene terephthalamide) (Nylon M5T) clearly shows crystal-to-crystal transition when the amorphous polymer (or as-spun fiber) is heated in the DSC or DMA [6].

![Poly(2-methylpentamethylene terephthalamide) (Nylon M5T)](image)
Figure 1. DSC heating curves of as-spun and drawn PEN fibers (draw ratio=5.2) [5]. The shape and the magnitude of the glass transition and the presence of cold crystallization indicates that the as-spun fiber is largely amorphous. The drawn fiber is ca. 50% crystalline {From Saw et al. (1977)[5]; reprinted with permission of the Society of Plastics Engineers}.

Figure 2. DMA measurements of as-spun and drawn PEN fibers (draw ratio 2.3 and 5.4) [5]. The as-spun fiber (amorphous and unoriented) exhibits a drop in the storage modulus between 100 and 140°C due to the amorphous glass transition, then the modulus increases due to cold crystallization. The modulus of the drawn fiber decreases much less and at a higher temperature range due to a higher glass transition temperature and smaller $\Delta C_p$ {from Saw et al. (1977) [5]; reprinted with permission of the Society of Plastics Engineers}

This is shown in Figures 3 (DSC) and 4 (DMA). As the as-spun fiber is heated, at around 180°C an exothermic peak can be observed (corresponding to the amorphous→crystal A transition). At around 200°C, crystal form A changes to crystal form B, and at 240°C crystal form B changes to crystal form C. Finally, crystal form C melts at ~300°C. WAXS and DMA measurements (Figure 4) support these conclusions. Also, modulated temperature DSC measurements (Figure 5) indicate that the crystal-to-crystal transitions proceed through melting of the given lower temperature crystal form with the subsequent cold crystallization
of the higher temperature crystal form. It is not easy to find a polymer in which the crystal forms change that easily from one to another, and these measurements were the first in the literature proving that the crystal-to-crystal transitions are not transitions within the solid state, but are a crystal→melt→crystal transitions (at least for Nylon M5T).

Figure 3. DSC heating curves of poly(2-methylpentamethylene terephthalamide) (Nylon M5T) as-spun fiber at various heating rates beyond the glass transition temperature [6]. The crystal-to-crystal transitions can easily be identified. At a heating rate of 40 °C/min the crystal form A→crystal form B transition is bypassed due to kinetic reasons, and crystal form A changes to crystal form C {from Menczel et al. (1996) [6], reprinted with permission of Springer-Verlag}.

c. Poly(vinyl alcohol)(PVA)

PVA is another important polymer from the point of view of thermal analysis of fibers. The gel spinning technique was also applied in the drawing procedure of PVA, but the maximum attainable draw ratio was 20x only [7], unlike polyethylene and polypropylene for which the maximum draw ratio attained is 300x and 57x, respectively. Later Cha and co-workers [8] increased this maximum draw ratio for PVA to ~45, but this was still much less than the draw ratio attainable for polyolefins. Garrett and Grubb [9, 10] studied the DMA recordings of PVA fibers gel-drawn to different ratios. They could raise the maximum draw ratio up to ~38x, but these increase draw ratios were achieved only at increased drawing temperatures (close to the melting point of the gel that was 228°C). However, an intense α-relaxation was observed in the DMA spectra of PVA, and the temperature of this relaxation (a crystalline relaxation) increased with increasing draw ratio. However, the temperature of this relaxation increased much faster with draw ratio than the melting range of PVA, and its magnitude
decreased. At high draw ratios the α-relaxation could not be resolved anymore. Garrett and Grubb [9, 10] suggested that the α-relaxation is a crystalline relaxation necessary for ensuring sufficient mobility in the crystals for drawing. Once this relaxation disappears, the drawing becomes extremely difficult. These authors suggested that a number of other polymers with strong hydrogen bondings cannot be gel-drawn to high draw ratios because they lack a similar crystalline relaxation that PVA has.

Figure 4. Tensile storage modulus of poly(2-methylpentamethylene terephthalamide) (Nylon M5T) [6] as-spun and drawn fibers as a function of temperature showing characteristic changes due to (1) the glass transition of the amorphous polymer (modulus drop); (2) sudden modulus increase due to cold crystallization (melt→crystal form A transition); (3) melting of crystal form A (modulus drop); (4) melt→crystal form B transition (modulus increase); (5) melting of crystal form B (modulus decrease); (6) melt→crystal form C cold crystallization (modulus increase); and (7) modulus decrease due to melting of crystal form C {from Menczel et al. (1996) [6], reprinted with permission of Springer-Verlag}

Figure 5. Reversing and non-reversing DSC curves of as-spun (amorphous) Nylon M5T fiber (R.H-Fl. is the reversing signal, NR. H-Fl. is the non-reversing DSC curve) {from Menczel et al. (1996) [6], reprinted with permission of Springer-Verlag}
c. Vectran (a thermotropic LCP fiber)

![Chemical structure of Vectran](image)

Figure 6. Heating DSC curves of as-spun and heat-treated Vectran filament {from Menczel et al. (1997) [16], reprinted with permission of Springer-Verlag}

Vectran is one of the most important high-performance fibers with superior mechanical properties. It is has similar mechanical properties as Kevlar and other aramids, but can be processed by melt spinning. And this is much less expensive than processing of aramids by dope spinning. Vectran is a liquid crystalline copolyester of p-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) developed by Celanese in the 1970s [11-15]. The high modulus, high tensile strength and stiffness, as well as the low coefficient of linear thermal expansion is due to the stiff polymer chains. These fibers cannot be drawn, because they are oriented after the spinning process. They are simply heat-treated ca. 10°C below the crystal→nematic transition ("melting point") (see Figure 6). This heat treatment increases the 3D-crystallinity in the fiber, and improves substantially the mechanical properties. A big advantage of these fibers that they do not exhibit shrinkage. The as-spun fiber shows a double melting peak, which was interpreted by some authors as the evidence of the simultaneous presence of two crystal forms. However, X-ray measurements did not prove this hypothesis, and later DSC measurements with changing heating rates [16] indicated that this is some kind of a crystal perfection during melting (see Figure 7).

2. Amorphous Fibers {Poly[2,2'-m-phenylene)-5,5'-Bibenzimidazole], PBI}

![Chemical structure of PBI](image)
PBI is a high temperature amorphous fiber, but it can crystallize on pressure treatment in a water/phenol mixture or when it is treated with formic acid. However, the commercial fiber is amorphous, the presence of crystallinity does not provide any advantage. It is extremely stable thermally and made from tetra-aminobiphenyl-(3,3’-diaminobenzidine) and diphenyl isophthalate. It is chemically resistant, and its integrity is retained even when it charred. Its moisture regain is high. It is used as high-performance protective apparel, aircraft wall fabrics, firefighter coats and suits, high temperature protective gloves, protective clothing for pilots, suits for race car drivers, etc.

Figure 7. Heating rate dependence of the heating DSC curves of as-extruded Vectran film {from Menczel et al. (1997) [16], reprinted with permission of Springer-Verlag}

Figure 8. Heating DSC curves of as-spun and drawn PBI fibers in constrained (fixed-length) and free-to-shrink (unconstrained) modes {from Menczel (2000) [17], reprinted with permission of Springer-Verlag}
It is produced by dry spinning (from a 25% solution in DMAC). Before application, the fiber is drawn. There is an additional sulfonation process to reduce the flame shrinkage of the fiber [18].

Figure 8 shows the DSC curves of as-spun and drawn PBI fibers. It is clearly seen that the glass transition temperature is much higher for the drawn fiber. Also, when the DSC measurement of the drawn fiber is done in fixed length state (“constrained”), $T_g$ is even higher. This is similar as the behavior of transitions in semicrystalline polymers, and again, can be explained by retention of orientation in the melt.

Figure 9 shows the DMA trace (storage modulus and $\tan \delta$) for the yarn from the as-spun fiber. Three processes can be observed in the modulus decrease. The highest temperature one (at around 400°C) is due to the glass transition, while the process that starts at around 250°C is probably due to water loss.

CONCLUSIONS

Thermal analysis is an excellent method to solve numerous fiber problems. This family of techniques helps to establish the structure-property relationship, and processing conditions. It is used in the industry and research for structural and chemical fingerprinting of commercial fibers. The importance of these techniques lately grows even more as recycling of fibers became an everyday job.

References:
[15] G.W. Calundann, U.S. Pat. 4,184,996