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# Polyolefins

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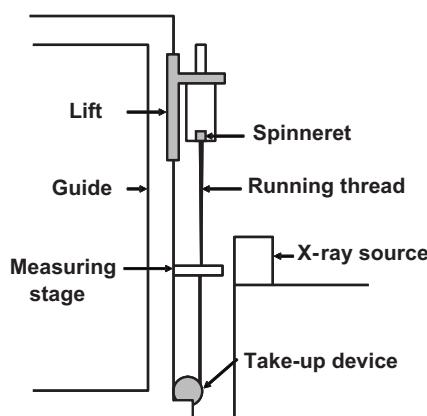
## 8.6 Polyethylene

### 8.6.1 High-Density Polyethylene

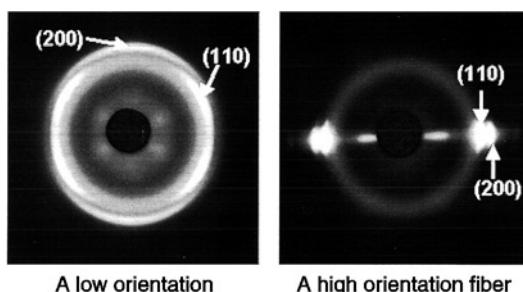
In 1968, Katayama, Amano, and Nakamura [51] of Asahi Kasei published a key investigation of crystallization during melt spinning of polyethylene in which they measured spinline temperature profiles and online X-ray diffraction using a rotating anode X-ray generator (Fig. 8.8). The X-ray diffraction investigation showed that the polyethylene crystallized in the spinline. They also observed a temperature plateau at which crystallization occurred. This experiment was later repeated by Dees and Spruiell [52], and the results were confirmed.

Katayama et al. [51] observed both the appearances of SAXS and WAXD reflections in high density as well as low density polyethylene spinlines. The SAXS patterns, which showed meridional reflections, indicated formation of lamellae, and the WAXD patterns, which showed equatorial reflections, indicated formation of crystals. The SAXS reflections appeared earlier in the spinline than the WAXD reflections. Katayama et al. [51] observed that at crystallization, the birefringence decreased for polyethylene. In a later study on roughly uniaxial film, Nagasawa et al. [53] of Ube Kosan found the birefringence of polyethylene to increase while crystallizing, which is more in line with other polymers.

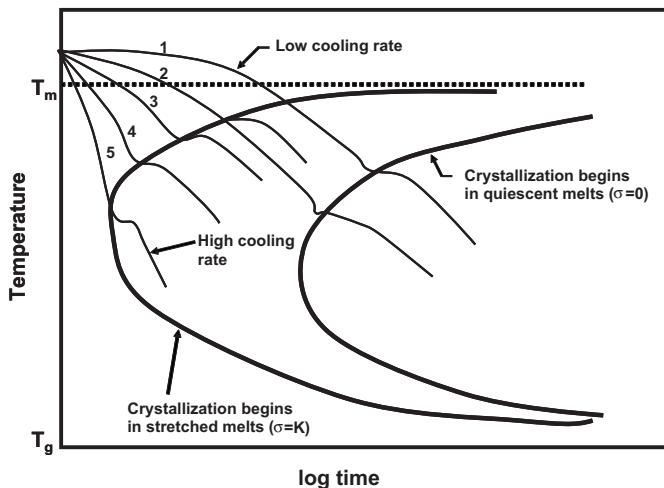
The crystal structure of polyethylene melt-spun filaments was found by all investigators [51–60] to be the Bunn orthorhombic structure (see Section 3.3). Typical WAXD patterns



**Figure 8.8** Experimental set up for online X-ray investigations of a running filament (Katayama et al. [51])



**Figure 8.9** Typical WAXD patterns for melt-spun polyethylene fibers



**Figure 8.10** Schematic illustration of continuous cooling transformation curves showing the effect of spinline stress on the rate of crystallization in polyethylene spinline compared to its quiescent melt (Spruiell and White [58])

of polyethylene melt-spun fibers are presented in Fig. 8.9. The rate of crystallization of polyethylene in the spinline was found to be much faster than in the quiescent state [58]. This may be demonstrated using the continuous cooling transformation (CCT) curves of Section 5.6 (see also Fig. 8.10). It is another example of the phenomenon of stress-induced crystallization.

The orientation of polymer chains and crystallographic axes in melt-spun polyolefin fibers has been investigated by various authors beginning with Kitao et al. [55]. These studies generally used the Hermans-Stein orientation factors [52, 55–58, 60] (see also Section 2.7.1)

$$f_j = \frac{\overline{3 \cos^2 \phi_j} - 1}{2} \quad (8.9)$$

Here  $\phi_j$  is the angle between the  $j$ -crystallographic axis and the fiber axis and the superimposed bar indicates averaging over all the polymer chains presented. The value of  $f_j$  varies between  $-0.5$  and  $1.0$ . It is zero for isotropy (i.e.,  $\cos^2 \phi_j = 1/3$ ),  $1.0$  for a perfect orientation parallel to the fiber axis and  $-0.5$  for a perfect orientation perpendicular to the fiber axis.

WAXD orientation investigations of melt-spun polyethylene fibers have been made by various researchers [51–60]. Generally, the  $(200)$  and  $(020)$  reflections or the  $(200)$  and  $(110)$  reflections are used for determining the orientation. Polyethylene has an orthorhombic unit cell (see Section 3.3), and from the Pythagorean Theorem we have

$$f_a + f_b + f_c = 0 \quad (8.10)$$

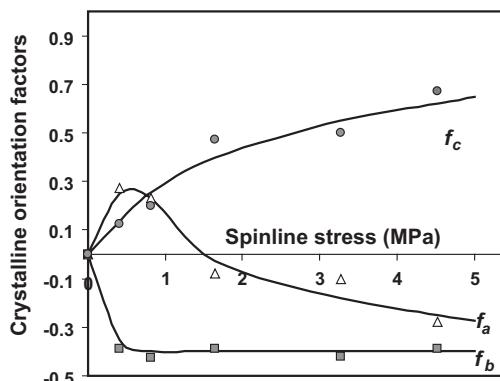
It was found, first by Kitao et al. [55], that at low draw-down ratios, the  $b$ -axis is almost perpendicular to the fiber axis while the  $a$ - and  $c$ -axes are slightly parallel to it. We have roughly

$$f_b \sim -0.4, \quad f_a \approx f_c \sim 0.2 \quad (8.11a)$$

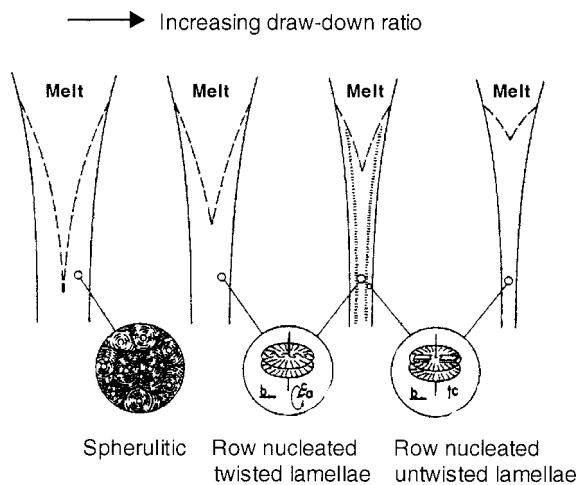
At higher draw-down ratios, we might have

$$f_b \rightarrow -0.4, \quad f_a \rightarrow -0.3, \quad f_c \rightarrow 0.7 \quad (8.11b)$$

This is shown in Figure 8.11 as a function of spinline stress [60].



**Figure 8.11** Hermans-Stein orientation factors as a function of spinline stress for melt-spun polyethylene fibers (C. H. Choi and White [60])

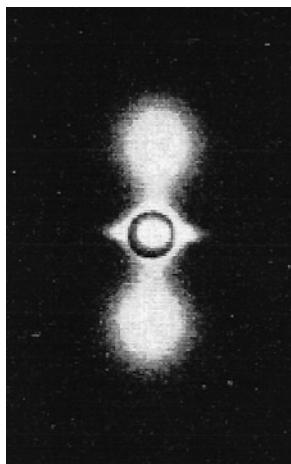


**Figure 8.12** A morphological model for melt-spun polyethylene fibers based on the Keller-Machin row structure (Dees and Spruiell [52])

Clearly, the values of  $f_c$  are much higher than for the glassy thermoplastics. Katayama et al. [51] and Dees and Spruiell [52] interpreted these results with a morphological model (Fig 8.12) similar to the Keller-Machin row structure [61], which was discussed in Section 4.2. In this morphological model, folded-chain lamellae grow out of a central shish-like row nuclei, and the growth direction coincides with the  $b$ -axis. At low draw-down ratios or spinline stresses, the growing lamellae are twisted and rotate with respect to the growth direction. At high draw-down ratios or spinline stresses, the lamellar twisting is much suppressed, and the chain-axis (or the  $c$ -axis) is predominantly oriented to the fiber direction.

Dees and Spruiell [52] have determined the birefringences of polyethylene melt-spun fibers and determined them as an increasing function of spinline stress. More recently, C. H. Choi and White [60] have correlated the Hermans-Stein orientation factors with spinline stress, because it has long been known that for polymer melts, the birefringence varies linearly with applied stress (see Section 7.6). This has also been found to be the case for melt-spun fibers formed from vitrifying thermoplastics [45–49] (see Section 8.5). It seems reasonable that the enhanced levels of birefringence and crystalline chain-axis orientation factor would be determined by the crystallization habit and stress-determined melt orientation at the position of crystallization.

Small angle X-ray scattering (SAXS) investigations of polyethylene melt-spun fibers show two meridional spot patterns, which indicate the formation of parallel lamellae [51, 52] (Fig. 8.13). One should expect the fiber morphology to be largely determined



**Figure 8.13** A typical SAXS pattern for melt-spun polyethylene filaments

by the spinline stress at solidification and not by the kinematics, that is, the draw-down ratio ( $V_L/V_o$ ).

### 8.6.2 Ultrahigh Modulus Polyethylene Fibers

Ultrahigh modulus polyethylene fibers can be produced by solution spinning technology [62]. This has been accomplished commercially by DSM in their product Dyneema®. Presumably, these fibers achieve significant chain extension (as compared to melt processed fibers) as well as high levels of orientation.

### 8.6.3 Polyethylene Copolymers

Polyethylene is copolymerized with comonomers such as butene-1, hexene-1, and octene-1 to produce linear low density polyethylene (LLDPE). These have densities of order  $0.91\text{ g/cm}^3$ . Both Dow Chemical (with DuPont-Dow) and Exxon-Mobil have been producing polyethylene copolymers with higher levels of these comonomers using special metallocene catalysts. Dow Chemical has been producing polyethylene copolymers with even higher octene-1 comonomer content with densities of the order 0.89, commonly called VLDPE. Shan and White [63] have made a comparative melt spinning study of HDPE, LLDPE, and VLDPE. The HDPE and LLDPE have similar Bunn orthorhombic unit cells and orientations. The VLDPE exhibits much lower crystallinities,

which seem roughly hexagonal. The birefringence levels of melt-spun fibers at the same spinline stress are markedly lower. The row structure morphology of twisted lamellae seems to be lost with increasing comonomer content.

### 8.6.4 Polyethylene-Polystyrene Blends

The melt spinning of polyethylene-atactic polystyrene blends were investigated by Min et al. [64]. They found that melt spinning produced a two-phase with parallel uniaxial oriented immiscible fibrillar phases, in which the continuous phase is determined by the composition. By extracting the polystyrene, very small diameter ( $\sim 1 \mu\text{m}$ ) polyethylene fibers can be produced.

X-ray diffraction investigations find that the polyethylene in the melt-spun blend fibers exhibits the Bunn orthorhombic crystal structure. Studies of crystalline orientation and the Hermans-Stein orientation factors indicate that the addition of polystyrene reduces the crystalline orientation and the extent of reduction increases with polystyrene content.

The mechanism leading to the low levels of polyethylene crystalline orientation in the melt-spun blend fibers is the distribution of the applied tension between the polyethylene and polystyrene phases. This we might write:

$$F_L = A_{PE} \sigma_{PE} + A_{PS} \sigma_{PS} \quad (8.12)$$

where  $A$  is roughly the volume fraction. If we write the stress on each phase as a product of an elongational viscosity  $\eta_{el}$  and a stretch rate  $dv/dz$ , then

$$F_L = (A_{PE} \eta_{el,PE} + A_{PS} \eta_{el,PS}) \frac{dv}{dz} \quad (8.13)$$

As we move down the upper threadline where both phases are molten, the melt viscosity of the polystyrene increases much more rapidly than that of the polyethylene (this is associated with the high glass transition temperature of the polystyrene) to maintain continuity. The stress concentrates more in the polystyrene and less in the polyethylene. When crystallization of the polyethylene occurs, the stresses on the polyethylene ligaments are much lower than the average  $F_L/A$  over the cross-section. This results in a reduction of polyethylene orientation below what would be expected.