HANSER

Polyolefins

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Leseprobe 3

Small angle X-ray scattering studies have shown lamellar structures in tubular blown polyethylene film. K. J. Choi et al. [66] proposed a morphological model for polyethylene tubular film based on non-parallel shish nuclei, each with perpendicular lamellae growing from the shishes (Fig. 9.15).

9.8 Isotactic Polypropylene Film

9.8.1 Cast Film

The structural characteristics of cast films of conventional isotactic polypropylenes has been described by Haudin and his coworkers [17, 69, 70]. These studies are unique among research in films because they consider structural microstructure gradients through the film thickness direction. Both industrial films and films prepared in their laboratories were studied.

All of the films exhibited spherulitic microstructures. The main crystalline form was the Natta-Corradini α-monoclinic structure with lesser amounts of the hexagonal β structure (Section 3.4). The film thus consists of α and β elliptical spherulites. The β spherulites had higher birefringence levels.

Optical microscopy could distinguish three regions. These were

- region in contact with the chilled roll,
- the core of the film and
- region in contact with air.

The relative thicknesses of the surface layers were about 20 to 30% of the film thickness, and the core 50–60%. The surface layers were higher in β content than the median layer. The outermost surface in contact with the chilled roll exhibited a transcrystalline morphology. This cross-sectional morphology was sensitive notably to the chilled roll temperature.

9.8.2 Tubular Blown Film

Isotactic polypropylene tubular blown film has been studied by Shimomura et al. [71] and by D. Choi and White [72]. They found that the film crystallized into the Natta-Corradini α-monoclinic crystal structure. They gave average values of orientation through the thickness unlike Duffo et al. [17, 69, 70].

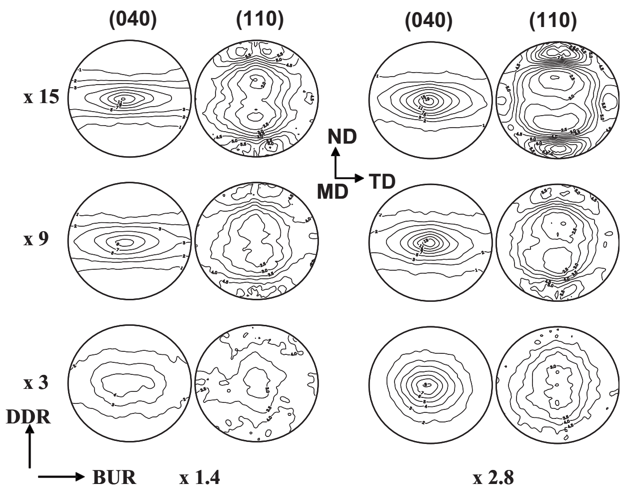

Figure 9.16 Typical pole figure patterns for isotactic polypropylene tubular blown films (D. Choi and White [72])

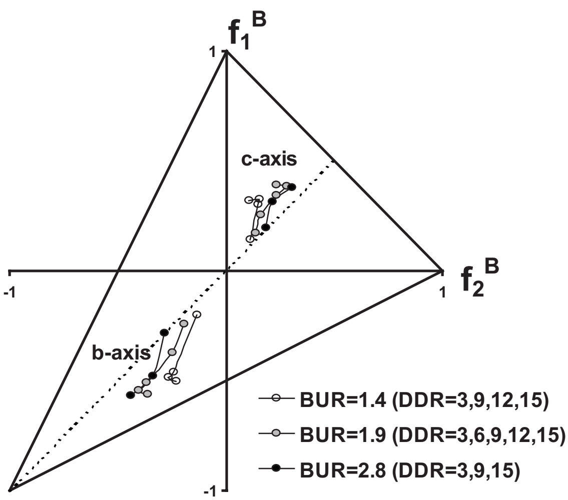

Figure 9.17 Biaxial orientation factors of isotactic polypropylene tubular blown films (D. Choi and White [72])

The crystalline orientation in isotactic polypropylene tubular blown films has been described by Shimomura et al. [71] and D. Choi and White [72]. The *b*-crystallographic axis tends to orient perpendicular to the surface of the film. Typical examples of pole figures and biaxial orientation factors are shown in Fig. 9.16 and Fig. 9.17, respectively.

Increasing draw-down ratio increases chain-axis (*c*-axis) orientation in the machine direction. Increasing blow-up ratio tends to increase chain-axis orientation in the transverse direction.

Annealed highly oriented uniaxial films of isotactic polypropylene become hard elastic films [73, 74]. They exhibit reversible elastic properties with a high modulus. Most strikingly, the transparent films become opaque when they are stretched due to the scattering of light by voids that are opened up. These voids apparently open up between the folded chain lamellae in the annealed films.

9.8.3 Biaxially Oriented Film

The double bubble process and tentering frame process have been used to make biaxially oriented films. There have, however, been few studies of crystalline orientation in highly stretched films [75–77]. Biaxially stretched isotactic polypropylene films are characterized by the crystallographic *c*- and a^*-axes being in the plane of the film and the *b*-axis being perpendicular to the surface of the film [77]. Thus,

$$f_{1c}^{B} = f_{2c}^{B} \to 0.5, \quad f_{1b}^{B} = f_{2b}^{B} \to -1.0$$

Generally, highly biaxially oriented films are characterized by high modulus and tensile strength and reduced elongations to break.

9.9 Syndiotactic Polypropylene Film

Syndiotactic polypropylene tubular blown films have been prepared by D. Choi and White [78]. Syndiotactic polypropylene unlike high density polyethylene and isotactic polypropylene does not exhibit a distinct freeze line on the bubble, but the bubble diameter gradually expands over a wide range. This is associated with the slow crystallization rates. High blow-up ratios are readily achievable in making syndiotactic polypropylene blown films.

Syndiotactic polypropylene blown films exhibit the Lovinger, Lotz et al. Form I orthorhombic crystal structure (Section 3.5). No changes in crystal structure were found such as those occurring in the case of melt-spun fibers [78] (Section 8.8). This is probably caused by the low stresses.

In syndiotactic polypropylene films, the *a*-axis tends to orient perpendicular to the film thickness direction (Fig. 9.18). High chain orientation in the transverse direction is rapidly developed by increasing blow-up ratio. Typical examples of biaxial crystalline orientation factors are shown in Fig. 9.19.

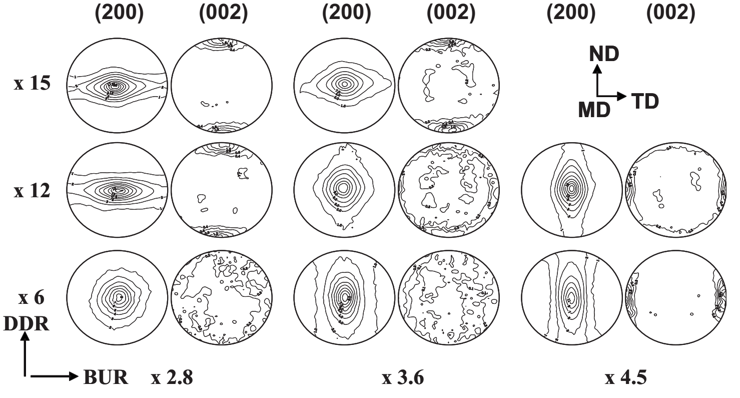

Figure 9.18 Typical pole figure patterns for syndiotactic polypropylene tubular blown films (D. Choi and White [72])

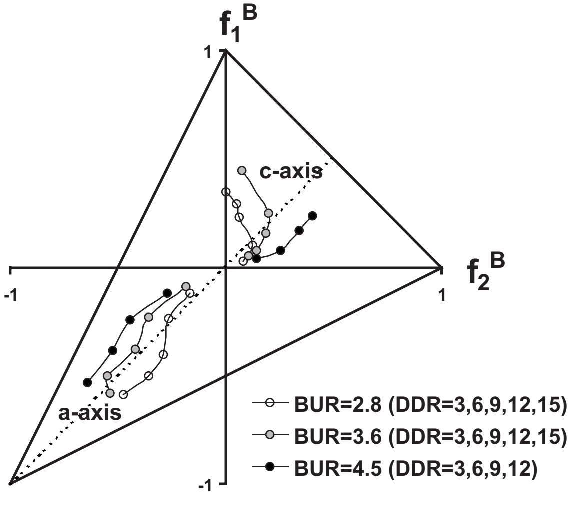

Figure 9.19 Biaxial orientation factors of syndiotactic polypropylene tubular blown films (D. Choi and White [72])

9.10 Isotactic Polybutene-1 Film

Isotactic polybutene-1 film was first investigated by Nagasawa et al. [62, 63]. They found that the molten films crystallized in the film line. Subsequent studies were made by Rohn [79], Hashimoto et al. [80, 81], Hong and Spruiell [82], and Johnson and Wilkes [83].

Hong and Spruiell [83] note that the films initially exhibit the Form II tetragonal crystal structure, which slowly ages to Form I hexagonal structure (Section 3.6). The transition can be enhanced by cold rolling or through introducing additives.

Johnson and Wilkes [84] in a more recent study discuss the lamellar structure of isotactic polybutene-1 films.

9.11 Isotactic Poly(4-Methyl Pentene-1) Film

Tubular blown films of isotactic poly(4-methyl pentene-1) have been prepared by Johnson and Wilkes [83, 84]. These were essentially uniaxial films (blow-up ratio: 1.0) and were characterized in terms of their lamellar structure and orientation. The levels of uniaxial orientation were observed to be quite high as found in their melt-spun fibers (Section 8.10)

9.12 Syndiotactic Polystyrene Film

There seem to be no published studies of cast or tubular film extrusion of isotactic polystyrene.

Cast syndiotactic polystyrene film was prepared by Hsiung and Cakmak [85]. It was virtually amorphous and resembled the low draw-down fibers of the same polymer by Hong and White [86]. Hsiung and Cakmak [85] found that their films crystallized when uniaxially stretched at 110 °C, which was 15 to 20 °C above T_g.

Single and double bubble tubular films of syndiotactic polystyrene have also been investigated by Kanai [87].

9.13 Summary and Conclusions

Studies on the structuring of polyolefin tubular blown films have not been developed as far as melt spinning. Some conclusions can be reached:

- Bubble inflation allows biaxial orientation to be developed.
- In cast film and single bubble tubular film extrusion, the processing conditions are mild, and only low orientations are developed.
- Tentering frame and double bubble processes develop high levels of biaxial orientation.
- Haze in tubular blown film is primarily due to surface roughness.
- For atactic polystyrene films, the birefringence development is determined by the stress field at vitrification as is the case for melt-spun fibers. The birefringence is proportional to the stress level. Enhanced mechanical properties may be obtained in biaxially oriented films.
- For polyethylene, there have been many studies of single bubble film. The Bunn α orthorhombic structure is formed. The birefringence and crystalline chain-axis orientation factors are determined by the stresses at the position of crystallization. The b-crystallographic axis tends to orient perpendicular to the surface of the film. The orientation-stress relationship for polyethylene tubular blown films is consistent with that for the melt-spun fibers. It may readily be concluded that the crystalline morphology depends upon the stress field at the frost line.
- In isotactic polypropylene, there is much less data on blown film extrusion compared to melt spinning. The Natta-Corradini monoclinic α-crystal structure is formed, and the b-crystallographic axis tends to orient perpendicular to the surface of the blown film.
- Structuring in cast films of isotactic polypropylene has also been studied. The cast films exhibit structural gradients in the film thickness direction. The monoclinic α-crystalline form is dominantly formed, and lesser amounts of hexagonal β spherulites are found in the surface layers.
- In syndiotactic polypropylene, the Form I orthorhombic crystal structure is formed, and the a-crystallographic axis tends to orient perpendicular to the surface of the blown film. High chain orientation in the film transverse direction is readily developed by increasing blow-up ratio.