The Preparation of Multiaxially Oriented Polyethylene Morphologies with High Mechancial Properties in Planar Directions

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Synopsis

The development of multiaxially oriented films of low molecular weight ($M_w \approx 59{,}000$) high density polyethylene with high mechanical properties in planar directions has been pursued by inducing fibrillar crystallization under curvilinear flow conditions in a contained geometry using an extrudomolding process and by simulating similar crystallization conditions in an optical plate–plate rheometer. The films, like the uniaxially drawn morphologies of the same low molecular weight high density polyethylene by solid-state extrusion, had a high modulus (12–20 GPa) and strength (0.25 GPa) along the residual flow lines but they exhibited also a modulus enhancement (5 GPa) in the transverse direction as a result of the orientation gradient of the molecular chains in the thickness directions.

INTRODUCTION

The development of high modulus polymers has been achieved by preparing anisotropic morphologies of oriented and extended molecular chains. These morphologies have been obtained with flexible polymers by inducing the high degree of molecular order using solid-state and melt or solution techniques, and also with semirigid and rigid polymers by fiber spinning from lyotropic solutions and injection-molding thermotropic melts.[1–6] However, in all processes, the level of molecular orientation is extreme in only one direction, and therefore the resultant mechanical performance is very directional. This type of unidirectional mechanical performance is beneficial in various applications, and many efforts have been made to maximize it, e.g., in fiber producing processes. In applications where a 2- or a 3-dimensional mechanical performance is required, the approach is more complex. About 15 years ago, Cleereman reported a rotational molding process to reduce and homogenize the residual orientation in injection-molded polystyrene products.[7,8] The process resulted in molded specimen with enhanced toughness, but no tensile modulus or strength enhancement was observed. More recently, workers at Bethlehem Steel Co. have designed a hydrostatic extrusion process to obtain biaxially oriented polypropylene films.[9] The extrudates, thick biaxially oriented tubes, produced through inverted conical disc, were split open to sheets and had enhanced impact strength. Like the Cleereman's process, their process is of low molecular deformation efficiency, and, as a result, the tensile properties of the sheet products are low.

Recently, we have undertaken in our laboratory the development of multiaxially oriented morphologies by an extrudo-molding technique to process the polymer at a temperature below its crystalline melting point under curvilinear

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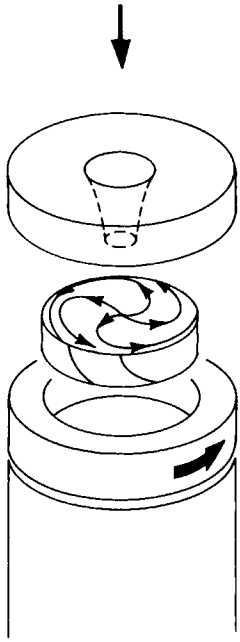


Fig. 1. Schematic diagram of the rotating mold cavity and the flow lines generated under the combined effects of rotation and compression.

flow conditions generated by the combined effects of compression and rotation in a contained geometry. Although the process has been demonstrated successfully for the preparation of multiaxially oriented morphologies with semi-

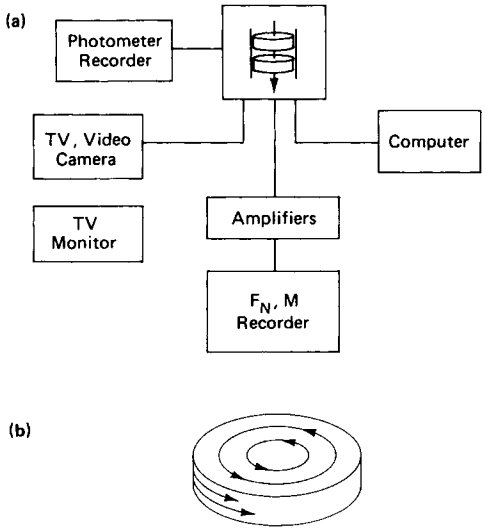


Fig. 2. Schematic diagram of (a) the plate–plate optical rheometer and (b) the flow lines generated under the curvilinear flow conditions between the plates.

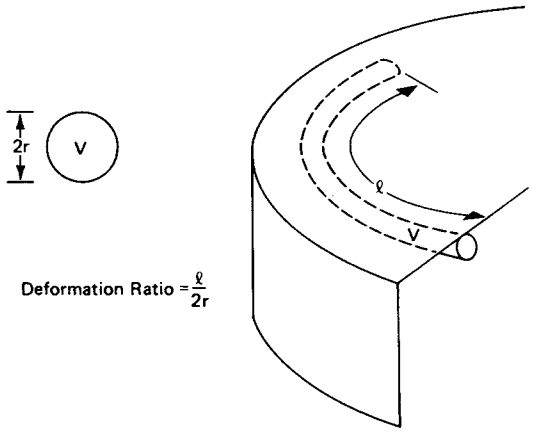
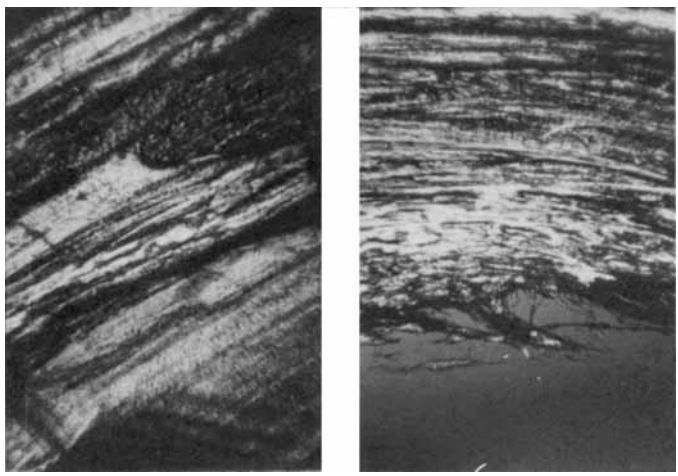


Fig. 3. Schematic of a deformed pellet.

crystalline and semirigid polymers,[10,11] we discuss in this report the results of our studies with high density polyethylene, a polymer which has been used extensively for the preparation of highly drawn morphologies.

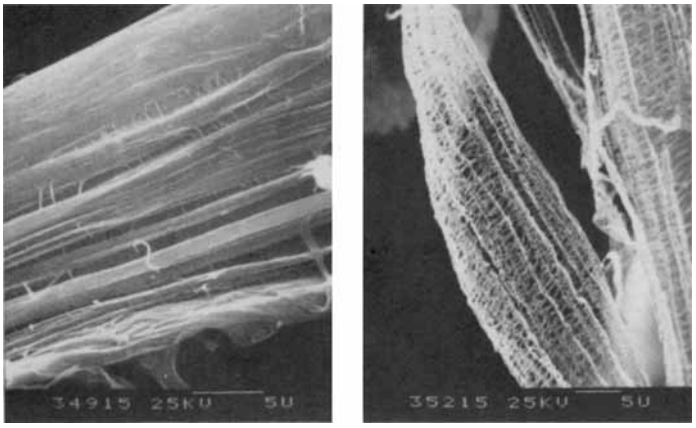
EXPERIMENTAL

The multiaxially oriented high density polyethylene (Alathon 7050, M_w = 59,000) films were prepared in a specially designed mold (Fig. 1) using a compression-molding machine (Morgan-Press). The two key features of the process are: (a) the controlled injection of the polymer melt in the mold cavity to avoid quenching of the melt and (b) the superposition of the compression and rotational forces, generated by rotating the lower point of the mold cavity during the in-



(a) (b)

Fig. 4. Optical micrographs of the high density polyethylene (a) melt under shear at 128°C and (b) crystallized polymer at 121°C under rotational-compression conditions. The micrographs were obtained with cross polarized light.



(a) (b)

Fig. 5. Scanning electron micrographs of the fibrillar morphology of (a) unetched and (b) plasma etched multiaxially oriented film specimens.

jection of the polymer to ensure controlled crystallization along the residual flow lines in the mold. The injection pressure was 200 atm. A temperature gradient of ~10°C was applied between the gate to the mold and the mold cavity which was heated to 120°C. The duration of rotation (~80 rpm) during the injection step was 15 s. After crystallization, the cavity was cooled to ambient to retrieve the specimen.

Similar processing conditions were simulated in a custom built parallel plate–plate optical rheometer (Fig. 2). The plate–plate fixture was made of optically clear quartz, and it was surrounded by a cylindrical wall to prevent the polymer melt from flowing past the two circular plates when high shear or compression (≤5 atm)—by closing the gap between the plates—was applied. The whole assembly was enclosed in a temperature controlled cavity. The optical observations were made using cross-polarized light. In a typical experiment, the polymer was placed between the plates and was heated to 160°C. After temperature equilibration for 5 min, the melt was compressed (≤5 atm) and was oriented by rotating the lower plate during recrystallization on cooling to 120°C. When the polymer crystallized completely, the rotation was stopped, and the film was retrieved after cooling to ambient. The shear rate at the periphery of the disc plate was 4×10^2 s^{-1}. The oriented films which were prepared in the optical rheometer had a thickness of ~150 μm.

PHYSICAL PROPERTY CHARACTERIZATION

The morphology of the oriented films was studied by scanning electron microscopy using a Hitachi S-500 SEM. The electron microscopy studies included also the examination of the surface morphology of oriented films which were plasma etched in an oxygen atmosphere for 20 min.

The tensile properties of the oriented films were determined with ribbon specimen cut along and across the flow direction using a custom made microtensile instrument. The Young modulus was measured at 1.3×10^{-3} s^{-1}, and the tensile strength is the average of three measurements. The impact strength

TABLE I
Physical and Mechanical Properties of Multiaxially Oriented Polyethylene Samples[a]

Flexular modulus (GPa)	12
along flow lines	
across flow lines	4
Tensile modulus (GPa)	12–20
along flow lines	
across flow lines	5
Tensile strength (GPa)	0.25
Strain to fracture (%)	3.4
Impact strength (lb·in.)	8
Melting point (°C)	138
Crystallinity (%)	86

[a] Film thickness 1.2 mm.

tests were performed with a falling ball tester (Gardner Instruments). The impact strength is the average value of five measurements.

Thermal analysis data were obtained with a DuPont Thermal Analyzer (Model 990). The percent crystallinity was determined assuming that the heat of fusion of perfect polyethylene crystals is 69 cal/g.[12]

To determine the extent of the molecular deformation in the extrudo-molded specimens, we performed shrinkage tests at fast heating rates (~100°C/min) above the melting point of the polymer. The samples—ribbons (1 cm long) cut along the flow direction—were placed in a glycerol bath which was preheated to 160°C. As soon as the samples were molten, they became transparent and shrunk. From the dimensional changes, the percent shrinkage and/or elastic recovery could be calculated using the equations

$$\%S = (L_T - L/L_T) \times 100 \tag{1}$$

$$\%R = (L_T - L/L_T - L_0) \times 100 \tag{2}$$

where L_T is the length of the oriented sample before testing, L the shrunk length, and L_0 the length before processing. The deformation ratio of the oriented films was determined by blending pellets of different color. Assuming volume conservation, the ratio was defined by the diameter of the pellet idealized as a sphere before melting and its deformed length idealized as a cylinder, as shown in Figure 3. From the ratio (DR) of cylinder length to pellet diameter and the percent recovery, the actual molecular deformation was determined using the equation

$$\text{molecular deformation (MD)} = R \times (\text{DR} - 1) + 1 \tag{3}$$

RESULTS

The melt flow crystallization studies with the optical rheometer provided useful information for deciding the processing conditions in the extrudo-molding experiments. When the polymer melt was sheared between the parallel plates, it exhibited flow birefringence along the circular shear flow lines on cooling at 128°C. Soon thereafter, fibrillar crystallization occurred which was completed on further cooling to ~121°C (Fig. 4). Under the processing conditions in the mold when the rotational flow—imposed by the rotating mold—was combined with the radial flow—resulting from the injection of the polymer at the center of the circular cavity—the fibrillar crystallization occurred along the residual

TABLE II
Shrinkage and Modulus Data of Uniaxially Oriented and Multiaxially Oriented HDPE (Alathon 7050)

Sample	EDR	% Recovery	MDR	Modulus (GPa)
Rod[a]	14	44	5.3	10
Rod[a]	24	46	11.0	27
Rod[a]	36	46	16.0	40
Film[b]		44–53	5.8–18.3	12–37
Film[c]		9	2	1.5

[a] Uniaxially oriented samples obtained by solid state extrusion.
[b] Multiaxially oriented samples obtained by extrudo-molding.
[c] Samples obtained by conventional injection molding.

ellipsoidal flow lines, shown in Figure 2. With the thicker specimens obtained in the mold cavity (1.2 mm thick), the ellipsoidal flow lines had an angle gradient also in the thickness direction.

As shown by the electron micrograph in Figure 5(a), the fibrillar morphologies of the multiaxially oriented films appear structureless at low magnification. On the contrary, the electron micrographs of the plasma etched specimens show that the fibrils have a shish-kebab type of morphology [Fig. 5(b)]. The central backbone of the lamellar fibrils is clearly seen; also, the fibrils appear to interpenetrate in adjacent fibrillar columns.

The Young modulus of the multiaxially oriented films along the flow direction was typically 12–20 GPa and increased to 35 GPa as the thickness of the film was reduced from 1.2 mm to 150 μm. The Young modulus across the flow direction was 3–4 GPa but decreased sharply as the thickness of the film was reduced. The tensile strength was 0.25 GPa, and the strain at fracture 3.4%. The impact strength of the multiaxially oriented films (1.2 mm thick) is reported relative to the impact strength of an unoriented film. An 8× increase was observed with the multiaxially oriented films. The mechanical properties are summarized in Table I, and they are compared to the property values obtained with uniaxially oriented polyethylene fibers which were prepared by the solid-state extrusion technique.[2] The melting point of the multiaxially oriented films was 138°C, and the calculated crystallinity 86%. The thermal analysis data are included also in Table I.

The shrinkage and the calculated molecular draw ratio data for the multiaxially oriented films are summarized in Table II and are compared to analogous data obtained previously with solid-state extruded rods of the same polyethylene grade. Also, the Young modulus data are included for comparison.

DISCUSSION

The development of polymer compositions with high mechanical performance in planar directions has been achieved to date predominantly by the construction of fiber-reinforced composite structures which, in general, involve elaborate and expensive laying up processes. Biaxial orientation, the most obvious approach for the development of homogeneous compositions with high mechanical performance in planar directions, has been used also extensively in various processes, e.g., extrusion and stretching. The products of such processes have enhanced

Fig. 6. Type of failure in impact strength tests with multiaxially oriented polyethylene films. The films crack along the residual flow lines in each layer of their laminated structures.

impact resistance but only moderate tensile strength and modulus. The low strength and modulus of the biaxially oriented fibers is attributed to the spherulitic structure—in the case of a semicrystalline polymer—which at low extension ratios, at which the biaxial orientation process typically operate, does not convert to a highly drawn fibrillar morphology which is a prerequisite for the development of ultrahigh tensile performance. The generation of a fibrillar morphology by a biaxial drawing process would result most likely in the destruction of the drawn specimen because of the lateral weakness of the fibrils along a particular plane and across the thickness of the specimen. Therefore, to obtain in planar directions the ultrahigh mechanical performance typically achieved by uniaxially drawing processes, e.g., melt or solid-state extrusion and drawing, it is essential to obtain a morphology in which the unidirectional orientation of the molecular chains in the plane of the specimen has an angle gradient in both the plane and thickness directions. This type of multiaxial orientation can be obtained by inducing fibrillar crystallization under curvilinear flow conditions generated by the combined effects of compression and rotation. As it was observed also in earlier rheo-optical studies with ultrahigh molecular weight polyethylene,[13] the fibrils grow under such conditions by row nucleation along the circular flow lines in the plane of the film. When processing in the

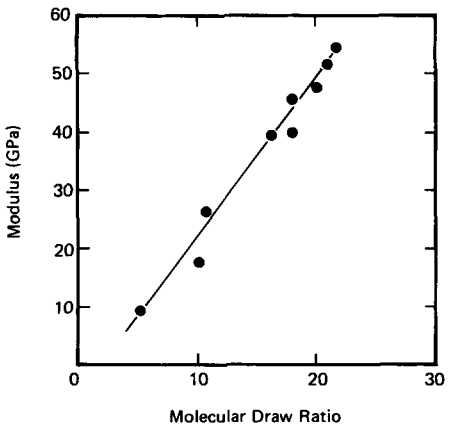


Fig. 7. Variation of modulus with molecular draw ratio (from Ref. 14).

rotating mold, the fibrillar crystallization occurs along the residual (ellipsoidal) flow lines resulting from the superimposed radial and circular flow conditions generated in the mold cavity. The orientation of the fibrils varies with the sample thickness, and, as discussed below, it plays an important role in the mechanical performance of the films.

The mechanical property data summarized in Table I indicate that the multiaxially oriented films have a laminated structure of fibrils in which the fibrillar orientation varies slightly in each layer of fibrils. The property dependence on the angle gradient of the fibrillar orientation in the thickness direction of the specimen is supported also by the enhancement of the impact strength (8×) and is illustrated also by the mode of failure upon impact. The films tend to crack along residual flow lines in each laminate, as shown in Figure 6, and eventually they fail mostly by delamination. This kind of failure reflects clearly the high planar tensile strength of the fibrillar films, which is comparable to the tensile strength value of uniaxially drawn filaments.

Previous studies on the preparation of oriented polymers have shown that (a) the efficiency of inducing and maintaining the chain elongation is important in producing high modulus products and (b) the modulus is a simple linear function of the molecular drawn ratio.[14] A simple test that gives a quantitative measure of the molecular extension, and therefore the efficiency of the process, is a shrinkage test performed at fast heating rates above the melting point of the polymer. The test has been used previously for the evaluation of the molecular extension in solid-state extruded polymers, and the results were astonishingly close to those obtained in independent studies by the small angle X-ray scattering technique.[15] In the present study, this simple test showed that the average shrinkage (~45%) was approximately equal to the shrinkage values determined with solid-state extruded ribbons of molecular drawn ratio 5–18. Again, the molecular drawn ratio of the multiaxially oriented films was dependent on the sample thickness, the high molecular drawn ratio associating with the thinner specimens (150 μm thick). In addition, the Young modulus values of the multiaxially oriented films along the flow direction were very close to the values predicted by the plot of molecular drawn ratio vs. modulus shown in Figure 7 and reproduced from Ref. 14. Although the processing conditions affect the efficiency of the deformation process and hence the mechanical performance of the deformed polymer, as shown by the higher molecular drawn ratio and modulus values, these data show also that the preparation of multiaxially oriented morphologies with similar high mechanical properties, but in more than one direction, is feasible and can be achieved by rapid and commercially available processes.

CONCLUSION

The development of homogeneous morphologies with high mechanical performance in planar directions has been achieved by inducing fibrillar crystallization under curvilinear flow conditions. The concept was demonstrated using a simple and rapid extrudo-molding process to prepare multiaxially oriented polyethylene films which were resistant to fibrillation and had high planar tensile and flexular properties.

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