Ultradrawing of Polystyrene by Solid-State Coextrusion: Shear-Induced Crystallization in Isotactic Polystyrene

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Synopsis

Polystyrene with a 60% isotactic dyad content (iPS) was subjected to two-stage solid-state coextrusion at 124 and 160°C. It was shown that only shear-induced crystallization occurred with the amount of crystallinity strongly dependent on draw ratio. The steep increase in crystallinity from 0 to 29% is accompanied by a marked increase in the absolute total birefringence from 0 to 30×10^{-3} and the tensile properties, from 2.5 GPa to 4.5 GPa, giving strong evidence for the necessity of a crystalline phase to achieve higher tensile moduli. Wide-angle X-ray scattering showed a higher crystal orientation for the extrudate produced at 124°C than for the one produced at 160°C. Thermal shrinkage experiments support a partial dissipation of orientation after extrusion at 160°C and on reextrusion in general. Electron microscopy revealed a fibrous nature for the solid-state coextrudates produced at both temperatures.

INTRODUCTION

In recent years, significant progress has been achieved in ultradrawing semi-crystalline thermoplastics, most commonly polyethylene, by a variety of methods including solid-state extrusion.[1-3] At temperatures well below the melting point of semicrystalline polymers, only low draw ratios (DR) are possible due to increasingly severe pressures required. The newly developed method of solid-state coextrusion[4] reduces these limitations, allowing also the drawing of heretofore intractable thermoplastics.[5] The process has also been applied to amorphous atactic polystyrene.[6] Further progress in ultradrawing of atactic polystyrene was achieved by a multistage solid-state coextrusion[7] allowing DR > 20.

Through its widespread application,[8] atactic polystyrene has grown into one of the largest volume of bulk polymers produced today, but there has not been any significant growth in the commercial development of products based upon isotactic polystyrene.[9] Severe processing conditions are associated with its high melting point, $T_m = 240°C$,[10] without significantly improved mechanical and optical properties.[9] It is expected that by solid-state coextrusion the severe processing conditions of iPS can be overcome and that extrudates of high DRs with improved tensile and physical properties can be obtained.

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EXPERIMENTAL

Materials and Extrusion

A polystyrene of 60% isotactic dyad content was used in this study (Polyscience, Inc., Warrington, PA, $M_w = 851,000$; $M_w/M_n = 5.93$). The polymer pellets were mold-pressed into films 0.6 mm thick at 250°C and at 20,000 psi ram pressure. The films were subsequently quenched in water to room temperature, which produced amorphous samples.

To aid coextrusion, two types of billets were prepared from commercially available rods: (1) high-density polyethylene (HDPE) billets of Ultra Ethylux, Westlake Plastics, Pittsburgh, PA, and (2) isotactic polypropylene (iPP) billets from Cadillac Plastic and Chemical Co., Linden, NJ. The $3/8$ in. diameter rods were split and grooved longitudinally in the same manner as described earlier.[7] For the first stage of coextrusion, the grooves were machined to accommodate films 6 mm wide; and for the second stage, grooves fitting the preextruded films were machined.

The split billets together with the inserted films were then press-fitted into the preheated barrel of an Instron rheometer and, after temperature equilibration, pushed through conical brass dies of included entrance angle of 20°. The nominal draw ratios of the dies (change in cross-sectional area) were varied between 3.8 and 9. For the second stage of coextrusion, films of an effective draw ratio (EDR) between 2.4 and 4.2 were chosen. The EDR was calculated from the displacement of ink markers before (l_0) and after (l_e) extrusion to EDR = l_e/l_0. Coextrusions were carried out at 160°C with iPP and at 124°C with HDPE as the coextrudate.

Thermal Analysis

The thermal analysis of the extruded samples was carried out in a Perkin–Elmer DSC 2. The sample weighed 10–12 mg; the heating rate was 10°C/min, and the sensitivity was 2 mcal/s.

Shrinkage experiments were performed at various temperatures in a glycerol bath. Ten-millimeter-long strips of the extruded films were floated for a sufficient time to reach equilibrium length. Subsequently, the films were cooled to room temperature and the shrinkage determined. The percent shrinkage S is defined as

$$S = \frac{l_e - l_s}{l_e} \times 100$$

and the percent recovery R as

$$R = \frac{l_e - l_s}{l_e - l_0} \times 100$$

with l_s being the length of extrudate after shrinkage.

Birefringence

The total birefringence was measured with a Zeiss polarizing microscope equipped with an Ehringhaus rotary compensator. The thickness of the shaved samples ($\pm 10\%$) was taken as the average of several micrometer measurements along the film.

Scanning Electron Microscope

The morphology of samples was examined along freeze-fractured surfaces formed in liquid nitrogen with a ETAC–SEM, Haywood, CA. The surfaces were sputter coated with approximately 300 Å of gold in the vacuum. The acceleration potential in the microscope was 20 kV.

Tensile Testing

Tensile properties of the polystyrene extrudates were determined with an Instron tester model TTM. The modulus was calculated from the slope of the stress–strain curve at 0.1% strain; the strain rate was about 1.7×10^{-4}/s. All films were stressed to break, and the corresponding strength at break was computed.

Wide-Angle X-Ray Scattering

A pin-hole camera with copper $K\alpha$ radiation was used to take wide-angle (WAXS) photographs. Generally, 4 to 5 strips of iPS film 1 cm long were placed on top of each other to obtain a sufficiently strong photographic pattern on 24 h of exposure.

RESULTS AND DISCUSSION

In recent work,[7] processing conditions for ultradrawing atactic polystyrene have been developed. So encouraged, an attempt has been undertaken to find conditions under which isotactic polystyrene can be coextruded to high draw ratios to achieve extrudates of enhanced directional properties. To this end, two types of billet materials were chosen as coextrudates for iPS, HDPE, and iPP. The extrusion temperatures were optimized at 124 and 160°C, respectively, for initially amorphous iPS. At both temperatures, it was possible to extrude the iPS to an effective draw ratio (EDR) of ~7. A higher EDR of ~12 was obtained by a two-stage process.

The thermal properties of the translucent coextrudate fibers of iPS were investigated by differential scanning calorimetry. The crystallinity was calculated from the area of the melting peak taking the heat of fusion of iPS crystals as H_f = 19.2 cal/g.[11] In all cases, a simple broad melting peak was observed, in contrast to the double peaks reported for solution cast 100% iPS and for blends of iPS and atactic PS.[12] The different melting behavior may be due to different crystal morphologies which is well known for polyethylene.[13] Table I shows the melting point to increase with the crystallinity to a maximum of 227°C. The glass transition temperature, on the other hand, does not change perceptibly with EDR and is found to be 99 ± 1°C.

TABLE I
DSC Results for Coextruded Films of Isotactic Polystyrene

Extrusion temp., °C	EDR	T_g, °C	T_m, °C	Percent crystallinity
a	1.0	100	—	0
160	2.2	98	217	4.9
	2.2[b]	98	—	0
	3.28	99	217	5.9
	5.64	101	218	16.0
	5.76	99	218	22.7
	5.76[b]	100	—	0
	6.56	100	227	26.0
	6.56[b]	100	—	0
124	3.2	100	217	1.0
	3.94	99.5	217	7.8
	5.50	99.5	218	7.8
	7.6	100	223.5	22.0
	7.6[b]	100	—	0
	8.2	99	218	9.8
	12.4	100	225	28.9
	12.4[b]	100	—	0

[a] Mold-pressed film.
[b] Film from extruder barrel, of the same thermal and pressure history, but not extruded.

Crystallinity develops only during extrusion and mainly near the die exit. Films of iPS of identical thermal and pressure history as the corresponding coextrudate exhibit no crystallinity (see Table I). Because of the short die res-
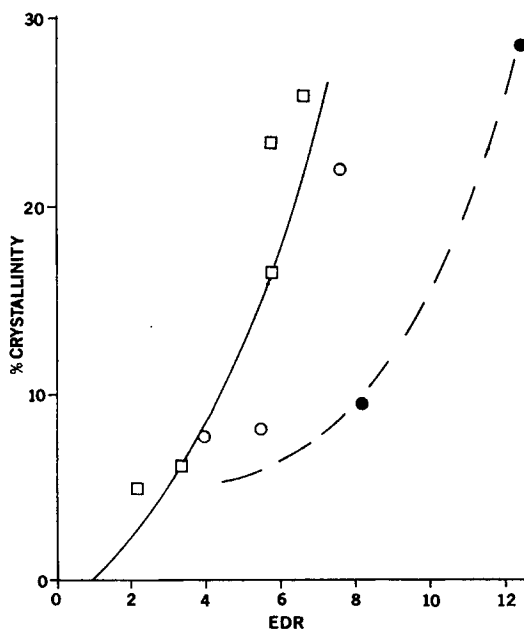

Fig. 1. Crystallinity as function of effective draw ratio (EDR) for 60% isotactic polystyrene obtained by solid-state coextrusion at 124°C (O) and at 160°C (□). Full symbols for the second-stage process.
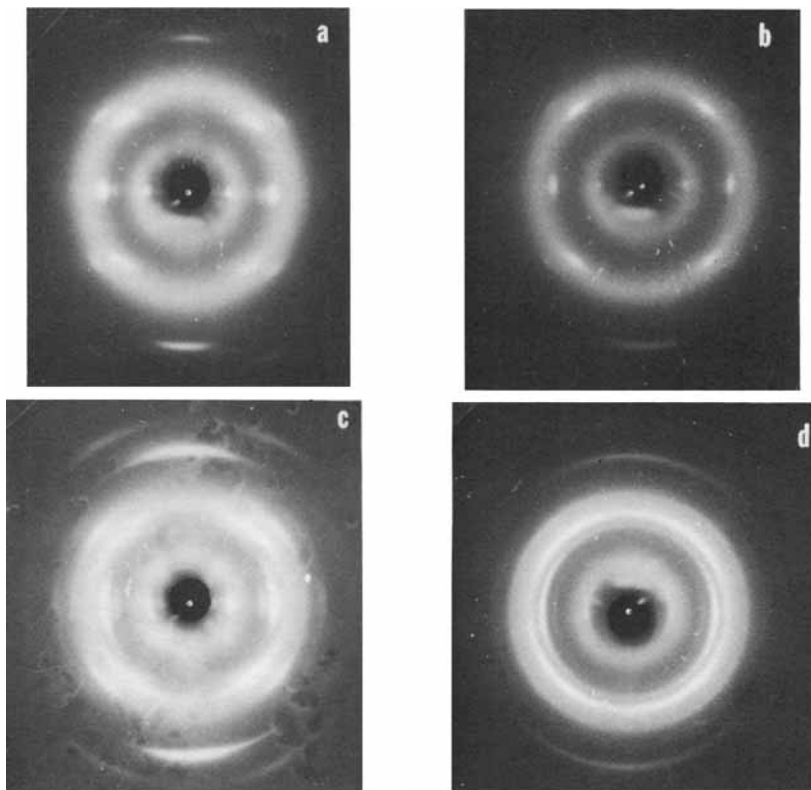
Fig. 2. Wide-angle X-ray photographs for solid-state coextruded iPS. Temp. 124°C: (a) EDR 7.6, (b) EDR 8.2. Temp. 160°C: (c) EDR 6.56, (d) EDR 10.8.

ident time, and relatively short cooling time of the extrudate upon exposure to air, the crystallization process is complete in less than 15 min. The highest degrees of crystallinity obtained here at crosshead speeds of 0.05 cm/min and NDR = 9 suggest high crystallization rates since comparable crystallinity can only be obtained after hours of isothermal treatment.[12,14] Further, the degree of crystallinity increases with EDR (Fig. 1) to reach a maximum of about 25% for the first step of coextrusion. A slightly higher degree of crystallinity (29%) is achieved for the second stage at higher EDR after an initially slow increase in crystallinity. The highest crystallinity was obtained where the flow profile, as reflected by deformed ink markers, exhibited deep parabolas typical of shear flow. However, no attempt has been made at this point to separate the effect of shear and extensional flows on the coextrusion of isotactic PS.

A qualitative examination of the crystalline orientation was undertaken by WAXS photography (Fig. 2). The reflections indicate that the iPS crystallographic C axis[15,16] is oriented along the extrusion direction. It is obvious from the photographs that the films extruded at 124°C [Figs. 2(a) and (b)] exhibit a significantly higher crystalline orientation than those extruded at 160°C [Figs. 2(c) and (d)]. Further, the extrudate obtained by the two-stage solid-state coextrusion at 160°C (d) displays considerably less orientation than the one-stage extrudate (c). This effect is not as apparent for iPS drawing at 124°C. This behavior may be explained in terms of increased relaxation for postdrawing at

the higher temperatures.   The high orientation achieved by the shear flow leads to rapid crystallization, but the connecting amorphous phase relaxes above the PS T_g causing a slight disorientation of the crystallite alignment with the extrusion direction.   At the lower temperature, the crystalline orientation is better generated and preserved because T_g is closer, thus effectively "freezing" the overall orientation.   Similar results had been found for the ultradrawing of atactic PS.[17]   This is consistent with a liquid–liquid transition temperature at $T_{ll} = 1.16 \times T_g$ for atactic PS.   Assuming that the same T_{ll} applies to isotactic PS, a considerably higher mobility is expected for 160 than 124°C and consequently a higher degree of orientation at 124°C because of the lesser relaxation.

Birefringence reflects the same trend for orientation of the iPS with increasing EDR, as does WAXS (see Fig. 3).   It reaches a maximum of $|3.05 \times 10^{-2}|$.   This is more than twice the value obtained for atactic PS at the same EDR and lower temperatures.   As birefringence responds to a combined amorphous and crys-
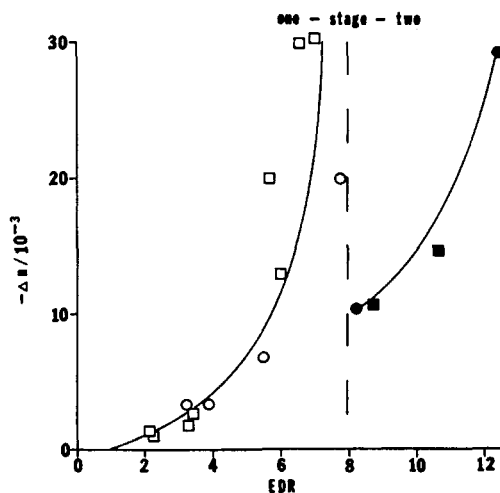

Fig. 3. Birefringence as function of draw ratio.   Symbols as in Fig. 1.
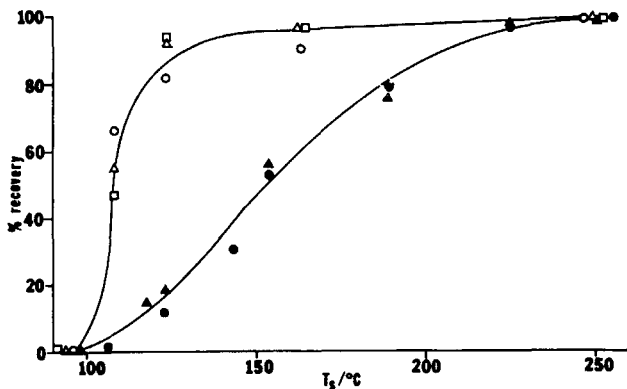

Fig. 4. Elastic recovery as function of shrinkage temperature T_s for iPS drawn at 124°C at EDRs of (□) 3.94, (△) 5.5, (●) 7.6, (○) 8.2, and (▲) 12.4.
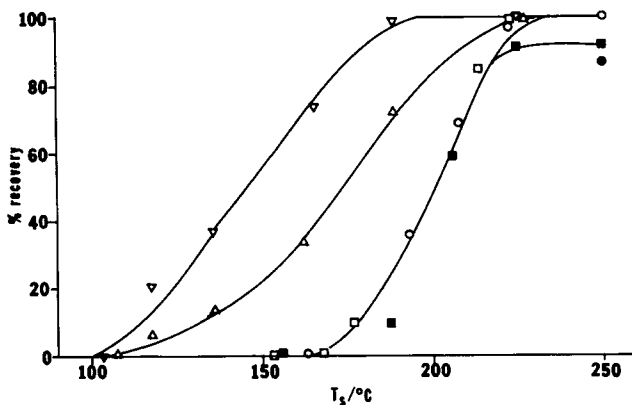
Fig. 5. Elastic recovery as function of T_s for iPS drawn at 160°C, at EDR of ($\triangledown$) 2.46, ($\triangle$) 3.28, ($\square$) 5.64, ($\bigcirc$) 6.56, ($\blacksquare$) 10.8, and ($\bullet$) 8.7.

talline orientation, a simple separation of the individual contributions is therefore not easily possible. However, a $\Delta n = -3.05 \times 10^{-2}$ is more than twice the value obtained for atactic PS at the same EDR and at lower draw temperatures.[17] This indicates that the major birefringence contribution may be attributed to the crystalline phase. This is consistent with the work of Krigbaum and Taga,[16] who found that the degree of crystallinity grows at the expense of amorphous orientation. A clear separation of the amorphous and crystalline orientation will require a quantitative WAXS analysis in conjunction with birefringence measurements, as scheduled for future experiments. These additional experiments should also elucidate the nature of the load bearing units in iPS.

Again, the results indicate that during both stages of coextrusion, high orientation, as reflected by birefringence and WAXS, can be achieved, however at widely different draw ratios. The difference in the degree of orientation for the two stages of coextrusion as seen by WAXS cannot be seen in the birefringence because it measures only the total orientation.

Thermal shrinkage tests have been widely used to evaluate models for drawn morphologies.[7,19–23] In Figure 4, the shrinkage results for extrudates obtained at 124°C are shown. At temperatures at or above the melting point, quantitative elastic recovery is observed, i.e., the drawn fibers contract back to their original shape. As the shrinkage temperature T_s was decreased, the less crystalline extrudates continued to exhibit high recoveries until near T_g, where immobilization set in. For the more crystalline extrudates, recovery drops off considerably below the melting point and ceases altogether just above T_g. This is thought to be due to the relaxation of the amorphous tie molecules below the melting point, whereas the crystalline phase remains ordered.

The extrudates obtained at 160°C (Fig. 5) also exhibit quantitative recovery at or above the melting point, but below the melting point all films showed a rapid decrease in recovery. The samples of highest crystallinity displayed the most rapid decrease in agreement with the relaxation being limited to the amorphous phase. At decreased crystallinity, the orientation of tie molecules increases, resulting in more efficient recovery.

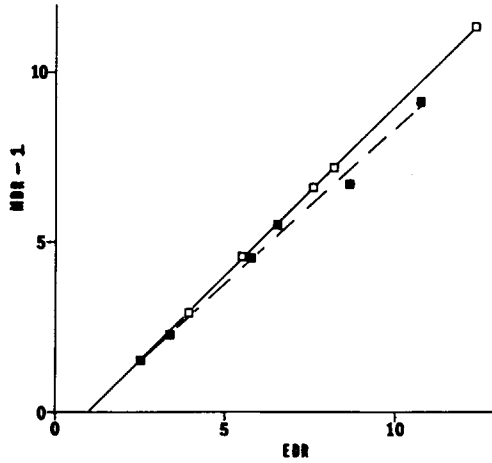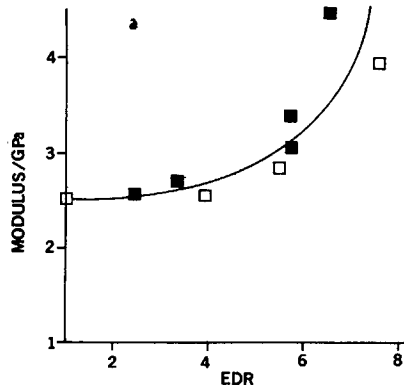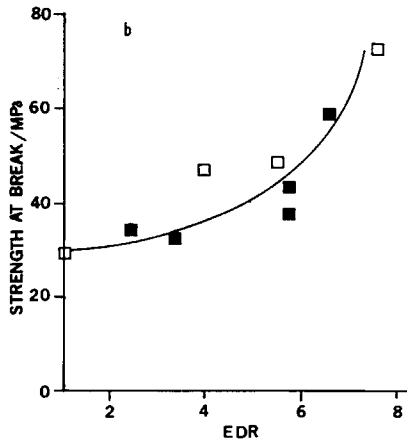The efficiency of the solid-state coextrusion may be calculated from molecular

Fig. 6. The efficiency of the coextrusion as reflected by the molecular draw ratio (MDR) as function of EDR at temperatures of (□) 124°C and (■) 160°C.

(a)

(b)

Fig. 7. Tensile properties as function of EDR: (a) Young's modulus; (b) yield strength. Symbols as in Fig. 6.
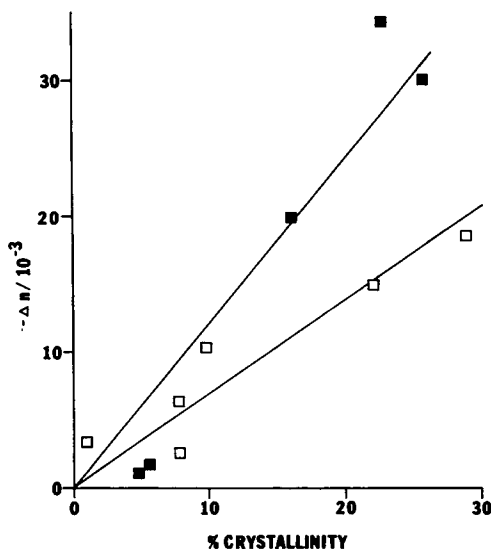
Fig. 8. Birefringence as function of crystallinity. Symbols as in Fig. 6.

draw ratio (MDR) from the measured recovery above the melting point; here pure chain extension is measured:

$$\text{MDR} = \frac{l_e - l_s + l_0}{l_0} = \frac{S \times \text{EDR}}{100} + 1$$

The results in Figure 6 are seen to confirm the above statements that the coextrusion into air at 124°C is more efficient than the one at 160°C.

The tensile properties are displayed in Figures 7(a) and (b). The moduli show a significant increase only for relatively high degrees of crystallinity reaching a maximum of about 4.5 GPa. The maximum is higher than for atactic PS[7,17] and more than one-third the theoretical modulus[24] calculated for 100% isotactic PS. This is a higher fraction than has been achieved for higher-modulus HDPE.[25] The modulus measurements point out again that the crystalline regions are necessary to tie the amorphous regions strongly together to achieve increased mechanical rigidity. The yield strength shows a trend similar to the moduli. The results for the two-stage extrudates are less clear, possibly due to
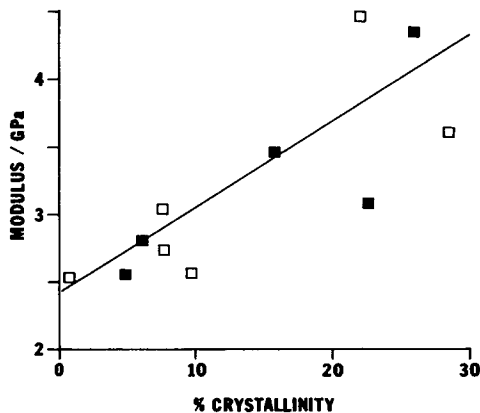

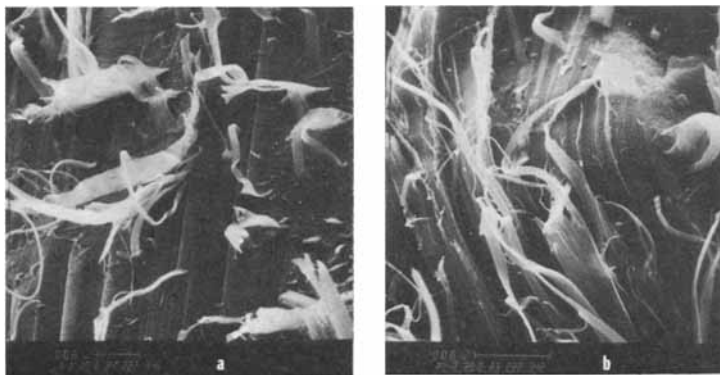Fig. 9. Modulus as function of crystallinity. Symbols as in Fig. 6.

Fig. 10. Electron micrographs of freeze-fractured surfaces of iPS coextrudates: (a) temp. 124°C, EDR 7.6; (b) temp. 160°C, EDR 10.8.

measuring errors and imperfections associated with rough surfaces. The strictly linear relationship between MDR and EDR reflects the high efficiency of the coextrusion process and indicates that the physical properties improve concomitantly with the orientation achieved and the induced crystallization. To illustrate this point, birefringence has been plotted vs. crystallinity in Figure 8 as well as modulus vs. crystallinity in Figure 9. As expected, linear relationships are obtained in both cases, with birefringence being more sensitive to the extrusion temperature. Importantly, the crystalline domain appears to be responsible for the improvement in physical properties.

The electron micrographs of Figures 10(a) and (b) demonstrate the fibrous nature of the drawn crystalline but clear iPS films. The fibers are aligned with the extrusion direction and are ribbonlike. The ribbons are thinnest for extrudates of high EDR and crystallinity. The extrusion temperature did not have any perceptible influence on the fibrous nature.

CONCLUSIONS

It has been shown that by solid-state coextrusion isotactic polystyrene can be drawn to high EDRs under moderate processing conditions comparable to those for atactic PS.[7,9,17] A rapid shear-induced crystallization to a high degree of crystallinity was observed. The process is more efficient than the more elaborate procedures for obtaining highly crystalline PS described in the literature.[11,12,14–16] The orientation in iPS extrudates was investigated by birefringence and wide-angle X-ray scattering. The results are consistent with an oriented crystalline phase connected by amorphous tie molecules. The molecules or segments in the amorphous domains are not in their random equilibrium conformation, resulting in thermal shrinkage well below the melting point of the crystalline regions. At higher drawing temperatures, partial relaxation after drawing reduces orientation. This is supported by thermal shrinkage experiments. The fibrous nature of the drawn extrudates was demonstrated by scanning electron microscopy. The maximum tensile properties are higher than for atactic PS equivalently drawn, leading to an overall improvement of physical and mechanical properties of iPS over atactic PS under similar mild processing conditions.

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