

Ultradrawing of Amorphous Polymers by Coextrusion Illustrated with Atactic Polystyrene

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Synopsis

Films of pure and high-impact atactic polystyrene were prepared by the recently developed technique of solid-state coextrusion. The films were produced at extrusion rates ≥ 4 cm/min at 126°C with a maximum extrusion draw ratio (EDR) of 11.6. These ultradrawn films are fibrous, have a high birefringence of -2.24×10^{-2} , and exhibit a 72% elastic recovery. The material has a tensile modulus of ~ 4 –5 GPa and a tensile strength to break of 85 MPa. Thermal analysis suggests a constant T_g .

INTRODUCTION

Polyethylene and other semicrystalline thermoplastics have been ultraoriented by several means, including solid-state extrusion.¹⁻⁴ The preparation of extrudates of high extrusion draw ratio at temperatures substantially below their melting points, however, is restricted by low extrusion rate and severe processing conditions, viz., high extrusion pressure.

Solid-state coextrusion,⁵ a new method developed recently in this laboratory, has alleviated to a large extent these limitations and furthermore has made possible the extrusion of less tractable thermoplastics. By the new technique cylindrical billets are split longitudinally and extruded through a conical die. A film strip of the same or different thermoplastic is also inserted within the split prior to extrusion. Upon extrusion, oriented films of the polymer inserted within the split may be obtained simultaneously with the surrounding substrates at much faster rates and lower temperature and pressure in comparison with the conventional extrusion of a single polymer. For example, oriented films of poly(vinylidene fluoride) of EDR ~ 6 have been prepared by conventional extrusion at 140–170°C and 0.23–0.49 GPa through a slit die. The same polymer was more effectively extruded between split billets of high-density polyethylene at 126°C and 0.09 GPa.⁶

Although the orientation of semicrystalline polymers by solid-state extrusion has attracted considerable interest, the deformation of amorphous polymers by this approach has heretofore not been examined. In this communication we report the application of the solid-state coextrusion technique to the preparation of oriented and fibrous films of atactic polystyrene. We also report on the properties of the oriented amorphous polystyrene films as coextruded on a double substrate of semicrystalline polyethylene.

EXPERIMENTAL

Cylindrical billets 0.95 cm in diameter of high-density polyethylene (du Pont Alathon 7050, $M_w = 59,000$, $M_n = 19,900$) were compression molded in vacuo at 160°C in a specially designed apparatus and split longitudinally into two halves.⁵ Films of polystyrene were obtained by compression molding at 170°C and quenching in icewater; the polymer grades and compositions are shown in Table I. A film strip of polystyrene having the geometric profile of the billet was imprinted with a 0.25-cm-square grid pattern in order to measure the extent of draw on coextrusion. The film (2 mm thick) was then inserted between the two halves of the split polyethylene billet, and the whole assembly was press fitted into the reservoir of an Instron rheometer and subsequently extruded at 126°C and 40 MPa through a conical brass die of included entrance angle of 20° and extrusion draw ratio 12.

The effectiveness of the coextrusion technique to produce extension and orientation of the amorphous polystyrene was evaluated by physical and mechanical tests on the extruded film strips. Thermal analysis of the extruded samples was performed with a Perkin-Elmer DSC-2B. The thermograms of the extruded samples, ~6 mg, were obtained at a heating rate of 10°C/min.

The total birefringence was measured with a Zeiss polarizing microscope equipped with an Ehringhaus compensator. Both the outer surface and the internal sample morphology of the extruded films were studied by scanning electron microscopy (SEM) with a JOEL 100CX "Temscan". The internal morphology was studied by examining a frozen fracture surface formed in liquid nitrogen by propagating a crack along the extrusion direction of the frozen sample. This morphology is shown in Figure 2. The surface of the extruded film is shown in Figure 3. Both surfaces were coated with approximately 300 Å of gold by vacuum evaporation and examined at a 100 kV acceleration potential in the microscope.

Shrinkage tests were performed on a hot-stage microscope with film samples 1 cm long. The films were floated on a glycerol bath to avoid adhesion between the polymer and the stage and heated from 100° to 160°C. Experiments were repeated three times, and results are reported with ±3% accuracy.

The tensile properties of the coextruded polystyrenes were measured on an Instron tester Model TTM in the extension mode. The modulus was determined from the tangent to the stress-strain curve at 0.1% strain for a strain rate of 3.3×10^{-4} /sec. Shrinkage tests were performed on 10-mm-long samples at different temperatures on a microscope thermostatted hot stage.

TABLE I
Molecular Characteristics of Polystyrenes Investigated

Polymer grade	$M_w \times 10^3$	$M_n \times 10^3$	M_w/M_n
PS (7% polybutadiene, 2% internal lubricant)	222	69.5	3.20
PS-HH 101 ^a Monsanto Company (high heat-resistance grade)	333.1	133.9	2.48

^a Sample kindly provided by Dr. J. H. Southern of Monsanto Company.

RESULTS AND DISCUSSION

Atactic polystyrene is a noncrystallizable amorphous polymer that provides a valuable system for studies of changes in physical and mechanical properties with molecular orientation. Sample brittleness is reduced upon orientation, and the clear but rigid oriented material may be widely usable.⁷

The technique of solid-state coextrusion is unique for the preparation of oriented thin films. They can be conveniently prepared on simultaneously extruded double substrates of different polymer composition under selected extrusion conditions. The resultant films were 0.08 mm thin and of measured maximum EDR 11.6. The extrusion draw ratio was obtained by observing changes on the square grid pattern (2.5 mm) imprinted on the polystyrene film before extrusion. The EDR was also calculated as a function of the extrudate length assuming constant volume deformation from the following equation⁸:

$$\text{EDR} = \left(\frac{R}{r}\right)^2 = \left(1 + \frac{3L \tan \theta/2}{r_{\text{fib}}}\right)^{2/3}$$

where θ is the entrance angle of the conical die, R is the radius at the entrance of the die, and L and r are the length and radius of the extruded assembly, respectively.

For comparison, attempts were made to conventionally extrude (solid plug) both pure and high-impact polystyrene over the temperature range from 90° to 130°C. This was not found possible because of the high viscosities. All subsequent deformations of polystyrene thus were done only by the solid-state coextrusion technique with high-density polyethylene.

Pure amorphous polystyrene upon coextrusion at temperatures from 90° to 120°C fractured at $\text{EDR} \geq 4$, whereas high-impact polystyrene showed similar behavior up to $\sim 116^\circ\text{C}$. Above these temperatures, the extrudates exhibited a kind of viscous fracture⁹ which was alleviated only when the extrusion was performed at $\geq 126^\circ\text{C}$. At 126°C the components of the extruded assembly (the

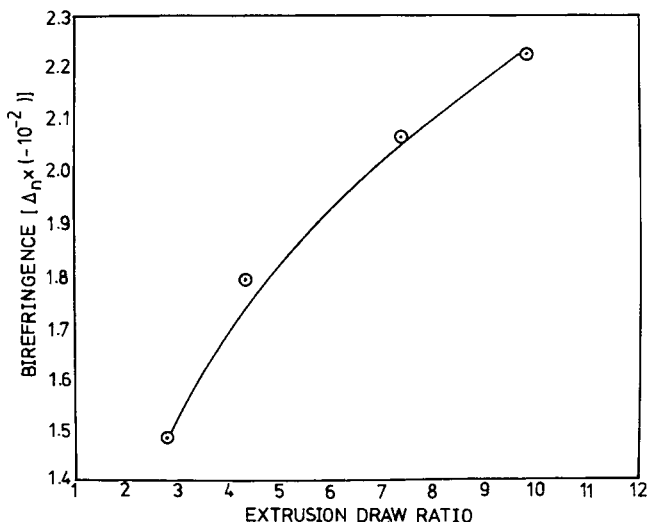


Fig. 1. Variation of total birefringence for polystyrene with extrusion draw ratio.



Fig. 2. Electron micrograph showing the fibrous nature of polystyrene oriented by solid-state extrusion. Magnification as indicated. Long arrow shows the extrusion direction.

two HDPE substrates and polystyrene fiber) maintained positional integrity only in the case of pure amorphous polystyrene.

The oriented amorphous polystyrene film of EDR 11.6 was freed from the surrounding HDPE substrates by simple delamination. For the deformation of high-impact amorphous polystyrene at the same temperature at the onset of extrusion, the polymers coextruded at the same rate; but as the EDR increased, they extruded at different rates until they reached their own steady state and different extrusion rates. The oriented polystyrene films thus obtained were of EDR 7 as it was calculated from the displacement of the markers. However, coextrusion of the high-impact polystyrene at 128°C proceeded with no differential flow, and oriented films of high-impact polystyrene of EDR 11.6 could also be obtained. Ram et al.¹⁰ have reported similarly high draw ratios by stretching amorphous polystyrene at >170°C, i.e., well above T_g . However, in this temperature range, molecular orientation is not high as in other such polystyrene drawing studies⁷ and is indicated by their birefringence data. Consequently,



Fig. 3. Electron micrograph showing the non-uniform deformation along the extrusion direction for polystyrene; A, undrawn; B, highly drawn. Long arrow indicates the extrusion direction.

we wish to keep the extrusion temperature close to T_g to ensure the highest possible molecular orientation, that is, to increase the efficiency of draw.

The structural changes of the amorphous polystyrene upon extrusion were assessed by physical and mechanical tests on the extruded film strips. The birefringence variation with EDR is depicted in Figure 1. The maximum obtained value, -2.24×10^{-2} , is attributed to the draw efficiency under the extrusion conditions of our studies. This value, being larger by one order of magnitude from the values reported by Ram et al.¹⁰ and Tanabe and Kanetsuna,¹¹ is similar to the values reported by Gurnee¹² and Andrews and Rudd.¹³ Gurnee¹² calculated the birefringence for a zigzag chain and a single random coil assuming firstly that the two systems have the same relationship between orientation and birefringence and secondly that a system of completely uncoiled parallel zigzag chains without deformation of bond angles is 100% oriented. Assuming that the orientation is directly proportional to the extension r/nl , where r is the straight line distance between the ends of the chain, n is the number of links in the chain, and l is the length of each link, he found for polystyrene filaments that the birefringence corresponding to 100% orientation is -0.3 , whereas a maximum bi-

refrindex of the range reported in this study corresponds to $\sim 30\%$ of this value. This value is reasonable considering the amorphous nature of polystyrene.

Electron microscopy has provided information for the structure of oriented, amorphous polystyrene at $\text{EDR} \geq 7$. Figure 2 clearly shows the fibrous structure of the extrudate with the fibrils aligned parallel to the extrusion direction. The fibers have a noncircular cross section and are ribbon-like. This is most obvious for the fibrils that have become partially detached in the fracture process. These fibers have an approximate cross-sectional aspect ratio of 3 to 1. The larger width is $\sim 1 \mu\text{m}$. Although the transformation from an isotropic to a fibrous morphology is known to occur during the deformation of semicrystalline polymers, such transformation is not well documented for amorphous polystyrene.

Molecular reorganization is not uniform over the extrudate surface. As shown in Figure 3, some areas are more drawn than others. Similar observations have been reported in the plastic deformation of poly(ethylene terephthalate) films as shown by the gold-marking techniques.¹⁴

We attempted to evaluate the amorphous orientation of the deformed polystyrene by wide-angle x-ray scattering experiments, but the results have been inconclusive. A method for the determination of orientation in amorphous polymers has been proposed by May.¹⁵ However, the technique is relatively tedious in comparison with the simpler technique of birefringence. Tanabe and Kanetsuna¹¹ investigated the orientation of melt-extruded atactic polystyrene monofilament and studied its relationship to their brittle-to-ductile transition.

Differential scanning calorimetry showed that crystallization does not occur during our deformation process. The thermograms of an unoriented, oriented ($\text{EDR} \sim 11.6$) and an unoriented sample of high-impact polystyrene which has been obtained from a previously heated to 190°C oriented sample are depicted in Figure 4. It is indicated that only the glass transition at 104°C occurs. This transition is easier to observe after orientation, but not perceptibly changed.

In addition, gel permeation chromatography data collected for the high-impact polystyrene product indicated that degradation did not occur during deformation. The results of GPC analysis for a series of samples of varying EDR are shown in Table II.

Shrinkability tests were performed over a temperature range from 100° to 160°C with the two polystyrene grades described in Table I. The results were very similar, irrespective of the polymer grade, and indicated that the rate and extent of shrinkage increase with temperature as shown in Figure 5. The percent shrinkage was calculated from the length retraction ΔX and expressed as $(\Delta X/X_0) \times 100$, where X_0 is the original sample length. Similarly, the percent elastic recovery was calculated from the expression $(\text{CDR}/\text{EDR}) \times 100$. CDR, the "contraction" draw ratio, is determined by the ratio X_0/X , where X is the length of the sample on shrinking. The variation of elastic recovery and shrinkability with heating temperature is shown in Figure 6.

The transformation of the shape of the samples during shrinking deserves mention and is illustrated in Figure 7. The originally oriented sample, (a), retracted along the extrusion direction, (b) and (c), and at temperatures $> 135^\circ\text{C}$ elongated perpendicularly to the extrusion direction to assume the oblong shape shown by (d) and (e) in the same figure. The variation in length and shape is

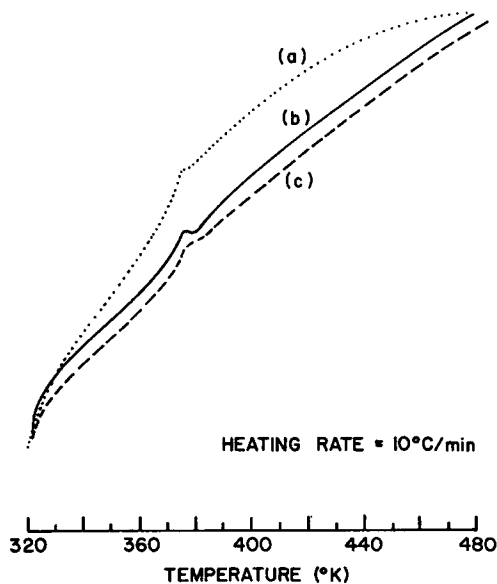


Fig. 4. DSC thermograms of (a) unoriented polystyrene film, (b) oriented polystyrene film, EDR ≈ 11.6 , and (c) unoriented polystyrene film obtained from an oriented polystyrene film, EDR ≈ 7 , melted at 190°C .

important since it illustrates the high efficiency of the extrusion process. The rate at which the oriented material returns to the random coil configuration will be governed by the molecular mobility of the sample. The molecular mobility above the glass transition temperature (T_g) is a function of the temperature difference $T - T_g$ and the experimental time scale, as seen in stress relaxation experiments. Given that the practical experimental time scale used in these experiments is constant at ~ 600 sec, the total amount of elastic recovery will be dependent on the temperature elevation above T_g . The higher the temperature, the greater the shrinkage due entirely to relaxation effects. Upon heating at $\geq 150^\circ\text{C}$ the sample retracted to its original oblong shape that it had in the unoriented film prior to extrusion.

The tensile properties of the extended fibers increased with orientation, in agreement with several independent conclusions.^{7,16} The tensile strength of a film of EDR ~ 11 was 70% higher than the value of the unoriented polystyrene (50 MPa). The modulus was 4–5 GPa, i.e., $\sim 30\%$ higher than the value of the unoriented material and is comparable to values reported by Andrews and Rudd for oriented polystyrene of similar birefringence.¹³

It is also interesting to note that the oriented films, as shown in Figure 8, exhibit

TABLE II
Gel Permeation Chromatography Analysis For Extruded High-Impact Polystyrene

Extrusion draw ratio	M_w	M_n	M_z	M_w/M_n	M_z/M_w
Original	257.700	88.640	519.400	2.907	2.015
2.5	331.600	101.700	674.200	3.260	2.033
4.0	259.900	82.430	543.700	3.153	2.092
7.0	265.500	88.980	551.300	2.995	2.068

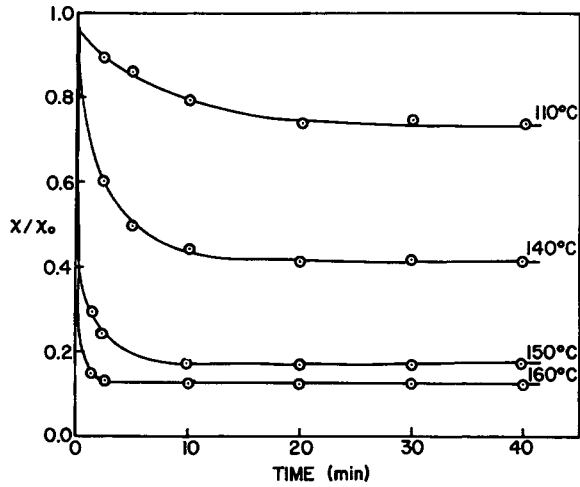


Fig. 5. Shrinkability of oriented polystyrene with temperature. X_0 is initial sample length, 1 cm; X is sample length on shrinking.

the dead bend effect, i.e., do not craze or fracture upon bending. Also, the presence of 7% polybutadiene and 2% internal lubricant in the high-impact polystyrene grade did not affect the draw efficiency under our experimental conditions. This assessment was made from the close similarity of birefringence and tensile property results for the two different polystyrenes (see Table I).

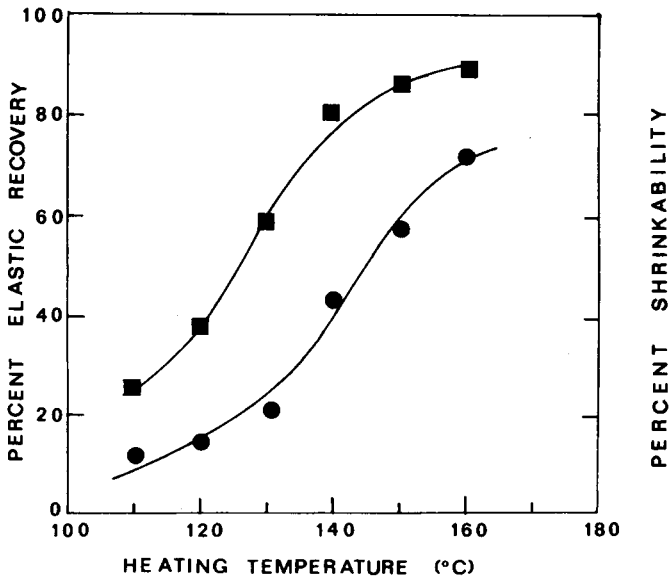
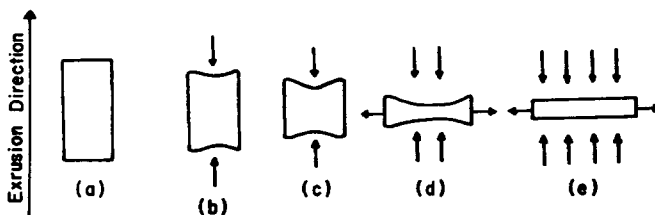
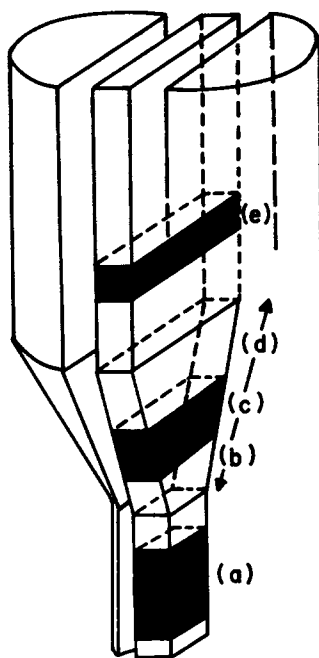


Fig. 6. Variation of elastic recovery (●) and shrinkability (■) for isothermal heating at the temperature indicated.



Variation of sample shape during a shrinkage test

(A)



(B)

Fig. 7. (A) Change of sample shape during a shrinkage test. (B) The shape recovery with respect to the originally undeformed film.

CONCLUSIONS

The recently developed technique of solid-state coextrusion has been employed for the preparation of thin oriented films of atactic polystyrene. This study illustrates the effective orientation of an amorphous polymer on coextruded double substrates that may result by this novel technique at selected conditions. These initial coextrusions with high-density polyethylene were conducted at 126°C and 40 MPa and yielded unflawed and continuous polystyrene films oriented at EDR_{max} 11.6. The films were 80 μm thick and exhibited the dead bend effect. The high orientation efficiency, indicated by the fibrous nature of the deformed film, is also demonstrated by the birefringence value 2.24×10^{-2} , a 72% elastic recovery (or 88% shrinkage), and mechanical tests. GPC indicates that the efficient deformation process did not degrade the polystyrenes.

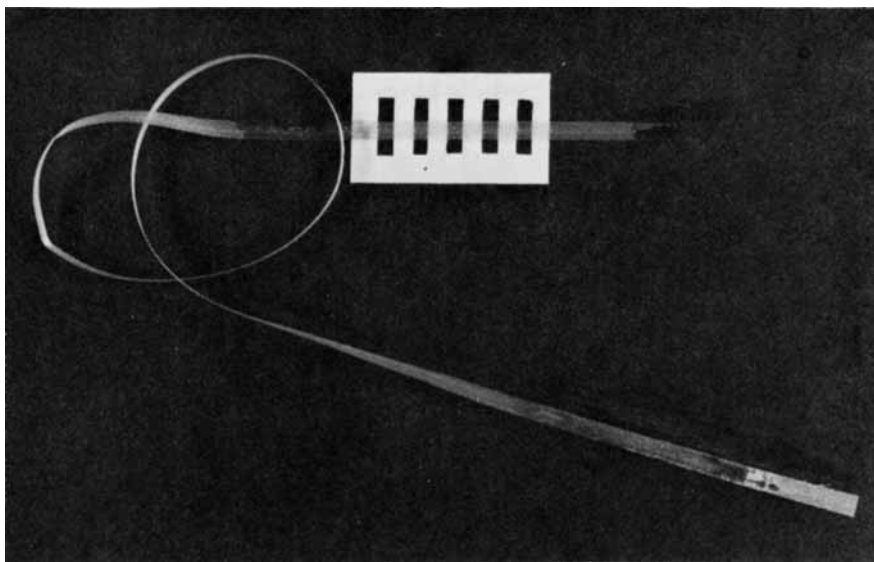


Fig. 8. Photograph of extruded polystyrene showing the stability in dead bend tests.

Finally, the presence of small amounts of additives in the polystyrene (i.e., polybutadiene and internal lubricant) influenced only to a small extent the lowest effective extrusion temperature (126°C) for the preparation of unflawed oriented films—an increase by 2°C was required for the extrusion of high-impact polystyrene—and did not affect the draw efficiency of $EDR \approx 12$ at temperature $>128^\circ\text{C}$.

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