

# Melt Spinning of Shear Modified Plasticized Polystyrene

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## SYNOPSIS

Polystyrene is not normally shear-modifiable. Addition of small amounts of plasticizer (butyl benzyl phthalate) result in changes in melt viscosity and elasticity during extrusion. Fiber spinning experiments are shown to provide useful indications of the rheological state of polymers that are sensitive to shear history. Here, the density, modulus and work to rupture of lightly plasticized polystyrene is shown to vary with extrusion history of the material.

## INTRODUCTION

Polystyrene is not generally regarded as a fiber-forming polymer. The atactic configuration of this polymer prevents crystallization during orientation, its relatively low  $T_g$  renders it unattractive for textile uses, and its brittle character makes it difficult to cold-draw to high extensions. It was nevertheless of interest to study the melt-drawing behavior of plasticized polystyrene, as a follow-up to our previous work, in which the effects of plasticizer on the shear modification of polystyrene were investigated.<sup>1</sup>

Shear modification is a process in which the rheological nature of a thermoplastic can be altered, to some extent, without changes in molecular weight distribution.<sup>2</sup> Shearing, as in an extruder, may cause changes in melt elasticity, viscosity, the onset of extrusion defects, and other properties. Various applications include reduction of the haze of extruded polyethylene film and the production of ultra-oriented high-density polyethylene.<sup>3</sup>

Styrenic polymers have not been reported to benefit from shear modification processes. This is due at least in part to the stiffness of the polymer chain, which is relatively difficult (compared to polyethylene) to disentangle or to orient in the liquid state. Our earlier work<sup>1</sup> has shown that the addition of small amounts of plasticizer renders polystyrene more amenable to shear modification. Melt elasticity (extrudate swell) was shown to be affected by prior extrusion history if small concentrations of plasticizer were added to the polymer. In this report we examine the effects of plasticizer and shear history on fiber-forming properties of a commercial polystyrene because fiber properties can be a sensitive indicator of the entanglement state of the polymer that is being extruded.

Another incentive for this study stems from the gel-spinning processes that are used commercially to produce ultra-oriented polyethylene. In these operations dilution of the polymer in solvent is believed to facilitate chain untangling and the achievement of the requisite very high draw ratios.<sup>4,5</sup> It has also been shown that shear modification can be employed to reduce the dilution level needed for effective disentanglement during tensile drawing.<sup>3</sup> The latter concept is applied here to polystyrene, which is inherently not a fiber former, to determine whether this idea can be extended more generally.

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**Table I** Molecular Weights of Polystyrenes

Sample	Content of Plasticizer (wt %)	Shear Times	$M_n$ $10^{-5}$	$M_w$ $10^{-5}$	$M_z$ $10^{-5}$	SD(N) <sup>a</sup> 10 <sup>-5</sup>	SD(W) <sup>a</sup> 10 <sup>-5</sup>
PS	0	0	1.19	2.50	4.22	1.25	2.07
PPS	10	0	1.39	2.65	4.28	1.32	2.08
SPPS	10	2	1.32	2.38	3.77	1.18	1.82

<sup>a</sup> SD(N), SD(W) = standard deviations of number and weight distributions, respectively.

## EXPERIMENTAL

The materials used include a commercial polystyrene (PS) and butyl benzyl phthalate (BBP) plasticizer. The plasticized polystyrene (PPS) containing 10 wt % BBP was mixed on a roll mill at 170°C for less than 10 min. Shear modification of the plasticized PS, here labeled SPPS, was in a laboratory-scale single-screw extruder equipped with 4.2 : 1 compression ratio screw, and a flat entry capillary die of 3.18 mm diameter with a length to diameter ( $L/D$ ) ratio of 4. The mixture was sheared twice through the extruder at 190°C and a screw speed of 34.6 rpm, to obtain the sample labeled SPPS.

Filaments were produced with a screw extruder containing a 3 : 1 compression ratio screw and flat entry capillary die of 1.27 mm diameter with an  $L/D$  ratio of 25. Extrusion was at 190°C with a screw speed of 13.1 rpm. The extrudate passed through air to be taken up on a godet and was then directly collected on a spool. The godet speed was adjusted to achieve the desired stretching of the filament. Draw-down ratio was measured as the ratio of take-up speed ( $V_t$ ) to the exit speed of the filament from extruder die ( $V_0$ ).

The fiber cross-section area was estimated by weighing a bundle of filaments of known length (5 m) and measuring its density using a specific gravity device attached to a balance. Scanning electron micrographs of the fracture region of the filaments were taken with a JEOL JSM-840 scanning electron microscope.

Molecular weights of three samples with or without plasticizer were determined by size exclusion chromatography. Molecular weight data are given in Table I. Clearly, the shear modification process resulted in some molecular weight degradation in

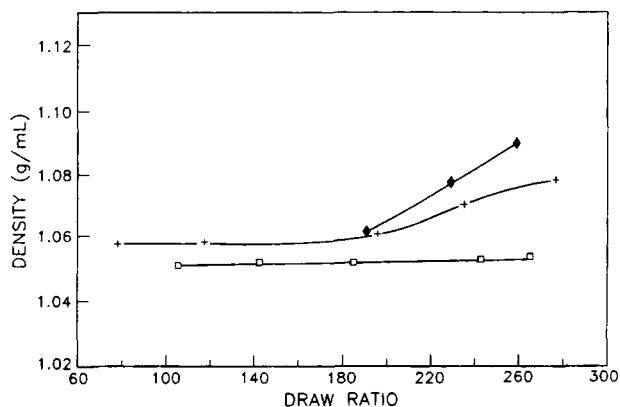
the high molecular weight region ( $M_z$  is significantly lower for SPPS than for PS or PPS).

## RESULTS AND DISCUSSION

The curves in Figure 1 represent the variation of the density of the three types of specimens with draw ratio. The density of 10% BBP-PS without drawing is calculated to be 1.057 g/cm<sup>3</sup> from the densities of pure PS (1.05 g/cm<sup>3</sup>) and BBP (1.120 g/cm<sup>3</sup>).

At higher draw ratios, the densities of the filaments are in the following increasing order: polystyrene < plasticized polystyrene < shear-modified plasticized polystyrene. Extrusion and shear modification have only affected the plasticized polymer. This behavior is as expected since the presence of plasticizers or diluents is expected to facilitate disentanglement in shear fields.<sup>2</sup>

It should be remembered here that the apparent drawing ratios in these experiments reflect differ-

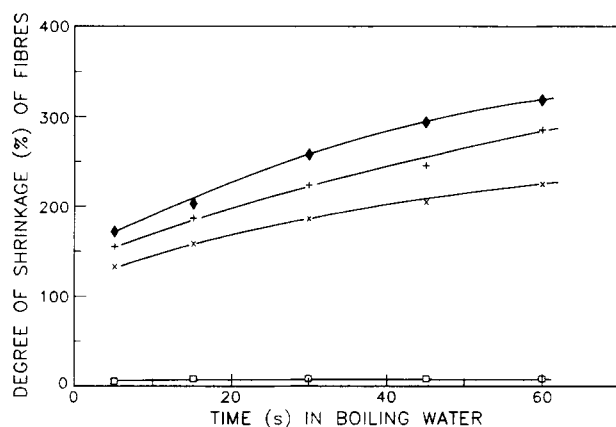


**Figure 1** Dependence of fiber density on draw ratio PS ( $\square$ ), PPS (+), SPPS ( $\blacklozenge$ ).

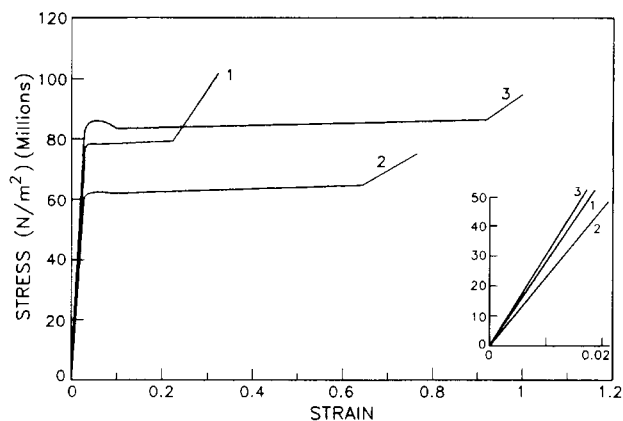
ences in extrusion and take-up speeds. Most, if not all, of the extension will have occurred in the molten polymer. Nevertheless, alignment of the polymer molecules is more easily achievable in the presence of plasticizer. The observed behavior is consistent, also, with the concept that shear modification has reduced the frequency or intensity of entanglements, thus further facilitating molecular orientation.

The degree of shrinkage of PS, PPS, and SPPS versus immersion time in boiling water is shown in Figure 2. The PS fibers exhibited very little shrinkage and were obviously produced with almost no residual stress, despite their high draw ratio. By contrast, plasticized and shear-modified, plasticized polystyrene exhibited high retractions at about the same draw-down ratios. Presumably, extension of PS filaments was accomplished with very little molecular orientation in the drawing direction. This is in sharp contrast to the behavior of the PPS and SPPS materials, in which intermolecular restraints are reduced by the presence of the small concentration of BBP and by some disentanglement in the previous shear modification processes. The observed differences will also reflect the lower higher  $T_g$  of PS, compared to PPS or SPPS.

Figure 3 shows typical stress-strain curves, at a stretching speed of 40 mm/min, for filaments of PS, PPS, and SPPS. All materials exhibit a yield stress at this extension rate. All specimens had about the same extension ratio. PPS exhibited the lowest modulus and yield stress. Somewhat surprisingly, SPPS has a modulus and yield stress as high as that



**Figure 2** Degree of shrinkage (percent) of various filaments in boiling water. Specimen: (Draw ratios are in brackets) PS (265) (□), PPS (278) (+), SPPS (260) (◆), SPPS (191) (×).



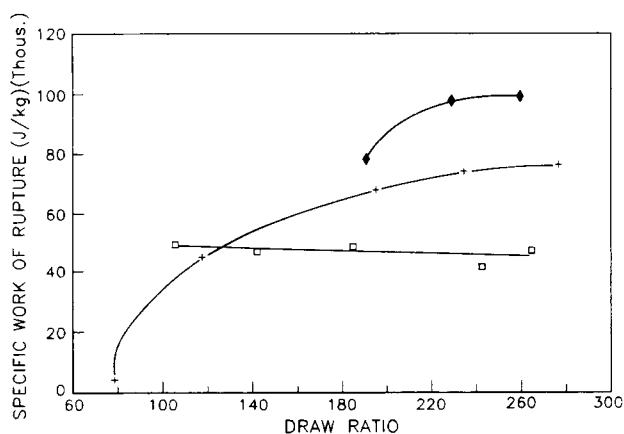
**Figure 3** Typical stress-strain curves of polystyrene fibers (stretching speed = 40 mm/min). Sample (draw ratio): (1) PS (265), (2) PPS (278), (3) SPPS (260). (Specimen gauge length here = 2.5 cm). The inset shows the initial portions of the curves.

of unplasticized polystyrene. This must reflect the higher orientation in the latter sample.

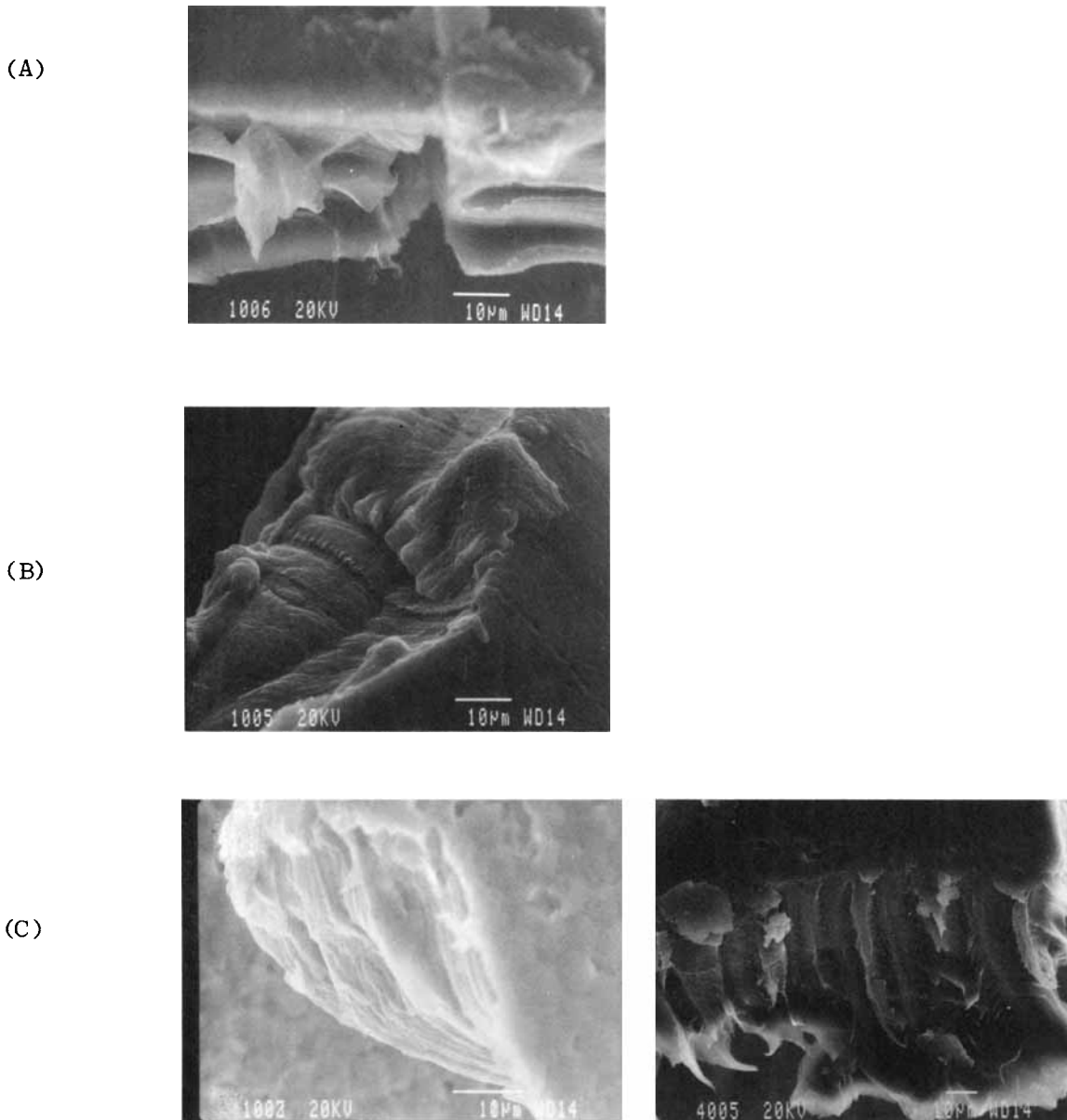
The work to rupture,  $W$ , is defined as the energy needed to break the fiber and is equal to the area under the load-elongation curve. A more useful comparative parameter is the specific work to rupture  $W_{sp}$ , defined as<sup>6</sup>

$$W_{sp} = \frac{W}{(\text{mass/unit length}) \times (\text{initial length})}$$

with units here of J/kg. The effects of draw-down ratio on  $W_{sp}$  of the various samples is shown in Figure 4. The toughness of PS is unaffected by the ex-



**Figure 4** Influence of shear modification on the specific work of rupture. Symbols are as in Figure 1.



**Figure 5** Scanning electron micrographs for fiber fracture surfaces. (A) PS, (B) PPS, (C) SPPS.

tension ratio, while that of the plasticized polymer is highly influenced. The shear-modified, plasticized polymer has a higher specific toughness than that of the plasticized material, at the same draw ratio.

Scanning electron micrographs of fracture surfaces of the different filaments show clearly different features (Fig. 5). The plasticized and shear-modified plasticized fibers exhibited laminar textures that are absent in the unmodified polystyrene. The shear-

modified product, in particular, contains much more ordered material.

### CONCLUSIONS

Earlier work from this laboratory has shown that dilution and mechanical shearing processes can be

combined to obtain relatively disentangled polyethylenes that can be used to make articles with high orientations and superior mechanical properties.<sup>3</sup> The same general phenomena can be seen in the case of the polystyrene studied here. This procedure would appear to have no practical consequences in the case of polystyrene, but it may be of value with other polymer melts.

Fiber spinning experiments appear to provide useful indications of the rheological state of polymers that are sensitive to shear history.

This research was supported by the Natural Sciences and Engineering Research Council of Canada.

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*Received March 22, 1990*

*Accepted May 10, 1990*