Biaxial Orientation Behavior of Polystyrene: Orientation and Properties

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ABSTRACT: Square sheets of extrusion grade polystyrene (PS) were biaxially stretched using a laboratory biaxial stretcher. The effects of process parameters such as stretch ratio, drawing sequence, drawing speed, and temperature were studied. Birefringence, mechanical properties, and thermal shrinkage of the stretched sheets were the focus of this study. A high orientation was achieved at high stretch ratio, and orientations from uniaxial to equi-biaxial were obtained by controlling the relative magnitude of stretch ratio in machine (MD) and transverse (TD) directions. Stretching increased tensile strength and elongation at break significantly, which indicated an improvement in the toughness of the oriented PS sheets. Those properties were correlated with biaxial orientation factors: a rapid increase was observed for both tensile strength and elongation at break for birefringence levels above −0.005, and below, a plateau was observed. The shrinkage strain and stress were found to correlate well with the biaxial orientation factors. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 487–496, 2003

Key words: polystyrene; orientation; structure–property relations

INTRODUCTION

It is well known that polymer mechanical properties can be enhanced by uniaxial or biaxial orientation. Blown films generally generate low to moderate levels of orientation, and high levels of biaxial orientation can be achieved using biaxial orientation processes, such as tentering,[1] roll-drawing,[2] or double bubble blowing processes. It is also known that orientation to moderate levels improves the ductility of polymers such as PS and polyethylene terephthalate (PET).

A series studies were conducted in our laboratory on an extensive investigation on the biaxial orientation as well as the development of morphology upon stretching of different polymers. Our objective is to establish processing–structure–properties correlations. Depending on the nature and draw states of polymers, various morphologies and orientation levels can be imparted to a polymer and, therefore, various property enhancements can be achieved.

Extensive studies on biaxially oriented polymers were mainly focused on PET.[1,3,4] Those studies used in general an in-house designed and built rig, allowing two perpendicular directions independent motion for the biaxial stretching. The results obtained in those studies upon uniaxial and biaxial stretching PET were described in terms of a molecular network model.[1,3,4]

However, little efforts were performed on other polymers. In addition, the development of a new commercially available laboratory biaxial stretcher allows significant improvements and possibilities in biaxial stretching of polymers. The focus of the present study is polystyrene (PS).

Studies on PS biaxial orientation can be dated back to the middle of 60s and late 70s. Most of them were concerned about cast film or monofilaments, and focused on uniaxial orientation,[5–8] which improved the mechanical properties in the stretch direction. The molecular chains were found to extend parallel to the direction of fiber axis, which suppressed the formation and growth of cracks in PS monofilaments, resulting in a more ductile behavior.[7]

Studies on biaxial stretching of polystyrene were first performed by Thomas and Cleereman,[9] followed by Jones,[6] Matsumoto et al.,[10,11] and DeVries et al.[12] Matsumoto et al.,[11] for example, reported that the tensile force–elongation curves for uniaxially stretched PS showed a yield in the direction of draw, and were brittle in the other direction, whereas for biaxially oriented PS, a yield was observed in all directions. In a more extensive study reported by Choi et al.[13] on uniaxially and biaxially stretched PS, it was found that the elongation at break was more sensitive to orientation than the other mechanical properties. They also reported a brittle-to-ductile transition at a value of biaxial orientation factors of 0.0025 for biaxially oriented sheets and at a value of 0.015 in the machine direction for uniaxially stretched ones. From morphological analysis, they found that the fracture

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TABLE I
Samples Studied in This Study

Sample	Temperature (°C)	Preheating time (s)	MD stretching ratio	TD stretching ratio	Draw rate	Sequence
PS1.5	120	120	1.5	1.5	10%/s	Sequential
PS2	120	120	2	2	10%/s	Sequential
PS3	120	120	3	3	10%/s	Sequential
PS4	120	120	4	4	10%/s	Sequential
PS5	120	120	5	5	10%/s	Sequential
PS6	120	120	6	6	10%/s	Sequential
PS7 (broken)	120	120	7	7	10%/s	Sequential
PS24	120	120	2	4	10%/s	Sequential
PS26	120	120	2	6	10%/s	Sequential
PS42	120	120	4	2	10%/s	Sequential
PS46	120	120	4	6	10%/s	Sequential
PS62	120	120	6	2	10%/s	Sequential
PS64	120	120	6	4	10%/s	Sequential
PS2S	120	120	2	2	10%/s	Simultaneous
PS4S	120	120	4	4	10%/s	Simultaneous
PS6S	120	120	6	6	10%/s	Simultaneous
PS0.1	120	120	6	6	2%/s	Sequential
PS0.2	120	120	6	6	4%/s	Sequential
PS0.2(broken)	120	120	8	8	4%/s	Sequential
PS0.8	120	120	6	6	16%/s	Sequential
PS115a	115	120	2	2	11%/s	Sequential
PS115b(broken)	115	120	4	4	11%/s	Sequential
PS115c(broken)	115	120	6	6	10%/s	Sequential
PS125a	125	120	2	2	10%/s	Sequential
PS125b	125	120	4	4	10%/s	Sequential
PS125c	125	120	6	6	10%/s	Sequential

surfaces of ductile sheets exhibited many fibrils, while brittle fracture did not.[13] However, the causes for this brittle-to-ductile transition were rarely reported,[7] and experimental and theoretical efforts to understand it are still in progress.[14] It is worth mentioning that no other properties, such as shrinkage, were investigated in all these studies.

The aim of this work is to use a state-of-the-art biaxial stretcher to mimic real industrial process, and to study more extensively the biaxial stretching behavior of polystyrene. Our objective is to study the effects of a wide range of stretch ratios, drawing sequence, and drawing temperatures and rates on the oriented structure of biaxially oriented PS sheets and correlate
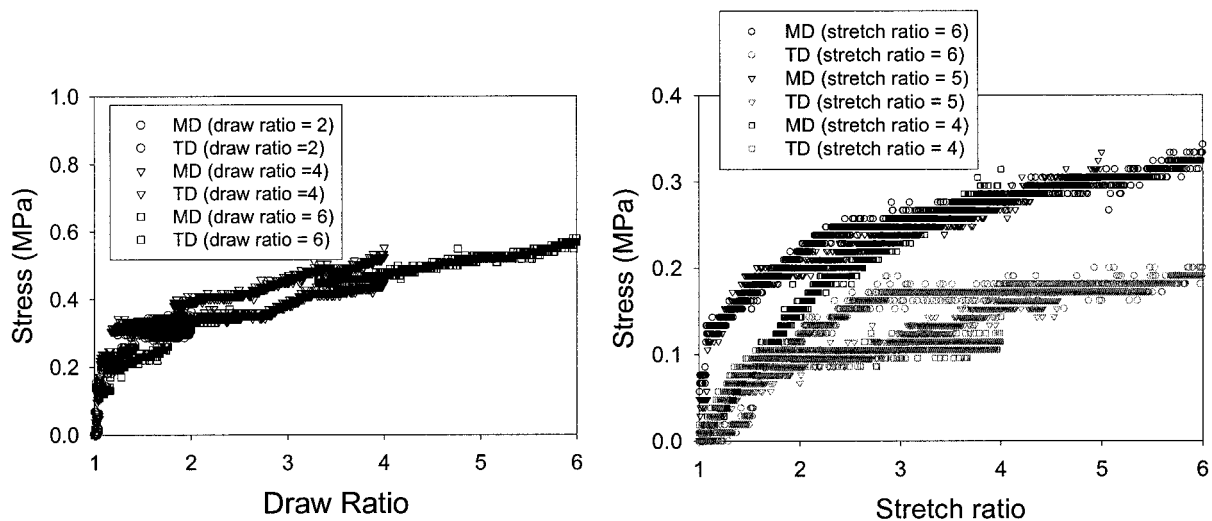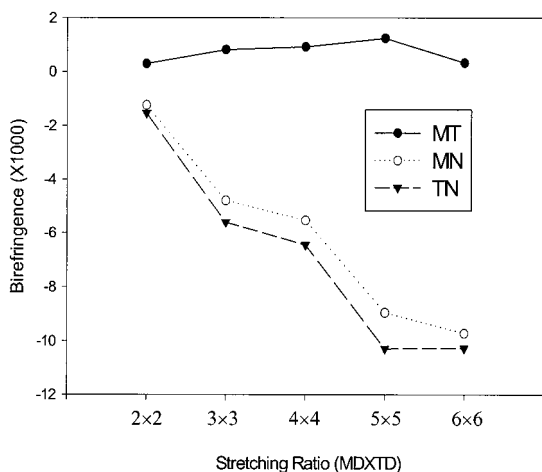

Figure 1 Deformation stress for equibiaxially stretched PS sheets: (a) simultaneous; (b) sequential (first draw in MD then in TD).

Figure 2 Effect of stretch ratio on birefringence for sequential equibiaxial stretch.

EXPERIMENTAL

The polymer used in this study was Crystal Polystyrene 1200 from Nova Chemicals. Its melt flow index was 1.6 g/10 min and linear mold shrinkage 0.004–0.007 mm/mm; 10 × 10 cm × 1 mm PS sheets were prepared by compression molding press at a temperature 230°C. The PS sheets were biaxially stretched in a Bruckner biaxial laboratory stretcher. Stretch ratios (the ratio of final stretched length to initial length) ranging from 1 to 6 were successfully obtained in this study. Most samples were stretched sequentially, the simultaneous stretching mode was used for some samples for comparison. Several stretch rates (2%/s, 4%/s, 10%/s, and 16%/s) were used. The experiments were performed at the temperatures of 115, 120, and 125°C, and specimens were preheated at the designed temperature for 2 min before stretching. A complete list of the samples investigated is given in Table I. The best temperature to stretch samples was found to be 120°C, and it was not possible to stretch the sheets more than 2 × 2 at 115°C. The highest stretch ratio that could be reached at 120°C was 6 × 6 for sequential stretching. At a stretch ratio of 7 × 7, the first direction stretch went well, but the sheet torn upon stretching in the second direction.

The orientation of the biaxially stretched sheets was characterized using birefringence. The absolute values of birefringence along the machine, transverse, and normal direction were measured by an incident multiwavelength double-beam and photodiode array assembly, combined with an in-house developed software. Details of the measurements technique can be found in our previous publications.[15,16]

this orientation with mechanical properties and thermal shrinkage.

The biaxial orientation factors defined by White and Spruiell, f_M^B and f_T^B measure the level of molecular orientation corresponding to machine and transverse directions, respectively. Those factors for an amorphous polymer can be obtained from birefringence measurements as:[17]

$$f_M^B = \Delta n_{MN}/\Delta^\circ \text{ and } f_T^B = \Delta n_{TN}/\Delta^\circ \quad (1)$$

where Δ° is the intrinsic birefringence of PS, which was taken as $\Delta^\circ = -0.125$.[18]

The tensile tests were performed according to ASTM D 882-97, a standard test method for tensile properties of thin plastic sheeting. A crosshead speed of 50 mm/min and a 0.1 kN load cell with rubber clamps were used. A video extensometer with a 50-mm specimen gauge length and a 50-mm grip separation distance was employed. A sample size 20 mm in width and 120 mm in length was used.

A standard test method for unrestrained linear thermal shrinkage of plastic film and sheeting, ASTM D 2732-96, was used to measure the shrinkage of the stretched samples. Specimens were put into a 110 and 160°C oil bath, and the immersion kept for 120 s. The samples were cleaned and the dimensions measured in the machine and transverse directions. The percentage shrinkage was calculated as:

$$(\%) \text{ Shrinkage} = \frac{L_{initial} - L_{final}}{L_{initial}} \quad (2)$$

where $L_{initial}$ and L_{final} are the length before and after thermal treatment.

The shrinkage stress was also measured using Instron tensile machine equipped with an oven. The samples were inserted between the jaws, which were adjusted to bring the film taut without any measurable tension. The temperature of the oven was set at 110°C, and the samples were kept at this temperature for 2
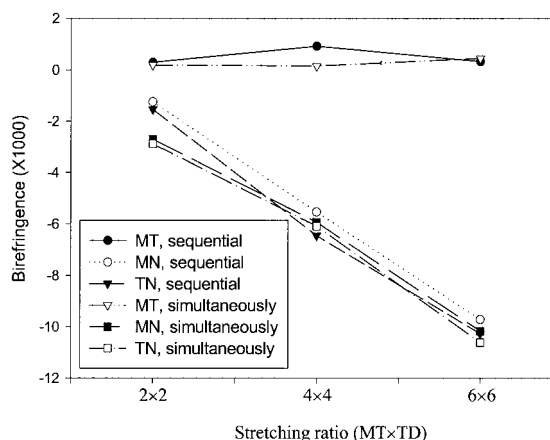
Figure 3 Comparison between sequential and simultaneous equibiaxial stretching.
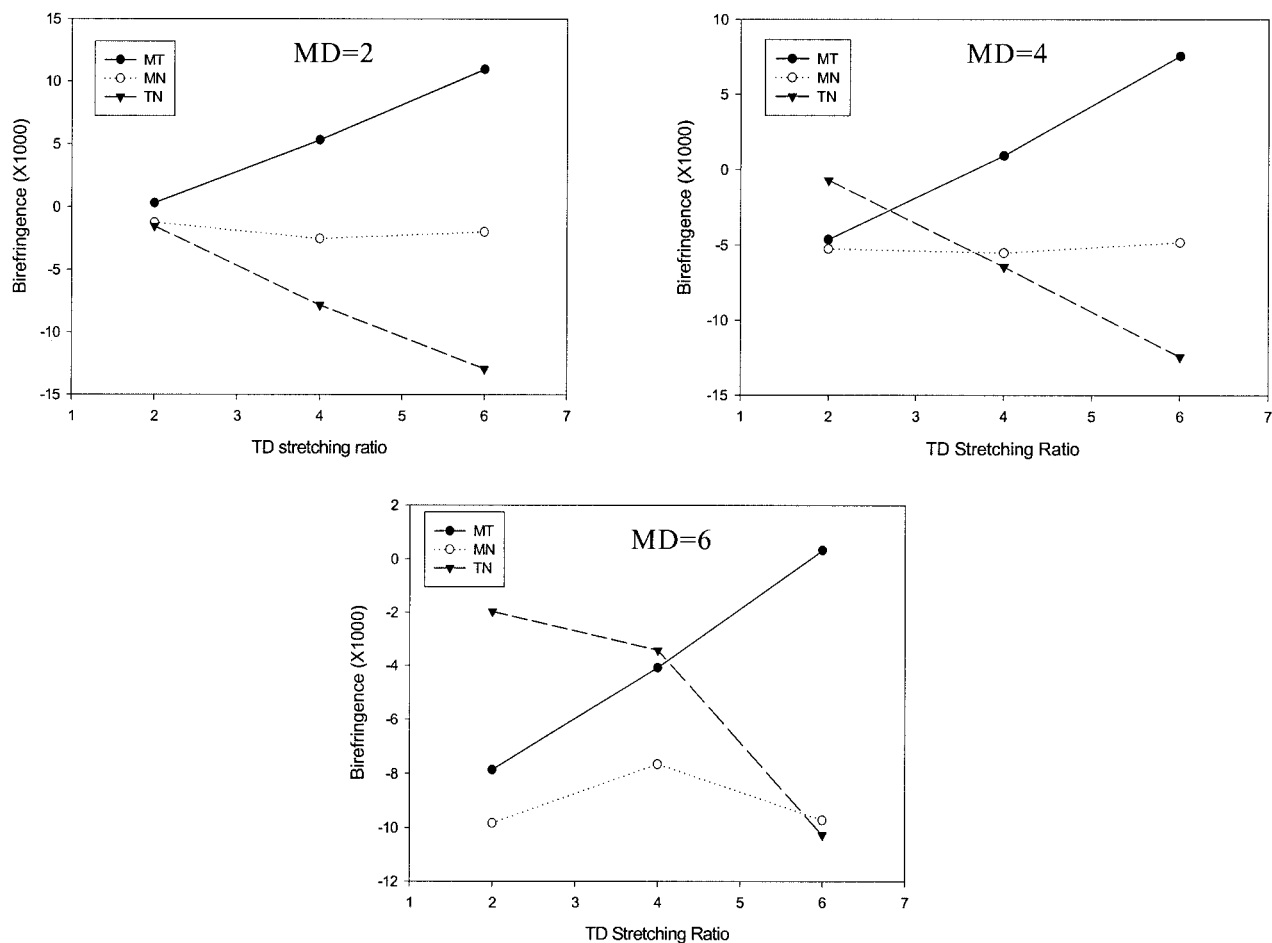
Figure 4 Effect of TD stretch ratio on birefringence for biaxial stretching with constant MD stretch ratio.

RESULTS AND DISCUSSION

Development of deformation stress and orientation structure

The samples in this study were all stretched at a constant rate. Typical nominal deformation stresses as a function of draw ratio for simultaneous and sequential equibiaxially stretched samples are shown in Figure 1(a) and (b), respectively. An equal stress was observed for machine and transverse directions in the

min or longer. At a higher temperature, above 130°C, the shrinkage occurred instantly, and the shrinkage force resulted in breakage of the samples; in that case, the shrinkage stress was not possible to measure. In another set of experiments, a minimum crosshead speed of 0.5 mm/min, and a 0.1 kN load cell were used and the stress as a function of time was monitored. To avoid films sliding, sand paper was used between the sample and the clamps. The shrinkage stress was computed as the maximum in the shrink stress recorded. In some cases, after the peak in shrink stress, the films were cooled rapidly using liquid nitrogen and the stress (cold stress) recorded.

case of simultaneous stretch. The higher the stretch ratio, the higher the stress. However, for sequential stretching, a lower stress was found in the second stretch (transverse direction), as shown in Figure 1(b). In the sequential process, the stress in the first direction will partially relax during stretching in the second direction, so the final stress in the first direction should be lower than the initially measured one.

The birefringence Δn_{TN}, Δn_{MN}, and Δn_{MT} were determined as a function of the stretch ratio. The results for sequential equibiaxial stretching (first stretch in MD then TD) are shown in Figure 2. The negative intrinsic birefringence for PS results in a negative value of birefringence. It is seen that Δn_{MT} is close to zero, and the magnitude of Δn_{TN} is slightly higher than Δn_{MN}, both of them increase with increasing the stretch ratio. The comparison between sequential and simultaneous stretching is shown in Figure 3. For simultaneous stretching, Δn_{TN} is almost identical to Δn_{MN}, and located between corresponding sequential Δn_{TN} and Δn_{MN}. The difference between the two directions in the case of sequential stretching is due to the fact that the orientation formed in the first stretch direction (MD) may partially relax during stretch in
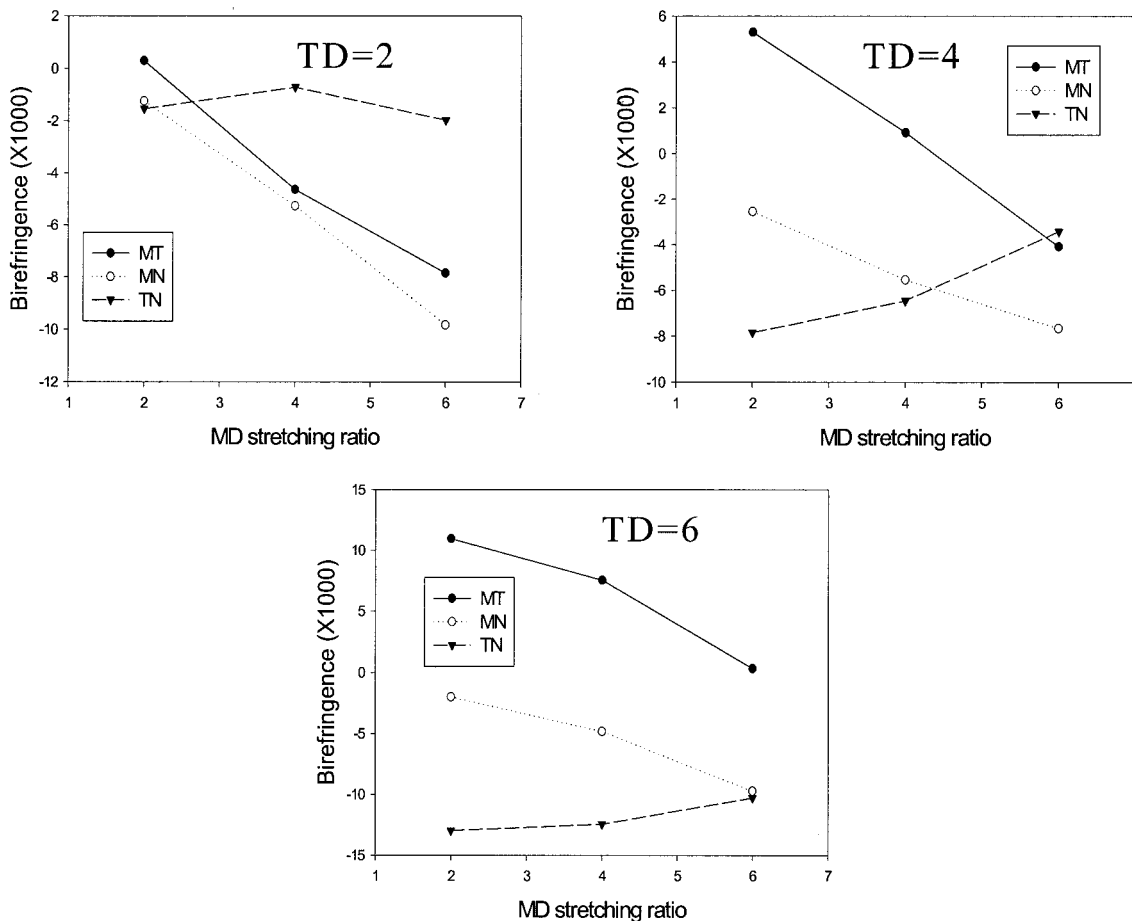
Figure 5 Effect of MD stretch ratio on birefringence for biaxial stretching with constant TD stretch ratio.

the second direction (TD). Even though the MD stresses observed in the sequential cases are higher than TD stresses (as shown in Fig. 1), the MD orientation is lower than that of TD.

When MD stretch direction was maintained at a constant stretch ratio (2, 4, or 6), the effect of the TD

Figure 6 Distribution of biaxial orientation factors.

stretch ratio on the birefringence is illustrated in Figure 4. As expected, orientation in TD increases with TD stretch ratio, the higher the orientation in the first stretch direction, the lower the attainable orientation in the second stretch direction. For example, a Δn_{TN} of -0.013 was obtained for the MD stretch ratio of 2 and TD stretch ratio of 6, while a Δn_{TN} of -0.010 for the same TD stretch ratio, but with an initial MD stretch ratio of 6. However, MD orientations at different TD stretch ratios are almost constant, indicating first-formed MD orientation is slightly influenced by the following TD stretch.

Figure 5 shows the same results as above, but with keeping the TD draw ratio constant and changing the MD stretch ratio. Δn_{TN} is observed to be much more sensitive to the MD stretch ratio than Δn_{MN}'s response to the TD stretch ratio above. Keep in mind that MD is the first stretch direction. From these result, it can be speculated that the stretch in the first direction probably converted a part of the amorphous phase to a rigid amorphous phase; then, during the following stretching, the oriented rigid amorphous phase was less deformable, and only the less oriented amorphous phase can be oriented highly in the second stretch. The
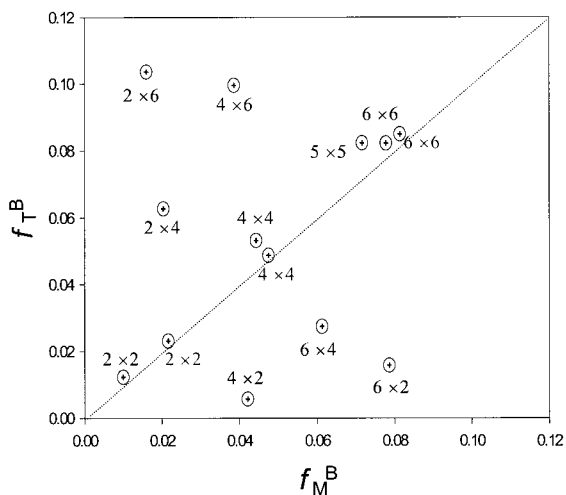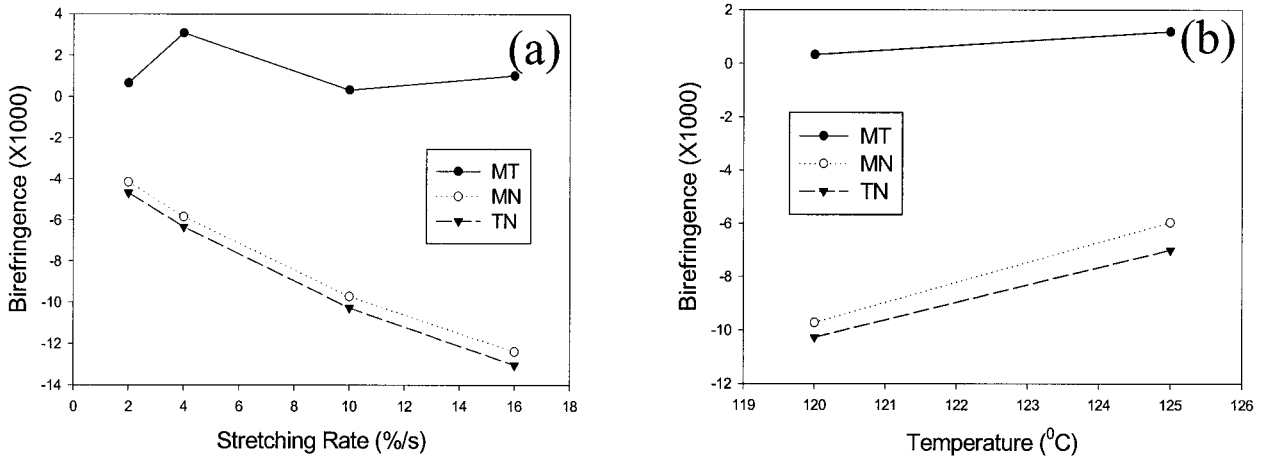
Figure 7 Effect of (1) stretch rate and (2) temperature on birefringence (MD × TD = 6 × 6).

higher the stretch ratio used in the first direction, the higher the amount of rigid oriented phase formed in that direction, and therefore, the less the amorphous chains left to be stretched in the second direction. Thus, sheet drawability during second stretching was highly dependent on the structure of the initial one-way drawn sheet.

The biaxial orientation factors f_M^B and f_T^B calculated using eq. (1) are shown in Figure 6. The equibiaxial orientation with respect to MD and TD are along the diagonal, the intermediate states locate between the coordinate axes and the diagonal. By controlling stretching configurations, different levels of orientation from uniaxial to biaxial can be achieved. The
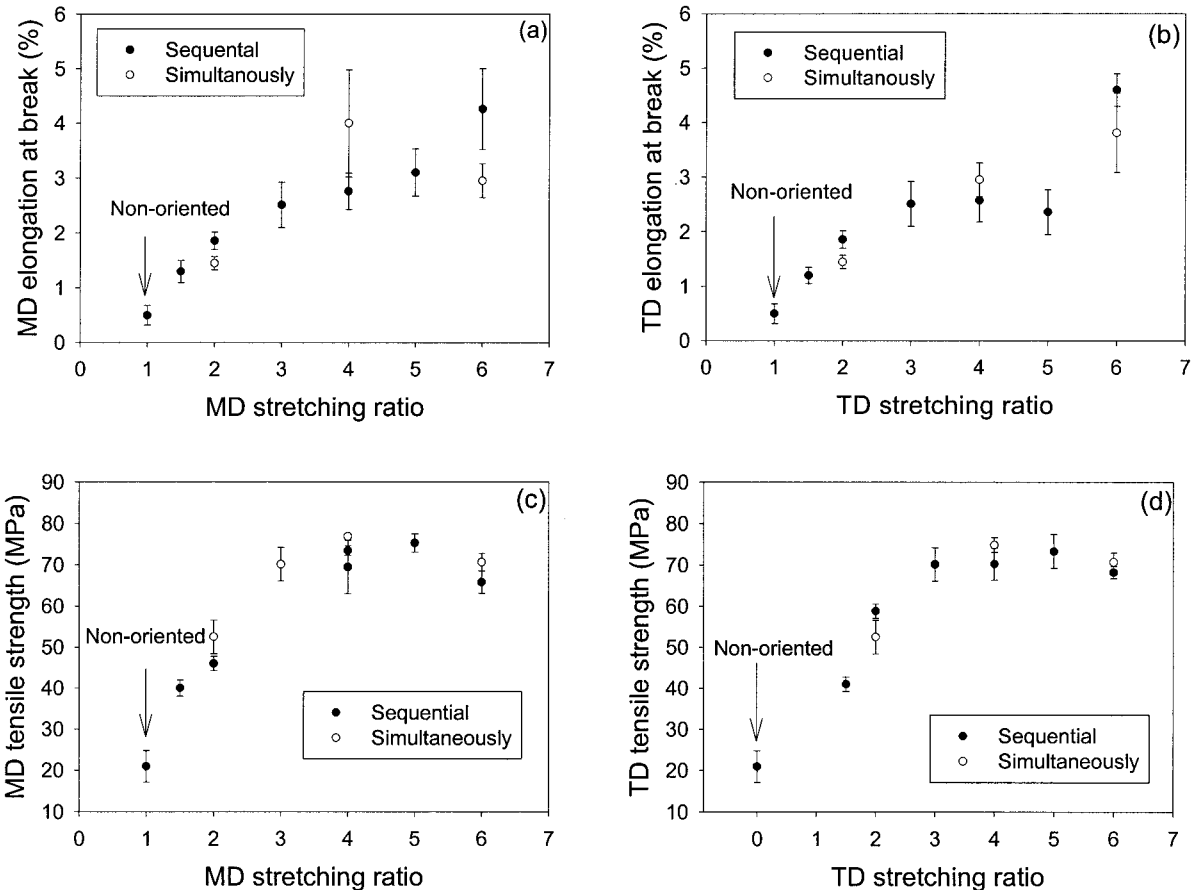

Figure 8 Effect of stretch ratio on mechanical properties for equibiaxial stretch.
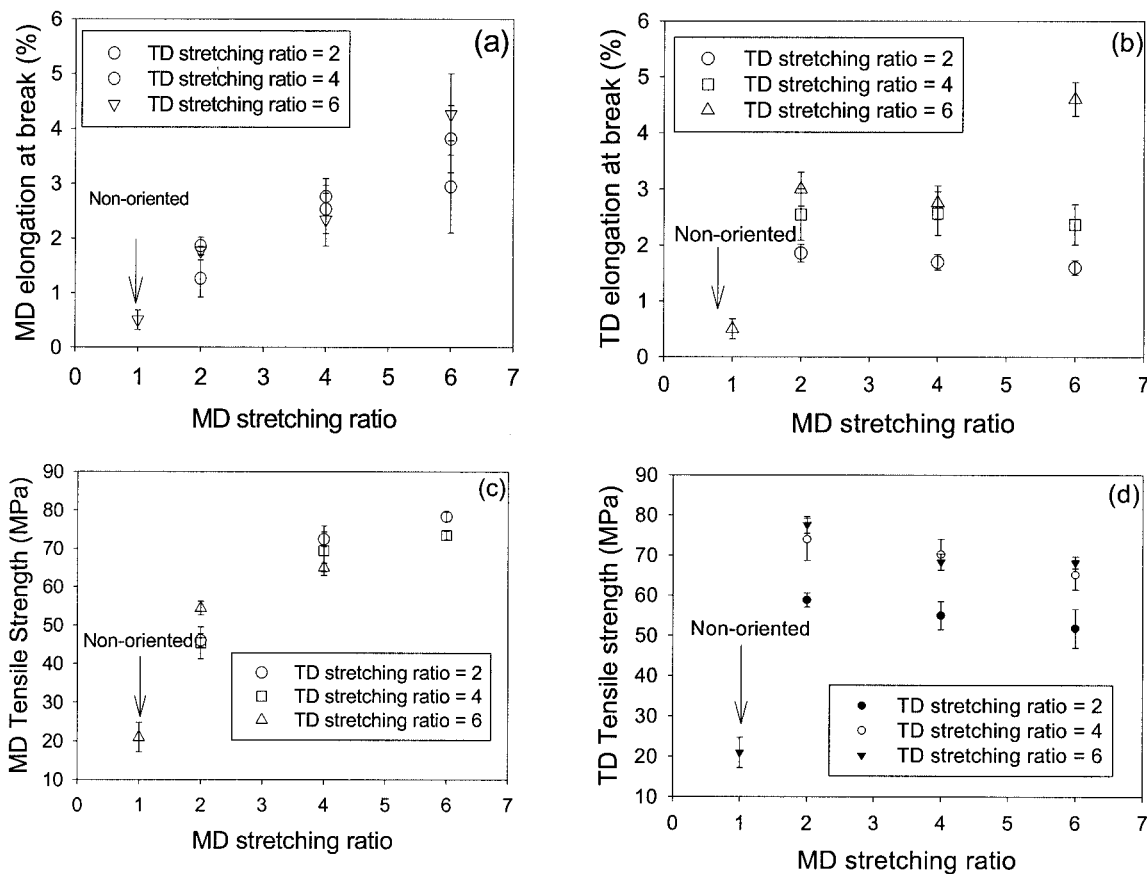
Figure 9 Effect of stretch ratio on mechanical properties for nonequibiaxial stretching.

highest biaxial orientation factor obtained for equibiaxial orientation was 0.085 at a stretch ratio of 6 × 6, the highest f_M^B was 0.08 and the highest f_T^B was 0.103 and were obtained for stretch ratios of MD × TD = 6 × 2 and MD × TD = 2 × 6, respectively.

The effect of stretch rate and temperature on birefringence for the same stretch ratio of MD × TD = 6 × 6 is shown in Figure 7(a) and (b), respectively. An increase in stretch rate or a decrease in temperature favors both MD and TD orientation. This is due to the fact that the lower the stretch rate or the higher the draw temperature, the higher is the time allowed for the oriented structure to relax. Thus, to obtain a high level of orientation, a rapid stretch rate at the lowest possible temperature to high stretch ratio is required.

Mechanical properties and its correlation with orientation

Elastic–brittle deformation behavior, with small elongation at break below 1%, was observed for the nonstretched PS. For the stretched PS sheets, an elastic response followed by a yielding was occasionally observed. The improvements in modulus are in the range of measurement errors; however, the tensile strength and elongation at break were found sensitive

to orientation, and hence, the analysis of the mechanical properties is focused on these two properties.

For equibiaxially oriented PS samples, the dependence of tensile strength and elongation at break on stretch ratio is shown in Figure 8(a)–(d). Comparable tensile strength and elongation at break was observed for MD and TD directions. Tensile strength increased from 40 MPa up to 80 MPa with increasing the level of orientation, especially at the stretch ratio range from 1.5 to 3.0, where the increase is significant. The highest elongation at break obtained was around 4.5%, not as high as reported in the literature.[12] However, considering the increase in tensile strength and elongation at break, it can be projected that stretching improved significantly the toughness. The mechanical properties do not change much above a stretch ratio of 3, even though higher orientation can be achieved at higher stretch ratio.

When keeping one direction (MD or TD) at a constant stretch ratio, the influence of stretch ratio in the other direction on the mechanical properties is illustrated in Figures 9(a)–(d). The tensile strength and elongation at break in one direction are sensitive to the stretch ratio in that direction, but not much influenced by the stretch ratio in the other direction. When MD
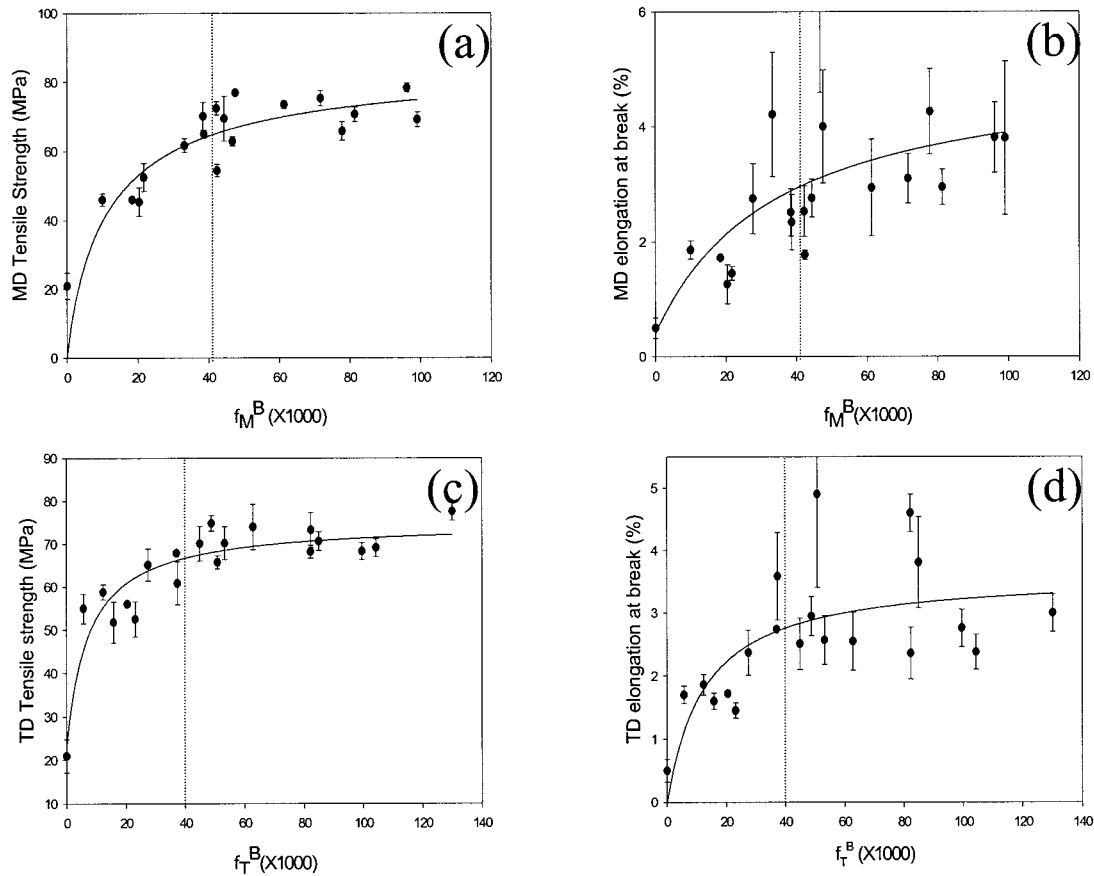
Figure 10 Correlation of mechanical properties with orientation factors.

stretch ratio was maintained at 2, 4, or 6, while that in the other direction was varied, the MD tensile strength did not change significantly, while TD strength increased with increasing TD stretch ratio. The same behavior was observed when TD stretch ratio was constant and the MD one varied. Significantly different mechanical properties for MD and TD directions, depending on relative TD and MD stretch ratio, can be obtained by controlling TD and MD stretch ratio.

Correlation of mechanical properties with biaxial orientation factors is shown in Figure 10(a)–(d). Beyond f_M^B (f_T^B) = 0.04, which corresponds to Δn = −0.005, a plateau is observed. Once the plateau is reached, the mechanical properties are no longer dependent on orientation levels. In this study, when both MD and TD stretch ratio are beyond 3, any increase in

stretch ratio does not further contribute to the enhancement of mechanical properties. This is particularly true for tensile strength.

Shrinkage behavior

A direct correlation between shrinkage and stretch ratio or orientation is of an particular interest in PS oriented sheets applications. The shrinkage ratio measured at 160°C is compared with actual stretch ratio induced in the sheets in Table II. The stretch ratio as measured by shrinkage is a lower than the actual stretch ratio, which is in agreement with some other published results.[19] To exactly retract sample to its original size, higher temperature and sufficient time are necessary. From Table II, it can be observed that

TABLE II
Shrinkage Measured at 160°C and Stretch Ratio Determined by Shrinkage

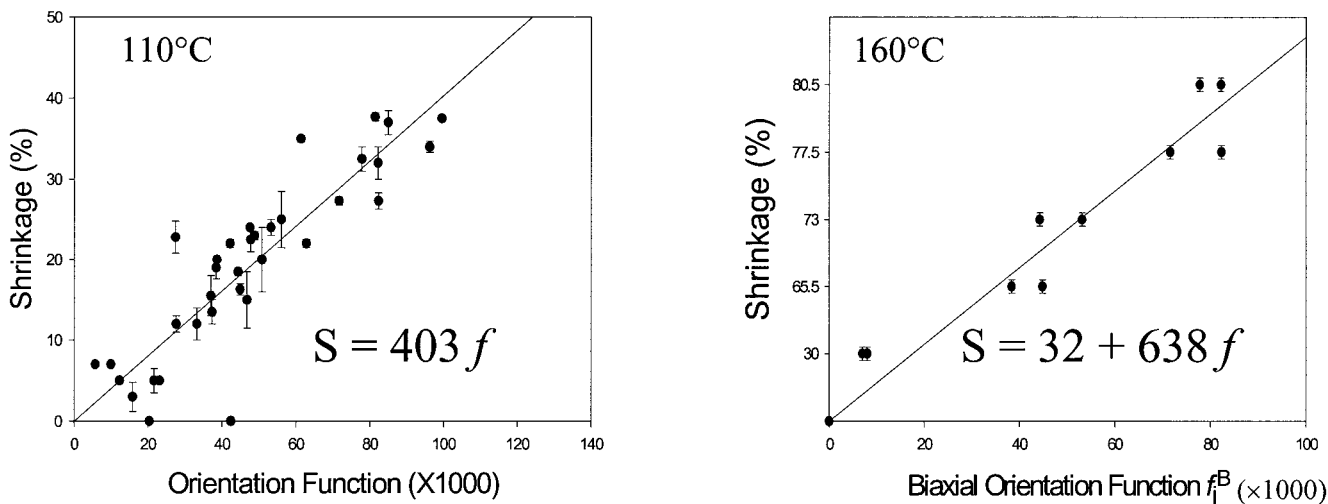| Samples	Shrinkage (%) (MD × TD)	Stretch ratio by shrinkage (MD × TD)	Real stretch ratio (MD × TD)
PS1.5	30 × 30	1.43 × 1.43	1.5 × 1.5
PS3	64 × 65	2.78 × 2.86	3 × 3
PS4	72 × 74	3.57 × 3.85	4 × 4
PS5	77 × 78	4.45 × 4.50	5 × 5
PS6	81 × 81	5.13 × 5.33	6 × 6

Figure 11 Correlation of shrinkage with biaxial orientation factors at 110 and 160°C.

stretch ratios from shrinkage at 160°C are close to actual stretch ratios in the low stretch ratio range. For higher draw ratios, the differences are more and more significant. This is probably due to the occurrence of disentanglement at higher draw ratio, and longer relaxation times are needed to retract to the original size. The technique of measuring stretch ratio by thermal shrinkage can be approximately valid only at low orientation levels.

For oriented amorphous polymers, the two main thermal processes during heat up are (1) release of stored elastic energy (intrachain energy), which is exothermic; and (2) heat of disorientation (interchain entropic energy) which is endothermic. Correlations between shrinkage strain and orientation factors are shown in Figure 11. A good correlation was observed between shrinkage strain and the orientation factors for the two temperatures of 110 and 160°C, shrinkage in this case can be regarded as a measure of orientation.

The shrinkage force was studied by monitoring the stress while keeping the sample at a constant length between the two fixed clamps. Load vs. time for PS oriented sheets under constrained annealing and annealing followed by quenching is shown in Figure 12. Several regimes in this load–time graph are observed. After a long flat low load region, a plateau region, which was reported to be directly proportional to reversible entropic elastic force,[20] is observed. The higher the drawing temperature used, the lower the reversible entropic stress. This plateau was also sensitive to the stretch ratio: it disappears at a low stretch ratio, and the higher he stretch ratio, the more distinct was this region (not shown here). A high peak stress corresponding to a large shrinkage region was observed when heating the oriented PS above T_g. The recovery of elastic energy will produce an irreversible stress that will shrink the samples, as observed in Figure 12. After the peak, a decrease in stress, which is
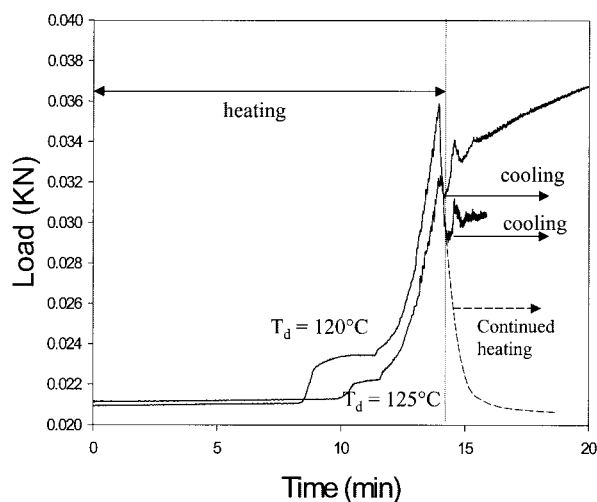

Figure 12 Load development in heating or heating then cooling process for the samples drawn at two different temperatures. The temperature of the oven was set at 110°C. Draw ratio = 6 × 6, draw rate = 10%/s.
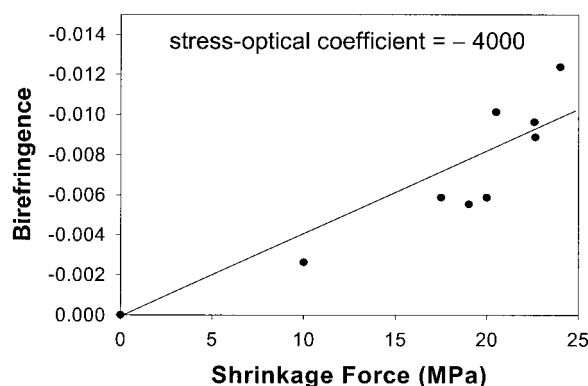

Figure 13 Correlation of shrinkage stress measured at 110°C with orientation factors.

the result of relaxation, is observed. After a sufficient heating time, the stress relaxes to a very low value. The peak value upon heating was referred to as shrinkage stress. If the samples are cooled rapidly after the peak stress, a second peak followed by a steady plateau was seen.

Shrinkage stress vs. orientation is shown in Figure 13. The orientation in polymeric glasses may be determined by application of rheo-optical laws relating stress and birefringence in the melt state and allowing the birefringence to be frozen near T_g. According to the stress optical law, a linear relationship between normal stress and birefringence can be predicted; from the slope, the stress-optical coefficient can be obtained. The value of the stress optical coefficient determined from the line in Figure 13 is 4000 Brewster. Values for the stress-optical coefficient of PS in the glass states have been obtained by several investigators.[21–23] These values are in the range of +7.50 to +11.00 Brewster. However, the stress-optical coefficient for PS melt was found to be 4100 to 4500.[24–26] The value obtained here is close to literature values for PS melt.[24–26]

CONCLUSIONS

PS sheets having a wide range of orientations, from uniaxial to equibiaxial, were produced. The stretch level in the second stretch direction was sensitive to the orientation structure and level formed in the first stretch direction. High stretch rates, low temperatures, and high stretch ratios favored the formation of high levels of orientation. The orientation structure and level formed in the first stretch direction directly influenced the orientation in the second stretch direction. Stretching enhanced tensile strength and elonga-

tion at break significantly up to an orientation factor of f_M^B (f_T^B) = 0.04. Finally, shrinkage strain and stress showed a good correlation with orientation factors.

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