Drawing and Annealing of Polypropylene Fibers: Structural Changes and Mechanical Properties

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Synopsis

A study has been carried out on the influence of cold drawing (25°C), hot drawing (140°C), and annealing (140°C) on the structure and mechanical properties of a series of four different well-characterized melt spun polypropylene filaments. The influence of the interaction between melt spinning and drawing variables was given special attention. Cold drawing increased the orientation in the samples, disrupts the initial monoclinic crystal structure and the morphology of the filaments, and it results in extensive fibrillation. Annealing restored the monoclinic structure but eliminated only a small part of the fibrillation. Hot drawing produced changes which were qualitatively similar to the combined effects of cold drawing and annealing. The orientation and morphology of the as-spun filaments were found to have major effects on drawing behavior and the mechanical properties of the drawn fibers for a given draw ratio. It was found, however, that the mechanical properties (tensile strength, tangent elastic modulus, and elongation to break) of the melt spun, hot drawn and cold drawn, and annealed fibers could all be correlated with birefringence measurements.

INTRODUCTION

Since polypropylene is among the most important synthetic fibers, studies of the processing operations used in its fabrication are of considerable interest. In the production of polypropylene fibers, continuous filaments are first formed by melt spinning; these filaments are then drawn. The structure and properties of the final fibers are determined by the details of both operations. We are involved in an extensive program on the formation of polypropylene fibers. In the first part of this study, we investigated structure development in melt spinning of a wide range of polypropylenes.[1-3] The present paper involves a study of drawing of melt spun fibers under a range of conditions and an evaluation of resulting fiber structure and mechanical properties.

The earliest published studies of the drawing of polypropylene fibers were those of Sobue and Tabata,[4] Hall,[5] Wyckoff,[6] and Sheehan, Cole, and Wellman.[7,8] These authors were concerned with the crystallographic character and degree of disorder in drawn fibers and films as well as methods for producing very high strength fibers. A second generation of studies was carried out by Samuels[9-11] who investigated the variation in orientation and morphology during drawing by means of wide-angle x-ray diffraction (WAXS), small-angle x-ray diffraction (SAXS), birefringence, and small-angle light scattering (SALS). Mechanical properties of drawn fibers were measured and correlated with orientation. The drawing of polypropylene fibers has also been investigated by Kamide[12] who studied the influence of drawing temperature and molecular weight on the mechanical properties of polypropylene fibers. Peterlin and his colleagues[13,14] have made transmission-electron-microscope studies of the drawing of polypropylene

Journal of Applied Polymer Science, Vol. 22, 3121–3133 (1978)

0021-8995/78/0022-3121$01.00

and attempted to interpret morphology variations. A recent study of the drawing of polypropylene is given by Cansfield, Cappaccio, and Ward.[15]

There have been extensive studies of the drawing of fibers (and films) formed from various polymers. Varying views of structural and property changes resulting from drawing have been expressed by Peterlin[16,17] and Samuels[9–11] among others.

In most previous studies of drawing, the initial filaments are low-orientation spherulitic materials or else specification of the initial structure is neglected. Only a few studies from our own laboratories[3,18,19] have dealt extensively with the influence of the spinning conditions on the subsequent drawing behavior and mechanical properties of the drawn fibers. Most of this work has been restricted to a single grade of high-density polyethylene fibers. The purpose of the present study was to examine the effect of the initial orientation and morphology on the drawing behavior and mechanical properties of two polypropylenes with considerably different average molecular weight.

EXPERIMENTAL

Materials

The fibers investigated in this paper were the same as those prepared in our earlier paper.[1] Two Hercules Profax polypropylene types were used. These materials and their structural characteristics are summarized in Table I. The polymers have melt indices 0.42 (Profax 6823) and 12.0 (Profax 6323) and are designated in subsequent discussion as H-0042 and H-1200, respectively. The H-0042 was extruded at 0.5 g/min through a single spinneret hole and taken up at 50 and 550 m/min. The H-1200 was extruded at 2.0 g/min and taken up at 200 and 550 m/min. In all cases the spinning was carried out at 230°C. For more details of the spinning conditions, see our earlier paper.[1] Crystallinities and orientation factors of the as-spun filaments are summarized in Table I.

Drawing and Annealing Treatments

The fiber drawing operation was carried out using an Instron tensile testing machine. Samples of initial length one inch were stretched to three different stages of drawing; 1) 1 in. beyond the natural draw ratio (defined by the disappearance of necks), 2) approximately 1 in. prior to fracture, and 3) intermediate between the above two. In the case that no necking was observed, the first stage corresponded to a draw ratio of 2.0. The drawing operations were carried out at both room temperature and 140°C. This resulted in the draw ratios shown in Table II. A crosshead speed of 2 in./min was used during drawing.

The cold drawn fibers were subsequently annealed at 140°C for 15 min.

Structural Characterization

WAXS patterns were obtained using a Philips Norelco x-ray generator and a flat plate camera. The radiation used was Ni filtered Cu $K\alpha$ of wavelength 1.542 Å.

SAXS patterns were obtained using a modified Kiessig camera with pinhole collimation. The camera was mounted on a Rigaku General Electric rotating

TABLE I
Melt Spun Fibers used in Drawing Experiments

	Spun fiber characteristics							
Fiber	Base polymer	$[\eta]$ decalin/ 137°	M_w	Diameter (μm)	Crystallinity (density measurements)	Orientation factors f_c	Orientation factors f_b	Birefringence $\times 10^3$
H-0042-50	Profax 6823	2.5	314,000	116	55.8	0.49	−0.40	16.3
H-0042-550	Profax 6823	2.5	314,000	38	57.4	0.91	−0.48	19.9
H-1200-200	Profax 6323	1.7	194,000	255	53.1	0.19	−0.11	2.7
H-1200-550	Profax 6323	1.7	194,000	77	53.5	0.63	−0.43	12.1

TABLE II
Draw Ratios Selected for Drawing Studies

Specimen	Draw ratios I	II	III
H-1200-200	4.0	6.8	9.5
H-1200-550	2.5	4.9	6.2
H-0042-50	2.0	4.1	6.2
H-0042-550	2.0	2.9	3.8

anode x-ray generator. Patterns with a resolution of 400 Å were obtained with a custom made collimator.

The birefringence of the fibers was determined on an Orthoplan Polarizing Microscope with a Leitz Berek Compensator.

Densities and apparent crystallinities were determined using an isopropyl-alcohol–water-gradient density column as described by Tung and Taylor.[20]

Mechanical Properties

Fiber mechanical properties were measured using an Instron tensile tester at room temperature. Fibers of initial gauge length of 1 in. were stretched at a cross-head speed of 0.5 in./min.

STUDIES OF STRUCTURAL CHANGES

Crystalline Form and Crystallinity

Figure 1 illustrates the effect of cold drawing, hot drawing, and cold drawing plus annealing on the WAXS patterns of the H-1200 sample spun with a take-up velocity of 200 m/min. It can be seen that cold drawing transformed the monoclinic form of the as-melt spun filament into a more oriented but disordered structure. The x-ray pattern of the cold drawn sample exhibits a high degree of line broadening which may be considered to result from a decrease of crystallite size and greatly enhanced lattice strains and defects. The structure of this disordered cold drawn sample probably may be considered similar to that of the smectic form produced by rapid quenching from the melt.[1–4,6,7] Samples which were hot drawn or cold drawn and then annealed exhibit a highly oriented well-formed monoclinic structure [Figs. 1(c) and 1(d)].

Densities of hot drawn fibers and cold drawn and annealed fibers are slightly higher than those of the as-melt spun filaments indicating small increases in crystallinity. Crystallinity values of about 61% were observed.

Orientation

Typical WAXS patterns for the three stages of drawing (varying draw ratios) are shown in Figures 2 and 3. Figure 2 shows patterns from the hot drawn samples while Figure 3 shows patterns from the cold drawn and annealed samples. The WAXS patterns generally indicate increases in crystalline orientation brought about by drawing. In the case of H-1200-200, these changes are substantial. In the case of H-0042-550 which is already highly oriented in the as-spun condition, the increase in orientation is small. The higher the initial or-

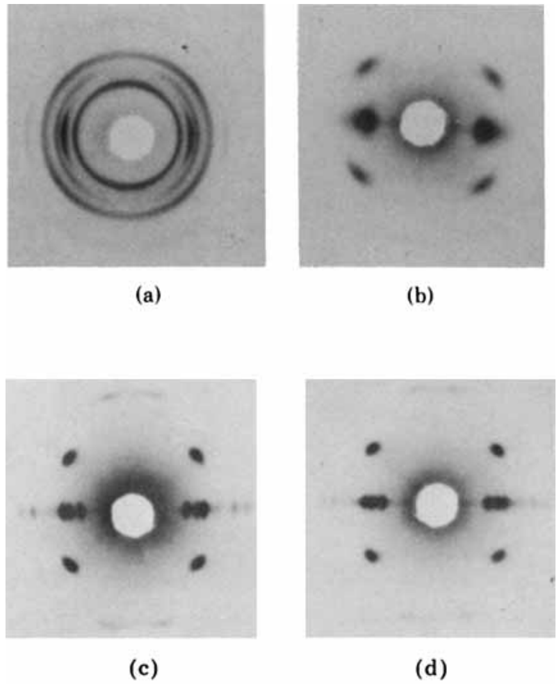


Fig. 1. WAXS patterns of H-1200-200. (a) As-spun; (b) cold drawn, 25°C; (c) hot drawn, 140°C; and (d) cold drawn and annealed 15 min at 140°C.

ientation in the spun filament, the lower is the draw ratio needed to develop a given high level of orientation. Generally orientation is observed to increase most during the first stage of drawing. It continues to increase somewhat as one moves from drawing stage I to stage II, but there is little apparent change in crystalline orientation during the third stage of drawing. Examination of Figures 2 and 3 shows that there are slight differences in the way that orientation develops in the hot drawn samples as compared to the cold drawn and annealed samples. However, these differences do not appear to be nearly as significant as the effect of initial condition.

Bimodal orientation is observed in the as-melt spun fibers.[1-3,21-24] This is associated with crystallization under uniaxial stress. In both the hot drawn and cold drawn and annealed fibers, the bimodal orientation gradually disappears.

In Figure 4, we plot the birefringence as a function of draw ratio for the fibers. Generally, birefringence first increases and then levels off with increasing draw ratio.

SAXS Measurements and Morphology

SAXS patterns in the as-spun condition of the low orientation H-1200-200 filament and the highly oriented H-0042-550 filament are shown in Figure 5. The H-1200-200 pattern consists of a ring with considerably stronger meridional than equatorial intensity. The position of the ring corresponds to a long period of spacing of 125 Å. The H-0042-550 filament exhibits a definite two-point pattern with strong intensity maxima on the meridian, corresponding to a long

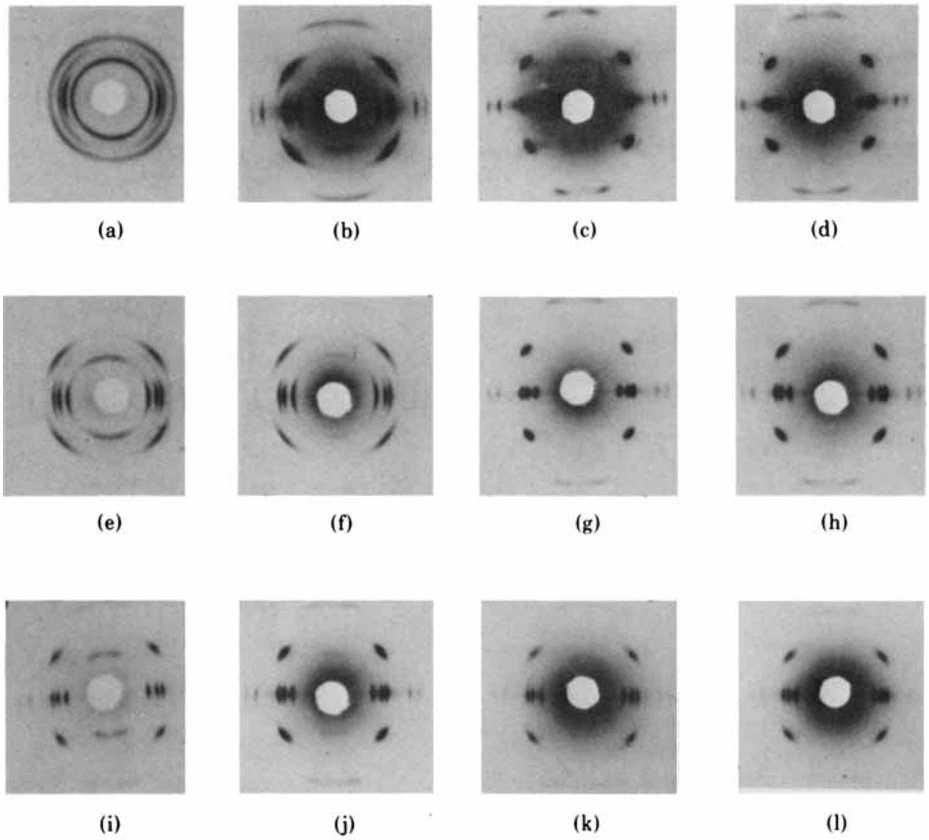
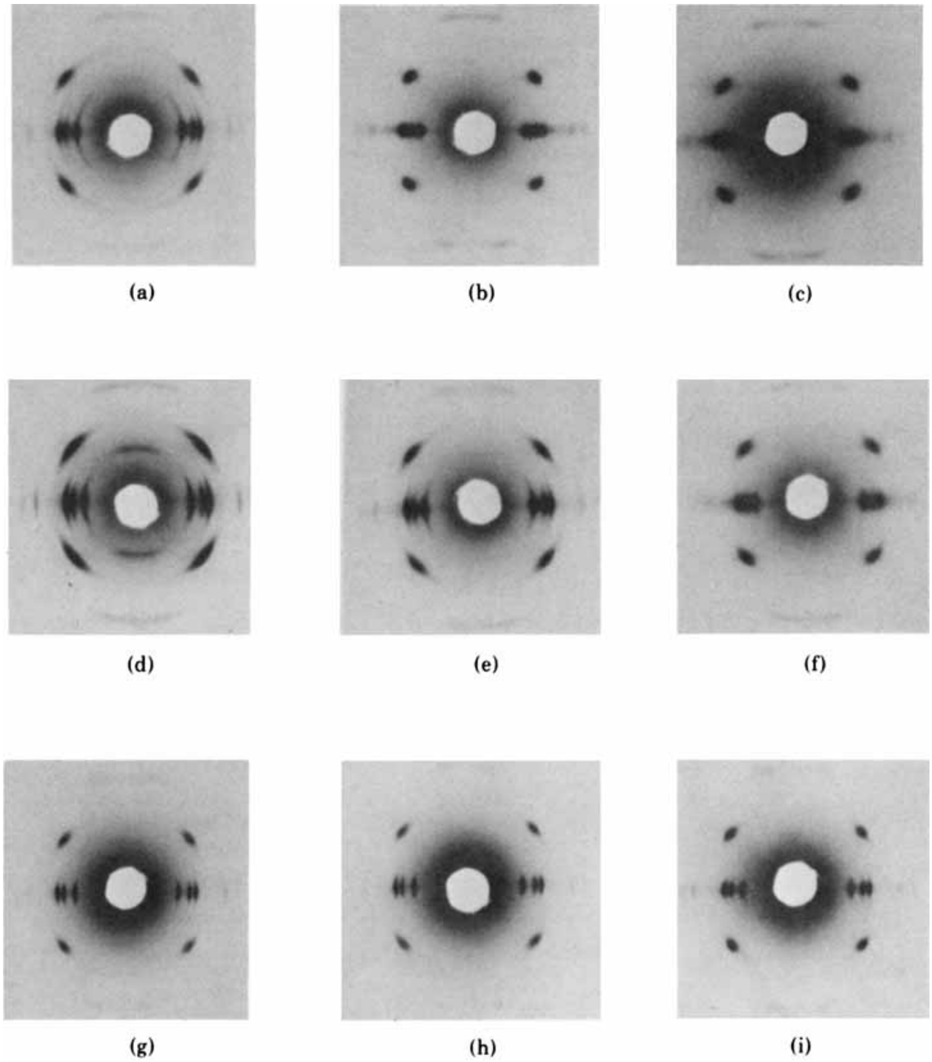


Fig. 2. Typical WAXS patterns for hot drawn fibers. (a) H-120-200, draw ratio (D.R.) = 1.0 (as-spun); (b) H-1200-200, D.R. = 4.0; (c) H-1200-200, D.R. = 6.8; (d) H-1200-200, D.R. = 9.5; (e) H-0042-50, D.R. = 1.0; (f) H-0042-50, D.R. = 2.0; (g) H-0042-50, D.R. = 4.1; (h) H-0042-50, D.R. = 6.2; (i) H-0042-550, D.R. = 1.0; (j) H-0042-550, D.R. = 2.0; (k) H-0042-550, D.R. = 2.9; and (l) H-0042-550, D.R. = 3.8.

period of 137 Å. Based on a more complete array of results[1–3] together with the efforts of prior investigators[11,25,26] we have previously concluded that low orientation samples have a slightly distorted spherulitic morphology while high orientation samples have a "row" or "cylindritic" morphology. Presumably, there is a gradual transition from the spherulitic morphology to the row structure.

The effect of cold drawing, hot drawing and cold drawing plus annealing on the SAXS pattern is shown in Figure 6 for the H-1200-200 sample. For the cold drawn fiber, there is diffuse equatorial scattering. The annealed cold drawn fiber shows reduced diffuse equatorial scattering and the development of a two-point pattern on the meridian corresponding to a long period of 147 Å. The SAXS pattern of the hot drawn fiber is similar to that for the cold drawn and annealed fiber except that the meridional scattering corresponds to a somewhat larger dimension of about 200 Å.

The SAXS patterns for the drawn H-0042-550 samples are similar to that of the H-1200-200 sample described above except that there is somewhat less equatorial diffuse scatter. The long-period spacings also differ; for a draw ratio of 2.4 the long period of the cold drawn and annealed sample was 150 Å and that of the hot drawn sample was 192 Å.



(a) (b) (c) (d) (e) (f) (g) (h) (i)

Fig. 3. Typical WAXS patterns for cold drawn and annealed fibers. (a) H-1200-200, D.R. = 4.0; (b) H-1200-200, D.R. = 6.8; (c) H-1200-200, D.R. = 9.5; (d) H-0042-50, D.R. = 2.0; (e) H-0042-50, D.R. = 4.1; (f) H-0042-50, D.R. = 6.2; (g) H-0042-550, D.R. = 2.0; (h) H-0042-550, D.R. = 2.9; and (i) H-0042-550, D.R. = 3.8.

The SAXS patterns described above are similar to those reported by Sze, Spruiell, and White[19] on melt spun, cold drawn, and annealed high-density polyethylene fibers. The general view we have formed of structural changes occurring during drawing correspond to those of these authors, White, Dharod, and Clark,[18] and Peterlin.[14,16,17] Based on the WAXS results (Fig. 1), cold drawing disrupts the entire structure including the unit cell level as well as the morphology. It fibrillates the initially spherulitic or row structured filament producing microfibrils, fibrils, and superfibrils. This explains the diffuse equatorial scattering and the reduction of intensity and disappearance of the meriodional small angle reflections which exist for the as-spun filaments. Annealing removes residual internal strains, increases perfection in the unit cell, increases crystallite sizes, and restructures an axial periodicity with a new

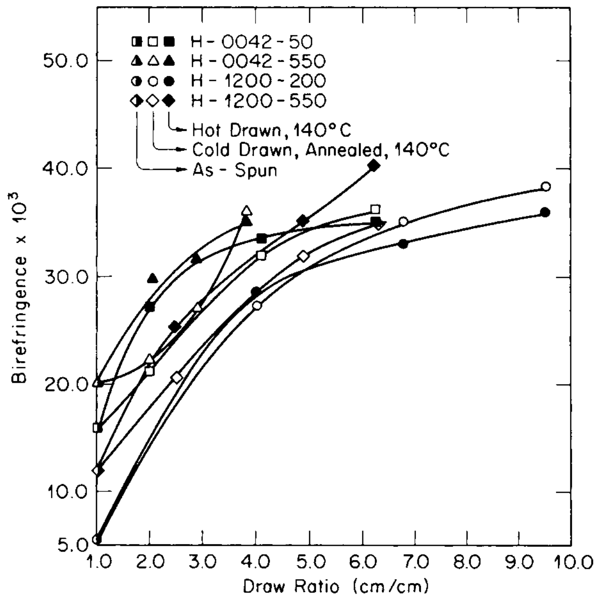
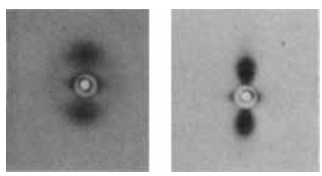
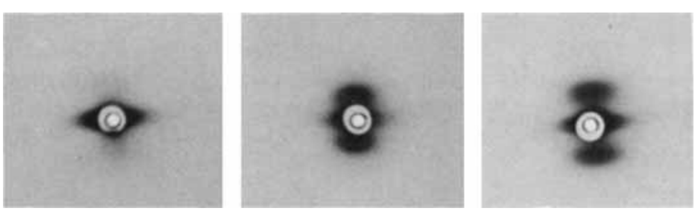


Fig. 4. Birefringence as a function of draw ratio and processing path for polypropylene fibers.



(a) (b)

Fig. 5. SAXS patterns of as-spun filaments. (a) H-1200-200, and (b) H-0042-550.



(a) (b) (c)

Fig. 6. SAXS patterns of drawn H-1200-200 fibers with D.R. = 6.8. (a) Cold drawn, 25°C; (b) hot drawn, 140°C; and (c) cold drawn and annealed 15 min at 140°C.

long-period spacing. During this process small voids separating the microfibrils appear to heal. These changes are consistent with the changes observed in both the WAXS and SAXS patterns. Hot drawing is viewed as causing a less severe disruption of the structure than cold drawing. The fibrillation and destruction of the morphology is less extensive. Perhaps, however, hot drawing involves disruption of the morphology followed by rapid healing by simultaneous annealing processes. The samples with low as-spun orientation seem to exhibit greater fibrillation than those with high as-spun orientation. This difference can be largely rationalized on the basis of the lower draw ratios needed to develop similar mechanical behavior in the high orientation precursor.

Mechanical Properties

Figure 7 shows stress strain curves for typical melt spun and drawn (hot) fibers. Other examples of the stress-strain behavior of the melt spun fibers were presented in our previous paper.[1] The stress exhibits an almost linear rising regime, followed by a yield value and slowly changing stress, corresponding to the regime of neck development and then a regime of rising stress and failure. Aside from increases in tensile strength and decreases in elongation to break, the major difference between the H-1200-200 sample and those samples having higher spin orientation is a reduction in the necking elongation with increasing orientation.

The drawn fiber exhibits a higher modulus, no apparent yield point and a considerably lowered elongation to break but increased tensile strength compared to the filament from which it was drawn. These qualitative similarities exist in all drawn and annealed fibers.

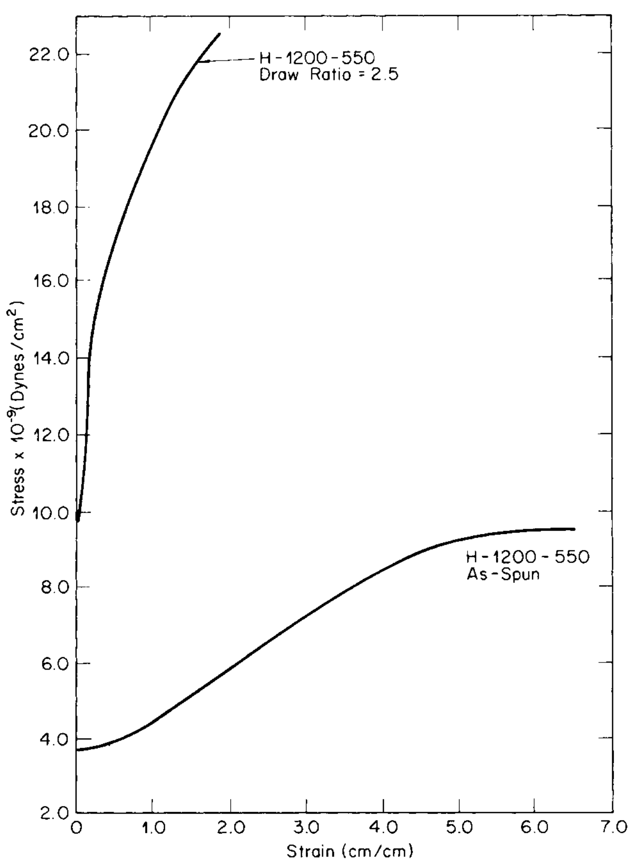


Fig. 7. Stress-strain curves for melt spun and hot drawn H-1200-550 fibers.

The mechanical properties of the drawn fibers were found to depend on both the drawing conditions and the melt spinning conditions as shown in Figure 8 for the case of tensile strength. Though the mechanical properties show a regular behavior with draw ratio, a general correlation of the properties with draw ratio is not possible because of the dependence of the mechanical properties on the structure of the starting spun filament and the processing path.

It would seem more reasonable to correlate mechanical properties with some measure of fiber structure. Samuels[11] suggested that the state of orientation and not the fabrication draw ratio should be used to characterize the mechanical properties of fibers and film. In Figures 9–12, we plot modulus, tensile strength and elongation to break as a function of fiber birefringence. We include melt spun, hot drawn, and annealed cold drawn fibers in each plot. The ability to correlate the mechanical properties with the birefringence is surprisingly good.

Somewhat different correlations are proposed by Samuels[9–11] using amorphous and two-phase averaged orientation factors. We believe there is little difference between his and our own correlations. His f_{av} is nearly proportional to birefringence. The main contribution of the present results is to extend such correlations to a wide range of starting morphologies. The fact that polymers with two different average molecular weights were included makes the correlation even more remarkable.

Finally, it is of interest to examine the distribution of the results from different starting materials. Figure 12 shows the elongation to break data for the drawn samples plotted so that the values for each starting material can be identified. It is clear that the results for the various as-spun samples are each spread throughout the birefringence range and are not clustered together at some point in a narrow band of birefringence values. Also, the scatter of the data about the curve appears similar for all the starting conditions. Similar behavior is observed for the tensile strength and modulus data.

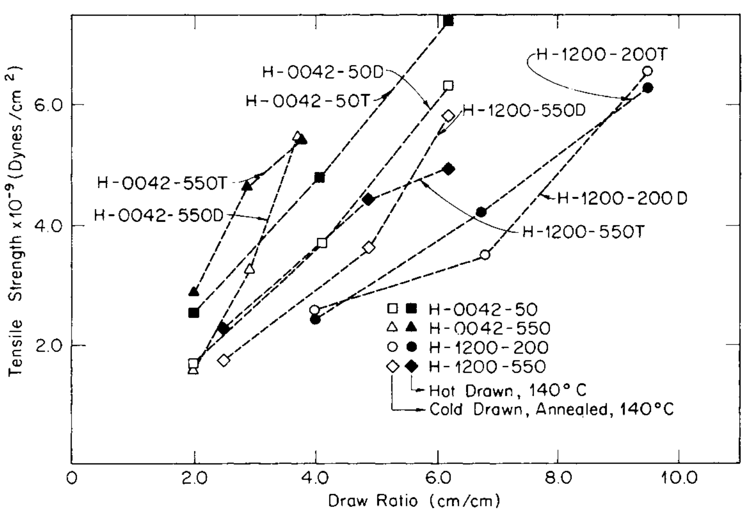


Fig. 8. Tensile strengths of drawn fibers as a function of draw ratio. D series was drawn at 25°C; T series was drawn at 140°C.

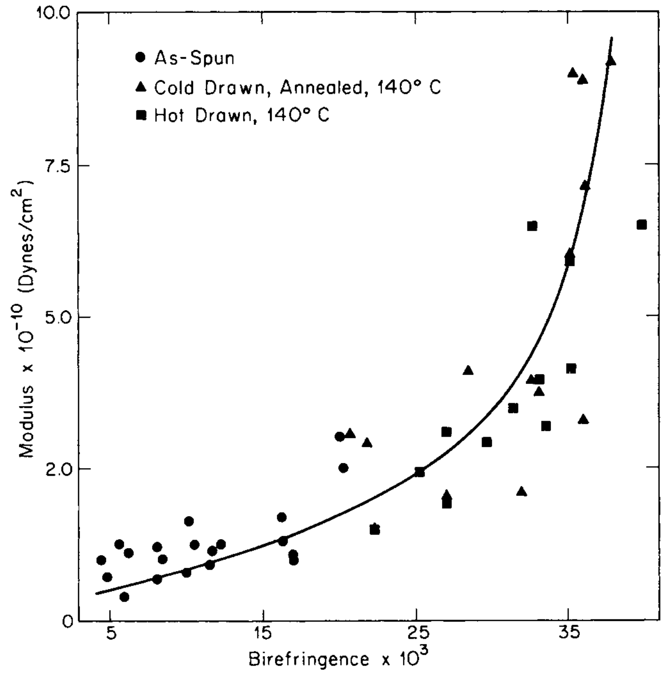


Fig. 9. Modulus as a function of birefringence for melt spun, hot drawn and cold drawn, and annealed fibers.

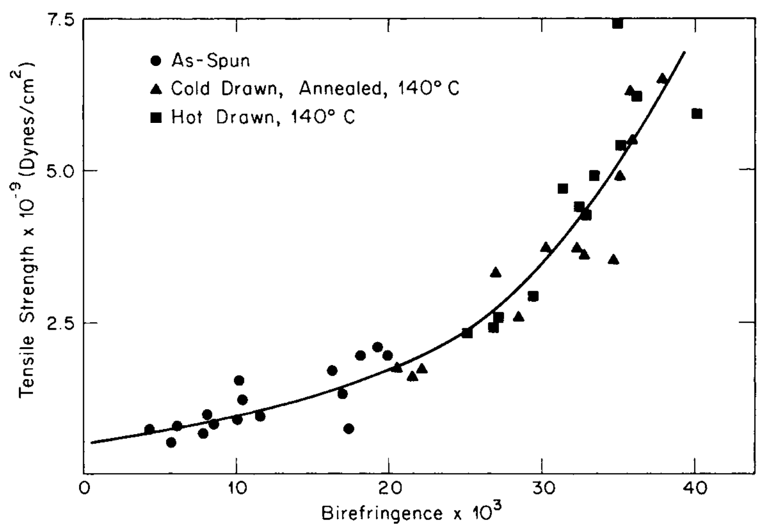


Fig. 10. Tensile strength as a function of birefringence for melt spun, hot drawn and cold drawn, and annealed fibers.

CONCLUSIONS

A study has been carried out of the hot drawing, cold drawing, and annealing of polypropylene filaments having different starting morphology due to different spinning conditions and average molecular weight. The different starting morphologies have great effect upon the drawing behavior of the filaments.

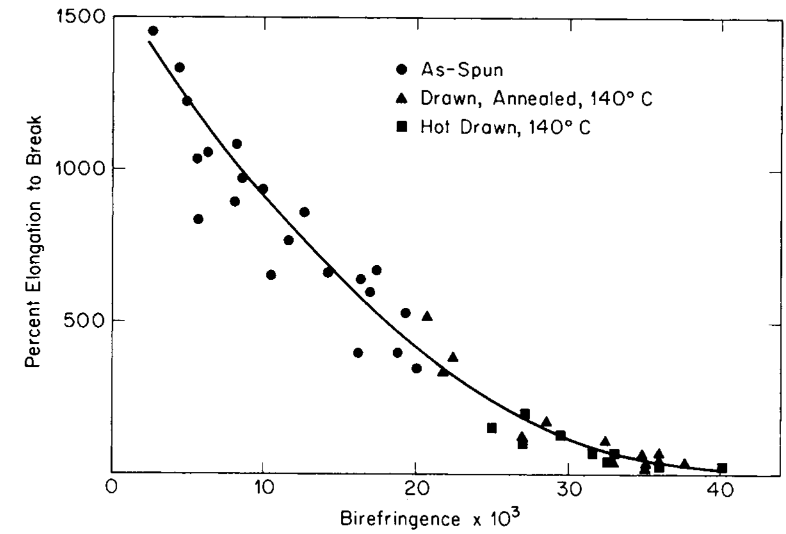


Fig. 11. Elongation to break as a function of birefringence for melt spun, hot drawn and cold drawn, and annealed fibers.

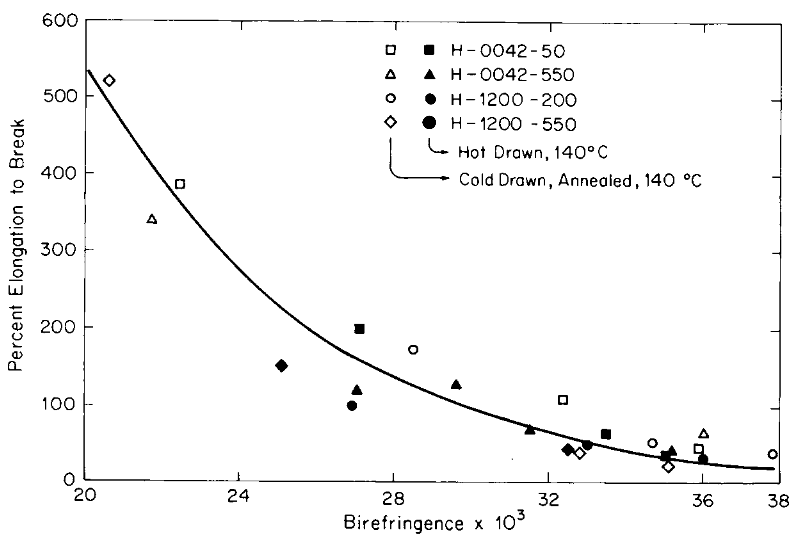


Fig. 12. Elongation to break as a function of birefringence for drawn polypropylene fibers showing the initial spinning conditions for each result.

Remarkably, it was found that the mechanical properties of the spun and drawn fibers could all be correlated with the birefringence developed in them by the processing conditions, independent of the processing path.

This research was supported in part by the National Science Foundation under NSF Grant No. ENG 75-16974. The polymers used were kindly supplied by Hercules.

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Received April 28, 1977
Revised July 22, 1977