The Influence of Processing Parameters on the Structural and Mechanical Properties of Drawn Polypropylene Fibres: A Factorial Design Approach

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ABSTRACT: This article reports a study of multi-stage polypropylene fiber drawing (stretching) as a continuous, but independent stage of the overall fiber-forming process. The fibers were drawn according to a factorial experimental design, once appropriate spinning conditions had been devised. The structures of the drawn fibers were studied using wide-angle X-ray diffraction and birefringence measurements. In addition, the fibers were characterized with respect to filament tenacity, elongation to break, specific secant modulus, and extent of shrinkage at 130°C. All these properties were quantitatively assessed as responses to nine specially selected process control parameters in the drawing equipment. For every property analyzed, the temperatures of the hot plates in the draw frame were found to exert no significant influence, whereas the temperatures of the initial rollers were in most cases significant. Furthermore, the speed of the final roller also played an influential role, and a number of interactions between process parameters were identified as significant. Explanations are advanced for the parts played by significant process parameters on the properties of the drawn fibers. The article also demonstrates the advantages of factorial experimental design in determining correct settings for process parameters to give drawn fibers with the properties desired. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3606–3616, 2012

Key words: statistical analysis; factorial experimental design; drawing; polypropylene; fibers

INTRODUCTION

It has been known for nearly 50 years that, in common with other types of fiber, the conditions for processing polypropylene (PP) fibers exert a critical influence on their structure and mechanical properties.[1] The crystallization and deformation processes that occur in melt spinning and subsequent drawing (stretching) of PP fiber have subsequently been closely investigated.[2,3] Indeed, the topic is still the subject of research activity.[4,5] Furthermore, there is considerable interest in the effect of particulate additives on PP fiber structure and properties. These additives include pigment particles, incorporated prior to spinning to color the fibers,[6,7] carbon nanotubes, incorporated with a view to fiber reinforcement[8] and clay nanoparticles, incorporated to improve fiber tenacity and fire resistance.[9,10] Nevertheless, the adoption of statistical experimental design to PP fiber processing has been far less widely reported.

In previous papers,[11–13] we have described the application of statistical experimental design to determine the significance of a variety of process control parameters on the structural and mechanical properties of melt-extruded (as-spun) PP fibers. However, as-spun fibers lack the mechanical performance required for commercial applications, and to achieve this performance the fibers must be drawn. Drawing, under the correct conditions, leads to extensive transformation of the microstructure within the filaments, so that a variety of desirable mechanical properties can then be attained, such as high strength, low elongation and enhanced recovery. The structural changes within the filaments involve greater alignment of the PP chains and crystalline domains along the fiber axis and a consequent increase in the degree of crystallogaphic order. Moreover, the paracrystalline structure often present in as-spun fibers is transformed to the α-monoclinic crystalline form.

The principal factors influencing the properties of drawn PP fibers are the structure of the as-spun fiber precursors and the drawing conditions imposed on them. These conditions include the number of drawing stages (commercial PP fiber production often involves two-stage drawing), the draw ratio achieved at each stage, draw temperatures, and draw speeds. The impact of all these factors is discussed elsewhere.[14]

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TABLE I
Grade of PP

Manufacturer	Name	MFI (g/10 min)
Targor	1101N	13.8
Borealis	HF445J	19.5
Petrofina	PPH9069	22.4
Borealis	VC35	34.2

The structural features of the as-spun fibers can be conveniently evaluated in terms of the degree of crystallographic order and the degree of orientation of the PP chains in the direction of the fiber axis. Drawability is also considered to be an important parameter: this is usually taken as the maximum draw ratio achievable.[15] Thus, as-spun fibers of high crystallinity and high macromolecular chain orientation possess limited capacity for further deformation during drawing. Such as-spun fibers are hence not desirable in commercial processing. By contrast, paracrystalline PP fibers have been identified as suitable for the production of high-tenacity drawn fibers,[15,16] and indeed some evidence has also accrued that low PP chain orientation is also desirable.[17]

This article concentrates on multi-stage PP fiber drawing, as a continuous, but independent stage of the overall fiber-forming process. The effects of a variety of drawing parameters are examined systematically under fixed spinning conditions. However, to undertake this systematic examination, preliminary experiments were conducted to investigate the drawability of as-spun fibers, appropriate spinning conditions for the drawing process, and the structural transformation during first-stage drawing. The experiments on drawability and on first-stage drawing have been described elsewhere.[11,17] The work on the appropriate spinning conditions is included in this article.

EXPERIMENTAL

The grades of PP used are given in Table I, along with values determined for melt flow index (MFI).

Raw PP granules were melt extruded from pilot-plant scale Labspin equipment supplied by Extrusion Systems. Descriptions of PP fiber extrusion using this equipment are available elsewhere.[13,18] The extruded fiber was immediately fed to a draw-frame, specially constructed by Extrusion Systems, of scale commensurate with that of the extrusion equipment. As shown in Figure 1, the draw-frame consisted of four hot drawing rollers, three hot plates, a spin finish applicator, and a winder. Each roller, of diameter 16 cm, was equipped with a freely rotating separator of diameter 3.5 cm, to separate the wraps of filaments on the same roller.

Tensile testing was conducted using an M5 tensile tester (Nene Instruments, UK) in a conditioned room at a temperature of (20 ± 2)°C and a relative humidity of (65 ± 3)%. Filaments with an initial length of 20 mm were stretched at a constant speed of 20 mm min^{-1}. Values of fiber tenacity, specific secant modulus,[16] and elongation to break were determined. Five measurements were made for each sample. The determination of wide angle X-ray diffraction data and of optical birefringence data has been described elsewhere.[12,18]

The thermal shrinkage of drawn fibers was determined using an MK4 oven (chamber size, 25 × 11 × 8 cm), from Testrite, UK. One end of the specimen carrier consisted of a clamp, while at the other end was a pulley. Ten folds of each sample were tied together with two knots as markers. One end of the bunch was fixed to the clamp, whereas the other end was allowed to hang freely on the pulley, by pulling with a 10 g weight. The weight provided a constant tension bearing, so that the sample did not touch the chamber surfaces. Samples were heated for 120 s at 130°C. The distance between the two marker knots was measured before and after heat treatment. Thermal shrinkage was calculated as $[100(L_o - L)/L_o]\%$, where L_o and L are the lengths before and after heat treatment.

Experimental trials were conducted using factorial design in the manner reported in our previous papers. Details of the trials are given in the succeeding sections of this article. The principal methods of analysis used were effects plots and analysis of variance (ANOVA). The ANOVA was carried out with the use of "MINITAB" software. The main effects reveal the relative magnitude and direction of the effects of individual process control parameters.[19] The ANOVA provides a quantitative index, the *F*-value, for judging the significance of factor effects, within a chosen level of risk, α. In accordance with common practice, a level of risk, $\alpha = 0.05$, has been used in our work. From the *F*-value, the probability,

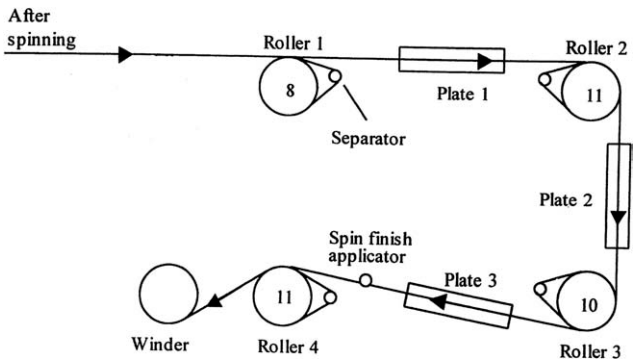

Figure 1 Schematic diagram of the drawing process for the PP fibers. The number in each roller refers to the number of times the filament is wrapped around the roller and its associated separator.

TABLE II
Spinning Factors and Levels for the Screening Experiment

Spinning factors	Setting 1	Setting 2	Setting 3	Setting 4
Metering pump speed, MPS (rpm)	3	9	6	12
Quenching air speed, QAS (%)	60	40	50	30
Spinning temperature, ST (°C)	260	250	240	230
Speed of godet 1, SG1 (m min^{-1})	240	150	200	100
Melt flow index, MFI (g/10 min)	13.8	22.4	19.5	34.2
Hole size of spinneret, HS (mm)	0.35	0.35	0.40	0.40
Spin finish speed, SFS_S (rpm)	0.30	0.40	0.35	0.50

P, of the significance of each effect is determined and compared with α.

SELECTION OF SPINNING CONDITIONS

To investigate the drawing process as a continuous, but independent stage, suitable spinning conditions were first established. A screening experiment involving both spinning and drawing was conducted. The experiment comprised seven spinning factors with four different settings (i.e., combinations of these factors) and eleven drawing factors at two levels, as shown in Tables II and III, respectively.

The selection of the spinning factors and settings was based on the features of the melt extrusion equipment and on experience from previous work.[12,13] The range of factors, including the melt flow index (MFI) of the PP grade, was chosen to be as broad as possible, while still maintaining the smooth operation of the equipment. The use of only two levels of spinneret hole size, HS, 0.35 and 0.40 mm, was limited by the availability of suitable spinnerets. The four settings shown in Table II take on board a number of considerations. The lowest spinning temperature is adopted for the PP grade of highest MFI (Setting 4), to avoid any PP decomposition. In addition, increases in metering pump speed (MPS) are matched by corresponding decreases in the speed of the godet 1 (SG1), to obtain a wide range of draw-down ratios. (Draw-down ratio indicates the ratio by which the filaments have been stretched in transit from the spinneret to SG1, which is located immediately after the cooling chamber).

TABLE III
Drawing Factors and Levels for the Screening Experiment

Drawing factors	Level 1	Level 2
Temperature of roller 1, TR1 (°C)	60	80
Temperature of plate 1, TP1 (°C)	60	80
Temperature of roller 2, TR2 (°C)	125	135
Temperature of plate 2, TP2 (°C)	135	140
Temperature of roller 3, TR3 (°C)	125	135
Temperature of plate 3, TP3 (°C)	135	140
Temperature of roller 4, TR4 (°C)	40	115
Speed of roller 2, SR2 (m min^{-1})	300	400
Speed of roller 3, SR3 (m min^{-1})	390	500
Speed of roller 4, SR4 (m min^{-1})	490	500
Spin finish speed for drawing SFS_d (rpm)	2.5	5.0

The 11 factors associated with the drawing process (Table III) were selected to cover all the drawing factors used during the three stages of drawing that can be achieved on the draw frame. The use of only two levels for each factor kept the overall size of the experiment to a manageable level.

An L16 design matrix[20] was adopted for the screening experiment. The 16 trials were conducted in a continuous spin-draw mode. Details of the trials are provided in Table IV. The trials were conducted over 2 days, each day taking up a block of eight trials. The four settings of the spinning conditions were treated as four levels of a single factor under the heading "Spinning Setting."

The tenacity, specific secant modulus, and elongation to break of the processed PP filaments were characterized as responses of the screening experiment. The results are presented in Figure 2 in the form of effects plots for the main factors selected. The main effects plots reveal the relative magnitude and direction of the effects of the individual process control parameters.[19] It is clearly evident that, under the conditions employed, the effects on the responses of the spinning conditions far outweigh those of the drawing conditions and block factor. In particular, Setting 4 resulted in high fiber tenacity, high modulus, and low elongation at break. Setting 4 was, therefore, chosen for the fixed spinning conditions for the subsequent investigation of the drawing process.

The structural parameters determined for the PP fibers produced with Setting 4 are worthy of comment. To compare crystallographic order among our samples of PP fiber, we have, in accordance with the proposal of Zanetti et al.,[21] determined values of $(W_{[1/2]})^{-1}$, the reciprocal of the half-height width, for the X-ray diffraction peak at $2\theta = 14$–$15°$. The value of $(W_{[1/2]})^{-1}$ for the fibers produced from Setting 4 is 1.0. This value can be compared with values obtained in previous work[12] of up to 1.38 for samples of PP fiber exhibiting a high degree of

TABLE IV
Experimental Array for Selection of Spinning Conditions

Sample no.	Spinning setting[a]	TP1 (°C)	TP2 (°C)	TP3 (°C)	TR1 (°C)	TR2 (°C)	TR3 (°C)	TR4 (°C)	SFS_d (rpm)	SR2 (m min^{-1})	SR3 (m min^{-1})	SR4 (m min^{-1})
1	1	60	135	135	60	125	125	40	2.5	300	390	490
2	1	60	135	135	60	135	135	115	5.0	400	500	500
3	1	80	140	140	80	125	125	40	2.5	400	500	500
4	1	80	140	140	80	135	135	115	5.0	300	390	490
5	2	60	135	140	80	125	125	115	5.0	400	390	490
6	2	60	135	140	80	135	135	40	2.5	300	500	500
7	2	80	140	135	60	125	125	115	5.0	300	500	500
8	2	80	140	135	60	135	135	40	2.5	400	390	490
9	3	60	140	135	80	125	135	40	5.0	300	500	490
10	3	60	140	135	80	135	125	115	2.5	400	390	500
11	3	80	135	140	60	125	135	40	5.0	400	390	500
12	3	80	135	140	60	135	125	115	2.5	300	500	490
13	4	60	140	140	60	125	135	115	2.5	400	500	490
14	4	60	140	140	60	135	125	40	5.0	300	390	500
15	4	80	135	135	80	125	135	115	2.5	300	390	500
16	4	80	135	135	80	135	125	40	5.0	400	500	490

[a] Spinning settings are listed in Table II.

crystallographic order, and 0.30–0.35 for paracrystalline samples. The sample produced from Setting 4 possesses, therefore, a moderate degree of crystallographic order. The degree of overall orientation of the constituent PP chains can be assessed from birefringence values, Δn. The value of Δn for the sample produced from Setting 4 was (1.4×10^{-3}) and is lower than any of the values reported from our previous work.[12,17] These results support earlier evidence that low PP chain orientation is desirable for obtaining high drawability in as-spun fibers,[17] whereas work by Wang et al. has stressed only the importance of paracrystallinity in as-spun PP fibers.[15,16]

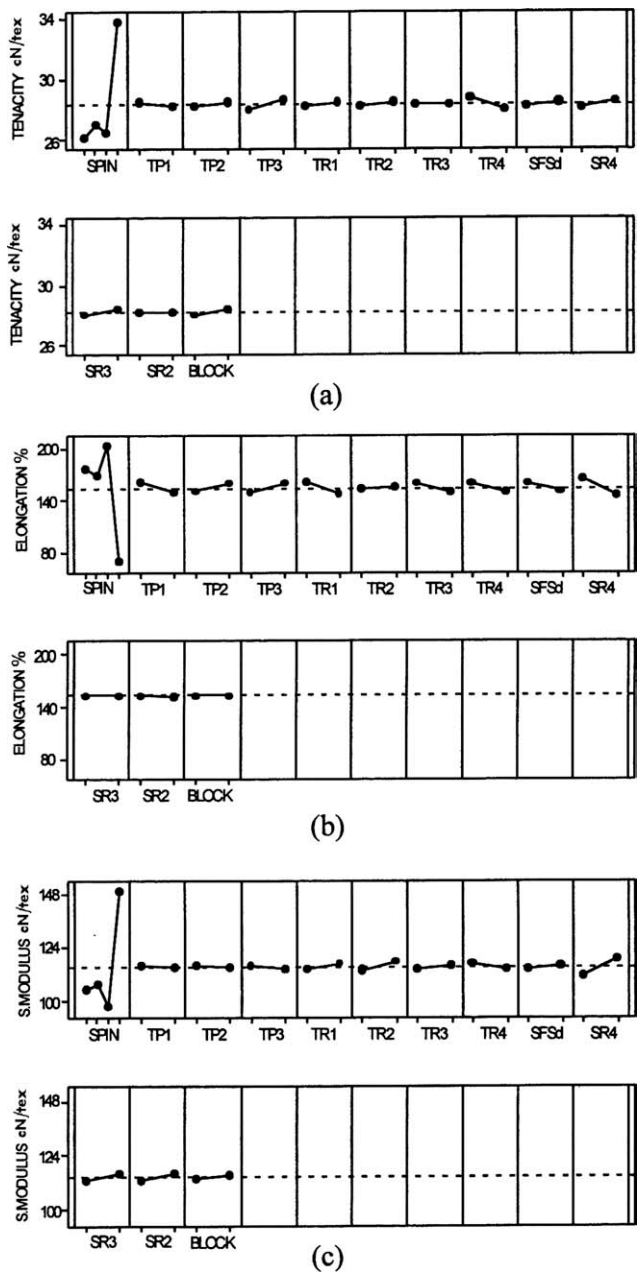

Figure 2 Main effects for (a) tenacity, (b) elongation, and (c) specific secant modulus of the PP fibers produced in the screening experiment.

TABLE V
Factors and Levels for Spinning and Continuous Multi-Stage Drawing

Factors	Level 1	Level 2
Metering pump speed, MPS (rpm)	12	
Quenching air speed, QAS (%)	30	
Spinning temperature, ST (°C)	230	
Speed of godet 1, SG1, (m min^{-1})	100	
Melt flow index, MFI (g/10 min)	34.2	
Spinneret hole size, HS (mm)	0.4	
Speed of spin finish for spinning, SFS_s (rpm)	0.5	
Temperature of roller 1, TR1 (°C)	40	80
Temperature of roller 2, TR2 (°C)	120	140
Temperature of roller 3, TR3 (°C)	125	140
Temperature of plate 1, TP1 (°C)	40	80
Temperature of plate 2, TP2 (°C)	120	140
Temperature of plate 3, TP3 (°C)	120	140
Speed of roller 2, SR2 (m min^{-1})	300	400
Speed of roller 3, SR3 (m min^{-1})	500	600
Speed of roller 4, SR4 (m min^{-1})	550	650

CONTINUOUS SPINNING AND MULTI-STAGE DRAWING

Table V lists the 16 control parameters for experimental trials on the continuous process of PP fiber spinning and subsequent multi-stage drawing. Seven of the control parameters govern the spinning process and were fixed at the levels adopted for Setting 4 in the screening experiment. The remaining nine parameters, associated with the drawing process, were varied between two levels. These variables could be accommodated in the MINITAB software package, whose maximum capacity is nine main factors. The experiment did not include TR4, the temperature of Roller 4, as any effect from TR4 would relate to a thermal treatment after the actual drawing process. Moreover, the spin finish was applied to the drawn filament just before it reached Roller 4, and hence SFS_d was also excluded.

The setting of the two levels for the drawing parameters was based on our previous preliminary work on PP fiber drawing.[11,17] It will be noted that the lower level speed of SR4, the speed of Roller 4, is less than that of the higher level speed, SR3, of the immediately preceding roller. Filament relaxation could thus also be examined.

An L32 fractional factorial design was adopted,[20] as shown in Table VI. The 32 trials were conducted in blocks of eight trials each over four consecutive days. The processed fibers were characterized in terms of their structure, and mechanical and thermal properties, as listed in Table VII.

TABLE VI
Experimental Array for Spinning and Continuous Multi-Stage Drawing

Sample no.	TR1 (°C)	TR2 (°C)	TR3 (°C)	TP1 (°C)	TP2 (°C)	TP3 (°C)	SR2 (rpm)	SR3 (rpm)	SR4 (rpm)
1	40	120	125	40	120	120	300	500	550
2	40	120	125	40	120	120	300	500	650
3	40	120	125	40	140	140	400	600	550
4	40	120	125	40	140	140	400	600	650
5	40	120	140	80	120	120	400	600	550
6	40	120	140	80	120	120	400	600	650
7	40	120	140	80	140	140	300	500	550
8	40	120	140	80	140	140	300	500	650
9	40	140	125	80	120	140	300	600	550
10	40	140	125	80	120	140	300	600	650
11	40	140	125	80	140	120	400	500	550
12	40	140	125	80	140	120	400	500	650
13	40	140	140	40	120	140	400	500	550
14	40	140	140	40	120	140	400	500	650
15	40	140	140	40	140	120	300	600	550
16	40	140	140	40	140	120	300	600	650
17	80	120	125	80	120	140	400	500	650
18	80	120	125	80	120	140	400	500	550
19	80	120	125	80	140	120	300	600	650
20	80	120	125	80	140	120	300	600	550
21	80	120	140	40	120	140	300	600	650
22	80	120	140	40	120	140	300	600	550
23	80	120	140	40	140	120	400	500	650
24	80	120	140	40	140	120	400	500	550
25	80	140	125	40	120	120	400	600	650
26	80	140	125	40	120	120	400	600	550
27	80	140	125	40	140	140	300	500	650
28	80	140	125	40	140	140	300	500	550
29	80	140	140	80	120	120	300	500	650
30	80	140	140	80	120	120	300	500	550
31	80	140	140	80	140	140	400	600	650
32	80	140	140	80	140	140	400	600	550

TABLE VII
Response Data for the Spinning and Continuous Multi-Stage Drawing Experiments

Sample no.	$(W_{1/2})^{-1}$ $(^0)^{-1}$	Δn ($\times 10^3$)	Tenacity (cN tex^{-1})	Elongation (%)	Modulus (cN tex^{-1})	Shrinkage (%)
1	0.92	31.6 (0.4)	40.5 (4.1)	92 (15.4)	200 (6.9)	19.1 (0.6)
2	0.90	32.2 (0.2)	48.3 (0.9)	55 (4.3)	238 (3.4)	18.4 (0.3)
3	0.80	31.4 (0.2)	47.8 (2.3)	79 (4.5)	212 (6.9)	16.6 (0.8)
4	0.82	33.0 (0.6)	50.0 (1.2)	57 (13.4)	242 (7.4)	19.4 (0.3)
5	0.85	31.5 (0.0)	45.7(l.1)	77 (9.2)	187 (0.0)	15.2 (0.9)
6	0.82	33.1 (0.3)	50.4 (2.4)	63 (8.1)	243 (6.4)	19.1 (0.1)
7	0.90	31.8 (0.7)	40.4 (l.5)	68 (7.1)	205 (0.0)	16.0 (0.3)
8	0.93	32.6 (0.6)	47.8 (1.8)	63 (6.4)	234 (7.8)	17.9 (0.2)
9	0.99	31.3 (0.7)	43.0 (0.4)	70 (7.8)	209 (6.9)	14.2 (0.8)
10	0.96	31.8 (0.4)	46.6 (1.9)	59 (5.6)	217 (6.0)	16.3 (0.2)
11	0.85	31.5 (0.4)	41.6 (0.7)	86 (4.7)	199 (6.9)	15.6 (0.3)
12	0.85	31.9 (0.3)	47.2 (1.7)	63 (4.1)	199 (9.8)	18.1 (0.7)
13	0.90	31.5 (0.7)	40.4 (l.0)	81 (10.3)	181 (5.6)	15.0 (0.1)
14	0.87	32.1 (0.5)	48.2 (2.4)	66 (4.0)	228 (7.8)	16.3 (0.6)
15	1.10	31.4 (0.7)	44.5 (2.0)	49 (2.0)	180 (6.0)	11.1 (0.3)
16	0.98	32.0 (0.5)	47.7 (l.7)	54 (6.3)	228 (6.0)	11.5 (0.7)
17	0.87	32.2 (0.6)	48.2 (0.6)	59 (2.2)	232 (7.8)	19.1 (0.8)
18	0.90	31.9 (0.2)	41.1 (0.7)	83 (9.5)	205 (5.6)	16.6 (0.6)
19	0.97	32.6 (0.3)	46.7 (0.7)	66 (3.5)	221 (7.4)	16.7 (0.3)
20	1.00	31.6 (0.4)	44.8 (l.1)	60 (4.4)	188 (6.0)	14.7 (0.1)
21	0.97	32.8 (0.3)	50.4 (1.5)	41 (5.0)	218 (7.8)	17.7 (0.4)
22	0.97	31.7 (0.5)	45.2 (1.3)	80 (4.8)	181 (6.9)	13.4 (0.8)
23	0.88	32.5 (0.8)	50.2 (0.8)	49 (4.7)	225 (6.0)	12.5 (0.2)
24	0.92	31.9 (0.7)	43.0 (0.4)	71 (4.4)	199 (6.9)	12.5 (0.5)
25	0.95	33.4 (0.5)	52.6 (2.2)	40 (2.8)	228 (6.0)	10.3 (0.1)
26	0.98	32.0 (0.3)	46.9 (1.3)	64 (5.8)	210 (6.9)	9.3 (0.3)
27	0.96	33.1 (0.4)	53.1 (2.6)	40 (1.4)	234 (6.4)	9.3 (0.1)
28	0.99	32.2 (0.6)	45.1 (1.2)	70 (6.5)	231 (6.9)	8.5 (0.4)
29	1.00	33.0 (0.2)	53.3 (1.3)	43 (3.1)	226 (6.0)	8.6 (0.3)
30	1.00	32.3 (0.3)	45.0 (1.2)	64 (6.2)	208 (7.4)	8.4 (0.3)
31	0.96	33.9 (0.8)	53.3 (1.2)	42 (2.7)	259 (6.0)	9.4 (0.1)
32	0.95	32.1 (0.4)	53.0 (0.5)	47 (1.0)	232 (7.4)	8.0(0.0)

The values in brackets are the standard deviations of three measurements for Δn and five measurements for the other responses.

Structure of the drawn filaments

The results of structural characterization of the drawn fibers using birefringence and WAXS measurements are displayed as effects plots in Figure 3. It can be noted that all the main factors presenting statistically significant effects are associated with the rollers in the draw frame and not the hot plates.

The effect plot in Figure 3(a), for crystallographic order, indicates that as many as five main process control parameters significantly influence crystallographic order: TR1, TR2, SR2, SR3, and SR4. The two-factor interactions assigned to Column 12 also appear significant. ANOVA confirmed that the effects from all these factors are statistically significant at the normal level of risk, $\alpha = 0.05$, and that none of the other main factors is significant (Table VIII). The significant main factors reveal that crystallographic order is influenced predominantly by the temperature and extent of drawing during the first two stages. The significance of SR4 may be more marginal ($P = 0.039$). It is noteworthy that the temperatures of the hot plates have no significant effect, and indeed they exert no significant effect on any of the other fiber properties we examined.

The positive effects of initial drawing temperatures (TR1 and TR2) suggest that increases in temperature raise the mobility of the PP chains, so that they can move sufficiently close to one another to arrange themselves into crystal lattices. The negative effect of SR2 on crystallographic order is considered to arise from the time spent by the PP filaments in contact with Roller 2, as SR2 increases. An increase in SR2 significantly reduces the time of heat transfer to the PP filament from Roller 2. On the other hand, SR3 has a positive effect on crystallographic order, which we attribute to crystallization induced by increased orientation of the PP chains. The effect is probably most significant at this stage of the drawing process, when the filaments are well heated. The negative effect observed for SR4 is considered to arise from the effect of relaxation. The low level speed selected for SR4 is smaller than the high level speed selected for SR3, which immediately precedes it. Where SR3 > SR4, therefore, the filament would experience relaxation. After the two-stage drawing

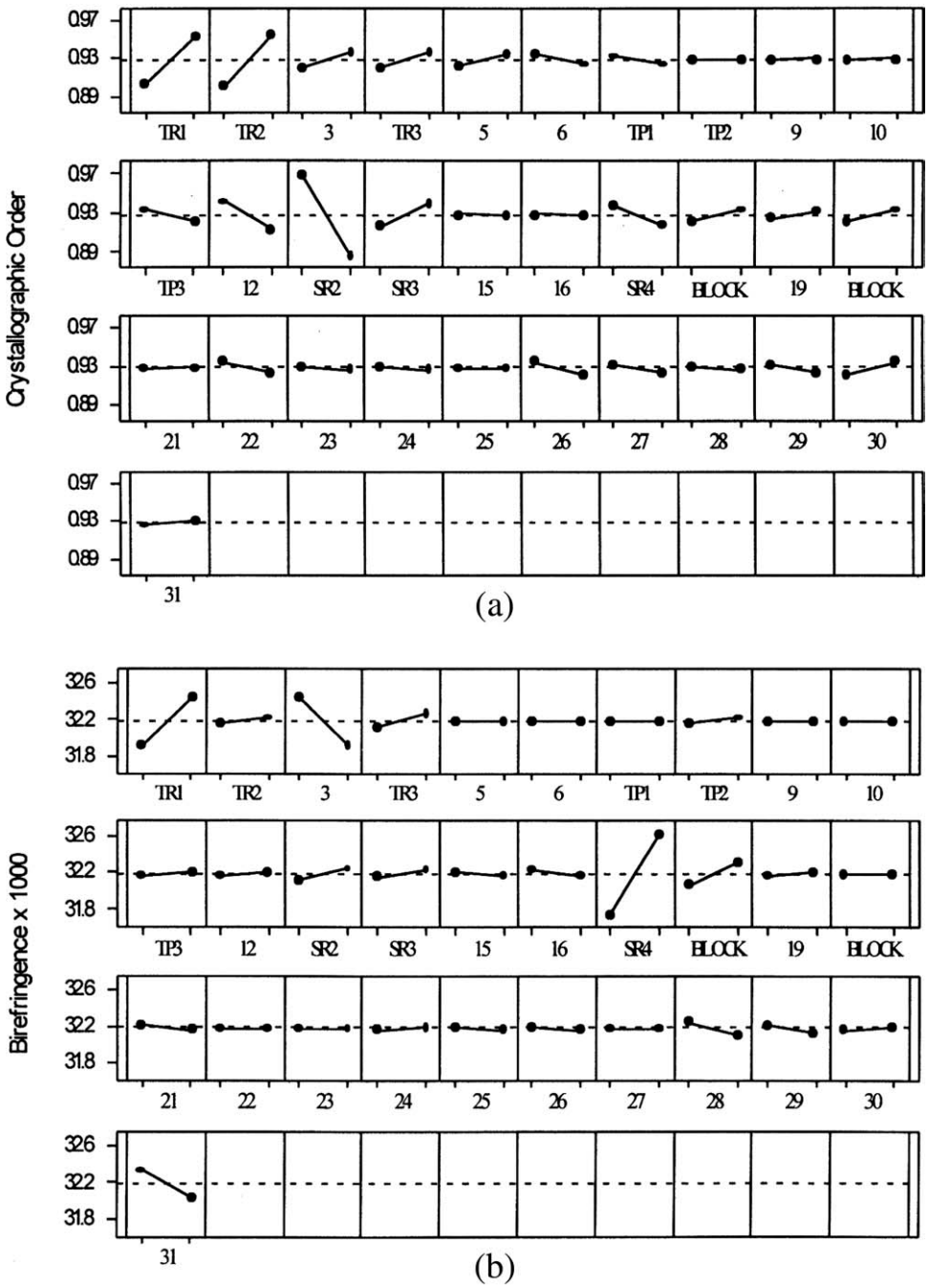

Figure 3 Effects plots for (a) crystallographic order and (b) birefringence of the drawn PP filaments.

process, a certain degree of relaxation at the elevated temperature acquired by the filament is equivalent to heat treatment (annealing) of the drawn fibers, which reduces any defects (e.g., microvoids) arising from drawing, and increases crystallographic order.[22,23]

Column 12 of the effects plot, Figure 3(a), suggests a significant interaction effect, which is confirmed by ANOVA (Table VIII). However, due to the fractional factorial nature of the experimental design, the column contains four two-factor interactions: TR3*TP2, TP1*TP3, SR2*TR1, and SR3*TR2. Unambiguous identification of the significant interaction (or interactions) present in Column 12 cannot, therefore, be carried out, without further experimental trials. Nevertheless, since the temperatures of the hot plates, as main factors, have no significant effects on structural properties, it is unlikely that they will be represented in a significant interaction. On this basis we can, therefore, rule out interactions, TR3*TP2 and TP1*TP3. All four main factors represented in the remaining two interactions, SR2*TR1 and SR3*TR2, are individually significant themselves, so we cannot suggest with any confidence which of these

TABLE VIII
Summary of the ANOVA Results for the Continuously Processed Filaments[a]

$(W_{[1/2]})^{-1}$	Factor	TR1	TR2	SR2	SR3	SR4	C12
	±	+	+	−	+	−	−
	P	0.000	0.000	0.000	0.009	0.039	0.005
Δn	Factor	TR1	SR4	C3	C18	C31	
	±	+	+	−	+	−	
	P	0.000	0.000	0.000	0.000	0.000	
Tenacity	Factor	TR1	SR3	SR4	C3	C31	
	±	+	+	+	−	+	
	P	0.000	0.000	0.000	0.000	0.001	
Elongation	Factor	TR1	TR2	SR3	SR4		
	±	−	−	−	−		
	P	0.003	0.020	0.047	0.000		
Modulus	Factor	SR4	C3				
	±	+	−				
	P	0.000	0.000				
Shrinkage	Factor	TR1	TR2	TR3	SR4	C3	
	±	−	−	−	+	+	
	P	0.000	0.000	0.002	0.004	0.003	

[a] For each response factor listed in the first column, the rows list those process parameters statistically significant at a risk level $\alpha = 0.05$, the direction of the effect (either positive or negative) and the *P*-value of the effect. The letter C refers to the column in the corresponding effects plot in Figure 4.

interactions is significant, or whether indeed both are significant. It is noteworthy, however, that both interactions link the speed of a particular roller with the temperature of the preceding roller.

The effects plot for the degree of PP chain orientation [Fig. 3(b)] and the corresponding ANOVA (Table VIII) show that the only significant process control factors are SR4 and TR1. It should be noted that an increase in SR4 favors enhanced PP chain orientation but, by contrast, apparently reduced crystallographic order. It is noteworthy too, though, that a significant negative interaction effect appears in Column 31 of the effects plot. This column is represented by the interaction, SR3*SR4. It is difficult to reconcile the negative effect associated with this interaction with the positive effect of SR4 on its own. However, the explanation may lie in the levels of the settings chosen for SR3 and SR4. Since the high level of SR3 is above the low level of SR4, relaxation (rather than further drawing) of the filaments was possible between Rollers 3 and 4 in some trials.

The significant effect of TR1 on overall PP chain orientation may be explained tentatively as follows. A relatively high temperature at the start of the fiber drawing process provides sufficient thermal energy to promote alignment of the polymer chains in the subsequent drawing stages.

The unexpected significance of the block effect revealed in Column 18 is puzzling. Of all the properties we investigated, the block effect appears to be significant only for chain orientation. A true block effect originating in the fiber processing is likely to be observed in all (or nearly all) these properties. We, therefore, suggest that the effect may arise from random error involved in the birefringence measurements.

Column 3 of the effects plot also reveals a significant interaction effect. This column contains four two-factor interactions: TR1*TR2, TP1*TR3, TP2*TP3, and SR2*SR3. As stated above, the temperatures of the hot plates are unlikely to be represented in significant interactions. However, on the basis that a significant main factor is likely to be represented in a significant interaction, we also tentatively suggest that the significant interaction confounded in Column 3 is TR1*TR2, and not SR2*SR3. If this interaction is significant, it would indicate that a large difference in temperature between the first and second rollers in the draw frame confers increased mobility too quickly to the PP chains, and their alignment starts to be impaired.

Mechanical properties

Figure 4 displays the effects of the processing factors on some key mechanical properties: fiber tenacity [Fig. 4(a)], elongation to break [Fig. 4(b)], and specific secant modulus [Fig. 4(c)]. No block effect is observed in any of the four responses. The corresponding ANOVA results are listed in Table VIII, alongside the structural responses. As with the structure of the filaments, all the main factors presenting statistically significant effects are associated with the rollers in the draw frame and not the hot plates. This feature demonstrates clearly that structural changes in the filaments during drawing have occurred on the rollers rather than the plates. These

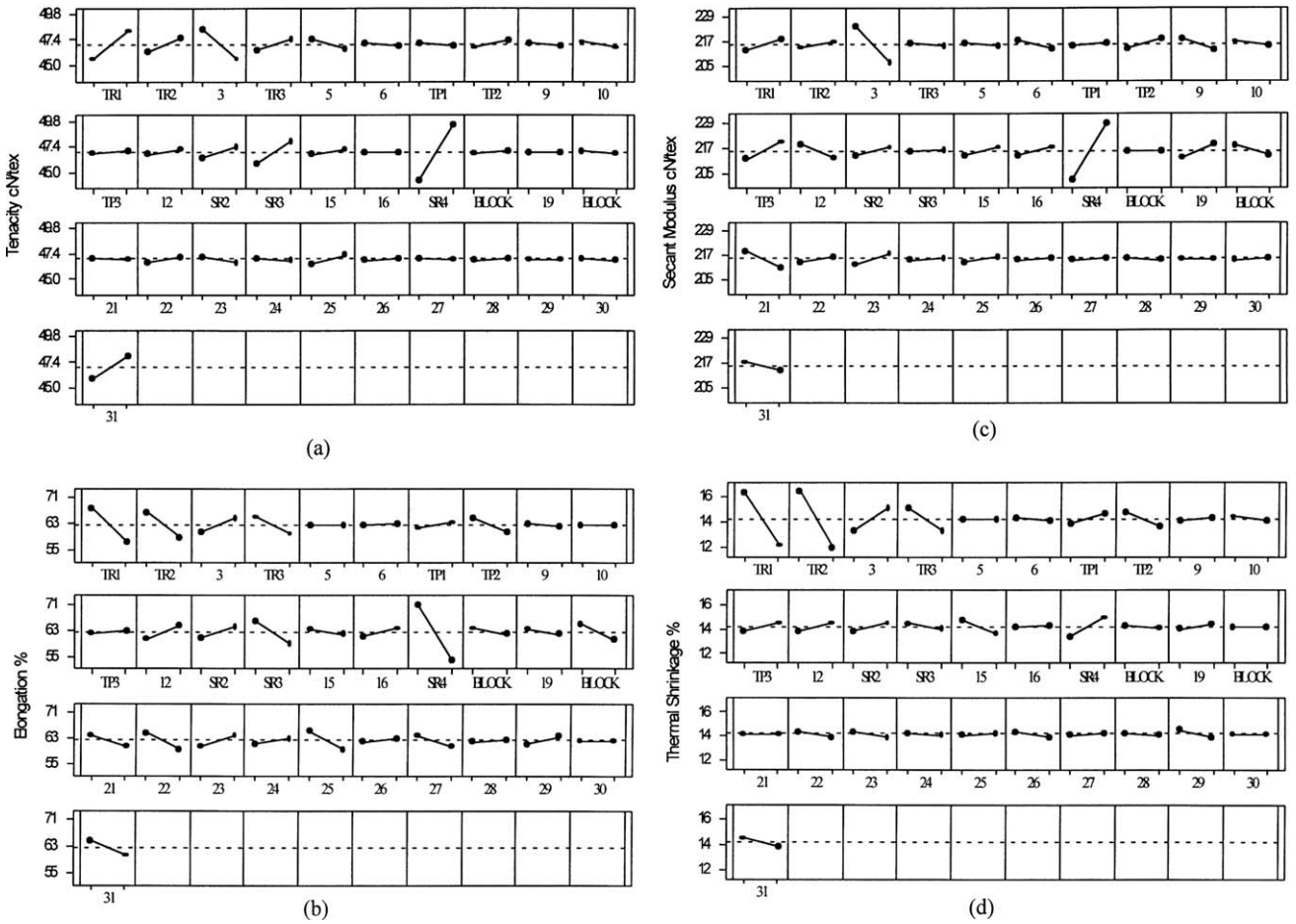

Figure 4 Effects plots for the mechanical and thermal properties of the continuously processed PP filaments: (a) tenacity, (b) elongation, (c) specific secant modulus, and (d) thermal shrinkage.

changes are normally quite rapid at elevated temperatures during drawing.[15] In addition, the rollers are all located before the plates, and contact between the filaments and the rollers is considerably longer than that between the filaments and plates (0.72–3.12 s with the rollers, and 0.05–0.30 s with the plates). Therefore, by the time the filaments are transported outside the region of the rollers, structural transformation has already been completed, and so is not further affected by the temperature of the plates.

Most of the parameters which exert a significant influence on fiber tenacity also exert a significant influence on overall PP chain orientation (Table VIII). These parameters are TR1 and SR4, as well as the interactions in Columns 3 and 31. The directions of the influences are also the same, with the exception of Column 31, identified as SR3*SR4. Additionally, SR3 is a further processing factor with a significant effect on fiber tenacity, but it is not significant for chain orientation. By contrast, half of the factors significantly influencing crystallographic order do not significantly affect fiber tenacity. This result emphasizes the importance of chain orientation in governing fiber tenacity. It can be noted too that this result agrees with those which have been obtained for as-spun fibers.[13,24]

Nevertheless, it is also observed that SR3 appears to influence fiber tenacity but not chain orientation. The interaction in Column 31, identified as SR3*SR4, influences tenacity in a positive direction, just like its constituent main parameters. It is apparent, then, that SR3 is important in influencing the ultimate fiber tenacity, while not influencing PP chain orientation. As yet, we have no clear explanation to account for this observation.

Elongation is influenced in a negative direction by the main factors, SR3, SR4, and TR1, a result consistent with the positive effect of these factors on fiber tenacity. It is also influenced in a negative direction by TR2. The influence of TR2 may be a consequence of its effect on the mobility of the PP chains, to move closely enough to one another, to form crystal lattices, as described above. Specific secant modulus, by contrast, is apparently influenced only by SR4 and the interaction in Column 3. It appears, then, that the conditions for the final stage of drawing are crucial in determining the specific secant modulus of the drawn fiber. It is noteworthy that the direction

of each of these influences matches the direction of influence on PP chain orientation.

Thermal shrinkage of the drawn fiber is negatively influenced by the temperatures of the rollers in the draw frame: increased temperatures result in reduced thermal shrinkage. As with all the other structural and mechanical properties examined, SR4 also plays a key role, in this case in a positive direction. The interaction in Column 3 also influences shrinkage in a positive direction. These results can be explained in terms of concepts underlying the thermal setting and molecular tension of the filaments achieved during drawing. Thermal setting, formation of a stable structure at an elevated temperature, can be achieved through crystallization, which is favored by increased temperature of the rollers, especially the initial ones, as discussed above. Low shrinkage is, therefore, related to a high degree of crystallographic order. Increased molecular tension is produced in highly drawn filaments, where there is a high degree of chain orientation, as reflected in the positive effect of SR4. Release of this tension through structural relaxation at 130°C gives rise to a higher value of thermal shrinkage from a high degree of orientation.

The influence of the interaction in Column 3, which we have tentatively assigned as TR1*TR2, may perhaps be explained on the basis that too large a difference in temperature between Rollers 1 and 2 confers increased mobility too quickly to the PP chains. There is a consequent impairment to their alignment, and hence to crystallization, with the result that shrinkage is enhanced.

CONCLUSIONS

Following our previous work on the melt spinning of PP fibers, fractional factorial design has been extended to the drawing of these fibers. Using comprehensive statistical analysis, the drawn fibers have been characterized with respect to structural characteristics, mechanical properties, and the extent of shrinkage at 130°C. The relationships between these properties and key processing parameters have been rationalized in terms of microscopic structure, as determined by crystallographic order and the overall orientation of the PP chains.

For all the properties analyzed, it was evident that the temperatures of the hot plates in the draw frame exerted no significant influence. It has also been shown that, under the conditions used in our work, most of the process parameters influencing the tenacity of the drawn fibers also exert a significant influence on the overall chain orientation. By contrast, only half the factors influencing crystallographic order have an effect on tenacity. It should perhaps be noted that, whereas overall orientation takes into account all the PP chains in each filament, crystallographic order includes only those in crystalline phases. These results serve to highlight the importance of those chains, or chain segments, present in noncrystalline regions in playing a key role in influencing fiber tenacity.

Specific secant modulus is markedly influenced by the speed of the final roller in the draw frame. In contrast to fiber tenacity, the temperatures of the individual rollers do not apparently exert any significant influence on the modulus. Indeed, the only other significant factor appears to be the difference between Rollers 1 and 2, though further experiments would be needed before this suggestion can be confirmed.

All three main factors exerting a positive influence on tenacity exert a negative influence on elongation to break. This result is perhaps not surprising, when it is recalled that fibers of higher tenacity generally possess lower elongation to break.

The extent of thermal shrinkage at 130°C is significantly influenced by the temperatures of the rollers in the draw frame. Higher temperatures are likely to favor the formation of more stable structures through enhanced crystallization. The significant influence of the speed of the final roller can be explained in terms of increased molecular tension.

The benefits to PP fiber processing technology of factorial experimental design and statistical analysis have been demonstrated in this article. The advantages of this approach include economy in the range of experimental trials needed and the ability to take into consideration any interactions between processing parameters as well as the processing parameters themselves. For nearly all the fiber characteristics discussed in this article, at least one interaction has been shown to be significant. Our approach can, therefore, be usefully applied both to the sound design of experimental trials to achieve a set of desired fiber properties and to the provision of further insights into processing–structure–property relationships in drawn PP fibers.

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