The Influence of Fiber Processing Parameters on the Structural Properties of As-spun Polypropylene Fibers: a Factorial Design Approach

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ABSTRACT: The structures of polypropylene fibers, spun according to a factorial experimental design, have been studied with the aid of wide angle X-ray diffraction and birefringence measurements. From statistical analysis of the results, the fibers have been characterized in terms of their crystallographic order and the overall orientation of their constituent polymer chains. These properties have been quantitatively assessed as responses to seven specially selected process control parameters in the extrusion equipment used to process the fibers. For both crystallographic order and overall orientation, the metering pump speed (MPS) at which the fibers are extruded and the speed (WS) at which the extruded fibers are wound exert significant effects. Moreover, the interaction, WS × MPS, between these two control parameters also significantly influences orientation. For crystallographic order, two further significant parameters are the melt flow index (MFI) of the grade of polypropylene used and the temperature (ST) at which the polymer melt passes through the spinneret. The roles of these two factors in the development of crystallites within the fibers are discussed. No interaction effects, however, appear to be significant for crystallographic order. Models that specify the direction of change of the significant parameters for increasing or reducing both responses are given.
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Key words: statistical approach; processing; structural properties; polypropylene; fibers

INTRODUCTION

The production and application of polypropylene (PP) fiber are increasing rapidly,[1] and this increase appears set to be maintained for a number of years to come. PP fibers have now been developed for numerous applications, which include carpet backings, carpet face yarns, geotextiles, bulk bags, and sports surfaces.[2] PP fibers are also being developed for an extensive range of biomedical and hygiene applications, many of which require nonwoven PP fiber products.[2,3] There is, therefore, a commercial need to be able to tailor the properties of PP fiber for particular applications.

Many of these applications require the enhancement of PP fiber mechanical performance. For example, our group has sought to achieve the enhancement of fiber tenacity and initial modulus through the incorporation of a small proportion of liquid crystalline polymer.[4] The work has also demonstrated that, by altering fiber processing conditions, significant improvements in the mechanical properties of pure PP fiber itself can be obtained.[5] However, although PP fiber was melt-extruded on a pilot-plant scale, subsequent drawing (stretching) of the fiber was performed on a bench-top draw-frame at only low speeds, typically 40 m min^{-1} or less.[4,5]

It is evident from our own work and that of others[6,7] that there is a need for better control and understanding of PP fiber processing, to obtain a desired range of mechanical properties. This need is especially strong, for example, in the use of PP fiber products for biomedical applications, as in materials for implants and sutures. It would be highly desirable, therefore, to confirm which of the many individual control parameters exert a significant influence on PP fiber processing and, furthermore, to establish which interaction effects, if any, between two or more control parameters also play significant roles. To obtain this information reliably and with economy in the number of experimental trials, a statistical approach that integrates factorial experimental design and comprehensive statistical analysis is required.[8,9] The utility of this approach has already been illustrated,[10] as has the application of neural networks to our research.[11]

The control parameters involved in fiber melt-spinning have been extensively discussed by Ziabicki.[12] He divided the melt-spinning variables into three groups: primary (independent) variables, which govern the course of the melt-spinning process and the resulting fiber structure and properties, secondary

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variables governing spinning conditions, and resulting (dependent) variables, which include structure and mechanical properties. In our work, however, a simpler approach has been adopted, to render the experimental trials more manageable.

In a previous paper, we demonstrated the usefulness of a fractional factorial design approach[13] to establish the significant control parameters regulating crystallographic order in "as-spun" PP fibers: i.e., fibers which had been melt-extruded, but not subsequently drawn. An L16 array was used, which involved 16 trials with seven process control parameters: melt flow index (MFI), spinneret hole size (HS), metering pump speed (MPS), spinning temperature (ST), quenching air speed (QAS), application speed of spin finish (SFS_s), and winding speed (WS). Following the proposal of Zanetti et al.,[14] the degree of crystallographic order was represented by $(W_{1/2})^{-1}$, the reciprocal of the half-height width at $2\theta = 14$–15^o in the X-ray diffraction patterns, obtained from wide-angle X-ray scattering (WAXS).[13]

We have also used fractional factorial designs to ascertain the significant control parameters influencing the orientation of the polymer chains comprising the PP fibers, as assessed from birefringence measurements.[10] It was apparent that, of the individual control parameters, only MPS and WS exercised any significant effects. However, we also demonstrated that birefringence values were influenced too by MPS × WS, i.e., the interaction between the two main control parameters. There is, therefore, a considerable synergistic relationship between them. The identification of this synergy provides a good example of the merits of a systematic statistical approach, in contrast to the "one-factor-at-a-time" approach often employed.[13,15]

In this paper, we report further work on the application of the factorial design approach to the investigation of the factors controlling crystallographic order in as-spun fibers. Using these results and those obtained on the orientation of the fibers' constituent polymer chains,[10] we seek to demonstrate how the factorial design approach can both optimize the processing of as-spun PP fibers with regard to particular structural features and also throw further light on fiber structural changes during fiber processing.

EXPERIMENTAL

Raw PP granules were spun on a pilot-plant scale Labspin extruder supplied by Extrusion Systems Limited. The equipment has been described elsewhere.[5,13] There are three heating zones in the barrel of the extruder, one in the metering pump and two in the die head, which contained a filter package and a spinneret of 55 circular holes. Alterations to spinning temperature were effected by adjusting the heaters in the metering pump and die head. The extruded filament was cooled in a flow of ambient air in a quenching chamber. An aqueous based spin finish, VICKERS 1031, kindly provided by Benjamin Vickers and Sons Limited, was applied following the cooling of the filament. The spin finish was diluted five times with water before application.

Two grades of PP granule were used: PPH9069, supplied by Petrofina, and VC18, supplied by Borealis. The MFI values were determined as 22.4 ± 0.2 g/10 min and 17.7 ± 0.2 g/10 min, respectively. Each value was determined from 33 measurements, using the method described in ASTM D1238, under conditions of 2.16 kg/230°C.

An L16 design matrix,[9] comprising the seven process control parameters[13] and two levels for each parameter, was used for the fractional factorial experimental design. To extend design space, the two levels were separated as far apart as possible from one another, but still such that the as-spun fiber could be reliably produced. Details of the experimental design have been given elsewhere.[13] The 16 trials, whose details are listed in Table I, were conducted in a random order. The trials were conducted over 2 consecutive days, each day taking up a block of 8 trials. Duplicates of the complete set of initial trials were also conducted in a random order. In addition, a set of confirmatory trials (listed in Table II) was carried out, to test the correctness of the model and to evaluate the significance of interactions between pairs of control parameters. In the confirmatory trials, QAS and SFS_s, were omitted, as discussed below.

Optical birefringence data were obtained by means of a Pluta polarizing microscope with a compensation system (a Wollaston prism set at a subtractive position). Birefringence values, Δn, were obtained directly using the equation:

$$\Delta n = (\Delta z \lambda)/(ZD)$$

where Δz refers to the displacement of the fringe caused by the anisotropy of the filament sample, Z is the spacing between adjacent fringes, D is the diameter of the filament, and λ is the wavelength of the incident light (546.1 nm).[16] Triplicate measurements were made on each PP sample.

The determination of the wide angle X-ray diffraction data has been described elsewhere.[13]

The principal methods of statistical analysis employed were main effects plots and analysis of variance (ANOVA). The ANOVA was conducted using MINITAB software. The main effects plots reveal the relative magnitude and direction of the effects of individual process control parameters.[8] The ANOVA provides a quantitative index, the F-value, for judging the significance of factor effects, within a particular level of risk, α. In line with common practice, the level of risk $\alpha = 0.05$ has been used in our work. From the

TABLE I
Experimental Array for the Spinning of PP Filaments[a]

Standard order	HS (mm)	MFI (g/10 min)	ST (°C)	MPS (rpm)	QAS (%)	SFS_S (rpm)	WS (m min^{-1})	$(W_{1/2})^{-1}$ $(°)^{-1}$ Original series	$(W_{1/2})^{-1}$ $(°)^{-1}$ Duplicate series	Δn (×1000) Original series	Δn (×1000) Duplicate series
1	0.35	17.7	230	3	30	0.35	100	0.31	0.32	8.6	7.9
2	0.35	17.7	230	12	30	0.50	400	0.30	0.33	8.5	13.9
3	0.35	17.7	260	3	50	0.35	400	0.31	0.33	25.4	21.9
4	0.35	17.7	260	12	50	0.50	100	0.33	0.31	3.9	2.2
5	0.35	22.4	230	3	50	0.50	100	1.03	1.08	9.2	11.0
6	0.35	22.4	230	12	50	0.35	400	1.25	1.04	10.9	14.5
7	0.35	22.4	260	3	30	0.50	400	1.10	1.17	22.3	16.1
8	0.35	22.4	260	12	30	0.35	100	0.48	0.44	4.4	4.2
9	0.40	17.7	230	3	50	0.50	400	0.98	1.18	19.5	21.5
10	0.40	17.7	230	12	50	0.35	100	0.32	0.33	3.9	2.5
11	0.40	17.7	260	3	30	0.50	100	0.32	0.31	8.0	6.9
12	0.40	17.7	260	12	30	0.35	400	0.30	0.32	8.3	8.0
13	0.40	22.4	230	3	30	0.35	400	1.38	1.26	18.1	19.0
14	0.40	22.4	230	12	30	0.50	100	1.05	1.08	3.9	6.2
15	0.40	22.4	260	3	50	0.35	100	0.54	0.53	8.7	8.9
16	0.40	22.4	260	12	50	0.50	400	1.00	0.97	10.8	13.5

[a] HS, hole size of the spinneret; MFI, melt flow index; ST, spinning temperature; MPS, speed of the metering pump; QAS, quenching air speed; SFS, application speed of spin finish; WS, winding speed; $(W_{1/2})^{-1}$, crystallographic order; Δn, birefringence.

F-value, the probability, *P*, of the significance of each effect is determined and compared with α.

RESULTS

In a previous paper,[13] we argued that control of the structure of as-spun PP fibers will be more effective if quantitative relationships can be provided between fiber structure and spinning conditions. One important aspect of fiber structure is crystallographic order. An increase in the degree of crystallographic order is, however, manifest by a variety of features in an X-ray diffraction pattern: an increase in the intensity of the peaks, a decrease in peak width, and a decrease in the background area below the peaks. In accordance with the proposal by Zanetti et al.,[14] we have determined values of $(W_{1/2})^{-1}$, the reciprocal of the half-height width, for the peaks at $2\theta = 14–15°$. These values are reported in Tables I and II. For the crystalline samples, this peak corresponds to diffraction by the (110) plane. However, the nature of the other prominent peaks in the X-ray diffraction patterns has been taken into ac-

TABLE II
Experimental Array for the Third Series[a]

Standard order	HS (mm)	MFI (g/10 min)	ST (°C)	MPS (rpm)	WS (m min^{-1})	$(W_{1/2})^{-1}$ $(°)^{-1}$	Δn (×1000)
1	0.35	17.7	230	3	400	1.14	27.2
2	0.35	17.7	230	12	100	0.35	3.4
3	0.35	17.7	260	3	100	0.35	12.2
4	0.35	17.7	260	12	400	0.36	10.3
5	0.35	22.4	230	3	100	1.02	10.4
6	0.35	22.4	230	12	400	1.33	9.8
7	0.35	22.4	260	3	400	1.24	32.5
8	0.35	22.4	260	12	100	0.36	3.3
9	0.40	17.7	230	3	100	0.34	7.7
10	0.40	17.7	230	12	400	0.34	10.2
11	0.40	17.7	260	3	400	0.49	32.2
12	0.40	17.7	260	12	100	0.36	2.7
13	0.40	22.4	230	3	400	1.49	31.7
14	0.40	22.4	230	12	100	0.90	3.8
15	0.40	22.4	260	3	100	0.50	10.3
16	0.40	22.4	260	12	400	1.01	11.6

[a] See the notes for Table I.

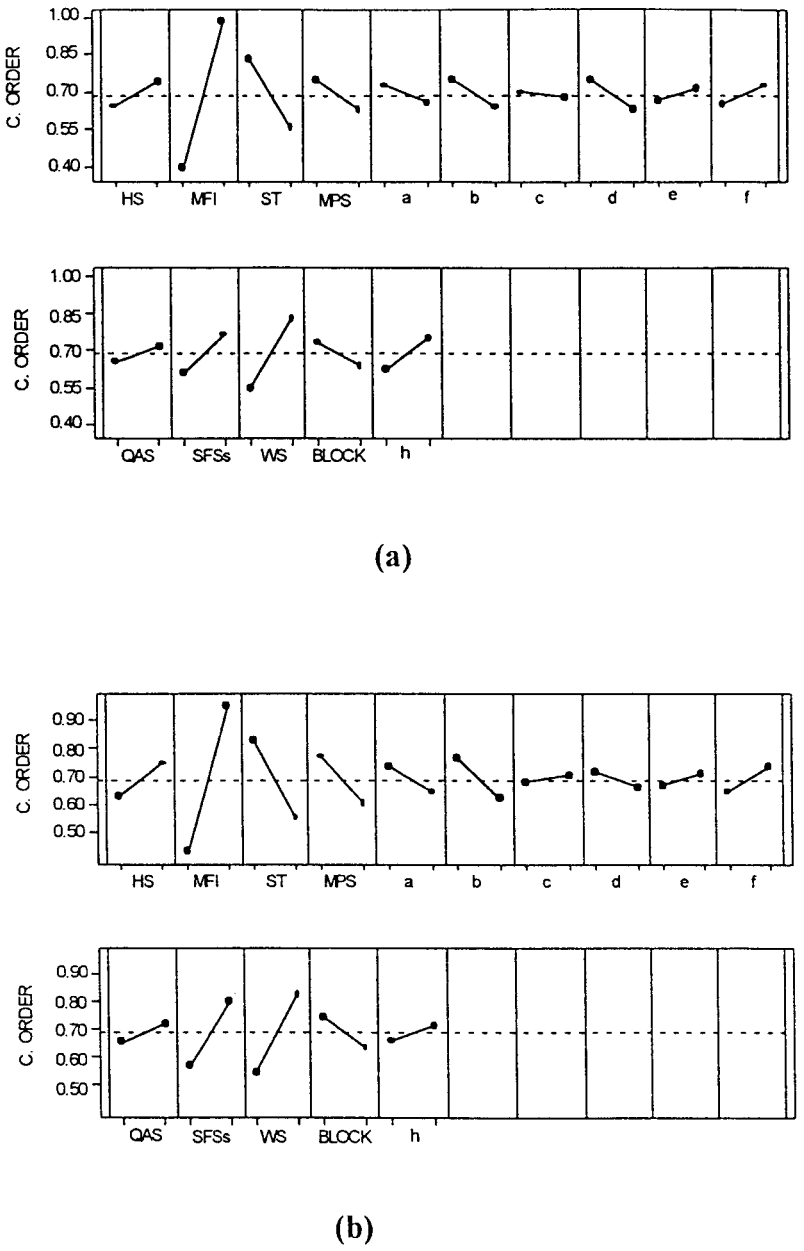

Figure 1 Effects plots for the response, degree of crystallographic order $(W_{1/2})^{-1}$. The uppercase letters along the x axis represent the main factors and block factors, and the single letters in lowercase represent the interactions. Plots (a) and (b) are for the original and duplicate series, respectively.

count, and the relative intensities of these peaks are discussed later.

Original and duplicate experimental trials

Figure 1 shows the results of statistical analysis of the effects caused by individual control parameters (main effects) and the interactions between them on the crystallographic order of the as-spun PP fibers, as determined by $(W_{1/2})^{-1}$. Seven of the columns are taken up by the main effects. The column labeled BLOCK takes into account any variation arising from the duration of the trials over 2 consecutive days. The remaining seven columns, labeled a–h, are taken up by interactions, but due to the fractional nature of the factorial design, several interactions are confounded in each of these columns. Thus, any significant interaction observed in columns a–h cannot be definitely assigned. From the effects plots, it can be noted that the original and duplicate sets of data generally agree quite closely with each other (note that the scales of the ordinates are slightly different). However, the effects from MPS, SFS_s, and an interaction in column b are somewhat more pronounced in the duplicate series than in the

TABLE III
Results from ANOVA Identifying the Statistical Significance of Factor Effects on Crystallographic Order

	DF		SS		MS		*P*	
Source	Original series	Duplicate series	Original series	Duplicate series	Original series	Duplicate series	Original series	Duplicate series
HS	1	1	0.04	0.06	0.04	0.06	0.279	0.119
MFI	1	1	1.36	1.07	1.36	1.07	0.000	0.000
ST	1	1	0.31	0.31	0.31	0.31	0.012	0.005
MPS	1	1	0.06	0.12	0.06	0.12	0.200	0.042
QAS	1	1	0.02	0.02	0.02	0.02	0.460	0.345
SFS_s	1	1	0.09	0.22	0.09	0.22	0.109	0.012
WS	1	1	0.31	0.30	0.31	0.30	0.012	0.006
b		1		0.09		0.09		0.063
BLOCK		1		0.05		0.05		0.139
h	1		0.07		0.07		0.169	
Error	7	6	0.19	0.10	0.03	0.02		
Total	15	15	2.45	2.34				

original series of trials. Furthermore, an interaction in column h is slightly more pronounced in the original series. Some clear conclusions can, though, already be reached: the main effects from factors, MFI, ST, and WS on $(W_{1/2})^{-1}$ are prominent, whereas those from factors HS and QAS are not. On the other hand, interaction column h in the original series and MPS, SFS_s, BLOCK and interaction column b in the duplicate series present effects whose prominence is unclear.

The effects were more rigorously examined using analysis of variance, ANOVA, of the $(W_{1/2})^{-1}$ data. The results are listed in Table III. The original and duplicate series were treated separately as independent experiments using a pooling technique:[8] the most prominent effects identified from the effects plots were singled out as analysis targets, whereas the least prominent effects were pooled. In Table III, 10 factors, the maximum that could be employed by the MINITAB software, were analyzed. Thus, no significant effects were likely to be omitted, and the error estimated by pooling was minimized. It will be noted that the BLOCK effect and the effect b are included only in the duplicate series, since the effects plots clearly indicate no significance of these effects in the original series. Similarly, the effect h is included only in the original series.

It can be seen from Table III that the effects of HS, for which the probability P is 0.279 and 0.119, respectively, in the two trials, and QAS ($P = 0.460$ and 0.345) are not statistically significant at $\alpha = 0.05$. Moreover, the values of P for the effects from the column BLOCK ($P = 0.139$) and column h ($P = 0.169$) are also appreciably greater than 0.05: these effects, then, are not significant either. In contrast, ST ($P = 0.012$ and 0.005) and WS ($P = 0.012$ and 0.006) are significant, and MFI is highly significant in both series. The effect of MPS appears marginally significant in the duplicate series ($P = 0.042$) but not significant in the original series ($P = 0.200$). The effect from column b appears marginally insignificant in the duplicate series ($P = 0.063$). For these two latter cases, further experiments were clearly required for more reliable conclusions to be reached.

The effect of SFS_s, while not significant in the original series ($P = 0.109$), does, surprisingly, appear to display significance in the duplicate series ($P = 0.012$). The spin finish was applied on the surface of already solidified PP fibers. Given that the finish was aqueous based, any significant effect exerted by it would then have to be attributable to one or more of its components diffusing into the bulk of the fibers. Diffusion, while possibly causing some fiber swelling, is unlikely to affect crystallographic order. However, the effects plot for SFS_s in the duplicate series, shown in Figure 1(b), indicates that greater level of spin finish increases crystallographic order. Unless the application of spin finish in the duplicate series caused slight cooling of the fibers, which may have enhanced crystallographic order to some extent, we suggest that the effect arises from normal experimental error or random significance belonging to the marginal statistical probability of α.

Overall, the ANOVA results are consistent with the more qualitative conclusions drawn from the effects plots of Figure 1. In the optimization of crystallographic order, the direction for changing the levels of each control factor can be deduced from the effects plots. Factor levels above the average line are selected for maximization of response and levels below the line for minimization. Hence, low levels of MFI and WS and high levels of ST should be used for minimization of crystallographic order in the as-spun fibers. Minimization of crystallographic order is likely to be desirable for improved mechanical performance in subsequently drawn fibers.[6,7]

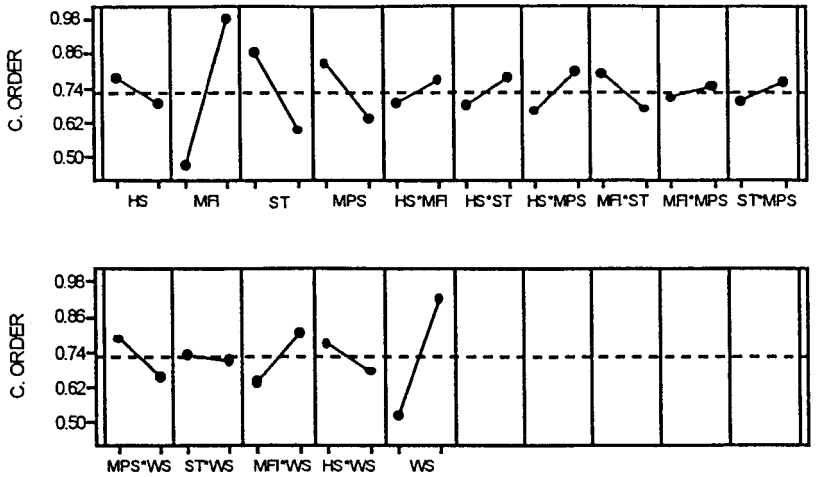

Figure 2 Effects plot of the response $(W_{1/2})^{-1}$ for the third series.

Confirmatory trials

As indicated above, some discrepancy between the results from the original and duplicate sets of trials has been observed concerning the statistical significance of some factor effects, and in particular some interaction effects may be statistically significant. Therefore, a third set of confirmatory trials was carried out under a new design to try to resolve these indeterminate cases. Unlike the design for the original and duplicate sets of trials, in which confounding was involved in the interaction columns, the new design had a higher resolution, so that two-factor interactions could be readily assessed. To achieve the higher resolution, factors QAS and SFS_s were omitted in the new L16 design.

The results for the confirmatory trials are shown in the effects plot in Figure 2 and in the ANOVA in Table IV. Again, the effects plot indicates that the main factors MFI, WS, and ST exhibit prominent effects, whereas HS does not. These observations are supported by the ANOVA in Table IV. MPS, on the other hand, produces an effect whose magnitude lies somewhere in the middle and thus may be marginally significant, as shown in Figure 2; this is confirmed by the ANOVA results ($P = 0.038$) in Table IV. The result serves to explain the discrepancy about the significance of MPS observed between the original and duplicate series of trials. The interaction effects by HS $\times$ MPS, MFI $\times$ ST, MPS $\times$ WS, and MFI $\times$ WS also appear to display some prominence in the effects plot. However, the ANOVA results in Table IV reveal that none of these interactions appears significant (in all cases $P > 0.05$), although MFI $\times$ WS may perhaps be only marginally insignificant ($P = 0.060$). Further analysis, in the form of an interaction effect plot, has provided additional evidence that the interaction, MFI $\times$ WS, is relatively weak.[17]

In summarizing the results of the three series of experiments and the corresponding analyses presented above, Table V lists a concise statistical model comprising the significant mean factors and their directions of change for optimizing crystallographic order of as-spun PP fibers. The model, which takes account of interaction effects as well as main effects, states that the factors MFI and WS should be set at low levels and that ST and MPS should be set at high levels, to minimize crystallographic order before subsequent fiber drawing. Maximization of crystallo-

TABLE IV
ANOVA of Main and Interaction Effects for the Third Series

Source	DF	SS	MS	*P*
HS	1	0.03	0.03	0.266
MFI	1	1.06	1.06	0.000
ST	1	0.31	0.31	0.009
MPS	1	0.15	0.15	0.038
WS	1	0.65	0.65	0.002
HS×MPS	1	0.08	0.08	0.100
MFI×ST	1	0.07	0.07	0.133
MPS×WS	1	0.07	0.07	0.115
MFI×WS	1	0.12	0.12	0.060
Error	6	0.13	0.02	
Total	15	2.67		

TABLE V
A Statistical Model for Maximization of Crystallographic Order

Factors	P^a	Factor levels
Melt flow index (MFI)	0.000	High
Winding speed (WS)	0.002	High
Spinning temperature (ST)	0.009	Low
Metering pump speed (MPS)	0.038	Low

*The *P* values are quoted from the third series.

graphic order is achieved when the factors are set in opposite directions.

A comparison between the results on crystallographic order and overall orientation[10] reveals that there are cases in which the two responses, $(W_{1/2})^{-1}$ and Δn, lie qualitatively in the same direction in the order–disorder spectrum. For example, in Table I, a high degree of crystallographic order coincides with a high degree of overall orientation in samples 7, 9, and 13, and a low degree of crystallographic order coincides with a low degree of orientation in samples 4, 8, and 10. There are also cases in which the two responses lie in opposite directions: a high degree of crystallographic order is coupled with a low degree of overall orientation in sample 14, and conversely for sample 3. Furthermore, crystallographic order is significantly influenced by a number of main factors: MFI, ST, WS, and, marginally, MPS. Overall orientation, on the other hand, is significantly influenced by only two main factors, WS and MPS, and also by the interaction between them.[10] It is evident, therefore, that the two response parameters reveal different aspects of fiber structure and respond differently to variations in processing conditions.

Peak intensities in the X-ray diffraction patterns

Significant differences in relative intensities of the X-ray diffraction peaks were observed among the as-spun PP fibers investigated. These differences occurred both among those fibers exhibiting true crystallinity and among those displaying paracrystallinity. Based on such differences, we may distinguish between peaks occurring at $2\theta < 20^{o}$ (one broad peak for the paracrystalline samples and three sharp peaks for the samples exhibiting crystallinity) and peaks at $2\theta > 20^{o}$ (a second broad peak for the paracrystalline samples and two peaks, sometimes unresolved, for the samples exhibiting crystallinity).[13] We have observed that, as the degree of crystallographic order of the PP fibers progressively increases from paracrystalline through transitional to crystalline states, those peaks at $2\theta < 20^{o}$ become more pronounced while those peaks at $2\theta > 20^{o}$ become less pronounced.[13] From a practical point of view, these changes in relative peak intensity allow some assessment of the degree of crystallographic order for samples within the paracrystalline group, since among these samples, the parameter $(W_{1/2})^{-1}$ varies very little: 0.30–0.33 in Table I and 0.34–0.36 in Table II.

Figure 3 illustrates X-ray diffraction patterns obtained for some of the paracrystalline samples, used in the original and duplicate experimental trials (Table I). For samples 3 and 11, the ratio of the intensity, I_{p1}, of the peak at $2\theta < 20^{o}$ to the intensity, I_{p2}, of the peak at $2\theta > 20^{o}$ differs: I_{p1}/I_{p2} is 1.74 for sample 3 and is 1.28 for sample 11. There is a clear indication, therefore, that sample 3 possesses a greater degree of crystallographic order than sample 11. If we consider the processing conditions for these two samples (Table I), we may note that MFI, ST, and MPS have identical settings. The only significant process control parameter that differs for the two samples is WS, greater in the processing of sample 3 than in that of sample 11. Now, it has already been shown that high levels of WS promote crystallographic order (Table V). Thus, the statistical model accords with the analysis of the two diffraction peaks.

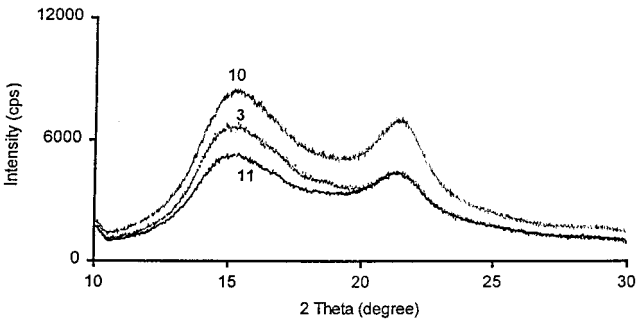

Figure 3 WAXS traces of paracrystalline samples.

Another example is provided by a comparison of the diffraction patterns of samples 10 and 11 in Figure 3. In the processing of these samples, the significant factors, MFI and WS, were set at the same levels, but the significant factors, ST and MPS, were set at different levels (Table I). The value of ST was lower in the processing of sample 10 than for sample 11, but the value of MPS was higher for sample 10. A lower value of ST promotes crystallographic order, whereas a higher value of MPS tends to diminish it. Thus, it may be expected that the crystallographic order in the two samples may be comparable. In fact, the ratio of the peak intensities, I_{p1}/I_{p2}, is determined as 1.28 for both paracrystalline samples, which suggests that they possess almost identical degrees of crystallographic order.

DISCUSSION

It is widely accepted that melt spun fibers contain a variety of structural elements of differing degrees of order. The structural elements exist in regions that range from totally noncrystalline regions through regions of increasing degrees of order to totally crystalline regions.[18] The proportions of these structural elements and their distribution within a fiber will depend very much on the fiber processing method. For example, they will differ greatly between as-spun fibers and those that have been subsequently drawn.

In practice, the identification of all these structural elements within a fiber is difficult and often even impossible, so this concept is usually simplified. In the case of PP fibers, it is often useful to separate the

structural elements into three broad groups: crystalline, paracrystalline, and noncrystalline. Such a categorization can readily arise from wide angle X-ray diffraction patterns of PP fibers, in which paracrystalline structures give broader peaks than do their more truly crystalline analogues. Paracrystalline structures represent a form of structural order intermediate between crystalline and noncrystalline. A liquid-crystalline model for the paracrystalline structure has recently been proposed, suggesting a liquid-like lateral packing of PP chains, together with a high degree of registry in the chain direction.[19]

Clearly then it is difficult to provide a complete picture of the internal structure of a PP fiber. WAXS probes the extent of the crystalline and paracrystalline regions and the internal arrangement of the polymer chain segments within them. The WAXS technique is especially suitable for studies of PP fibers, for these have a stronger tendency for crystallization than most other common polymer fibers.[20] Birefringence data, on the other hand, reveal the extent of the overall orientation of the molecular chains within the fibers. We now seek to enhance the picture in as-spun PP fibers through determining those individual control parameters and interactions between them in the melt spinning process that significantly influence crystallographic order and orientation.

The influence of MFI on crystallographic order highlights the importance of the PP grade used in the melt spinning process, and indeed the effect of MFI on melt spinning has been noted by other authors.[20,21] The MFI value of a grade of PP is dependent on several factors, including weight-average molar mass, molar mass distribution, and even impurities present associated with the use of catalysts. MFI can be considered, therefore, only as a nonspecific indicator of the significance of the grade of PP, and we cannot specify from our results which of the factors influencing MFI are chiefly responsible for its effect on crystallographic order. However, of the grades used in this work, the one with the higher MFI is very likely to possess the shorter polymeric chains.[20] Very long molecular chains are difficult to stretch and align because of their greater entanglement with one another. Shorter molecular chains, associated with a higher MFI, are therefore expected to favor crystallographic order,[20] as observed experimentally in the work described here.

The significant influences of WS and MPS on crystallographic order can be conveniently considered in terms of the effect of draw-down ratio (DDR). DDR indicates the ratio by which the filaments have been stretched (drawn) during their passage from the spinneret to the winder. A higher WS and a lower MPS contribute to a higher DDR, and hence to an increased and closer alignment of molecular chains along the fiber axis. The close alignment of PP chains during draw-down facilitates a better fitting of the chains into a crystal lattice, and thus to an increased crystallographic order. In addition, an increase in DDR also increases crystallization rate by strain-induced crystallization.[22,23]

The significant influence of ST on crystallographic order can be considered in terms of the thermal motion in the PP chains. At lower values of ST, the thermal motion is reduced, with the result that the chains can be more readily accommodated into well-defined crystal lattice structures, once the fibers have cooled after their emergence from the spinneret. Therefore, the degree of crystallographic order will be increased at lower values of ST.

The observed decisive effects of WS, MPS, and their interaction on overall orientation, Δn, can also be explained in terms of DDR. Increased drawing facilitates extension and alignment along the fiber axis of molecular chains in the noncrystalline regions.[24] It also promotes the orientation of crystallites. All these effects of intensified drawing improve the overall orientation and hence increase the birefringence, Δn. Therefore, the overall orientation of PP fibers at the spinning stage is primarily through external forces unlike the case of crystallographic order, which is also significantly influenced by the grade of raw material and spinning temperature. The existence of the highly significant interaction WS $\times$ MPS on Δn shows that, in addition to the significant main effects exerted independently by WS and MPS, there is also a considerable synergy between them. Although the direction of the interaction effect is consistent with those of the main factors on influencing overall orientation,[10] the interaction must additionally be considered when optimizing the overall orientation of as-spun PP fibers. It is also noteworthy, however, that the interaction effect does *not* appear to be significant in influencing crystallographic order, although the individual main effects WS and MPS do appear significant. The absence of a significant interaction effect on crystallographic order can perhaps be attributed to the apparently marginal significance of MPS itself.

As discussed above, the structural properties of as-spun fibers can be controlled at a macromolecular level through a statistical approach to the fiber extrusion process and the use of WAXS and birefringence measurements as characterization methods. Whereas WAXS probes the extent of the crystallites and their internal regularity in the arrangement of polymer chains, birefringence data reveal the extent of overall orientation attained through all the structural elements associated with the noncrystalline, as well as crystalline, parts of the fibers. The two methods complement each other and together provide a picture of the fiber structure more refined than that afforded by either method alone. By means of a statistical approach, effective control of the behavior of the poly-

mer chains during fiber processing can be achieved. Moreover, the statistical approach provides a basis for optimization of the spinning process in the direction of either increased or decreased crystallographic order and/or overall orientation of as-spun PP fibers. This, in turn, also provides a basis for quantitative modeling, such as neural network modeling.[11]

CONCLUSION

Fractional factorial experimental design has been applied to the melt-extrusion of PP fibers. Using a comprehensive statistical approach, the fibers have been characterized with respect to their crystallographic order and the overall orientation of their constituent polymer chains. The individual process control parameters significantly governing overall orientation are WS and MPS. It is noteworthy that the interaction MPS $\times$ WS between the two parameters is also significant with respect to overall orientation. Thus, enhancement of overall orientation is indeed driven primarily by the extent of spin drawing, as manifest by DDR.

The influences on crystallographic order are more varied. Nevertheless, WS and MPS again appear significant (although MPS only marginally), but so also do MFI and ST. These results provide not only further indication of the decisive influence of DDR in PP fiber melt spinning technology but also demonstrate the importance of the polymer chain length and spinning temperature on the development of crystallites.

Maximization of the responses can be achieved under conditions of high WS and low MPS for overall orientation and, additionally, of high MFI and low ST for crystallographic order. Minimization of these responses is achieved when the levels of the control parameters are changed in the opposite directions. It is to be noted that a low degree of crystallographic order in as-spun PP fibers has been considered beneficial for enhanced mechanical properties in subsequently drawn fibers.[6,7]

The benefits to PP fiber process technology of factorial experimental design and statistical analysis of the results have been exemplified in this paper, with respect to the structure of as-spun fibers. In a later paper, we aim to apply this approach to the mechanical properties of as-spun fibers and hence to provide further insights into processing–structure–property relationships.

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