The Influence of Isotacticity, Ethylene Comonomer Content, and Nucleating Agent Additions on the Structure and Properties of Melt-Spun Isotactic Polypropylene Filaments*

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SYNOPSIS

The influence of isotacticity, ethylene comonomer content, and nucleating agent additions on the structure and properties of melt-spun polypropylene filaments was studied for a series of polypropylenes having similar resin melt flow rates (MFR ≅ 35), average molecular weights, and polydispersities. In general, increasing the degree of isotacticity increases crystallinity and tensile modulus of the spun filaments, while increasing the copolymer content has the opposite effect. Nucleating agent additions also lead to greater crystallinity, but, under certain conditions, the addition of a nucleating agent can lead to lower tensile modulus in spite of higher crystallinity. For given spinning conditions, the tensile strength increased slightly with increased copolymer content but was little affected by tacticity in the range studied. Nucleating agent additions lowered the tensile strength of spun filaments. The effects of nucleating agents on the filament modulus and tensile strength were traced to their ability to raise the crystallization temperature and reduce the level of molecular orientation generated in the filaments. The reasons for the observed behavior are discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

This is the fifth paper in a series from our group dealing with the influence of resin characteristics on the structure and properties of melt-spun isotactic polypropylene filaments. Three of the earlier papers[1-3] dealt extensively with the influence of molecular weight and polydispersity and the interaction of these variables with the spinning process variables. It was shown that the processing, structure, and properties of polypropylene filaments are highly influenced by both molecular weight and polydispersity. A fourth paper[4] briefly examined the effects of changing the crystallization kinetics by adding a

nucleating agent or by copolymerizing with ethylene. The present paper extends this latter work to include the effects of varying the copolymer content and the tacticity of the homopolymer.

The prior work on the melt spinning of polypropylene was reviewed in our earlier papers;[1-4] the reader is referred to these papers for an overview of the subject and a detailed discussion of the key references.

EXPERIMENTAL DETAILS

Materials

Eight resin samples were provided by Exxon Chemical Company. Their characteristics are summarized in Table I. Three of the resins were homopolymers having different levels of isotacticity and three were random ethylene copolymers (RCPs) with nominal ethylene contents of 1.5%, 3.0%, and 5.0% (wt %). In addition, two resin samples, one a homopolymer

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Table I Characteristics of As-Received Resins

Sample Code	MFR	FTIR (% Ethylene)	Isotacticity[a] (%)	M_n	M_w	Polydispersity (M_w/M_n)
HT-PP	36	0	99	59,010	131,128	2.22
MT-PP	34.2	0	93	60,330	143,825	2.38
LT-PP	37	0	91	54,867	134,841	2.46
1.5% RCP	35	1.4	96	49,214	158,590	3.22
3.0% RCP	35.4	3.0	94	61,549	142,160	2.31
5.0% RCP	31	4.9	92	66,474	150,114	2.26
1% NA-PP	35	0				
3.0% RCP + 1% NA	36	2.6	94	67,852	144,412	2.13

[a] IR method of Luongo,[6] calibrated with heptane-insoluble data for the HT-PP and LT-PP samples.

and one a copolymer, had 1 wt % of a nucleating agent added. All resins were nominally 35 MFR resins with similar weight average molecular weights, and fairly narrow molecular weight distributions (MWD) as indicated by their polydispersities. It should be noted that the 1.5% RCP has a slightly broader MWD than the other resins.

The ethylene contents in the copolymers measured by an FTIR technique[5] are also given in Table I. The measured values are fairly close to the nominal compositions except for the 3% RCP with nucleating agent added (3.0% RCP + 1% NA), which is a bit low. The percent isotacticity values were also estimated from FTIR measurements using the approach of Luongo.[6] The technique assumes that the polymer is made up of an isotactic and an atactic phase whose relative amounts determine the ratio of certain IR absorption bands. In our case, we used heptane insolubles measured on the high tacticity homopolymer (HT-PP) and the low tacticity homopolymer (LT-PP) to calibrate the method. Thus the values listed for % isotacticity should be approximately equal to the values for heptane insolubles for each of the resins. It should be noted that all other values lie between the values for the two materials used for calibration. Furthermore, the values for the copolymers decrease with increasing ethylene content. The technique used here has a probable error of about ±2%, and it does not clearly evaluate the distribution of stereo inversions among the polymer chains. The most appropriate technique would be to use nuclear magnetic resonance spectroscopy to study the tacticity of both the heptane insoluble and the heptane soluble fractions. Unfortunately, this technique was not available to us.

Melting and Crystallization Behavior of the Resins

The melting and crystallization behavior of the resins were compared using a Perkin-Elmer differential

scanning calorimeter (DSC-7). Melting points were determined from scans made at heating rates of 20°C per minute. Values of the melting point were determined after removal of the influence of prior history by first heating to well above the melting point and cooling at a rate of 20°C per minute back to room temperature. Values given are for the peak of the melting endotherm.

The crystallization behavior was examined in both an isothermal and a nonisothermal mode. The nonisothermal mode consisted of cooling at a rate of 20°C per minute and measuring the crystallization temperature. Isothermal crystallization experiments consisted of (1) holding the sample at 200°C for 3 min, (2) cooling rapidly (80°C/min) to the chosen crystallization temperature, (3) holding at the crystallization temperature until crystallization is completed, and (4) determining the time for half the energy in the crystallization exotherm to be emitted (the crystallization half-time). More detailed studies and analyses of the crystallization behavior of these resins have been carried out, but these results will be described elsewhere.

Melt Spinning

Filaments were spun using the same equipment used in our earlier studies,[1-4] and the reader is referred to these articles for more detail. Generally, monofilaments were spun using an extruder equipped with a constant displacement melt pump which provided a constant extrusion rate. Molten polymer from the melt pump was forced through a filter mesh and then through a capillary die of diameter 0.762 mm and L/D = 5.0. The filament exiting the die was drawn down using an airjet drawdown device. Air pressure applied to this device produces high speed air which provides a drag force to draw the filament down. The amount of drag, and hence the take-up

Table II   Melting and Crystallization Temperatures of the Resins

Sample Code	Melting Temp., °C	Crystallization Temp., °C	Crystallinity[a] (20°C/min) %
HT-PP	167.0	114.9	59.4
MT-PP	162.3	100.7	52.2
LT-PP	161.2	103.6	48.6
1.5% RCP	154.2	106.6	49.1
3.0% RCP	142.7	90.1	43.5
5.0% RCP	133.0	92.8	25.8
1% NA-PP	163.1	123.7	54.2
3.0% RCP + 1% NA	149.1	113.5	46.6

[a] DSC technique.

velocity of the filament, can be controlled by varying the air pressure supplied to the drawdown device. Depending on the viscous properties of the polymer, spinning speeds up to about 6000 m/min could be obtained with air pressures up to about 80 psig. The spinline length from the capillary die to the airjet drawdown device was kept constant at 250 cm (2.5 m) for all experiments.

Filament Characterization

The as-spun filaments were characterized by density, birefringence, wide-angle X-ray diffraction, and tensile mechanical property measurements. The experimental procedures have been described in our previous papers.[1-4] Briefly, the density was measured in an isopropyl alcohol/water density gradient column maintained at 23°C. The birefringences were measured using a polarizing microscope equipped with a Berek compensator and a filar eyepiece. X-ray patterns were obtained using a flat plate camera and Ni filtered CuKα radiation. The tensile tests were run using fibers with an initial gauge length of 25 mm and a crosshead speed of 50 mm/min. The filaments were conditioned at room temperature for several days prior to testing. The reported results are the average of tests carried out on 10 tensile test specimens for each condition.

On-Line Measurements

The techniques used to measure the profiles of diameter and birefringence as a function of distance from the spinneret have been previously described.[2,7] The diameter profiles are measured with a Zimmer diameter monitor. This instrument operates on a noncontact electrooptic principle; it has a diameter resolution of ±0.5 μm. The birefringence profiles were measured by mounting a polarizing microscope

so that the spinning filament can pass through the microscope field of view. The microscope is mounted on a moveable stand so that it can be located at various distances from the spinneret. A Berek compensator is then used to measure the retardation of the filament at each position.

RESULTS AND DISCUSSION

Melting and Quiescent Crystallization Behavior of the Resins

The melting and crystallization behavior of the resins were studied in order to further characterize the resins and because the structure development during the melt spinning process and the resulting structure and properties of the as-spun filaments is known to be strongly affected by the crystallization behavior.[4,8-10]

The melting points of the resins are given in Table II. The data show that the melting points increase with increase of percent isotacticity and decrease with increase of ethylene content in a manner consistent with other results in the literature.[11-17] The addition of a nucleating agent would not be expected to influence the melting point directly, though it may have an indirect effect due to its effect on the crystallization temperature. It is known that crystallization temperature affects the lamella thickness of polymer crystals[18] and that lamella thickness affects the melting point through the equation:[19]

$$T_m = T^0_m \left(1 - \frac{2\sigma_e}{\Delta H_f l}\right) \tag{1}$$

where T_m is the melting temperature with a certain lamella thickness l, ΔH_f is the heat of fusion, and σ_e is the end surface free energy of the lamella crystal. The data in Table II indicate that the melting point

of the nucleated resins is consistent with the melting point of similar resins without nucleating agent (recall that the resin labeled 3% RCP + NA actually has only 2.6% ethylene).

The crystallization temperatures during cooling in the DSC at a rate of 20°C/min are also given in Table II. It should be noted that these data are not simply and directly related to the melting point data. In order to crystallize, a resin must cool below its melting point, but crystallization is also affected by other factors which control the rate of primary nucleation and subsequent growth of crystals. For the present resins, the presence of purposely added nucleating agents in two of the resins greatly increases their crystallization temperature, both in an absolute sense and relative to their melting points; i.e., nucleating agents reduce the supercooling required for crystallization. Based on the literature[11,12] increasing ethylene copolymer content would be expected to lower the crystallization temperature. However, it is to be noted that the present 3.0% RCP has a lower crystallization temperature than the 5.0% RCP. Generally, we would anticipate that increasing isotactic content would raise the crystallization temperature, as it raises the melting point.[15-17] However, the present medium tacticity homopolymer (MT-PP) crystallizes at a lower temperature than the low-tacticity homopolymer (LT-PP). Finally, the crystallization temperature of the 1.5% RCP seems a bit high relative to the LT-PP and MT-PP homopolymer resins. This may be a result of the high isotacticity of this sample (Table I).

The crystallinity of the resins developed by slow cooling in the DSC is also given in Table II. The crystallinity values were measured by DSC technique. These results show that the crystallinity increases with increased isotacticity and decreases with increased copolymer content as expected.[11,15] The addition of nucleating agent has relatively little effect on the crystallinities after slow cooling.

Figure 1 shows the crystallization half-times as a function of temperature, measured by DSC under isothermal conditions, for each resin. These data clearly show that the crystallization kinetics of the resins as measured by crystallization half-time at a given temperature are ordered in the same manner as the crystallization temperatures measured during cooling as described above. Samples with purposely added nucleating agents have shorter half-times at given temperature than their nonnucleated counterparts; higher tacticity also tends to decrease the half-time, and increasing copolymer content increases the half-time. The reversals of form for the 3.0% RCP and the MT-PP resins are also evident
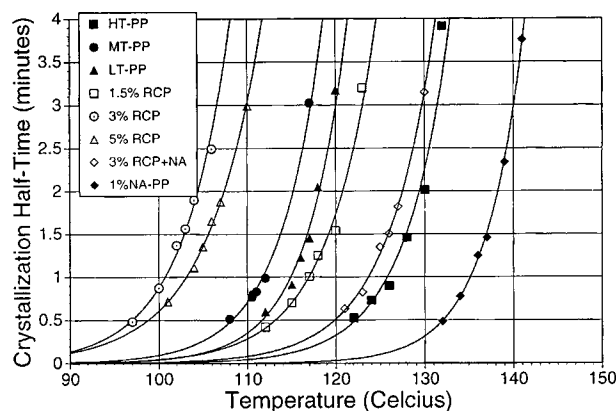

Figure 1 Crystallization half-times for the resins as a function of temperature.

in the results of Figure 1. The half-times of the 1.5% RCP indicate that this resin crystallizes faster than we would anticipate relative to the MT-PP and LT-PP resins.

In considering the above melting and crystallization results, the following points can be made. The melting point, crystallinity, and crystallization rate of a homopolypropylene resin are affected by percent isotacticity due to the difficulty of incorporating stereo inversions into the crystals. A similar argument can be advanced to explain the affect of ethylene copolymer content; the ethylene units are not readily incorporated into the crystals. Theoretical considerations[20,21] also suggest that the melting point and crystallinity will be lowered and crystallization rates will be reduced by introducing copolymer units or stereo inversions into the polymer chain. These trends are observed in the above results except for the reversals already mentioned. Specifically, the 5% RCP resin crystallized somewhat faster at a given temperature or at a higher temperature during slow cooling in the DSC than does the 3% RCP. Also, the LT-PP resin crystallizes slightly faster than the MT-PP resin. Furthermore, it is a bit surprising that the 1.5% RCP crystallizes more rapidly than either the LT-PP or MT-PP homopolymer resins.

One possible explanation for these effects is that the crystallization behavior is controlled as much by the distribution of stereo inversions (or copolymer units) among the polymer chains as by the average number of such inversions. If we consider two resins with the same average number of stereo inversions, there is likely to be a substantial difference between the behavior of the resins if one contains only chains with a uniform number of inversions per unit length, and one is a mixture of some atactic chains, and some chains which have very few stereo inversions.

The current isotacticity data do not allow us to determine if such a difference in distribution might exist in our resins. This would require detailed studies of the tacticity by the NMR technique of both the heptane-insoluble and the heptane-soluble fractions of the resins. These techniques were not available to us. But, since there are no reversals in the expected melting point results, we do not think that this is the most probable explanation.

We believe that the most likely explanation of the reversals of form mentioned above is due to unexpected variations in the spherulite nucleation rate. In studies described in detail elsewhere,[22] it has been shown that these reversals of behavior for the present samples can be, at least partially, accounted for by the presence of a noticeably higher spherulite nucleation density during quiescent crystallization of the 1.5% RCP and the 5.0% RCP compared to the 3.0% RCP and the MT-PP resin. This implies that there are more adventitious nuclei present in the 1.5% RCP and the 5% RCP resins. Spherulite growth rate measurements do not exhibit the reversals in the expected behaviors that are observed for the overall crystallization rates. It would appear, then, that the reversals are caused by fewer readily activated sites for nucleation of spherulites in the 3.0% RCP or the MT-PP resins. It is not clear why this is the case, but it may be suggested that this behavior is caused by some subtle difference, such as type or amount of catalyst residues.

Structure and Properties of As-Spun Filaments— Results

For the study of structure development during spinning, each resin was spun with an extrusion temperature of 210°C, a mass throughput of 1.55 ± 0.02 g/min (per hole), and three or more different take-up velocities that were obtained by applying different air pressures to the drawdown device. The processing conditions and some characteristics of the filaments are summarized in Table III. The indicated spinning speeds are determined from application of the continuity equation to the on-line diameter measured at 220 cm from the spinneret. The average diameters of the as-spun filaments were also measured. They are compared with the on-line diameters measured at 220 cm from the spinneret in Table III. It is noteworthy that the off-line diameters tend to be slightly larger than the final on-line values. This apparently is due to the elastic contraction in the filaments when the drawdown stress is removed.

The density and birefringence of the as-spun filaments are plotted versus the filament take-up velocity in Figures 2 and 3. Figure 2 shows that, in general, increasing isotacticity and the addition of nucleating agents increase the density developed in the filaments, while copolymerization decreases it. This would seem to correlate with the crystallinity and crystallization rate data for these resins described above.

The birefringence data, Figure 3, generally indicate a fairly complex behavior with the isotacticity and copolymer content not exhibiting clearly discernible trends. It is noteworthy that the nucleated samples tend to have lower birefringence, and hence lower molecular orientation, than their nonnucleated counterparts.

X-ray patterns of the as-spun filaments indicated that filaments prepared from all resins contained primarily the α-phase under all the spinning conditions studied. As with earlier results[1,3,4] filaments spun at lower speeds and lower spinline stress levels tend toward a contribution from the smectic mesophase. The patterns also showed that under similar spinning conditions the resins generally developed a similar level of crystalline orientation (though not the same level of crystallinity). An exception was that the nucleated homopolymer exhibited a noticeably lower level of crystalline orientation than the nonnucleated resins. This result is in agreement with the lower birefringence of the nucleated resin.

On-line measurements of diameter and birefringence profiles were carried out in order to provide additional understanding of the influence of tacticity, copolymer composition, and nucleating agent additions. Figure 4 presents on-line diameter and birefringence profiles for the HT-PP resin spun at three different air pressures applied to the drawdown device, and hence three different take-up velocities (see Table III). As take-up velocity increases, the filament draws down to its final diameter nearer the spinneret. The rapid rise in birefringence due to oriented crystallization also occurs nearer the spinneret with increase in take-up velocity. Although not shown here as a figure, the overall appearance of the data for the LT-PP resin is similar to that of Figure 4, but the drawdown occurs more slowly and the rapid rise in birefringence occurs further from the spinneret than for the HT-PP resin at each spinning speed. Furthermore, the final on-line birefringence is slightly lower in each case for the LT-PP resin than for its HT-PP counterpart.

Figure 5 illustrates that the addition of the ethylene copolymer tends to decrease the rate at which the diameter draws down and moves the point at which the rapid rise in birefringence occurs further from the spinneret. An exception for the present

Table III   Spinning Conditions and Characteristics of As-Spun Filaments

Resin Code	Air Pressure (psig)	Spinning Speed (m/min)	On-line Filament Diameter (μm)	Off-line Filament Diameter (μm)	Birefringence ($\times1000$)	Density (g/cm^3)	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation to Break (%)
HT-PP	5	2011	33.0	37.7	17.4	0.9012	1078	154	274
	10	2594	29.0	32.3	20.7	0.9045	1427	185	233
	25	3507	24.9	30.0	21.3	0.9077	1917	173	217
MT-PP	2	1608	37.0		18.7	0.8964	—	172	—
	5	1855	34.4	41.6	18.0	0.8991	1048	156	398
	7	1960	33.5		18.4	0.8975	1303	158	310
	10	2527	29.4	33.2	18.7	0.9023	—	—	309
	25	3086	26.6	31.7	18.6	0.9041	1301	155	275
	28	3234	26.0		19.5	0.9028	1430	155	236
LT-PP	5	2128	32.2	36.9	18.5	0.8943	643	157	230
	10	2559	29.3	33.7	19.7	0.8983	892	165	220
	25	3262	25.9	27.3	21.7	0.9019	1109	188	227
1.5% RCP	5	2070	32.6	38.0	18.5	0.8971	824	145	244
	10	2417	30.1	35.5	19.7	0.9013	1199	163	243
	25	3184	26.2	29.2	19.3	0.9030	1231	157	254
3% RCP	2	1323	41.0		19.5	0.8871	—	180	250
	5	2155	32.0	40.0	19.1	0.8921	624	171	276
	10	2689	28.5	33.9	18.5	0.8938	893	164	282
	25	3257	26.0		17.1	0.8963	—	—	270
	28	3638	26.6	31.7	17.5	0.8986	1003	157	288
5% RCP	5	1831	35.0	35.7	19.4	0.8915	641	192	181
	10	2914	27.7	31.5	20.3	0.8940	777	193	188
	25	3873	24.0	27.5	19.1	0.8960	877	182	191
1% NA-PP	5	2136	31.9	38.6	11.4	0.9080	959	94.6	340
	10	2735	28.2	33.0	14.9	0.9073	1057	127	322
	25	4078	23.1	29.5	18.4	0.9070	1348	157	238
3% RCP + NA	5	2020	33.0	37.7	15.3	0.8972	782	135	273
	10	2524	29.5	33.4	17.9	0.8984	856	151	228
	25	3167	26.3	29.7	19.6	0.9007	950	163	198

resins is the case of the 1.5% RCP. This will be discussed in more detail below.

The influence of increasing the crystallization kinetics by adding a nucleating agent is illustrated in Figure 6. For each spinning speed (air pressure applied to the drawdown device), the filament diameter draws down nearer the spinneret than for the HT-PP resin, and the rapid rise in birefringence accompanying oriented crystallization begins closer to the spinneret. A comparison of Figure 6 with Figure 4 illustrates that the influence of the nucleating agent in moving the point at which the crystallization occurs nearer the spinneret is much greater at low spinning speeds than at high spinning speeds. This is also evident from the on-line birefringence data shown in Figures 7 and 8. In Figure 7, data are shown for selected resins at similar spinning speeds of about 2100 m/min (5 psig pressure applied to the draw-

down device). Figure 8 shows data for all eight resins compared at higher take-up velocities (25 psig pressure applied to the drawdown device).

The tensile mechanical properties of the filaments are presented in Figures 9–11.

Discussion of the Structure and Properties of the As-Spun Filaments

The data of Figure 2 show that the crystallinity and density of as-spun filaments are functions of isotacticity and copolymer content. The influence of these variables on both the ultimate crystallinity possible and their effects on crystallization kinetics are important in determining the crystallinity of the spun filaments. Specifically, at spinning speeds below about 2500 m/min, the order of increasing filament density is: 3% RCP < 5% RCP < LT-PP
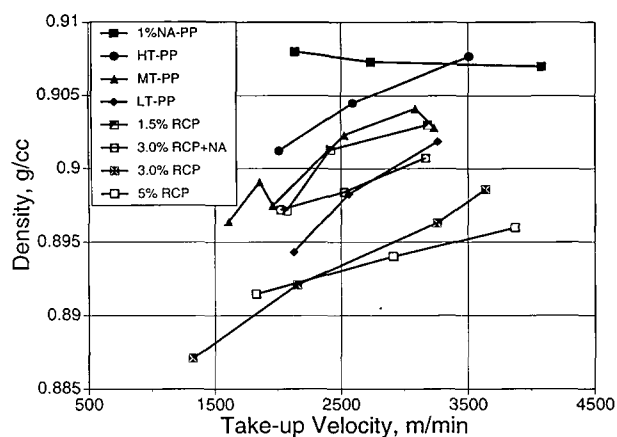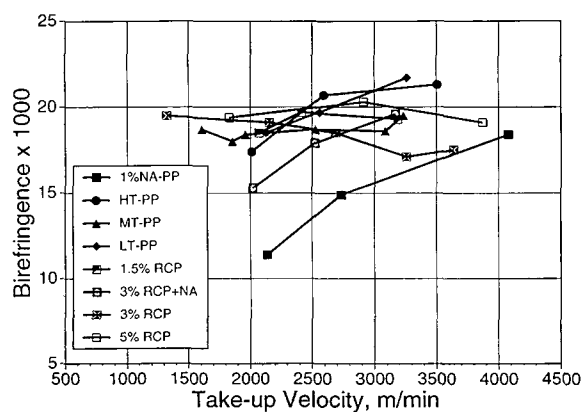
Figure 2 Effect of resin characteristics on the density of as-spun filaments.

Figure 4 Diameter and birefringence profiles for the HT-PP resin.

< 3% RCP + NA < MT-PP < 1.5% RCP < HT-PP < 1% NA-PP. If the ultimate crystallinity that is possible were alone controlling the filament crystallinity, then the order would be the same as that observed for the slow-cooled resins in Table II. But, in the spinline, the cooling rate is very high and crystallization kinetics therefore play an important role in determining the level of crystallinity achieved. With the exception of the MT-PP resin, whose density seems a bit high, and the 3% RCP + NA resin, whose density seems a bit low, the observed order of increasing filament density is the same as that of the crystallization half-times presented in Figure 1 and the crystallization temperatures in Table II. The deviations from this order are readily explained by the ultimate potential for crystallization modifying the order. The MT-PP resin has a relatively high potential for developing crystallinity, while the 3% RCP + NA resin has a relatively low potential for developing crystallinity. At

higher take-up velocities there are deviations from the order of filament densities observed at lower spinning speeds. These can be largely rationalized on the basis of the combined effects of greater stress-induced crystallization, higher cooling rates, and maximum crystallinity possible. For example, at high take-up velocities the density of the 3% RCP is higher than that of the 5% RCP. It would seem that stress-induced crystallization has increased the amount of crystallization occurring in the 3% RCP, thus raising its density, but the crystallinity of the 5% copolymer is limited due to the higher copolymer content. Also, the resins with nucleating agent added achieve higher crystallinities than their nonnucleated counterparts at low spinning speeds due to their high crystallization temperatures and overall high crystallization rates. Thus, they achieve nearly their ultimate potential for crystallization at low
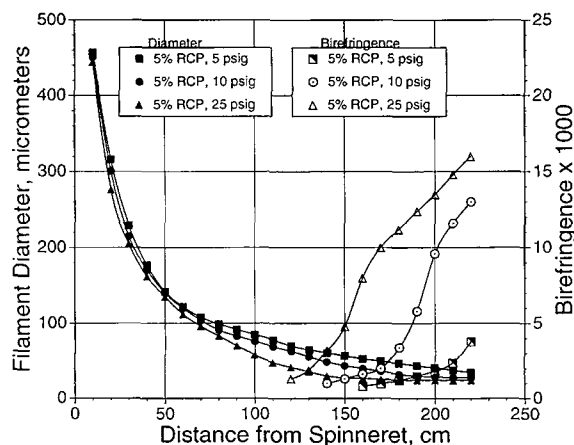

Figure 3 Effect of resin characteristics on the birefringence of as-spun filaments.

Figure 5 Diameter and birefringence profiles for the 5% RCP resin.
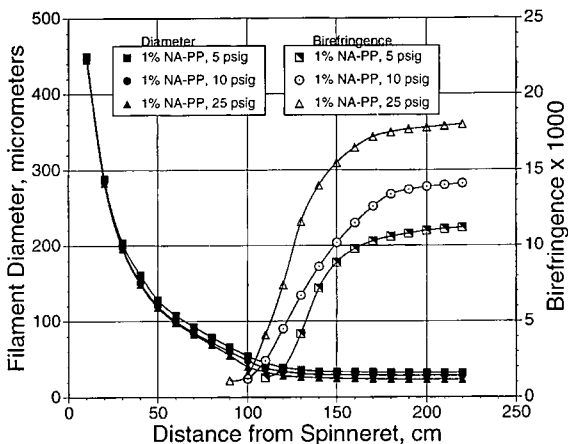
Figure 6 Diameter and birefringence profiles for the nucleated homopolymer.

Figure 8 Birefringence profiles for all resins spun at the highest spinning speeds.

spinning speed, something that the resins without nucleating agent cannot do. Higher spinning speeds have little or no further effect on their level of crystallinity and density. Stress-induced crystallization caused by higher molecular orientation at higher spinning speeds can have a marked effect on the crystallinity of the resins that do not contain nucleating agents due their influence on the crystallization rates. Thus, with higher spinline stress and higher molecular orientation, the resin crystallizes at a higher temperature in the absence of a nucleating agent, and the nucleating agent becomes less effective in raising that temperature further. The slight decrease in the crystallinity of the nucleated homopolymer as spinning speed increases, observed in Figure 2, probably results from the increased cooling rate of the filaments spun at the higher spinning speeds, without appreciable increase in
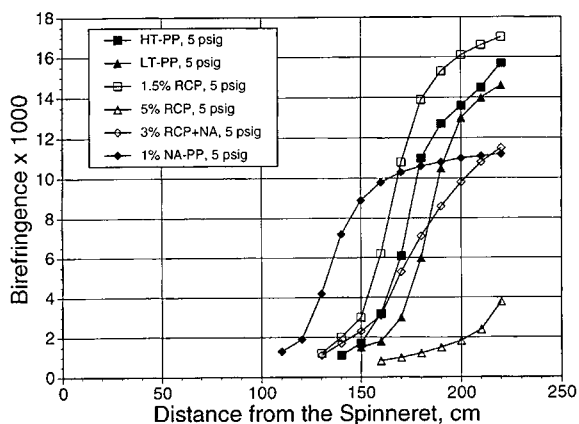
crystallization kinetics. The on-line data of Figures 6–8 also support the overall interpretation described here.

The final birefringence of the samples is not influenced very much by tacticity and copolymer content, but the addition of nucleating agent results in a substantially lower final birefringence. This is readily observed in Figure 3, which shows that the nucleated homopolymer has the lowest birefringence of the group of resins. The data of Figures 7 and 8 show that the high nucleation rate causes crystallization to begin closer to the spinneret. This necessarily means that the crystallization is occurring at higher temperature and lower stress, especially for the lower spinning speeds, than their nonnucleated counterparts. Crystallization at higher temperature and lower stress means that there is less molecular orientation in the melt at the point at which crystallization begins, and lower levels of mo-

Figure 7 Birefringence profiles for selected resins at spinning speeds of about 2100 m/min.

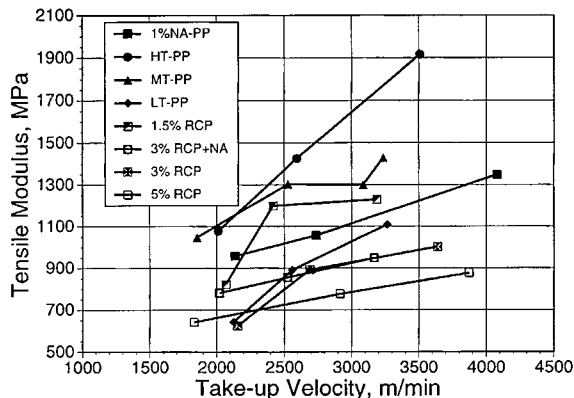**Figure 9** Effect of resin characteristics on the tensile modulus of as-spun filaments.

Figure 10 Effect of resin characteristics on the tensile strength of as-spun filaments.
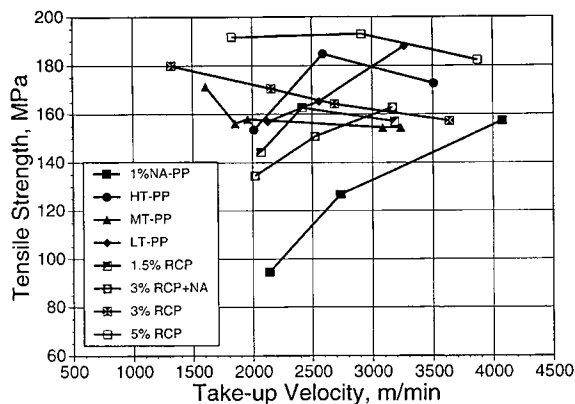

Figure 11 Effect of resin characteristics on the elongation-to-break of as-spun filaments.

lecular orientation are developed on crystallization. In the case of the 3% RCP + NA resin, the slower rate of crystallization caused by the copolymer effect offsets some of the effect of the nucleating agent, and this sample exhibits a birefringence, which is at an intermediate level. Considering the influence of copolymer, one might argue that the slower rate of crystallization causes the onset of crystallization to occur farther from the spinneret, Figures 7 and 8, where the spinline stress and molecular orientation in the melt is higher, resulting in relatively high birefringence. This is just the opposite of the argument for the nucleating agent effect.

The tensile modulus of polypropylene filaments is influenced by both crystallinity and molecular orientation. Figure 9 shows that the tensile modulus tends to increase with increase in tacticity and to decrease with increase in copolymer content. This effect is undoubtedly related to the increase in crystallinity with increased isotacticity and the decrease in crystallinity with copolymerization. Comparing Figure 9 with Figure 2 indicates that the tensile modulus correlates closely with the crystallinity for all filaments *except* those containing nucleating agents, which have high crystallinities and low moduli. However, the birefringence of the nucleated resins is lower than their nonnucleated counterparts, as shown in Figure 3. This suggests that the relatively low value of the tensile modulus for the nucleated resins is due to lower molecular orientation. This is especially noticeable in the case of the homopolymer resin.

It has previously been shown that the tensile strength of melt-spun filaments correlates with birefringence for homopolypropylenes of similar isotacticity, independent of the molecular weight and its distribution.[3] The tensile strengths shown in
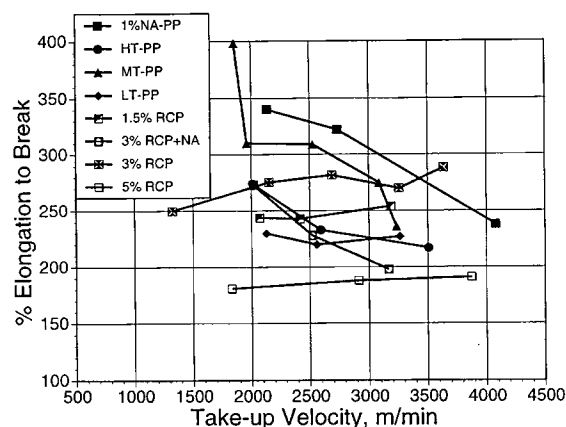
Figure 10 also tend to correlate with the birefringence data of Figure 3, as is shown in Figure 12. This figure shows the data for all samples studied in this paper superimposed on the prior data for samples of different polydispersity and average molecular weight which, were reported in reference 3. The latter data are indicated as "narrow," "medium," and "broad MWD" in Figure 12. The average standard deviation of each data point shown is indicated by the error bars in the upper lefthand corner of Figure 12. Within the error limits in both tensile strength and birefringence data, there is a strong correlation of tensile strength with birefringence for the entire range of plotted data. Furthermore, within the error limits, the other variables (including isotacticity, copolymer content, presence of nucleating agents, and crystallinity, as well as molecular weight and polydispersity) influence the tensile strength
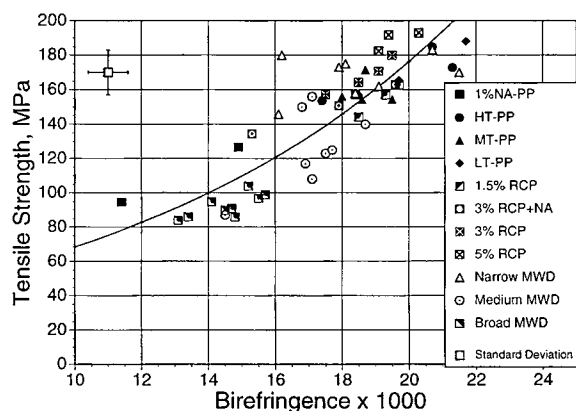

Figure 12 Correlation of tensile strength with birefringence for a wide range of polypropylene filaments.

only by their effect on the molecular orientation through their effect on its development during processing.

The elongation to break, Figure 11, tends to be the reverse of the tensile strength; i.e., samples with higher tensile strength tend to have lower elongation, and *vice versa*. This also implies that elongation to break tends to correlate with the birefringence as previously noted.[3]

Figures 6 and 7 show that the 1.5% RCP develops its birefringence unexpectedly close to the spinneret. Based on quiescent crystallization kinetics, the position at which the rapid rise in birefringence occurs for this resin should be slightly farther from the spinneret than that of the HT-PP resin. Figures 6 and 7 show that it actually lies closer to the spinneret than does the data for the HT-PP resin. This result appears to be related to the higher polydispersity of this sample compared with the other resins of the present group. Previous work from our laboratory[3] showed that broadening the MWD (increasing the polydispersity) causes the filament diameter drawdown and the rapid rise in birefringence to occur closer to the spinneret than for narrow MWD resins with similar melt flow rate (MFR). The major influence of polydispersity on the structure and properties developed was attributed to its effect on both the elongational viscosity of the resin and the ability of the high molecular weight tails in the distribution to enhance the stress-induced crystallization that occurs in the spinline.

CONCLUSIONS

The final structure and properties of as-spun polypropylene filaments are comprehensive results of all the factors that affect the morphology of the filaments—especially the level of crystallinity and the molecular orientation of the filaments. Many factors, both processing conditions and materials parameters, control these features. The present study emphasizes the influence of certain material parameters. In particular, the present paper reports the effects of degree of isotacticity, ethylene copolymer content, and the addition of nucleating agents for polymers of similar weight average molecular weight and polydispersity. The influence of changes of weight average molecular weight and polydispersity were featured in a recent publication.[3]

The structure and properties of melt-spun polypropylene filaments vary markedly with the presence or absence of nucleating agents, the level of isotacticity, and the ethylene copolymer content. The effects of isotacticity and copolymer content are a result of differences in both the rate of crystallization and the effect which these variables have on the ultimate level of crystallinity that is possible in the resin. Higher isotacticity tends to increase both the crystallization rate and the ultimate crystallinity that can be developed, while increasing ethylene copolymer content decreases the crystallization kinetics and the level of crystallinity that is possible.

Primarily through their influence on the crystallization start temperature and overall crystallization kinetics, nucleating agents cause crystallization to occur under lower stress levels and lower molecular orientation in the melt compared with an otherwise similar polymer that does not contain nucleating agents. Thus, nucleated resins develop higher levels of crystallinity but lower levels of molecular orientation than their nonnucleated counterparts. Somewhat similar, though less marked, effects were observed with an increase in degree of isotacticity or a decrease of copolymer content.

These differences in structure are clearly reflected in the tensile mechanical properties of the filaments. Higher crystallinity and molecular orientation lead to higher tensile modulus. In the case of the addition of a nucleating agent, a decrease in the level of molecular orientation obtained can, under certain conditions, offset the effect of increased crystallinity. The tensile strength and elongation to break tend to correlate with molecular orientation and are relatively independent of crystallinity.

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