

Production of Thermally Stable Polypropylene Fibers

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SYNOPSIS

Polypropylene (PP) fibers were made with a number of different processing conditions, such as one-stage drawing, two-stage drawing, and a combination of drawing, annealing, and relaxation. The thermal stability of these fibers in terms of shrinkage in length at 100, 130, and 150°C was studied. It was found that the thermal shrinkage can be greatly improved with multi-stage drawing and with annealing. The fibers that were two-stage-drawn, relaxed, and then annealed remained stable at 130°C while still having a fiber tenacity in excess of 0.8 N/tex. Thermal stability at 150°C was more difficult to improve. However, the fibers that were drawn in three stages with a final drawing temperature of 185°C showed thermal shrinkage at 150°C of less than 10%. Finally, it was found that the thermal shrinkage of PP fibers at 150°C can be greatly reduced by blending a minor component of a liquid crystal polymer into the PP fibers. With two-stage drawing and annealing, fibers with shrinkage at 150°C of only 2.9% were produced. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene (PP) fibers have a number of unique properties and applications.¹ Because of their low cost and excellent tensile mechanical properties, they are widely used in carpet backing, ropes, lifting bags, and many other domestic/industrial applications where a medium range of fiber tenacity is required, thereby bridging the gap between the conventional fibers and the more expensive high-performance fibers.

One of the main shortcomings of PP fibers is their poor thermal stability. The melting temperature of PP is around 165°C, and the PP fibers usually soften and lose strength at around 130°C. This softening temperature would be too low for many applications, since dimensional stability of the fibers beyond 200°C is often required. With sewing thread, e.g., the thermal stability should be high to avoid the problem of the thread being melted by the frictional heat.

Because of the low cost and the relatively high fiber strength, PP fibers can be used as a reinforcing

component for low-cost composite materials such as hose pipes and conveyor belts. For these applications, it is desirable that the thermal stability of the PP fibers be higher than 130°C, preferably higher than 150°C, as this would allow the use of a relatively wide range of matrix polymers.

This article describes the results of a study on the thermal stability of PP fibers. The as-spun fibers were made on a single-screw melt extruder and they were then processed by using different drawing, annealing, and relaxation procedures, such as one-stage drawing with annealing and relaxation and multi-stage drawing with different drawing temperatures. The effect of blending PP with a second component with a high thermal stability was also studied.

EXPERIMENTAL

The as-spun fibers were made by extruding the PP granules (Neste VP19) on a single-screw melt extruder (Labspin, Extrusion Systems Ltd), equipped with a 37 hole spinneret plate (capillary $D = 0.4$ mm). The extrusion temperature was 250°C and the extrusion rate was 3 m min⁻¹. The as-spun fibers were collected at 100 m min⁻¹ and they were then drawn on a laboratory-scale drawing unit consisting of two pairs of advancing rollers and a hot plate.

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In one-stage drawing, the as-spun fibers were fed at 6 m min^{-1} and they were drawn over the hot plate to the drawing rollers running at a higher speed. The drawing temperatures and ratios will be mentioned later in the Results section. In two-stage drawing, the as-spun fibers were partially drawn in the first stage; then, the partially drawn fibers were fed into the drawing unit again for a second-stage drawing at a higher temperature.

Annealing of the drawn fibers was carried out by placing the fibers (tightly wrapped on metal bobbins) inside a heated oven. The annealing temperature was usually set at 130°C as PP has the highest crystallization rate at this temperature. The annealing time was usually 5 h.

Relaxation of the fibers was carried out at 150°C by feeding the drawn fibers at 40 m min^{-1} and collecting them on the take-up rollers at the lowest speed just before the fibers began to loosen up. The extent of relaxation was calculated from the percentage increase in the fiber thickness in tex (weight in g of 1000 m fiber) of the relaxed and the original samples, respectively.

Thermal stability of the fibers was expressed as the thermal shrinkage of the PP fibers at various temperatures. One meter of the yarn was wrapped loosely on a metal frame and the percentage shrinkage in fiber length was measured after the frame was placed in boiling water or in a heated oven with temperature set at 130 and 150°C . The fibers were usually conditioned for 10 min.

Polyblend fibers made from mixtures of PP, poly(ethylene terephthalate) (PET), and various liquid crystal polymers (LCPs) were used to assess the thermal stability of PP fibers after the incorporation of the second component with high thermal stability. The preparation conditions for these fibers as well as some of the characterization methods can be seen in previous publications.²⁻⁴

RESULTS AND DISCUSSION

One-stage Drawn Fibers

In one-stage drawing, the as-spun fibers are stretched between two pairs of advancing rollers. The randomly oriented molecules of the as-spun structure align in the longitudinal direction of the fiber because of the draw line tension. At elevated temperatures which are usually applied for drawing, the initial imperfect structure of the as-spun fibers are destroyed and a more ordered molecular and crystalline structure is formed. However, because of

the relatively short residence time, the one-stage drawing process is usually incomplete and internal stresses are frozen in the partially oriented fibers. During prolonged use or in applications at elevated temperatures, the relaxation of internal stresses results in the loosening of the oriented structure and longitudinal shrinkage occurs due to the reorganization of the previously stretched macromolecules.

Table I shows the thermal shrinkage of the one-stage drawn fibers and that of the relaxed sample. It is clear that for the one-stage drawn fibers the thermal stability was poor even in boiling water. The shrinkage became worse at higher temperatures, with that at 130°C exceeding 10%.

Thermal shrinkage of the PP fibers can be greatly reduced after the fibers are relaxed at 150°C . This is natural as the relaxation process provided the opportunity to remove the internal stresses that were left frozen after drawing. As can be seen in Table I, after the relaxation process, the thermal shrinkage at 130°C changed from 10.7% for the control sample to 1.2% for the relaxed sample, showing a significant improvement in the thermal stability of the PP fibers. However, with the relaxation of the oriented structure, the fiber tenacity reduced from 0.816 N/tex for the control sample to 0.472 N/tex for the relaxed sample, representing a significant reduction in the tensile properties of the PP fibers.

Multistage Drawn Fibers

As pointed out earlier, during the drawing process, the polymeric chains are aligned in the fiber axis because of the draw line tension. Time and temperature are the two most important parameters affecting the extent of chain orientation. A high temperature is usually required to reduce draw line tension and to increase molecular movement. However, at a high draw temperature, the increased molecular movement leads to an increased extent of relaxation of the oriented structure. To some extent, this deorientation effect determines the upper limit of the

Table I Thermal Stability of the One-stage Drawn Fibers

Sample	Thermal Shrinkage (%)	
	At 100°C	At 130°C
Drawn at 155°C ($r = 8.34$)	-5.2	-10.7
Above sample relaxed by 19.7% at 150°C	+0.5	-1.2

Table II Thermal Stability of the Two-stage Drawn Fibers

Sample	Thermal Shrinkage (%)		
	At 100°C	At 130°C	At 150°C
$t_1 = 120, T_2 = 170^\circ\text{C},$ $r_1 = 8.14, r_2 = 1.26^a$ Above sample relaxed by 2.7% at 150°C	-3.6	-7.5	-21.7
	-0.2	-1.8	-19.8

^a T_1 and T_2 : first- and second-stage drawing temperatures, respectively; r_1 and r_2 : first- and second-stage draw ratios, respectively.

drawing temperature, and one-stage drawing is usually carried out at temperatures far below the melting point of the polymer.

When the as-spun fiber is partially drawn, the partially oriented structure is capable of withstanding a high draw line tension. In addition, because a partially oriented structure is thermally more stable, it is possible to apply a higher drawing temperature in the second-stage drawing. This process of combining an initial drawing at a relatively low temperature and a more complete drawing at a high temperature has been used to produce high-tenacity/

high-modulus fibers, producing the so-called super-drawn fibers.^{5,6}

Table II shows the thermal shrinkage results of the two-stage drawn fibers. It is clear that the shrinkage was much less for the two-stage drawn fibers than for the one-stage drawn ones. The relaxed sample showed an even higher thermal stability than that of the control sample. The fiber tenacity was 0.820 N/tex for the relaxed sample and 0.907 N/tex for the control sample. The reduction in fiber tenacity is significantly lower than that observed in the one-stage drawing. This may be attributed to the fact that with the anticipated high draw line tension and the high draw temperature a more stable structure is formed in the second-stage drawing. Also, by combining the two-stage drawing and the relaxation process, it is possible to produce fibers with both a high tenacity and a high degree of thermal stability.

Figure 1 shows the DSC curves of the as-spun, partially drawn, and two-stage drawn PP fibers. It is clear that with the two-stage drawing there was increased crystallinity for the PP fibers, thereby contributing to the high thermal stability of the two-stage drawn fibers.

Table III shows the thermal shrinkage of three-stage drawn fibers at different third-stage drawing temperatures. In the third-stage drawing, because the fibers possess a relatively high degree of orien-

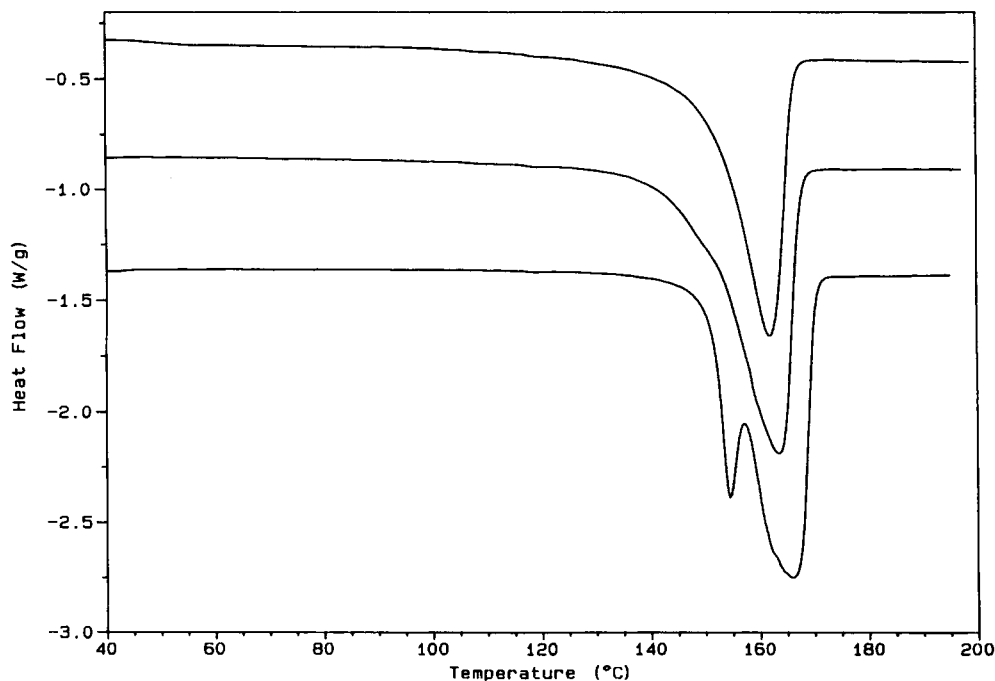


Figure 1 DSC curves of as-spun, partially drawn, and two-stage, fully drawn, PP fibers (temperature rate $10^\circ\text{C min}^{-1}$).

Table III Thermal Stability of the Three-stage Drawn Fibers

Drawing Temperature (°C)	Draw Ratio ^a			Tenacity (N/tex)	Thermal Shrinkage (%)	
	r_1	r_2	r_3		At 130°C	At 150°C
130	7.71			0.711		
150		1.18		0.812	-16.1	-46.5
170			1.33	0.885	-9.0	-41.4
175			1.41	0.863	-6.5	-27.9
180			1.35	0.931	-5.3	-24.2
185			1.29	0.798	-3.3	-9.8

^a The as-spun fibers were drawn at 130°C for the first-stage drawing; they were then drawn at 150°C before they were drawn in the third stage at temperatures between 170 and 185°C.

tation and crystallinity after the second-stage drawing, they can be drawn at temperatures above their melting temperature. As can be seen in Table III, with the increase in the third-stage drawing temperature, there is remarkable improvement in the thermal stability of the resultant fibers. The shrinkage at 150°C decreased sharply with the increase in the third-stage drawing temperature. With the sample drawn at 185°C, the fiber shrinkage at 150°C is less than one-quarter of that drawn at 170°C. As 185°C is 20° higher than the melting point of PP, it is possible that at this temperature the imperfect and thermally unstable structures are largely destroyed and stable structures are formed under the high drawing temperature.

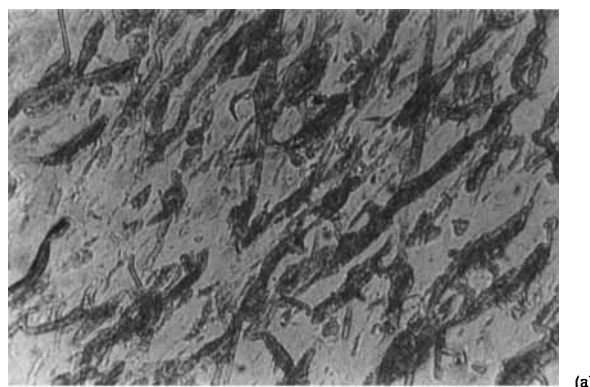
Effect of Annealing

Annealing of the drawn fibers at an elevated temperature over a period of time provides the opportunity for the macromolecules to resume a more relaxed configuration, thereby reducing the internal

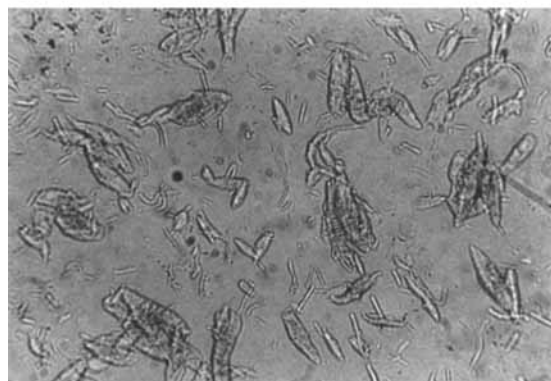
stresses in the fibers. It also provides the condition for the fiber to form a more perfect crystalline structure.^{7,8} As can be seen in Table IV, there was significant reduction in the thermal shrinkage of the two-stage drawn fibers after annealing at 130°C for 5 h. After the fibers were further relaxed at 150°C, they showed no shrinkage in boiling water, while the shrinkage at 130°C was reduced to only 1%. This result was further improved by a different arrange-

Table IV Effect of Annealing on the Thermal Stability of PP Fibers

Sample	Thermal Shrinkage (%)	
	At 100°C	At 130°C
Two-stage drawn, annealed at 130°C for 5 h ($r_1 = 8.14$, $r_2 = 1.26$, $T_1 = 120^\circ\text{C}$ and $T_2 = 170^\circ\text{C}$)	-0.9	-2.5
Above sample relaxed at 150°C	0	-1.0
Above sample two-stage drawn, relaxed at 150°C and then annealed at 130°C for 5 h	0	-0.2



(a)



(b)

Figure 2 Hot-stage photomicrographs ($\times 400$) of PP and Rodrun LC3000 polyblend fibers (PP/LCP wt/wt ratio 100/20): (a) as-spun fibers; (b) drawn fibers.

ment of the drawing, annealing, and relaxation processes. In Table IV, it can be seen that the fibers showed minimum shrinkage when they were two-stage drawn, relaxed, and then annealed at 130°C for 5 h. With this arrangement, the thermal shrinkage at 130°C was reduced to merely 0.2%.

Although it is not usually practiced in the processing of man-made fibers, by annealing the as-spun fibers at 130°C for 16 h, the fibers showed only 5.8% shrinkage at 150°C after the annealed fibers were drawn at 120 (×6) and 170°C (to the maximum extent) and then relaxed at 150°C. It is possible that when the as-spun fibers are annealed, the PP spherulite grows in diameter, and these larger and more perfect crystallites are deformed during the drawing process to form larger and more stable fibrils in the drawn fibers.⁹⁻¹¹

Polyblend Fibers

In all the above samples, the thermal stability of the PP fibers was poor at 150°C. This is more an inherited problem from the low melting temperature of PP than from the processing conditions. To improve the thermal stability of the PP fibers at this temperature, which can be important for such applications as rubber reinforcement, it was deemed necessary to modify the fiber structure by introducing a thermally stable component into the PP fibers.

In a few previous publications,²⁻⁴ attempts were made to study the effect of incorporating LCPs into PP fibers for improving the fiber strength and modulus. It was shown that with proper control of the processing conditions thin and long microfibrils of LCP can be formed in PP fibers, as can be seen in the hot-stage photomicrographs of PP/Rodrun LC3000 polyblend fibers containing 20% LCP (Fig. 2).

Table VI Thermal Shrinkage of PP/Polyester Polyblend Fibers: PP/PET Wt/Wt Ratio 80/20

Sample	Thermal Shrinkage (%)	
	At 130°C	At 150°C
Two-stage drawn sample, drawn at 120 (×6) and 170°C (maximum extent)		
PP	-6.8	-31.0
PP/PET	-7.0	-13.2
Above samples annealed at 130°C for 5 h		
PP	-2.6	-21.6
PP/PET	-2.2	-11.3

Table V shows the thermal shrinkage results of the PP and PP/LCP polyblend fibers. It is clear that with the addition of LCPs significant reduction in the thermal shrinkage of the PP fibers was brought about. For the two-stage drawn fibers, a significant reduction was observed at 130°C, although the thermal stability at 150°C was still poor for the fibers containing 10% LCP. All the fibers showed improved thermal stability after they were annealed at 130°C for 5 h. The fibers also showed improved thermal stability when the LCP concentration was increased to 20%. In fact, after two-stage drawing and annealing, the PP/Rodrun fiber (pp/LCP wt/wt ratio = 100/20) had thermal shrinkage of 0.5 and 2.9% at 130 and 150°C, respectively, which corresponds well with the requirement for applications in rubber reinforcement.

LCPs are quite expensive at the moment, and it would be advantageous if the improvement in thermal stability can be achieved by adding conventional

Table V Thermal Stability of Two-Stage Drawn Fibers from PP and PP/LCP Blends

Sample	Thermal Shrinkage			
	Two-stage Drawn Samples		Annealed at 130°C for 5 h	
	At 130°C	At 150°C	At 130°C	At 150°C
PP	-13.3	-35.3	-2.6	-18.3
PP/Vectra A900 (wt/wt ratio = 100/10)	-7.7	-25.9	-2.0	-11.9
PP/Vectra B950 (wt/wt ratio = 100/10)	-7.5	-25.2	-2.5	-14.2
PP/Rodrun LC3000 (wt/wt ratio = 100/10)	-7.0	-26.0	-1.8	-11.0
PP/Rodrun/PET (wt/wt ratio = 100/10/2)	-6.4	-19.0	-1.4	-7.9
PP/Rodrun LC3000 (wt/wt ratio = 100/20)	-4.4	-7.2	-0.5	-2.9

Monofilament fibers were used in this study. For preparation conditions, see refs. 2-4.

polymers into the PP fibers. Table VI shows the thermal stability of polyblend fibers made of PP and PET. For the two-stage drawn fibers, the thermal shrinkage at 130°C was only slightly improved for the polyblend fibers. At 150°C, however, there was a remarkable reduction in the thermal shrinkage of the polyblend fibers. This is more obvious for the annealed sample, which showed thermal shrinkage at 150°C of 11.3%, as compared to 21.6% for the control sample. This remarkable increase in the thermal stability reflected the contribution of the thermally stable polyester component in the polyblend fiber.

CONCLUSIONS

This study has shown that thermal stability of polypropylene fibers is strongly affected by the processing conditions. The fibers showed increased fiber strength and thermal stability from the multistage drawing. The relaxation process improved the thermal stability of the fibers; however, only with the multistage drawing process were the fibers capable of retaining a high strength after the relaxation process. It was found that the thermal shrinkage at 130°C can be completely removed by using a combined process of two-stage drawing, relaxation, and annealing. The shrinkage at 150°C was poor for most of the drawn fibers. This can be improved by either a process of three-stage drawing with a very high third-stage drawing temperature or by annealing the as-spun fibers and then drawing the annealed fibers with the two-stage drawing process. Finally, this study has also shown that the thermal stability of

polypropylene fibers can be greatly improved by blending a thermally stable component such as liquid crystal polymers or poly(ethylene terephthalate) into the polypropylene fibers.

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