# Dyeing Behavior of Polypropylene Blend Fiber. III. Effect of Drawing on Dyeability

# JIŘÍ AKRMAN,\* JOSEF PŘIKRYL

Department of Textile Chemistry and Fibers, University of Pardubice, CZ 532 10, Pardubice, The Czech Republic

Received 4 June 1998; accepted 25 August 1998

ABSTRACT: A modified polypropylene fiber was prepared containing 6% of a basic polymeric additive. The fiber was drawn to various ratios and its dyeability with an acid dye was tested. Structural changes due to the drawing were evaluated by application of eight different physical techniques: wide-angle X-ray diffraction, small-angle X-ray scattering, dark-field and optical microscopies, scanning electron microscopy, and density, birefringence, and tensile testing. Variations in dyeability were attributed to density variations from macrovoids in the specimen. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 719–727, 1999

Key words: polypropylene fiber; dyeing; additive; drawing; porosity

# INTRODUCTION

Our earlier articles,<sup>1–3</sup> dealt with the preparation of dyeable polypropylene (PP) fiber by the method of dispersion of a small amount of basic polymeric additive (see Fig. 1) followed by spinning of this dispersion. The modified PP fiber is dyeable with polar, water-soluble dyes in spite of the hydrophobic nature of the basic fiber-forming polymer. Ionized molecules of acid dyes are unable to penetrate through a PP layer; hence, there emerges a question as to their diffusion toward the center of the fiber. Ahmed<sup>4</sup> considered three possible mechanisms of dyeing of basically modified PP fibers:

- (a) The dye molecules diffuse in the fiber via the interconnected particles of the additive;
- (b) The dye molecules diffuse into the fiber in a nonionized state as the corresponding sulfonic acid; and
- (c) The dye diffuses into the fiber through sub-

microscopic crack fissures formed during spinning, drawing, and heat setting.

The diffusion via the additive particles is enabled by the character of the dispersion (a network-in-matrix type). In the continuous PP phase, the additive forms interconnected channels reaching to the fiber surface, which was confirmed by investigation of ultrathin sections of fibers using electron transmission microscopy.<sup>1</sup> The hypothesis of diffusion through the microchannels of the additive is supported by the nonlinear dependence of sorption upon the additive content and also by the ring-dyeing fibers containing lower amounts of the additive. This diffusion mechanism is also supported by the fact that more polar dyes (those with two sulfonic groups) exhibit a higher affinity to the fiber.<sup>2</sup>

Another experimental finding that supports the hypothesis of diffusion through the additive channels is the effect of plasticizers.<sup>3</sup> Compounds having a plasticizing effect on PP should facilitate the sorption of dyes. However, we found that an addition of dichlorobenzene, naphthalene, *o*-phenylphenol, and lauryl alcohol to the dyeing bath has an opposite effect—it lowers the degree of exhaustion of dye from the bath. The diffusion of

<sup>\*</sup> Present address: Research Institute of Organic Syntheses, CZ 532 18 Pardubice-Rybitví, The Czech Republic. Correspondence to: J. Přikryl.

Journal of Applied Polymer Science, Vol. 73, 719-727 (1999)

<sup>© 1999</sup> John Wiley & Sons, Inc. CCC 0021-8995/99/050719-09

dye into fiber in the form of nondissociated sulfonic acid of the dyestuff represents another possible dyeing mechanism since the sorption of dye increases with decreasing pH of the dyeing bath. In strongly acidic solutions, free sulfonic acids of dyestuffs are formed from the respective sodium salts, and these acids could diffuse into the fiber by a polysolution mechanism—in the nonionized state—and thus resemble a disperse dye. Nevertheless, experiments with the Acid Orange 7 free acid showed a much slower dyeing course as compared with that of the acidified solution of sodium salt of dyestuff.<sup>3</sup>

Another fact that initiated the present discussion was the experiments with the fiber in which basic dye-binding sites had been quaternized by the action of methyl iodide vapors. Sorption of dyes by the fibers pretreated in this way is independent of the pH value of the dyeing bath: The dyeing can be achieved in a bath of low acidity. The experimental results indicate unambiguously that the dyeing process is an ionic exchange, and the diffusion of a unionized sulfonic group plays a minor role.<sup>3</sup>

It could be anticipated that the dveing process is describable as a mere interaction of the dyestuff with the additive, the PP matrix presenting no barrier to the penetration of the dye molecules. However, investigation of various types of basically modified PP fibers showed<sup>4</sup> that the fiber samples produced at different spinning conditions are dyed to considerably different degrees of saturation. Similarly, the sorption of the dyes is dramatically influenced by the drawing of fibers. Any change in the fine structure results in changed dyeability. Variations in the rate and equilibrium properties of dyes occurred, reflecting the physical differences which exist between one batch of fiber and another. The main factors governing the dyeing behavior of polymers are the crystallinity, orientation, and size of crystalline regions as well as the mobility of the polymer chains characterized by the glass transition temperature. Thus, the total number of amorphous regions and the accessibility of these regions control the dye uptake and moisture absorption. The drawing induces compression in the interfibrillar amorphous layers with the result of the reduction of the molecular mobility. The reduced molecular mobility affects the properties overall, but, in particular, some properties more directly related to the mobility phenomena such as transport properties. Stress and enhanced temperature in drawing can also induce crystallization and growth of the crys-



**Figure 1** Preparation of *N*-substituted styrene–maleimide copolymers.

talline portion in the fiber. The diffusion of dyes is realized through the less ordered regions in the fiber.

The mechanism usually accepted for describing the drawing of PP fibers is based on the concept of instability of the microstructure in the initial stage of drawing and subsequent gradual restabilization on drawing it further. A region of small draw ratios where deformation occurred by spherulite deformation was followed by one of higher draw ratios where microfibrils as a new morphological unit were formed. For higher draw ratios, plastic deformation is accompanied by both microfibril formation and some spherulite deformation as reflected by changes in both orientation and crystallite size. At the morphological level, the originally chain-folded lamellar structure of nondrawn fiber is transformed on drawing into a microfibrillal one. Separation of crystal lamellae leads to microvoid formation. This is evidenced by the high intensity of diffuse small-angle X-ray scattering (SAXS) observed from the sample during deformation. Spinning and subsequent drawing of PP fibers containing foreign incompatible particles of the additive provides favorable conditions for the formation of microfractures and microcracks. The continuous and the dispersed phases exhibit different deformabilities as well as interfacial tension. The microfractures and pores loosen the structure and help to open up the fiber. It is clear that even small porosities in fibers can be important through their influence on other, diffusional properties like swelling, dyeing, absorption of moisture, and so on. Porosity in fibers may also affect their outward appearance: for instance, luster and depth of shade after dyeing. As a result, the dyeability increases with the draw ratio in contrast to fibers made from one



Figure 2 Decrease in elongation from draw ratio.

type of polymer where the system becomes more ordered and dyeability usually decreases with increasing draw ratio. The present article deals with changes of the inner structure of the modified PP fiber upon drawing and with their effect on dye uptake.

## **EXPERIMENTAL**

#### **Materials**

A normally spun 33 filament PP yarn (airquenched) containing 6 wt % of the additive<sup>2</sup> (Fig. 1) was drawn to different draw ratios at the temperature of a heated plate ( $110^{\circ}$ C) and the speed of 80 m/min on a laboratory drawing machine. All draw ratios reported were calculated from denier reduction.

## **Tensile Properties**

Load-elongation curves were obtained using an Instron 1122 tensile tester at a standard strain at 23°C and 50% relative humidity. The tenacities and the elongations at break of the PP fibers at various draw ratios are shown in Figures 2 and 3.

## Birefringence

Optical retardation of the fibers was measured with a Zeiss polarizing microscope equipped with an Ehringhaus compensator at a wavelength of 551 nm. A drop of silicon oil was used as the immersion liquid (refractive index 1.515) in the measurements. A Zeiss eyepiece screw micrometer was used for measurement of the fiber diameter. As the fibers were found to possess an unnaturally large diameter, correction was taken for the void volume: The birefringence calculation used the fiber diameter obtained from the draw ratio and diameter of the undrawn fiber. Using the optical birefringence combined with the X-ray method, we calculated the orientation of noncrystalline and crystalline regions and the average orientation. The last quantity mentioned was expressed by the orientation factor  $f_0$ :

$$f_0 = (\Delta n / \Delta n_i) \cdot (\rho_K / \rho)$$

where  $\rho_K$  and  $\rho$  are the densities of a fully crystalline fiber and the investigated one,  $\Delta n$  stands for the birefringence measured, and  $\Delta n_i$  is the birefringence of a fiber with an ideal orientation.

The value of the average orientation was then divided among the contributions of the crystalline and noncrystalline regions:

$$f_0 = \beta \cdot f_K + (1 - \beta) \cdot f_A$$

where  $\beta$  and  $f_K$  are the crystallinity and orientation factor of the crystalline regions determined by X-ray analysis, respectively, and  $f_A$  is factor of orientation of the noncrystalline regions. The results are summarized in Figures 4 and 5.

# Wide-angle X-ray Diffraction Studies (WAXS)

These measurements were carried out with a URD-6 (Carl-Zeiss) diffraction unit, pinhole collimation, nickel-filtered copper radiation (wavelength 154 pm) at the conditions for measuring the reflection and by the Bragg–Brentano method



Figure 3 Increase in tenacity from draw ratio.



Figure 4 Variations of orientation factor from draw ratio.

with a discriminator of impulse heights. To eliminate the effect of orientation, the measurement of the crystallinity and crystal magnitude (plane 110) was carried out with a rotatable holder (Figs. 6 and 7). In our study, we observed only the monoclinic  $\alpha$ -crystal modification of PP.

## Small-angle X-ray Scattering (SAXS)

The parameters that characterize the supermolecular structure—invariant—were assessed. The results of the measurements were analyzed in terms of the theoretical approaches by Porod, Glatter, and Guinier.<sup>5–7</sup> Quantitative analysis of the SAXS data were performed with the aid of a computer program.<sup>8</sup> SAXS measurements represent measurable regions of low-electron density, which are then interpreted as true voids. The



**Figure 6** Dependence of crystallinity on draw ratio of fibers.

results (porosity, inner specific area, microvoid size) are presented in Table I.

#### Density

The densities of the PP filaments were determined at 20°C with a density-gradient column<sup>9</sup> prepared from methanol-water mixtures calibrated with glass floats ranging in densities from 760 to 850 kg/m<sup>3</sup>. The values obtained must be taken with a certain reserve because it is not known to what extent the liquid (80% aqueous methanol in our case) penetrates into the fiber and fills its pores. The density values obtained were used to assess the porosity of fibers, the latter being considered as composed of four phases: crystalline PP, amorphous PP, additive,



Figure 5 Variation of birefringence from draw ratio.



**Figure 7** Dependence of crystal size in fibers on draw ratio.

Draw	SAXS	Specific	Microvoid
Ratio	Porosity(%)	Area(m²/g)	Size(nm)
$1.0 \\ 1.5 \\ 2.2 \\ 2.9 \\ 3.6$	0.28 0.33 0.32 0.50 2.14	3.18 3.35 3.04 3.21 2.11	$4.06 \\ 4.38 \\ 4.72 \\ 4.07 \\ 4.72$

Table ISAXS Porosity, Inner Specific Area,and Average Microvoid Size

and cavities filled with air. The calculation adopted the crystallinity degree obtained from X-ray diffraction and the density values of 850 and 936 kg/m<sup>3</sup> corresponding to wholly noncrystalline and wholly crystalline ( $\alpha$ -modification) PPs, respectively; the additive was present in the amount of 6% and its density<sup>2</sup> was 1054 kg/m<sup>3</sup>. The porosity, from density measurements, provides some information about "voids" that are not necessarily true voids, but rather local random regions of low-density material. In a sense, such voids represent statistical fluctuations in density. The porosity and density changes of the fibers with the draw ratio are depicted in Figures 8 and 9.

## **Dark-field Microscopy**

Dark-field microscope pictures (Fig. 10) were obtained with the use of a Zeiss polarizing microscope equipped with a Zeiss dark-field condenser attachment. A normal optical photograph of the



**Figure 8** Density changes of fibers induced by drawing.



**Figure 9** Draw ratio versus porosity (calculated from density).

fiber dyed with C.I. Acid Blue 45 was also taken (Fig. 11).

# Scanning Electron Microscopy

The morphology of the inner structure of the fibers was investigated using electron microscopy. A bundle of drawn fibers of a 2.9 draw ratio was broken over the edge of a scalpel in liquid nitrogen. The inner morphology of the fiber in the direction of the fiber axis was investigated by a peeling technique: The fiber surface was notched with a sharp razor blade and the surface layer was peeled off with a pair of tweezers (Fig. 12). Specimens were subsequently coated with a 10nm-thick gold film using a sputter coater. Investigations were carried out using a Tesla BS 340 scanning electron microscope. Images were obtained using the secondary electron signal.

## Dyeing

The dyeing was carried out at 95°C in a dyeing apparatus (Linitest) at infinite dye-bath conditions. The fiber sample of about 50 mg was immersed into the bath (450 mL) containing 800 mg/L Egacid Yellow 2R (C.I. Acid Yellow 42, supplied by Ostacolor a.s., Pardubice, Czech Republic). The bath acidity was adjusted at pH 3.5 using acetic acid. A series of such samples immersed in the dye bath for different periods of time provided data relating the dye concentrations in the fiber to the time of immersion in the dye bath. The equilibrium parameter of dyeing was expressed as the equilibrium sorption in mg/g and the dye-





Figure 10 Dark-field photomicrograph of void formation during drawing: (a) draw ratio 1, no observable light scattering on fiber; (b) draw ratio 3.6, light scattering on voids.

ing kinetics as the dyeing half-time defined as the time needed to reach half the equilibrium sorption (Figs. 13 and 14). The dye content in the fiber was measured using a Unicam SP 600 spectrophotometer and glass cells of 10-mm path length. The weighed sample (about 15 mg) was dissolved in a mixture of 5 mL chlorobenzene and 0.5 mL water in a boiling water bath. Then, the mixture was left to crystallize at room temperature for 2 h, whereafter its volume was adjusted to 50 mL by adding a 0.5% sodium hydroxide solution in an 80:20 ethanol-water mixture. After filtration, the extinction was measured at 435 nm using the analogous sample prepared from the undyed fiber as a reference.

## **Reflectance Spectra**

The reflectance measurements were carried out using a Datacolor 3890 spectrophotometer, the

yarn samples being wound onto cardboard to form  $2.5 \times 2.5$ -cm-square samples. The color strength is taken as the sum of the weighed functions in the visible region of the spectrum (400–700 nm) (see Fig. 15). Differences in the color strength were evaluated by visual assessment according to the gray scale using the sample with the maximum draw ratio as a standard (Fig. 16).

## **RESULTS AND DISCUSSION**

Figure 2 shows that the tenacity of the PP fibers increases with increasing draw ratios, which signifies that the tensile strength is very much related to the degree of alignment of the molecular chains parallel to the fiber axis. The value of the breaking elongation (%) falls sharply at an initial stage of drawing, but at higher draw ratios (draw ratio 2.9), the changes are not so significant and the fiber acquires mechanical properties similar to those of unmodified PP fiber (Fig. 1).

The birefringence, which reflects the overall orientation in the course of drawing, increases (Fig. 5). In the initial phases up to the draw ratio of 1.5, the orientation in the crystalline regions increases, but in amorphous regions, it decreases as mild deorientation occurs; this is consistent with a model of lamellae rotation as the controlling process in the low-draw region. Moreover, the additive particles are dispersed in the amorphous phase and prevent its orientation. In the further course of drawing, it is the increasing order of the noncrystalline regions which predominantly contributes to the overall orientation. (Fig. 4).

X-ray techniques provide a deeper insight into the structure of crystalline polymers. These meth-



**Figure 11** Optical micrograph of dyed PP fiber; draw ratio 2.9.





**Figure 12** Scanning electron micrograph of internal structure of fibers; draw ratio 2.9: (a) cross section—break; (b) microfibrillar texture.

ods permit the determination not only of the quantitative crystalline-phase ratio but also of the size of the crystallites. The crystalline structure originally formed is destroyed by the drawing, which is confirmed by the decreasing magnitude of the crystallites and the decrease in the crystalline portion (Figs. 6 and 7). The finding that drawing is accompanied by amorphization indicates that the drawing took place outside the optimum temperature interval. The starting fiber is also characterized by a high degree of orientation due to elongation in the nozzle during spinning (draft under die).

The orientation of fiber increases with the proceeding drawing and, apparently paradoxically, the dyeability also increases, as can be seen from both dyeing parameters—decreasing the halftime of the dyeing and increasing the equilibrium sorption (Figs. 13 and 14). The dye absorption is maximum where the apparent density of the fiber is minimum (Fig. 8), which leads to an idea that the mechanism of diffusion through voids and macrocracks is operating. Anomalously, low density indicates the presence of pores. The porosity calculated from the density reflects the color strength changes very well (Fig. 9). The steepest increase in porosity from 1.5 to 6% is observed in the middle range of the drawing ratios. This 6% of porosity together with the 6% of additive makes 12% of the volume of the PP fiber, giving ready accessibility for acid dyes.

From the point of view of practical dyeing processes, there follow two important consequences:

- 1. A nonuniform drawing may result in uneven dyeing. The differences in color strength, for example, can be evaluated according to the gray scale (Fig. 16).
- 2. There exists a certain optimal draw ratio at which the sorption of dyestuffs is at its maximum. This optimum draw ratio is 2.9 for the sample set studied (see Fig. 15). It was found that it also applies to other investigated dyestuffs, namely, C.I. Acid Yellow 25, Acid Yellow 61, Acid Red 114, Acid Blue 45, and Acid Blue 129.

The most valuable and useful information about the pore size and geometry is obtained from direct microscopic observation of the pore structure even though electron microscopy has its own problems, such as distortion during sectioning and nonrepresentative sampling. The section of the fiber broken in liquid nitrogen shows no perceptible pores or they are below the limit of reso-



**Figure 13** Draw ratio versus half dyeing time of C. I. Acid Yellow 42.



**Figure 14** Draw ratio versus equilibrium sorption of C. I. Acid Yellow 42.

lution, about 500 nm. The additive particles are not visible either since they coalesce with the structure of PP [Fig. 12(a)]. This proves the partial compatibility of the polymer blend. A normal microfibrillar texture was observed in the scanning electron microscope for drawn fibers [Fig. 12(b)]. This photograph shows no perceptible particles of the additive either. The latter can be seen only after dyeing the fiber with an acid dye (Fig. 11). In the drawn fiber, the additive is present in the form of particles elongated along the fiber axis and located between the PP microfibrils.

The fiber was examined with a dark-field microscope for any macrovoids that might be present. Figure 10 shows the following results: The unstretched fiber has no macrocracks. The



**Figure 15** Draw ratio versus color strength of dyed fibers of C. I. Acid Yellow 42.



**Figure 16** Draw ratio versus color difference of C. I. Acid Yellow 42.

stretched one exhibits a scattering at the macrovoids. The macrovoids are oriented in the direction of the fiber axis.

A technique for studying extremely small pores in fibers is based on the diffusive scattering of X-rays at small angles. This method appears to be suitable for only a very small pore range (less than 20 nm). The microporous structure is little developed in the samples investigated, which is confirmed by all the parameters observed (see Table I). The highest porosity of 2.14% was found with the sample drawn up to the maximum draw ratio. As this sample also has the lowest specific surface of pores, 2.11 m<sup>2</sup>/g, and the average magnitude of the pores is also small (4-5 nm), one can anticipate a broader distribution of magnitudes. An opposite dependence of porosity upon the inner surface of the pores with the PP draw ratio of 3.6 indicates that the greatest amount of pores have magnitudes above the limit of perceptibility by the X-ray method, that is, about 100 nm in this case. In the drawing process, it seems that the additive particles are not at the origin of micropore formation.

In the last phase of drawing (draw ratio above 2.9), a partial collapse of the overall porosity occurs (Fig. 9) but the microporosity increases (Table I). This can also be observed when measuring the fiber cross section and comparing it with the theoretical diameter of the fibers corresponding to the diameter decrease due to drawing. The fiber stretched to the maximum draw ratio showed a decrease in dyeability. Hence, it can be concluded that sorption of dyestuffs is affected by macrovoids of 100–500-nm magnitude.

Cross sections of the dyed fibers were observed under a microscope. The fibers with draw ratios of 2.9 and 3.6 were dyed uniformly over the whole cross section. On the other hand, the nonstretched fiber and that drawn to the ratios of 1.5 and 2.2 showed only ring-type dyeing. Hence, the contribution of macrovoids to the dyeing process consists of the fact that they enable uniform dyeing over the whole bulk of the fiber.

# **CONCLUSIONS**

Investigation of dyeing properties is valuable as a means of estimating the internal structure of a fiber, especially the state of amorphous and less ordered regions. In the case of modified PP fiber, it is important to correctly adjust the spinning and drawing parameters with regard to fiber porosity.

The morphological transformations occurring during the process were different in the high and low ranges of extension. These transformations can be identified from the structural data summarized as follows:

- 1. In the low-drawn regions (up to drawing ratio 1.5), the original structure present in the spun fiber is destroyed. The crystalline regions control the deformation.
- 2. In the intermediate stages of drawing (drawing ratios from 1.5 to 2.9), macro-

voids are formed. The macrovoids elongate in the fiber axis direction and the crystalline and noncrystalline regions are oriented as well. The spherulitic character of the fiber substructure is lost and the structure becomes microfibrillar. The dyeability increases.

3. In higher-draw regions (above 2.9), the drawing mechanism is changed. The plastic deformation is accompanied by partial collapse of the porosity, whereas, on the other hand, the microporosity increases. The dyeability is decreased.

# REFERENCES

- Akrman, J.; Kaplanová, M. J Soc Dyers Col 1995, 111, 159.
- Akrman. J.; Přikryl, J. J Appl Polym Sci 1996, 62, 235.
- Akrman, J.; Přikryl, J. J Appl Polym Sci 1997, 66, 543.
- 4. Ahmed, M. PP Fibres—Science and Technology; Elsevier: 1982; Chapter V.
- Small Angle X-ray Scattering; Glatter, O.; Kratky, D., Eds.; Wiley: London, 1982.
- 6. Glatter, O. J Appl Crystallogr 1980, 13, 7.
- 7. Vonk, C. G. J Appl Crystallogr 1975, 8, 340.
- Marcian, V.; Karnis, J. Chem Vlákna (Man-Made Fibres, Slovakia) 1986, 36, 83.
- 9. Beevers, R. B. Experiments in Fibre Physics; Butterworth & Co. Ltd.: London, 1970.