# Study on Dyeable Polypropylene Fiber and Its Properties

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**ABSTRACT:** A disperse dyeable polypropylene fiber has been prepared by admixing polystyrene to the polymer prior to extrusion. Polystyrene has been synthesized at suitable molecule weight and narrow mol wt distribution. The dyeability, mechanical properties, shrinkage, degree of crystallinity, and orientation of pure polypropylene or the blend fibers with different amount of polystyrene were investigated. In addition, the structure of the blend containing 4 and 6% polystyrene was also studied to explain the interesting dyeing behavior of the blend fibers. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3172–3176, 2001

Key words: dyeable fiber; polystyrene; polymer; molecular weight

## INTRODUCTION

Unmodified polypropylene fiber is difficult to dye due to the absence of dye sites in the molecular chain and high crystallinity. In recent years there has been considerable research to improve its dyeability. The dyeability of polypropylene fiber has been improved by blending or grafting with other polymers<sup>1-6</sup> or copolymerizing with other monomers<sup>8</sup> or metal complexes<sup>7,8</sup> that have been attempted. These different approaches have been discussed by Roshan Paul et al.<sup>9,10</sup>

Polypropylene, blended with small amount of polystyrene, is one of the most successful ways to improve its dyeability. Molkova et al.<sup>11,12</sup> have reported that shrinkage of polypropylene yarn could be increased by adding a small amount of polystyrene to isotactic polypropylene. Their aim was to

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reduce crystallinity to enable producing a highly shrinkage fiber. Polypropylene fiber and fiber spun from the blends of polypropylene and a small amount of polystyrene incorporated through melt blending prior to spinning were investigated for dveing performance in both untextured and textured forms by A. K. Sengupta, K. Sen, and colleagues.<sup>13,14</sup> The dyeing performance was improved with the addition of polystyrene, but the blend containing 5% polystyrene has a lower dye uptake than that with 2%. In this article, we shall prepare polystyrene and analyze the influence on dye uptake under different content of polystyrene. Furthermore, the contradiction with the results of A. K. Sengupta, K. Sen, and colleagues<sup>13,14</sup> will be explained.

#### **EXPERIMENTAL**

#### Materials

Styrene as a monomer and benzyl peroxide (BPO) as an initiator were of chemical grade. Sodium

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	Tensile Strength to Break (CN/dtex)	Elongation to Break (%)	Crystallinity (%)	Orientation (%)
Pure PP	3	19.6	58.8	90.1
PP/PS(98/2)	2.4	22.9	50.4	88.2
PP/PS(96/4)	2.2	24.5	44.3	87
PP/PS(94/6)	2.2	25.8	40.2	86.1
PP/PS(92/8)	2.1	26.5	38.1	85.6

Table I Influence of the Content of Polystyrene on the Properties of Blend Fibers

thiosulfate as a chain transfer agent was of analytical grade. Polyvinyl alcohol (PVA) as a protective agent was of commercial grade with the molecular weight between 75,000 and 79,000. Polypropylene (PP) as a basic polymer specified for fine fiber production was of suitable characteristics ( $M_w = 156,000, M_w/M_n = 2.1$ , degree of isotacity = 96%) from Dong Hua University Resin Factory. Silvatol as a deoil agent was of commercial grade from Ciba Co. The dyes used were C.I. Disperse Yellow 23 and C.I. Disperse Red 60 supplied by Shanghai Dye & Chemistry Factory No. 8. The commercial dyes were purified by the recrystallization method.<sup>13</sup> The stock solution was prepared by pasting 1 g of dye with a small quantity of dispersing agent and then adding distilled water to make 1% solution.

#### **Preparation of Polystyrene**

Styrene, BPO, and sodium thiosulfate were placed in a sealed glass tube with PVA and distilled water in a temperature-controlled water bath for 10 h to get the polystyrene at suitable molecular weight and narrow mol. wt distribution.<sup>15</sup> At the end of preparation, the product was washed with distilled water (40°C). Finally, the product was dried at 60°C under vacuum for 3 h.

#### **Preparation of Polypropylene Blends**

Polystyrene pellets in small proportions of 0, 2, 4, 6, and 8% were mixed and melted with isotactic polypropylene chips with a SHL-35 twin-screw extrusion machine at 160 to 250°C. The resultant chips were kept at 60°C under vacuum for 3 h.

#### Spinning and Drawing

The polypropylene and blend fibers were spun at  $200-250^{\circ}$ C by extruding the polypropylene and blend chips with a MST C-400 melt spinning machine with a 28 spinneret (L/D = 2; D = 1 mm),

and then drawn at  $100^{\circ}$ C with an FP-01 drawing machine at the ratio of 3.5 and obtaining the fiber with a dpf of 1.2 dtex.

## Dyeing

The fiber was scoured for 30 min with 1% owf Silvatol and 1% owf caustic soda at a material to liquor ratio of 1:100 at  $80^{\circ}$ C, followed by washing with distilled water and drying.

The fiber was dyed from finite bath (pH = 4.5) at a material to liquor ratio of 1 : 20 at 100°C in a beaker dyeing machine for 600 min to obtain equilibrium absorption of dye. After the completion of the dyeing cycle, the samples were washed three times in an acetone/water (50/50) mixture and rinsed twice with distilled water before dye estimation.

The estimation of dye on the fiber was done by extracting the dye from a known amount of dyed fiber using dimethyl formamide (DMF) at 110°C. The optical density of the extracted dye solution was measured by a 7520 spectrophotometer. From the optical value, the amount of dye in fiber was calculated through a calibration curve.

#### **Determination of Structure and Properties**

Boil-off shrinkage of different fibers was measured by immersing the fibers in boiling water  $(100^{\circ}C)$  for 5 min, and then they were removed and allowed to come to room temperature under ambient condition.

Degree of crystallinity was calculated from density measurement at 25°C by the density gradient column method with an MD-01 density determining instrument filled with a mixture of 1-propanol and water.

Degree of orientation was measured by the sonic velocity method with SOM-2 voice speed orientation determining instrument at 10 kHz.

Blended chips (4 and 6% polystyrene) were completely melt under 200°C and crystallized un-



**Figure 1** Influence of amount of polystyrene on dye uptake: (■) C.I. dispersed red 60; (●) C.I. dispersed yellow 23.

der 138°C. The behavior of crystallization for the blends was investigated and pictures were taken with special equipment that was made in our laboratory, equipped with an HM-C microscopic image manipulating instrument, VBSE 100 image dealing card, and numeral camera.

#### **RESULTS AND DISCUSSION**

Table I shows a proportional decrease and a proportional increase respectively with the increase of the content of polystyrene. But these values show the practical applicability of the polypropylene fiber in comparison with the values of all blend fibers.

There is a considerable effect on degree of crystallinity and orientation of the blend fibers. Table I also shows that the degree of crystallinity and orientation of blend fibers decreases heavily, especially for the degree of crystallinity. J. Radhakrishnan, U. P. Kanitkar, and colleagues<sup>16–19</sup> suggested that dye diffusion depended on two facts: the volume of the accessible region (amorphous region) and the tortuosity of the dye diffusion path. Because accessible region and the tortuosity are directly associated with degree of crystallinity and orientation, it is easy to dye when the degree of crystallinity and orientation decrease.

Figure 1 shows that under equilibrium condi-

tion of dyeing, the absorption of C.I. disperse yellow 23 on fiber is nearly the same as that of C.I. disperse red 60. Loosening the internal structure of the polypropylene fiber by incorporating small amounts of polystyrene results in a higher dye uptake. As the amount of polystyrene is increased from 2 to 8%, there is further increase of the dve uptake. It seems that there is a large conflict with the results of A. K. Sengupta, K. Sen, and colleagues.<sup>13</sup> They found that the sample containing 5% polystyrene had a lower dye uptake than that with 2%, although the latter had a higher crystallinity than the former. They postulated that the presence of rigid polystyrene segments in the matrix hindered molecular mobility. To explain their postulation, they found that shrinkage also decreased when the polystyrene content in the blend was increased from 2 to 5%, because an increase in shrinkage signified higher mobility of the molecular chains, which would facilitate diffusion of dye into the fiber.

Different molecular weight and mol. wt distribution would have different properties of polystyrene. The polystyrene with which A. K. Sengupta, K. Sen, and colleagues used as the additive was of commercial grade with a large molecular weight and wide mol wt distribution. However, Table II shows that there is a further increase in boil-off shrinkage when the polystyrene component is increased from 0 to 8%. This is due to the polystyrene used with low molecular weight and narrow mol wt distribution, which would facilitate dyeing of the blend fibers.

Referring to Figure 1 again, we see that certain interesting development in dyeing behavior among the blend fibers with various amount of polystyrene, different from those of tensile strength and elongation to break and shrinkage and degree of crystallinity and orientation, shall merit consideration. As the polystyrene component is increased from 0 to 8%, the dye uptake increases as a consequence. But dye absorption does not increase proportionally with the amount of polystyrene present in the blends. When the additive is changed from 4 to 6%, dye uptake increases obviously. Fibers with

Table II Influence of the Content of Polystyrene on the Shrinkage of Blend Fibers

	Pure PP	PP/PS(98/2)	PP/PS(96/4)	PP/PS(94/6)	PP/PS(92/8)
Shrinkage (%)	2.22	2.46	2.74	3.13	3.69



(a) PP/PS (96/4)

(b) PP/PS (94/6)

**Figure 2** Micrographs of polypropylene blended with polystyrene; (a) PP/PS (96/4); (b) PP/PS (94/6).

0 to 4% additive absorb less dyestuff because only small amounts of the additive component is present.

A truly compatible additive should form a solid solution with polypropylene. This does not happen in practice because of the strong tendency of polypropylene to crystallize. Moreover, polystyrene contains a benzoring, that is polar group, necessary to provide adequate binding. The structure of polypropylene blended with polystyrene greatly depends on the amount of additive. Jiri Akrman and Marie Kaplanova<sup>20</sup> reported that modified polypropylene fiber had been prepared by incorporating the styrene-amine resin Propimid into the polypropylene, followed by melt spinning. It was demonstrated with high-resolution transmission electron microscopy that such a network of microchannels of additive particles through which dye could diffuse could be formed at Propimid concentrations as low as 6% in polypropylene. Figure 2(b) shows that the microgragh of microchannels structure of modified polypropylene blended with 6% polystyrene is the same as modified polypropylene blended with 6% styrene-amine resin Propimid. We see that spherulites are formed, and many additive particles evenly distribute in the matrix, and the network of microchannels among particles is formed. The mechanism of diffusion of disperse dye molecules is along microchannels formed by the dispersed additive itself. As the amount of polystyrene is less than 4%, particles in the blend are isolated [Fig. 2(a)]. The structure characterized as a network in the matrix is necessary for the good dyeability of blend fibers.

# **CONCLUSION**

Dyeable polypropylene fiber has been prepared by mixing of polystyrene at low molecule weight and

narrow mol wt distribution with molten polypropylene, followed by spinning of the dispersion. Practically acceptable mechanical properties can be attained from the fiber blended with 2 to 8% polystyrene.

The degree of crystallinity and orientation are not only important to dye blend fibers, but a network of microchannels among additive particles is also important. Dyeing behavior among the blend fibers with various amounts of polystyrene, different from those of mechanical properties and shrinkage, increases irregularly. From the practical point of view, there is a need to use as little additive as possible to achieve a given color strength. This study shows that 6% polystyrene is at an optimum level due to formation of the network microchannels among additive particles.

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