

Yttria–Polystyrene–Polypropylene Composite for Fine Dyeable Fibers

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ABSTRACT: Fine polypropylene fiber has many excellent properties, but it is difficult to dye because of the absence of dye sites in the molecular chain and high crystallinity. Fine polypropylene/hybrid polystyrene (yttria) fiber melt-spun from blends of polypropylene and a small amount of nano-hybrid polystyrene with modified yttria incorporated was prepared to improve the dyeing properties. The dyeability, orientation, degree of crystallinity, phase morphology, and mechanical properties of pure polypropylene and the blend fibers were investigated. It was found that the crystallinity and morphology of these phases in the blend systems were

different. With the existence of nanohybrid polystyrene, the fine modified polypropylene filaments had practical mechanical properties, the amorphous region of the polypropylene/hybrid polystyrene (yttria) fiber increased, and the modified polypropylene fiber dyed easily and had good fastness to soaping because of the complexation of the disperse dye and yttrium in the blend system. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1563–1567, 2008

Key words: dyes/pigments; poly(propylene) (PP); polystyrene

INTRODUCTION

Polypropylene (PP) is one of the most important synthetic fibers because of its light weight and low water regain, its antimold, good chemical resistance, and mechanical properties [especially its fine filament (<1 dtex)], its good handle and wet and air permeability, and other advantages such as low cost and a large source. However, PP is difficult to dye because of the absence of polar groups, high crystallinity, and good stereoregularity; the applications of PP fiber are restricted in clothing.^{1,2} In recent years, there has been considerable research on improving its dyeability.^{3–7} Blending with other inorganic or organic materials is one of the most important methods; it breaks the regular aggregating structure of PP and introduces some groups with strong affinity to dyes. Sekar⁸ discussed these different approaches.

Blending PP with nanoparticles is an effective method to improve its dyeability. It was recently reported by Fan and coworkers^{9,10} that PP could be dyeable under the influence of nanoclay. However, it was also reported that the dyeing was uneven, and

this indicated that the nanoclay was not properly dispersed in the PP matrix because of high agglomeration and poor dispersion and because the particle size was not in the nanometer range.

Our colleagues have performed many studies on fine dyeable PP resins.^{11–14} A fine modified fiber, spun from blends of PP and a small amount of a polyolefin derivative before spinning, was prepared to improve the dyeing properties. However, its fastness to soaping was bad in practice because of a weak affinity between disperse dyes and the low-polarity polyolefin derivative, especially for medium-to-dark colors. To solve the bad fastness to soaping, we prepared another blend containing nanoyttria modified with a coupling agent and polystyrene (PS). In this article, the properties of a fine PP/hybrid polystyrene (yttria) [hy-PS (Y₂O₃)] fiber are reported.

EXPERIMENTAL

Materials

Y₂O₃ as an additive (100 nm) was acquired from Jiangsu Zhuoqun Nano Rare Earth Co., Ltd. (Jiangsu, China). The coupling agent organic titanate was chemical-grade. Styrene as a monomer and benzyl peroxide (BPO) as an initiator were chemical-grade. Sodium thiosulfate as a chain-transfer agent was analytical-grade. Poly(vinyl alcohol)

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(PVA) as a protective agent was commercial-grade with a molecular weight between 75,000 and 79,000. PP as a basic polymer specified for fine fiber production had suitable characteristics (weight-average molecular weight = 156,000, weight-average molecular weight/number-average molecular weight = 2.1, degree of isotacticity = 96%) and was obtained from Dong Hua University Resin Factory (Shanghai, China). Silvatol as a de-oiling agent was commercial-grade and was acquired from Ciba Co., Ltd. (Basel, Switzerland). The dyes used were C.I. Disperse Red 167 and C.I. Disperse Orange 30, and they were supplied by Dystar Co., Ltd. (Frankfurt, Germany). The commercial dyes were purified by a recrystallization method.¹⁵ The stock solution was prepared by the pasting of 1 g of dye with a small quantity of a dispersing agent and then the addition of distilled water to make a 1% solution.

Preparation of hy-PS (Y₂O₃) and PP blends

Styrene, BPO, sodium thiosulfate, and nanoyttria particles whose surface were modified with the coupling agent organic titanate were placed in a sealed glass tube with PVA and distilled water in a temperature-controlled water bath, with the temperature increasing progressively from 70 to 95°C, for 10 h. At the end of the preparation, hy-PS (Y₂O₃) was washed with distilled water (40°C) and dried at 60°C under vacuum for 3 h.

hy-PS (Y₂O₃) and PS pellets in small proportions were mixed and melted with isotactic PP chips in an SHL-35 twin-screw extrusion machine (Nanjing, China) from 160 (feeding zone) to 250°C. The resultant blend chips were kept at 60°C under vacuum for 3 h.

Fiber formation

The PP and blend fibers were melt-spun at 200–250°C by the extrusion of the PP and blend chips with an MST C-400 melt-spinning machine (Fujifilter, Tokyo, Japan) with a 28 spinneret (length/diameter = 2, diameter = 1 mm) and then drawn at 100°C with an FP-01 drawing machine (Shanghai, China) at a ratio of 3.5 to get the fiber with denier per filament (dpf) of 1 dtex.

Dyeing

Knitting fabric was prepared and scoured for 30 min with 1% owf Silvatol and 1% owf caustic soda at a material-to-liquor ratio of 1 : 100 at 80°C; this was followed by washing with distilled water and drying.

The fabric was dyed in a finite bath (pH = 4.5) at a material-to-liquor ratio of 1 : 20 at 100°C in a beaker-dyeing machine (Fong, Hongkong, China) for 10 h to obtain the equilibrium absorption of the dye. After the completion of the dyeing cycle, the sam-

ples were soaped for 30 min with a soaping agent (1% owf) at a material-to-liquor ratio of 1 : 50 at 80°C and then rinsed twice with distilled water before color estimation.

The estimation of the color darkness on the fabric (K/S value, where K is the absorption coefficient and S is the scattering coefficient) was measured with a Hitachi (Hongkong, China) 307 color photometer. The K/S value was calculated with the Kubelka-Munk formula:

$$K/S = \frac{(1 - R_\infty)^2}{R_\infty} = kc$$

where R_∞ is the reflecting ratio at a certain wavelength, k represents constant and c represents dye concentration in the fabric.

The estimation of fastness to soaping was measured with the method described by Huang.¹⁴

Determination of the structure and properties

PP, PP/PS, and PP/hy-PS (Y₂O₃) blended chips were completely melted under 220°C and crystallized under 138°C. The behavior of crystallization for the blends was investigated, and pictures were taken with a Nikon (Tokyo, Japan) SE/YS Alphaphot-2 YS2 polarizing microscope.

The degree of crystallinity was calculated from the density measurement at 25°C by the density gradient column method with an MD-01 density-determining instrument (Deqing, Zhejiang, China) filled with a mixture of 1-propanol and water.

The orientation was measured by the sonic velocity method on an SOM-2 voice speed orientation determining instrument (Shanghai, China) at 10 kHz.

The scanning electron micrographs of the PP/PS and PP/hy-PS (Y₂O₃) blend fibers were taken with a JSM-5600LV scanning electronic microscope (JEOL, Tokyo, Japan).

RESULTS AND DISCUSSION

Polar light microscopy (PLM) micrographs of the blend crystal

The dyeability of PP fiber is closely associated with its chemical composition, aggregating construction, and morphological structure, which is dependent on the components of the blend and their compatibility.

Figure 1 shows PLM micrographs of PP, PP/PS, and PP/hy-PS (Y₂O₃) blend crystals. The formation of even spherulites of pure PP, a distinct black cross, and a clear interface between crystals can be observed in Figure 1(a). After the blending with PS or hy-PS(Y₂O₃), many circular granules of PS dispersed in the regular spherulites, and the black cross was affected by the existence of other components

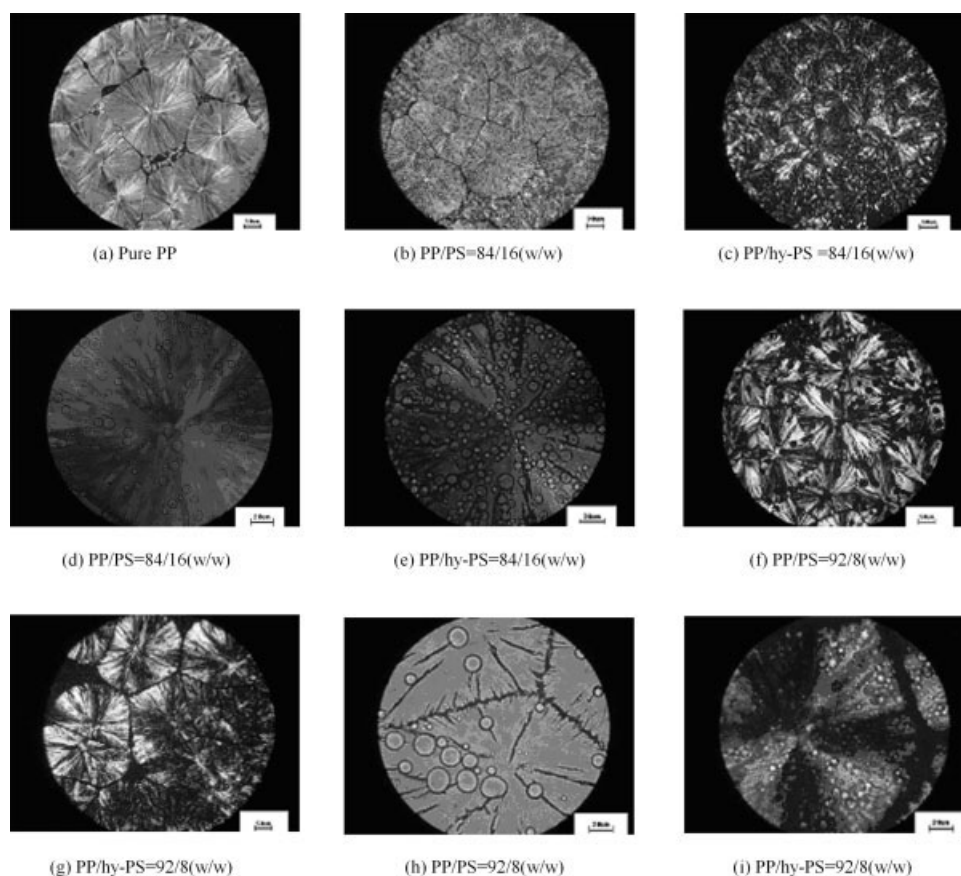


Figure 1 PLM micrographs of PP, PP/PS, and PP/hy-PS (Y_2O_3) blend crystal. (d,e,h,i) Amplified micrographs are included.

[as shown in Fig. 1(b,c,f,g)]. The round, dispersed phase of PS scattered evenly in the PP crystals, not aggregating massively among PS granules. The PP/hy-PS (Y_2O_3) system had better compatibility than the PP/PS system, and this could be confirmed by the phenomenon of a more blurry interface of PP/hy-PS (Y_2O_3) than that of PP/PS. Compared with PP/PS, the size of the dispersed phase and PP spherulites became smaller, the number of the dispersed phase obviously increased, and it scattered more evenly in PP/hy-PS (Y_2O_3). All this demonstrated that nanoytria particles in the blends were well dispersed and helped to disperse PS.

Crystallinity, orientation, and scanning electron microscopy of the blend fiber

The dyeing effect relies considerably on the degrees of crystallinity and orientation of the blend fiber. As the degree of crystallinity increases, the volume of the accessible region decreases, and the dye uptake decreases. As orientation of the blend fibers increases, the dispersing tortuosity from the fiber surface to the center becomes longer, and the dye uptake decreases.^{16,17}

Table I shows that the PP/hy-PS (Y_2O_3) fiber had a larger sonic velocity modulus and a smaller degree

of crystallinity than the PP/PS fiber, and the PP/PS fiber had a larger sonic velocity modulus and a smaller degree of crystallinity than the PP fiber. It might be speculated that nanoytria particles scattered in the interface of the PP phase and the PS phase acted as a wetting agent,¹⁸ and this helped the fiber to be drawn. On the other hand, nanoytria particles hindered the process of the axial arrangement of the PP molecule chain; the growth of the crystal slowed down because of the obstruction between hy-PS (Y_2O_3) and PP. As the degree of crystallinity

TABLE I
Orientation and Crystallinity of PP/PS and PP/hy-PS Blend Fibers

Sample	Draw ratio	Sonic velocity (km/s)	Sonic velocity modulus (gf/d)	Crystallinity (%)
PP (100)	3.4	4.26	204.59	59.35
PP (100)	3.8	5.88	390.96	66.77
PP/PS (92/8)	3.4	4.35	213.61	57.81
PP/PS (92/8)	3.8	6.25	441.41	63.66
PP/hy-PS (92/8)	3.4	5.63	358.66	57.30
PP/hy-PS (92/8)	3.8	7.27	597.68	60.28

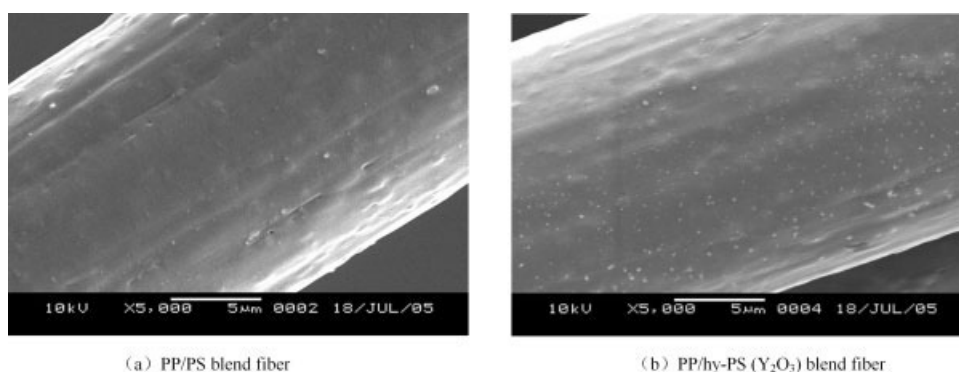


Figure 2 Scanning electron microscopy images of the surface morphology of PP/hy-PS (Y_2O_3) and PP/PS blend fibers.

of the PP/hy-PS (Y_2O_3) fiber decreased, the amorphous region increased, and this facilitated the diffusion of the dye into the blend fiber.

There were no solid granules on the surface of the PP/PS fiber besides a little dust, but some grooves could be found [Fig. 2(a)]. However, the sample blended with nanoyttria particles showed a different surface morphology [Fig. 2(b)]. There were a large number of fine, white granules on the surface of the PP/hy-PS (Y_2O_3) fiber, scattering evenly, not agglomerating among nanoyttria particles in the polymer. Compared with PP/PS, the PP/hy-PS (Y_2O_3) fiber had a smoother surface. PS and PP have different shrinkage properties. When the blend fibers were drawn at a certain tensile stress, nanoyttria particles in the interface of the phases, acting as a wetting agent, helped the PS phase to disperse in the blend fiber.

The presence of hy-PS (Y_2O_3) in PP reduced the degree of crystallinity and introduced the interfaces between the phases. These interfaces and amorphous areas formed tunnels in the fibers, and the interfaces increased the surfaces for disperse dye adsorption.

Dyeability and spinnability of the fine PP/hy-PS (Y_2O_3) fiber

Apolar PP is difficult to dye because disperse dyes have strong polarity. To improve its dyeability, it is necessary to blend it with other compositions with a strong affinity to dyes. A rare earth is usually used to improve dye uptake. It has been demonstrated by many researchers^{19–22} that dye uptake and fastness to soaping can be improved by a rare earth. When a rare earth is added to a dye bath, a dye with a molecular weight is formed by a complex reaction between the rare-earth ion and lone-pair-electron-supplying groups, such as $-CN$, $-N=N-$, $-NR_1R_2$, and $-OCO-$, which commonly appear in the disperse dye structure (Table II). Table III shows the K/S value and fastness to soaping of a PP/hy-PS

(Y_2O_3) blend (92/8) and PP/PS blend (92/8) dyeing with disperse dyes. Compared with the PP/PS blend, the PP/hy-PS (Y_2O_3) blend had a larger K/S value and better fastness to soaping. We suggest that some Y_2O_3 reacted with the acid, and yttric salt was formed first when the PP/hy-PS (Y_2O_3) fiber was dyed in an acid dye bath; then, a complex reaction occurred between yttric salt and the disperse dye. These reactions helped the blend fiber to improve its dye uptake and fastness to soaping.

On the other hand, good spinning processability and acceptable mechanical properties of modified fibers are important for practical applications. Spinning tests for PP, PP/PS, and PP/hy-PS (Y_2O_3) blends were carried out with the spinning tester. The spinnability of the blends was acceptable for the fine fiber process. PP/hy-PS (Y_2O_3) showed good spinnability like PP and PP/PS systems. This blend produced a stable spinning line in the tested output range from 240 to 250°C. These filaments also showed good tensile strength at break and drawability. Table IV lists the denier and mechanical data. All the drawn filaments reached less than 1 dtex/f. Table IV shows that the tensile strength and elonga-

TABLE II
Structures of the Disperse Dyes

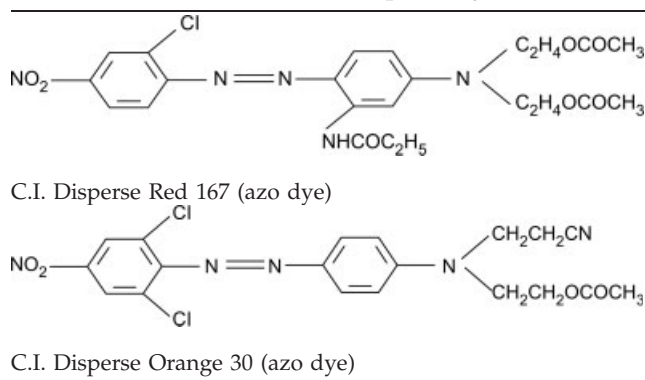


TABLE III
Dyeing Properties of PP/PS and PP/hy-PS (Y₂O₃) Blends

Sample	Dye	Concentration of dye (% owf)	K/S	Fastness to soaping (off-color of oriented sample)	Fastness to soaping (staining of white fabric)
PS/PP	C.I. Disperse Red 167	0.1	0.7045	3-4	4-5
PS/PP	C.I. Disperse Red 167	2	2.0039	4-5	4
PP/hy-PS (Y ₂ O ₃)	C.I. Disperse Red 167	0.1	0.8564	4	4-5
PP/hy-PS (Y ₂ O ₃)	C.I. Disperse Red 167	2	2.4629	4-5	4
PS/PP	C.I. Disperse Orange 30	0.1	0.4157	3	4-5
PS/PP	C.I. Disperse Orange 30	2	1.1284	4	3-4
PP/hy-PS (Y ₂ O ₃)	C.I. Disperse Orange 30	0.1	0.5495	3-4	4-5
PP/hy-PS (Y ₂ O ₃)	C.I. Disperse Orange 30	2	1.7957	4-5	3-4

tion at break of a modified PP filament were close to those of PP fiber. Therefore, PP/hy-PS (Y₂O₃) (92/8 w/w) is a successful modification for fine dyeable PP filaments.

CONCLUSIONS

Fine PP/hy-PS (Y₂O₃) fiber of less than 1 dtex was spun from blends of PP and a small amount of nanohybrid PS with modified Y₂O₃. The phase morphology of the blending systems was different. Nanoyttria particles in the PP/hy-PS (Y₂O₃) blending system dispersed evenly and helped to disperse PS. The PP/hy-PS (Y₂O₃) blending system had better compatibility between phases than PP/PS; the interface of PP/hy-PS (Y₂O₃) was not distinct, and nanoyttria particles scattered evenly in the polymer. Compared with PP/PS, the PP/hy-PS (Y₂O₃) fiber had a smoother fiber surface.

The PP/hy-PS (Y₂O₃) blend showed stable spinning processability, and the fine fibers made of the blend showed a mechanical performance similar to that of PP filaments. The dyeing effect relied considerably on the degree of crystallinity and orientation of the blend fibers. Changes in the degrees of crystallinity and orientation of the PP/hy-PS (Y₂O₃) fiber resulted in an increase of the amorphous region. The study showed that the PP/hy-PS (Y₂O₃) fiber had a larger K/S value and better fastness to soaping

because of the complexation of the disperse dye and yttrium in the blend system.

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TABLE IV
Processability and Mechanical Properties of the Modified PP Drawn Filaments

Sample	Denier of the drawn filament (dtex/f)	Strength to break (cN/dtex)	Elongation to break (%)
PP	0.91	3.84	32.4
PP/PS	0.98	3.54	38.9
PP/hy-PS	0.95	3.45	37.5