

Blends of Polypropylene and Modified Polystyrene for Dyeable Fibers

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ABSTRACT: Blends of polypropylene (PP) and modified atactic polystyrene (PS) with good processability were studied for dyeable fine and superfine fibers. Acrylic acid and butyl acrylate monomers were added to PS by radical suspension copolymerization. The dispersion of the additives in the PP crystal was investigated. The rheology curves of the blends were similar to that of PP under the testing conditions. Fine and superfine PP filaments were processed from these blends, and they had practical mechanical properties. The dyeability of the fabrics from the fibers was studied. The

increased amorphous content and the interface between PP and modified PS allowed the dyes to penetrate the fibers. These two effects helped to improve the color intensity. The color fastness was also improved by the presence of polar groups introduced by the modified PS components. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2360–2366, 2005

Key words: fibers; morphology; poly(propylene) (PP); polystyrene

INTRODUCTION

Because of its low cost, low density, good chemical resistance, and processability, polypropylene (PP) is widely applied in the plastic and fiber industries. Fine and superfine PP filaments are ideal materials for garments because of their special moisture transferability, soft hand, and other advantages. Recent studies on modified PP fibers have focused on functional modifications, such as dyeability, hydrophilicity, anti-static properties, and flame resistance.

Blending is an efficient process for the dyeable modification of PP. Wide ranges of additives have been tried. Akerman and Prikryl¹ selected a basic polymeric additive to improve the dyeability of PP fibers and studied the effect of drawing on the acid dyeability of the fibers. Gupta and Bhuvanesh found that the addition of a small amount of polystyrene (PS) to fiber-grade PP could increase the fiber shrinkage and improve the texturability and dyeability.² A variety of copolymers with polar groups have been used to modify the dyeability of PP fibers.^{3–6} Compatibilizers, such as polypropylene-*g*-maleic anhydride, have been

proved not only to improve the compatibility between PP and polar polymers but also to help the color fastness because of the presence of anhydride groups at the interface, to which polar agents can attach. These reports show that the key to obtaining a successful blend fiber from PP blends is to have a friendly interface and stable blend morphology, which are controlled by the additive properties and the processing conditions.

A resin for fine and superfine filament requires good spinnability and drawability. During our former studies of PP/PS blends, we added up to 8 wt % atactic PS with a controlled molecular weight to modify PP fibers. These blends had good spinnability and improved dyeability. The as-spun filaments also showed improved drawability. Fine and superfine fibers with increased disperse dye accessibility were produced and successfully industrialized.^{7–9} Unfortunately, because of a lack of polar groups, the color intensity and fastness needed further improvement. For this purpose, studies of copolymers of styrene and acrylic acid or acrylate were carried out.¹⁰ The goal of this study was to increase the dyeability of PP fibers through the blending of PP with modified PS while maintaining acceptable blend processability and fiber mechanical performance. The key factors for obtaining satisfactory blending filaments, including the additive component, blend morphology, and processing conditions, were investigated. The dyeing of fabrics made of the blends was used to evaluate the dye accessibility to these fibers.

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TABLE I
Influence of the Copolymer Composition (Molar Ratio) on T_g (°C) of the PS Additives and T_m (°C) of the Blends

Blends (94/6, except for pure PP)	Modified PS code	Modified PS description	Styrene/second monomer (mol %) in the copolymer	T_g (°C) of modified PS	T_m (°C) of the blends
PP	N/A	N/A	N/A	N/A	166.8
PP/PS	PS	Polystyrene	N/A	102.0	166.5
PP/PS-AA	PS-AA	Poly(styrene- <i>co</i> -acrylic acid)	95.6/4.4	102.0	166.4
PP/PS-SA	PS-SA	Poly(styrene- <i>co</i> -sodium acrylate)	94.2/5.8	115.0	166.9
PP/PS-BA	PS-BA	Poly(styrene- <i>co</i> -butyl acrylate)	88.9/11.1	88.6	166.7

N/A = not applicable.

EXPERIMENTAL

Materials

Specially designed isotactic PP for fine and superfine filaments, with a melt-flow rate of 25–35 g/10 min, were supplied by the resin plant of Donghua University (Shanghai, China). Styrene and butyl acrylate were chemical-grade, and they were pretreated for the removal of stabilizers and moisture and were sealed in a refrigerator. Acrylic acid, sodium hydroxide, and the initiator benzyl peroxide (BPO) were analytical-grade. The protective agent poly(vinyl alcohol) (PVA) was commercial-grade and had a molecular weight of 75,000.

Silvatol was a commercial deoiling agent and part of dyes; Terasil Blue 3RL-02 (C.I. Disperse Blue 56), Terasil Blue W-RBS (D.I. Disperse Blue 337), and Terasil Pink 3G (D.I. Disperse Red 302) were commercial grades from Ciba Special Chemical. Other dyes, including Disperse Red E-4B (C.I. Disperse Red 60) and Yellow E-3RL (D.I. Disperse Yellow 23), were from the Shanghai Dye Chemical Plant (Shanghai, China) and Dianix Red UN-SE (mixture), Dianix Yellow GRN-SE (mixture), Dianix Rubin ETD 300 (mixture), and Dianix Black EX-SE 300 (mixture) were from Dystar.

Preparation of modified PS

Modified PS samples were prepared with suspension polymerization.¹² The monomers (styrene/second monomer = 88:12) and the initiator BPO were premixed and added to a PVA solution with a bath ratio of 1:3. The polymerization was carried out at 90°C for 8 h with a fixed stirring rate. The number-average molecular weight (M_n) and distribution were determined with a Shimadzu LC-2A gel permeation chromatography system (Kyoto, Japan). M_n was 1.5×10^5 , and the molecular weight distribution was 1.7.

Preparation of the blends and fibers from PP/modified PS

Compounding of the PP/modified PS blends

PP pellets were dried in a vacuum dryer at 80°C for 8 h before they were compounded with PS and mod-

ified PS with a twin-screw extruder (diameter = 35 mm) at 220°C. The blends were then pelletized and vacuum-dried at 100°C for 8 h before being spun.

Spinning and drawing

As-spun filaments made of PP blends were processed with a Fujifilter MST C400 spinning tester (Tokyo, Japan) at take-up speeds of up to 400 m/min. The as-spun filaments were drawn with a Barmag Sprinzwirn 3013 drawing twisting machine (Chemnitz, Germany) at winding speeds of up to 800 m/min. Drawing ratio of 3–5 were tried to identify the drawability of the as-spun filaments. Yarns with a single end titer of about 1.0 dtex/f were collected for evaluation.

Preparation of the fabrics

Three knitting fabrics were processed with drawn filaments made of PP, PP/PS (94/6 w/w),⁷ and PP/poly(styrene-*co*-sodium acrylate) (PS-SA; 94/6 w/w) for the dyeability evaluation.

Measurement and characterization

Determination of the copolymer components by fourier transform infrared (FTIR) and the PS glass-transition temperature (T_g) and blend melting temperature (T_m) shifts by differential scanning calorimetry

The PS concentration of the copolymers was calculated on the basis of the band intensity ratios implied by their FTIR spectra, according to the calibrated curve of the component ratio versus the band intensity ratios.¹³ Moreover, T_g of the PS copolymers and T_m of the PP/modified PS blends were tested with a PerkinElmer DSC-7 (Wellesley, MA) accordingly. The results are listed in Table I.

Determination of the dispersion of modified PS in the PP phase and the effect on the spherulites

The blend chips were completely melted at 200°C and were isothermally crystallized at 138°C. The crystallization for the blends and the dispersion of modified

PS in PP were observed. Photographs of the crystal morphology and normal light for the modified PS domain dispersion were taken with a polarized microscope. Photographs of the domain dispersion were taken with a normal microscope.

Rheology property test of the PP/modified PS blends

The PP/modified PS blends were dried at 120°C in a vacuum oven for 8 h before the rheology test was performed with a Kayeness rheology meter (Franklin, MA). The curves of the test temperatures ranging from 230 to 250°C and the shear rates ranging from 1 to 10⁴ S⁻¹ were studied to cover the processing conditions (shown later in Fig. 3).

Evaluation of the fiber mechanical properties and structure factors

The drawn fibers were tested with an XL-1 type of strain–stress tester (Shanghai, China); the gauge was set to 10 mm, and the elongation speed was adjusted between 35–50 mm/min to ensure a break time of approximately 20 s.

The crystallinity was calculated from the density measured at 25°C by a density gradient column method with an MD-01 density tester (Deqing, Zhejiang, China). The reagent was a mixture of 1-propanol and distilled water.

The orientation of the fibers was calculated with the sonic velocity method with an SOM-2 sonic speed orientation tester (Shanghai, China) at a frequency of 10 kHz.

Dyeability test of the fabric samples

A composite dye of C.I. Disperse Red 60 (Disperse Red E-4B) and C.I. Disperse Blue 56 (Terasil Blue 3RL-02) with a 1:1 ratio was applied. The knitting fabrics were scoured, washed, and dried. The fabrics were dyed from a finite bath (pH 7) with a material/liquor ratio of 1:100 at 100°C in a beaker dyeing machine for 120 min. The dyeing bath had a density of 2.5 wt % of the bath. The samples were then soap-washed and dried for an optical density test with a Gretag Macbeth Color Dye 7000A (New Windsor, NY). The readings in *L** (grayness index), *a** (red–green index), and *b** (yellow–blue index) and the color shift (*dE**) were recorded and compared with those of the PP fabric:

$$dE^* = \sqrt{(dL^*)^2 + (da^*)^2 + (db^*)^2}$$

where *dL** is equal to *L**_{sample} – *L**_{standard}, *da** is equal to *a**_{sample} – *a**_{standard}, and *db** is equal to *b**_{sample} – *b**_{standard}. The subscript “sample” refers to the modified PP fabric, and the subscript “standard” refers to the control sample (PP fabric).

A CWR light source (cold white light) was applied to compare the color densities of three fabrics: PP, PP/PS (6 wt %), and PP/PS–SA (6 wt %).

A fabric of PP/PS–SA (6 wt %) was also evaluated via the color fastness property tests of washing, rubbing, soap washing, ironing, and sweat fastness per ref. 11.¹¹ Three series of dyes of different structures and molecular weights were used. The Dianix series dyes were from Dyster, the Terasil series dyes were from Ciba Special Chemical, and the others were from the Shanghai Dye Chemical Plant. The dyeing and finishing treatment were the same as the aforementioned procedures.

RESULTS AND DISCUSSION

Differently modified PS samples were applied as additives to PP with the intention of obtaining fine and superfine PP filaments with maintained mechanical properties and improved dyeability. The viscosity, morphology, and interfacial structure of the PP/modified PS blends were significant factors for the spinnability and dyeability. Here, the effects of the copolymer additives on the blend rheology and morphology are discussed.

Domain dispersion of modified PS in the PP matrix

PP and modified PS formed an immiscible polymer blend. With optical microscopy, we observed the domain size and domain dispersion of modified PS in the PP matrix (Fig. 1). The dispersed PS phases were spread uniformly in the continuous PP phase as round particles. The diameter of the dispersed phases ranged from 1 to 5 μm. The diameter of the poly(styrene-*co*-butyl acrylate) (PS–BA) phase in PP [Fig. 1(c)] was larger than that of the other modified PS additives.

PP crystal morphology in the PP/modified PS blends

With a polarized light source, pictures of spherulites were taken, as shown in Figure 2. In the PS and PS–BA systems, as Figure 2(b,c) shows, the spherulite shape of the PP crystallite was very similar to that of pure PP [Fig. 2(a)]. There were visible particles within the spherulite areas, but these particles did not change the morphology of the spherulite much. In the blends of PP and poly(styrene-*co*-acrylic acid) [PS–AA; Fig. 2(e)] and PP/PS–SA [Fig. 2(d)], the bound areas between the spherulites were clearer, with some dark areas between the spherulites. The size of the spherulite of PS–SA was much smaller than that of the other system. We suppose this was because the PS–SA copolymer was more immiscible with PP than PS. When PP crystallized, the copolymers with polar groups tended to be expelled from the PP crystal area. With the growth of the spherulite, the additives aggregated outside the spherulite, hindering PP

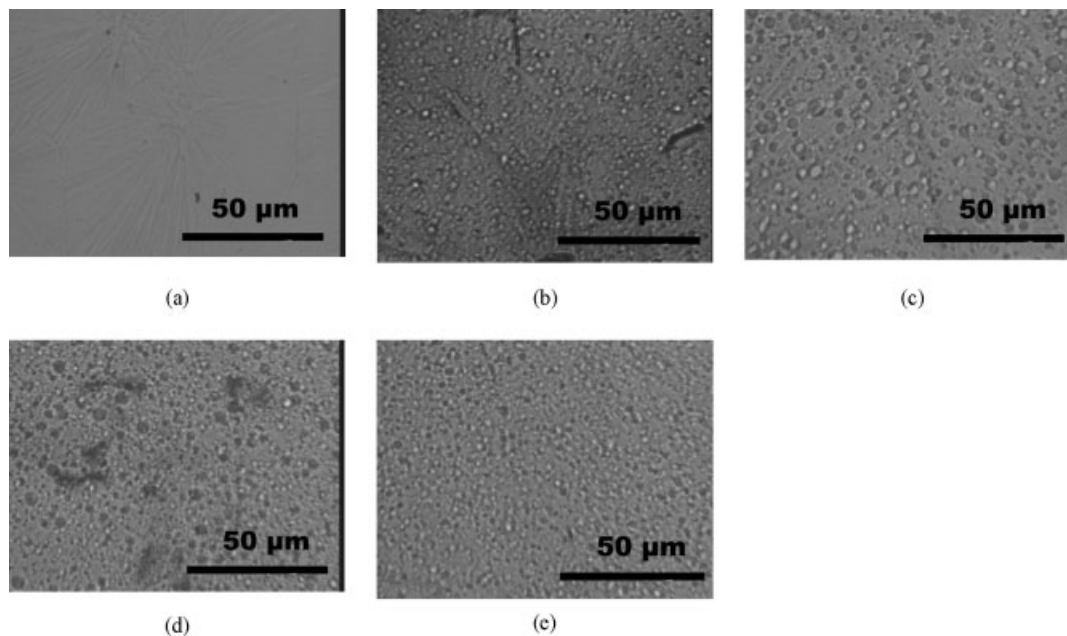


Figure 1 Domain size and domain dispersion of modified PS in the PP/modified PS blends: (a) PP without an additive, (b) PP/PS, (c) PP/PS-BA, (d) PP/PS-SA, and (e) PP/PS-AA.

chains from moving closer and crystallizing into the spherulite structure. Therefore, more dark area formed, which concerned the amorphous parts of PP and the additives. As for T_m of PP in the blends (Table I), all the readings were identical to that of pure PP, and the modified PS additives did not affect the PP crystal type. The amorphous parts between the spherulites and the interfaces between PP and the additives within the

spherulite areas both helped with the penetration of the dye staff into the PP fibers, and this in turn helped to improve the color density.

Rheology properties of the PP/modified PS blends

The rheology curves of the PP/modified PS blend were tested at 245°C in a shear rate range of 10^1 – 10^4 s $^{-1}$

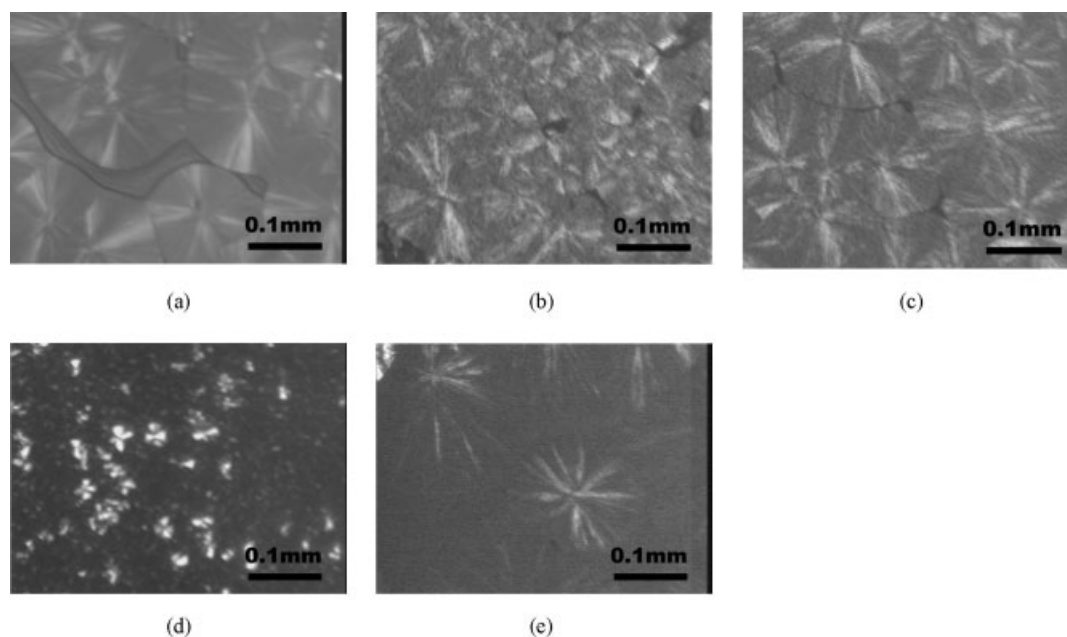


Figure 2 PP crystal in the PP/modified PS blends under polarized light: (a) PP without an additive, (b) PP/PS, (c) PP/PS-BA, (d) PP/PS-SA, and (e) PP/PS-AA.

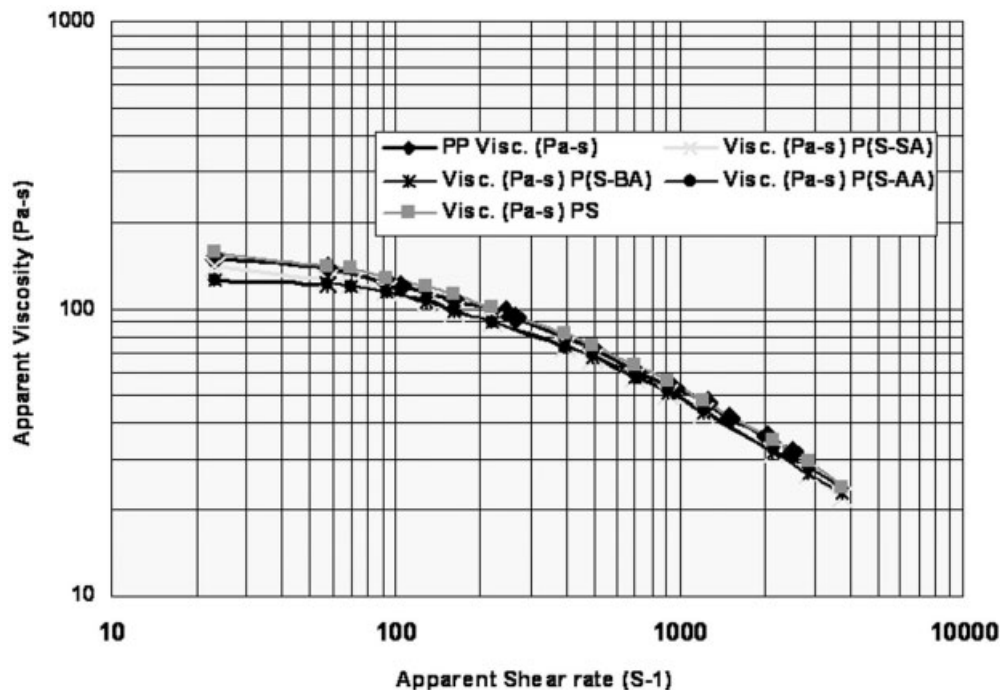


Figure 3 Rheology curves of the PP/modified PS blends at 245°C.

(Fig. 3), along with a blend of PP and PP/PS for comparison. PP/PS produced a curve very similar to that of PP. Generally, all the blends showed rheology performances close to those of the PP/PS and PP systems, with slight lower viscosities, especially in the low-shear end. We suggest that the reduced viscosity was caused by the easier interfacial slide between the additives and the PP matrix. This also explains why under a higher shear rate, the blend viscosity became closer to the PP performance. The rheology information helped us to identify the spinning/drawing process settings for the blends.

Spinnability of the PP/modified PS blends

Spinning tests for the PP/modified PS blends were carried out with a Fujifilter MST-C400 spinning tester. Yarn with 28 filaments was taken up at a 400 m/min winding speed. The as-spun filaments were not as

transparent as pure PP fiber when they came from the spinnerets. The whitening effect happened, more or less, in all the blends. It may have come from the interfaces between PP and modified PS when the phases separated. The drawing test with a Barmag Sprinnzwirn 3013 was carried out at draw ratios ranging from 3 to 5. The spinnability of the blends was generally acceptable for fine and superfine fiber processes. PP/PS-SA showed spinnability identical to that of PP/PS. This blend produced a stable spinning line in the tested output range and from 245 to 250°C. The as-spun filaments also showed good strength and potential drawability. Table II lists the titer and tensile data and some structure factors of the drawn filaments. Most of the drawn filaments reached 0.8–1 dtex/filament. They also showed tensile strength similar to that of PP fibers. All the blend fibers showed lower crystallinity than pure PP fibers did and maintained similar strength at break. This might be explained by the slightly higher orientation with respect

TABLE II
Titer of Drawn Filaments Made of PP/Modified PS

PP/modified PS code	Denier of the drawn filament (dtex/f)	Elongation at break (%)	Strength at break (cN/dtex)	Crystallinity (%)	Orientation (%)
PP	0.9	31.8	3.75	60.1	86.0
PP/PS	0.8	39.3	3.92	42.2	88.1
PP/PS-SA	1.0	38.9	3.88	39.6	90.7
PP/PS-BA	1.2	36.4	3.47	38.2	89.2

TABLE III
Color Intensity Reading of Fabrics Made of Dyeable Modified PP Filaments

Fabrics	Reflection (CWR)						
	L^*	a^*	b^*	dL^*	da^*	db^*	dE^*
PP	64.26	11.45	-13.00				
PP/PS (6 wt%)	44.65	18.22	-20.33	-19.61	6.77	-7.33	22.00
PP/PS-SA (6 wt%)	36.16	16.67	-22.76	-28.10	5.22	-9.76	30.20

to that of the pure PP fibers. The elongation at break was a bit higher.

Dyeability of the fine and superfine PP/modified PS filaments

The dyed fabrics of PP/PS-SA (6.0 wt %), PP/PS(6.0 wt %), and PP were parallel tested with CWF (cold-white-light, indoor-standard) light sources (Table III). Fabric made of PP/PS-SA (6.0 wt %) showed improved color intensity over fabrics made of PP or PP/PS. With the PP fabrics taken as the standard, the light reflection of a PP/PS-SA sample reached $dE^* = 30$, and this meant that the modified fabric got much deeper color than pure PP. It also showed improvement in comparison with the fabrics from PP/PS; this suggested an effect of polar groups on fiber dyeability. Figure 4 presents the curves of the light reflection of the specimens within a visible-light range under a CWF source. Throughout the entire visible-light wavelength range, the reflection was effectively reduced. To ensure the dye seat function of polar groups, we performed a further test of the color fastness.

The washing, rubbing, soaping, ironing, and sweating fastness of dyed fabrics from a group of dyes was tested. The results are listed in Table IV. Normally, the PP fabrics could be dyed to level 4, but with very low soaping fastness, and this resulted in little chance of practical applications. With the addition of 6 wt %

modified PS, the average fastness of all the tests reached level 4 or higher.

As PP has no polar groups in the molecular chain, the main interaction between a dye and PP can only be van der Waals forces, which are relatively weak; this explains the acceptable dye instance of the PP fabrics and the extremely low fastness of soaping. With the addition of modified PS, we suppose that there was increased interaction between the dye and fiber for the following reasons, which explain the results from the aforementioned color fastness test.

The presence of modified PS in PP reduced the fiber crystallinity and introduced the interfaces between the phases. These interfaces and amorphous parts formed the tunnels into the fibers, and the interfaces increased the surfaces for dye adsorption.

The phenyl structure of PS can form the π bond with the groups supplying protons. Besides, the acrylic acid or sodium acrylate polar groups from the modified PS also help to increase the interactions between the fiber and dye. The proton-supplying groups, such as $-\text{OH}$, $-\text{NH}_2$, and $-\text{NHR}$, which commonly appear in the dye structure, can easily form hydrogen bonds with the carboxyl groups induced by acrylic acid or acrylate during the normal dyeing and finishing processes. These increase both the color intensity and fastness. Thus, modified PS is a successful candidate for improving the dyeability of fine and superfine PP filaments.

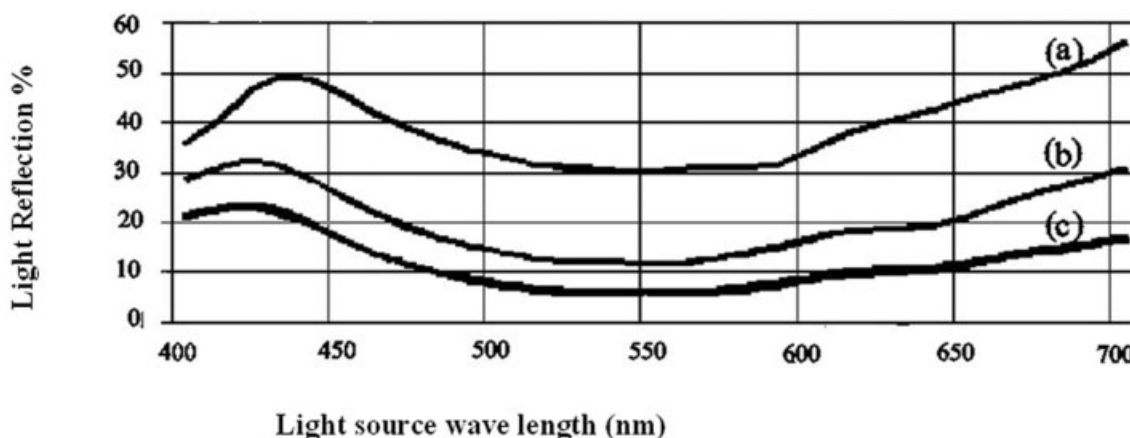


Figure 4 Light reflection of the fabrics for color reading (with CWF as the light source): (a) PP as a standard reference, (b) PP/PS (94/6 w/w), and (c) PP/PS-SA (94/6 w/w).

TABLE IV
Color Fastness Analysis of Fabrics Made of Dyeable Modified PP Filaments

Dye	Ironing (110°C)	Soaking	Rubbing		Soaping		Sweat stain	
			Dry	Wet	Shift	Stain	Shift	Stain
Dianix Red UN-SE (Mix)	4-5	4-5	4-5	4	4	4-5	4	4-5
Dianix Yellow GRN-SE (Mix)	4-5	4-5	5	4-5	4	4-5	4-5	4-5
Dianix Rubine ETD 300 (Mix)	4-5	4-5	4-5	4	4	4-5	4-5	4-5
Terasil Pink 3G (C.I. Disperse Red 302)	4-5	4-5	5	4	4	4-5	4-5	4-5
Yellow E-3RL (C.I. Disperse Yellow 23)	4-5	4-5	4-5	4-5	4	4-5	4	4-5
Dianix Black EX-SE 300 (Mix)	4-5	4-5	5	4-5	4	4-5	4-5	4-5
Red E-4B (C.I. Disperse Red 60)	4-5	4-5	5	4-5	4	4-5	4	4-5
Terasil Blue W-RBS (C.I. Disperse Blue 337)	4-5	4-5	4-5	4-5	4	4-5	4-5	4-5

CONCLUSIONS

The PP/modified PS blends showed good processability, and the fine and superfine fibers made of these blends showed improved dyeability and mechanical performance similar to that of PP filaments.

Modified PS additives dispersed uniformly in the PP matrix as spherical-like particles of approximately 1–5 μm . During the spinning, the dispersed modified PS phases were first extended with the PP continuous phase into fibrils; because of the viscosity difference with PP, they further broke down into smaller particles lining in the trace of the former fibrils. Some additives affected the PP crystal morphology and reducing the T_m of PP in the blends.

All the PP/modified PS blends showed a rheology performance similar to that of PP, especially at a higher shear rate at 245°C. A blend with PS-SA had stable processability. Its as-spun fiber had good drawability, and the drawn filaments reached 0.8–1.0 dtex/f.

The interfaces and increased amorphous phase of the blends induced by modified PS, together with the presence of polar groups from the acrylic acid or acrylate part, significantly increased the dyeability of the fibers. The light reflection of the dyed fabric made of

PP/PS-SA (94/6 w/w) was reduced by 30% in comparison with that of PP and by 10% in comparison with that of PP/PS. It was proved to be an efficient additive for improving the dyeability of fine and superfine PP filaments while maintaining satisfactory processability and mechanical properties.

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