Shade Darkening Effect of Polyorganosiloxane Modified with Amino and Hydroxy Groups on Dyed Polyester Microfiber Fabric

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ABSTRACT: The novel polyorganosiloxane material S-101 modified with amino and hydroxy groups is synthesized. Shade darkening effect of modified polyorganosiloxane on dyed polyester microfiber fabric is investigated by reflectance spectrum, color yield (K/S), and the color differences (ΔE). The colorimetric data of CIELAB is discussed. The results show that the novel material of silicone polymer modified with amino and hydroxy groups has excellent shade darkening effect on dyed polyester microfiber fabric. The rates of the color yield increase ($I\%$) of all dyed fabric with four dyes (Disperse Yellow S-4RL, Red GS, Blue 2BLN, and Black SF-R) exceed 10%. The shapes of the reflectance spectra curves of the dyed fabrics before and after treated with S-101 are not noticeable change. The dyed fabrics with the polymer have not significant effect on the wash fastness and wet rubbing fastness. The low reflectance thin film on dyed fabrics is formed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1256–1262, 2007

Key words: polysiloxanes; modification; polyester; thin films

INTRODUCTION

In a broad sense, a polyester microfiber is defined as a fiber or filament of linear density of less than 1 dtex. However, even finer fibers, between 0.01 and 0.4 denier class are produced. The polyester microfibers are used in various applications, for example in high-grade woven and knitted fabrics with a soft hand and water or oil-absorption fabrics, such as towels and typewriter ribbon. Wiping cloth, filter cloths, and clean-room garments utilize the large fiber surface. Moisture-permeable, waterproof, softness, and smoothness high-density woven fabrics are used in the garment area.[1,2] Not surprisingly, the physical and mechanical properties of these various microfibers are quite different from those of conventional fibers, and this is particularly true of their dyeing characteristics.[3] The surface of polymer microfiber increases markedly with decreasing filament linear density. The visual and instrumental depth of dyed microfiber may differ because of their light reflection properties. It is difficult that the polyester microfiber fabrics are deeply dyed because of light reflection, especially black and blue shade. To increase the depth of dyed microfiber, a number of attempts have been made to select special dyestuffs, choose dyeing processes, and modify surface with the low reflective index polymers.[4,5]

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It is common knowledge that polyorganosiloxane is an extremely important class of materials used for coating, adhesives, impact-resistance plastics, etc.[6,7] In application, polyorganosiloxane has many specific properties by virtue of its good water repellency, lubricity, high flexibility, excellent thermal stability, and low reflective index. The silicone polymers containing cationic groups concerning interpenetrating polymer networks (IPN) and graft copolymers are applied to improve the wash fastness of dyed fabric.[8] When the polyorganosiloxane is modified with amino and hydroxy groups, the difference in polarity between —Si—O— and —NH—, —OH is very large. The modified polyorganosiloxane could form thin film of low reflectance index on dyed microfiber polyester fabric.

In this article, the new polyorganosiloxane S-101, silicone polymer modified with amino and hydroxy groups, is synthesized through ring-opening polymerization of cyclosiloxane. Shade darkening effect of modified polyorganosiloxane on dyed microfiber polyester fabric is investigated. The colorimetric data and the reflectance spectrum of dyed microfiber fabric treated with S-101 are also discussed.

EXPERIMENTAL

Materials

Octamethyl cyclotetrasiloxane (D_4) was obtained from Xinghuo Petrochemical Plant of Jiangxi (Jiujiang, China) and fractionated under reduced pressure before used. *N*-(*β*-aminoethyl)-*γ*-aminopropyl dimethoxysilane (602), the hydrophilic organosiloxane polymer DH-800, nonionic surfactant NP-9 and NP-4 were obtained from Shanghai Handa Chemical Company (Shanghai, China). KOH (D4 polymerization catalyst) was obtained from Shanghai Chemical Reagent Plant (Shanghai, China).

Disperse Yellow S-4RL (CI Disperse Yellow 30) and Disperse Red GS (CI Disperse Red 153) were obtained from Zhejiang Jihua Dyestuff Chemical Company (Hangzhou, China). Disperse Blue 2BLN (CI Disperse Blue 56) and Black SF-R (None ascribed) were obtained from Zhejiang Longsheng Group (Shangyu, China). The scoured polyester microfiber fabrics (warp: 75dtex/24F, weft: 77 dtex/300F) were obtained from Zhejiang Jinqiu Textile Company (Shaoxing, China).

Preparation of polyorganosiloxane modified with amino and hydroxy group

The D4, and KOH were added into the reactor according to the recipe and sufficiently mixed with stirring at room temperature. The recipe is given in Table I. The polymerization mixture was heated to 85°C for 60 min in nitrogen atmosphere. Then the mixture was heated to 120°C, 602 were first dissolved in a certain amount of water and added into the reactor according to the recipe. The polymerization was conducted at 120°C for 7 h. Then a certain amount of water was added three times in this sequence: after 7 h, then after 60 min, after 120 min. The polyorganosiloxane modified with amino and hydroxy groups was achieved. The polymerization reaction was shown in Scheme 1.

Preparation of silicone emulsion

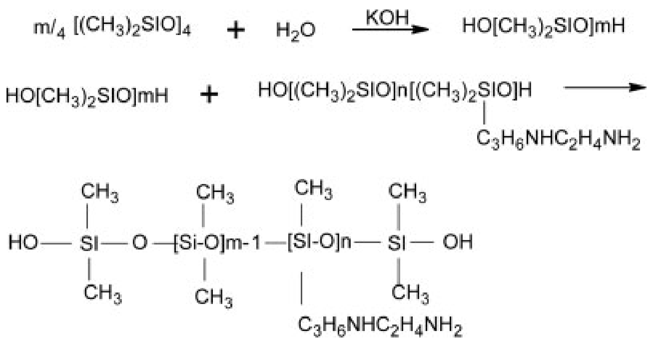
The emulsion agents, nonionic surfactant NP-9 and NP-4 and the hydrophilic organosiloxane polymer DH-800 were first dissolved in a certain amount of water. The modified polyorganosiloxane were added according to the recipe and sufficiently mixed with stirring at room temperature for 2 h. Translucent emulsion containing 15% resin was achieved. The polymer emulsion was called S-101.

Dyeing

The dyeing solution was prepared by using 1, 2, 5% (owf) of dye based on weight of fabric, respectively. The fabrics were dyed in an IR dyeing machine

TABLE I
Ingredients of Polymer Emulations (g)

Samples	D_4	602	KOH	DH-800	OP-9	OP-4	Water
S-101	11	1.1	0.005	7.9	8	2	170



Scheme 1

(PYROTEC-2000), the liquor ratio being 1 : 10. Fabrics were immersed in the dye bath at room temperature and the temperature was increased to 130°C at a rate of 1°C/min. Dyeing was carried out at this temperature for 60 min. After dyeing, the dyed samples were treated for 15 min in 0.5 g/L sodium hydrosulfite and 1.0 g/L sodium carbonate solution at 75°C. Then, all the samples were rinsed with water until the rinsing water was clear and dried.

Treating method to the fabric

The dyed samples were padded with the solutions of different concentration S-101 to give 75% wet pick-up. The dry temperature and time were 95°C and 3 min, respectively. The cure temperature was 165°C, and cure time was 1.5 min. To compare, the dyed samples without polymer were cured under the same conditions.

Color yield analysis

The color yield (K/S) of the dyed fabric was determined by Datacolor SP600$^+$ spectrophotometer. The tristimulus values of dyed samples were measured in the visible region of the spectrum from 360–700

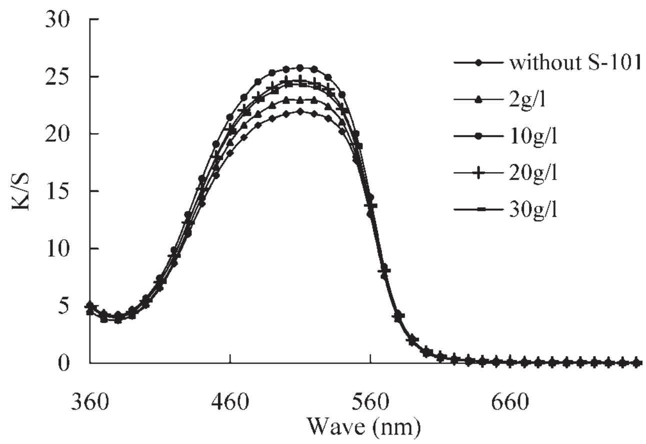


Figure 1 K/S versus wave of dyed fabric with Disperse Red GS (2% owf) treated with different concentration of S-101.

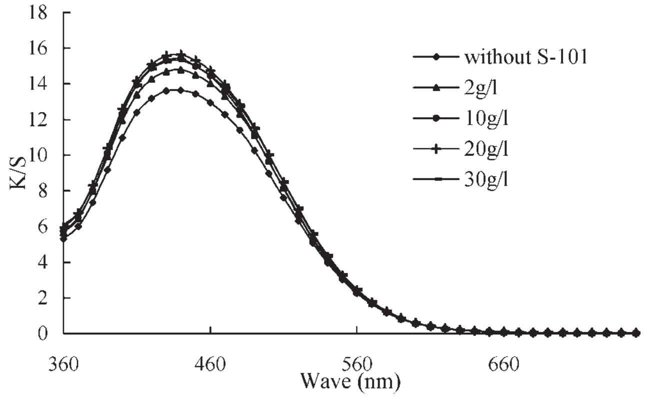


Figure 2 *K/S* versus wave of dyed fabric with Disperse Yellow S-4RL (2% owf) treated with different concentration of S-101.

nm and the reflectance at the wavelength of maximum absorption (λ_{max}) was used to calculate the color yield of dyed fabrics by the Kubelka–Munk Equation [eq. (1)]:[9]

$$K/S = \frac{(1-R)^2}{2R} \tag{1}$$

where *K* is the absorption coefficient of the substrate, *S* is the scattering coefficient of the substrate, and *R* is the reflectance of the dyed fabric at λ_{max}.

Measurements

Color fastness of the dyed samples treated with and without the S-101 polymer was determined according to the respective international standards: fastness to washing, ISO 105 C04 (1989); fastness to perspiration, ISO 105 E04 (1994); fastness to rubbing, ISO 105 X12 (1993).

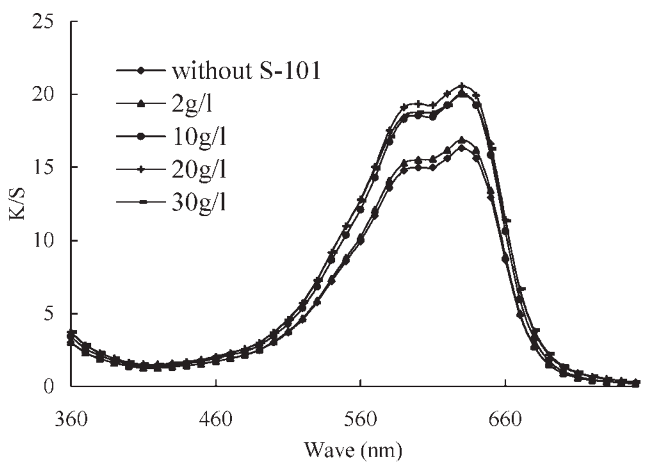


Figure 3 *K/S* versus wave of dyed fabric with Disperse Blue 2BLN (2% owf) treated with different concentration of S-101.

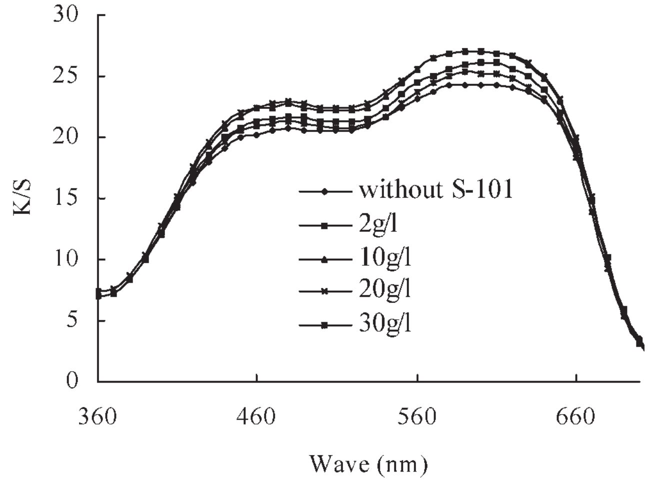


Figure 4 *K/S* versus wave of dyed fabric with Disperse Black SF-R(2% owf) treated with different concentration of S-101.

RESULTS AND DISCUSSION

Surface shade darkening effect of S-101 on the microfiber fabric

The polyorganosiloxane is prepared through ring-opening polymerization of cyclosiloxane. After octamethyl cyclotetrasiloxane (D_4) and 602 were polymerized with KOH as catalyst, surfactant admicelles structure of modified polyorganosiloxane emulsion was formed: hydrophobic core containing —Si—O— and hydrophilic shell containing —NH—, —OH groups. The polyorganosiloxane could form firmly thin film on the fiber due to the existence of —NH—, —OH groups. To investigate surface shade darkening effect of S-101, the Disperse Yellow S-4RL, Disperse Red GS, Disperse Blue 2BLN, and Disperse Black SF-R were used for the fabric. The dyed samples were padded with the solutions of different concentration silicone polymer (2, 10, 20, 30 g/L), respectively. The color yield (*K/S*) of the dyed fabric

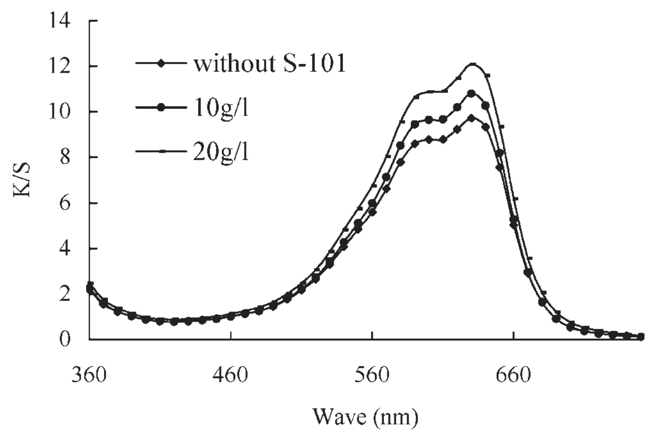


Figure 5 *K/S* of dyed fabric with Disperse Blue 2BLN (1% owf).

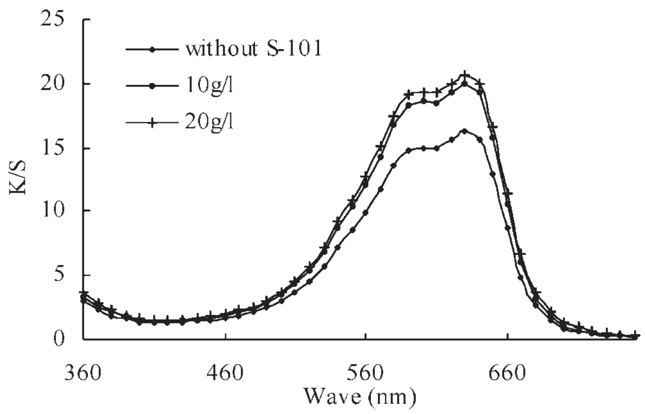


Figure 6 *K/S* of dyed fabric with Disperse Blue 2BLN (2% owf).

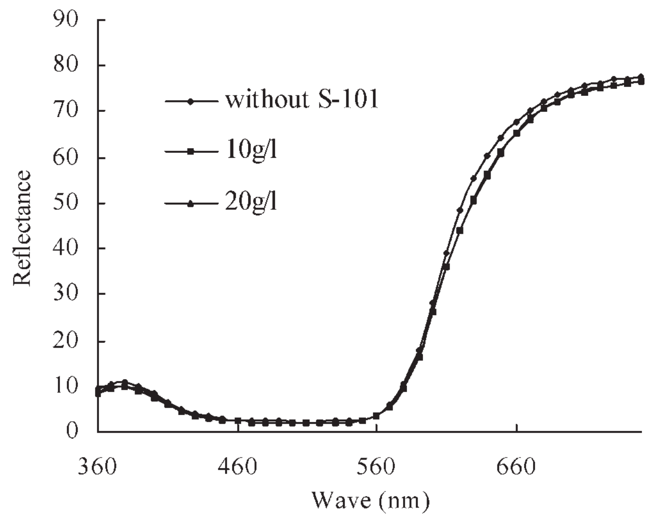


Figure 8 Reflectance spectra of dyed fabric with Disperse Red GS.

was determined by Datacolor SP600$^+$ spectrophotometer. The color yields (*K/S*) of dyed fabric treated with different amount of S-101 in the visible region of the spectrum from 360 to 700 nm are shown in Figures 1–4. It is clear that the color yields were remarkable increase with S-101 using all four disperse dyes in the visible region of the spectrum. The *K/S* rapidly increase with increasing the concentration of silicone polymer from 2 to 10 g/L in the wavelength of maximum absorption (λ_{max}), and then stay constant or small drop at 20 and 30 g/L. It shows that S-101 was excellent low reflectance resin. When the concentration of S-101 increased from 2 to 10 g/L, the thin film on the surface of dyed fabrics was formed. The thin film led to the *K/S* remarkable increase. It imparted low reflectance surface of fiber. The thin film of fiber surface became thicker when the concentration exceeded 20 g/L. The *K/S* slightly decreased.

To further investigate the dye concentration on the shade darkening effect of S-101, the Disperse Blue 2BLN was selected. Figures 5–7 exhibit the *K/S* of dyed fabrics with Disperse Blue 2BLN at difference dye concentrations 1%, 2 and 5% (owf) treated with and without S-101, respectively. It can be seen that the *K/S* had remarkable increase with S-101 at all difference dye concentrations. The *K/S* rapidly increased with raising the concentration of S-101 from 10 to 20 g/L at Disperse Blue 2BLN 1% (owf) (Fig. 5). The *K/S* stayed constant with raising the concentration from 10 to 20 g/L at Disperse Blue 2BLN 5% (owf) (Fig. 7). The results indicate that surface shade darkening effect of S-101 was related to the dye concentration.

Effect of the polymer on reflectance spectrum of dyed fabrics

Reflectance spectra of the dyed fabrics before and after treated with S-101 were measured. Both the shapes of the reflectance spectra curves and the min-

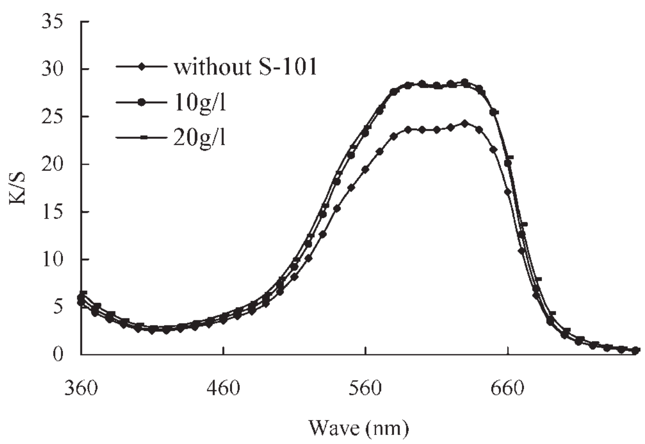


Figure 7 *K/S* of dyed fabric with Disperse Blue 2BLN (5% owf).

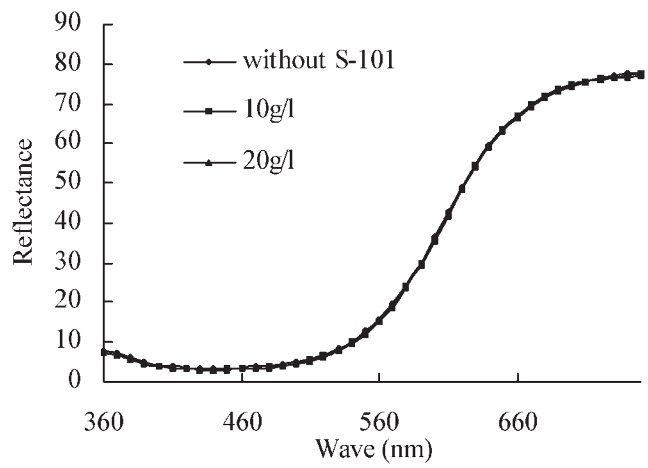


Figure 9 Reflectance spectra of dyed fabric with Disperse Yellow S-4RL.

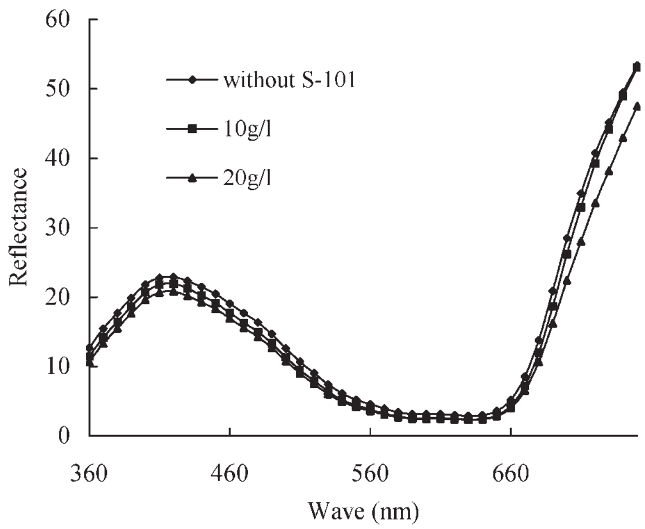


Figure 10 Reflectance spectra of dyed fabric with Disperse Blue 2BLN.

imum reflectance wavelength of dyed fabrics treated without and with S-101 had not noticeable change (Figs. 8–11). However, the reflectance of dyed fabrics treated with S-101 had a little decrease. Figures 12 and 13 show the reflectance spectra of dyed samples with Disperse Blue 2BLN and Disperse Black SF-R at difference dye concentrations (using 10 g/L S-101), respectively. It is clear that the higher the dye concentration was, the lower the reflectance indexes were.

The colorimetric data of the dyed fabrics

The colorimetric data of the dyed fabric was determined by Datacolor SP600$^+$ spectrophotometer. The color parameters L, a, b, were calculated by the tristimulus values X, Y, and Z. L refers to brightness-darkness with values from 100 to 0 representing

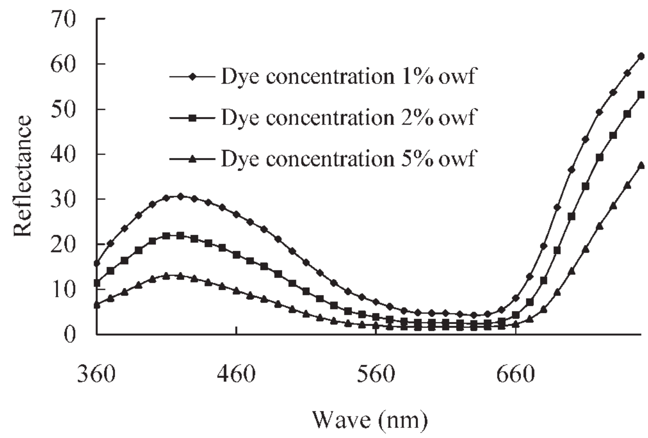


Figure 12 Reflectance spectra of dyed fabric with different concentrations of Disperse Blue 2BLN treated with S-101.

white to black. The a values run from negative (green) to positive (red). The b values run from negative (blue) to positive (yellow). The color differences (ΔE) were calculated using the measured values of CIELAB [eq. (2)].

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \quad (2)$$

where ΔL, Δa, and Δb are the difference in the color parameters before and after treated with the S-101 polymer.

The color yield increase ($\Delta K/S$) and the rates of the color yield increase (I%) were calculated using eqs. (3) and (4), respectively.

$$\Delta K/S = (K/S)_1 - (K/S)_0 \quad (3)$$

$$I\% = (K/S)/(K/S)_0 \quad (4)$$

where $(K/S)_0$ and $(K/S)_1$ represent K/S of dyed fabrics before and after treated with S-101, respectively.

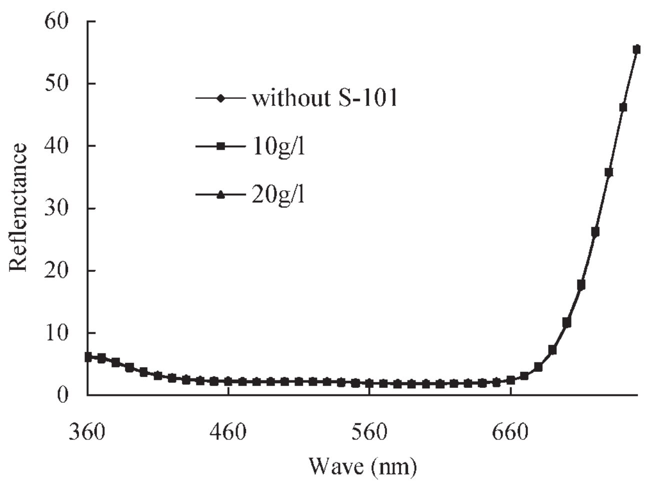


Figure 11 Reflectance spectra of dyed fabric with Disperse Black SF-R.

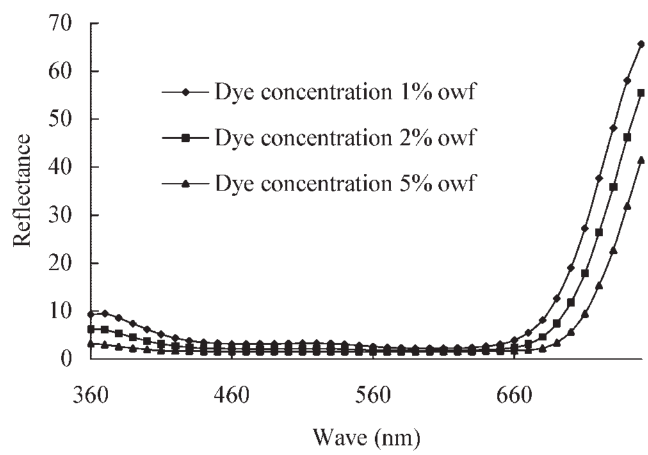


Figure 13 Reflectance spectra of dyed fabric with different concentrations of Disperse Black SF-R treated with S-101.

TABLE II
Colorimetric Data of Dyed Fabric with Disperse Red GS (2% owf)

	K/S	Δ*K/S*	*I*%	*L*	*a*	*b*	Δ*L*	Δ*a*	Δ*b*	Δ*E*
Without S-101	21.95	0	0	40.03	54.91	33.15	0	0	0	0
10 g/L S-101	25.75	3.8	17.31	38.43	53.95	33.26	−1.6	−0.96	0.11	2.33
20 g/L S-101	24.65	2.7	12.3	38.71	53.62	32.74	−1.32	−1.29	−0.41	2.61

TABLE III
Colorimetric Data of Dyed Fabric with Disperse Blue 2BLN (2% owf)

	K/S	Δ*K/S*	*I*%	*L*	*a*	*b*	Δ*L*	Δ*a*	Δ*b*	Δ*E*
Without S-101	16.32	0	0	31.72	1.59	−34.03	0	0	0	0
10 g/L S-101	20.02	3.70	22.67	29.62	2.87	−35.16	−2.10	1.28	−1.13	1.21
20 g/L S-101	20.56	4.24	25.98	28.86	2.92	−34.63	−2.86	1.33	−0.6	1.82

Colorimetric data of dyed fabric with the Disperse Red GS, Disperse Blue 2BLN, Disperse Yellow S-4RL, Disperse Black SF-R (2% owf) before and after treated with the polymer are summarized in Tables II–V, respectively. The results in Tables II–V show that *K/S* values of all dyed fabrics remarkably increased after treated with the polymer. The rates of the color yield increase (*I*%) of all dyed samples with four dyes (2% owf) after treated with polymer exceed 10%. The *I*% of dyed fabric with Disperse Blue 2BLN after treated with 10 and 20g/L S-101 polymer increased 22.67% and 25.98%, respectively. The *I*% of dyed fabric with Disperse Red GS after treated with 10 g/L polymer also increased 17.31%. However, when the concentration of the polymer was raised, *K/S* was no noticeable change. *L* values of dyed fabrics show that all *L* values decreased after dyed fabrics were treated with the polymer. This means that the color of dyed fabric became dark. The *a* values of dyed fabric with Disperse Red GS and Disperse Black SF-R treated with S-101decreased. This means the increase in color green component instead of red color. The *b* values of dyed fabric with Disperse Blue 2BLN treated with S-101 decreased. This means the increase in color blue component instead of yellow color. The *b* values of dyed fabric with Disperse Yellow S-4RL treated with S-101 increased. This means the increase in color yellow component instead of blue color. The color differences (Δ*E*) increased after dyed samples were treated with the S-101 polymer. When the shades of the dyed fabrics were compared visually, which of the treated fabric with S-101 polymer shew a noticeable depth shade compared with its untreated counterpart. The noticeable increase of the *K/S* of the dyed fabric with the S-101 polymer may be due to forming the film on dyed fabric.

Fastness properties of dyed fabric treated with the polymer

The fastnesses of dyed fabric treated with and without S-101 are summarized in Table VI. It can be seen that the fastness of dyed fabrics before and after treated with S-101 were similar. The wet rubbing fastness, wash fastness, and fastness to perspiration of the dyed fabric treated with S-101 had not further improvement. However, the fastnesses properties did not deteriorate.

TABLE IV
Colorimetric Data of Dyed Fabric with Disperse Yellow S-4RL (2% owf)

	K/S	Δ*K/S*	*I*%	*L*	*a*	*b*	Δ*L*	Δ*a*	Δ*b*	Δ*E*
Without S-101	13.59	0	0	50.15	38.11	47.45	0	0	0	0
10 g/L S-101	15.30	1.71	12.58	49.76	38.49	48.97	−0.39	0.38	1.52	1.61
20 g/L S-101	15.57	1.98	14.57	49.30	38.83	48.60	−0.85	0.72	1.15	1.61

TABLE V
Colorimetric Data of Dyed Fabric with Disperse Black SF-R (2% owf)

	K/S	Δ*K/S*	*I*%	*L*	*a*	*b*	Δ*L*	Δ*a*	Δ*b*	Δ*E*
Without S-101	24.26	0	0	16.34	0.11	−2.53	0	0	0	0
10 g/L S-101	27.10	2.84	11.71	15.44	0.03	−2.59	−0.90	−0.08	−0.06	0.85
20 g/L S-101	27.10	2.84	11.71	15.37	0.04	−2.46	−0.97	−0.07	0.07	0.99

TABLE VI
Fastness Properties of Dyed Fabrics (2% owf) Treated with and without S-101

		Fastness to rubbing		Fastness to washing		Fastness to perspiration	
Disperse dyes	Samples	Dry	Wet	SP	SC	SP	SC
Red GS	Without S-101	4–5	4	4	4	4	4
	S-101 (10 g/L)	5	4	4	4	4	4
Blue 2BLN	Without S-101	5	4	4–5	4	4–5	4–5
	S-101 (10 g/L)	5	4	4–5	4	4–5	4–5
Yellow S-4RL	Without S-101	5	4	4	4	4	4
	S-101 (10 g/L)	5	4	4	4	4	4
Black SF-R	Without S-101	4–5	4	3–4	3–4	3–4	3–4
	S-101 (10 g/L)	4–5	4	3–4	3–4	3–4	3–4

SP, staining on polyester; SC, staining on cotton.

CONCLUSIONS

1. The novel material of polyorganosiloxane modified with amino and hydroxy groups, S-101, was synthesized through ring-opening polymerization of cyclosiloxane. S-101 had excellent shade darkening effect on dyed polyester microfiber fabric.
2. After the microfiber fabrics were dyed with the four dyes (Disperse Yellow S-4RL, Red GS, Blue 2BLN, and Black SF-R), the color yields (*K*/*S*) of dyed samples treated with S-101 had remarkable increase in the visible region of the spectrum. The *K*/*S* rapidly increased with increasing the concentration of silicone polymer from 2 to 10 g/L. It shows that low reflectance thin film on dyed fabrics was formed.
3. The shapes of the reflectance spectra curves of dyed fabrics treated without and with S-101 had not noticeable change. The reflectance of dyed fabrics treated with S-101 had a little decrease. The treatment with the polyorganosiloxane polymer had not significant effect on the wash fastness and wet rubbing fastness.

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