Research Article

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Study on structure and properties of natural indigo spun-dyed viscose fiber

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Abstract: To improve the level dyeing property and colorfastness of natural pigment-dyed cellulose fiber, a study on the structure and properties of natural indigo spun-dyed viscose fiber was carried out systematically. Herein, the natural pigment-dyed cellulose fiber was prepared by wet-spinning technique, and the microstructure of the colored fiber was comprehensively studied. Fabrics with different color depths were obtained by adjusting the color value and the content of indigo pigment. The natural indigo was evenly embedded in the viscose fiber, and the results indicated the existence of a direct ratio relationship between the performance of natural indigo and the color depth of the fiber. The level dyeing property and colorfastness of the fabric were tested. The fabric exhibited excellent dyeing uniformity, as indicated by the relative standard deviation of the surface color depth value on the fabric, which was no more than 2.39%. The colorfastness of natural indigo spun-dyed fiber was outstanding even when mordant was not used in the production process. The colorfastness to artificial light could reach grade 5, the fastness to washing with detergent reached grade 3–4, the fastness to rubbing reached grade 4–5, and that to high temperature reached grade 4–5. These results can possibly promote the future use of natural dyes in the fiber produced by a spun-dyeing technique.

Keywords: natural dye, mass coloration, level dyeing property, colorfastness, cellulose

1 Introduction

Textile industry uses excessive amount of water for coloring and postprocessing (1,2), and the water consumption and environmental pollution have led to the requirement of severe control tendency on account of the emission of toxic and stubborn concentrated dye solution. Classical synthetic dyes are stable to light, heat, and oxidants; and they are nonbiodegradable (3) and thus constitute the main contaminant of effluent (4). In contrast, natural dyes such as lycopene, curcuma, and indigo are extracted from plants, animals, and minerals without any chemical treatment (5). Moreover, the residual pigment after dyeing could be utilized as an ideal fertilizer in agricultural fields (6). Natural dyes can be effective against both gram-positive and gram-negative bacteria and can be used as eco-friendly antifungal and antibacterial agents on various textile products, exhibiting the application prospects in the field of garment manufacturing for kids and for developing health-care products and foodstuffs (7). The advantages of natural dyes, including environment friendly, biodegradable, nontoxic, and nonallergenic, make them a promising substitute for synthetic dyes. Therefore, dyeing of textiles using natural dyes is an effective and acceptable way to reduce pollution caused by various processes performed in the textile industry (8,9).

However, natural dyeing technology still offers inevitable disadvantages. For instance, it is difficult to reproduce shades by using natural dyes/colorants, as these agro-products vary from one crop season to another, place to place, species to species, maturity period, etc. Furthermore, natural dyeing requires skilled craftsmanship; thus, it is more expensive than synthetic dyeing. The low color yield of natural source dyes necessitates the use of more dyestuffs, larger dyeing time, and excess cost for mordant and mordanting. Moreover, the shade, color depth, and colorfastness of natural dyes obtained by conventional dyeing technology are unsatisfactory (10,11).

Similarly, the natural light resistance of many natural dyes, in particular, those extracted from petals, varies from poor to average. Moreover, nearly all natural

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dyes require the use of mordant to fix them onto the textile substrate. Furthermore, a substantial portion of mordant remains unexhausted in the residual dye bath, leading to a serious effluent disposal problem (12). Indigo, as one of the largely used historical dyes, is insoluble in water, which needs to be reduced in an alkaline solution to a leuco sodium salt (13). Thus, the reduction process and the reducing agents are the main research areas for the development of indigo dyes. Notably, the nonreproducibility and poor colorfastness of indigo have partly been improved. For instance, Son *et al.* (14) used sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) as a reducing agent to dye indigo onto the polyester fiber. Although it showed better colorfastness to washing with detergent, $\text{Na}_2\text{S}_2\text{O}_4$ was oxidized to nonrenewable products such as sulfite and sulfate that caused various problems during dyeing (14,15). Therefore, in order to overcome these issues, Hossain *et al.* (16) dyed cotton with three different types of sweet fruits (date palm, banana, and apple) as reducing agent. Even though the fabric possessed suitable colorfastness to rubbing and washing with soap, the colorfastness to light was still undesirable. Furthermore, Saikhao *et al.* (17) used environment friendly, nontoxic, inexpensive, and biodegradable reducing sugars as a green substitute for $\text{Na}_2\text{S}_2\text{O}_4$ and the colorfastness to rubbing improved. Although the release of sulfite and sulfate into the wastewater was correspondingly reduced, the reducing sugar was inferior to $\text{Na}_2\text{S}_2\text{O}_4$ in terms of color strength and washing ability under strong alkali conditions. Therefore, low water consumption and pollution-free dyeing method still need further systematic explorations.

Mass coloration technique, namely, spun-dyeing or dope dyeing, is defined as a method of coloring manufactured fibers by incorporation of colorant in the spinning composition before extrusion into filaments (18). The spun-dyeing technique exhibits the advantages of cost-effectiveness, uniformity of coloration, and superior colorfastness (9,19). Compared to the traditional fiber dyeing method, spun-dyeing technology can solve the problem associated with color defects due to poor colorfastness to rubbing, the fastness to washing with soap, and obtained high color uniformity in the spun-dyed fiber. More importantly, the technology omits the dyeing process of downstream products and significantly reduces the consumption of water and energy in the entire textile industry (J. Zheng, July 2013, Production method of colored regenerated cellulose fiber, P.R.C. patent 102041573B). An analytical and statistical description for the eco-friendly spun-dyed modal fiber was presented by Terinite and Manda, following the method of life cycle assessment (20).

Compared to conventionally dyed fabric, the energy use of spun-dyed modal fabric was reduced to half and the carbon footprint declined by 60%. Moreover, the water consumption also got halved and showed significantly less (40–60%) environmental impacts. A technique, which is commonly used in spun-dyeing process, involves the addition of a vat dye to the spinning dope (19), in which the vat dye gets reduced to a leuco compound before addition to spinning dope and then the leuco compound is oxidized to the vat dye form during or after cellulose regeneration. Thus, small particles obtained by grinding the insoluble indigo can directly be used to color the fiber in the spun-dyeing process.

In this study, the natural indigo was *in situ* injected into viscose fiber during the spinning process in order to overcome the poor colorfastness of natural pigments after dyeing cellulose fiber. Furthermore, the relationship between the added content of natural indigo dye and the depth of coloration of cellulose fiber was analyzed. Finally, microstructure analysis techniques were employed to investigate the distribution of natural indigo in colored fiber.

2 Materials and methods

2.1 Preparation

2.1.1 Preparation of indigo-dispersed color paste

Natural indigo (Meisheng Biomaterials Co., Ltd.) was added to deionized water, stirred uniformly, and ground in a ball mill at a rate of 100 rpm for 4 h to obtain a certain size of indigo-dispersed color paste (Figure 1).

2.1.2 Preparation of spun-dyed fiber

The dynamic light scattering method was applied to obtain the particle size (D) and its distribution using a Z3000 instrument (PSS Company, USA) at 25°C. The indigo particles with an average particle size of 329.0 nm were evenly distributed in water. Before spinning, the color paste and viscose solution (Xinxiang Bailu Co., Ltd.) were blended and evenly mixed using a dynamic mixer and a static mixer. The homogeneous mixture was sprayed into a coagulation bath through a spinneret, solidified, and wound into a 30-hole two 120D viscose filaments. A weft plain stitch fabric of 55.62 g m^{-2} was knitted on a cylindrical

Figure 1: The particle size distribution of indigo dispersed in color paste.

machine (YC21D hosiery machine; Changzhou Depu Textile Technology Co., Ltd.).

2.2 Color measurement

Natural indigo pigment was dissolved in chloroform and diluted, and the contents were oscillated for 30 min under ultrasonication to obtain the sample solution. The absorbance of the indigo pigment sample solution was measured in a 1-cm cuvette using a spectrophotometer (722E; Shanghai Spectrometer Co., Ltd.) at the wavelength of 601.5 nm (the wavelength of the maximum absorbance of indigo is in the range of 400–700 nm). In contrast, the pure chloroform solvent was used as a reference solution.

The knitted fabric samples with colored fiber obtained by adding different contents of natural indigo were tested using a DataColor SF600 spectrophotometer. The test aperture was 6.0 mm, the light source was D65/10°, and the compressed thickness of the sample was greater than 1 mm. Measurements were taken at three different points on each sample to obtain the average.

2.3 Microstructure of natural indigo spun-dyed fiber

In order to observe and characterize the microstructure of natural indigo-colored fiber under an electron microscope (MERLIN Compact, Germany), the cross-section and the

outer surface of the spun-dyed fiber were obtained in liquid nitrogen (20), which was followed by a gold-spraying treatment.

2.4 Level dyeing property test

The surface color depth values (K/S) of n points were measured on a piece of fabric, and the average value of the K/S of the fabric was calculated according to Eq. 1. The K/S values of the n measurement points were calculated for the spun-dyed fabric. Furthermore, the level dyeing property of the spun-dyed fabric was evaluated by testing the relative standard deviation S_r of the surface color depth values, as shown in Eq. 2. The smaller the S_r value, the better the uniformity of the dyed fabric.

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad (1)$$

$$S_r = \sqrt{\frac{\sum_{i=1}^n \left(\frac{x_i}{\bar{x}} - 1 \right)^2}{n-1}} \quad (2)$$

where n is the number of points measured, $n = 20$ in this experiment; $x = K/S$; S_r is the relative standard deviation of the K/S value of each point with respect to its average value.

2.5 Colorfastness test

The spun-dyed fabric was tested for the colorfastness by washing with soap according to ISO105-C10 standard, during which pure white cotton cloth was used as the adjacent fabric. The size of the spun-dyed fabric and the adjacent fabric was 4 cm × 10 cm individually. The sample was washed at 60°C for 30 min to achieve colorfastness to washing with soap tester (SW-12J; Laizhou Electronic Instrument Co., Ltd.), at a bath ratio of 1:50, where 5 g L⁻¹ of soap powder and 2 g L⁻¹ of sodium carbonate were added. Washed samples were rinsed with pure water and suspended for drying.

The colorfastness of the spun-dyed fabric to artificial light was tested according to ISO105-B10 standard, in which the sample was cut into a rectangular shape of size 30 cm × 12 cm and was fixed in a frame. The colorfastness test toward light was carried out using a weathering colorfastness tester (NF1-YG611E-III; Western Chemicals (Beijing) Technology Co., Ltd.), and the exposed

and the unexposed sample fabrics were compared for colorfastness evaluation.

The colorfastness to croaking test was subjected according to ISO105-X12, using a rubbing tester for colorfastness (Y571L; Laizhou Electronic Instrument Co., Ltd.). During dry rubbing colorfastness test, the spun-dyed sample was rubbed for 10 cycles at a running speed of one reciprocating cycle per second. For the wet rubbing colorfastness test, the sample was completely immersed in distilled water and then the excess water was removed until the ratio of water to cloth was 95%. Further, similar procedure for the test was followed as that for the dry rubbing colorfastness test. The colorfastness of the fabric was evaluated using a DataColor colorimeter.

The colorfastness to heat was tested according to AATCC117 standard, using an oven (GZX-9070MBE). After being kept in a vacuum oven at 180°C for 30 s, the fabric was cooled down to room temperature and then the colorfastness was evaluated using the DataColor colorimeter.

3 Results and discussion

3.1 Color value and color depth of spun-dyed fiber

Noteworthy, the color value is one of the main quality parameters of natural pigments. It clearly reflects the level of pigment content and the strength of coloring ability. The formula for calculating color value is as follows:

$$E_{1\text{ cm}, 601.5\text{ nm}}^{1\%} = \frac{A}{m/f \div 0.01} \quad (3)$$

where $E_{1\text{ cm}, 601.5\text{ nm}}^{1\%}$ is the absorbance at 601.5 nm, when the concentration of the sample solution to be tested was 0.01 g mL⁻¹ in a 1-cm cuvette; A – absorbance of the test sample; f is the volume of solvent (mL); m is the weight of pigment in solution (g).

Noteworthy, the color value of natural pigment changes with different plants, places of origin, and batches. To obtain spun-dyed fiber with steady color depth, a

specific parameter should be used to control the industrial production. The color performance of natural pigment in fiber can be described as P , which is proportional to the color value of pigment and the addition of pigment into the fiber. It is represented as follows:

$$P = E \times c \times \frac{V}{M} \quad (4)$$

where P is the color performance of natural pigment in fiber; E is the color value of the natural indigo powder; c is the pigment concentration in the paste (g mL⁻¹); V is the volume of pigment paste injected into the mixer per minute (mL min⁻¹); and M is the mass of injected cellulose per minute (g min⁻¹).

Table 1 summarizes that based on the results, the color value of the pigment powder was obtained, and P could be calculated by using Eq. 4. The color depth of the spun-dyed fiber was measured by using DataColor described in Section 2.2. The relationship between the performance of the pigment in fiber and the color yield of the colored fiber is shown in Figure 2.

The linear regression equation was obtained according to Figure 2.

$$K/S = 0.03 P - 1.56 \quad (5)$$

Clearly, the performance of indigo in the fiber is positively linear with the color depth of the fiber and is significantly correlated. Integration of Eqs. 4 and 5 indicates that the color depth of the fiber can be controlled by changing the content and the color value of the indigo pigment.

$$K/S = 0.03EcV/M - 1.56 \quad (6)$$

3.2 The microstructure of the spun-dyed fiber

The SEM micrographs of the outer surface of cellulose fiber were obtained and are shown in Figure 3.

Notably, the spinning process of the natural indigo spun-dyed viscose fiber is the same as that for the

Table 1: The color value of the natural indigo

Serial number	Wavelength (nm)	M (g)	A	f	Color value	Color value arithmetic mean
1	601.5	0.0027	0.458	200	339.26	331.36
2	601.5	0.0045	0.463	333	342.96	
3	601.5	0.0064	0.479	416	311.85

Figure 2: Relationship between the color depth K/S of the spun-dyed fiber and the performance P of pigment in the fiber.

nondyed ordinary viscose; for this reason, the irregular grooved cylinder of their side morphology is captured in each image. Figure 3a exhibits that the nondyed viscose fiber is smooth and straight. However, Figure 3b–d demonstrates that the surface of the spun-dyed viscose fiber is inlaid with a large amount of pigment. Owing to the addition of natural indigo, the surface roughness of the fiber

becomes larger. With the increase in the performance of the pigment, the number of particles adhering to the surface of the fiber also increases, and the cohesion between the particles of the fiber increases, thereby affecting the gloss properties of the fiber and improving the quality of the yarn. Wang et al. (21) also presented similar result, which indicates that in the generation of spun-dyed fibers, some pigments get deposited on the surface of the fibers. In the SEM images of spun-dyed alginate fibers, the outer surface of fibers was given. With the increase in the added content of fluorescent pigments, more particles could be observed on the outer surface (21).

The cross-sectional SEM image of nondyed viscose fiber and the indigo pigment spun-dyed viscose fiber is displayed in Figure 4. The microstructure analysis of the natural indigo-dyed fiber in this study combined with the existing literature indicates that mass coloration technology can lead to the even mixing of the fine pigment particles with spinning solution, thus leading to the generation of evenly dispersed fibers. With the increase of pigment content, the density of the protuberant globules in the image increases. As a result, the pigment particles are embedded in the viscose fiber and are dispersed evenly. Similar results can also be obtained from literature study (22), which reported that carbon black (CB)/latex

Figure 3: The outer surface of the fiber. The magnification of the image is 20k times. (a) Viscose fiber, $P = 0$. (b) Spun-dyed viscose fiber, $P = 76.96$. (c) Spun-dyed fiber, $P = 153.92$. (d) Spun-dyed fiber, $P = 307.84$.

Figure 4: Cross-section of the fiber under different conditions. The magnification of the image is 20k times. (a) Viscose fiber, $P = 0$. (b) Spun-dyed viscose fiber, $P = 76.96$. (c) Spun-dyed fiber, $P = 153.92$. (d) Spun-dyed fiber, $P = 307.84$.

Table 2: 20 K/S data of different regions on natural indigo spun-dyed viscose fabric

Serial number	K/S ($P = 76.96$)	K/S ($P = 153.92$)	K/S ($P = 230.88$)	K/S ($P = 307.84$)
1	1.475	3.188	5.694	8.153
2	1.498	3.096	5.761	8.130
3	1.481	3.111	5.683	8.158
4	1.449	3.194	5.511	8.158
5	1.455	3.284	5.688	7.839
6	1.415	3.176	5.676	7.961
7	1.464	3.128	5.700	8.042
8	1.441	3.211	5.459	8.147
9	1.467	3.178	5.425	8.127
10	1.476	3.362	5.496	8.283
11	1.492	3.235	5.497	8.393
12	1.457	3.108	5.492	8.539
13	1.437	3.217	5.477	8.333
14	1.426	3.124	5.432	8.215
15	1.493	3.104	5.501	8.197
16	1.423	3.260	5.439	8.212
17	1.436	3.240	5.480	8.319
18	1.444	3.140	5.587	8.123
19	1.41	3.189	5.544	8.434
20	1.453	3.338	5.761	8.346
Average	1.455	3.194	5.565	8.205
S_r (%)	1.79	2.39	2.08	1.98

particles were small and uniformly distributed in aqueous media. A clear microstructure of zeolite in the composite was spotted by SEM (23). Zhang et al. prepared polylactic acid (PLA)-modified CB composite pigments by sol-gel method and then employed the open-ring polymerization method to introduce PLA molecules onto the CB surface (24). Though the “spun-dyed” film was researched rather than the spun-dyed fiber of PLA, the microstructure obtained was still strongly connected.

3.3 Level dyeing properties

The color depth K/S of 20 points on the spun-dyed fabric was measured by using DataColor following the method described in Section 2.4. The average color depth and the standard deviation were calculated by using Eqs. 1 and 2.

Table 2 presents the K/S values, indicating that the average value of the data of the 20 regions on the natural indigo spun-dyed viscose fabric ($P = 76.96$) is 1.455, and the value of S_r is 1.79%. The value S_r is small, which indicates that the dyed fabric has good uniformity, which is consistent with the visual result.

3.4 Colorfastness of spun-dyed fiber

Table 3 lists the results of colorfastness of fabric to rubbing, washing with soap, artificial light, and heat. During the spinning process, the pigment paste and viscose solution were evenly blended and then spun into fiber. The pigment was wrapped inside and effectively retained in the fiber, which resulted in significant improvement in the colorfastness to washing with soap and rubbing. The highest grade of the colorfastness to washing with soap reached 4–5, which is attributed to the fact that the indigo pigment particles are insoluble in water as well.

The natural indigo pigment itself exhibits excellent stability to sunlight and high temperature, which contributed to the grade 4–5 of the colorfastness to light and the colorfastness to heat, respectively (Figure 5).

Figure 5: The structure of the indigo molecule.

All results of colorfastness were above grade 3–4. Therefore, the requirements for subsequent finishing of the fabric could be successfully achieved. As a result, the natural indigo paste can be successfully used to color the viscose fiber to develop a fabric with high colorfastness to rubbing, washing with soap, sun exposure, and high temperature.

Table 3: Colorfastness of the spun-dyed fiber under different conditions

Category		Samples	CIE ΔE	Fastness grade
Colorfastness to washing with soap	Discoloration	$P = 76.96$	2.18	3–4
		$P = 153.92$	1.72	4
		$P = 230.88$	1.16	4–5
		$P = 307.84$	1.71	4
	Cotton stain	$P = 76.96$	1.99	4
		$P = 153.92$	1.84	4
		$P = 230.88$	2.20	3–4
		$P = 307.84$	2.07	4
Colorfastness to heat	Discoloration	$P = 76.96$	0.83	4–5
		$P = 153.92$	1.01	4–5
		$P = 230.88$	1.08	4–5
		$P = 307.84$	0.74	4–5
Colorfastness to light	Discoloration	$P = 76.96$	0.36	5
		$P = 153.92$	0.53	4–5
		$P = 230.88$	0.52	4–5
		$P = 307.84$	0.27	5
Colorfastness to dry rubbing	Dry rubbing	$P = 76.96$	1.64	4
		$P = 153.92$	0.29	5
		$P = 230.88$	0.30	5
		$P = 307.84$	0.55	4–5
	Cotton stain	$P = 76.96$	0.55	4–5
		$P = 153.92$	0.68	4–5
		$P = 230.88$	2.40	3–4
		$P = 307.84$	2.19	3–4
Colorfastness to wet rubbing	Wet rubbing	$P = 76.96$	0.44	4–5
		$P = 153.92$	1.59	4
		$P = 230.88$	1.48	4
		$P = 307.84$	1.31	4
	Cotton stain	$P = 76.96$	2.22	3–4
		$P = 153.92$	2.10	4
		$P = 230.88$	2.27	3–4
		$P = 307.84$	2.97	3–4

4 Conclusion

In this study, a spun-dyeing technique was designed to improve the colorfastness and level dyeing property of natural colorant-dyed fabric. Consequently, the natural pigment could be dispersed evenly in fiber via the spun-dyeing technology. It solved the limitation of the colorfastness to washing and rubbing. In general, the spun-dyeing technology can be used in dyeing fiber with many natural colorants, and the key technique is to process the natural colorants into dispersing color paste. Noteworthy, the particle in the disperse color paste should be small enough to easily pass through the spinneret. The microstructure was confirmed by SEM image, exhibiting uniform and even dispersion of the natural indigo particles.

The conception and calculation of color performance were suggested and confirmed by the linearity relation between the color depth of spun-dyed fiber and the value of color performance. The formula is suitable and valuable to obtain a steady color depth in producing spun-dyed fiber in the manufacturing factory.

The spun-dyed technique is very environmentally friendly, which is attributed to its low consumption of water and energy, which has been reported by many researchers. Furthermore, the utilization rate of natural colorants in the spun-dyeing process is also very high, which is more significant for natural dyes because of their high price. In particular, it is meaningful for natural colorants, mordant was not used in this research. Though the heavy metal in mordant is an origin of pollution, the mordant application is often an easy way to improve the

colorfastness in the conventional dyeing process while using natural dyes.

Some other types of natural dyes can also be prepared by the spun-dyed method, and the characteristics property should be further researched and discussed, in particular, for the soluble natural colorants combined with cellulose fiber.

The development of natural spun-dyed fibers is conducive to the protection of natural resources and the ecological environment.

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