Fibers and Polymers 2006, Vol.7, No.3, 250-254

Preparation and Dyeing of Superfine Down-powder/Viscose Blend Film

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(Received March 23, 2006; Revised July 28, 2006; Accepted August 7, 2006)

Abstract: Superfine down-powder/viscose blend films were prepared and characterized for their dyeing properties. Down-powder with average size of 2.56 μm were suspended in viscose dope and blend films were obtained by solution casting. When the blend films were dyed with acid dye, the dye uptake and K/S values increased with the increase in down-powder content. Amino-acid analyses showed that amino acid component of the down were not affected during the film formation, which confirmed the changes of dye uptake and K/S value.

Keywords: Blend film, Down-powder, Viscose, Dyeing

Introduction

There has been a great interest in investigating fibers based on regenerated protein to develop new textile fibers and to recycle redundant protein materials in recent years [1-6]. In most of these studies, protein fibers was extruded [5] from keratin using complicated chemical methods or S-sulfo keratin [6] and other polymers were blended to produce blend fibers through melt or wet spinning. However, the protein was prone to decompose in the process of spinning and the inherent microstructure of protein was destroyed inevitably. Therefore the protein biofibers might lose the original properties of the protein. On the other hand, since protein powder could keep the original properties of materials without destroying the microstructure, it has been widely applied in modern industries and hi-tech related fields with some special properties [7-9]. Silk powder was produced as one of the useful physical forms of silk fibroin protein which had some special properties compared with the fiber and silk films for biomaterial applications [10,11]. It has been also applied to finish yarn-dyed cotton fabrics which offered good drape characteristics and moisture absorbing properties [12]. Previously, we developed and characterized wool powder [13,14]. With the purpose of producing protein/polymer blend fiber without losing its original properties, we produced superfine down powder by a special mechanical pulverizer and applied it to the spinning of viscose fiber to produce down-powder/viscose blend filaments. In order to investigate the spinnability and explore its new properties, the powder was added into viscose dope to produce superfine down-powder/viscose blend films and the blend films were dyed with acid dyes. Dye uptakes were measured during the process of dyeing, K/S values and color changes of lightness L^*, saturation C^*, hue angle h and color difference ΔE_{LCh}^* of the dyed films were also measured. Amino-acid analysis was used to test the change of amino group of the blend films so as to explain the color changes of the films. In this way we could assess the compatibilities of the blend materials and show the original properties of the protein fiber in the composite, which was a good preparation of the spinning of down-powder/viscose blend filaments.

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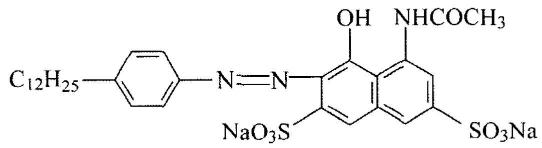
Experimental

Materials

Down fibers peeled from duck were supplied by Maolong-wuzhong Down Co. Ltd., Shaoxing, China. The viscose spinning dope was produced by Hubei Chemical Fiber Factory, China. One of commercially available acid dyes, C.I. Acid red 138, was employed. Its chemical structure is shown as follows:



Preparation and Characterization of Superfine Down Powder

Down fiber was cut into short pieces on a rotary blade and then the pieces were ground into white superfine down powder. Laser particle analyzer (Chengdu Jingxin Powder Analyse Instrument Co., Ltd. JL-1166, China) was used to measure the average particle size and size distribution of the superfine down powder. The surface morphology of the down powder was observed using a scanning electron microscope (Hitachi, model X-650, Japan) at 10 kV with gold coating on the samples.

Preparation and Morphology of Superfine Down Powder/Viscose Blend Films

Superfine down-powder was evenly suspended in distilled water with a liquor of 10:1 with vigorous stirring on a magnetic agitator and subsequently the blend solution was added into viscose spinning dope. The weight of the blend solution was changed to produce blend films with various powder contents. The powder/dope mixture was stirred by an agitator and de-aerated for an hour to make the powder blend evenly in the mixture without any bubbles. The blend mixture was cast onto a clean glass plate at a standard room condition and films were formed in a coagulating bath comprised of sulfuric acid, sodium sulfate, and zinc sulfate. Finally the films were peeled off from the plate, washed with distilled water for several times, and dried at room temperature. Blend films with 3 %, 6 %, 8 %, 10 %, 20 %, and 30 % powder contents were prepared. The morphology of the blend film was also observed using a SEM (Hitachi, model X-450, Japan) at 20 kV with gold coating on the samples.

Dyeing of the Blend Films

The dyeing of blend film follows a traditional exhaust dyeing procedure. The dye bath contained 5 % (o.w.f.) acid dye with a liquor ratio of 40:1. The films were immersed into the dyeing solution at 40 °C, heated up to 98 °C at a rate of 1.5 °C/min, and then maintained at 98 °C for 60 min. The pH of dyeing bath was adjusted to 4 by sodium acetate. For comparison, wool fabric was dyed under same conditions. Spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd. LENGGUANG 721, China) was used to measure the absorbance of the dye solution at different time intervals, the dye uptake was then calculated as the weight percentage of dye in the solution, and the exhaustion curves were obtained at the same time.

Color Measurement

Color characters of dyed films such as L^*, C^*, h, ΔE_{LCh}^*, and K/S values were measured using a Computer Color Matching System (Datacolor International, SF600, Switzerland), using illuminant D_{65} and 10° standard observer condition. Relative colour strengths (K/S values) is measured based on the equation of Kubelka-Munk:

$$K/S = (1-R)^2/2R \qquad (1)$$

where K refers to the coefficient of absorption, S is the coefficient of scattering, and R is the reflectance of the dyed blend film.

Amino-acid Analysis

Amino-acid analysis was carried out with a HITACHI 835-50 amino-acid analyzer in CCTCC (China Centre for Type Culture Collection).

Results and Discussion

Preparation and Characterization of Superfine Down Powder

Figure 1 shows the particle size and frequency distribution of the superfine down-powder. It was apparent that the particle size of the powder was between 0.5 μm and 12 μm, but the 80 % of the powder was under 3.5 μm, where particle sizes of 1 μm and 1.5 μm of the whole powder kept

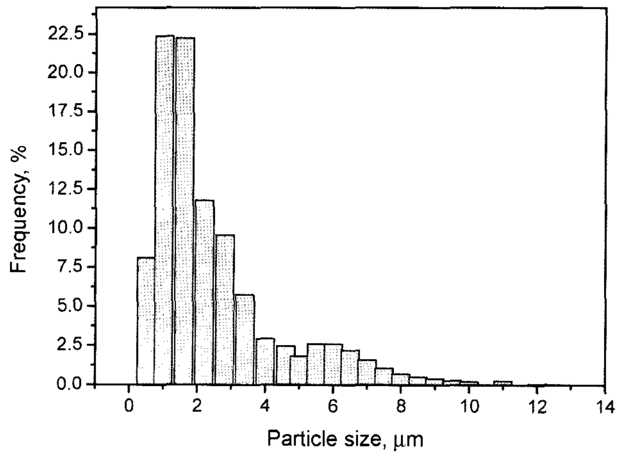


Figure 1. Size distribution of down powder.

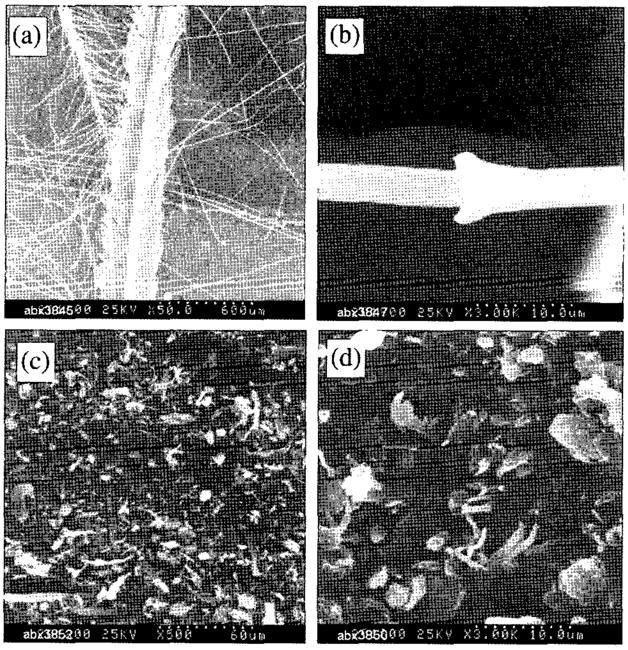


Figure 2. SEM photos of down fiber (a) ×50 and (b) ×3000 magnification; and down powder (c) ×500 and (d) ×3000 magnification.

22.4 % and 22.26 %, respectively. The average particle size of the powder was calculated to 2.56 μm. In order to get a clear surface morphology of superfine down powder, SEM photos were taken for both the down fiber (a) and (b) and superfine down powder (c) and (d) with different magnifications, as shown in Figure 2. It was obvious that down fiber was cut into small pieces and superfine powder was obtained. Compared with down fiber, whose diameter was about 30 μm from photo (b), the diameter of superfine down powder were extremely small, and the down fiber was ground into small powder evenly from photo (c), the dimension of the powder was under 10 μm as the photo (d) showed, but most

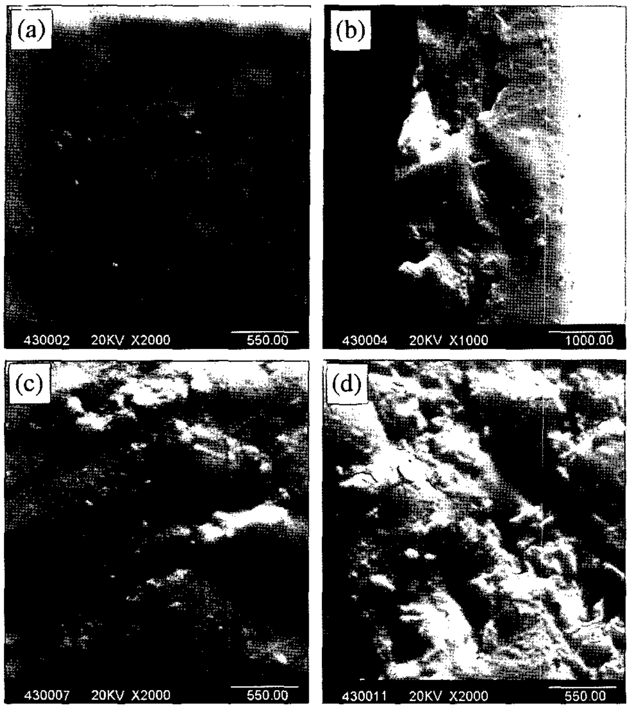


Figure 3. SEM photos of viscose film and superfine down powder/ viscose blend film: plane (a) and cross-section (b) of viscose film; plane(c) and cross-section (d) of blend film.

of them was smaller than 10 μm. Most of the down fibers were ground into small pieces and some of them into needles.

Morphology of Blend Films

Figure 2 shows the SEM photos of viscose film and superfine down-powder/viscose blend film. (a) and (b) were the taken from the plane and cross-section of viscose film, obviously that viscose could be molded into film with smooth surface and cross-section, whereas in the SEM photos of blend film (c) and (d), superfine down-powder could be found both in the plane and cross-section of blend film, and it was distributed evenly.

Dye Uptake of the Blend Films

As a kind of protein fiber, down-fiber could be dyed by acid dyes easily, so it is expected that the down-powder/ viscose blend films could be dyed with acid dyes. In this paper, the blend films, viscose film, and wool fabric were dyed by acid dyes under the same experimental condition and the exhaustion curves of all the samples were shown diagrammatically in Figure 4. From Figure 4, it was evident that viscose film could be hardly dyed with acid dyes, because it only absorbed 18 % of dye even in the end. However, the dyeing rate of wool fabric was much quicker and the dye uptake reached 99.5 %. The dye uptake curves had apparently the same trend in the dye uptake of the blend films. The slope of each curve was steep at the first few

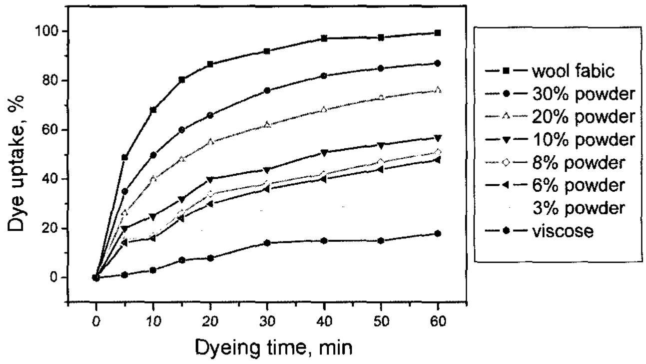


Figure 4. Dye uptake of down powder/viscose blend films with different powder contents as a function of dyeing time.

minutes and slowed down after that. The dye uptake was enhanced obviously as the plume powder content increased. The dye uptake of the film with 30 % down powder reached 87 % at the end of the dyeing process, which was nearly the same as the dye uptake of wool fabric which showed excellent dyeing affinity to the acid dye. The dye uptake was found to be enhanced unexpectedly for the film with only 3 % down powder. Conclusively the superfine down-powder/ viscose films could be dyed by acid dye and optimum dye uptake would be attained if the powder content was larger than 10 %.

Color Evaluation of the Dyed Blend Films

In order to evaluate the color character of dyed films, the K/S values and changes in color of L^*, C^*, h, and $\Delta E_{LCh}{}^*$ of all samples were tested. The results were shown in Figure 5 and Table 1. In Figure 5, the K/S value curves of all the blend films with powder content of 3 %, 6 %, 8 %, 10 %, 20 %, and 30 % were shown at the wavelength from 400 nm to 700 nm, it was obviously that the K/S values of the dyed viscose were just little above 0 and kept constantly, while the other dyed blend films increased K/S values with a maximum K/S at the wavelength of 510 nm. The more powder content the blend films had, the higher K/S values were attained. Table 1 shows that the powder content had a strong effect on

Table 1. Effect of powder content on the color of down powder/ viscose blend films

Powder content, %	L^*C^*h color system			Color differences, $\Delta E_{LCh}{}^*$
	L^*	C^*	h	
0	84.2	13.6	56.9	-
3	66.4	40.1	24.6	34.5
6	58.2	52.8	23.8	49.5
8	55.7	54.6	24.7	52.2
10	53.2	59.3	26.2	57.2
20	48.6	61.4	29.8	61.1
30	46.2	58.9	29.8	60.7

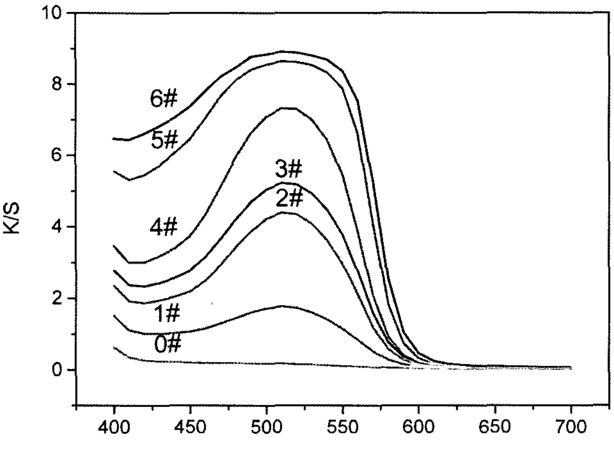


Figure 5. K/S curves of down powder/viscose blend films with different down powder contents: 0#: viscose film, 1#: 3 %; 2#: 6 %; 3#: 8 %; 4#: 10 %; 5#: 20 %; 6#: 30 %.

color characters of all the blend films. The lightness (L^*) decreased as the powder content increased, while the saturation of color (C^*) rose apparently but the hue angle *h* had little changes as the powder content increased. The color differences ΔE_{LCh}^* increased gradually with the increasing powder content.

Amino Acid Analysis

All the results above indicate that the dye uptake and color values of the films with different superfine down-powder contents are largely determined by the content of amino group of the fiber. We can assume that the blend films would contain different contents of amino groups which could change the dye properties of the films. Amino-acid analysis was taken on the blend films with powder content of 6 %, 10 %, 15 %, 20 %, and 30 %. For comparison, the amino-acid of pure down-powder was also tested. 17 kinds of amino-acids and ammonia were tested and the results were presented in Table 2. It was apparent that all the amino acid content increased greatly as the powder content increase except for the film with 30 % powder content. Compared with the amino-acid content of down-powder, the real amino-acid contents in the blend films were lower than the added content. The discrepancy was bigger as the powder content increased. This suggests obviously that the powder might disappear somewhat in the molding of the film in the coagulating bath. Though the amino group content of wool is just 0.8-0.9 mmol per gram, 0.1 mmol amino group per gram is enough for the fiber to be dyed with acid dye and yield acceptable color. Since the amino group content of film with 6 % down powder was calculated to be 0.288 mmol per gram, we could claim that all the blend films could be dyed with acid dyes.

In order to show the relations among the dye uptake, K/S values, and amino acid content of the blend films, all the three data with different powder contents were compared in Figure 6. Dye uptake data shown were tenfold of its original values so as to make the comparison more evident. It was evident that the K/S values and dye uptake increased in

Table 2. Amino acid content of blend films with different down contents

Amino-acid, mg/100 g	Down content, %					
	6	10	15	20	30	100
Asparagine	176.24	317.92	491.58	762.29	753.53	5360.00
Threonine	131.08	246.11	380.65	608.72	595.92	4200.00
Serine	295.10	620.39	921.78	1448.37	1406.65	1047.00
Glutamic acid	332.63	710.21	1079.59	1739.79	1691.25	1116.00
Glycocoll	184.90	303.35	469.94	778.90	765.22	6140.00
Alanine	128.74	234.80	338.45	520.05	501.42	3560.00
Cystine	41.62	76.09	126.08	197.97	229.88	6110.00
Valine	287.13	474.06	633.19	882.70	864.33	6450.00
Methionine	16.12	94.23	100.22	111.23	106.09	620.00
Isoleucine	183.41	334.63	425.27	615.68	614.01	4730.00
Leucine	200.85	373.08	588.14	950.26	951.82	7200.00
Tyrosine	54.56	46.18	113.92	135.23	148.94	2700.00
Phenylalanine	150.14	244.07	334.00	546.19	533.34	4880.00
Lysine	46.03	90.23	96.09	153.93	148.98	1390.00
Ammonia	98.77	71.47	152.79	249.17	200.26	1490.00
Histidine	-	16.72	20.27	33.39	34.38	400.00
Arginine	263.70	358.50	477.40	622.58	643.96	6620.00
Proline	305.77	567.06	859.29	1366.55	1419.99	9260.00
Total	2896.79	5179.19	7608.65	11723.00	11609.97	92740.00

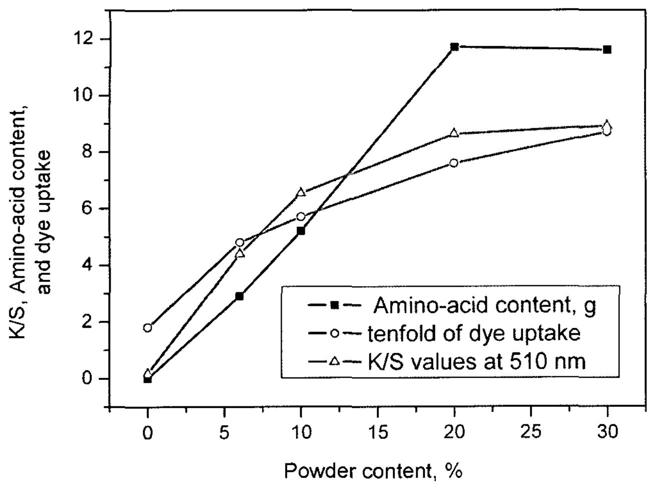


Figure 6. Comparison of K/S, amino-acid content, and dye uptake of down powder/viscose films with different powder content.

proportion to the amino acid content. Since in the dyeing process under the acid condition, anions of the acid dyes are combined with amino groups of the films through ionic bonds, more amino groups can attract the anionic dyes more quickly and consequently the dye uptake increases.

Conclusions

The average particle sizes of the superfine down powder were around 2.56 μm with 80 % of power sample having the powder diameter smaller than 3.5 μm. and the powder distributed evenly as seen in the SEM photos. The powder could be applied to improve the acid-dyeability of viscose. With the increase of powder content in the blend films, the films absorbed dye more quickly and the dye uptakes were enhanced greatly. K/S values of all the blend films showed a maximum at the wavelength of 510 nm and the K/S peak values increased with increase in powder content. L^* was decreased and C^* and $\Delta E_{LCh}{}^*$ were increased as the powder content increased, while hue angle *h* hardly changed. Amino acid content of all the blend films increased with the powder content and the increase of the content of amino group in the films led to the improvement of the dyeing properties of the blend films such as dye uptake, K/S values, and color values for acid dyes.

Acknowledgements

This project is funded by "The founding for Innovation Team of the Natrural Science Foundation of Hubei Province" and "the funding for supporting the elitistsof new Centuty from the Ministry of Education of China"".

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