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The Effects of Cultivars and DAPs(Days After Planting) of Kenaf Plants on Lignin Contents and Dyeability of Their Fibers

Jeon Sook Rhie · Hyeja Yoo†* · Christine M. Ladisch**

Dept. of Clothing & Textiles, Chonbuk University
*Dept. of Clothing & Textiles, Seowon University
**Dept. of Consumer Science & Retailing, Purdue University

품종과 재배기간이 다른 케나프 섬유의 리그닌 함량과 염색성

이전숙 · 유혜자†* · Christine M. Ladisch**

전북대학교 의류학과, *서원대학교 의류학과
**Dept. of Consumer Science & Retailing, Purdue University

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Abstract

The effects of cultivar and DAPs on the lignin content and dyeability of the kenaf fibers were investigated. Four kenaf fiber samples were prepared from two cultivars, *Tainung 2* and *Everglades 41*, and their 60 and 120 DAPs(days after planting) for the experiments. The lignin contents of the kenaf fibers of *Tainung 2*(T2) and *Everglades 41*(E41) were 11.29~12.78%. Both T2 and E41 kenaf fibers had comparable amount of lignin, and klason lignin of the fibers was 2.5~3 times as much as much as acid-soluble lignin. In both T2 and E41, 120 DAPs kenaf have 1% more lignin than 60 DAPs kenaf. The moisture regains of the four kenaf fiber samples were almost the same as 10.25±0.05%. The absorbances of residual solution after dyeing for 1~180 minutes with Red 81 at maximum wavelength 520 nm and Green 26 at 600 nm were measured. Comparing to Green 26, the dyeing rate of Red 81 was rapid and equilibrium state was reached in 12 minutes. The CIE L*, a*, b*, ΔE and K/S values of the kenaf fibers dyed with Red 81 and Green 26 were measured as well. The dye exhaustion ratio of 60 DAPs kenaf was higher than that of 120 DAP.

Key words: Kenaf, Cultivar, Days after planting, Contents of lignin, Dye-uptake; 케나프, 품종, 재배기간, 리그닌 함량, 염착량

I. Introduction

Kenaf is a member of the hibiscus family(*Hibiscus cannabinus L*) and closely related to cotton and jute. Because of its biodegradability and environmental compatibility(Warnock & Ferguson, 1996), the demand of kenaf has increased. The kenaf has become a potential natural fiber source for both apparel and industrial applications(Han et al., 2003: Ramaswamy & Easter, 1997; Tao et al., 1999). Kenaf consists of an inner core part and an outer bast part. The outer bast part can be separated by decortication of kenaf stem. And then, the kenaf fiber can be taken by retting(Kuroda et al., 2005; Lee et al., 2003: Morrison et al., 1996; Parikh et al., 2002; Sharma et al., 1999). The main composition of kenaf fibers are cellulose, hemicellulose and lignin which is a complex, amorphous and aromatic biopolymer. Lignin is found in all vascular

†Corresponding author
E-mail: hjyoo@seowon.ac.kr

plant mostly between the cells and also within the cells and in the cell walls. Lignin is also a complex polymer of phenylpropane units of molecular weight 15,000 or more(McCrady, 1991, Wang & Ramaswamy, 2003). The large molecules in lignin are heavily cross linked and makes vegetables firm and crunchy. Lignin is a material that binds the fiber bundles and hardens the cell walls of plants, and also makes fiber bundles coarse and stiff. The coarseness and stiffness make kenaf fiber processing difficult. Lignin can be removed partly by alkaline treatment(Carr et al., 2005; Kuroda et al., 2005; Morrison et al., 1996; Nishima et al., 2002: Wang & Ramaswamy, 2005).

Lignin is generally classified into guaiacylpropane, syringylpropane and hydroxyphenylpropane structures according to the products of oxidation decomposition(Morrison et al., 1999; Nishima et al., 2002). The lignin contents can be obtained by measuring contents of klason lignin and acid-soluble lignin by H_2SO_4 carbonizing separation method.

The differences in fiber quality of kenaf are known to results from cultivar, location, climate, maturity, days after planting, etc. In this research, four samples of kenaf fiber were prepared from two kinds of cultivar, Tainung 2 and Everglades 41, and their 60 and 120 DAPs(days after planting). The effects of cultivar and DAPs on the lignin content and dyeability of the kenaf fibers were investigated.

II. Experimental

1. Preparation of Kenaf Fiber Samples

Two kinds of kenaf cultivar, *Tainung 2*(T2) and *Everglades 41*(E41) were obtained from M.M. Warnock in University of Arkansas. Their DAPs were 60 and 120. The bastes of these four kenaf were retted in 2% NaOH aqueous solution at 100°C for one hour. They were rinsed two or three times in warm and hot water to clean and then were kept in room temperature for drying. The dried kenaf fibers were carded with a hand card and the carded fibers were scoured after being weighted.

The fibers were scoured by soaking in aqueous solution of 5%(owf) NaOH, 1%(owf) Na_2SiO_3 and 1%(owf) AATCC soap and gently boiling for 3 hours at 100°C. After scouring, the kenaf fibers were bleached by soaking in aqueous solution of 5%(owf) H_2O_2, 14%(owf) Na_2SiO_3 and 1%(owf) Triton X-100 at 85C for 1 hour. The fiber-to-liquor ratio in the scouring and bleaching bath was 1:20(w/v). Deionized water was used for scouring, bleaching and dyeing.

2. Measuring of Lignin Content

Measuring of lignin contents of the kenaf fibers were carried out by Chemical Analysis & Testing Standard Procedure No. 003(Determination of Klason lignin in Biomass) and No. 004(Determination of Acid Soluble Lignin in Biomass). This test methods were recommended by Alternative Fuels Division of NREL(National Renewable Energy Laboratory).

The air dried kenaf fibers were dried at 105°C in drying oven for 2 hours. About 1g of fiber after weighing was put in a test tube and 15 ml of 72% sulfuric acid was added carefully, and then kept for 2 hours at 20°C while stirring every 15 minutes. It was transferred to 1*l* ground flask and diluted by 560ml of deionized water to decrease acid concentration to 3%. Then it was boiled gently for 4 hours in the flask with a reflux condenser.

The solution was cooled and vacuum filtered with filtering crucibles and volume of filtrate was measured. Half of the filtrate was remained for acid-soluble lignin determination. The other half of filtrate was put into a crucible and was dried at 105°C for 2 hours. After cooling in a desiccator, the dried residue was weighed precisely(W2). This residue contained klason lignin and acid insoluble ash. To get a content of klason lignin, the dried residue was burnt to ashes in a furnace at 575±25°C for 3 hours. The ash was cooled in a desiccator and then weighed precisely (W3). To calculate the acid-soluble lignin, absorbance in 205nm of the diluted filtrate was measured by a spectrophotometer.

3. Moisture Regain

The moisture regain, % of retted kenaf fibers was measured in accordance with ASTM D 2654(Stan-

dard test methods for moisture in textile materials).

4. Dyeing Procedures

The scoured and bleached kenaf fibers were dyed in a shaking dyebath with dyes of C.I. Direct Red 81(Red 81) and C.I. Direct Green 26(Green 26). Red 81 is a diazo type dyestuff and its molecular weight is 663. It has two anionic sulfonate group as shown in <Fig. 1>. Green 26 has tri azo structure and larger molecular weight than Red 81 as 1306. It has four anionic sulfonate, carboxylic and hydroxyl group as shown in <Fig. 1>.

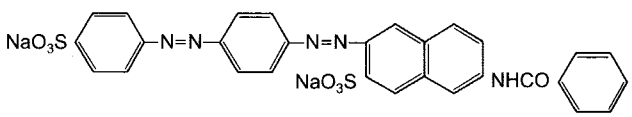
Dyeing was carried in a dye-bath of 1%(owf) dye and 5%(owf) Glauber's salt at 90°C for 1, 2, 3, 4, 5, 7, 9, 12, 24, 48, 96, 180minutes. Fiber-to-liquor ratio was 1:50(w/v) in a dyebath and dyeing was carried out twice with the same procedure for duplication.

The Spectrocolorimeter(Color-Eye 3100, Macbeth, U.S.A.) was used for color measurement. Absorbance values of the residual solution and ΔE, L, a, b and K/S values of the fibers dyed were investigated. Maximum wavelength of absorbance was shown at 520nm in the Red 81 solution and at 600nm in the Green 26 solution.

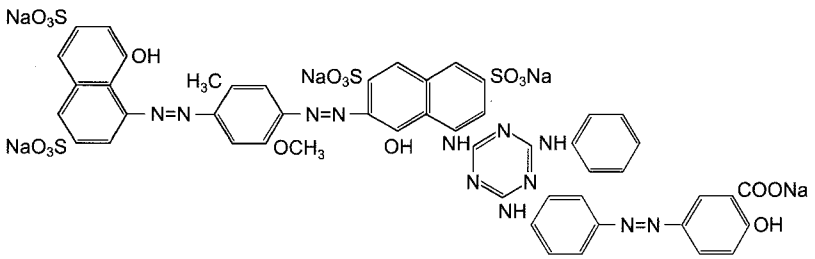
III. Results and Discussion

The contents of klason, acid soluble and total lignin in the 4 samples of the retted kenaf fibers were measured and shown in <Table 1>.

It shows that both T2 and E41 kenaf fibers have almost the same total amount of lignin and klason lignin of the fibers was 2.5~3 times as much as acid soluble lignin. It accords with Akin et al.(1997)'s report that cultivars did not affect the chemical components and lignification. The lignin content was changed with the DAPs. In both E41 and T2, 120 DAP kenaf has 1% more than 60 DAP, but their acid soluble lignin amounts are same. The longer the kenaf plants grow, the more lignin they have and the harder they become because lignin binds together the fiber bundles in kenaf. On the other hand, the moisture regains of four samples of kenaf fibers were



(a) C.I. Direct Red 81(Red 81)



(b) C.I. Direct Green 26(Green 26)

Fig. 1. The chemical structures of dyes used for kenaf fiber dyeing.

Table 1. The lignin contents of the retted kenaf fibers

Types of lignin	Tainung 2(T2)		Everglades 41(E41)	
	60 DAP	120 DAP	60 DAP	120 DAP
klason lignin(%)	8.28	9.51	8.18	9.24
acid soluble lignin(%)	3.37	3.27	3.11	3.28
total(%)	11.65	12.78	11.29	12.52

almost same as 10.25±0.05% regardless of cultivar and DAP.

Dyeing was carried in dyebath of 1%(owf) Green 26 and Red 81 at 90°C for 1, 2, 3, 4, 5, 7, 9, 12, 24, 48, 96, 180 minutes, respectively. Red 81 is a dyestuff of disazo type and its molecular weight is 663. It has two anionic sulfonate group. Green 26 has trisazo structure and large molecular weight as 1306. It has four anionic sulfonate, carboxylic and hydroxyl group. <Fig. 2> and <Fig. 3> indicates the absorbances(from 340nm to 740nm) of the residual solutions after dyeing E41(DAP 60) kenaf fiber with C.I. Direct Red 81 and Green 26 respectively.

As showing <Fig. 2> and <Fig. 3>, the absorbances of residual solutions in the control dyebath were 0.883 at 520nm in Red 81 and 0.286 at 600nm in Green 26 before dyeing and were decreasing with dyeing time. <Table 2> and <Table 3> indicate the absorbances of residual solution after dyeing with Red 81 at wavelength 520nm and Green 26 at 600nm for 1~180 minutes respectively. Comparing to Green 26, the dyeing rate of Red 81 was rapid and equilibrium state was reached in 12 minutes. The reason is that the molecular weight of Red 81 is small.

The dye exhaustion ratios based on the results of <Table 2> and <Table 3> were represented in <Fig. 4> and <Fig. 5>. Dye exhaustion ratio of kenaf fiber was low as about 30% in Red 81 but was reached as

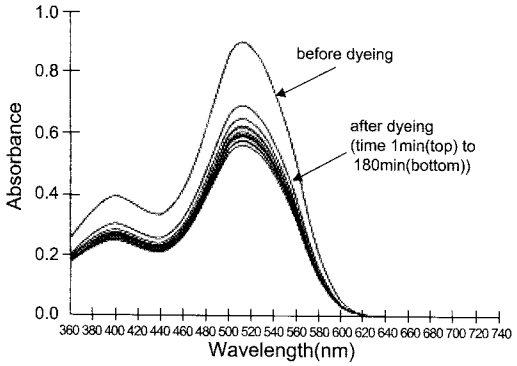


Fig. 2. The spectrophotometric absorbance curves of residual solutions after dyeing E41(DAP 60) kenaf fiber with C.I. Direct Red 81.

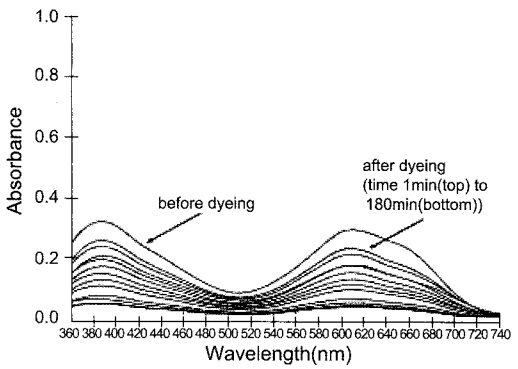


Fig. 3. The spectrophotometric absorbance curves of residual solutions after dyeing E41(DAP 60) kenaf fiber with C.I. Direct Green 26.

Table 2. The absorbance of residual solution of C.I. Direct Red 81 at 520nm

Dyeing time (min)	Tainung 2		Everglades 41	
	60 DAP	120 DAP	60 DAP	120 DAP
1	0.682	0.700	0.680	0.691
2	0.653	0.659	0.665	0.656
3	0.625	0.627	0.618	0.639
4	0.615	0.616	0.615	0.617
5	0.588	0.599	0.590	0.602
7	0.573	0.588	0.575	0.574
9	0.564	0.569	0.560	0.575
12	0.556	0.569	0.550	0.562
24	0.566	0.571	0.578	0.571
48	0.586	0.577	0.576	0.573
96	0.594	0.574	0.587	0.585
180	0.585	0.588	0.574	0.588

Table 3. The absorbance of residual solution of C.I. Direct Green 26 at 600nm

Dyeing time (min)	Tainung 2		Everglades 41	
	60 DAP	120 DAP	60 DAP	120 DAP
1	0.211	0.227	0.221	0.224
2	0.201	0.212	0.197	0.213
3	0.176	0.193	0.185	0.199
4	0.168	0.190	0.166	0.199
5	0.148	0.178	0.155	0.179
7	0.123	0.152	0.133	0.171
9	0.111	0.145	0.119	0.162
12	0.093	0.138	0.092	0.144
24	0.064	0.095	0.071	0.112
48	0.051	0.069	0.054	0.077
96	0.041	0.050	0.042	0.059
180	0.037	0.043	0.036	0.047

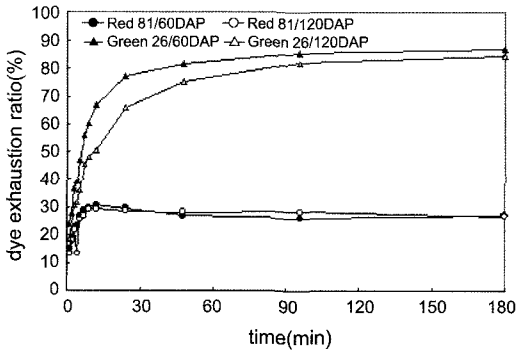


Fig. 4. Dye exhaustion ratio of T2 kenaf fiber.

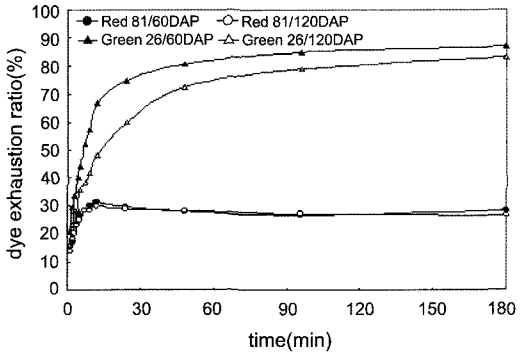


Fig. 5. Dye exhaustion ratio of E41 kenaf fiber.

much as 88% in Green 26.

<Table 2> showed that dyeing equilibriums of Red 81 were reached in 12 minutes. But dyeing rate of Green 26 was very slow and their dyeing equilibriums were reached in over 48 minutes. Even though the exhaustion ratio was lower, the absorbance in Red 81 appeared higher than in Green 26.

Both cultivars of E41 and T2 showed similar dyeability. In case of Red 81 of which exhaustion ratio was low, the kenaf fiber of 60 DAP and 120 DAP were showed similar dyeability. But, in Green 26, the dyeing rate of 60 DAP kenaf fiber was faster and the dyeability was better than 120 DAP. This result tallies with Miyata's report(2003) that there were effects of the kenaf(Zhejiang No.1 cultivar from China) plant days on the sorption of direct dyes and the orientation.

The CIE L*, a*, b*, ΔE of the kenaf fibers dyed with Red 81 and Green 26 were represented in <Table 4>. When the kenaf fiber was dyed with Red 81, ΔE values of T2 and E41 of 60 DAP were 44.79 and 43.00 and ΔE values of T2 and E41 of DAP 120 were 40.87 and 41.78 respectively. Kenaf fibers of DAP 60 showed better dyeability than DAP 120. When the kenaf fibers were dyed with Green 26, ΔE values of T2 and E41 of DAP 60 were 38.50 and 38.21 and ΔE values of T2 and E41 of DAP 120 were 33.38 and 35.70. These are in a good agreement with the results of dye exhaustion. In other words, dye exhaustion ratio and the surface color of the fiber of 60 DAP kenaf were better than 120 DAP.

<Fig. 6> shows K/S values of the dyed kenaf fiber. The K/S values were obtained by reflectance ratio in

Table 4. The color values of the dyed kenaf fiber

Dyestuff	cultivar of kenaf	DAP of kenaf	L	a	b	ΔE
C.I. Direct Red 81	Tainung 2	60	54.92	34.41	8.75	44.79
	Everglade 41	60	54.41	32.84	7.48	43.00
	Tainung 2	120	56.06	32.19	7.87	40.87
	Everglade 41	120	57.88	32.59	7.11	41.78
C.I. Direct Green 26	Tainung 2	60	52.76	-15.19	3.54	38.50
	Everglade 41	60	51.32	-14.72	3.28	38.21
	Tainung 2	120	54.12	-14.73	4.32	33.38
	Everglade 41	120	54.86	-15.11	4.06	35.70

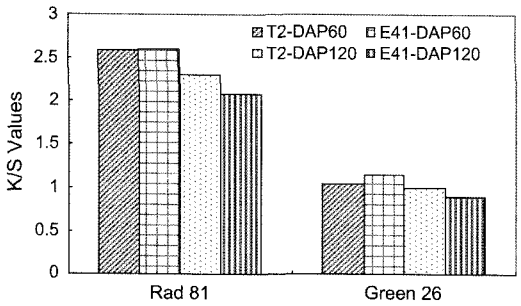


Fig. 6. K/S Values of the dyed kenaf.

Red 81 at maximum wavelength 520nm and Green 26 at 600nm. According to ΔE values in <Table 4> and K/S values in <Fig. 6>, the exhaustion ratio in Red 81 appeared lower than in Green 26, but the surface was dyed deeper. This is because Red 81 has smaller molecular size than Green 26.

IV. Conclusions

The lignin contents of four kinds of kenaf fibers taken from two kinds of cultivar of *Tainung 2* and *Everglade 41* and two different DAPs(days after planting) of 60 and 120 were investigated and their lignin contents were measured as 11.29~12.78%. The lignin content was changed according to the DAPs, and 120 DAP kenaf has 1% more than 60 DAP in both *Tainung 2* and *Everglade 41*. But their acid soluble lignin amounts were same and have 2.5~3 times as much klason lignin as acid soluble lignin. The moisture regains of the four kenaf fibers were almost same as 10.25±0.05%.

The scoured and bleached kenaf fibers were dyed with direct dyes of C.I. Direct Red 81(Red 81) and C.I. Direct Green 26(Green 26). The dyeing rate of Red 81 was rapid and equilibrium state was reached in 12 minutes. The dyeing rate of Green 26 was very slow and it's dye uptake was increased continuously. equilibrium state of Green 26 was reached in over 48 minutes regardless of cultivar. The maximum absorbance of control dyebath of Red 81 was 0.883 at 520nm and Green 26 was 0.286 at 600nm. The absorbance in Red 81 appeared higher but the exhaustion ratio appeared lower than in Green 26. The dye exhaustion ratios of Red 81 and Green 26 were 30% and 88%, repectively.

Both cultivars of *Everglade 41* and *Tainung 2* showed similar dyeability. In the case of Red 81 of which exhaustion ratio was low, the kenaf fiber of 60 DAP and 120 DAP showed similar dyeability, but in Green 26, the dyeing rate of 60 DAP kenaf fiber was faster and the dyeability was better than 120 DAP.

It was found that the dyeability and lignin contents of kenaf were not affected by their cultivars, but could be affected by their DAPs.

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요 약

케나프의 품종과 재배기간에 따라 섬유의 리그닌 함량과 염색성 변화를 검토하였다. Everglaze 41와 Tainung 2, 두 종류의 케나프 품종을 각각 60일과 120일간 재배한 4종류의 시료를 준비하였다. 4종류의 시료의 리그닌 함량은 11.29~12.78%였으며, 품종에 따라서는 차이가 나타나지 않았고 재배기간에 따라서는 60일 재배한 케나프보다 120일간 재배한 섬유의 리그닌 함량이 1% 정도 더 많았다. 케나프 섬유의 염색성은 분자량이 다른 C.I. Direct Red 81과 C.I. Direct Green 26, 두 종류의 염료로 4종의 케나프를 1~180분 동안 염색하였다. 소정의 시간 동안 염색한 후 여액의 흡광도를 측정하여 염착속도를 고찰하였으며 염색된 섬유의 표면색을 측정하였다. 본 연구의 실험결과, Red 81로 염색한 경우, 염착속도가 매우 빨라서 품종에 관계없이 12분 정도에 평형에 도달하였으며 Green 26으로 염색한 경우 염색시간 48분 이상에서 평형에 도달했다. 한편, 염료소모율은 각각 30%와 88%로 Green 26에 대한 소모율이 높았다. 품종에 따라서는 차이가 없었으나 재배기간에 따라서는 약간의 염색성 차이를 보였다. 즉, Red 81로 염색한 경우는 60일과 120일 재배한 케나프의 염색성이 비슷했으나 Green 26으로 염색했을 경우에는 60일 재배한 섬유가 120일 재배한 섬유에 비해 염착속도도 빠르고 표면색도 더 진하게 염색되었다.