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Improving Dyeability of Safflower Yellow Colorants on Cellulose Fibers

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홍화 황색소의 셀룰로오스 섬유에 대한 염착성 증진

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Abstract

To improve poor dye uptake of safflower yellow colorants, cellulose fibers were pretreated with chitosan. The effect of chitosan pretreatment on the dyeability of safflower yellow colorants to cotton, ramie, and rayon was investigated in terms of dye uptake, color, and colorfastness. Irrespective of fiber types, dye uptake increased continuously with increase in chitosan concentration. Chitosan pretreatment improved dye uptake up to 5.6 times for cotton, 7.2 times for ramie, and 3.7 times for rayon. For cotton and ramie, the shade of dyed fabric changed YR color to Y color with increase in chitosan concentration. Dyed rayon fabrics showed Y color irrespective of chitosan concentration. Shades got darker and deeper with increasing chitosan concentration. Shades of chitosan pretreated fabrics were shifted differently depending on dyeing temperature within same fabrics. In common, the color of all dyed fabrics changed to YR at 50 and 70°C while Y color at 30 and 90°C. V and C value decreased with increase in dyeing temperature and resulted in darker and duller color, in general. Light fastness was fair while washing fastness was poor. It was confirmed that ultrasonic dyeing method enhanced dye uptake more than 30% for cotton and ramie fabrics compared to the conventional automatic machine dyeing method. However, no difference in dye uptake between two dyeing methods was found for rayon.

Key words: Safflower yellow colorants, Dyeability, Cationization, Colorfastness, Ultrasonic dyeing; 홍화 황색소, 염색성, 양이온화, 키토산, 염색견뢰도, 초음파염색

I. Introduction

The flower petals of safflower(*Carthamus Tinctorius* L.) have long been used as coloring materials. Although it has yellow and red components, mainly the red component(carthamin) has been used for cosmetics and textiles(Kanehira et al., 1990). The water-soluble yellow components of safflower petals have been hardly used for a dye and are currently using as a natural food colorants. We became to notice its potentiality as a resource of yellow natural dye. A growing interest in the use of natural dyes in textile coloration has gained. The stringent environmental standards imposed by many countries. Ecofriendly and biodegradable dyes derived from natural resources have emerged as important alternatives to synthetic dyes. Meanwhile, natural dyeing of cellulose fibers

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such as cotton, ramie, and rayon has always posed challenges because they are not easy to dye from plant colorants, in general. Many researches have been done to improve the dyeability of cellulose fibers. Among them, using metallic mordants posed serious ecological constraints. Cationization using ecofriendly chitosan has been reported as a feasible way to improve dyeability of cotton fiber(Shin & Yoo, 1998). Chitosan is a cationic biodegradable and nontoxic biomaterial derived from the shell of shrimp, prawn, crab, etc. and has been applied in textile area as a finishing agent to impart antimicrobial properties(Shin et al., 1999) and to improve dyeability(Shin & Yoo, 1998) and shrink resistance(Vilchez et al., 2006). On the other hand, new ultrasonic dyeing method has been proved as a way of improving poor dye uptake of natural dyes(El-Shishtawy et al., 2003; Vankar et al., 2007).

In this work, effects of chitosan pretreatment on the dyeability of safflower yellow colorants to cotton, ramie, and rayon fibers were investigated in terms of dye uptake, CIE Munsell color, and fastness. Also, ultrasonic dyeing method was applied for chitosan pretreated fabrics and assessed the enhancing effect of dye uptake compared to conventional machine dyeing method.

II. Experimental

1. Materials

Bleached and scoured cotton, ramie and rayon fabrics were used. Characteristics of the fabrics are presented in <Table 1>. Chitosan(KL-245, Kitolife Co., Korea) obtained commercially has 95% degree of deacetylation and 145,000(Mw) of molecular weight.

2. Methods

Safflower yellow colorant was extracted in distilled water at 40°C for 2 hrs two times using a constant temperature shaking bath. The first and second extracts were mixed together, concentrated with a vacuum evaporator, and freeze-dried at -40°C to obtain colorants powder.

Table 1. Characteristics of fabrics used

Sample	Weave	Fabric count (wxf/inch^2)	Weight (g/m^2)	Thickness (mm)
Cotton	plain	95×86	80	0.20
Ramie	plain	60×46	118	0.32
Rayon	plain	104×75	55	0.11

Fabric samples were padded with chitosan solution(0.5~2.0%, owb) in 2% acetic acid in two dips and two nips method, dried at 70°C for 2 min, cured at 115°C for 3 min, washed, and dried for dyeing. Add-on was calculated from fabric weights before and after chitosan treatment.

For machine dyeing, the fabrics pretreated with chitosan were dyed in 1%(owb) dye solution at varied temperatures(30, 50, 70, & 90°C) for 40 min in a liquor ratio of 1:100 with infra-red automatic dyeing machine(Ahiba Nuance, Data Color International, USA). For ultrasonic dyeing, the fabrics pretreated with 2% chitosan concentration were dyed in 1% (owb) dye solution at 50°C for 40 min in a liquor ratio of 1:100 using a ultrasonicator(35 kHz, Sung-Dong Co., Korea). After dyeing, fabrics were rinsed with distilled water and dried for further evaluation.

Fastness to washing was evaluated using Launder-Ometer by AATCC method 61-1984(1A). The color change and staining of test samples were assessed by the Gray Scale and Chromatic Transference Scale, respectively. Light fastness was assessed in terms of color difference(ΔE) and color change against the Gray Scale according to AATCC method 16-1998 with Fade-Ometer(Atlas Electric Devices Co, USA). Color differences were measured with a Macbeth Coloreye after irradiating for 5, 10, 20, and 40 hours.

Color values were evaluated in terms of K/S values and CIELAB(Illuminant D65/10°Observer) with a Macbeth Coloreye 3100 spectrophotometer at 400 nm(λ max). Color difference(E) and H V/C values were obtained from L*a*b* data using the CIE Munsell conversion program.

III. Results and Discussion

1. Effect of Chitosan Concentration

<Table 2> shows add-on of the chitosan-pretreated cotton, ramie, and rayon fabrics. The add-on increased

Table 2. Add-on(%) of the fabrics pretreated with chitosan

Sample	Chitosan conc.(%)			
	0.5	1.0	1.5	2.0
Cotton	0.54	1.21	1.65	2.67
Ramie	0.29	0.76	0.83	0.94
Rayon	1.56	1.89	2.05	2.05

with increasing chitosan concentration generally. However, the amount of add-on is different at same chitosan concentration depending on fiber types. Rayon showed the highest add-on and followed by cotton and ramie as in the order. This attributed to microstructural features of fiber such as crystallinity, pore size, surface area, and so forth. Among three fibers, rayon has the lowest crystallinity and large surface area due to rough fiber surface caused by manufacturing method, leading to the highest add-on. In contrast, ramie has the highest crystallinity and smooth fiber surface, resulting in the lowest add-on among three fibers. Further study seems to be necessary for investigating the relationship between fiber structure and chitosan add-on.

<Fig. 1> shows the effect of chitosan concentration on dye uptake. Dyeing was carried out in pH 5.8 without adjusting pH. K/S values of the untreated cotton, ramie, and rayon fabrics were 1.77, 1.56, and 2.05, respectively. The dye uptake of each fiber increased progressively with increase in chitosan concentration. It improved up to 5.6 times for cotton, 7.2 times for ramie, and 3.7 times for rayon.

It is known that the major yellow components of safflower petals are safflomin A, safflower B, and safflomin C(Sato et al., 2005). These components become aglycon state, i.e., colorants, in acidic solution by eliminating glucose attached to them and (-) charges are formed on the surface of colorants(Cho, 1997). The improvement of dyeability attributed to forming dye sites by amine groups in chitosan molecules. In acidic solution, safflower yellow colorants with (-) charge make binding to the NH_3^+ groups of chitosan. Therefore, dye uptake depends on the amount of NH_3^+ groups accessible to colorants. After chitosan pretreatment, ramie showed the highest dye uptake and followed by cotton and rayon. This result is opposite to chitosan add-on. It is speculated that

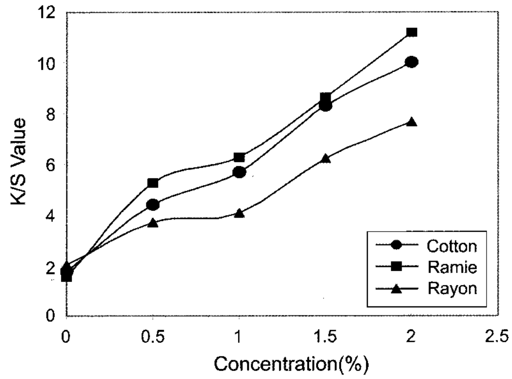

Fig. 1. Effect of Chitosan concentration on the dye uptake(Dyeing conc.; 1% owb, 30, 40 min).

ramie has relatively more NH_3^+ groups accessible to colorants on the surface than other fibers, even though it showed low chitosan add-on. This made higher dye uptake than other two fibers. On the other hand, there seemed to be less available NH_3^+ groups accessible to colorants on the surface of rayon fiber even though it showed higher add-on of chitosan. Discrepancy between chitosan add-on and the amount of NH_3^+ groups accessible to colorants attributed to the binding of amine groups in chitosan with hydroxyl groups in cellulose, which is limited by crystallinity, pore size, surface area, and so on. More binding of amine groups with hydroxyl groups in cellulose occurred, less available amine groups to colorants would exist on the surface of fiber.

<Table 3> shows the effect of chitosan concentration on the color of the dyed fabrics. The L* value indicates perceived lightness in CIELAB color space. The L* scale runs from 0(black) to 100 (white); the higher the L reading, the lighter the color. The a* value indicates red(+a*) and green(-a*) while the b* value indicates yellow(+b*) and blue(-b*). H V/C of the Munsell system represent hue, value, and chroma; hue is the quality of color described by the words red, yellow, blue, and so forth; value is the quality of a color classified as equivalent in lightness; chroma is the quality classified as equivalent in dullness.

For cotton, the shade changed from YR color of the untreated sample to Y color by chitosan pretreatment. Reddish character of the untreated sample is

Table 3. The effect of chitosan concentration on the color of dyed fabrics

Sample	Chitosan conc. (%)	H V/C	L*	a*	b*	ΔE*
Cotton	Untreated	5.9YR 8.3/3.0	83.46	7.84	16.35	-
	0.5	0.2Y 7.0/5.2	71.06	8.34	32.96	20.74
	1.0	1.1Y 6.7/5.7	67.74	8.17	37.04	25.90
	1.5	0.6Y 6.2/6.7	62.99	10.86	42.77	33.56
	2.0	0.7Y 6.1/7.1	61.21	11.48	42.03	36.70
Ramie	Untreated	8.9YR 7.8/4.0	78.42	7.56	24.05	-
	0.5	10.0YR 6.7/5.9	67.35	10.03	36.90	17.14
	1.0	0.8Y 6.3/6.0	63.72	9.28	38.52	21.39
	1.5	0.4Y 5.9/6.3	59.37	10.81	40.05	25.09
	2.0	0.6Y 5.7/7.1	57.20	12.02	45.13	30.24
Rayon	Untreated	1.5Y 8.3/4.2	83.13	4.05	29.16	-
	0.5	1.3Y 7.5/5.4	75.24	6.43	35.36	10.32
	1.0	1.7Y 7.2/5.8	72.52	7.03	38.37	18.06
	1.5	0.9Y 6.7/6.5	67.47	9.45	41.62	20.73
	2.0	1.1Y 6.5/6.9	65.46	10.11	44.80	24.37

dye conc.; 1% owb, 30°C, 40min, 1:100

attributed to the adsorption of red colorants. During water extraction of yellow colorants, it seems to be inevitable that small amount of red colorants extracted together with yellow colorants. Compared with b* value of the untreated samples, the chitosan pretreated samples got more yellow character, indicating by much higher b* value, with the increase of chitosan concentration. This indicates that dyeing sites (NH_3^+ groups in chitosan) are more accessible to yellow colorants because the concentration of yellow colorants are much higher than red colorants. As chitosan concentration increased, the color changed to darker, indicated by decrease in L* value, as dye uptake increased. Even though b* value did not change much, a* value changed more at higher chitosan concentration, indicating more red character at higher chitosan concentration. On the other hand, b* value increased remarkably up to 0.5% of chitosan concentration and not much change thereafter, indicating more increase of yellow character at lower chitosan concentration. As chitosan concentration increased the color of the cotton fabric changed to darker and deeper, resulting decrease in V value and increase in C value.

For ramie, the shade of dyed fabric changed YR color to Y color with increase in chitosan concentration. As same as cotton, L* value decreased with the increase of chitosan concentration, resulting darker color. b* value increased more than a* value by chitosan pretreatment, indicating more yellow character in the shade of dyed fabric. V values decreased and C values increased with the increase in chitosan concentration, resulting that the dyed ramie fabric color got darker and deeper.

For rayon, the improvement of dye uptake was relatively low compared with ramie and cotton. The color was less shifted compared with cotton and ramie, showing all Y color. b* value increased more compared with a* value, getting more yellow character by chitosan pretreatment. V decreased and C increased, resulting darker and deeper color as chitosan concentration increased. As chitosan concentration increased, color difference of each fiber increased progressively. Cotton showed the largest color difference and followed by ramie and rayon. From the results, it was confirmed that chitosan pretreatment affected the color of dyed fabrics.

2. Effect of Dyeing Temperature

<Table 4> shows dye uptake and color depending on dyeing temperature. Regardless of fiber type, dye

uptake was not changed significantly in the temperature range applied in this study. However, the color of dyed fabrics was shifted depending on dyeing temperature, as shown in <Table 4>. In general, the color of all dyed fabrics showed Y color at 30 and 90°C while YR color at 50 and 70°C at which higher a* value appeared. a* values of the dyed fabrics are the lowest at 90°C, indicating less red character. As temperature increased, L* and b* values for cotton and ramie decreased, indicating that the color of dyed fabrics became lighter and less yellow character. For rayon, L* and b* values decreased up to 70°C and then increased slightly at 90°C, indicating the color became a little darker and less red character. As described above, some quantity of red colorants (carthamin) extracted together with yellow colorants. Carthamin adsorbed on cellulose fiber at these temperatures(50 and 70°C), shifting the shade of dyed fabrics from Y color to YR color. At 30°C, it seems not high enough to occurr the adsorption of carthamin on cellulose fiber. The red colorants is very unstable to heat and colorants solution is discolored mostly at 90°C(Kanehira et al., 1990). Therefore, care should be taken for setting optimum dyeing temperature for safflower yellow colorants. Both of color and dye uptake of the dyed fabrics must be considered. V and C value decreased with increase in dyeing temperature and resulted in darker and duller color, in general. With increasing dyeing temperature, color difference of ramie and rayon fabrics increased but that of cotton was marginal.

3. Colorfastness to Washing and Light

<Table 5> shows the colorfastness rating of chitosan pretreated fabrics. Washing fastness is very poor for all of the dyed fabrics. It is considered that chitosan coated on the fabric surface washed away during

Table 4. Effect of dyeing temperature on dye uptake and color of the chitosan pretreated fabrics

Sample	Dyeing temp. (°C)	K/S	H V/C	L*	a*	b*	ΔE*
Cotton	30	5.69	1.1Y 6.7/5.7	67.74	8.17	37.04	25.99
	50	5.71	9.3YR 6.3/5.1	63.47	9.94	30.96	24.86
	70	5.72	9.0YR 6.0/4.5	60.70	9.07	26.57	24.98
	90	5.91	1.0Y 5.7/3.9	58.37	5.53	25.00	26.64
Ramie	30	6.25	0.8Y 6.3/6.0	63.72	9.28	38.52	20.70
	50	6.59	8.6YR 5.8/5.5	58.52	12.11	32.25	22.00
	70	7.23	8.4YR 5.4/4.8	54.04	11.15	28.03	24.96
	90	7.74	0.8Y 5.2/4.4	53.13	7.14	28.19	25.63
Rayon	30	4.09	1.7Y 7.2/5.8	72.52	7.03	38.37	14.36
	50	4.10	9.7YR 6.8/5.1	69.01	9.03	32.05	15.25
	70	4.35	9.6YR 6.4/4.7	64.53	8.54	28.61	19.15
	90	4.63	2.2Y 6.4/4.4	64.77	4.45	29.50	18.37

(Chitosan con.; 1%, dye conc.; 1% owb, 40min, 1:100)

Table 5. Colorfastness of chitosan pretreated fabrics

Sample	Washing			Irradiation time(hr)			
	Color Change	Staining		5	10	20	40
		First	Second				
Cotton	1	5	5	2-3	2-3	1-2	1
Ramie	1	5	5	3	3	2-3	2
Rayon	1	5	5	3	2-3	1-2	1

laundering and so colorants bonded with chitosan washed away together. Crosslinking agent such as glutaldehyde was applied with chitosan in our laboratory, but the result showed no significant effect on washing fastness. Low lightfastness attributed to unstable characteristics of safflower yellow colorants. More work should be done for improving colorfastness.

4. Effect of Ultrasonic Dyeing on Dye Uptake

Dye uptakes obtained by using conventional automatic machine dyeing(CD) and ultrasonicdyeing(UD) methods are compared in <Fig. 2>. Fabrics pretreated with 2% chitosan concentration were dyed at 1%(owb) dye solution at 50°C for 40 min in a liquor ratio of 1:100. It was confirmed that ultrasonic dyeing method enhanced more than 30% of dye uptake for chitosan pretreated cotton and ramie fabrics, comparing with conventional automatic machine dyeing. Ultrasound induces cavitations in liquids, which enhances chemical and physical processes. Cavitation causes formation and collapse of microbubbles and microbubbles slowly grow and implode violently to generate localized high pressures and temperature. This activated state is effective in chemical reaction between the fiber and the dye by forming shock waves and shear forces(Vankar et al., 2007). The enhancing effect of ultrasound in dyeing is attributed to the de-aggregation of dye molecules leading to faster dye diffusion inside fibers(Kamel et al., 2003). On the other hand, ultrasonic dyeing method did not enhance dye uptake for rayon, which is a regenerated cellulose fiber. It is speculated that

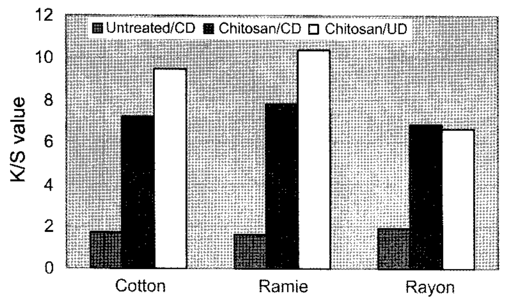

Fig. 2. Effect of dyeing method on dye uptake.

microstructure such as pore size and surface area might be limited for facilitating the diffusion of dye molecules even though ultrasonic power increases their diffusion rate.

IV. Conclusions

Irrespective of fiber type, dye uptake increased continuously with increase in chitosan concentration. Chitosan pretreatment improves dye uptake up to 5.6 times for cotton, 7.2 times for ramie, and 3.7 times for rayon. For cotton and ramie, the shade of dyed fabric changed YR color to Y color with increase in chitosan concentration. For rayon, the shade of dyed fabrics showed Y color irrespective of chitosan pretreatment and concentration. The shades were darker and deeper by chitosan pretreatment. Shades of the chitosan pretreated fabrics were shifted differently depending on dyeing temperature within same fabrics. In common, the shade of dyed fabrics changed to YR color at 50 and 70°C while Y color at 30 and 90°C. V and C values decreased with increase in dyeing temperature and resulted in darker and duller color, in general. Light fastness of the chitosan pretreated fabrics was fair and washing fastness was poor and. It was confirmed that ultrasonic dyeing method enhances dye uptake more than 30% for cotton and ramie fabrics.

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요 약

홍화 황색소의 면, 마, 레이온과 같은 셀룰로오스 섬유에 대한 염착량을 증진시키기 위하여 키토산 전처리를 행하였다. 키토산 전처리가 염착성, 색상, 염색견뢰도에 미치는 영향을 조사하였다. 섬유 종류에 관계없이 키토산 전처리는 염착성을 증진시켰으며, 농도가 증가함에 따라 계속 증가하엿다. 2% 처리농도에서 미처리와 비교할 때 면은 5.6배, 모시는 7.2배, 레이온은 3.7배 염착량이 증가하였다. 키토산 전처리한 면과 모시는 YR 색상에서 Y 색상으로 변화하였으며, 레이온의 경우에는 전처리와 상관없이 Y 계열의 색상을 보였다. 키토산 전처리에 의해 색상은 노란색이 강하여졌으며 더 진하고 깊은 색상으로 변하였다. 키토산 전처리 직물은 염색온도에 따라 색상이 변화하였는데 공통적으로 50, 70°C에서는 YR 색상을 30, 90°C에서는 Y 색상을 나타냈다. 염색온도가 높을수록 색상은 진하고 칙칙하였다. 세탁견뢰도는 아주 낮았으며, 일광에 매우 약한 홍화 황색소의 특성을 고려할 때 일광견뢰도는 양호한 편이었다. 기존의 자동염색기로 염색하는 경우와 비교할 때 초음파 염색법이 면과 모시의 염착량을 30% 이상 증진시키는 효과가 있음을 확인하였다. 레이온의 경우, 두 방법간의 염착량 차이는 없었다.