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Fabric Dyeing with Lichen *Parmotrema austrosinence* and Improvement of Dyeability by Chitosan Treatment

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Parmotrema austrosinence(지의류)를 이용한 직물염색과 키토산 처리에 의한 염색성 향상

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Abstract

Three fabrics, 100% silk, nylon and cotton each, were dyed with a lichen dye solution prepared by a fermentation method under conditions of varying dyebath pH and temperature. To verify the effect of chitosan on fabric dyeing, the 100% cotton fabric was treated with a chitosan solution before dyeing. The K/S, CIE L*, a*, b*, ΔE and Munsell values of the dyed samples were measured. Colorfastness of each sample was also investigated. The maximum K/S value was measured at 520nm wavelength for the dyed silk fabric and at 480nm for the dyed cotton and nylon. The K/S values for the dyed silk fabric were much greater than those of the other fabrics. The dyed silk fabric showed a red tone on the Munsell color system, and the dyed nylon and cotton fabrics a yellowish red tone. Dye affinity to fabrics was better in a neutral or acidic dyebath. As dyeing temperature increased, K/S values increased for the dyed nylon and cotton fabrics but not for the silk. Dyeability of cotton fabrics could improve by Chitosan treatment. As for most natural dyes, colorfastness of all dyed samples was poor. The silk fabric showed an excellent dry cleaning fastness of Grade 5.

Key words: Lichen pamotrema austrosinence, Chitosan treatment, Dye affinity, Colorfastness, Fabric dyeing; 지의류, 키토산, 염색성, 염색견뢰도, 직물염색

I. Introduction

Many different natural dyes have been used throughout the human history. Ancient civilization, such as the Egyptian, Greek, Roman, Chinese, Mesopotamian, and Indian culture, possessed excellent empirical dyeing technologies.

Natural dyes have their origin in animals, vegetables and minerals. Among them, the most useful dyes come from plants; their roots, barks, leaves, berries, twigs, branches, tubers and nut hulls were used as dye materials(Kramer, 1972) in traditional natural dyeing. It is inexpensive, easy to apply and eco-friendly. However, for commercial uses, it has limitations due to the shortage of supply materials, small production scale, poor fastness and unlevel dyeing.

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The current trend values "nature and body friendliness" in products and has become the major issue in all industries. In this respect, the use of natural dyes in commercial products has brought a new interest (Lesch, 1970; Nam, 1998).

Lichen is a plant composed of two completely different organisms, green or blue-green algae; they are related to free-living algae and colorless fungal threads called hyphae(Hale, 1969, 1974; Park, 1982; Seaward, 1997). Lichen is created between fungus and alga. When fungus and alga are compatible, they can craft a body of lichen called thallus. Thus each fungus and alga forms a unique type of thallus body (Canas et al., 1997; Louwhoff & Crisp, 2000).

People have learned how to use lichen in many useful ways. It is edible except for a few kinds that are poisonous. Drug companies extract antibiotic substance from lichen. It can also tell us whether the air is clean because most lichen dies when the air gets polluted. However, one of the most creative uses of lichen was to use it to dye wool fabrics. There are many examples of wool dyed with lichen. The dyed color can be subtle in tone as well as bright and cheerful(Canas et al., 1997; Lee et al., 2000; Park, 1990). American Indians also used lichen as dyes. They obtained dye liquor by boiling lichen in water for several hours, or by treating it with ammonia water for one or two weeks without heat. Shade of color can vary depending on the length of dyeing time(Hale, 1969, 1974; Park, 1990; Seaward, 1997). Although interest in natural dyes has been increasing recently, little research has been done with natural dyes for their usefulness.

The major objectives of this study are to find an effective method for extracting dyestuff from lichen *Parmotrema austrosinence* and appropriate dyeing conditions for the natural dye. For our experiment, we used lichen *austrosinence* that belongs to genus *Parmotrema*. It shows wavy, broad-lobed soredia. No black cilia occur on the lobe margins. This lichen frequently possesses a white margin in the underside (Canas et al., 1997; Louwhoff & Crisp, 2000).

II. Experimental

1. Fabrics and Lichen

The fabrics used in the experiments were silk, nylon and cotton woven fabrics made of 100% of the fiber content, respectively. They were desized and scoured before dyeing. The lichen *Parmotrema Austrosinence* was obtained from Mt. Gaya, Kyoungsangnamdo province in S. Korea. The characteristics of the fabric samples are shown in <Table 1>.

2. Dyeing Procedure

1) Ammonia Fermentation of Lichen

Lichen was thoroughly washed to remove the soil. Commercial ammonia water(35% by volume) was diluted with the liquor ratio of three to one. *Parmotrema Austrosinence*(20g) was put in the glass container and 300cc of prepared ammonia water was added slowly. For fermentation, the ammonia treated sample was incubated for 7 days at 40°C. A reddish dye solution was obtained after incubation(Lee, 1987; Lee et al., 2000; Lee & Kim, 1998).

2) Dyeing

The fermented fabric was dyed in dyebath with a liquor ratio of 30:1. Dyeing was carried out under different conditions of pH (4, 7 and 10) and temperature(30°C, 50°C and 80°C) for 80 minutes. The dye cycle was programmed as shown in <Fig. 1> for 50°C <Fig. 1(a)> and 80°C <Fig. 1(b)>. In the case of dyeing at 30°C, the temperature was maintained for

Table 1. Characteristics of the sample fabrics

Fiber Composition	Weave	Fabric count (ends×picks)	Weight (g/m^2)	Thickness (mm)
Silk 100%	Plain	162×108	86	0.23
Nylon 100%	Plain	102×88	58	0.11
Cotton 100%	Plain	84×79	95	0.26

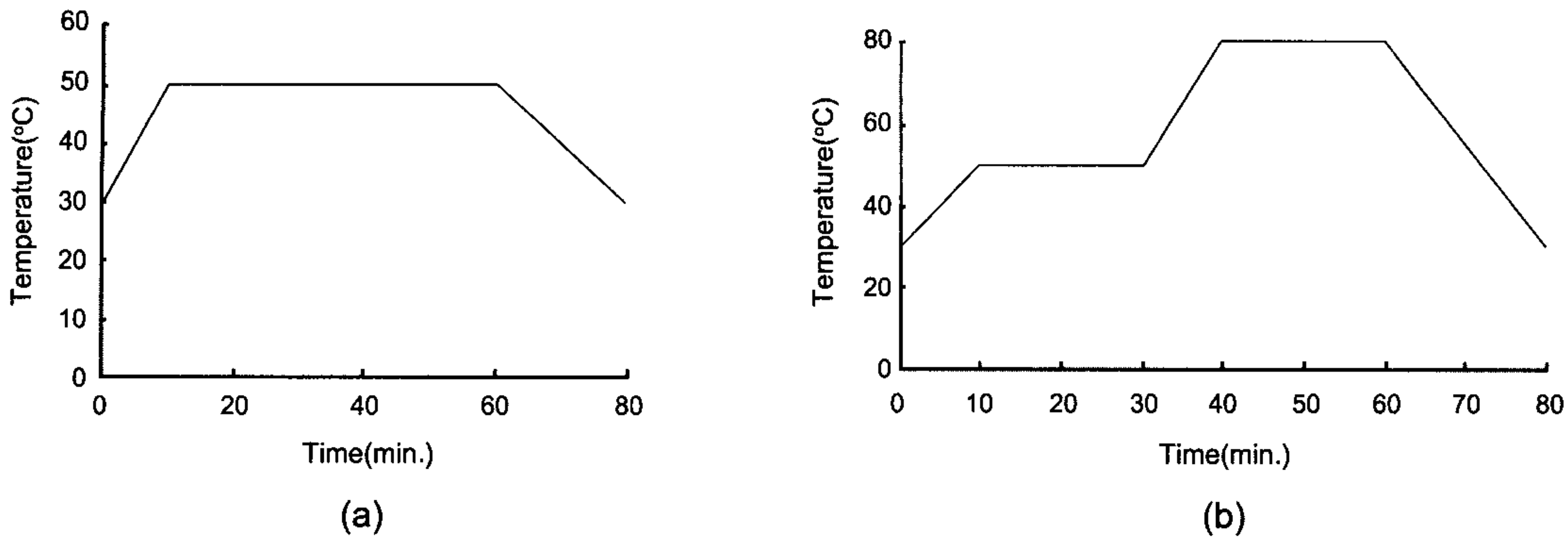

Fig. 1. Dyeing cycles using lichen at 50°C (a) and 80°C (b).

80minutes throughout. After dyeing, samples were washed three times with distilled water and dried in the air at room temperature.

3. Chitosan Treatment

Cotton fabrics were pretreated with chitosan before dyeing to verify its effect on fabric dyeing. The 70% deacetylized chitosan(obtained from Tokyo Chem., Japan) was treated in 40% NaOH at 100°C under nitrogen gas for one hour to raise the degree of deacetylation of chitosan. The treated chitosan was rinsed with a 1% acetic acid aqueous solution and washed with distilled water twice. The degree of deacetylation was measured by the hydrochloric acid method and was 85%. Deacetylized chitosan was dissolved in 2% acetic acid to make a 0.3% concentration on the weight of the fabric(Kim & Jeon, 1995; Yoo & Lee, 2001). Fabric samples were dipped in the chitosan solution for 30minutes at 30°C and padded to reach a 100% add-on. Chitosan treated fabrics were cured in a drying oven for 10minutes at 90°C, followed by a washing and drying.

4. Color Measurement

The prepared samples were measured for their K/S, CIE Lab(ΔE, L*, a*, b*) and Munsell values by a spectrocolorimeter(Technocolor, JS-555, Japan). Color difference(ΔE) was obtained by measuring the L*, a*, b* values for both undyed and dyed fabrics. K/S values were measured at every 20nm of wavelength from 400nm to 700nm, and the wavelength that showed the minimum reflectance or maximum absorbency was obtained. For silk it was 520nm and 480nm for all other fabrics. Also, colorfastness to laundering (KS K 0430) was measured for nylon and cotton fabrics and colorfastness to dry cleaning for silk. Colorfastness to light(KS K 0700) was measured using a carbon-arc Fade-Ometer for all fabrics.

III. Results and Discussion

Three woven fabrics of different fiber contents were dyed using dyebath that was prepared with fermented *Parmotrema austrosinence* lichen in an aqueous ammonia solution under several different dyeing conditions. Chemically, *Parmotrema austrosinence* lichen is known as a lecanoric acid. Lee and Kim (1998) reported that a red liquid colorant was obtained by fermenting lichen in an ammonia solution. The chemical structure of lecanoric acid is shown in <Fig. 2>.

In <Tables 2, 3 and 4>, color values are shown of the silk, nylon and cotton fabrics dyed in a dye solu-

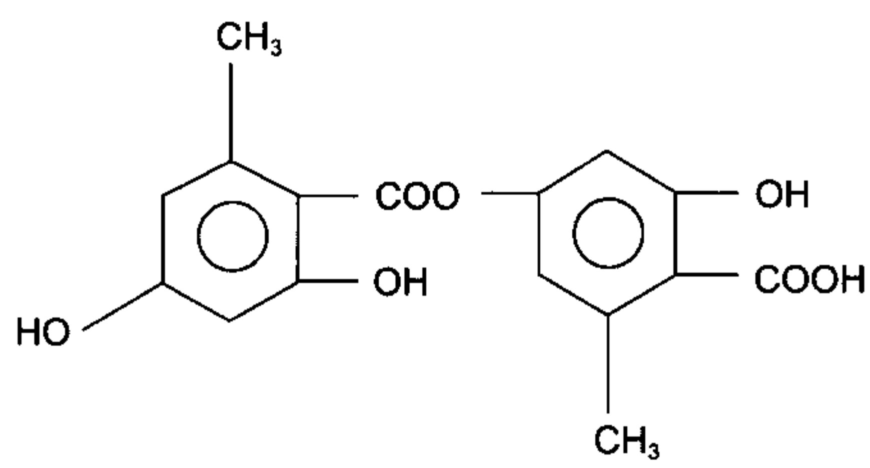

Fig. 2. Chemical structure of lecanoric acid.

Table 2. Dyeability of silk fabrics dyed with *Parmotrema austrosinence* lichen under different dyeing conditions at 80 min. dyeing time

Silk		CIE Lab				Munsell color values	
		ΔE	L*	a*	b*	H	V/C
Undyed		-	96.77	-0.60	6.32	2.0Y	9.8/1.4
30°C	pH 4	57.71	43.63	25.47	14.43	7.8R	4.7/6.1
	pH 7	57.72	45.63	29.14	14.44	6.5R	4.9/7.4
	pH 10	54.09	49.87	29.35	12.15	5.5R	5.3/7.3
50°C	pH 4	59.16	40.34	21.93	13.74	8.4R	4.5/5.9
	pH 7	62.21	39.87	28.07	14.25	7.1R	4.2/6.9
	pH 10	58.15	44.12	27.54	13.38	6.8R	4.7/6.6
80°C	pH 4	56.04	42.94	20.26	12.29	8.8R	4.6/5.1
	pH 7	61.92	38.20	23.96	13.84	8.3R	4.2/6.0
	pH 10	57.58	42.81	23.47	14.43	8.6R	4.7/6.1

Table 3. Dyeability of nylon fabrics dyed with *Parmotrema austrosinence* lichen under different dyeing conditions at 80 min. dyeing time

Nylon		CIE Lab				Munsell color values	
		ΔE	L*	a*	b*	H	V/C
Undyed		-	97.34	-2.71	-5.81	3.9Y	10.2/0.5
30°C	pH 4	39.00	62.70	12.98	8.86	2.3YR	6.6/3.7
	pH 7	38.57	65.56	19.67	7.96	8.4R	7.0/4.9
	pH 10	38.85	66.05	20.66	8.59	8.9R	7.2/5.0
50°C	pH 4	45.72	55.25	13.80	8.15	1.5YR	6.1/3.9
	pH 7	46.24	57.69	21.88	8.28	7.9R	6.3/5.4
	pH 10	39.55	64.08	18.49	8.65	9.5R	6.9/4.8
80°C	pH 4	47.31	53.98	13.94	9.41	2.2YR	6.0/3.9
	pH 7	50.73	51.59	18.55	9.33	10.0R	5.6/4.7
	pH 10	47.67	55.79	19.76	10.16	10.0R	6.2/5.2

Table 4. Dyeability of cotton fabrics dyed with *Parmotrema austrosinence* lichen under different dyeing conditions at 80 min. dyeing time

Cotton		CIE Lab				Munsell color values	
		ΔE	L*	a*	b*	H	V/C
Undyed		-	95.10	0.14	0.03	1.9Y	10.1/0.7
30°C	pH 4	28.55	71.66	15.64	5.05	0.7YR	7.5/3.8
	pH 7	31.83	66.97	13.61	5.09	0.6YR	7.0/3.7
	pH 10	21.34	76.03	8.03	5.47	2.8YR	8.3/3.1
50°C	pH 4	34.00	64.88	14.83	5.19	1.9YR	6.8/3.9
	pH 7	33.35	65.01	12.75	5.73	2.0YR	6.9/3.6
	pH 10	23.77	73.47	8.16	5.78	3.9YR	7.6/3.0
80°C	pH 4	40.02	57.54	13.18	4.55	2.5YR	5.9/3.7
	pH 7	38.40	59.22	12.20	4.74	3.3YR	6.3/3.5
	pH 10	24.73	72.38	8.33	5.36	3.7YR	7.9/2.4

tion with extracted *Parmotrema austrosinence* lichen. In the Munsell color system, dyed silk fabrics showed a hue in the red range, whereas nylon fabrics red or yellow-red, and cotton fabrics yellow-red. The hue of dyed fabrics appeared to change from red range to yellow red with increasing dyebath temperature. However, when the dyebath temperature was high, dyebath pH showed little effect on the hue of the dyed fabrics. The hue of dyed silk was brownish red when it was dyed in acidic or neutral dyebath, whereas a more reddish hue was noted when dyed in a basic dyebath. The ΔE values of silk were higher than those of nylon and cotton. The a* values(represent redness) of silk were higher than those of other fabrics and showed a decreasing trend as dyebath temperature increased to 50°C and 80°C from 30°C.

<Fig. 3> illustrates the trend of K/S values of each fabric dyed under different dyebath conditions of pH and temperature. Silk fabrics showed the maximum absorbency at wavelength of 520nm, whereas nylon and cotton fabrics at 480nm. Therefore, for silk, K/S values were calculated from reflectance rate in the wavelength of 520nm and for nylon and cotton at 480nm.

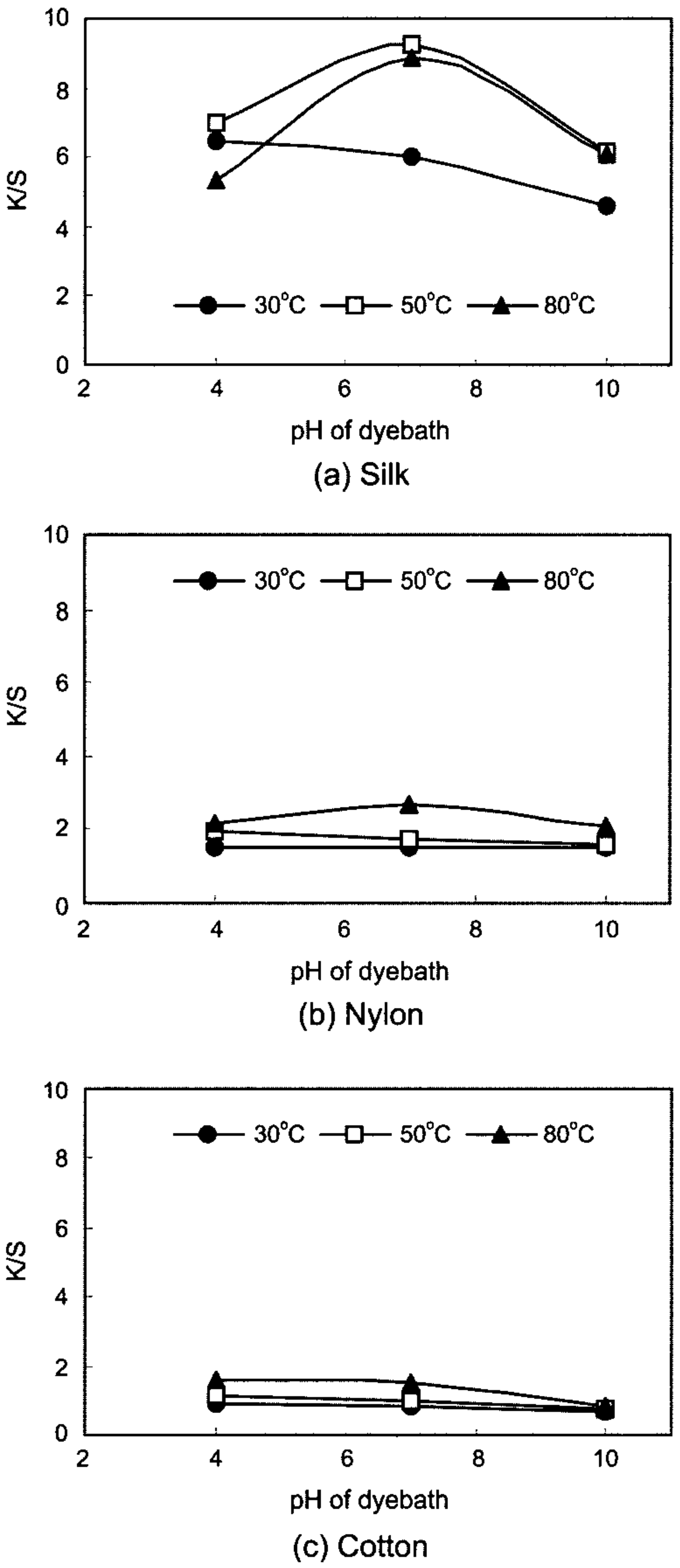

Fig. 3. K/S values of fabrics dyed under different dyeing conditions.

<Fig. 3(a)> illustrates that silk fabrics dyed in neutral dyebath at 50°C and 80°C show a much higher K/S values, thus better dyeability, than in acid or basic dyebath at the same temperature levels. The same trend was noted in <Fig. 3(b)> for nylon fabrics dyed in neutral dyebath at 80°C, but at a much reduced K/S value than for silk; K/S values of dyed silk were much greater than those of the other fabrics, resulting in higher dye affinity for *Parmotrema austrosinence.*

K/S values of dyed silk fabrics at 50°C dyebath were a little higher than at 80°C under all pH conditions. In the case of nylon and cotton, K/S values increased as dyeing temperature was higher, but the differences were small. not significant

<Fig. 4> shows dyeing results of the silk, nylon and cotton fabrics at pH 4, 7 and 10 at 80°C, the highest dyebath temperature applied, for 80minutes. K/S values for fabrics dyed in neutral dyebath were higher than those for fabrics dyed in acidic or basic dyebath. It seems that fabrics dyed in neutral dyebath of *Parmotrema austrosinence* exhibited higher K/S values, thus resulting in better dyeability.

<Fig. 5> represents dyeing results of the silk, nylon and cotton fabrics at neutral dyebath with pH 7 at 30°C, 50°C and 80°C for 80 minutes. K/S values for nylon and cotton fabrics showed an increasing

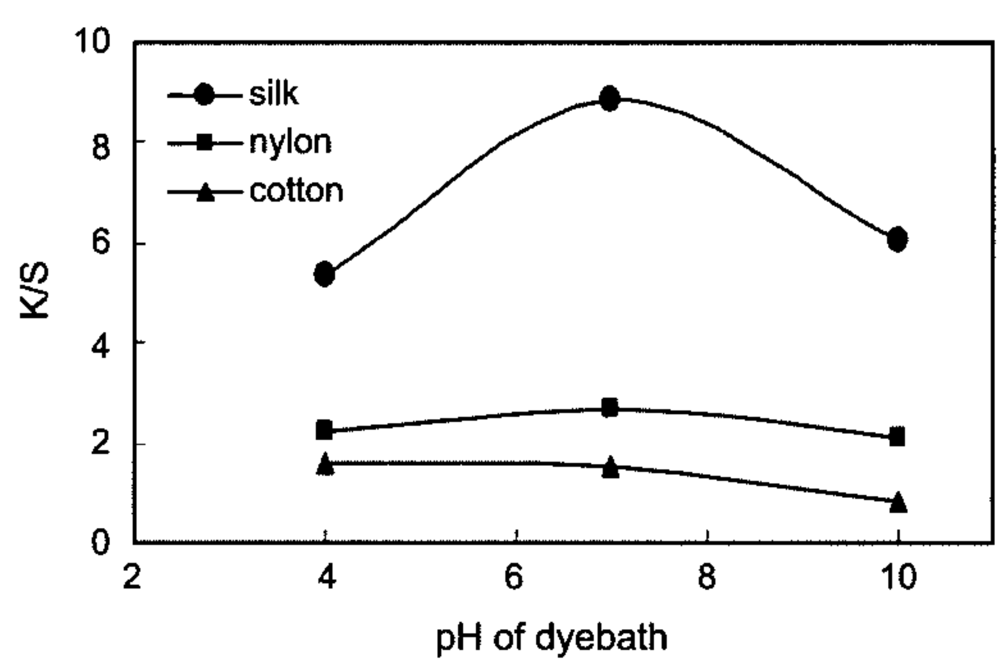

Fig. 4. K/S values of the fabrics dyed in dyebath of 80°C for 80 minutes.

trend as temperature rose, but for silk fabrics the highest K/S value was observed at 50°C dyebath temperature rather than at 80°C. However, the difference was small as compared with that between 30°C and 50°C.

<Table 5> compares dyeability of chitosan treated 100% cotton fabrics with that of untreated ones. K/S and ΔE values of chitosan treated fabrics were greater than those of untreated ones. Hue values of the Munsell color, however, did not change with chitosan treatment. This result clearly shows that chitosan treatment improved dyeability of 100% cotton fabrics.

<Fig. 6> displays dyeability of silk, nylon, cotton fabrics and chitosan treated cotton fabrics with their ΔE values. As dyeing temperature increased, ΔE values of the fabrics grew larger. Nylon fabrics showed better dyeability than cotton but lower dyeability than silk. It appears that dyeability of cotton fabrics improved by chitosan treatment to the level comparable to the dyeability of nylon fabrics at 30°C.

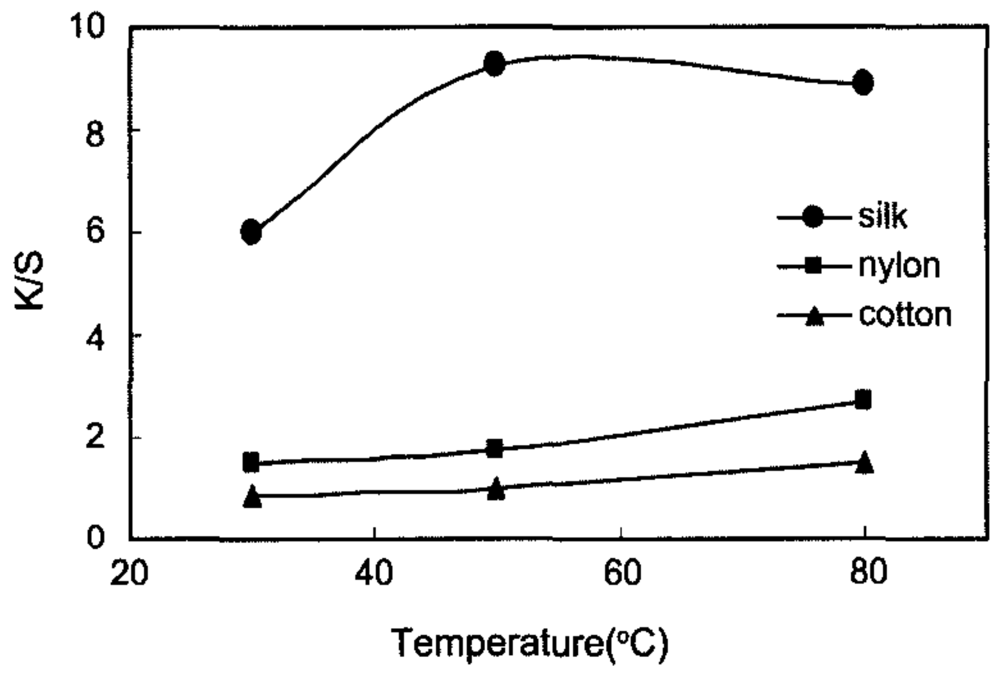

Fig. 5. K/S values of the fabrics dyed in dyebath of pH 7 for 80 minutes.

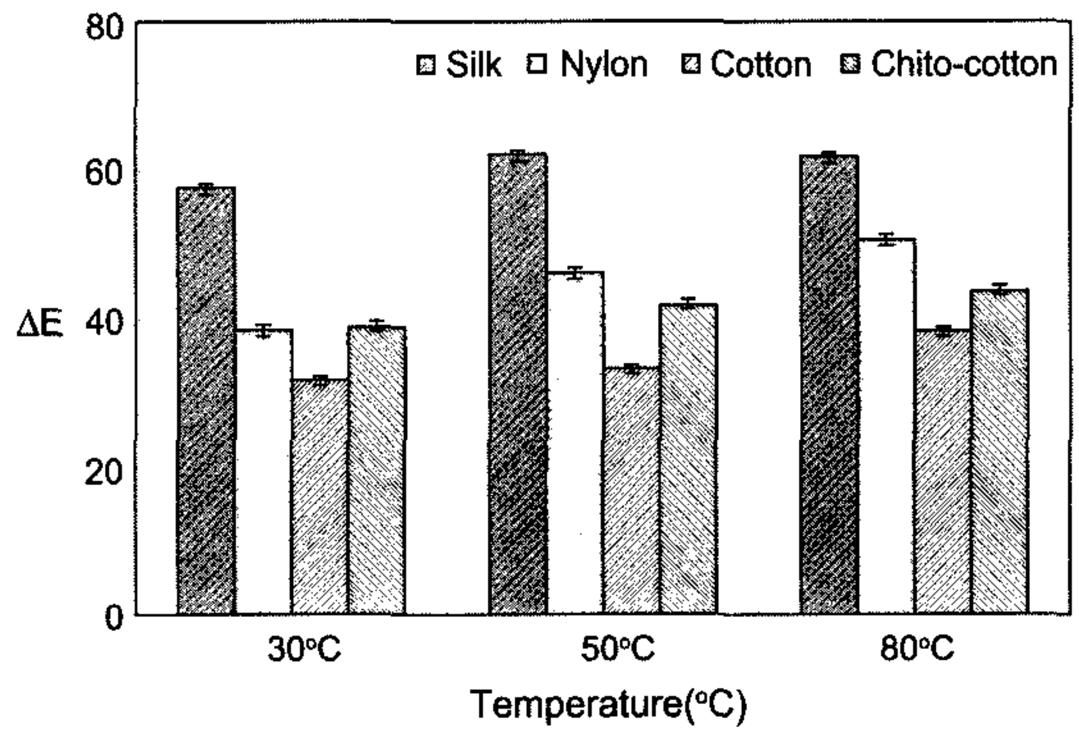

Fig. 6. ΔE values of the fabrics dyed in lichen dyebath at pH 7.

Table 5. Dyeability of chitosan treated cotton at the dyebath pH 7

Cotton		K/S (480mm)	ΔE	L*	a*	b*	Munsell color values	
							H	V/C
Un-Treated	30°C	0.852	31.83	66.97	13.61	5.09	0.6YR	7.0/3.7
	50°C	1.002	33.35	65.01	12.75	5.73	2.0YR	6.9/3.6
	80°C	1.500	38.40	59.22	12.20	4.74	3.3YR	6.3/3.5
Chitosan Treated	30°C	1.510	38.90	59.21	15.94	5.23	0.6YR	6.4/3.9
	50°C	1.774	41.89	56.77	13.51	3.59	2.2YR	6.2/3.5
	80°C	2.186	43.76	53.60	12.69	3.49	3.7YR	5.7/3.4

Dyeing time : 80 minutes

Table 6. Colorfastness of the fabrics dyed with lichen at pH 7 for 80 min.

Fabrics	Temp.(°C)	Grades of Colorfastness		
		Light	Laundering	Dry cleaning
Silk	50	2	-	5
	80	2	-	5
Nylon	50	1-2	3	4-5
	80	2	4	5
Cotton	50	1-2	1-2	4-5
	80	2-3	2-3	5
Chitosan treated-Cotton	50	2-3	3	5
	80	2-3	3-4	5

<Table 6> shows colorfastness to light, laundering, and dry cleaning of the three fabrics dyed with *Parmotrema austrosinence* lichen. Like most other fabrics dyed with natural dyes, the lichen dyed fabrics showed poor colorfastness to light. However, chitosan treated cotton fabrics showed improved colorfastness to light as compared with that of untreated fabrics. The colorfastness to laundering of dyed cotton fabrics was poor, resulting in colorfastness grades of 1-2 and 2-3. Colorfastness of dyed nylon fabrics showed higher grades of 3 to 4 than cotton fabrics. Chitosan treated cotton fabrics showed improved colorfastness to laundering also. Colorfastness to dry cleaning was excellent in all dyed fabrics, resulting in grades of 4-5 or 5.

IV. Summary and Conclusions

Three woven fabrics made of 100% silk, nylon and cotton were dyed in dyebath that was prepared by fermentation of *Parmotrema austrosinence* in aqueous ammonia solution under several different dyeing conditions. Dyed silk fabrics showed color hue in the red range, nylon in red or yellow-red, and cotton in yellow-red in the Munsell color system. The hue of dyed fabrics changed from red to yellow red as dyebath temperature increased.

Silk fabrics dyed in lichen dyebath showed the maximum absorbency at 520nm wavelength while nylon and cotton fabrics at 480nm. Silk showed higher dye affinity for *Parmotrema austrosinence* than nylon or cotton fabrics. K/S values of dyed silk fabrics at dyebath temperature of 50°C were a little higher than at 80°C, under all pH conditions in this study. For nylon and cotton, K/S values increased with rising dyebath temperature.

At dyebath pH of 4, 7, and 10 at 80°C, dyeability of cotton and nylon fabrics was higher at pH 4 or 7 than at pH 10; for silk fabrics dyeability at pH 7 was better than at pH 4 or 10. All fabrics dyed better in neutral dyebath of pH 7. When the fabrics were dyed in dyebath pH 7 at 30°C, 50°C and 80°C, nylon and cotton fabrics dyed better as dyeing temperature increased, but K/S values of silk fabrics were a little better at 50°C than at 80°C. The K/S and ΔE values of chitosan treated cotton were greater than those of untreated cotton. It seems clear that chitosan treatment improved dyeability of cotton fabrics.

Fabric colorfastness to light when dyed with *Parmotrema austrosinence* lichen was poor in all fabric types used. Likewise, colorfastness to laundering of dyed cotton fabrics was poor, resulting in low colorfastness grades of 1-2 and 2-3. However, nylon fabrics showed better colorfastness to laundering with a grade of 3 to 4. Cotton fabrics showed improved colorfastness to light and laundering by chitosan treatment. Colorfastness to dry cleaning of all dyed fabrics was good with a colorfastness grade of 4-5 or 5.

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요 약

국내에서 자라는 지의류의 한 종류인 *Parmotrema austrosinence*를 채취하여 염액을 제조하고, 제조된 염액을 사용하여 견직물, 나일론직물과 면직물을 염색하였다. *Parmotrema austrosinence*를 암모니아수에 넣고 발효시켜 얻은 염액을 사용하여 pH를 4, 7, 10으로, 염색온도를 30°C, 50°C, 80°C로 각각 조절한 후 염색을 하였다. 면직물은 견직물과 나일론직물에 비해 염색성이 낮게 나타났다. 면직물의 염색성 향상을 위해 키토산 액으로 처리하고 염색성과 염색견뢰도의 변화를 검토하였다. 염색된 시료들의 염색성은 K/S 값, ΔE와 Munsell값을 측정하여 평가하였다. 염색된 시료들의 K/S값은 견직물의 경우에는 520nm에서, 나일론직물과 면직물은 480nm에서 최대 흡광파장을 나타냈다. 견직물 염색포의 K/S값은 4.6~9.3으로 1.0~2.7인 나일론직물이나 0.8~1.6인 면직물에 비해 매우 높게 나타나 견직물이 *Parmotrema austrosinence* 염액에 대해 우수한 염색성을 가짐을 확인하였다. 염색온도가 높아질수록 먼셀 색상값이 red나 yellow red에서 yellow쪽으로 이동하는 색상변화가 나타났다. 견직물의 경우, 염색온도가 50°C와 80°C일 때의 염색성이 비슷하였으며, 다른 직물의 경우에는 염색온도 상승에 따라 K/S값도 높아졌다. 따라서 지의류를 사용한 적정 염색온도는 견직물의 경우 50°C, 다른 직물의 경우 80°C임을 확인하였다. 염색된 시료의 먼셀 색상은 견직물에서는 R(red) 영역에서, 나일론 직물에서는 YR(yellow red)~R 영역에서, 면직물은 YR 영역으로 나타났다. 면직물과 나일론직물은 중성 또는 산성염액에서 염색이 잘 되었고, 견직물의 경우는 중성 염액에서의 염색성이 가장 우수하였다. 염색성이 낮게 나타난 면직물은 키토산 가공에 의해 염색성과 염색견뢰도를 향상시킬 수 있음을 확인하였다. 염색된 시료들의 일광견뢰도와 세탁견뢰도는 대체로 낮게 나타났으나 드라이크리닝 견뢰도는 4-5급 또는 5급으로 모두 우수하였다.