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Effects of introduced chemical groups on the dyeability of cotton fabrics with *Phellodendron amurense* Rupr.

Heain Kim, Soomin Park*

Department of Textile Engineering, College of Engineering, Pusan National University, Pusan 609-735, Republic of Korea

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Abstract

The dyeability of cotton fabrics with natural basic dye, *Phellodendron amurense* Rupr. was improved by applying anionic and hydrophobic groups on cotton fibers. The dye uptake was increased by interactional force and the change of fine structure by fiber modification. After introducing cross-linking using formaldehyde, the wash fastness had been improved. The wash fastness relied on the degree of swelling of fabric during washing and the number of the entrapped dyes.

Keywords: Natural dye; Amur cork tree; Cotton; Modification; Wash fastness

1. Introduction

Natural dyes are usually deeper and softer in color shades than synthetic dyes. With the increase of worldwide concern for the environment, use of natural dyes is being widely studied. Natural dyes may overcome many defects of synthetic dyes such as harmfulness to the human body and water pollution [1,2]. However, natural dyes show very low dye exhaustion on cotton fiber compared to silk or wool, and no satisfying result has been obtained in spite of many experimental attempts of repeating dyeing and mordant treatment.

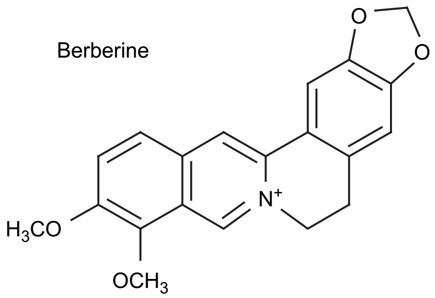
Several studies have been conducted on applying anionic [3] and hydrophobic groups on cotton fibers, and shown that these groups can improve dyeability and color fastness of cotton fabrics with basic dye. These treatments on cotton fibers, however, have not been studied for natural dye.

This study reports an investigation of the wash fastness of *Phellodendron amurense* Rupr. on modified cotton fabrics. The effects of cotton modification on changes of shade and the improvement of wash fastness were also studied. The wash properties were evaluated in terms of Kubelka–Munk (*K*/*S*) values, obtained before and after washing.

2. Experimental

2.1. Materials

The natural dye used was *P. ammurence* Rupr. (from the amur cork tree). Scheme 1 shows the chemical structure of the chief colorant, Berberine. Extraction of chief colorant, Berberine (Scheme 1), was carried out in the following



Scheme 1. Chemical structure of the chief colorant.

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* Corresponding author. Tel.: +82 51 510 2412; fax: +82 51 512 8175.
E-mail address: soominpark@pusan.ac.kr (S. Park).

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procedure. Amur cork tree bark (10 g) and methanol (300 ml) were put in a 1-l round-bottom flask fitted with a reflux condenser, refluxed for 1 h at 67 °C, and this procedure was repeated 2–3 times. The resultant extract was mixed, filtered, and concentrated to 20 ml. In the preparation of cotton derivatives, scoured cotton fabrics (66.3 g/m^2) having the following specifications were used: warp density, 35 threads/cm; weft density, 31 threads/cm; weight, 105 g/m^2; warp count 16.5 tex weft counts 14 tex and plain weave. All chemicals were of the highest purity grade.

2.2. Preparation of cotton derivatives

In the following treatments, the pick up ratio of PDC (padding–drying–curing) method was 100% and the bath ratio of deposition method was 1:30. The introduction of various chemical groups into cotton fabrics was identified by an FT-IR spectrophotometer (Impact 400D, Nicolet) and was reported in the previous paper [4].

Acid groups on cotton fibers were applied by carboxyethylation, sulfonation, and carboxymethylation. In the case of carboxyethylation of cellulose (CEC), cotton fabrics were dipped in an aqueous solution with 15% acrylic acid and 0.45% ammonium chloride. Fabrics were padded, mounted on a frame, dried for 5 min at 70 °C, and cured for 30 min at 140 °C. For the sulfonation of cellulose (SFC), fabrics were dipped in an aqueous solution of 0.01 M sodium metaperiodate for 30 min at 30 °C. Dialdehyde cotton fabrics were treated in an aqueous solution with 5% sodium hydrogen sulfite for 60 min at 85 °C. In the case of carboxymethylation of cellulose (CMC), cotton fabrics were treated in an aqueous solution with 2% sodium chloroacetic acid and 2% sodium hydroxide for 30 min at 10 °C, and then were treated continuously for 45 min at 60 °C. All treated fabrics were washed and air-dried at room temperature.

Hydrophobic groups were applied on cotton fibers by esterification and urethane formation. In the case of esterification, cotton fabrics were treated in DMF (*N*,*N*-dimethylformamide) solution containing 0.2 M acetyl chloride, 0.2 M propionyl chloride, and 0.2 M butyryl chloride. Esterification included treatments of acetyl chloride for 150 min at 50 °C, of propionyl chloride for 75 min at 90 °C, and butyryl chloride for 75 min at 90 °C. All modified fabrics were washed in DMF solution and air-dried at room temperature. In order to introduce hydrophobic groups by urethane formation of cellulose (UFC), phenyl isocyanate and toluene diisocyanate were used as aromatic compounds and butyl isocyanate and hexamethylene diisocyanate were used as aliphatic compounds. Cotton fabrics were treated in DMF solution including 0.15 M butyl isocyanate, 0.1 M hexamethylene diisocyanate (HMDI) and 0.12 M phenyl isocyanate for 60 min at 130 °C. A 5 ml of 2,4-toluene diisocyante (TDI) in 30 ml dimethyl sulfoxide (DMSO) solution was also applied to the cotton fabrics for 240 min at 30 °C. Finally, they were washed and air-dried at room temperature.

For the cross-linking of cotton fabrics, untreated or carboxymethylated cotton fabrics were soaked in 3, 6, 9, and 12% (v/v) aqueous solution of formalin with 2% magnesium chloride for 20 min at 27 °C, dried for 7 min at 70 °C, and were cured for 5 min at 150 °C.

2.3. Dyeing procedure

Dyeing was processed in a bath containing 1 ml/50 ml extracts of amur cork tree bark and 2% acetic acid for 60 min and then 5% sodium carbonate was added to the dye bath for 45 min. Dyed fabrics were washed and air-dried at room temperature.

2.4. Color strength

Macbeth Coloreye 700 spectrophotometer (illuminant D65, 10° observer) was used to evaluate samples based on the Kubelka–Munk analysis (*K*/*S*). The *K*/*S* values obtained before and after washing indicate the concentration of adsorbed and fixed dye of the samples. AATCC 61 No. 1A method was used for washing fastness test.

3. Results and discussion

3.1. Effects of anionic groups

Table 1 shows the *K*/*S* values of anionized cotton fabrics such as CEC, CMC, and SFC, which were dyed using amur cork tree extract. The anionized cotton fabrics showed an increase in *K*/*S* values compared with those of the untreated cotton fabrics. The *K*/*S* values of untreated cotton fabrics are low and this is caused by the weak interaction force between the dyes from the amur cork tree extract and the cotton fibers. When the anionizing agent is applied on cotton fibers, anion sites of treated cotton fibers enhance the formation of ionic bonds with cationic dyes. Anionization of cotton fibers improves the dye adsorption as shown in Table 1. *K*/*S* values of the CMC fabric show great influence on dyeability when comparing the values of CEC and SFC fabrics. This result indicates that the increase of adsorbed dye does not seem to have any relationship to the strength of the acid groups introduced by anionization.

In the case of washed samples, all *K*/*S* values were low. This is due to the weak bonding forces between dyes and

Table 1
K/*S* values and wash fastness (WF) of cotton fabrics with introduced acid groups

Cotton modification	Color strength (*K*/*S*)		WF
	Adsorbed[a]	Fixed[b]	
Unmodified	1.47	0.29	1
Carboxyethylation	6.01	0.54	<1
Carboxymethylation	10.93	1.39	<1
Sulfonation	5.84	0.37	<1

[a] *K*/*S* values of samples before washing at λ_{max}.

[b] *K*/*S* values of samples after washing at λ_{max}.

anionized cotton fibers. Adsorbed dyes are desorbed easily during the washing process.

3.2. Effects of hydrophobic groups

By introducing acid groups to the cotton fibers, the amount of adsorbed dyes was increased but it could not protect the desorption of dyes in the process of washing; thus, in order to improve the bonding force between the dyes of amur cork tree extract and the cotton fibers, it was proper to introduce hydrophobic groups on cotton fibers.

Table 2 shows the *K*/*S* values obtained before and after the washing of cotton fabrics with hydrophobic groups introduced by urethane formation. In the case of esterificated cotton fabrics, the *K*/*S* values of the samples were higher than that of the unmodified one regardless of the kind of alkyl groups introduced. This result shows that applying hydrophobic groups on cotton fibers by esterification can increase adsorption of dye and decrease desorption of dye. In the case of carboxymethylated and esterificated cotton fabrics, the dyed samples show higher *K*/*S* values than the values of the uncarboxymethylated and esterificated samples. Moreover, the washed samples show high *K*/*S* values. Hydrophobic groups are hindrances for the permeation of dyes into fibers; however, the dyeability of cotton fabrics esterificated after carboxymethylation is enhanced by decrystallization in the process of carboxymethylation [5]. In these results, the increase of dye uptake results from the interactional force of the anionic and hydrophobic groups, introduced by modification, and the dye, as well as the change of fine structure. The decrease of desorption seems to be correlated with the degree of swelling of the fabric during washing and the interaction between dyes and acid groups. This indicates that the coexistence of acid groups and hydrophobic groups is more effective to the increase of dye uptake and the reduction of desorption than the introduction of carboxymethyl or hydrophobic groups. Regardless of caboxymethylation, the *K*/*S* values of dyed and washed samples followed the order of the number of carbon introduced in esterification, that is, acetic ester < propionic ester < butyric ester.

Table 2
K/*S* values and wash fastness (WF) of cotton fabrics with hydrophobic groups introduced by esterification

Cotton modification	Esterificated cotton with moieties	Color strength (*K*/*S*)		WF
		Adsorbed[a]	Fixed[b]	
Uncarboxymethylated	–	1.47	0.41	1
	Acetyl group	3.24	0.68	<1
	Propionyl group	4.33	1.09	<1
	Butyryl group	4.46	1.24	<1
Carboxymethylated	–	10.68	0.42	<1
	Acetyl group	10.94	3.57	<1
	Propionyl group	11.07	5.02	1
	Butyryl group	11.25	5.61	1

[a] *K*/*S* values of samples before washing at λ_{max}.
[b] *K*/*S* values of samples after washing at λ_{max}.

Table 3 shows the *K*/*S* values obtained before and after the washing of UFC with hydrophobic groups introduced by urethane formation. These results indicate that hydrophobic groups applied by urethane formation are more effective to the increase of absorbed and fixed dyes than that of the hydrophobic groups applied by esterification. The *K*/*S* values of UFC samples are higher than those of untreated samples. UFC fabrics with aromatic compounds show high adsorption of dye and low desorption of dye when compared to the fabrics with aliphatic compounds. Without regard to the type of isocyanate, one containing a higher number of carbon and diisocyanate group was more effective than the one with a lower number of carbon and monoisocyanate group. The increase of dye uptake and the decrease of desorption were due to the increase of the interactional force between the fiber and the dye, the change of fine structure, and the decrease in the degree of swelling of the fabric during washing. Aromatic isocyanates containing a resonant structure in molecules were especially effective. HMDI and TDI forming cross-linkages in cotton fibers have high values for absorbed and fixed dye (see Table 3). It seems that treating only with TDI, an aromatic diisocyanate, also showed high values for absorbed and fixed dye. These results indicate that dye uptake and desorption are related to the quantity, structure, strength, and size of the hydrophobic groups and acid groups introduced. The desorption of dye is influenced by the interactional force between the groups introduced and the dye, the formation of cross-linkages and the degree of swelling during washing process.

Fig. 1 shows the *K*/*S* values of the samples before and after washing with various concentrations of TDI, the most effective group on the dyeability. As the concentration of TDI increased up to 1 ml/30 ml. From 2 ml/30 ml, *K*/*S* values decrease gradually.

Fig. 2 shows the concentrations of combined TDI in cotton fabrics with various TDI concentrations. The combined TDI converted the change of weight between used and reacted cellulose into quantity per glucose unit. As the concentration of TDI was increased, the combined TDI increased greatly, up

Table 3
K/*S* values and wash fastness (WF) of cotton fabrics with hydrophobic groups introduced by urethane formation

Cotton modification	Urethane-formed cotton with reagent	Color strength (*K*/*S*)		WF
		Adsorbed[a]	Fixed[b]	
Uncarboxymethylated	–	1.47	0.41	1
	Butyl isocyanate	2.67	1.27	2
	Hexamethylene diisocyanate	3.41	2.01	2 – 3
	Phenyl isocyanate	4.31	2.65	2 – 3
	Toluene diisocyanate	6.74	5.86	4
Carboxymethylated	Butyl isocyanate	10.67	0.42	<1
	Hexamethylene diisocyanate	7.85	4.38	2
	Phenyl isocyanate	8.19	5.86	3 – 4
	Toluene diisocyanate	9.63	7.27	3 – 4
		10.89	9.98	4

[a] *K*/*S* values of samples before washing at λ_{max}.
[b] *K*/*S* values of samples after washing at λ_{max}.

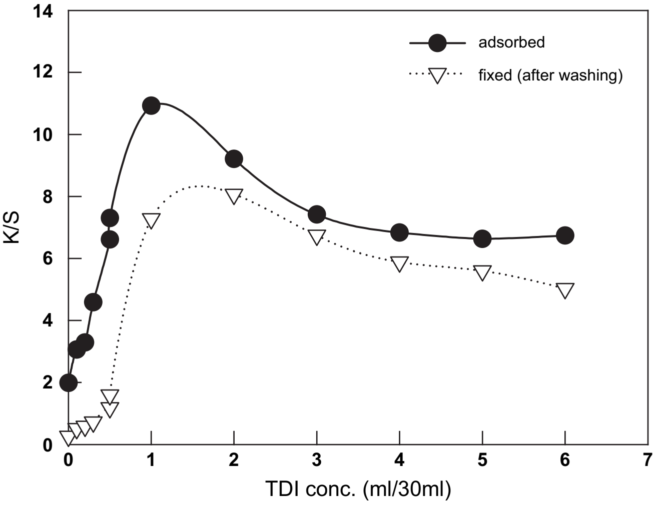

Fig. 1. *K*/*S* values of cotton fabrics treated with 2,4-toluene diisocyanate and dyed.

to 2 ml/30 ml. In the reaction of tri-hydroxy groups (C2, C3, and C6) per glucose in the cotton fiber, the hydroxy group of C6 may react preferentially, because of primary alcohol when compared with those of C2 and C3. The concentration of combined TDI is 0.068 mol/g.u., and if the crystallinity of cellulose is 70%, from these results the reaction of TDI per glucose may react by the ratio of 2-hydroxy per 9-glucose.

3.3. *Effects of cross-linking*

In order to investigate the only effect of the introduction of cross-linking, the introduction of cross-linking was carried out by formalin. Fig. 3 shows the *K*/*S* values of the samples before and after washing with various concentrations of formalin as a cross-linking agent for the cotton fiber. As the concentration of formalin is increased, the *K*/*S* values of dyed sample before washing are decreased and those values of the sample after washing are increased. The *K*/*S* values of the dyed sample with the treatment of 3% HCHO are increased slightly. These results indicate that the initially introduced cross-links stabilized the swollen structure, thereby increasing the effective area and dyeing site of samples cross-linked in the swollen state [6]. As the concentrations of formalin are increased, the *K*/*S* values of the dyed sample are decreased. This resulted due to the reduction of swelling or the adsorbed area of dye by the decrease of pore size, but also by the blocking of micropores. In the case of the sample after washing, the increase of *K*/*S* values are caused by entrapped dye during washing and in increasing the binding force of the dye [7]. The ratio of this increase is merely 20%. Thus, it may be possible to generalize that in order to enhance dye uptake and wash fastness, anionic groups and hydrophobic groups, as well as appropriate cross-linking must be introduced into the cotton fabrics.

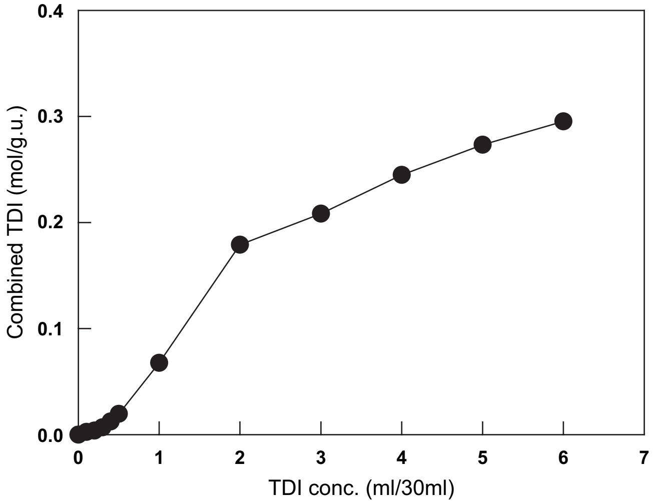

Fig. 2. Amount of combined 2,4-toluene diisocyanate in cotton fabrics treated with various concentrations of 2,4-toluene diisocyanate.

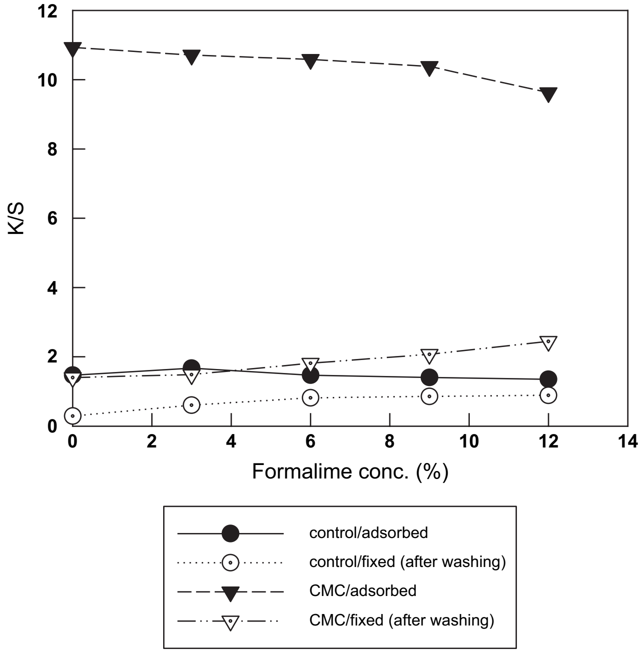

Fig. 3. Effect of cross-linkage introduced by formalin on the *K*/*S* values of cotton fabric unmodified or carboxymethylated.

4. Conclusions

In order to improve dyeability in the dyeing of cotton fabrics with *P. ammurence* Rupr. (amur cork tree), various chemical groups were introduced to cotton fiber. The effects of these chemical groups were addressed in this study. The dye uptake was increased by interactional force (i.e., ionic force and hydrophobic force) and the change of fine structure by modifying cotton fibers. The wash fastness depended on the degree of swelling of fabric during washing and entrapped dye caused by cross-linking. The most effective modification of cotton fibers was anionization followed by the introduction of hydrophobic groups. As the hydrophobic groups were introduced, the one containing a higher (diisocyanate group and aromatic compound) become more effective than the one with a lower number of carbon (monoisocyanate group and aliphatic compound).

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