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Dyeing Characteristics and UV Protection Property of Green Tea Dyed Cotton Fabrics
–Focusing on the Effect of Chitosan Mordanting Condition–

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Abstract: There is increasing interest in the many beneficial aspects of green tea to human such as anti-carcinogenic, anti-aggregant, anti-allergic, anti-bacterial, anti-mutagenic, and anti-oxidant activities. Besides these beneficial aspects, it has been reported that green tea ingredients, especially polyphenolic families (i.e., catechin), have some UV protection property both in vivo and in topical applications. In this study, green tea extract was used as a dyeing stock for cotton and the UV protection property of the dyed cotton fabric was examined. To increase the affinity of cotton fiber to the polyphenolic components in the green tea extract, a natural biopolymer, chitosan, was used as mordanting agent. The effects of chitosan concentration in mordanting on the dyeing characteristics and the UV protection property were examined. Chitosan mordanted green tea dyed cotton showed better dyeing characteristic and higher UV protection property compared with the unmordanted green tea dyed cotton. As the chitosan concentration in mordanting increased, the dyeing efficiency and the UV protection property also increased. Therefore, adapting chitosan mordanting in green tea dyeing can increase the UV protection property of cotton fabrics to some extent.

Keywords: Green tea, Chitosan, Dyeing characteristics, Cotton fabric, UV protection properties

Introduction

Ultraviolet radiation (UVR) is considered a major factor causing skin cancer and other skin and eye diseases [1]. As the UV dosage and the outdoor activity increased over years, a fair amount of genotoxic and cytotoxic effects of UVR on human have been reported [1-5].

Overdose of UV can cause various skin, eye, and even DNA damages [1-5]. Ultraviolet consists of three parts; UV-A, UV-B, and UV-C. Overdose of UV-A (320-400 nm) can cause chronic reactions and damages such as an acceleration of skin ageing, a promotion of photodermatosis, and phototoxic reactions with various materials, and is a possible carcinogen [4,5]. Overdose of UV-B (280-320 nm) can cause acute chronic reactions and damages such as skin reddening or sunburn, increase risks of melanoma, eye damage, and even DNA damage in case of high dosage [4,5]. UV-C is intercepted by ozone layer and cannot reach to the earth surface [4]. Although UV-A was considered less harmful than UV-B, UV-A can penetrate on skin deeper and can cause DNA damages in a wider range of cell types [1]. Therefore, it is need to develop a proper mean to protect human skin and eye from both UV-A and UV-B radiation.

Textiles have been considered a primary tool in shielding UVR, however, the UV protection efficiency is varied with fiber type, thickness, fabric count, yarn count, fabric structure, color, and etc. Cotton, the most preferable fiber type worn during the summer, provides a relatively low UV protection, especially in case of thin cotton having a low fabric count. For example, thin muslin and poplin showed the UPF value less than 5 [6]. Therefore, it is need to develop a proper treatment to increase the UV protection property of cotton fabric. Titanium oxide and zinc oxide are two main chemicals used in increasing UV protection property of textiles [7-12], however, only synthetic fibers can be incorporated during the preparation of spinning dope. These chemicals cannot be incorporated in this way in case of natural fiber such as cotton. Surface coating is an alternative way in incorporating these chemicals onto cotton, however, possible damages or allergic reactions on human skin can happen in tight and sweaty situation. Therefore, a proper and innovative method needs to be developed to enhance UV protection property of cotton fabric.

In this study, green tea dyeing was employed to increase UV protection property of cotton. Green tea is a natural material and has many beneficial characteristics on human [12]. Green tea has an active phenolic moiety called "catechin" in its extracted components [12], which would exert a proper UV protective property. Figure 1 shows the various structures of catechin identified. (+)-Catechin, (−)-epicatechin (EC), (−)-epigallocatechin (EGC), (−)-epicatechin gallate (ECG), (−)-epigallocatechin gallate (EGCG), (−)-gallocatechin gallate (GCG) have been identified as an active agents in green tea [12]. Green tea beverages has 30-42 % catechin components when measured in weight % of extract solids, followed by carbohydrates, flavanols, and etc. [12]. In recent study, Morley *et al.* found that the green tea polyphenols, especially (−)-epigallocatechin gallate (EGCG), can protect human cellular DNA from UV and visible radiations induced damages in cultured human cells as well as in human peripheral blood

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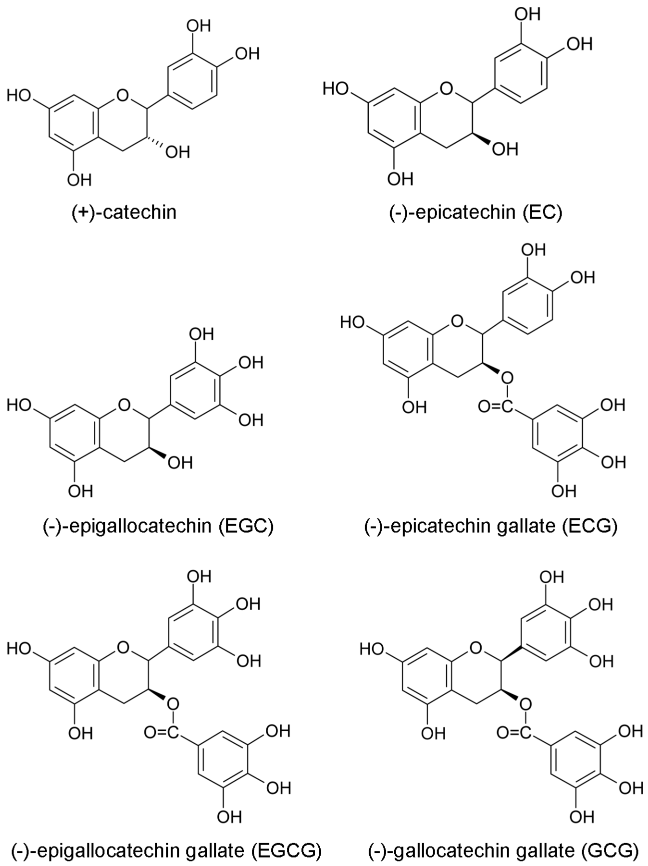

Figure 1. Structures of (+)-catechin and (−)-epigallocatechin gallate.

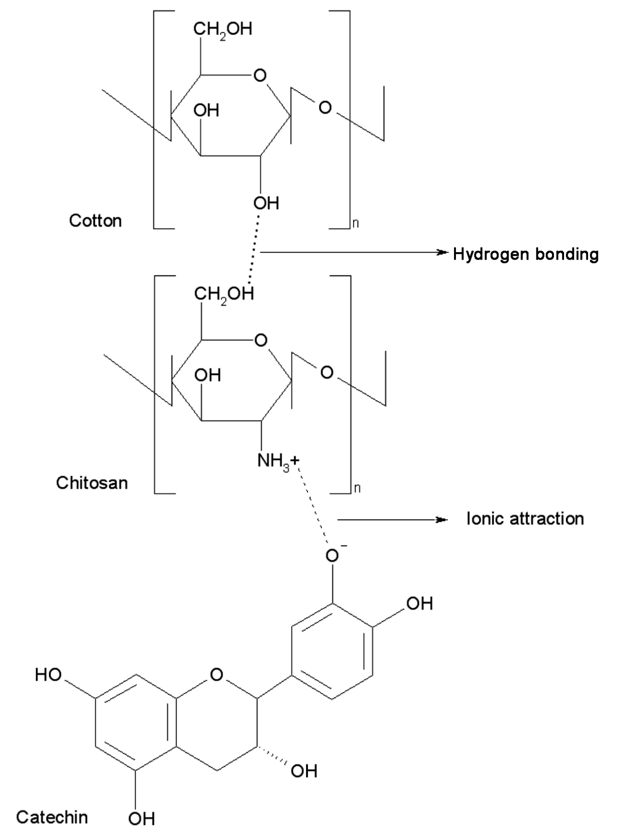

Figure 2. Suggested binding mechanism between cellulose and catechin.

cells after green tea ingestion [14]. It is very surprising that green tea has a protective effect against UV not only in the topical application but also in the *in vivo* application. The UV-protective effects of green tea in case of both oral and topical applications were also reported in animal and human studies [15-18]. Green tea polyphenol decreased the penetration of UV and also decreased DNA photodamage and affected photoimmunology [17]. Katiyar and Muktar studied the relationship between the tea consumption and the various types of cancer, and found that the skin cancer induced by UVR was inhibited better than other types of cancer [17]. Beside of UV-protective effect, green tea extract has been extensively studied because of its powerful anti-carcinogenic, anti-aggregant, anti-allergic, anti-bacterial, anti-mutagenic, and anti-oxidant activities [13,18-23]. Therefore, using green tea extract in enhancing UV protection property of cotton would be a novel method in terms of biocompatibility and physiological benefits, and in addition, this process can be done environment-friendly way.

However, cellulose has a low affinity to catechin because both components would exists in anionic forms in aqueous solution, a mordanting agent will be needed to increase the catechin uptake to cotton. Conventionally, heavy metal ions such as copper, cadmium, iron, aluminium, and tin were used in mordanting fabrics to enhance the natural dye uptake and the fastness [24-27]. However, these heavy metals can cause an environmental problem and be a potential risk in skin contact, and therefore, will not serve a proper role in this study. Therefore, chitosan was used in this study in mordanting cotton to increase the affinity of cotton fabric to green tea extract active moiety, i.e., catechin families. Chitosan, (1→4)2-acetamido-2-deoxy-β-D-glucose, is a derivative of chitin, extracted from crustacean shells [28]. Chitosan showed a variety of physiological beneficial properties, an enhanced reactivity, and a hydrophilicity, since a primany amine of glucose ring was isolated from acetyl group of chitin through deacetylation [28]. Chitosan exists as cation in the acidic condition, this cationic ammonium groups exert an anti-bacterial property. Therefore, chitosan is a proper material in treating fabrics which will closely contact with human skin. Cellulose would attract chitosan by hydrogen bonds, and phenolic components in green tea extract would attracted to chitosan by ionic attraction as suggested in Figure 2.

Experimental

Materials

Green tea powder was purchased from BosungDawon, Bosung, Korea. Chitosan (Brookfield, 1 % sol. in 1 % acetic acid, viscosity > 200 cps) was purchased from Sigma-Aldrich (Milwaukee, WI, USA) and acetic acid was used as reagent grade (DaeJung Chemical Co., Korea).

Cotton muslin with plain weave (thickness 0.13 mm, weight 64.5 g/m^2, fabric count 90 × 81/inch^2) was used.

Mordanting Cotton Fabric with Chitosan

Cotton fabric was treated with chitosan to enhance the uptake of phenolic moiety, i.e. catechin, uptake in the green tea dye bath. Chitosan was dissolved in acetic acid solution (0.5 % aq.) by 1-10 g/l to find out the effect of chitosan mordanting on the uptake of green tea extract active moiety. Cotton fabrics were dipped into chitosan solutions for 10 min, padded, and cured at 115 ^{o}C, for 3 min.

Dyeing Using Green Tea Extract

Green tea extraction was done by boiling green tea powder with 10 fold water for 1 hr. Unmordanted and chitosan mordanted cotton fabrics were dyed at liquor ratio, 1:30 o.w.f., in the green tea extracted solution. Dyeing conducted at the room temperature for 15 min, and then, at 95 ^{o}C for 90 min, subsequently. Two kinds of dyeing baths were prepared, an undiluted 100 % green tea extract solution and a diluted 50 % green tea extract solution. 50 % green tea extract solution was made by diluting the 100 % green tea dye bath with the same amount of tap water. After dyeing, dyeing batch was cooled down to the room temperature, and the dyed textiles were washed several times with tap water until no colorants came out and air-dried under the shade.

Color Measurement

To evaluate the dyeability of green tea extract on the various fiber types, $L^*a^*b^*$ was measured using spectrophotometer (Gretag Macbeth Color-Eye® 3100, USA). And ΔE was calculated from following equation;

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2} \quad (1)$$

$$\Delta L = L_1 - L_2 \quad (2)$$

$$\Delta a = a_1 - a_2 \quad (3)$$

$$\Delta b = b_1 - b_2 \quad (4)$$

Surface reflectance values were also measured using spectrophotometer (Gretag Macbeth Color-Eye® 3100, USA). All measured sample showed the greatest $\lambda_{max.}$ value at 400 nm. The K/S was calculated by the following equation (Kubelka-Munk equation) [29];

$$K/S = \frac{(1-R)^2}{2R} \quad (5)$$

R: surface reflectance, K: light absorption, S: light scattering.

Evaluation of UV Protection

Transmittances of both UV-A and UV-B through the original cotton, the chitosan mordanted cotton, and the green tea dyed cotton were measured using UV transmittance analyzer (Xenon Arc., Labsphere Co., USA). UV in the range of 315-400 nm was measured for UV-A transmittance and UV in the range of 290-320 nm was measured for UV-B transmittance. UV protection percentage was calculated from the following equation;

$$\text{UV transmittance (\%)} = (T/B) \times 100 \quad (6)$$

$$\text{UV protection (\%)} = 100 - \text{UV transmittance (\%)} \quad (7)$$

where T is UV transmitted through the fabric sample and B is UV transmitted without the fabric.

Results and Discussion

Dyeing Characteristics of Chitosan Mordanted Green Tea Dyed Cotton Fabrics

Green tea dyed cotton fabrics showed a reddish yellow color, and the color became darker as the chitosan mordanting concentration increased. In our preliminary study, cellulosic fibers showed reddish yellow color by green tea extract dyeing, while protein fibers showed greenish yellow color by green tea extract dyeing. Yellow value increased to the maximum at the highest chitosan mordanting concentration (10 g/l) and in undiluted 100 % green tea extract bath. It was found that cellulose fibers showed low affinities to green tea colorants, while protein fibers showed high affinities to green tea colorants in our preliminary study and other studies [30,31]. Therefore, a proper mordanting agent would be required to increase the affinity of cotton fabric to green tea colorants. Chitosan, a natural biopolymer, was used in this study to increase the affinity of cotton fabric to green tea colorants. Since chitosan was first dissolved in acetic acid aqueous solution and then applied to cotton, primary amines in chitosan would exist in $-NH_3^+$ cationic form. These $-NH_3^+$ cat ions would attract the anionic phenolic compounds in the green tea extract solution. The proposed mechanism of chitosan mordanting was suggested in Figure 2.

Table 1 shows the $L^*a^*b^*$ and ΔLab values of green tea extract dyed cotton fabrics mordanted with chitosan by various concentrations. L^* decreased gradually as the mordanted chitosan concentration increased both in a diluted 50 % bath and in an undiluted 100 % bath. In case of unmordanted cotton, L^* showed a lower value in 100 % bath than in 50 % bath, which means the better dyeing result in 100 % bath. On the other hand, the similar dyeing results were observed both in 50 % green tea dye bath and in 100 % green tea dye bath upon chitosan pre-treatment, which means chitosan mordanting promoted the green tea extract colorant uptake. Therefore, it would require the lower concentration of green tea extract bath for the similar result. This tendency is more dominant as chitosan concentration increases.

In Figure 3, ΔE of chitosan treated and dyed fabric increased as the increase in chitosan mordanting concentration. In

Table 1. $L^*a^*b^*$, ΔLab, and ΔE values of green tea extract dyed cotton fabrics upon various chitosan mordanting concentration and upon different dye bath concentration

Fabric	Chitosan conc. (g/*l*)	Green tea dye bath conc. (50 %)						
		L^*	a^*	b^*	ΔL	Δa	Δb	ΔE
Control	–	91.05	3.08	−10.81	–	–	–	–
Dyed	0	84.75	2.27	6.77	−6.30	−0.81	17.58	18.69
	1	78.38	4.79	11.78	−12.67	1.71	22.59	25.96
	2	77.18	5.38	13.85	−13.87	2.30	24.66	28.39
	3	76.45	5.61	13.60	−14.60	2.53	24.41	28.56
	4	74.85	6.46	13.82	−16.20	3.38	24.63	29.67
	5	74.49	6.40	15.12	−16.56	3.32	25.93	30.95
	6	73.84	6.64	14.92	−17.21	3.56	25.73	31.16
	7	71.02	7.49	16.65	−20.03	4.41	27.46	34.27
	8	71.41	7.24	16.11	−19.64	4.16	26.92	33.58
	9	69.02	8.00	17.86	−22.03	4.92	28.67	36.49
	10	69.37	7.91	17.67	−21.68	4.83	28.48	36.12
	Chitosan conc. (g/*l*)	Green tea dye bath conc. (100 %)						
		L^*	a^*	b^*	ΔL	Δa	Δb	ΔE
Control	–	91.05	3.08	−10.81	–	–	–	–
Dyed	0	80.89	3.30	11.51	−10.16	0.22	22.32	24.52
	1	78.57	4.49	13.50	−12.48	1.41	24.31	27.36
	2	76.34	5.77	14.87	−14.71	2.69	25.68	29.72
	3	78.80	4.58	12.19	−12.25	1.50	23.00	26.10
	4	75.03	6.07	14.59	−16.02	2.99	25.40	30.18
	5	71.06	7.61	16.65	−19.99	4.53	27.46	34.27
	6	70.47	7.15	17.76	−20.58	4.07	28.57	35.44
	7	72.95	6.64	16.82	−18.10	3.56	27.63	33.22
	8	70.53	7.32	18.30	−20.52	4.24	29.11	35.87
	9	69.59	7.45	17.61	−21.46	4.37	28.42	35.88
	10	71.40	6.90	17.29	−19.65	3.82	28.10	34.50

50 % green tea dye bath concentration, the ΔE value increased from 18.69 to 36.12 as chitosan mordanting concentration from 0 to 10 g/*l*. In 100 % green tea dye bath concentration, the ΔE value increased from 24.52 to 34.50 as chitosan mordanting concentration from 0 to 10 g/*l*. Since the initial ΔE of the unmordanted and dyed fabric is higher in 100 % green tea dye bath than that in 50 % green tea dye bath, the ΔE increase is more visible in 50 % green tea dye bath than in 100 % green tea dye bath. Similar ΔE values in high concentration of chitosan mordants (from 7 g/*l* to 10 g/*l*) were shown in both 50 % and 100 % green tea dye bath, which implies chitosan mordanting can increase the effect of green tea dyeing in low green tea bath concentration. Kwon *et al*. also showed the chitosan treatment increased the natural dye absorption of cotton using Loess [32].

Figure 4 shows the K/S values of chitosan mordanted green tea dyed cotton fabric with different mordants concentration. As mordanting chitosan concentration increased, the K/S also increased. The K/S values of cotton dyed in undiluted 100 % green tea extract bath are generally higher than those

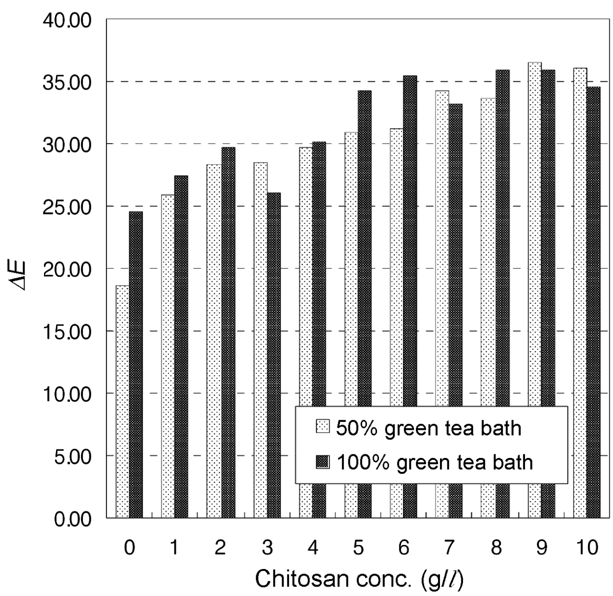

Figure 3. ΔE of chitosan mordanted geen tea dyed cotton fabrics.

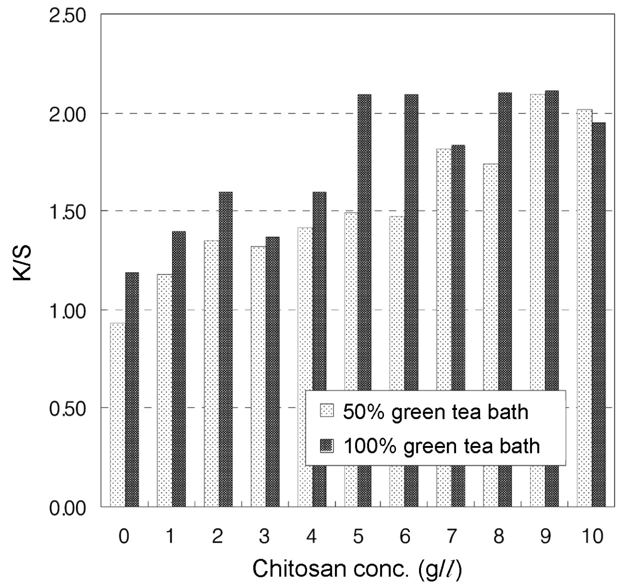

Figure 4. K/S of chitosan mordanted green tea dyed cotton fabrics.

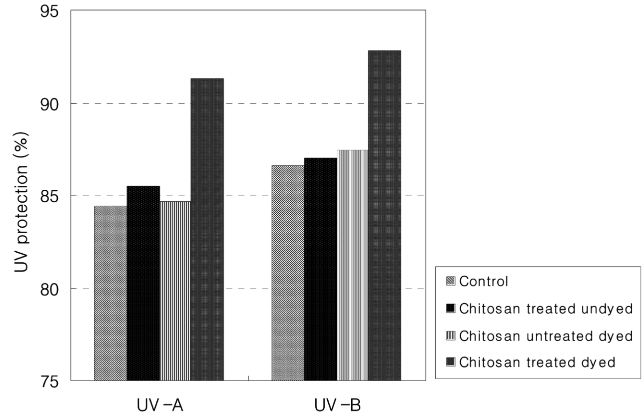

Figure 5. UV-A and UV-B protection of the control, the chitosan treated undyed cotton*, and the chitosan treated green tea dyed cotton fabric**. * 1 (g/*l*) chitosan 0.5 % (w/w) acetic acid solution (aq.) treatment, ** 1 (g/*l*) chitosan 0.5 % (w/w) acetic acid solution (aq.) treatment and dyed in 50 % green tea extract bath.

of cotton fabrics dyed in 50 % green tea extract bath, however, the difference became small at the highest chitosan mordanting concentration, 10 g/*l*.

Therefore, chitosan mordanting effectively increased the green tea extract colorant uptake of cotton fabric. And the concentration of chitosan increased, both ΔE and K/S values increased subsequently.

UV Protection Property of Green Tea Dyed Cotton Fabric

UV protection property of four different types of cotton fabrics were measured; 1) Chitosan untreated and undyed (control), 2) chitosan treated (10 g/*l*) and undyed, 3) chitosan untreated and dyed, 4) chitosan treated (10 g/*l*) and dyed. Figure 5 and Figure 6 show the UV protection effect of green tea dyed cotton manifestly. Three types of fabrics, 1), 2), and 3), did not show any significant increase in UV protection property both in UV-A and UV-B, 84.4 %, 85.5 %, and 84.7 %, respectively, in UV-A protection and 86.6 %, 87.0 %, and 87.4 %, respectively, in UV-B (Figure 5). In case of 3) chitosan untreated and dyed cotton in 100 % dye bath, the UV-B protection was slightly increased compared to those of control and the chitosan treated and undyed fabric, however, the increase is very small (less than 1 %). On the other hand, the fourth fabric, the chitosan mordanted and green tea dyed fabric, showed the increase in UV protection in both UV-A and UV-B (91.3 % and 92.8 %). This increase range is similar with UV protection value of green tea dyed cellulose using metal mordants [31]. Therefore, the following conclusion can be induced. First, green tea extract dyeing can increase the UV protection property of the dyed fabric. Second, chitosan mordanting can increase the uptake of UV protective moiety in green dye bath and chitosan mordanting itself does not affect the UV protection

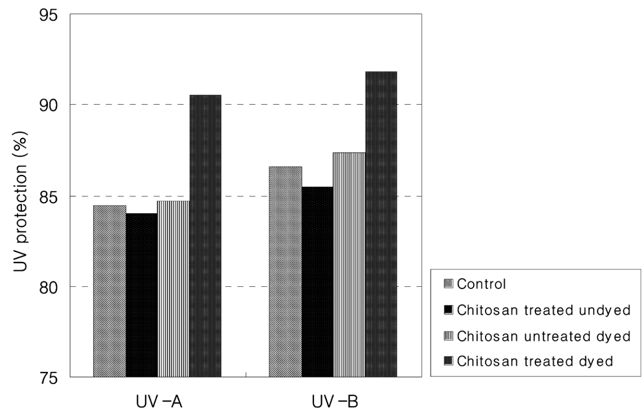

Figure 6. UV-A and UV-B protection of the control, the chitosan treated undyed cotton*, and the chitosan treated green tea dyed cotton fabric**. * 1 (g/*l*) chitosan 0.5 % (w/w) acetic acid solution (aq.) treatment, ** 1 (g/*l*) chitosan 0.5 % (w/w) acetic acid solution (aq.) treatment and dyed in 50 % green tea extract bath.

of the mordanted fabric. It was reported that Kwon *et al.* used chitosan in natural dye mordanting using Loess and found chitosan mordanting can be used in natural dyeing to increase the dyeabiltiy. Song and Song and Shin and Choi used metal mordants to increase the green tea colorant uptake to the cellulosic fiber [30,31], however, using metal mordants would not be desirable since their potential toxicity during usage and the environmental problem. As reported in Song and Song's work, some metal mordanted cellulose resulted in the lower UV protection property and the reason for that is not mentioned. Therefore, it was proven that chitosan can be used as mordants in green tea dyeing of cellulosic fiber and the green tea dyeing can be used in increasing the UV protection property of dyed fabric [30].

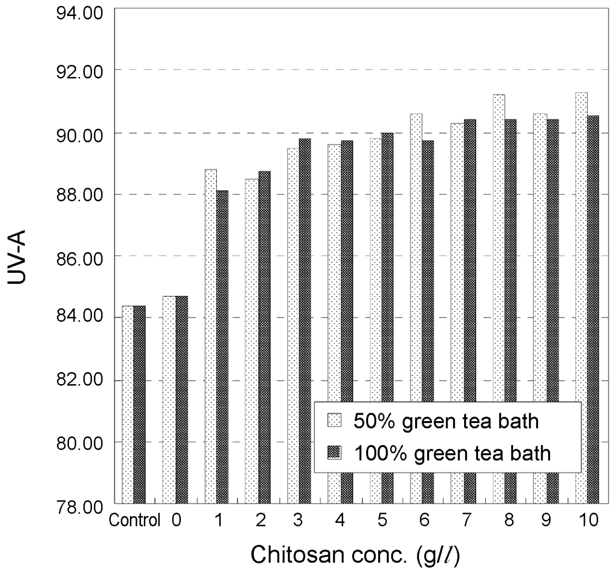

Figure 7. UV-A protection of chitosan-mordanted green tea dyed cotton fabrics in 50 % and 100 % green tea extract dye baths respectively.

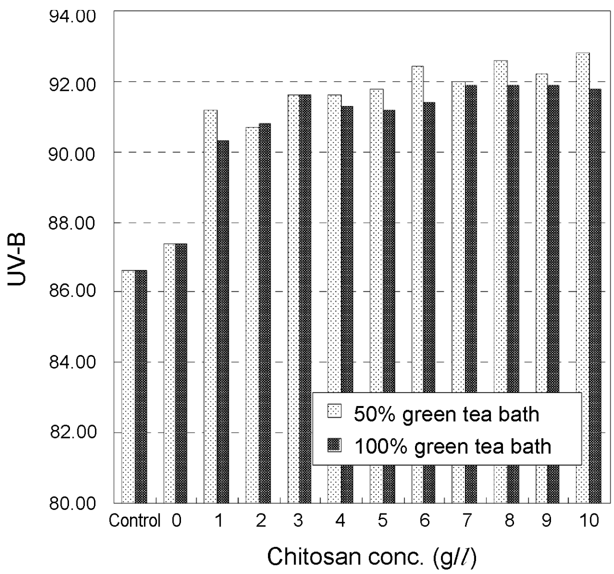

Figure 8. UV-B protection of chitosan-mordanted green tea dyed cotton fabrics in 50 % and 100 % green tea extract dye baths respectively.

The Effect of Chitosan Mordant Concentration on the UV Protection Property of Green Tea Dyed Cotton Fabric

UV-A and UV-B protection properties of chitosan mordanted green tea dyed cotton fabrics were shown in Figure 7 and Figure 8, respectively.

As chitosan mordanting concentration increased, the UV-A protection increased gradually. In case of chitosan concentration, 10 g/*l*, over 90 % UV-A protection property was observed (91.3 % protection in a diluted 50 % green tea dye bath, 90.5 % protection in an undiluted 100 % green tea dye bath). In case of chitosan mordanted cotton farbrics, green tea dyeing bath concentration did not affect the UV-A protection property, while dyeing bath concentration affected the UV-A protection property in case of unmordanted cotton fabrics (Figure 7).

In case of UV-B, the UV-B protection increased slightly as chitosan concentration increased (Figure 8). Over 90 % UV-B protection property was observed in all concentration range of chitosan mordanting (1-10 g/*l*). And green tea dye bath concentration did not affect the UV-B protection property as in UV-A (92.8 % protection in case of 50 % dye bath and 91.8 % protection in case of 100 % dye bath at 10 g/*l* chitosan mordanting concentration). Only unmordanted cotton showed the different UV-B protection property upon green tea dye bath concentration as shown in Figure 8 (87.4 % at 50 % green tea extract dye bath and 89.9 % at 100 % green tea extract dye bath). It can be assumed that chitosan mordanting increased the absorption of green tea active moiety responsible for UV protection property. And the higher concentration of chitosan mordanting resulted in the higher UV-A and UV-B protection of green tea dyed cotton fabrics, probably the increase of catechin family uptake, which would be responsible for UV protection of green tea extract [14-18]. Song and Song also measured the UV protection property of green tea extract dyed cellulosic materials, cotton, linen, and Hanji, using metal mordants and found the increase in UV protection property upon green tea dyeing [31]. And they suggested that the active moiety such as catechin and organic flavonoid compounds in green tea extract are responsible for the UV protection property of green tea dyed fabric [31]. Without metal mordants, only 3.5 % increase in UV-A protection and 4 % increase in UV-B protection of dyed cellulose were observed. With various metal mordants treatment, about 5-8 % increase in UV-A and UV-B was observed, which is similar increase range with the chitosan mordanted green tea dyed cotton in our study (5.3-6.9 % increase in 10 g/*l* chitosan mordanting concentration). Therefore, chitosan can be used as a non-toxic substitute for metal mordants without causing an environmental problem.

Conclusions

Cotton fabrics were successfully dyed by green tea extract upon chitosan mordanting, and UV protection property of the chitosan mordanted green tea dyed cotton was increased. The following conclusions were made from this study;

1. Chitosan mordanting can effectively increase the ΔE and the K/S, that is, the dyeing efficiency of green tea dyeing onto cotton fabrics. As chitosan concentration increased, the ΔE and the K/S of cotton fabrics by green tea extract increased gradually.

2. Chitosan mordanting can effectively increase the UV protection property of both UV-A and UV-B of green tea

dyed cotton fabrics. Chitosan mordanted undyed cotton and chitosan unmordanted dyed cotton did not show an increase in UV protection property. Therefore, it can be assumed that chitosan increased the uptake of active moiety, catechin, in green tea, which would be responsible for the UV protection and subsequently increased UV protection property of the chitosan mordanted green tea dyed fabric.

3. As chitosan mordanting concentration increased, UV protection property increased in both UV-A and UV-B. Around 7 % UV protection increase from control was observed upon chitosan mordanting, which is similar value of the green tea dyed cellulose fabric using a specific metal mordant.

Therefore, it can be concluded that green tea dyeing can be used in developing UV protective cotton textiles, and the chitosan mordanting process would be necessary in green tea dyeing of cotton to increase not only the dyeing efficiency but also the UV protection property of cotton fabrics.

Acknowledgements

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