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〈Research Paper〉

Ultraviolet Protection Property of Green Tea Extract Dyed Fabrics

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녹차추출물로 염색한 직물의 자외선 차단성에 관한 연구

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Abstract— Nowadays, interests of ultraviolet(UV) protection increased, since the UV dosage on the earth surface has increased over years. Overdose of UV can cause various skin, eye, and even DNA damages. Therefore, it is need to develop a proper mean to protect human skin and eye from UV radiation. In this study, the UV protective effect of green tea extract dyed fabrics with various fiber types were examined. Green tea has an active moiety called "catechin" having benzene rings in its structure, which would exert a proper UV protective property. Green tea dyed fabrics showed the increase in UV protection, and silk showed the highest increase in UV protection (from 52.2% to 84.5% in UV-A, from 66.1% to 90% in UV-B). The order of UV-A protection increase is silk, wool, nylon and acrylic, PET, and cotton. The order of UV-B protection increase is silk nylon, wool, acrylic, cotton, and PET. In case of silk and nylon, the UV protection property gradually increased as the concentration of green tea extract increased. As a result, it was proven that green tea extract dyeing can improve UV protection property of dyed fabrics in environment-friendly and biocompatible manners.

Keywords: *green tea extract, catechin, UV protection, green tea extract dyeing, biocompatible*

1. 서 론

Green tea has been extensively studied nowadays, since its various advantageous characteristics such as anti-carcinogenic, anti-oxidant, anti-bacterial, anti-allergic activities, and so on[1-6]. Among these advantages of green tea, UV protection property has been found and studied mainly for biomedical applications[7-10]. The main component contributing UV protection property of green tea is catechin moiety, which exists in various forms such as (+)-catechin, (-)-epicatechin, (-)-epigallocatechin, (-)-epi catechin gallate, (-)-epigallocatechin gallate, (-)-gallocatechin gallate [5]. Fig. 1 shows the structure s of (+)-catechin and (-)-epigallocatechin. It has been found that human cellular DNA can be pro-tectedby green tea extract against UV and visible light induced damages[9]. The protection effect of green tea against UV is valid not only in topical application but also in oral consumption [7-8), 10)].

Katiyar et al. reported the UV protection effect of green tea in oral and topical applications in human as well as animal study [8]. Since the harmfulness of UV and dosage of UV on the earth surface increase over years, the application of green tea extract on textile material should be considered.

UV radiation has various genotoxic and cytotoxic effects on human skin and many researches have been studied focusing on the harmful effects of UV [11-15]. Overdose of UV can cause various skin, eye, and even DNA damages [11-15]. Ultraviolet radiation (UVR) consists of three parts; UV-A, UV-B, and UV-C. Overdose of UV-A(320-400nm)

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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[14-15].

Overdose of UV-B(280-320nm) 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[14-15]. UV-C is intercepted by ozone layer and cannot reach to the earth surface[14].

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[15]. Therefore, it is need to develop a proper mean to protect human skin and eye against both UV-A and UV-B radiation.

For the reasons described above, the UV protection property of green tea extract dyed fabrics were examined in this study. The relationship between the dyeability and the UV protection property of various fiber type green tea dyed fabrics were investigated and the dyeability and UV protection property of various fiber types were studied. The effect of concentration of green tea extract bath when dyeing fabrics having various fiber types were also examined.

The purposes of this study are identifying the dyeability and the UV protection property of green tea dyed fabrics, defining the difference in dyeability and UV protection property of green tea dyed fabrics over different fiber types, and examining the optimum concentration of green tea extract bath in dyeing various fabrics. The environmental friendliness and biocompatibility of developed green tea dyed fabrics for UV protection would be another beneficial characteristic sinceonly synthetic UV protection materials such as titanium oxide, zinc oxide, and benzophenones have been used as UV protector in textile application and it is hard to apply these materials in natural fabrics[15-19]. There have been some studies related to UV protection of green tea extract dyed fabrics, however, it is restricted only in cotton and Hanji[21]. In this study, the dyeability of various natural and synthetic fabrics in green tea extract bath in the relation with the UV protection property of dyed fabrics.

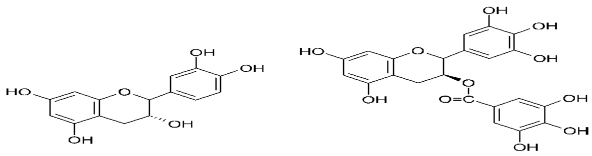

Fig. 1. Structures of (+)-catechin and (-)-epigallocatechin gallate.

2. Experimental

2.1 Materials

Green tea powder were purchased from Bosung-Dawon, Bosung, Korea. Cotton, silk, nylon, PET, wool, and acrylic fabrics were purchased from KATRI, Seoul, Korea. The property of each fabrics are shown in Table 1.

2.2 Method

2.2.1 Preparation of green tea extract

Green tea extraction was done by boiling green tea powder with 10 fold water for 1 hr at 100 ℃. To find out the effect of dye bath concentration on the dyeability and UV protection property, the

Table 1. Characteristics of standard fabrics used in experiments

	Counts (Tex)		Weight	Thickness	Density
	warp	weft	(g/m^2)	(mm)	(threads/cm)
Cotton	15	12	64 ± 5	0.13	180 X 162
Silk	2.31/2	2.31/2	26.15 ± 5	0.08	276 X 192
Wool	19	19	102 ± 5	0.28	142 X 136
Nylon	7.8	7.8	60 ± 5	0.10	214 X 150
PET	8.3	8.3	70 ± 5	0.09	210 X 191
Acrylic	16	16	95 ± 5	0.22	149 X 139

green tea extract solution was diluted 20%, 40%, 60%, and 80% by water and this green tea extract dye bath conc. was used in this study.

2.2.2 Green tea dyeing

Fabrics were dyed at liquor ratio, 1:30 o.w.f., in the green tea extracted solution. Dyeing was conducted at the room temperature for 15 min., and then, at 95℃ for 90min., subsequently. After dyeing, dyeing batch was cooled down to the room temperature, and the dyed fabrics were washed several times with tap water and air-dried.

2.2.3 Color measurement

To evaluate the dyeability of green tea extract on the various fabric types, L*a*b* was measured using spectrophotometer(Gretag Macbeth Color-Eye® 3100, USA). Surface reflectance values were also measured using the same spectrophotometer. All measured sample showed the greatest max. value at 400 nm. The K/S was calculated by Kubelka-Munk equation[22].

2.2.4 Evaluation of UV protection

Silk among natural fabrics and nylon among synthetic fabrics showed good dyeabilities and fair increases in UV protection value in the preliminary experiment and both fabrics have amide linkages. Therefore, UV protection measurement of silk and nylon was done according to the different green tea batch concentration, 20, 40, 60, 80, and 100%. UV protection of wool, cotton, acrylic, and PET were measured in the condition of undyed and 100% green tea batch concentration.

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

UV transmittance (%) = (T/B) 100
UV protection (%) = 100 UV transmittance (%)

T : UV transmitted through the fabric sample
B : UV transmitted without the fabirc

3. Result and Discussion

3.1 Dyeing characteristics of green tea dyed fabrics have various fiber types

Dyeing characteristics of various fabric types were shown in Table 2 Considering K/S value, the order of dyeability is as follows, wool, silk, cotton, nylon, acryl, and PET. Dyeing mechanism of catechin to various fibers are suggested in Fig. 2 Since catechin has more than four hydroxyl groups in the structure, hydrogen bonding would be a main attractive force between catechin and the fabric. Wool, silk, cotton, and nylon, the fibers capable of forming hydrogen bonding, showed higher K/S values than PET and acrylic, the fibers uncapable of forming hydrogen bonding. Ionic bonding could be a secondary attraction between catechin and the fiber, because the increased uptake of catechin was observed in chitosan treated cotton in my previous study of green tea dyeing[23]. However, since the fabrics were dyed in the neutral state, the ionic bonding would not be the main dye uptake force in this experiment. Among wool, silk, cotton, and nylon, the wool and silk showed the higher K/S values than cotton and nylon, even though all four fibers can form hydrogen bonds with catechin family. Because catechin is relatively large size for dye, it would be hard for catechin moleculeto penetrate into the compactly arranged fiber structure such as cotton and nylon. Therefore, only limited dyeability was shown in these fibers. On the other hand, wool fiber, which has a large amount of amorphous region showed the highest K/S.

As the green tea dye bath concentration increased, wool showed a relatively linear increase in K/S and silk also showed an increase in K/S (Fig. 3). Cotton and nylon showed a fair increase in K/S until dye bath 20%, however, no meaningful further increase was not observed. Acryl and PET were hardly dyed, which showed the lowest K/S and no change over the increased dye bath concentration.

Table 2. Dyeing characteristics of various fabrics by green tea extract

Fabric Type	Green tea dye bath conc.	L*	a*	b*	△L	△a	△b	K/S
Cotton	Control	91.05	3.08	-10.81	-	-	-	0.7138
	20%	84.69	2.20	4.91	-6.36	-0.88	15.72	0.9352
	40%	85.81	2.07	3.95	-5.24	-1.01	14.76	0.8269
	60%	84.75	2.27	6.77	-6.3	-0.81	17.58	0.9310
	80%	85.35	1.91	6.42	-5.7	-1.17	17.23	0.8126
	100%	85.45	2.12	5.83	-5.6	-0.96	16.64	0.9462
Silk	Control	88.73	-0.09	3.27	-	-	-	0.0987
	20%	79.86	2.59	18.00	-.87	2.68	14.73	0.9334
	40%	78.68	3.07	19.96	-10.05	3.16	16.69	1.1516
	60%	77.83	3.68	21.74	-10.90	3.77	18.47	1.4290
	80%	77.69	3.94	21.87	-11.04	4.03	18.60	1.4687
	100%	77.33	4.52	22.20	-11.40	4.61	18.93	1.5302
Wool	Control	86.41	-0.93	9.00	-	-	-	0.3518
	20%	75.38	4.12	22.35	-11.03	5.05	13.35	1.1645
	40%	74.70	4.79	23.98	-11.71	5.72	14.98	1.9041
	60%	72.97	5.79	25.30	-13.44	6.72	16.30	2.2972
	80%	72.30	6.11	25.81	-14.11	7.04	16.81	2.4771
	100%	71.86	6.45	26.20	-14.55	7.38	17.2	2.6540
Nylon	Control	89.26	-0.24	3.19	-	-	-	0.0858
	20%	83.10	0.33	17.51	-6.16	0.57	14.32	0.8325
	40%	83.16	0.94	16.73	-6.10	1.18	13.54	0.7788
	60%	80.18	2.76	18.25	-9.08	3.00	15.06	1.0394
	80%	80.42	2.66	17.80	-8.84	2.90	14.61	0.9786
	100%	82.32	1.89	14.73	-6.94	2.13	11.54	0.7065
PET	Control	90.07	-0.10	2.32	-	-	-	0.0649
	20%	88.37	-0.12	6.06	-1.70	-0.02	3.74	0.1358
	40%	88.55	-0.11	5.65	-1.52	-0.01	3.31	0.1277
	60%	88.76	-0.27	5.46	-1.31	-0.17	3.14	0.1220
	80%	88.47	-0.18	6.09	-1.60	-0.08	3.77	0.1421
	100%	88.73	-0.17	5.72	-1.34	-0.07	3.40	0.1318
Acrylic	Control	89.09	-0.62	3.68	-	-	-	0.1183
	20%	85.95	0.03	10.14	-3.14	0.65	6.46	0.2919
	40%	87.42	-0.43	7.53	-1.67	0.19	3.85	0.2136
	60%	87.65	-0.84	7.82	-1.44	-0.22	4.14	0.2249
	80%	86.78	-0.90	9.45	-2.31	-0.28	5.77	0.2787
	100%	87.38	-0.90	8.24	-1.71	-0.28	4.56	0.2362

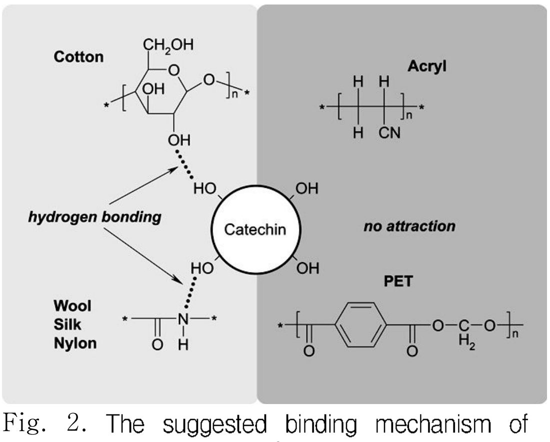

Fig. 2. The suggested binding mechanism of catechin to the various fiber types.

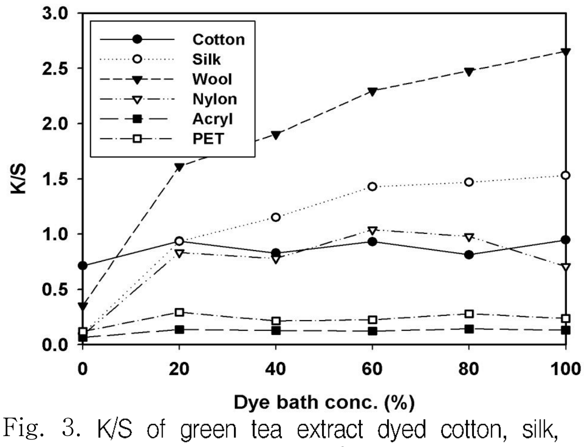

Fig. 3. K/S of green tea extract dyed cotton, silk, wool, nylon, PET, and acrylic fabrics.

3.2 UV protection property of green tea dyed fabrics with different fiber types

The suggested mechanism of UV protection by green tea treated fabrics are shown in Fig. 4. Some UV rays would absorbed and scattered by the fabric itself. The UV cutting ability is varied with fiber type, yarn type, weave, color, fabric thickness, fabric surface structure, and so on. For example, thin silk used in this experiment transmitted 47.8 of UV-A and 33.9% of UV-B. UV-A has a longer wavelength and can penetrate deeper, so more UV-A penetrates through the fabric than UV-B does. By green tea extract treatment of the same silk fabric, the UV-A penetration diminished to 15.5% and UV-B penetration diminished to 10.0%. The increased UV protection ability would be due to the increased catechin uptake. There is no report about the mechanism of catechin in UV cutting. Many researchers only reported the result of UV cutting ability of green tea applied skin or fabrics[7-8), 10)].

The following mechanism can be speculated as suggested in Fig. 4 Catechin familiy has many phenyl groups in its structure, which would have an ability to absorb UV rays. For example, 2,2′-dihydroxy-4-methoxy-benzophenone is a representative UV-absorber used in many industrial purpose[24)-26)]. The structural similarities of catechin and 2,2′-dihydroxy-4-methoxy-benzophenone can be observed. However, the harmful effects of benzonphenone family was reported[27)], therefore, it would not be proper to use 2,2′-dihydroxy-4-methoxy-benzophenone in skin contact situation. On the other hand, catechin is safe and many clinical studies proved the UV protection ability of green tea for topical and oral uses.

The effects of UV protection were shown in Fig. 5 and Fig. 6 All fiber types showed an increased UV-A and UV-B protection although the extent was varied with fiber type. In case of silk fabric, a marked increase were shown both in UV-A and UV-B protection(from 52.2% to 84.5% in UV-A protection, from 66.1% to 90% in UV-Bprotection). Nylon and wool showed a fair amount of increase both UV-A and UV-B. In case

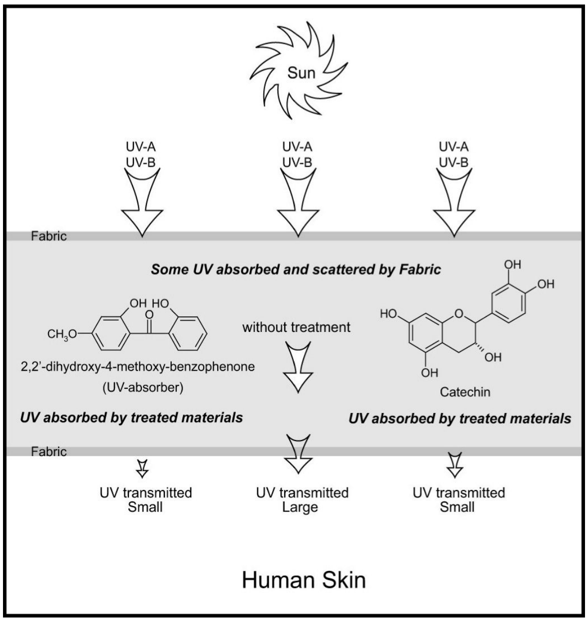

Fig. 4. The illustration of the suggested UV protection mechanism of catechin treated fabrics.

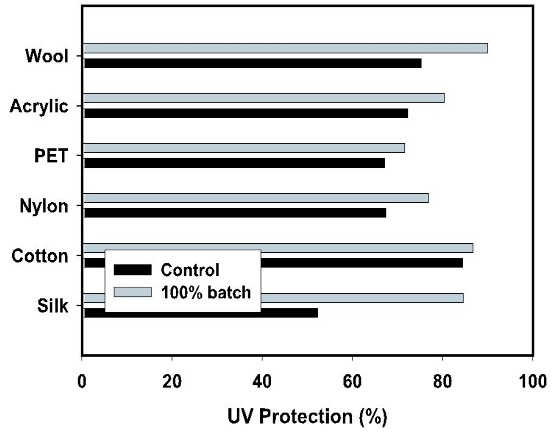

Fig. 5. UV-A protection effect of green tea dyed fabrics with various fiber types.

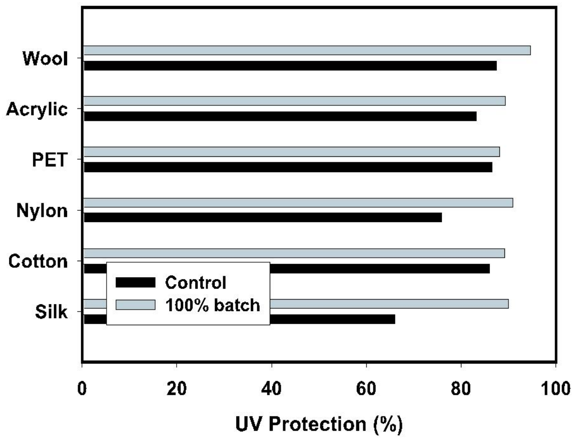

Fig. 6. UV-B protection effect of green tea dyed fabrics with various fiber types.

of nylon, UV-A protection increased from 67.4% to 76.9%, and UV-B protection increased from 75.8% to 90.9%. In case of wool, UV-A increased from 72.3% to 80.4%, and UV-B protection increased from 83.2% to 89.4%. The different UV protection is in the difference of green tea extract uptake amount among fabrics. However, the higher dyeability does not always mean the higher UV protection. The order of the increase in UV-A protection is silk, wool, nylon and acrylic, PET, and cotton, and the order of the increase in UV-B is silk, nylon, wool, acrylic, cotton, and PET.

On the other hand, the order of dyeablity is wool, silk, cotton, nylon, acrylic, and PET. This result indicates that the color exerting component uptake and the catechin uptake onto textile materials could be somewhat different. Silk and wool, fabrics dyed in dark color, showed the highest increase in UV protection. In general, the darker dyed fabrics showed a better UV protection except cotton. It seemed that the original cotton showed the fairly high UV protection value and the further increase in UV protection was not significant upon green tea dyeing. In case of silk, wool, and nylon, a fair amount of increase in UV protection was observed.

Therefore, green-tea dyed fabrics can effectively protect human body compared to the undyed fabric. As mentioned earlier, the harmful effects of UV radiation have been increasing over years, a proper mean to prevent UV penetration without the incorporation of any harmful UV absorbing or scattering chemicals would be very valuable. A simple treatment of fabrics with green tea extract would be very beneficial at this point.

3.3 The effect of green tea dye bath concentration on the UV protection property

Silk and nylon was dyed at the various concentrations and UV protection of silk and nylon were measured to know the relationship between green tea extract uptake and UV protection ability. Silk and nylon were chosen to study the concentration dependent UV protection because these two fabrics showed good increases in UV protection property after treating them in 100% green tea extract bath.

For silk fabric, a gradual increase in UV protection was observed as the concentration of green tea extract dye bath increased(Fig. 7). In case of nylon, the same result with silk was observed. The increase range was not that prominent compared to that of silk fabric because nylon showed the lower dyeability than silk, which means the lower uptake of catechin(Fig. 8).

Therefore, it would be needed the high concentration of green tea extract bath to get the higher increase of UV protection property.

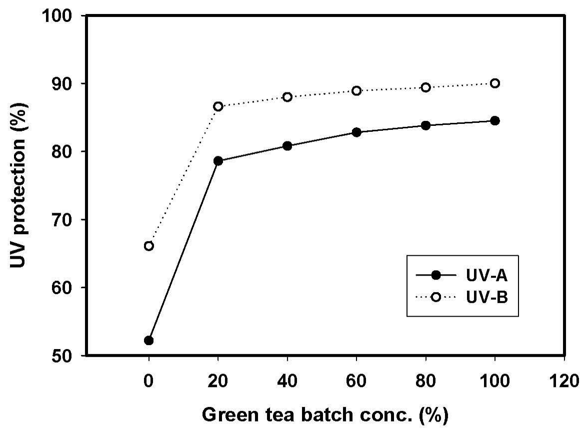

Fig. 7. UV-A and UV-B protection effect of green tea dyed silk fabrics at the various green tea extract concentrations.

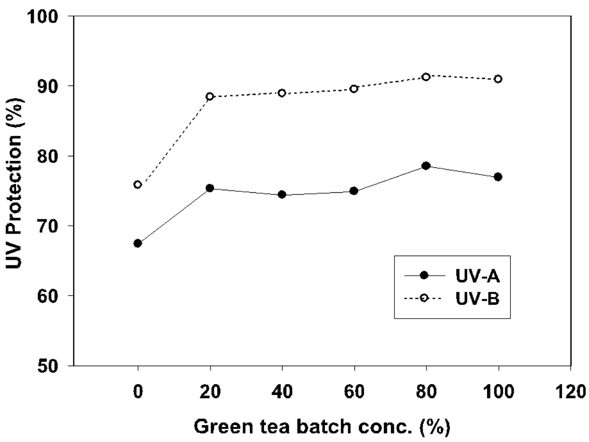

Fig. 8. UV-A and UV-B protection effect of green tea dyed nylon fabrics at the various green tea extract concentrations.

4. Conclusions

Green tea dyeing successfully increased UV protection property of fabrics and the following conclusions can be made from this study.

1. Wool showed the highest dyeability followed by silk, cotton, nylon, acrylic. PET was hardly dyed by green tea extract. As the dye bath concentration increased, the K/S value of wool and silk increased and the other fibers did not.
2. Green tea extract dyeing can effectively increase the UV protection property of dyed fabrics.
3. Fabrics having amide moiety such as wool, silk, and nylon showed a better dyeability by green tea extract and showed a better UV protection property.
4. Wool fabrics showed a best dyeability of green tea extract. However, the maximum increase of UV protection property was observed in silk among tested fabrics.
5. In case of silk, as the concentration of green tea extract increased, the UV protection property increased gradually.
6. Green tea extract dyeing can be used in developing UV-protective fabrics in environmental-friendly and biocompatible manners.

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References

1. H. Hibasami, Y. Achiwa, T. Fujikawa, and T. Komiya, Induction of programmed cell death (apoptosis) in human lymphoid leukemia cells by catechin compounds, *Anticancer Res.*, **16**, 1943(1996).
2. M. Hirose, Y. Mizoguchi, M. Yaono, H. Tanaka, H., T. Yamaguchi, and T. Shirai, Effects of green tea catechins on the progression or late promotion stage of mammary gland carcinogenesis in female Sprague-Dawley rats pretreated with 7,12-dimethylbenz()anthracene, *Cancer Lett.*, **112**, 141(1997).
3. S. K. Katiyar, R. Agarwal, and H. Mukhtar, Protection against malignant conversion of chemically induced benign skin papillomas to squamous cell carcinomas in SENCAR mice by a polyphenolic fraction isolated from green tea, *Cancer Res.*, **53**, 5409(1993).
4. S. K. Katiyar and H. Mukhtar in "Metabolic consequences of changing dietary patterns", (A. P. Simopoulos Eds.), World Rev. Nutr. Diet., Basel, Karger, vol.79, pp.154-184, 1996.
5. B. C. Nelson, J. B. Thomas, S. A. Wise, and J. J. Dalluge, The separation of green tea catechins by micellar electrokinetic chromatography, *J. Microcolumn Separations*, **10**(8), 671(1998).
6. V. W. Setiawan, Z-F. Zhang, G-P. Yu, Q-Y. Lu, Y-L. Li, M-L. Lu, M-R. Wang, C-H Guo, S-Z. Yu, R. C. Kurtz, and C-C Hsieh, Protective effect of green tea on the risks of chronic gastritis and stomach cancer, *Int. J. Cancer*, **92**, 600(2001).
7. C. A. Elmets, D. Singh, K. Tubesing, M. Matsui, S. Katiyar, and H. Mukhtar, Cutaneous photoprotection from ultraviolet injury by green tea polyphenols, *J. Am. Acad. Dermatol.*, **44**(3), 425(2001).
8. S. K. Katiyar, F. Afaq, A. Perez, and H. Mukhtar, Green tea polyphenol (-)-epigallocatechin-3-gallate treatment of human skin inhibits ultraviolet radiation-induced oxidative stress, *Carcinogenesis*, **22**(2), 287(2001).
9. N. Morley, T. Clifford, L. Salter, S. Campbell, D. Gould, and A. Curnow, The green tea polyphenol (-)-epigallocatechin gallate and green tea can protect human cellular DNA from ultraviolet and visible radiaton-induced damage, *Photodermatol. Photoimmunol. Photomed.*, **21**, 15 (2005).
10. P. K. Vayalil, A. Mittal, Y. Hara, C. A. Elmets, and S. K. Katiyar, Green tea polyphenols prevent ultraviolet light-induced oxidative damage and matrix metalloproteinases expression in mouse skin, *J. Invest. Dermatol.*, **122**(6), 1480 (2004).
11. A. Ablett, D. C. Whiteman, G. M. Bolye, A. C. Green, and P. G. Parsons, Induction of metall-

othionein in human skin by routine exposure to sunlight: Evidence for a systemic response and enhanced induction at certain body sites, *J. Invest. Dermatol.*, **120**(2), 318(2003).
12. B. L. Diffey, Human exposure to solar ultraviolet radiation, *J. Cosmet. Dermatol.*, **1**(3), 124 (2002).
13. J. Garssen, M. Norval, A. El-Ghorr, N. K. Gibbs, C. D. Jones, D. Cerimele, C. De Simone, S. Caffieri, F. Dall'Acqua, F. R. De Gruijl, Y. Sontag, and H. Van Loveren, Estimation of the effect of increasing UVB exposure on the human immune system and related resistance to infectious diseases and tumors, *J. Photoch. Photobio. B*, **42**(3), 167(1998).
14. G. Reinert, F. Fuso, R. Hilfiker, and E. Schmidt, UV-protecting properties of textile fabrics and their improvement, *Text. Chem. Color.*, **29**(12), 36(1997).
15. C. Teng and M. Yu, Preparation and property of poly(ethylene terephthalate) fabrics providing ultraviolet radiation protection, *J. Appl. Polym. Sci.*, **88**, 1180(2003).
16. I.Leaver, The mechanism of photoprotection of wool by UV absorbers of the 2-hydroxybenzophenone class, *J. Appl. Polym. Sci.*, **33**, 2795(1987).
17. B. Milligan and L. Holt, Ultraviolet absorbers for retarding wool photodegradation: Sulphonated long-chain substituted 2-hydroxybenzophenones, *Polym. Degrad. Stab.*, **5**, 339(1983).
18. B. Milligan and L. Holt, Ultraviolet absorbers for retarding wool photodegradation: Sulphonated 2-hydroxybenzophenones and 2,2-dihydroxybenzophenones, *Polym. Degrad. Stab.*, **10**, 335(1985).
19. J. Riedel and H. Höcker, Multifunctional polymeric UV absorbers for photostabilization of wool, *Text. Res. J.*, **66**(11), 684(1996).
20. H. Yang, S. Zhu, and N. Pan, Studying the mechanisms of titanium dioxide as ultraviolet-blocking additive for films and fabrics by an improved scheme, *J. Appl. Polym. Sci.*, **92**, 3201 (2004).
21. Y. Shin and H. Choi, Characteristics and dyeing properties of green tea colorants(Part III) Dyeing properties of cotton and green tea colorants-, *J. Kor Soc. Clo. Text.*, **23**(4), 510 (1999).
22. D. P. Law, A. B. Blakeney, and R. Tkachuk, The Kubelka-Munk equation: some practical considerations, *J. of near Infrared spectroscopy*, **4**(1), 189(1996).
23. S. H. Kim, Dyeing characteristics and UV protection property of green tea dyed cotton fabrics, -Focusing on the effect of chitosan mordanting condition-, *Fibers and Polymers*, **7**(3), 255(2006).
24. I. H. Leaver, Mechanism of photoprotection of wool by UV absorbers of the 2-hydroxybenzophenone class, *J. Appl. Polym. Sci.*, **33**(8), 2795(1987).
25. B. Milligan and L. A. Holt, Ultraviolet absorbers for retarding wool photo-degradation: Sulphonated long-chain substituted 2-hydroxybenzophenones, *Polym. Degrad. Stab.*, **5**(5), 339(1983).
26. J-H. Riedel and H. Hoecker, Multifunctional polymeric UV absorbers for photostabilization of wool, *Text. Res. J.*, **66**(11), 684(1996).
27. H. Yang, S. Zhu, and N. Pan, Studying the mechanism of titanium dioxide as ultraviolet-blocking additive for improved scheme, *J. Appl. Polym. Sci.*, **92**(5), 3201(2004).