[보 문]

Journal of the Korean Society of Clothing and Textiles
Vol. 25, No. 10 (2001) p.1738~1744

Development of Surface Modified Tencel Fabrics through the Control of Fibrillation(Part II)
- Fibrillation control effect through reactive dye treatment -
피브릴화 조절을 통한 다양한 감성의 텐셀소재 개발(제2보)
-반응성 염료에 의한 피브릴화 조절 효과-

Dept. of Clothing and Textiles · Human Ecology Research Institute, Chonnam National University
Younsook Shin · Kyounghee Son

전남대학교 의류학과, 생활과학연구소
신 윤 숙 · 손 경 희

(2001. 9. 26 접수)

Abstract

본연구의 목적은 반응성 염료를 이용한 텐셀섬유의 피브릴화 조절 효과를 표면 형태, 감량율, 역학적 성질 및 태의 변화의 측면에서 고찰하는데 있다. 반응성 염료에 의한 가교는 섬유의 비결정영역의 구조를 변화시켜 피브릴화를 억제하였으며 또한 효소의 작용에 영향을 주어 감량율을 감소시켰다. 반응성 염료에 의한 가교는 역학적 성질 중 특히 전단강성, 압축에너지, 압축레질리언스를 증가시켰다. 염색후 효소처리한 시료는 다른 시료보다 numeri와 fukurami 값이 높아 더 나은 종합태를 보였다. 공정순서에 따라 약간씩 차이가 있는 촉감을 나타냈다.

Key words: fibrillation control, reactive dyes, crosslinking, mechanical properties, total hand; 피브릴화 조절, 반응성 염료, 가교, 역학적 성질, 태

I. Introduction

Tencel shows a tendency towards fibrillation during wet abrasion because of its high orientation and lack of lateral cohesion. This fibrillation property has been manipulated to give various fabric hand such as soft touch and peach skin effect by using enzyme treatment.[1,2] On the other hand, fibrillation adversely affects the hand and appearance of a garment after repeated laundering.[3] For wider use of Tencel, it is necessary to control fibrillation. Reactive compounds such as easy care finishing agents have been applied to control fibrillation by inserting crosslinks inside fiber.[3] Effects of reactive dyes and crosslinking resins on enzymatic hydrolysis have been studied for cellulose fibers such as cotton, viscose rayon, linen, etc.[4,5] Those compounds have also been applied to Tencel fiber for investigating the feasibility of fibrillation control.[3,6] However, the effects of crosslinking on hand-related mechanical properties and the influence of these properties' changes on primary hand qualities such as koshi (stiffness), numeri (smoothness) and fukurami (fullness and softness) have not been widely studied.

The objective of this study is to investigate the fibrillation control effects of reactive dyes on enzymatic hydrolysis, mechanical properties, and hand qualities of the cellulase-treated Tencel fabrics.

II. Experimental

1. Materials

The fabric used was a desized and scoured 100% Tencel (3/1 twill, 110×74/inch², 237g/m², 0.39mm). Three reactive dyes (Cibacron Red F-R, Yellow C-2R and Red C-2G) were supplied by Ciba Specialty Chemicals Korea Ltd. Cellulase (Bio-Blue, Pacific Co., Ltd., Korea) from *Tricoderma viride* with an activity of 23.0 units/mg solid was used. Lubricant (Modarez ACA, Protex Korea Co., Ltd., Korea) was used during mechanical fibrillation. Aftertreatment softener was a protein type (Racset KG, Samwon Co., Ltd.) composed of collagen and polyoxyethylene alkylether. Chemicals for preparing buffer and analysis were first grade. All other chemicals were reagent grade.

2. Fabric Treatment

1) Dyeing

Dyeing was done at a liquor ratio of 1:10 in launder-Ometer at 60℃. Samples were dyed in a dyebath containing dye (1, 3% owf) and 10% owb sodium sulfide for 30 min, fixed for 60 min after adding 6% owb sodium carbonate in the bath and washed. Soaping was done in a bath containing 0.2% owb soaping agent (Lipotol RF-101, Korea Fine Chemical Co., Ltd.) at a liquor ratio of 1:50 for 15 min at 90℃. Dye uptake was assessed by measuring K/S value at λ_{max} on a Macbeth Colorimeter.

2) Enzyme Treatment

Enzyme treatment was done in a bath containing 3g/*l* of cellulase at 60℃ for 60 min using a rotary drum washer. Optimum pH of 5.0 was established with 0.9M NaOH/1.4M CH_3COOH solution. To terminate the enzymatic reaction, the fabrics were treated with hot water (80℃) for 10 min and rinsed twice with warm water (40℃) for 10 min and then dried.

3) Fibrillation

Fibrillation treatment was done before cellulase treatment to produce fibrils effectively in a bath containing lubricant (2g/*l*) at 80℃ for 60 min.

4) Softener treatment

The cellulase-treated samples were treated in a bath containing 3% owf softener at 40℃ for 30 min with a liquor ratio of 1:30.

3. Evaluation

1) Surface change

A scanning electron microscope (JEOL JSM-5400)

Table 1. Mechanical property parameters and measuring units

Property	Parameter	Definition	Unit
	LT	tensile linearity	–
Tensile	WT	tensile energy	gf · cm/㎠
	RT	tensile resilience	%
Bending	B	bending rigidity	gf · ㎠/cm
	2HB	bending hysteresis	gf · ㎠/cm
Shearing	G	shear stiffness	gf/cm · deg
	2HG	hysteresis at φ=0.5°	gf/cm
	2HG5	hysteresis at φ=5°	gf/cm
Compression	LC	compressional linearity	–
	WC	compressional energy	gf · cm/㎠
	RC	compressional resilience	%
Surface	MIU	coefficient of friction	–
	MMD	mean deviation of MIU	–
	SMD	geometrical roughness	micron
Thickness	T	thickness at 0.5 gf/㎠	mm
Weight	W	weight per unit area	mg/㎠

determined fiber surface changes at ×2000.

2) Weight loss

Fabric weight loss was determined on the conditioned weight of the fabric sample.

$$\text{Weight Loss (\%)} = [(W_0 - W)/W_0] \times 100$$

where W_0 and W represent weight before and after cellulase treatment, respectively.

3) Mechanical and Hand properties

The low stress mechanical properties (tensile, shear, bending, compression and surface) of the treated fabrics were measured using the KES-FB. Mechanical property parameters and measuring units are listed in Table 1. From the measured values of mechanical properties, primary hand values (HV) were determined by KN-101-WINTER for men's winter suiting materials.[7] Total hand value (THV) was determined by KN-301-WINTER.

III. Results and Discussion

1. Effect on Fibrillation

The surface differences between undyed and reactive dyed are clearly visible in SEM pictures shown in Fig. 1. Red F-R is monofunctional, Yellow C-2R is bifunctional and Red C-2G is trifunctional.

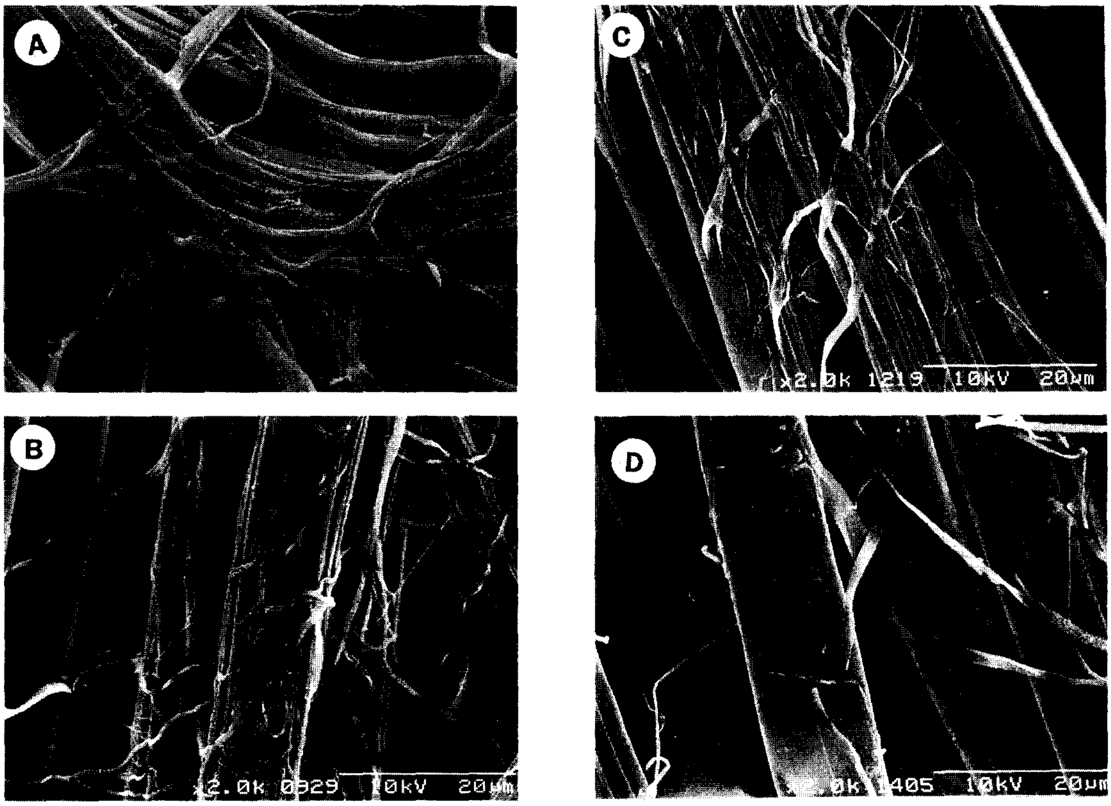

Fig. 1. SEM pictures(×2000) of experimental fabrics: A; undyed/fibrillated fabric, dyed/fibrillated fabric(B; 1% Red F-R, C; 3% Red F-R, D; 3% Red C-2G).

Comparing the undyed and fibrillated sample with the dyed and fibrillated samples, reactive dye reduced fibrillation of the Tencel fiber. Trifunctional reactive dye (sample D) reduced fibrillation more effectively than monofunctional reactive dye (sample C). Reduced fibrillation is the indication of crosslinking.[3] And less fibrils are observed at higher dye concentration irrespective of functionality of the dye. The more dye ingredients are added, the more chances of crosslinking of cellulose fibrils would exist.[3] This result is consistent with weight loss data which will be explained later. The effect of process order can be observed in SEM pictures shown in Fig. 2. The dyed/cellulase-treated sample showed a very clean surface, while the cellulase-treated/dyed sample, which is processed in reverse order, has many more fibrils on the surface.

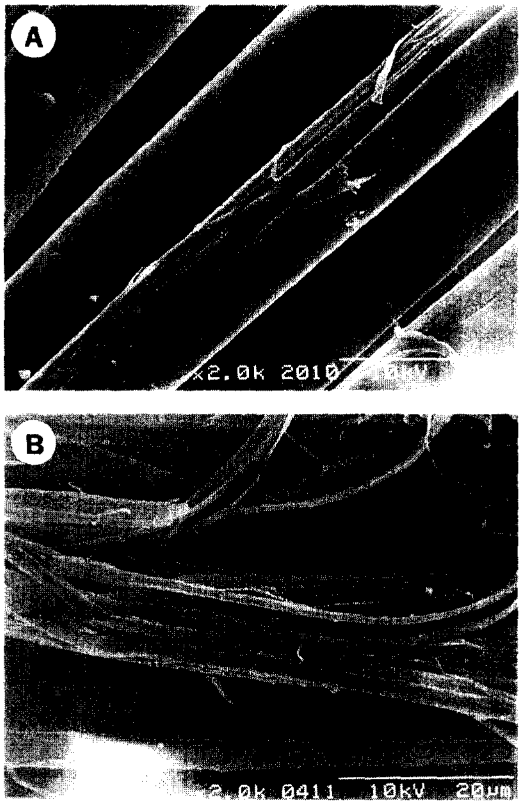

Fig. 2. SEM pictures(× 2000) of experimental fabrics: A; dyed(3% Red C-2G)/fibrillated/Cellulase-treated fabric, B; fibrillated/cellulase-treated/dyed(3% Red C-2G).

2. Effect on Weight Loss

Three different dyes in terms of the number of functional group are used to investigate the influence on enzymatic hydrolysis. Weight loss of the dyed/cellulase-treated samples are compared in Table 2. Considering that the weight loss of the dyed/cellulase-treated is lower than that of the undyed/cellulase-treated fabric, crosslinking with reactive dyes obviously suppresses enzymatic attack. Crosslinking reduced the amount of fibrils and this may affect the cellulase reaction, resulting in lower weight loss. Weight loss is decreased even more greatly as the number of functional group and dye concentration increase. Dyes having more functional groups gave lower weight loss. This implies that bi- and trifunctional reactive dyes create a certain amount of crosslinking, thus producing a protective effect against enzymatic degradation.[5] As dicussed above, SEM pictures (Fig. 1) showed reduced fibrillation, indicating

Table 2. Weight loss of the dyed and cellulase treated fabrics

Dye	Dye conc. (%, owf)	K/S value	Weight loss(%)
	undyed[a]	–	2.02
Red F-R	1	11.8	1.34
	3	24.0	0.79
Yellow C-2R	1	15.9	1.14
	3	25.6	0.57
Red C-2G	1	14.9	1.02
	3	26.7	0.39

[a] cellulase-treated

crosslinking. Reactive dyes form covalent bonds with the hydroxyl groups of cellulose, thus changing the structure of cellulose in the amorphous regions and this influences enzymatic hydrolysis. Taylor et al.[1] found that reactive dyes have a decelerating influence on enzymatic hydrolysis of cotton. And Ueda et al.[8,9] found that anionic dyes such as direct and reactive dyes absorbed on the cotton substrate inhibit cellulase catalytic reaction. They speculated that these dyes attribute to disturbance or deactivation of cellulase by the electrostatic potentials introduced on the substrate by the adsorption of ionic dyes. The position of functional groups also may affect crosslinking. For example, closely situated reactive groups can not make crosslinking even though the dye is polyfunctional. Nicoli et al.[5] reported that the effect of reactive dyes on enzymatic hydrolysis varied depending on the stereochemical structure and size of molecule and the internal mobility of the chromophore.

Table 3. Mechanical properties of the treated fabric

Properties	C	D/C	C/D	D/C/S	C/D/S
LT	0.67	0.69	0.68	0.62	0.57
WT	10.97	11.00	11.70	11.13	11.23
RT	50.21	53.88	53.03	63.14	65.47
B	0.181	0.180	0.182	0.144	0.139
2HB	0.066	0.063	0.059	0.035	0.027
G	0.51	0.54	0.54	0.32	0.33
2HG	0.37	0.35	0.36	0.10	0.13
2HG5	2.16	2.39	2.44	0.49	0.60
LC	0.49	0.43	0.45	0.44	0.48
WC	0.21	0.38	0.21	0.34	0.24
RC	34.21	37.97	38.19	49.01	46.09
MIU	0.204	0.200	0.233	0.190	0.196
MMD	0.016	0.014	0.016	0.011	0.010
SMD	3.85	3.55	3.54	3.35	3.49
T	0.600	0.688	0.611	0.747	0.623
W	23.872	24.237	23.832	24.377	23.970

S: softener treated

3. Effect on Mechanical Properties

In order to investigate change in the mechanical properties by reactive dye treatment, either dyed/cellulase-treated (D/C) or cellulase-treated/dyed (C/D) fabrics are compared with the undyed/cellulase-treated (C) fabrics in Table 3. Trifunctional reactive dye (Red C-2G) was used because it was the most effective for controlling fibrillation. The effect of processing order was also investigated.

Compared to the undyed/cellulase-treated fabrics, the dyed/cellulase-treated fabrics show slightly higher tensile resilience (RT) and tensile energy (WT). This indicates that crosslinking by reactive dye improves resilience and dimensional stability of the fabric. Tensile linearity (LT) is similar irrespective of processing order. Softener increased tensile resilience, resulting in the improvement of recovery from tensile deformation. Processing order does not significantly affect tensile properties.

Bending rigidity (B) is not affected but bending hysteresis (2HB) is decreased slightly. This means that reactive dye improves bending recovery. As expected, softener increases flexibility and elasticity of the treated fabrics, resulting in the decrease of bending rigidity and bending hysteresis. The cellulase-treated/dyed sample shows slightly lower bending hysteresis than the dyed/cellulase-treated sample.

Shear rigidity (G) is increased slightly in the dyed (D/C and C/D) samples. In general, crosslinking increases shear rigidity, making fabrics difficult to deform in bias direction and resulting in better silhouette and drape of a garment. Softener decreases shear rigidity and shear hysteresis (2HG and 2HG5) remarkably. Processing order does not affect shear properties. The cellulase-treated/dyed sample produces lower shear hysteresis than the dyed/cellulase-treated sample.

Compressional energy (WC) is increased distinctively in the dyed/cellulase-treated sample and compressional resilience (RC) is increased slightly in both dyed/cellulase-treated and cellulase-treated/dyed samples. High compressional energy indicates high fullness of the treated fabric. Increase in compressional resilience contributes to the improvement of recovery from compressive deformation. From these results, processing order is evaluated as an important factor for increasing the volume of the treated fabric. On the other hand, softener significantly increased compressional resilience. It has been widely accepted that softener improves resilience and fullness.

Surface properties seem to be affected by processing order more than fibrillation control. The fabric dyed after cellulase treatment gave higher friction coefficient (MIU) than the fabric dyed before cellulase treatment, which has more fibrils on the surface (Fig. 2C).

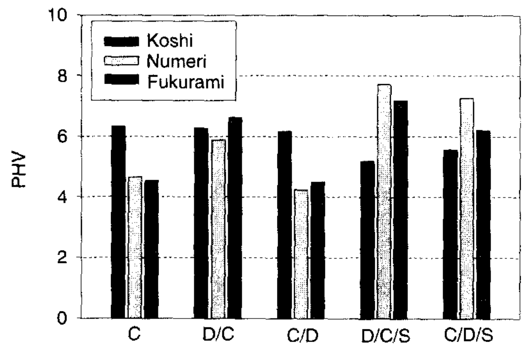

Fig. 3. Effect of finishing process on the primary hand values.

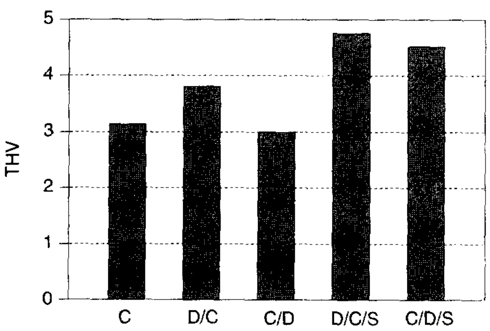

Fig. 4. Effect of finishing process on the total hand values.

4. Effect on Hand

Primary and total hand values are compared in Figs 3 and 4. The dyed/cellulase-treated sample shows higher numeri (smoothness) and fukurami (softness and fullness) values as shown in Fig 3, thus producing smoother, softer, fuller, and more resilient hand. Reactive dyeing does not affect koshi (stiffness) value. Evaluating subjectively, the dyed/cellulase-treated fabric tends to give a fuller touch while the cellulase-treated/dyed sample gives a slightly stiffer touch. Softener makes the treated fabrics less stiff, fuller, smoother, and softer, as expected. The total hand value is higher in the dyed/cellulase-treated sample than in the cellulase-treated/dyed sample. Nevertheless, each fabric treated in a different order gave a slightly differentiated hand quality.

IV. Summary

Reactive dyeing impedes enzymatic hydrolysis of Tencel fiber, thus decreasing the weight loss. Weight loss is decreased as the number of the functional group and dye concentration increase. Fibrillation is controlled more effectively by bi- and trifunctional reactive dyes than monofunctional reactive dye. Crosslinking by trifunctional reactive dye improves resilience and dimensional stability of the treated fabric. Crosslinking increases shear rigidity, making fabrics difficult to deform in bias direction of and resulting in better silhouette and drape of a garment. Compressional energy is increased distinctively in the dyed/cellulase-treated sample and compressional resilience slightly increased in both dyed/cellulase-treated and cellulase-treated/dyed. Surface properties seem to be more affected by processing order. The dyed/cellulase-treated sample shows higher numeri and fukurami values, thus resulting in smoother, softer, fuller, and more resilient hand. Each fabric treated in a different order gave a slightly differentiated hand guality.

Acknowledgement

This study was financially supported by the Chonnam National University in 1998. The authors deeply appreciate the support.

References

1. Taylor, J. M., and Harden, A. L., The dyeing of Tencel and Tencel A100 with poly-functional reactive dyes, Proceedings of 1998 Int'l Conference and Exhibition of AATCC, 545−555, 1998.
2. Kumar, A., and Harnden, A., Cellulase enzymes in wet processing of Lyocell and its blend, *Text. Chem. Color. & Am. Dyest. Reptr.*, **1**, 35−41, 1999.
3. Nicoli, M., Nechwatal, A., and Mieck, K. P., Textile crosslinking reaction to reduce the fibrillation tendency of Lyocell fibers, *Textile Research J.*, **66**, 575−580, 1996.
4. Buschle−Diller, G., and Traore, M. K., Influence of direct and reactive dyes on the enzymatic hydrolysis of cotton, *Textile Research J.* **68**, 185−192, 1998.
5. Choe, E. K., Park, S. Y., Cha, H. C., and Jeon, B. D., Effect of pre−existing dyes and fabric type on cellulase treatment of cotton fabrics, *Textile Research J.*, **67**, 155−162, 1997.
6. Collier, B. J., Effects of finishing and dyeing on Lyocell and Lyocell−blend fabrics, *Text. Chem. Color & Am. Dyest. Reprtr*, **1**, 40−45, 1999.
7. Kawabata, S., The Standardization and Analysis of Hand Evaluation, 2nd ed., *Textile Machinery Society of Japan*, Japan 1980.
8. Ueda, M., Koo, H., Wakida, T., Yoshimura, Y., and Igarashi, T., Cellulase treatment of cotton fabrics, *Textile Res. J.*, **64**, 70−74, 1994.
9. Ueda, M., Koo, H., Wakida, T., and Yoshimura, Y., Cellulase treatment of cotton fabrics part II; Inhibitory effect of surfactants on cellulase catalytic reaction, *Textile Res. J.*, **64**, 615−618, 1994.