

# Structural Changes in Tencel by Enzymatic Hydrolysis

YOUNSOOK SHIN,<sup>1</sup> KYOUNGHEE SON,<sup>1</sup> DONG IL YOO<sup>2</sup>

<sup>1</sup> Department of Clothing and Textiles, Chonnam National University, Kwangju, 500-757, Korea

<sup>2</sup> Department of Textile Engineering, Chonnam National University, Kwangju, 500-757, Korea

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**ABSTRACT:** The NaOH-, fibrillation-, and cellulase- treated Tencel fabrics were characterized by weight loss, tensile strength, scanning electron microscopy (SEM) analysis, X-ray diffraction analysis, measurements of moisture regain and dye adsorption (K/S value), degree of polymerization (DP), and copper number. Weight loss increased and tensile strength decreased with increase in cellulase concentration and treatment time. At a similar weight loss, tensile strength retentions of the NaOH-pretreated samples were better than those of the NaOH-nontreated samples because of more uniform enzymatic hydrolysis. SEM photographs showed more surface peeling and interfibrillar splitting as enzymatic hydrolysis progressed. Crystalline structure and degree of crystallinity were not much changed by cellulase treatment. As enzymatic hydrolysis progressed, moisture regain and K/S value increased slightly due to increase of specific surface area by fibrils. DP initially decreased as enzymatic hydrolysis progressed and then leveled off. Copper number increased largely at an initial stage of degradation and then decreased gradually. The NaOH-pretreated samples showed higher degree of crystallinity, DP, moisture regain, and K/S value, but lower copper number than the NaOH-nontreated ones. These results were attributed to extraction of short chain molecules in the amorphous region during NaOH pretreatment and change of amorphous region into the open-up structure. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1644–1651, 2000

**Key words:** Tencel; cellulase; scanning electron microscopy analysis; X-ray diffraction analysis; crystallinity; accessibility; degree of polymerization; copper number

## INTRODUCTION

Tencel is a cellulosic fiber produced from wood pulp via a novel solvent-spinning process designed to minimize environmental impact.<sup>1,2</sup> It has a high modulus, leading to low laundering shrinkage, and shows higher strength in both wet and dry states than viscose rayon.<sup>3</sup> However, it exhibits a distinct tendency to fibrillate when subjected to abrasion in the wet conditions. This is caused by the longitudinal splitting of the highly

oriented crystalline fiber.<sup>4,5</sup> This fibrillation property can be manipulated to achieve surface modification, including the peach skin and other soft touch effects. Various processes are being suggested to create different aesthetics to Tencel fabrics.<sup>6–8</sup>

Cellulases have been applied to improve hand and appearance of cellulosic fabrics.<sup>9–11</sup> Enzymatic hydrolysis of cellulosic materials is somewhat complicated and not fully understood.<sup>12</sup> It is known that cellulases cleave  $\beta$ -1,4 glucosidic linkage to yield glucose as the final product.<sup>13</sup> The fine structure and morphology of cellulosic fibers largely determine the course of the enzymatic degradation reaction.<sup>14</sup> For example, enzyme

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Correspondence to: Y. Shin.

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penetration occurs more easily in cotton cellulose than in regenerated cellulose fiber due to the larger pore size of cotton cellulose.<sup>15</sup> Therefore, enzymatic hydrolysis of Tencel fiber will be different from other celluloses due to differences in the fine structure and morphology, although based on identical chemical composition.

In this study, we treated Tencel fabrics with cellulase after mechanical fibrillation and investigated the effect of NaOH pretreatment on enzymatic hydrolysis. Weight loss and tensile strength of the treated fabrics were determined depending on cellulase treatment conditions. Scanning electron microscopy (SEM) analysis was carried out to study morphological changes of the treated fabrics. X-ray diffraction analysis, measurements of moisture regain, and dye adsorption (K/S value) were used to elucidate microstructural changes occurred by cellulase treatment. The degree of polymerization (DP) and copper number were also measured to estimate effect of hydrolysis.

## EXPERIMENTAL

Desized and scoured 100% Tencel fabric (3/1 twill,  $110 \times 74/\text{cm}^2$ , Dong-kuk Co., Ltd., Korea) weighting  $236 \text{ g/m}^2$  (thickness 0.36 mm) was used. 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. Chemicals for preparing buffer and analysis were first grade. All other chemicals were reagent grade.

NaOH pretreatment involved in applying the fabrics in a 8% sodium hydroxide solution at room temperature for 1 min under tension, rinsing, and neutralizing with a 5% acetic acid solution, followed by rinsing with distilled water and then air drying. Tencel fabrics were fibrillated with a rotary drum washer in a bath containing lubricant (2 g/L) at 80°C for 60 min with a liquor ratio of 30 : 1. Cellulase treatment was done in a 9M NaOH/14M CH<sub>3</sub>COOH solution of pH 5.0 at 60°C for 15–120 min in a rotary drum washer. To terminate the enzymatic reaction, the fabrics were treated with hot water (80°C) for 10 min and then rinsed twice with warm water (40°C) for 10 min.

Weight loss was determined on a dry weight basis. Tensile strength was measured in the warp direction by ASTM D-1682-64 on a Tensile Tester (AGS-500D, Shimadzu, Inc.). A scanning electron

microscope (SEM: JSM 5400, JEOL Inc.) was used to observe morphological change.

X-ray diffraction spectra were collected with an X-ray diffractometer (XRD-1200, Rikaku, Inc.) using Ni-filtered Cu-K $\alpha$  (1.5418 Å) radiation at 40 kV and 20 mA. Crystallinity was calculated according to

$$\text{Degree of crystallinity (\%)} = \frac{I_c}{I_c + I_a} \times 100$$

where  $I_c$  and  $I_a$  represent diffraction intensity against crystalline and amorphous regions, respectively. Separation between crystalline and amorphous scattering was done assuming that X-ray scattering of each image has the Gaussian distribution to scattering angle ( $2\theta$ ). Air scattering and background radiation were removed for each sample.

Moisture regain was measured according to ASTM D-629-59T. Specimens were dried in a vacuum oven at 50°C for more than 24 h, transferred to a desiccator containing dehydrating agent for allowing to cool to room temperature and weighed ( $W_2$ ). The same specimens were conditioned at  $20 \pm 1^\circ\text{C}$ , 60% relative humidity for more than 24 h and weighed ( $W_1$ ). Moisture regain was obtained from

$$\text{Moisture regain (\%)} = \frac{W_1 - W_2}{W_2} \times 100$$

Fabric samples were dyed in a bath containing 1% owf dyestuff (C. I. Reactive Red 183) and 2% owb sodium sulphate at room temperature for 30 min. Subsequently, 10% owb sodium carbonate was added in the dye bath for fixation and held for 50 min. After washing and drying, dye uptake of the dyed samples was assessed by measuring the K/S value at  $\lambda_{\text{max}}$  (502 nm) on a Macbeth Colorimeter.

DP was determined by the standard method: ASTM D-1795-94. 0.1 g of sample was dissolved in 100 mL of 0.5M cupriethylenediamine hydroxide solution and viscosity was measured with a Ubbelohde viscometer at  $25 \pm 0.01^\circ\text{C}$ . From intrinsic viscosity  $[\eta]$ , DP was calculated by the Mark-Houwink equation:

$$[\eta] = 0.98 \times 10^{-2} DP^{0.9}$$

Copper number was measured by titration with ammonium ceric sulfate using ferroin indicator to investigate cellulose chain damage.<sup>16</sup>

**Table I Weight Loss and Tensile Strength Retention of the Fabrics Treated with Cellulase**

Treatment		Weight Loss (%)		Tensile Strength Retention (%)	
Conc. (g/L)	Time (min)	NaOH Nontreated	NaOH Pretreated	NaOH Nontreated	NaOH Pretreated
3	15	0.98	1.29	88	88
	30	1.44	1.76	80	85
	60	2.23	2.52	78	81
	90	2.83	3.14	70	76
	120	3.37	3.62	67	72
8	15	1.27	1.58	80	86
	30	1.83	1.98	73	83
	60	2.86	2.94	67	77
	90	3.67	3.72	61	71
	120	4.83	4.90	55	68
Control				100 (86.2 Kgf)	

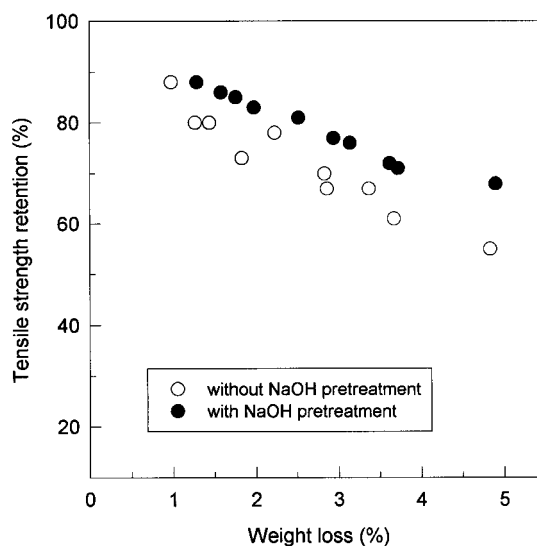
## RESULTS AND DISCUSSION

### Effect of Hydrolysis on Weight Loss and Tensile Strength

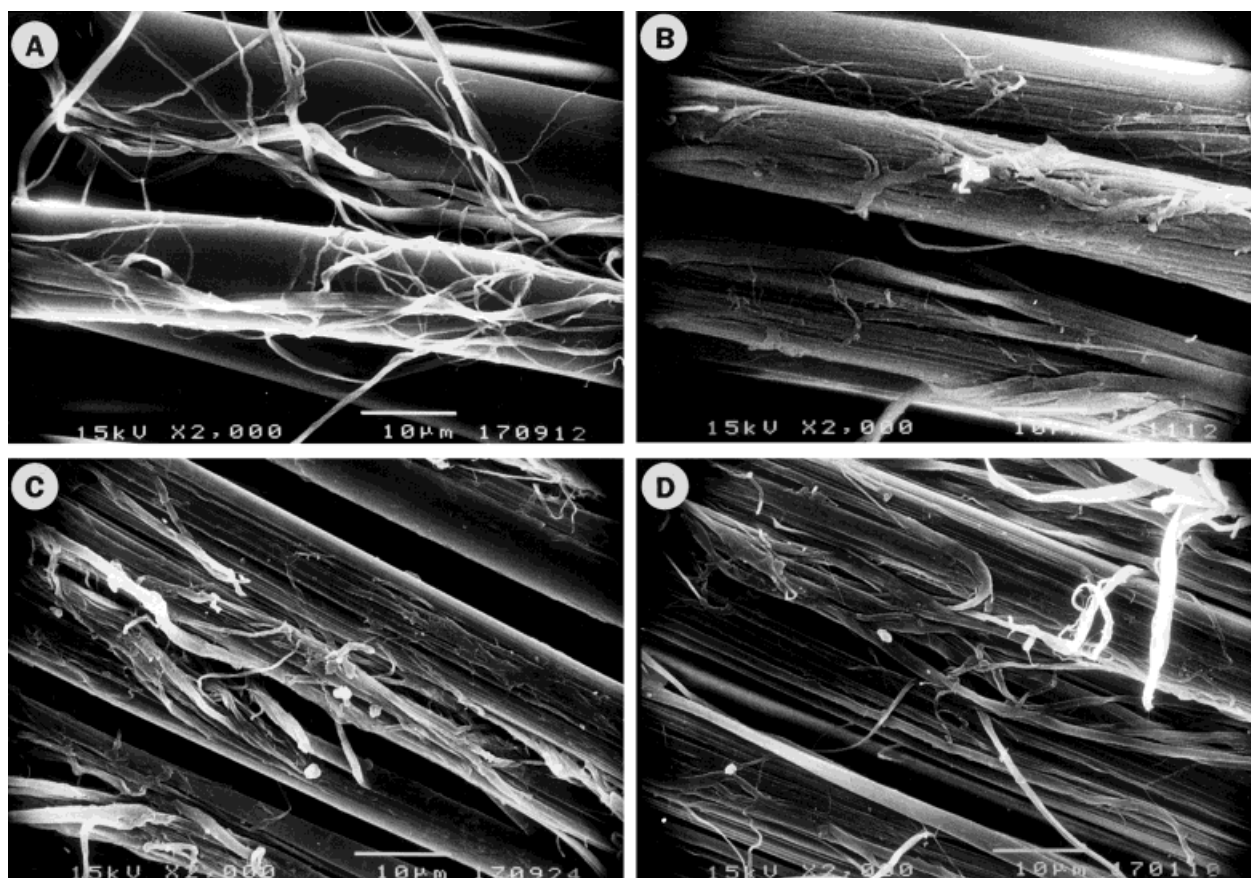
Changes in weight loss and tensile strength retention of the treated fabrics depending on treatment conditions are summarized in Table I. NaOH-treated and -nontreated fabrics were subjected to mechanical fibrillation before cellulase treatment. Irrespective of NaOH pretreatment, weight loss increases as cellulase concentration and treatment time increases. Weight loss is attributed to the removal of surface fibrils produced during mechanical fibrillation and cellulose chain scission followed by extraction of short molecular chains from amorphous region. This chain scission leads to strength reduction.

The NaOH-pretreated samples show slightly higher weight loss than nontreated counterparts at the same cellulase treatment conditions. Swelling treatments such as mercerization have an accelerating effect on enzymatic degradation because they make the cellulosic structure more accessible to the enzyme molecules.<sup>17</sup> Difference in weight loss between NaOH-pretreated and -nontreated samples is less pronounced with increase of cellulase concentration and treatment time. Namely, an accelerating effect of NaOH pretreatment on enzymatic degradation is diminished with the increase of cellulase concentration and treatment time. At the same cellulase treatment conditions, tensile strength retentions of the NaOH-pretreated samples are better than those

of the NaOH-nontreated counterparts in spite of higher weight loss of NaOH-pretreated samples. As shown in Figure 1, improvement of tensile strength with NaOH-pretreated samples is more pronounced at higher weight loss. It is considered that improved tensile strength of the NaOH-pretreated samples is attributed to uniform enzymatic reaction. Mercerized cotton also showed higher weight loss and tensile strength than nonmercerized cotton at the same treatment conditions due to more uniform and easier penetration of enzyme.<sup>18,19</sup>



**Figure 1** Relationship between weight loss and tensile strength retention.



**Figure 2** Longitudinal SEMs ( $\times 2000$ ) of the fabrics treated with cellulase. (A) Untreated after fibrillation (60 min); (B) 3 g/L, 60 min; (C) 3 g/L, 120 min; (D) NaOH-pretreated, 3 g/L, 120 min.

### Morphological Changes

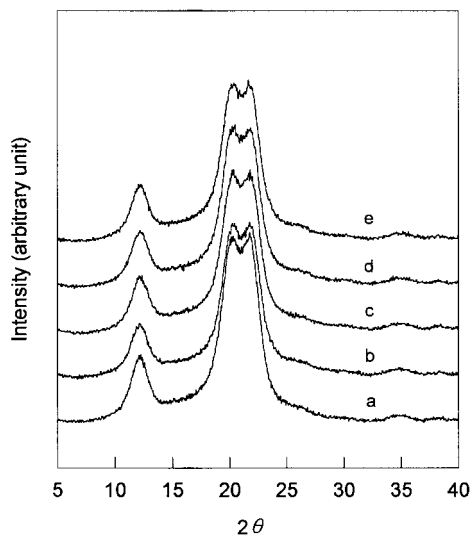
Figure 2 shows SEM pictures of the samples fibrillated and treated with cellulase. The untreated sample, which is not shown here, had a smooth and rod-shaped surface. Long fibrils are observed in the sample fibrillated mechanically (A). Those long fibrils are removed by further treatment with cellulase and microfibrils exist on the fiber surface (B). More extensive peeling and deeper inter-fibrillar splitting are observed in the sample (C) treated with longer time. These kinds of fiber damage create accessible areas to moisture and dye molecules and increase strength reduction discussed earlier. Also, the morphological changes are reflected changes in moisture regain and dye adsorption discussed later. We observed more uniform peeling with the NaOH-pretreated samples, which showed better strength retention.

### Changes in Crystalline Structure and Crystallinity

Figure 3 shows the X-ray diffractograms of scoured (a) and cellulase-treated (b–e) samples without NaOH pretreatment. The scoured sample (a) has three peaks. They are located near  $2\theta$  angles of 12.1, 20.2, and 21.8, and are characteristics of the 101,  $10\bar{1}$ , and 002 reflections of cellulose II, respectively.<sup>20</sup> Therefore, it is considered that Tencel has cellulose II crystalline structure. No significant difference in X-ray diffractograms is observed between untreated (a) and cellulase-treated samples (b–e). We confirmed that cellulase treatment does not affect the crystalline structure of Tencel. It is known that cellulase treatment does not affect crystalline structure of other cellulosic fibers such as cotton, polynosic rayon, and linen.<sup>19,21</sup>

Figure 4 shows X-ray diffractograms of the NaOH-pretreated (a) and NaOH/cellulase-treated samples (b–e). Peak intensity of  $10\bar{1}$  and 002





**Figure 3** X-ray diffractograms of the fabrics treated with cellulase: (a) untreated; (b) 3 g/L, 15 min; (c) 3 g/L, 60 min; (d) 3 g/L, 120 min; (e) 8 g/L, 120 min.

planes increases greatly compared to the NaOH-nontreated counterparts in Figure 3. This indicates that NaOH pretreatment caused to change lateral order slightly. X-ray diffractograms of NaOH-pretreated samples do not indicate any significant change in the overall form of the curves and characteristic three-peak location after cellulase treatment. This means that the cellulose II crystalline structure of Tencel does not change by NaOH pretreatment and following cellulase treatment.

The degree of crystallinity of the treated samples is summarized in Table II. Irrespective of NaOH pretreatment, crystallinity remains unchanged in the range of weight loss obtained in this study. Dohi et al.<sup>22</sup> reported that cotton showed an increase in crystallinity by 4.6% at weight loss of 13.6%, whereas crystallinity of Tencel increased by 3.0% at weight loss of 55.2%. It appears that crystallinity does not change significantly at low weight loss. This may be because an endwise attack has occurred by cellulase at an accessible cellulose chain on the crystallite surface and this particular chain completely disintegrates before deterioration of the next chain molecule.<sup>23</sup>

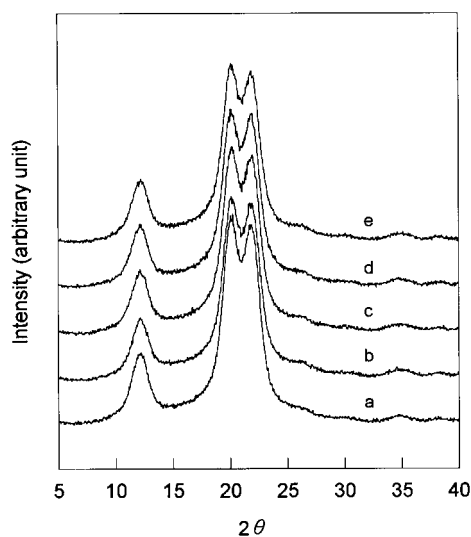
Irrespective of cellulase treatment conditions, the NaOH-pretreated samples showed higher crystallinity by about 3.5% compared to nontreated ones. Short chain molecules in amorphous region are extracted out during NaOH pretreatment, reducing amorphous region and relative

increase in crystallinity. This interpretation is supported by change in DP, which we will discuss later. Lenz et al.<sup>24</sup> also reported that dilute NaOH treatment does not reduce the crystallite orientation factor but reduces the amorphous orientation factor, leading to relative increase in crystallinity.

### Changes in Accessibility

Moisture regain and dye adsorption (K/S value) data give an estimate of accessibility in dry and wet states, respectively. Changes in moisture and dye sorption reflect changes in crystallinity, pore structure, and accessible internal surface area. Figure 5 shows the change in moisture regain depending on weight loss of the cellulase treated samples. Moisture regain of both NaOH-pretreated and -nontreated samples increases slightly with increase in weight loss. Buschle-Diller et al.<sup>23</sup> found that no significant change in the moisture sorption properties after enzyme treatment was attributed to no increase of accessible amorphous regions. Since crystalline structure and crystallinity of the samples treated with cellulase were not much changed, we speculated from SEM pictures shown in Figure 2 that the increase of moisture regain is caused by the increase of specific surface area due to fibrils and interfibrillar splitting.

The NaOH-pretreated samples both before and after cellulase treatment show slightly higher moisture regain than nontreated counterparts. Considering relative reduction of amorphous re-



**Figure 4** X-ray diffractograms of the fabrics treated with NaOH/cellulase: (a) untreated; (b) 3 g/L, 15 min; (c) 3 g/L, 60 min; (d) 3 g/L, 120 min; (e) 8 g/L, 120 min.

**Table II Degree of Crystallinity of the Fabrics Treated with Cellulase**

Treatment		Weight Loss (%)		Degree of Crystallinity (%)	
Conc. (g/L)	Time (min)	NaOH Nontreated	NaOH Pretreated	NaOH Nontreated	NaOH Pretreated
3	15	0.98	1.29	—	76.613
	60	2.23	2.52	73.164	76.606
	120	3.37	3.62	73.209	77.532
8	120	4.83	4.90	73.014	77.578
Control				74.085	77.584

gion by NaOH pretreatment, moisture regain of the NaOH-pretreated samples is expected to decrease but it is higher than that of the NaOH-nontreated samples. This is because the fiber structure changed into a relatively more open-up structure due to NaOH pretreatment and became more accessible to moisture as same as in cotton. NaOH treatment, whether slack or tensioned, increases accessibility of cotton to deuterium exchange because structural relaxation in amorphous region becomes larger with the transition to cellulose II structure.<sup>25</sup>

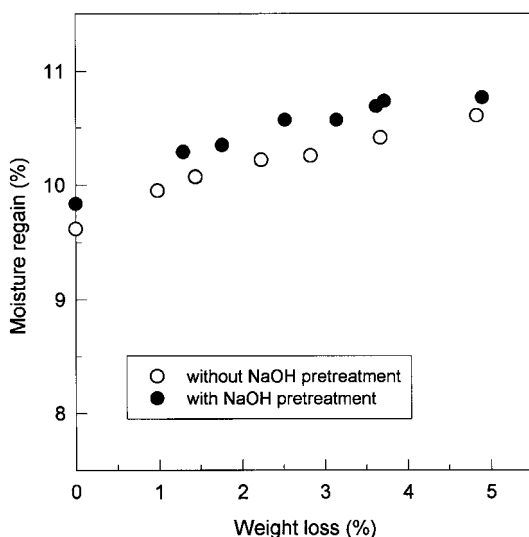
Figure 6 shows the effect of weight loss on dye adsorption (K/S value) of the cellulase-treated samples. Whether NaOH pretreated or nontreated, the K/S value increases slightly as weight loss increases. Dohi et al.<sup>22</sup> dyed cotton and Tencel after cellulase treatment, and found that the

K/S value of cotton decreased with increase of weight loss, whereas the K/S value of Tencel increased. Within the limits of weight loss obtained in this study, a slight increase of the K/S value with progress of enzymatic hydrolysis is also attributed to an increase of specific surface area due to fibrils. This interpretation is supported by the SEM observations discussed earlier (Figure 2).

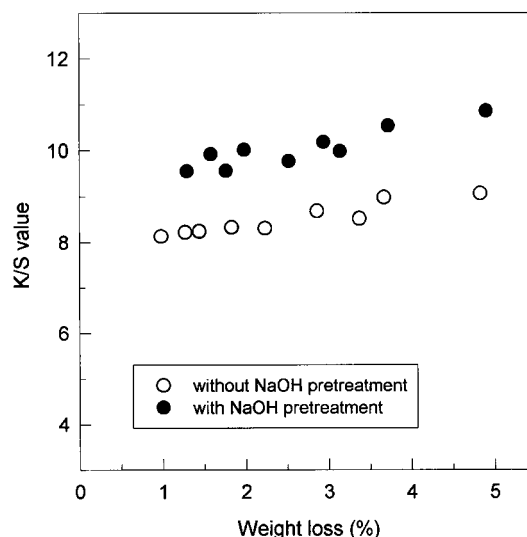
The NaOH-pretreated samples show relatively higher K/S values at comparable weight losses than the NaOH-nontreated ones. This is also because the amorphous region became an open-up structure by NaOH pretreatment.

#### Effect of Hydrolysis on Degree of Polymerization and Copper Number

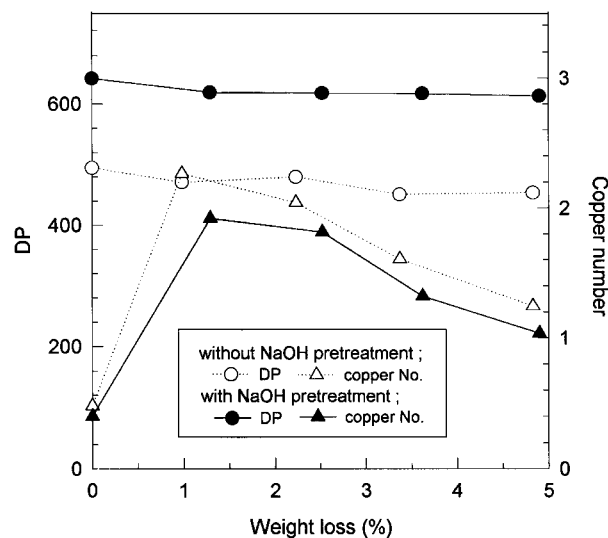
DP and copper number of the treated samples are shown in Figure 7. DP decreases initially and



**Figure 5** Effect of weight loss on moisture regain of the fabrics treated with cellulase.



**Figure 6** Effect of weight loss on K/S value of the fabrics treated with cellulase.



**Figure 7** Relationship between weight loss and DP and copper number.

then levels off, whereas copper number increases to a great extent at the initial stage of degradation and then decreases gradually. At the initial stage of enzymatic hydrolysis, relatively short cellulose chains are formed and at the same time, number of reductive end groups increases. Enzyme attacks cellulose chains randomly at the initial stage, resulting in a decrease in DP and an increase in copper number. As enzymatic hydrolysis progresses, copper number decreases with no change in DP. This supports the view that an accessible cellulose chain completely disintegrates and then the degradation continues with the next chain molecule.<sup>23</sup>

The NaOH-pretreated samples show higher DP and lower copper number than nontreated ones at the same cellulase treatment conditions. This agrees with a relative increase in crystallinity due to NaOH pretreatment discussed earlier. Since short molecular chains are extracted out during NaOH pretreatment, DP and crystallinity increase, whereas number of reductive end groups decreases and thus copper number decreases. This also supports the view that the NaOH-pretreated samples show better tensile strength retention than nontreated ones at a comparable weight loss.

## CONCLUSIONS

The NaOH-, fibrillation-, and cellulase-treated Tencel fabrics were evaluated for weight loss and

tensile strength. SEM analysis was carried out to study morphological change of the treated fabric. The X-ray diffraction method, moisture regain, and K/S value were used to elucidate crystalline structural changes that occurred by cellulase treatment. DP and copper number of the cellulase-treated samples were also measured to estimate effect of hydrolysis.

Weight loss increased and tensile strength retention decreased with increase in concentration and time of cellulase treatment. At a similar weight loss, tensile strength retentions of the NaOH-pretreated samples were better than those of nontreated ones due to more uniform hydrolysis.

SEM analysis indicated that with progress of enzymatic hydrolysis, fibrils were produced and damage occurred deep into the fiber. X-ray diffraction studies showed that crystalline structure and degree of crystallinity were not much changed by cellulase treatment. On the other hand, as enzymatic hydrolysis progressed, moisture regain and K/S value increased slightly due to increase of specific surface area by fibrils. DP initially decreased with enzymatic hydrolysis and then leveled off. Copper number increased, however, to a great extent at an initial stage of enzymatic hydrolysis and decreased gradually.

The NaOH-pretreated fabrics showed higher degree of crystallinity, DP, moisture regain, and K/S value, but lower copper number than the NaOH-nontreated ones at the same cellulase treatment conditions. These results were attributed to extraction of short molecular chains from amorphous region during NaOH pretreatment and change of amorphous region into the open-up structure.

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