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# Effect of NaOH Treatment on the Interfibrillar Swelling and Dyeing Properties of Lyocell (TENCEL®) Fibres

## Abstract

The effect of interfibrillar swelling on swelling degree, carboxyl content, split number, weight loss and dyeing properties by using NaOH solution up to 2.5 M concentration of lyocell fibres was investigated. The Split number and weight loss show the behaviour of fibres during alkali treatment, whereas the water retention value (WRV), carboxyl content and dyeing give information about the properties of samples after alkali treatment. By increasing alkali concentration, the swelling degree, weight loss, split number, total colour difference and K/S values of fibres increased when compared to untreated samples; on the other hand carboxyl content decreased.

**Key words:** alkali, cellulose, dyeing, fibre, lyocell, swelling.

## Introduction

Lyocell is regenerated from cellulose by using the wet spinning process, where N-methylmorpholine-N-oxide monohydrate solution is used as a dissolving agent [1].

During textile processing alkali treatments were applied to cellulosic materials in order to improve dye uptake, drape, luster, appearance and dimensional stability.

Carboxyl groups are mainly responsible for strength losses in the presence of alkali, leading to decreased performance parameters [2 - 3]. It is important to determine the content of oxidised groups of cellulose for process and quality control during pulping, fibre production and textile finishing [4].

Alkali treatments change the structure, morphology, accessibility and reactivity in cellulosic fibres depending on factors such as alkali concentration, treatment temperature, the physical state of the material and its degree of polymerisation [5 - 9].

In the literature, selected concentrations of NaOH solution were used to treat lyocell textile materials. But the swelling and dyeing tendency of lyocell textile materials in a range of NaOH treatment was not investigated. It is important to make a distinction between the swelling of fibres during and after alkali treatment to define the end concentration of only

interfibrillar swelling and to find relations between fibre properties in this range.

In our study, the weight loss and split number of lyocell fibres during NaOH treatment as well as the dyeing properties, swelling degree and carboxyl content after NaOH treatment were investigated in the range of only interfibrillar swelling by increasing the solution concentration up to 2.5 M.

## Experimental

### Materials

Lyocell (TENCEL®) staple fibre without spin finishing was kindly supplied by Lenzing AG-Austria. The titer and length of the fibres were 1.3 dtex and 38 mm, respectively. Analytical grade sodium hydroxide (NaOH, > 99%) was purchased from Fluka (Buchs, CH), sodium chloride (NaCl, ≥ 99.5%) from Merck and C.I. Direct red 81 (dye content ca. 50 %) from Sigma-Aldrich.

### Methods

#### Alkali treatment

Fibre samples were immersed in an aqueous alkaline solution with a liquor ratio of 1:33 at a certain concentration for 2 h at room temperature. The fibre was washed with running tap water and then neutralised with an acetate buffer containing 0.01 mol/l of acetic acid and 0.01 mol/l of sodium acetate (pH 5.0). The fibre sample was sufficiently washed with distilled water until the pH value of the solution indicated 7.0 and conductivity was less than 3 mS/m. Then the fibres were dried in an oven at 60 °C for 1 h.

The alkali treatment used by Zhang et al. 2005 was modified so that instead of us-

ing hot water to wash the samples, cold tap water was used [10].

#### Water Retention Value (WRV)

The swelling degree of fibres in the water was determined by a centrifugal method according to the literature [11 - 12]. The measurement was performed four times for each sample to obtain a mean value.

#### Determination of carboxyl content by methylene blue sorption

A weighed cellulose sample of known water content was suspended in an aqueous methylene blue chloride solution (300 mg/l) and borate buffer of pH = 8.5 for 20 h. The visible absorbances of the dye liquor for each sample were measured by a Hitachi U-2000 Spectrophotometer at a wavelength of 664.5 nm. The molar quantity of dye taken up by the fibre was assumed to correspond to the fibre carboxyl content, expressed in mmol/kg [13]. The measurement was performed three times for each sample to obtain a mean value.

#### Moisture content (MC) in percent [14]

In order to determine the weight loss of fibres during alkali treatment, the moisture content of the fibres was first calculated. The moisture content of the fibres was calculated according to equation (1). Firstly, the fibres were conditioned at 20 °C at 65% relative humidity for 24 h and weighed ( $w_1$ ). Then they were dried at 105 °C for 4 h. The fibres were weighed again ( $w_2$ ) after cooling down in a desiccator with P<sub>2</sub>O<sub>5</sub>.

$$MC = \text{Moisture content of fibres, \%} = \frac{(w_1 - w_2)}{w_2} \quad (1)$$

The measurement was performed three times for each sample to obtain a mean value.

### Weight loss in percent

The weight loss of the fibres during alkali treatment was determined. The fibres were conditioned at 65% relative humidity and 20 °C for 24 h. 0.25 g of the fibres in the conditioned state ( $w_m$ ) was swollen in 20 ml of alkali solution for 2 h. The fibres were washed with running tap water and neutralised with an acetate buffer containing 0.01 mol/l of acetic acid and 0.01 mol/l of sodium acetate (pH 5.0). The fibres were washed firstly with running tap water and then distilled water until the pH value of the solution indicated 7.0 and conductivity of the fibres was less than 3 mS/m. Then the fibres were dried in an oven at 105 °C for 4 h. The weight of the dried fibres was measured ( $w_3$ ). The weight of the dried fibres ( $w_d$ ) was calculated according to equation (2).

$$w_d = w_m - (w_m \times MC) \quad (2)$$

The weight loss of the fibres was calculated according to equation (3).

$$\text{Weight loss} = (w_d - w_3) / w_d \quad (3)$$

The measurement was performed three times for each sample to obtain a mean value.

### Dyeing procedures

The untreated and NaOH treated lyocell fibres were dyed with a mixture of 2 g/l Direct Red dye 81 and 0.5 g/l NaCl dyeing solution with a liquor ratio of 1:40, using a Werner Mathis AG LABOMAT dyeing machine at a continuous and alternate agitation of 30 r.p.m. The samples were dyed by the exhaust method.

The dyeing profile is shown in Figure 1. The temperature was increased from room temperature to 100 °C with a gradient of 5 °C/min. The temperature was held constant at 100 °C for 30 min and cooled down to 60 °C with a gradient of 3.5 °C/min. The dyed samples were rinsed with running tap water until no colour release from the fibres to water is observed. Then the fibres were air-dried. The measurement was performed three times for each sample to obtain a mean value.

### CIELAB

Shade, colour depth and colour difference between NaOH treated and untreated lyocell fibres were determined from their CIELAB colour coordinates, measured with a tristimulus colorimeter (Minolta Chroma-Meter CR-200, 0 °C viewing angle, sample diameter 8 mm) with D65 illuminant. When a color is expressed in CIELAB,  $L^*$  defines lightness,  $a^*$  denotes the red/green value and  $b^*$  the yellow/blue value. The difference in lightness was calculated by  $\Delta L^* = (L_2^* - L_1^*)$ , where  $L_2^*$  is the lightness of the sample (dyed fibres) and  $L_1^*$  is the lightness of standard untreated and undyed lyocell fibre.

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (4)$$

### Colour strength

Relative colour strengths ( $K/S$  values) were calculated by the Kubelka-Munk function [15 - 16] by subtracting the  $K/S$  values of the dyed samples from the undyed & untreated sample:

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

$$\left(\frac{K}{S}\right)_{corr} = \left(\frac{K}{S}\right)_D - \left(\frac{K}{S}\right)_{U'} \quad (6)$$

where  $K$ =absorption coefficient,  $S$ =scattering coefficient,  $R$  = fraction of light

reflected at a wavelength of maximum absorbance,  $(K/S)_D = K/S$  values of dyed sample,  $(K/S)_U = K/S$  values of the undyed sample and  $(K/S)_{corr} = K/S$  values corrected for reflectance from the undyed & untreated sample.

The reflectance values of the dyed samples were obtained at a wavelength of 530 nm by using Specord® 50, Analytik Jena AG spectrophotometer with integrating sphere.

## Results and discussion

Weight loss and split number correspond to the behaviour of lyocell fibres during alkali treatment. However, WRV (swelling degree), carboxyl content and dyeing results correspond to the behaviour of lyocell fibres after alkali treatment.

The WRV, carboxyl content, weight loss and split number of the fibres after NaOH treatment are shown in Figure 2. As the carboxyl content of the fibres decreased by increasing the NaOH concentration up to 2.5 M, the weight loss, split number and swelling degree of the fibres increased. It can be concluded that the weight loss of the fibres were mainly due to loss of the carboxyl group containing fibre molecules fibre. By increasing NaOH concentration up to 2.5 M, alkali penetrates more deeply inside the fibre because of interfibrillar swelling, resulting in a higher split number due to a less homogeneous distribution of alkali inside the fibre [17 - 18]. Increase in weight loss by increasing NaOH concentration is consistent with an increasing split number since a higher split number means more separation between macrofibrils and a decrease in the connection

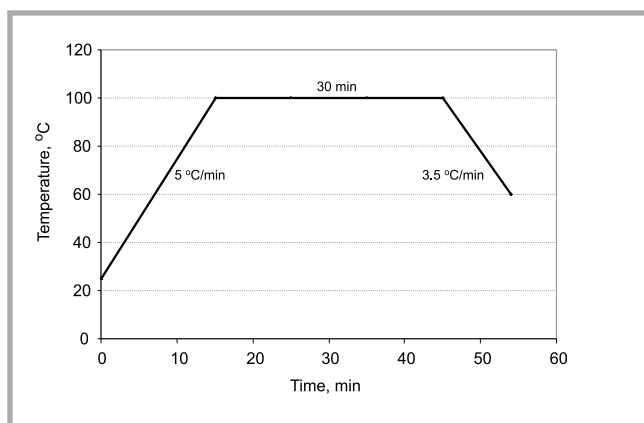


Figure 1. Dyeing temperature profile.

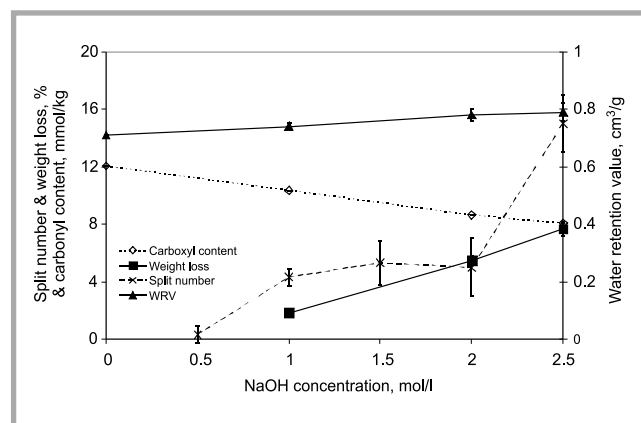
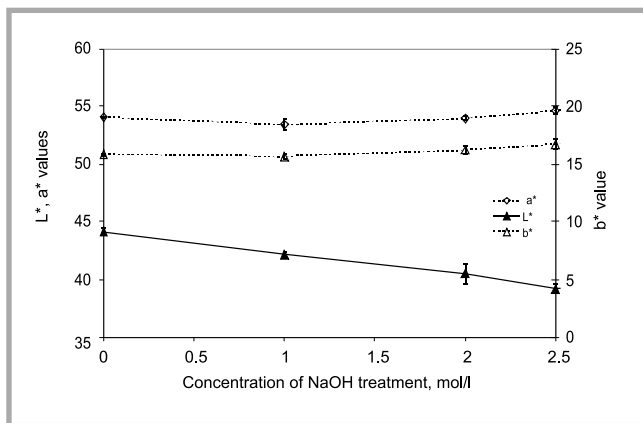
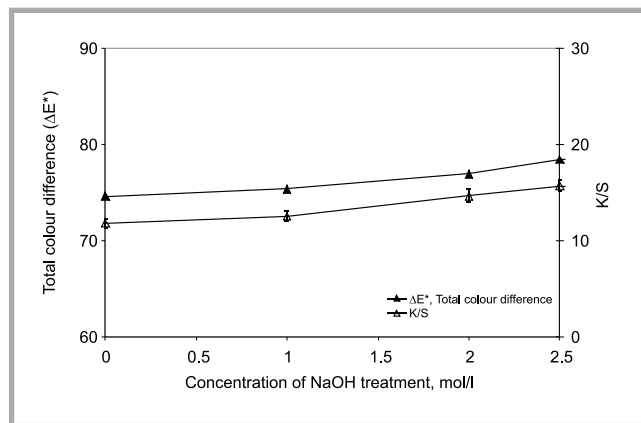


Figure 2. Weight loss (%), split number (x) of lyocell fibres during NaOH treatment and carboxyl content (mmol/kg) (o), water retention value (cm<sup>3</sup>/g) (▲) of lyocell fibres after NaOH treatment.



**Figure 3.** Change of CIELAB coordinates;  $L^*$ : lightness (100=white, 0=black) ( $\blacktriangle$ ),  $a^*$ : red/green coordinate (positive=red, negative=green) ( $\diamond$ ),  $b^*$ : yellow/blue coordinate (positive=yellow, negative=green) ( $\Delta$ ).



**Figure 4.** Color strength measured by  $K/S$  ( $\Delta$ ), Total colour difference ( $\Delta E^*$ ) ( $\blacktriangle$ ) obtained from CIELAB.

of these macrofibrils owing to the loss of carboxyl content.

At/in a 2.5 M NaOH solution the lyocell fibres were split into their highest split number. 2.5 M was also the highest concentration in terms of the highest alkali retention value and fibre diameter value; in other words for the swelling of the fibre during alkali treatment. By increasing the concentration up to 2.5 M, the stress developed in the fibre increased due to interfibrillar swelling. It was proposed that the split number gives us an idea of the distribution of alkali inside fibre, which results in stress and local weakness, and therefore under pressure a fibre can be split into its fibrils [19].

Figure 3 shows the lightness ( $L^*$ ), red/green value ( $a^*$ ) and yellow/blue value ( $b^*$ ) of the untreated-dyed and NaOH treated-dyed lyocell samples. Lightness was decreased by increasing NaOH concentration, which means darker colours were obtained for the NaOH treated samples. The yellow/blue value ( $b^*$ ) and red/green value ( $a^*$ ) of the samples changed slightly compared to the untreated sample, therefore the NaOH treated samples had slightly more blue and red colour compared to the untreated dyed sample.

The relative colour strength of the dyed fibres, expressed as  $K/S$ , measured by the light reflectance technique and total colour difference ( $\Delta E^*$ ), measured by CIELAB, are shown in Figure 4 in relation to NaOH concentration.  $\Delta E^*$  and  $K/S$  values showed direct relation. As the NaOH concentration increased, the total colour difference between the untreated and NaOH treated samples and colour strength of the fibres increased.

Similar results of an increase in colour strength by increasing NaOH concentration was found for NaOH-urea mixture treated lyocell woven fabrics dyed with a mixture of C.I. Direct Red 81 and C.I. Direct Green 26 [20]. UVITEX BHT optical brightener was used to measure dye penetration depth into lyocell, viscose and modal fibres. Dye accessibility of the fibres increased after 2.63 M NaOH treatment of lyocell fabric so that deeper intrusion of dye could be shown visually and numerically determined. As a result, alkali treatment enhanced accessibility to the fibre internal zones of the lyocell fibre [21]. As the NaOH concentration increased, the WRV of the lyocell woven fabrics and pilling formation resistance for the lyocell knitted fabrics also increased [22 - 23].

## Conclusions

NaOH treatments increased the WRV of lyocell fibres. Darker red colours for lyocell fibres were obtained by CIELAB and  $K/S$  measurements by increasing the concentration of NaOH treatment. The Weight loss of the fibres increased in relation to the decrease in carboxyl group containing fibre molecules. fibre.

The results presented here are supposed to represent the behaviour of lyocell fibres after NaOH treatment, but not other textile structures. Other textile structures like yarn, fabric and fabric type would also be an important criterion to consider, which would have different results than fibres. It is important to expand the scope of this study by using

- higher alkali concentrations to see the effect of intrafibrillar swelling,

- different alkali types and
- different types of regenerated cellulosic fibres. These studies are underway and will be reported at a later time.

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