

## SPLITTING TENDENCY OF CELLULOSIC FIBRES

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In alkali solutions, the splitting of lyocell and viscose fibers into their microfibrils was studied in this work. Ball bearing method, ultrasonic treatment and shear method were tried to analyse splitting of fibers. Viscose fiber show less splitting tendency than lyocell fiber. Various alkali types like LiOH, NaOH, KOH (0.5 M - 12 M) and TMAH, TbuOH (0.25 M – 2.8 M) and their mixtures with urea (0.26 M –

4.26 M) were used as swelling agents. The dependency of swelling time and temperature on splitting was also investigated. It was found that split number of a lyocell fiber ranges up to 44.

Keywords: alkali, fiber, fibrillation, lyocell, swelling, viscose

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### Introduction

Cellulose is a raw material with a wide variety of end uses in the chemical industry for producing man-made textile fibers. Commercial methods of manufacturing man-made cellulosic fibres include viscose, lyocell, cuprammonium and several alternative processes. Viscose production is based on deriving cellulose with carbon bisulphide [Cook 1984]. Lyocell process includes considerably less production steps and that the tedious production of viscose spinning mass is avoided. Lyocell is the most environment friendly process for producing cellulosic fibres [Kampl et al 1995]. The continuous recycling of the solvent in lyocell process means that the chemical operating costs of the direct dissolution process are low, and the lack of an alkali-ripening step means that the molecular weight of the cellulose forming the final fibre is higher than achieved in carbon disulphide viscose process [Moncreiff RW. 1970]. Different production processes and therefore different production conditions for conventional viscose, modal, and new lyocell fibers cause differences in the structure of the fibers despite the same chemical composition [Fink et al. 1998]. Lyocell differs from other

cellulose regenerated fibres by its high crystallinity, high longitudinal orientation of crystallites, high amorphous orientation, low lateral cohesion between fibrils, low extent of clustering, relatively large void (pore) volume [Schurz 1994, Schurz *et al.* 1994, Crawshaw et al 2000 a, b].

Fibrillation of cellulosic fibres seems to be related to the fibrillar structure of the fibre and the degree of crystallinity. Fibres with a lower degree of fibrillar structure (standard viscose, HWM fibre), and fibres with a helical arrangement of the fibrils (cotton) show a less pronounced tendency to fibrillate than fibres where both a marked fibrillar structure can be observed and the fibrils are arranged longitudinally along the fibre axis (polynosic, lyocell) [Nemec 1994]. The fibrillation tendency is directly related to the degree of swelling of lyocell fiber regardless of the alkali type [Zhang et al., part 1]. Fibrillation was inhibited by decrease in fiber swelling [Zhang et al., part 1], decrease in temperature [Zhang et al., part 2], alkali pre-treatment in sodium or potassium hydroxide of 5mol/l due to the fiber reorganization [Zhang et al. 2005] and crosslinking treatments at lower degree of

swelling [Zhang et al. part 5, Okubayashi accepted].

In this study, splitting tendency of lyocell fiber into its macrofibrils has been investigated. Different method trials like ball bearing method, ultrasonic and shear test were applied to induce splitting of lyocell fiber. Different concentrations of alkali metal hydroxides and their mixtures with urea were used. The mixture of DMDHEU and  $MgCl_2$  is generally used for crosslinking of cellulosic fibres. However in this study DMDHEU and its mixtures with LiCl or  $MgCl_2$  were tested on their ability to split lyocell fiber into its macrofibrils.

## Experimental

### Materials

Lyocell and viscose staple fibers without spin finishing were kindly supplied by Lenzing AG (in Austria) and were used for the experiments. The titer and the length of the fibers were 1.3 dtex and 38 mm, respectively. Analytical grade lithium hydroxide (LiOH, >99%), sodium hydroxide (NaOH, >98%), potassium hydroxide (KOH, >99%), tetramethyl ammonium hydroxide (TMAH, 25%, 2.8 M), tetrabutyl ammonium hydroxide (TbuOH, 40%, 1.5 M), lithium chloride (LiCl), technical grade urea (50g/l, 100 g/l) were purchased from Fluka, magnesium dichloride ( $MgCl_2$ ) used as catalyst was purchased from Merck, 1,3 dimethylol dihydroxyethylenurea (DMDHEU, 75%, Fixapret® CP) used as crosslinker for cellulose fibers was purchased from BASF.

### Methods

#### Ball Bearing Method

This method has been used to induce fibrillation of cellulosic fibres. A mass of fibers (0.5 g) was placed in a metal pot with 50 ml solution and 20 metal ball-bearings (of 0.5 cm diameter and 1 g weight) [Taylor 1991]. The pot was capped and tumbled end-over-end at 42 rpm and at fixed temperatures for 2 h. The fibers were then neutralized with a buffer

solution containing 0.01 mol/l acetic acid and 0.01 mol/l sodium acetate (pH 5.0), rinsed with hot water at 50°C and with cold water continuously. After the fibers were dried in an oven at 60°C for 1 h, fibril numbers in fibers were counted on 0.038 mm segments using an optical microscope. Ten fibers from each sample were used to obtain mean values [Zhang et al., part 1].

#### Inducement and assessment of splitting of cellulosic fibers – Shear Method

For splitting test, one fiber was placed on the microscope slide shown in Figure 1. Alkali solution was dropped on the fiber and fiber was swollen for 1 min. A cover glass was put on to the fiber. The cover glass was pressed onto fiber by putting a weight which had a circle shape at its down side. This weight was placed on the sample resulting in downward weight ranged between 7.4-9.8 N. The area of cover glass (20 mm×20 mm) was used to calculate the downward pressure.

The downward pressure on fiber would be

$$\text{between } \frac{(0.75\text{kg} \times 9.8\text{m/s}^2)}{4 \times 10^{-4}\text{m}^2} = 18.4\text{kPa} \text{ and } \frac{(1\text{kg} \times 9.8\text{m/s}^2)}{4 \times 10^{-4}\text{m}^2} = 2.5\text{kPa}.$$

Then the photos of the fibers were taken by Reichert optical microscope and the split numbers were counted. To evaluate the degree of of splitted fibers, numbers were used. The number 0 means no splitting was observed. 1 means the fiber is unique but some lines were observed on fiber which means splitting is about to start. 2 and higher numbers show how many splits were counted from the fibers. Three fibers were used and their mean value was taken for the average number of split number of a fiber swollen in each type of alkali.

#### Ultrasonic Treatment

Ultrasonic treatment was determined by sonifier named as Sonorex Digital 10 P, Bandelin. A mass of fibers (0.1 g) was immersed in alkali solutions in glass tubes. Glass tubes were placed in the sonifier and a

strong sonic wave ( $\times 10\%$ ) was radiated onto the fiber for varying duration of times and temperatures. Then, shear method was used to induce splitting so that effect of ultrasonification on splitting tendency of cellulosic fibres was investigated.

### Fibre Diameter

Swelling of a fiber in the aqueous medium was determined on the basis of fibre diameter measurements. The diameters of fibers were swollen for 1 min so that the fiber diameter stabilizes and then fibre diameters were measured by Reichert projection microscope. 20 fibers were counted and mean value was taken for each type of alkali swollen in each type of alkali.

Linear density of a fibre used in this study was 0.13 tex. This value means that 1000 m of a fibre weighs 0.13 g. Weight of one fiber is calculated as following:

$$W_{fiber} = (0.13g \times 38mm) / (1000 \times 10^3 mm) = 4.94 \times 10^{-6} g$$

If we assume a fibre's cross section as circular, Equation (1) can be used for calculating fibre diameter (d).

$$W_{fiber} = DL\rho(d/2)^2 \quad (1)$$

Here,  $W_{fiber}$  is the weight of one fiber,  $D$  is the density of lyocell,  $L$  is the length of the fibre and  $d$  is the fibre diameter. Since it is known that lyocell has 38 mm length, and  $1.52 \text{ g/cm}^3$  fibre density [Bourban et al 1997], diameter of dry fiber used in this study was calculated as 0.0104353 mm by using Equation (1).

### Alkali retention value (ARV)

The fiber samples, 0.5 g in weight, were put into alkali solutions for 2 h at room temperature. The fibers were then centrifuged at  $4000 \times g$  for 10 min and weighed ( $W_w$ ). The fibers were washed with hot water at  $50^\circ\text{C}$  and cold water, then they were neutralized with the 0.01 M acetate buffer (pH 5) solution, rinsed with hot and cold water again. The fibers were dried in an oven at  $105^\circ\text{C}$  for 4 h and the weight was measured ( $W_d$ ). Solvent

retention value in alkali solution (ARV) was calculated by Equation (2).

$$ARV = (W_w - W_d) / W_d \cdot D_{alk} \quad (2)$$

Here,  $D_{alk}$  is a density of the alkaline solution and it was assumed that  $D_{alk}$  is equal to the density of alkali inside the fiber. The measurement was repeated 4 times for each sample to obtain mean value [Zhang et al 2004, part 1].

### **Results and Discussion**

The fibrillation tendency is directly related to the degree of swelling of lyocell fiber regardless of the alkali type [Zhang et al., part 1]. The shear method applied to induce splitting permits the use of high alkali concentrations compared to the ball bearing method. Conditions of high swelling degree of lyocell and viscose fibers in various alkali solutions were selected from the literature [Zhang et al., part 1].

Figure 1 shows the relation between split number in ball bearing method and ARV of lyocell fiber against concentration of alkali. The highest split number of lyocell fiber was observed when it was swollen in TMAH solution. ARV and split number of lyocell fiber show the same trend for TMAH solution. Above 5 M concentration of alkali solutions, splitting of lyocell fiber wasn't observed. This indicates that splitting is no more directly related to swelling after 5 M concentration of alkali solutions.

Figure 2 and Figure 4 show the relation between fiber diameter and ARV of lyocell and viscose, respectively. Both of them show the swelling degree of fiber so that they show the same trend as it was expected.

Figure 3 shows the relation between split number and ARV of viscose fiber against concentration of alkali. It was found that viscose fiber doesn't have the splitting tendency in alkali solutions. It was also mentioned that viscose fibers didn't fibrillate under the experimental conditions used in Zhang et al., part 1 's work. This may be due to the different fibrillar structure of viscose fibers [Nemec 1994].

Figure 5 shows the split number of lyocell treated with 50 g/l urea and its mixtures

with different type of alkali solutions for 1 min and 1 hour at room temperature. Lyocell fiber showed higher splitting when urea-alkali mixtures were used than only using urea. It was shown that split number of lyocell fiber can change by its swelling time with no direct correlation. Time dependency of splitting could also have been observed due to the applied splitting method.

Table 1 shows the split number of lyocell fiber swollen in DMDHEU and LiCl mixture. 1 split of lyocell fiber was observed when 4 M LiCl was used whereas 27 split was observed when mixture of 4.26 M DMDHEU and 0.71 M LiCl was used.

Table 2 shows the split number of lyocell fiber swollen in DMDHEU and  $MgCl_2$  mixture. No split was observed when mixture of 4.26 M DMDHEU and 0.71 M  $MgCl_2$  was used. On the other hand, when LiCl was used instead of  $MgCl_2$ , 27 split was observed. 1 split was observed when only  $MgCl_2$  was used. It was observed that  $MgCl_2$  is more effective than LiCl on splitting of lyocell fiber.

Figure 6 shows the split number of lyocell fiber swollen with 1 M TMAH in ultrasonic and also without using ultrasonic, by only applying shear method. After using ultrasonic, fibers were splitted by applying shear method because it was found that only ultrasonic didn't split lyocell fiber into its fibrils. Temperatures of 40°C, 80°C and different times were used for swelling of fiber in ultrasonification to identify the temperature and time dependence on splitting tendency of lyocell fiber. It was found that, there wasn't a strong correlation between time and split number of lyocell fiber at room temperature without using ultrasonic. Split number slightly increased when temperature increased from 40°C to 80°C in ultrasonic for the same ultrasonic application time (30 min). Split number increased further by the increase of temperature when ultrasonic application time was 90 min. When 40°C or 80°C was used in ultrasonification, there was no significant dependence of time on splitting tendency of lyocell fiber.

Figure 7 shows the split number of urea-alkali mixtures when ultrasonic was used for different temperatures for 1 hour. When the temperature of ultrasonic was changed from

40°C to 80°C, split number increased for TMAH-urea mixture, remained constant for both urea solution and KOH-urea mixture and decreased for TbuOH-urea and NaOH-urea mixtures.

Figure 8 and 9 show the photos of lyocell fiber treated with 0.5 M TbuOH in ball bearing method by using balls and without using balls, respectively. Splitting of lyocell fiber couldn't have been achieved by using ball bearing method since this method applies the friction directly on the fiber so that fibrils are peeled from the surface of fiber which is called as fibrillation.

The maximum split number was observed as 44 when lyocell fiber was swollen at 80°C for 1 h in ultracentrifuge. If we assume that each splitted fibre has the same diameter,  $d_{fibre}$ ,  $\approx 0.010$  mm, the area of a fibre's cross section would be as Equation (3).

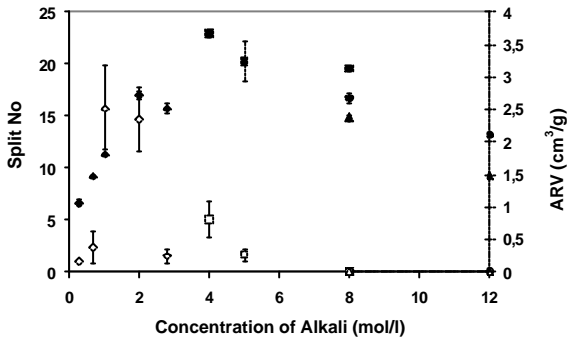
$$A_{fibre} = A_{fibril} \times \text{split number} \quad (3)$$

Fibers and splitted fibrils are assumed to have circle shapes so that equations (4) and (5) are used.

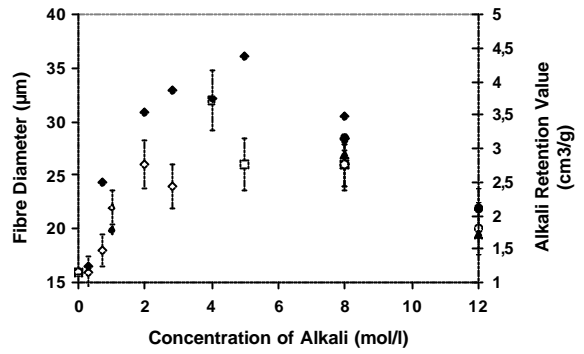
$$A_{fiber} = p(d_{fiber}/2)^2 \quad (4)$$

$$A_{fibril} \times \text{SplitNumber} = p(d_{fibril}/2)^2 \times 44 \quad (5)$$

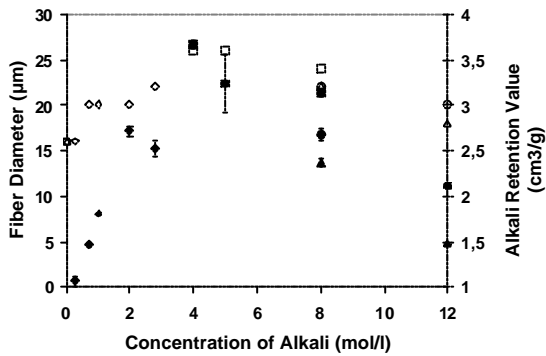
Here,  $d_{fibril}$  is the diameter of each splitted fibril and found as  $1.5 \times 10^{-3}$  mm by using equation (2). The diameters of a fiber, macrofibril, microfibril and an elemental fibril was suggested to be 10-30  $\mu\text{m}$ , 0.5-1  $\mu\text{m}$ , 100nm and 5-20 nm, respectively [Schuster et al 2003]. When the diameter of each splitted fibril,  $1.5 \times 10^{-3}$  mm, is compared with this literature, it can be assumed that this study show the achievement of lyocell fiber splitting into its macrofibrils.



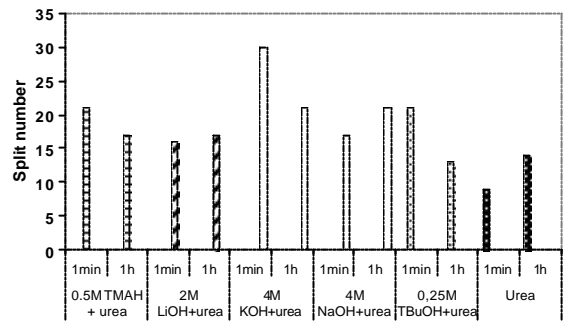
**Figure 1.** Plots of split number (TMAH ?, LiOH ?, KOH ?, NaOH ?) and ARV (TMAH ?, LiOH ?, KOH ?, NaOH ?) of lyocell fiber against concentration of alkali (mol/l)



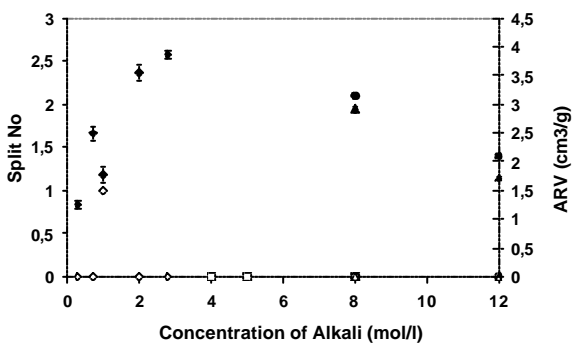
**Figure 4.** Plots of fibre diameter (µm) (TMAH ?, LiOH ?, KOH ?, NaOH ?) and ARV (cm<sup>3</sup>/g) (TMAH ?, LiOH ?, KOH ?, NaOH ?) of viscose against concentration of alkali (mol/l)



**Figure 2.** Plots of fiber diameter (µm) (TMAH ?, LiOH ?, KOH ?, NaOH ?) and ARV (cm<sup>3</sup>/g) (TMAH ?, LiOH ?, KOH ?, NaOH ?) of lyocell fiber against concentration of alkali (mol/l)



**Figure 5.** Split number of lyocell fiber treated with different urea-alkali mixtures for different times at room temperature (urea has concentration of 50 g/l)



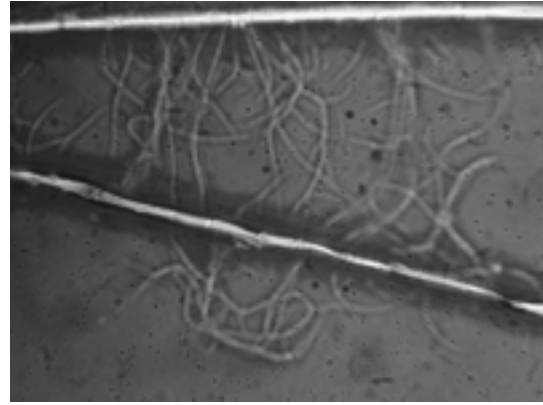
**Figure 3.** Plots of split number (TMAH ?, LiOH ?, KOH ?, NaOH ?) and ARV (cm<sup>3</sup>/g) (TMAH ?, LiOH ?, KOH ?, NaOH ?) of viscose against concentration of alkali (mol/l)

**Table 1.** Split number of lyocell fiber treated with DMDHEU and LiCl at room temperature

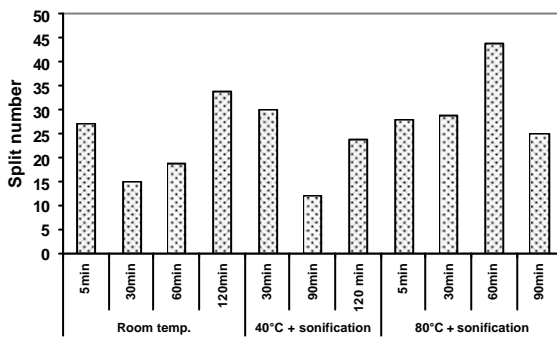
DMDHEU (conc.)	LiCl (conc.)	Split No
4.26 M	0 M	0
4.26 M	0.71 M	27
0 M	0.71 M	0
4.26 M	4 M	0
0 M	4 M	1

**Table 2.** Split number of lyocell fiber treated with DMDHEU and MgCl<sub>2</sub> at room temperature

DMDHEU (conc.)	MgCl <sub>2</sub> (conc.)	Split No
4.26 M	3.15 M	0
0.85 M	0.63 M	11
0.43 M	0.32 M	23
0.26 M	0.19 M	23
0 M	3.15 M	17
0 M	0.63 M	1
0 M	0.32 M	1
0 M	0.19 M	1
4.26 M	0.71 M	0



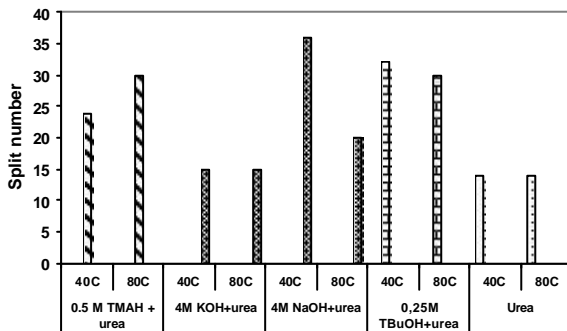
**Figure 8.** Lyocell fiber treated in 0.5 M TbuOH with ball bearing method by using balls



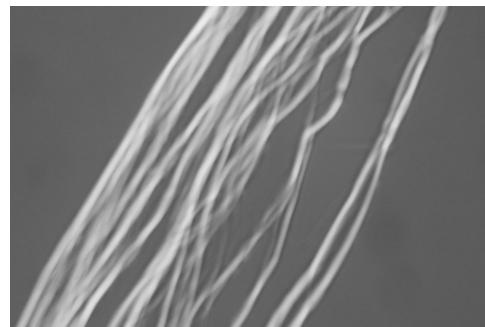
**Figure 6.** Split number of lyocell fiber treated with 1 M TMAH at room temperature, ultra-sonification at 40°C, ultrasonication at 80°C for different times.



**Figure 9.** Lyocell fiber treated in 0.5 M TbuOH with ball bearing method without using balls



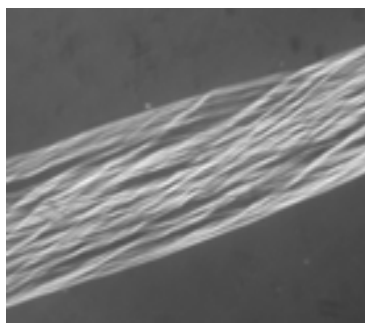
**Figure 7.** Split number of lyocell treated with different urea-alkali mixtures for different temperatures of the ultrasonication at 1 hour (urea has concentration of 50 g/l)



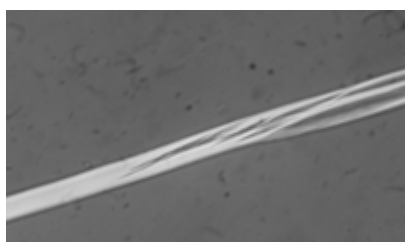
**Figure 10.** Lyocell fiber treated in 2 M TMAH at room temperature and then splitted by shear method (split number is 15)



**Figure 11.** Lyocell fiber treated with the mixture of 0.26 M DMDHEU and 0.19 M  $MgCl_2$  at room temperature and then splitted by shear method (split number is 2)



**Figure 12.** Lyocell fiber treated with 1 M TMAH in ultrasonification at 80°C for 90 min and then splitted by shear method (split number is 24)



**Figure 13.** Lyocell fiber treated with 0.7 M TMAH at room temperature and then splitted by shear method (split number is 3)

## Conclusions

Different methods were tried to establish a method for splitting of lyocell fiber. Ball bearing method was found too harsh for fiber so that fibrillation occurs instead of splitting. Putting a weight on fiber was found to establish splitting of lyocell fiber which was named as shear method. Neither splitting nor fibrillation occurred by using ultrasonic treatment alone.

Shear method was applied to fibers and split numbers were evaluated after using ultrasonification. Different time durations and temperatures were investigated for treatment of lyocell fiber in ultrasonification. The effect of ultrasonification was found not to be effective on splitting of lyocell fiber so that it was concluded that it isn't required to induce splitting.

In this work, splitting tendency of lyocell and viscose fibers was investigated. Splitting tendency of lyocell fiber was found to depend on the splitting test conditions like temperature, swelling time, alkali type and alkali concentration. Viscose fiber was found to show much less splitting tendency than lyocell fiber. Since viscose fiber has different fibrillar structure compared to lyocell fiber which has fibrils arranged longitudinally along the fibre axis, fibrillation tendency of viscose was found to be lower than lyocell [Nemec 1994].

Mixtures of DMDHEU with LiCl or  $MgCl_2$  are used for crosslinking of cellulosic fibers to retard fibrillation. It was shown that DMDHEU and catalysts can also act as swelling agents so that splitting can be observed for lyocell fiber.  $MgCl_2$  was found to be more effective agent in splitting of lyocell fiber than LiCl.

These results indicate new aspects of the interactions between textile chemicals and cellulose fibres.

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