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Swelling Behaviour of Cellulosic Fibres – Part I: Changes in Physical Properties¹⁾

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Abstract

The swelling and dissolving properties of textile materials are characterised in cotton and regenerated cellulosic fibres of lyocell and viscose (NMMO- and xanthogenate-type). The swelling, fractionation and dissolution mechanisms and their effect on polysaccharide substrate were studied with different solutions, while applying setting treatment. The differences in physical properties before and after treatment were followed by changes in diameter, mass loss and WRV (water regain).

Key words: cellulosic material, salt-alkali, fibre, swelling, physical properties.

Introduction

There is a need for pretreatments for cellulosic materials, which can be based on enzymes, physical methods or chemical methods of swelling, dissolution and fractionation mechanisms [1 - 2]. Based on this knowledge, the character of the pretreatments can determine dissolution behavior and its mechanism. Swelling is similar to dissolution – swelling happens when fibre molecules and water molecules change position up to a limited value, while dissolution is set off with the breakage of intermolecular bonds. By swelling, the fibre diameter increases mainly in dimension, whereas only very little longitudinal swelling occurs. The result of swelling is a lowering of crystallinity as well as an increase in accessibility [3]. Calcium ions ($\text{Ca}^{2+} > \text{Ba}^{2+} > \text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{NH}_4^+$) are the most effective cation, while thiocyanate ions ($\text{SCN}^- > \text{I}^- > \text{Br}^- > \text{NO}_3^- > \text{SO}_4^{2-}$) are the most effective anion for dissolving cellulose. In general, the best salt for forming a salt solution of cellulose features a cation which binds many water molecules, and an anion which binds little water [4]. In 1966 Åsnes and Wickman investigated the treatment of cotton fabrics inter alia with a concentrated calcium thiocyanate solution and also with a caustic soda solution including lithium thiocyanate [5]. The changes in fibre characters after setting treatment with several solutions at different concentrations were investigated, and the physical changes in the fibre properties are described here [6 - 10]. The extent of the swelling/dissolution was determined on the basis of fibre diameter measurements and by determination of mass loss during the treatment. Furthermore, the accessibility and surface related properties were determined. Based on this data, the treatment will be applied to cellulosic fabrics for further investigation into changes in physical properties.

Experimental

Materials

To measure the changes in fibre diameter, samples were taken from plain woven fabrics of standard lyocell called Tencel® Standard (CLY), and viscose which is called Lenzing Viscose® (CV), supplied by Lenzing AG, Lenzing, Austria. The cotton fibres were extracted from cotton yarn supplied by Getzner Textil AG, Bludenz, Austria.

The CLY desized fabrics have a mass per unit area of 133.5 g/m², end spacing of 34 yarn/cm (warp) and 28 yarn/cm (weft). The CV desized fabrics presented a mass per unit area of 143.4 g/m², end spacing of 35 yarn/cm (warp) and 28 yarn/cm (weft). The desized, scoured and bleached cotton woven fabric presented a mass per unit area of 125.4 g/m², an end spacing of 47 yarn/cm (warp) and 25 yarn/cm (weft).

For other tests loose fibres of standard desized lyocell (38 mm, 1.3 dtex) and standard desized viscose (39 mm, 1.3 dtex) were used. Cotton yarn desized, scoured and bleached (14.5 tex) was used. All materials were kept 24 h in a room of standard atmosphere (20 ± 2 °C, RH 65%) before use.

Methods

The swelling solutions, their mixture combinations, concentration and pH values are described in Table 1.

Swelling test

The cross-sectional swelling of the cellulosic fibres in various solutions and concentrations (Table 1) was investigated following changes in fibre diameter. A minimum of 10 fibres were placed on a microscope glass with 1 ~ 2 drops of selected swelling solutions. After two minutes, samples were covered with a glass cover and the fibre diameter was measured by a Reichert projection microscope, using an objective of 40/0.65 and reproduction scale of 500,

with a ruler attached. For comparison reasons, swelling in immersion oil and water was measured. The diameter measurements were performed randomly for lyocell and viscose, whereas this was done in the thinnest part of the cotton fibres due to its kidney-shaped cross-section [11 - 12].

Humidity content

0.50 g ± 0.02 g of untreated samples of CLY, CV and Co fibres were weighed (m_1) after acclimatisation for 24 h (20 °C ± 2 °C, RH = 65%). The samples were dried at 105 °C for 4 h in a conventional oven, placed overnight in a desiccator (P₂O₅, RH = 0%) and weighed (m_2). Each measurement had 4 repetitions and the humidity content was calculated as described in Equation 1.

$$H.C. = \frac{m_1 - m_2}{m_2} \cdot 100\% \quad (1)$$

where H.C. = humidity content in %, m_1 = mass in g in conditioned state including moisture and m_2 = mass in g without moisture.

Water Retention Value (WRV)

0.50 g ± 0.2 g of untreated and treated dry samples of CLY, CV and Co fibres were immersed in deionized water for 1 h until equilibrium, and centrifuged at 4000G (Heraeus Multifuge IL) for 10 min. They were then weighed (m_3), and next dried in a conventional oven at 105 °C. Finally, they were placed overnight

Table 1. Swelling solutions.

Code	LiSCN solution concentration, M	NaOH solution concentration, M	pH-value
B1	0.7	-	5.9
B2	1.6	-	6.4
B3	2.3	-	6.3
B4	3.1	-	6.5
B5	3.9	-	6.3
M1	0.7	1	12.6
M2	0.7	2	12.6
M3	0.7	3	12.4
M4	0.7	4	12.3
M5	0.7	5	12.4

in a desiccator (P_2O_5 , RH = 0%) and weighed (m_4). Each measurement had 4 repetitions and the water retention value was calculated as described in Equation 2.

$$WRV = \frac{m_3 - m_4}{m_4} \cdot 100\% \quad (2)$$

where WRV = water retention value in %, m_3 = mass in g after centrifuging and m_4 = mass in g after drying.

Mass loss

Samples with $0.50 \text{ g} \pm 0.02 \text{ g}$ were weighed after acclimatisation (m_5) for 24 h in a climate room (RH = 65%). The samples were immersed for 1 h in 40 ml solution, washed five times with cold running tap water and then lightly hand-squeezed. This was followed by neutralisation with 20 ml of 5% citric acid for 10 min and washed/squeezed five times. After neutralisation and rinsing, the samples were centrifuged in a Multifuge IL Heraeus for 10 min with 4000G (4660 r.p.m.) and then weighed (m_3). The samples were dried in a conventional oven at 105°C for 4 h, placed overnight in desiccator (P_2O_5 , RH = 0%) and weighed (m_4). Each measurement had 4 repetitions and the mass loss of the treated fibres was calculated as described in Equation 3.

$$M.L. = \frac{\frac{m_5 \cdot 100\%}{100\% + H.C.} - m_4}{\frac{m_5 \cdot 100\%}{100\% + H.C.}} \cdot 100\% \quad (3)$$

where $M.L.$ = mass loss in %, m_5 = mass in g, in conditioned state, $H.C.$ = humidity content in % obtained from Equation 2 and m_4 = mass in g after drying without moisture.

Results and discussion

Fibre swelling

Figure 1.a shows the change in fibre diameter caused by different concentrations from 0.7 - 3.9 M of LiSCN solutions (B1 - B5), with an increasing order of concentration, where CLY and CV fibres showed a constant increasing swelling rate overlapped by Co fibres that grow exponentially with increasing

concentration of LiSCN in the solution up to 3 M.

The swelling diameter difference between Co fibres treated with 0.7 M LiSCN solution (B1) and 3.1 M LiSCN solution (B4) of about $7 \mu\text{m}$, while for CLY and CV fibres the range of difference was only $2 \mu\text{m}$. However, the fibre diameter of cotton showed an increasing growing rate of diameter up to the concentration of 3 M solution (B4), and after that the swelling reached nearly the same values obtained with 1.5 M solution (B2), indicating that 3 M LiSCN solution is the concentration that allows maximum swelling in cotton fibre.

Figure 1.b shows the changes caused by LiSCN-NaOH solutions with increasing NaOH concentration from 1 to 5 M (M1 - M5). The treated CLY, CV and Co fabrics of showed an increasing swelling rate with increasing NaOH concentration, where CV fibres had the highest swelling rate and Co fibres the lowest.

Regenerated fibres of CLY and CV treated with LiSCN-NaOH solutions reached a plateau of swelling at approximately 3 M of NaOH. From 3 M solution, the LiSCN present in the LiSCN-NaOH solution hindered the swelling of fibres, and the same limit values were given in literature for splitting tendency as an indicator of inhomogeneous swelling or swelling limit [14 - 15].

Moisture content

The moisture content calculated was 11.7% for CLY fibres, 11.7% for CV fibres and 5.5% for the cotton yarn. The moisture content determined was applied in the mass loss calculations.

Mass loss in fibres

Figure 2 shows the mass loss values for CLY, CV and Co fibres treated with NaOH, LiSCN and LiSCN-NaOH solutions. CLY fibres in 0.7M LiSCN solution (B1) featured a mass loss of 4% more than CV and Co fibres. The mass loss in 3M NaOH solutions increased for all three types of fibres.

The amount of mass loss of the CLY and CV fibres was twice or more reduced in LiSCN-NaOH solutions than in NaOH solution. Solution containing 0.7 M of LiSCN and increasing NaOH concentrations of 1 M (M1) and 3 M (M3) decreased the mass loss in comparison with NaOH solutions with the same concentrations. The mass loss reached the limit of decreasing in LiSCN-NaOH mixture solution with 3 M of alkali (M3).

The results allow to state that LiSCN-NaOH solutions diminish the mass loss for CLY and CV fibres up to a concentration limit of 3 M for NaOH present in this mixture solution.

Water Retention Value (WRV)

CLY and CV fibres treated with NaOH solutions showed increasing values of WRV up to the concentration of 3 M (M1 - M3). The same regenerated fibres decreased the values of WRV in NaOH solutions at 5 M concentration (M5). Furthermore, while showing differentiate behavior, Co fibres possessed increasing values of WRV up to 5 M in NaOH solutions.

In general, the three types of fibres treated with LiSCN-NaOH solutions showed continuously increasing values of WRV up to a concentration of 5 M of NaOH. The presence of NaOH in the LiSCN solutions showed some clear tendencies. First, the solution of 0.7 M LiSCN (B1) and the solution with low NaOH concentration in the LiSCN-NaOH with 1 M NaOH (M1) - showed similar rates of WRV, indicating low interaction or boosting of the mixture. Second, the presence of 3 M NaOH in LiSCN solution (M3) decreased the WRV for CLY and CV fibres by approximately 64%, when compared to NaOH solution. Third, the presence of 5 M NaOH in LiSCN solution (M5) increased the WRV for CLY and CV fibres by 8 - 12%, when compared to NaOH. Lastly, for Co fibres, the presence of NaOH in the LiSCN solutions (M1, M2, M3) showed comparable rates of WRV to those treated

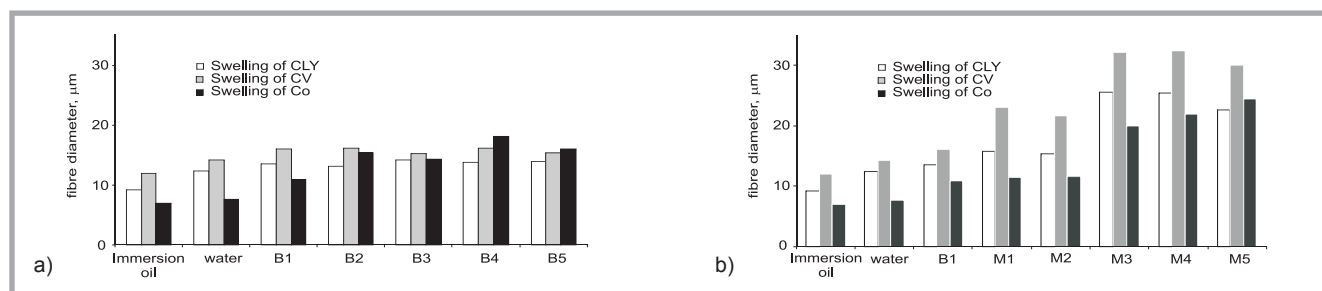


Figure 1. Influence of LiSCN solution concentration on fibre swelling, in order of increasing solution concentration; a) LiSCN solution, b) LiSCN-NaOH solution.

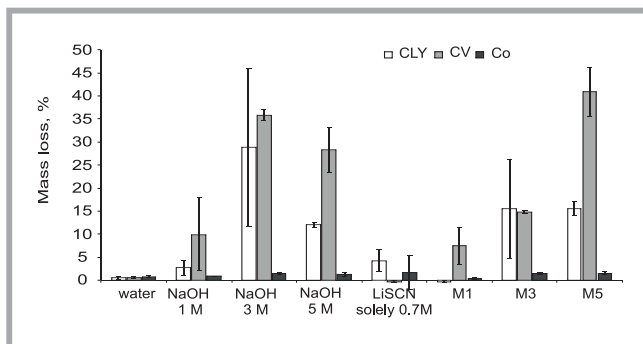


Figure 2. Mass loss of CLY, CV and Co fibres treated with NaOH and LiSCN-NaOH swelling solutions.

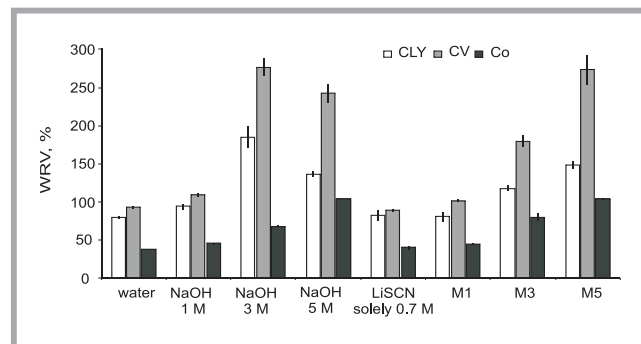


Figure 3. Water retention value of CLY, CV and Co fibres treated with NaOH and LiSCN-NaOH swelling solutions.

with NaOH solutions, besides gradually raising the WRV with increasing NaOH concentrations.

The WRV values of Co fibres treated with LiSCN-NaOH solution seem to be influenced by the LiSCN-NaOH mixture. It can be attributed to the conversion of cellulose I to cellulose II in the presence of NaOH (mercerization). Due to the very stable conformation formed, the structure can not be further disturbed by swelling liquids.

On the other hand, the differences in the void systems and continuous modification of the amorphous region of regenerated fibres of CLY and CV can lead to a large difference in WRV in sole solution or mixture solution treatments.

Conclusions

The LiSCN solution treatment showed an increased average of 7 μm in Co fibre diameter, but a 2 μm increase in CLY and CV fibre diameter. The fibres treated with LiSCN-NaOH solution displayed a growing increase in fibre diameter with increasing NaOH concentration. The LiSCN-NaOH mixture can be a booster for swelling properties, with slight differences in the fibre swelling behavior of cotton and regenerated cellulosic fibres.

The weight loss values obtained for fibres treated with NaOH, LiSCN and LiSCN-NaOH solutions identify the extent of swelling/dissolution. NaOH solution treatment caused a higher weight loss in fibres than the LiSCN-NaOH mixture solution of the same concentration of NaOH. It can be concluded that the NaOH present in the LiSCN solution only boosted the fibre swelling without causing the dissolution characterised by weight loss. Especially for CLY and CV fibres treated in LiSCN-NaOH solutions, did the mass loss decrease twofold up to 3 M of NaOH (M3), when compared to the fabrics treated with NaOH solutions, where the mass loss increased gradually up to 3 M of NaOH.

In general, the LiSCN-NaOH treatment applied to all the fibres showed growing rates of WRV with increasing concentration of NaOH, thus the increase in pore volume is affected by alkali strength. Regenerated cellulosic fibres of CLY and CV showed higher WRV with NaOH treatment than LiSCN-NaOH, where the LiSCN can be competing with NaOH for accessible sites, causing the lower values. On the other hand, Co fibres treated in LiSCN-NaOH solutions with increasing NaOH concentration of 1, 3 and 5 M (M1, M3 and M5) showed the same WRV as the NaOH treatment yet showing constant increase with increasing NaOH concentration. The conversion of cellulose I to cellulose II during NaOH treatment of cotton can be imposing the action of the limitation factor.

Mixture solutions of LiSCN-NaOH showed potential applications and additional studies will be described in Part II of this paper, where some selected solutions are applied in woven fabrics. The experiment was extended to fabrics to study the swelling properties of cellulosic materials in order to identify possible setting treatment for dimensional stabilisation. The effects of such treatments modify the physical, chemical and mechanical properties, and consequently the fabric accessibility is also modified, which can be capitalised in the textile finishing industry.

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Editorial note

- 1) Part II of the article will be prepared by the Authors in the foreseeable future and will be published in 'Fibres & Textiles in Eastern Europe' and will deal with fabric modification based on some solutions selected from Part I. The final chemical, mechanical, and physical properties of the fabrics processed will be discussed.

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