We are IntechOpen, the world's leading publisher of Open Access books
Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Alkali Treatments of Woven Lyocell Fabrics

Ján Široký, Barbora Široká and Thomas Bechtold
University of Innsbruck, Research Institute for Textile Chemistry and Physics
Austria

1. Introduction

We are surrounded by textile fabrics every second of our daily life. Being produced in enormous amounts, these products were considered simple mechanical constructions for a long time. During the last few decades aspects of functional products and smart textiles directed more scientific attention towards a more profound understanding of the relations between fabric structure and performance properties.

The overall properties of a textile fabric structure are determined by a series of constructive parameters built in at different levels of material design. For example the wetting behaviour and the final water uptake of a fabric will be determined by:

- type of fibre material and fibre properties chosen to produce the fabric e.g. cellulose fiber, polyolefine type fibre
- technical construction of the yarn *e.g.* spinning process, turns per meter, yarn count
- fabric construction, *e.g.* plain weave, single jersey.

As a result an enormous variability of designs can be chosen for a certain application. The best performance of a product will be achieved by appropriate choice of the right technical design parameters for a certain application.
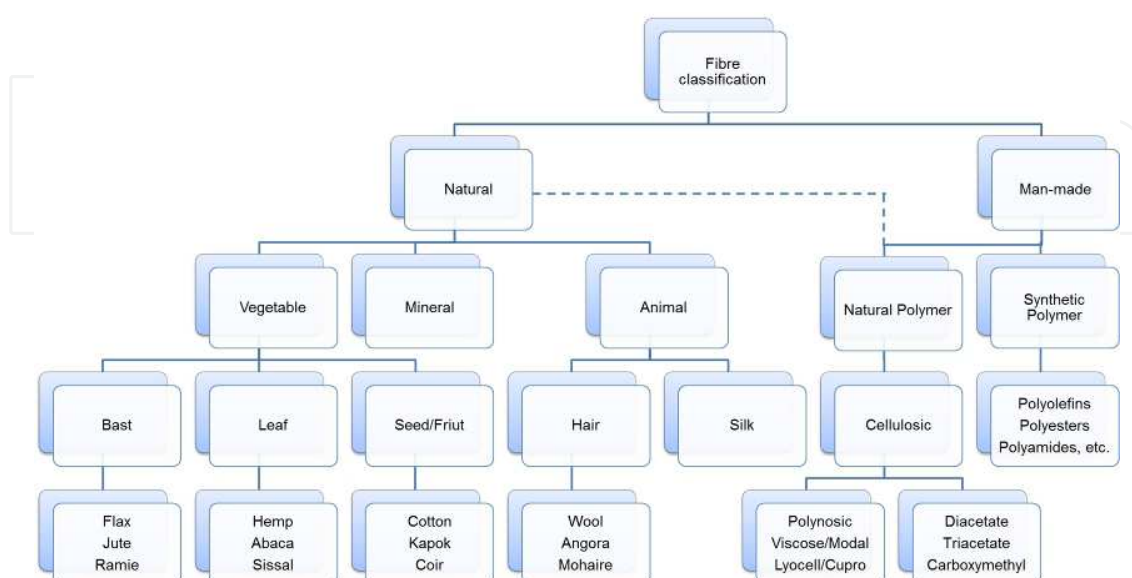

Fig. 1. Classification of textile fibres.

Textile fibres can be divided into two main categories, natural and man-made, as it is depicted in Fig. 1; in addition, there is another category which lies in between, and shares some features of both categories – it is termed 'regenerated fibres' and includes regenerated cellulosic fibres, which are typically wood pulp converted into continuous filaments by dissolving the wood in suitable solvents from which they can be regenerated.

Cellulose fibres exhibit a unique position among the textile fibres, due to their hydrophilicity and their ability to change their dimension by swelling. Swelling occurs in water, polar solvents and in particular in aqueous alkali hydroxide solutions, which are widely applied in textile finishing processes of cotton and regenerated cellulose fibres. Due to their high swelling capability regenerated cellulose fibres are highly sensitive during the alkaline treatment, thus a careful selection of alkalisation conditions for such fabrics is required. This particular behavior of cellulose to swell extensively in alkaline solutions results in a different performance in comparison to synthetic fibres. Herein, the chapter is dedicated to detailed discussion of the fibre behavior and the resulting effects/impacts onto regenerated man-made fabrics, for example lyocell fabric, during alkalisation.

2. Regenerated cellulose

It is difficult to verify when cellulosic materials were used the first time for clothing, because of the biodegradability, but the oldest cotton textiles found go back to 5800 BC and were found in a cave in Tehuacän in ancient Mexico;(Abu-Rous, 2006) other important sources like flax, linen, hemp or wool were also used in early history. For instance, Babylonia was the first country to process and trade in wool (Babylonia = land of wool) and also, the proof of using leather of different skin in clothes and shoes by discovery of the oldest European mummy; Ötzi the Iceman – man who lived about 5,300 years ago, on the border between Austria and Italy. (Hollemeyer et al., 2008; Kutschera & Rom, 2000)

Regenerated cellulose fibres are the first artificial fibres ever made. Processes capable of dissolving the cellulose derived from wood or cotton linters were first discovered by Schnöbein (1845, nitrocellulose soluble in organic solvents), Schweizer (1857, cellulose in cuprammonium solution), Cross, Bevan and Beadle (1885, cellulose sulfidized in sodium hydroxide; 1894, cellulose triacetate in chloroform) followed by commercial production of acetate fibres started in 1919; in 1955 they were joined by triacetate. The introduction of modifiers by Cox in 1950 and the development of high-wet-strength fibres initiated by Tachikawa in 1951 again increased the variety of cellulosic man-mades. In the 1960s, high wet modulus type rayon fibres were developed to improve resistance to alkali and to increase wet fibre mechanical properties and dimensional stability of fabrics. In the 1970s, new kinds of rayon fibres were produced - Avtex Avril III (a multilobal fibre), Rayonier's Prima and Courtaulds' Viloft (a hollow fibre with high water-holding capacity). In the late 1970s due to increasing investment in pollution control, which became cost-determining, several companies (Courtaulds, Lenzing, Enka) started to examine the application of carbon disulfide-free, direct solution systems for cellulose. Several direct solvent systems, such as dimethylsulfoxide/para-formaldehyde, N-methylmorpholine-N-oxide (NMMO) and N,N-dimethylacetamide lithium chloride were investigated, but only NMMO became of practical importance. Lyocell fibre made from an NMMO-solution is today a newest class of man-made cellulosic with very promising properties.

The main raw material from which regenerated cellulosic fibres are manufactured is purified wood pulp; mainly produced from wood and linters, but also from annual plants. For its conversion into textile fibres, it must be dissolved in a suitable solvent from which it can be regenerated as continuous filaments after the solution has been extruded through a fine orifice. At present, the following three methods are mostly used: the viscose process; the lyocell process; and the cuprammonium process.

Most of the world's man-made cellulose fibres are produced via the viscose process; these fibres are called 'rayons' because of the basic fibre-forming process, which involves cellulose regeneration from a cellulose xanthate, a chemical derivative of cellulose and carbon disulfide. The viscose process is characterized by high versatility, which is the result of various modifications that can be made at different stages of the process. The degree of polymerization of cellulose used, additives to modify the viscose solution, coagulation (controlled by coagulation bath additives, exerting an effect on the orientation and alignment of the cellulose molecules in the direction of the fibre axis), and stretching applied during fibre processing, can lead to a huge range of rayon forms and properties. These variations and their consequences on the end products are given in details in Morton and Hearle (1993).

With regard to the macrostructure of viscose fibres, regenerated cellulosics are different in their morphology to cotton as they have no lumen and are non-fibrillar (Fig. 2), which is directly due to the manufacturing process.
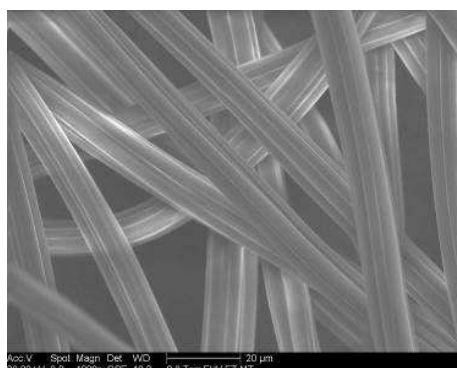

Fig. 2. Scanning electron microscope (SEM) micrographs of viscose fibres.

Lyocell is the generic name of a new generation of regenerated cellulosic fibres made by a solvent spinning process. The development of this fibre was driven by the desire for an environmentally friendly process to produce cellulosic fibres with an improved performance profile and cost compared to viscose rayon, utilizing renewable resources as raw materials.

This cellulosic fibre is derived from wood pulp (typically eucalyptus) produced from sustainably managed forests; the wood pulp (good quality, DP = 400-1000) is mixed at 70-90 °C with approximately 80% (v/v) *N*-methylmorpholine-*N*-oxide (NMMO) solution in water with a small quantity of degradation inhibitor. NMMO is capable of physically dissolving cellulose without any derivatisation, complexation or special activation, and it is able to break the inter- and intra-molecular hydrogen-bonds of cellulose.

In the ternary system, cellulose is dissolved in a narrow region and the solution is stabilised using suitable chemicals, *e.g.* isopropyl gallate. The homogenous solution (*dope*) with a minimum of undissolved pulp particles and air bubbles, is put into the evaporator vessel (evaporation of water) operated under vacuum to reduce temperature (ca 90-120 °C), due to the amine oxide solvent in solution degrading if it is overheated. Before spinning, the solution is passed through two stages of filtration. For spinning, the solution is supplied to each jet (a small *air gap* with thousands of tiny holes), and it is then extruded and spun through an air gap (*fibre* or *tow* is obtained) into a spin bath containing dilute amine oxide solution. The fibres are *drawn* or *stretched* in the air gap by the pull of *traction units* or *godets*. Afterwards, the fibres are washed and from the excess liquor and NMMO is recovered by filtration, purification and concentration. Lyocell fibre differs from viscose rayon in the fibre structure and morphology (Fig. 3).
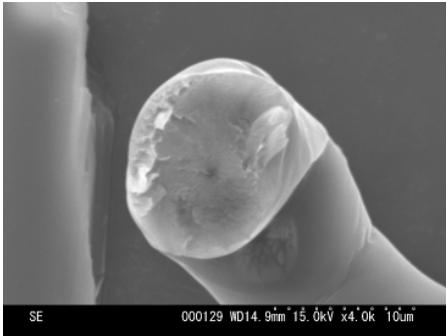

Fig. 3. Lyocell fibre SEM micrograph.(Zhang, 2004)

	Viscose Process	Lyocell Process
Derivatisation	CS_2, NaOH	----
Solvent	NaOH	NMMO
Toxicity	Very toxic (CS_2)	Non-toxic
Spinning Bath	H_2SO_4, $ZnSO_4$	H_2O
Pulps	Small variety	Large Variety
Recovery	Complex	Simple

Table 1. Comparison of the viscose and lyocell processes.(Harvey, 2007)

Production of fibres using this process has very little impact on the environment mainly in terms of chemical used and is a benign technology process. The manufacturing process recovers >99% of the solvent, additionally, the solvent itself is non-toxic and all the effluent produced is non-hazardous. The environmental impact of the viscose and lyocell processes are compared in Table 1. Lyocell is designed as a fully biodegradable cellulosic polymer with beneficial properties, which will be mentioned later. Despite all of these benefits, the production of lyocell was in 2002 only *ca.* 2.5% of the total regenerated cellulosic fibre production (total of 2.76 million tonnes), as shown in Fig. 4.(Abu-Rous, 2006)

The lyocell process is less flexible then the viscose process due to the high orientation of the obtained polymer after the air gap. However, there are other possibilities to influence the structure and properties of lyocell fibres using physical process parameters.

Lyocell fibres have the thinnest and longest crystallites, even the amorphous regions are oriented along the fibre axis, and its crystallinity is of high degree (up to 60-70%). These

fibres have a microfibrillar structure because a portion of the molecular chains aggregate to form microcrystals while recrystallizing along the chains, whereas the remaining chains exist in the amorphous phase as links between these two phases.(Okano & Sarko, 1984) In the crystalline regions of cellulose II polymers, the layered structure is very regular, so the length of hydrogen bonds between molecules is the same.
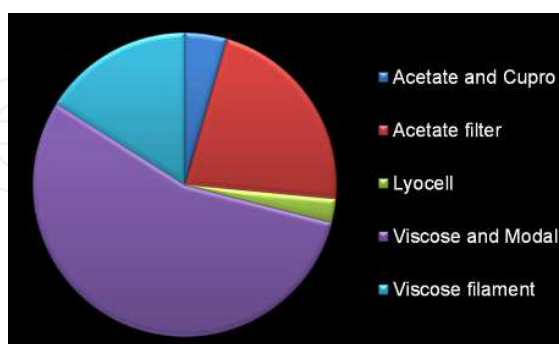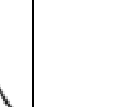

Fig. 4. World production of cellulosic fibres in tonnes.

Although, the physical properties of lyocell are unique among all kinds of rayons (Table 2) remarkably when wet, problems of lyocell properties occur as well.(Woodings, 1995) The weaker lateral links between crystallities are consequence of the highly crystalline lyocell structure and as a result of wet abrasion, at the surface of fibre the separation of fibrous elements known as *fibrillation* (Fig. 5) occurs. Basically, it is the longitudinal splitting of a single fibre filament into microfibers of 1-4 μm in diameter. It can also yield the 'peach skin' touch of fabrics, characteristic surface touch of lyocell fibre, but unwanted and uncontrolled fibrillation can worsen the fabric quality, for example, entanglement of microfibers causes a serious problem of pilling.

Fig. 5. Fibrillation of lyocell fibre. (Zhang, 2004)

Man-made cellulose fibres, such as viscose or lyocell, morphological structure can be described as a network of elementary fibrils and their more or less random associations; this is called a "fringe fibrillar" structure which is basically one of the macro-conformations of polymer chains depicted in Fig. 6. Schuster et al. (2003) used Ultra Small Angle Neutron Scattering (USANS) to yield information on lyocell fibres and their proposed structure at different dimensional levels is given in Fig. 7. In general, lyocell fibre is distinguished by its high crystallinity, high longitudinal orientation of crystallites, high amorphous orientation,

Property	Regular rayon	Cuprammonium	'Y'-shaped rayon[a]	Modal	Polynosic	Lyocell fibre [b]
Fibre cross-section						
Dry tenacity (cN/tex)	20-24	15-20	18-22	34-36	40-45	40-44
Wet tenacity (cN/tex)	10-15	9-12	9-12	19-21	30-40	34-38
Extension at break (%, dry)	20-25	7-23	17-22	13-15	8-12	14-16
Extension at break (%, wet)	25-30	16-43	23-30	13-15	10-15	16-18
Water imbibitions (%)	90-100	100	100-110	75-80	55-70	65-70
Cellulose DP	250-350	450-550	250-350	300-500	550-700	550-600
Initial wet modulus (at 5 %)	40-50	30-50	35-45	100-120	140-180	250-270

[a]The 'Y'-shaped rayon data are based on Courtaulds' Galaxy fibre;
[b]The solvent-spun rayon data are based on Courtaulds' Tencel fibre

Table 2. Physical properties of selected commercially available rayon fibres.
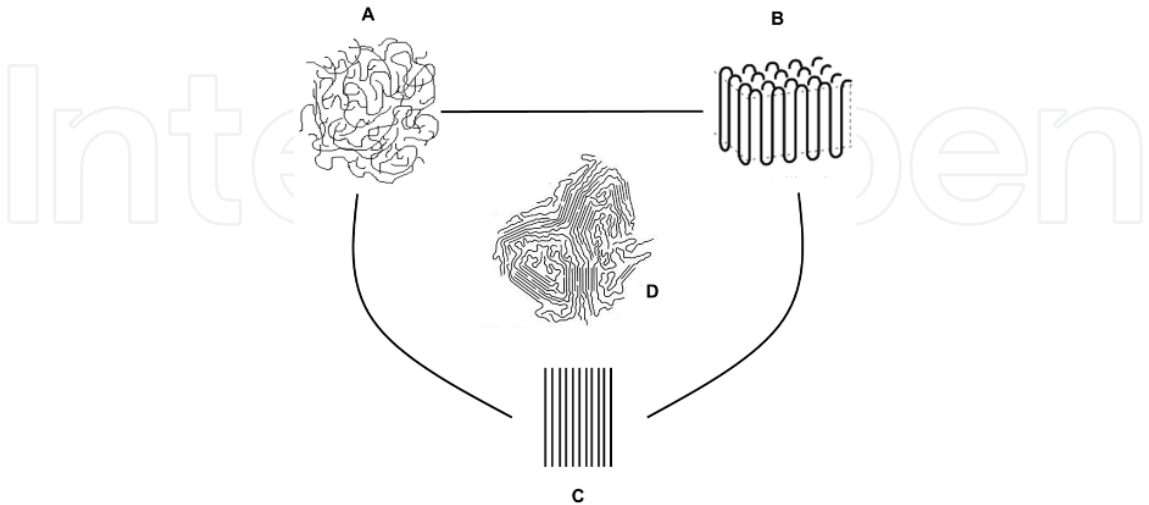

Fig. 6. Illustration of the macro-conformations of polymer chains. A, amorphous; B, regular chain folding; C, chain-extended which represents the limiting cases, and the middle part D, fringe micelle represents the intermediate structure.

low lateral cohesion between fibrils, low extent of clustering and relatively large void (pore) volume in comparison to other cellulosic regenerated fibres.
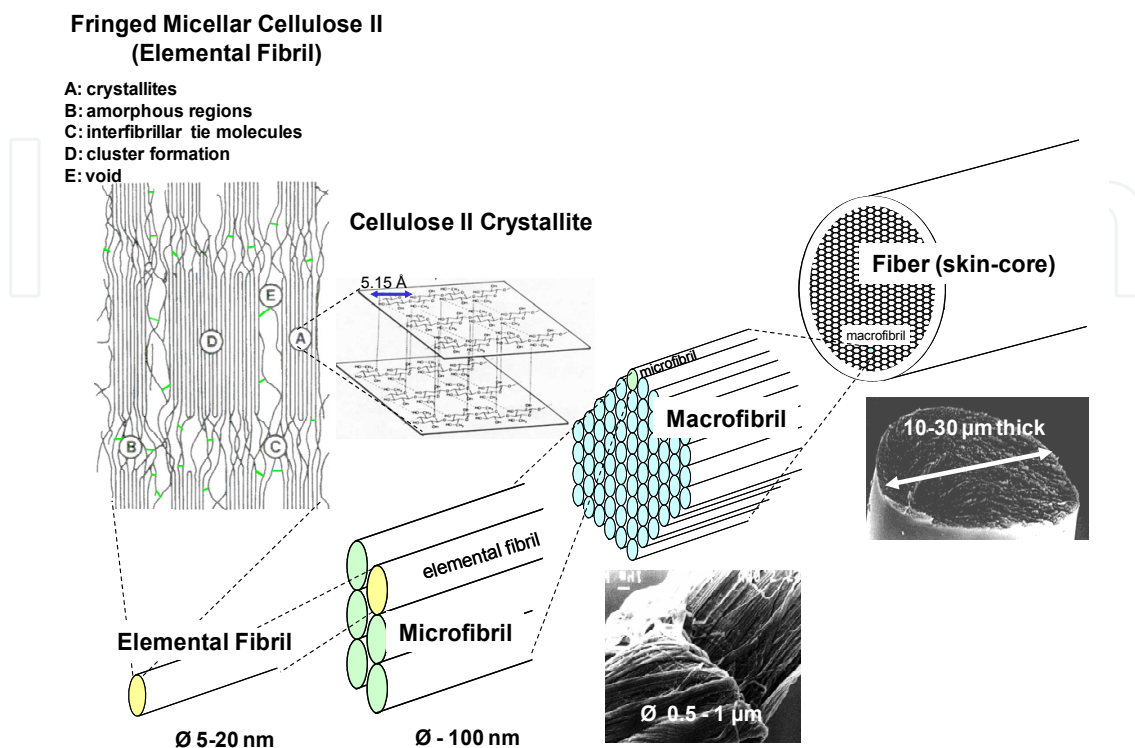

Fig. 7. Lyocell fibre structure at different dimensional levels.(based on Schuster et al. (2003))

There is a wide range of possibilities or processes to influence the fiber structure and its properties such as changing the parameters (*e.g.* type of pulp and molecular weight of polymer, dope composition, air gap length, l/d ratio of spinning nozzle, spinning speed, draw ratio, spinning bath composition, *etc.*) during the fibre formation. One of the processes for lyocell fibres mentioned herein is a "softer" precipitation, involving a two-stage precipitation in alcohol and water. By this process a decrease of crystallinity and orientation of lyocell fibers is obtained and, therefore, the fiber structure and core-shell structure is affected.(Klemm et al., 2005) It is also known that the structure and properties of regenerated fibers, like density, crystallite size, orientation, pore number and volume and therefore, skin-core structure as well, can be influenced with applied physical process (spinning) conditions. Recently, a skin-core model for lyocell fibers was proposed by Biganska(Biganska, 2002) where three-component system is presented. A system with compact fiber core, a porous middle zone and a semi-permeable fiber skin. However, Gindl et al. (2006) showed that only two different parts within lyocell fiber do exist, skin and core. They observed that studied fibers have uniform skin-core orientation, in contrast, Kong et al. (2007) obtained non-uniform skin-core orientation by X-ray diffraction as claimed due to the differences of used beam size (5 × 5 μm vs. 500 nm). This non-uniformity resulted in the higher average orientation of the fiber skin than of the core. Additionally, it was shown that the skin-core model of lyocell fibers is influenced by the increased shear forces on the outer region of the fiber during passing the spinning dope through the spinneret, which generates higher crystal orientation at the skin.

3. Activation treatments of cellulose

Activation methods (Table 3) in general are those that only open and widen existing capillaries, voids and interstices, those that are capable of splitting up fibrillar aggregations, *and* those that are able to disrupt crystalline order and/or change the crystal modification in order to increase accessibility and reactivity of fibrous cellulose substrates, *e.g.* fibres or fabrics.(Krässig, 1993b)

Treatment		Action
Degradation	Chemical	Hydrolysis-acid or enzymatic
		Oxidation
	Thermal	Applied at different temperatures in various media
	Radiation	Exposure to UV/VIS or high-energy radiation
Mechanical		Milling – dry and wet, grinding, beating, cutting
		Freezing, ultrasonic agitation
Solvent exchange		From water-swollen state introducing inert media towards providing reactive water-swollen state
Inclusion		As solvent exchange but introducing inert liquids to maintain reactive water-swollen state
Swelling		inter- and intra-fibrillar swelling
		swelling agent/solvent

Table 3. Treatments which have an activating effect onto cellulose fibrous substrates.

Degradation treatment of cellulose substrate can be performed with numerous chemical reaction routs, which of major significance is hydrolysis and oxidation, or with applying different source of energy such as *UV/VIS*, *γ*-irradiation or thermal treatment. *Mechanical* treatment is commonly employed by grinding, milling, beating or cutting to reduce size as well as increase accessible and reactive internal surface of cellulose with varying of activating time and/or temperature.

Activation of cellulose substrates also occurs in water-free organic environments followed by solvent exchange or by inclusion in a subsequently performed reaction. The *solvent exchange* treatment represents the action from water-swollen state with introduction of media which are unable to swell cellulose itself (inert to cellulose). Very similar is *inclusion* treatment which maintains the reactive water-swollen state by introducing inner liquids (*e.g.* benzene) applying the solvent exchange. Examples of chemicals used which provide highly swelling systems causing *intra-fibrillar* as well as *intra-crystalline swelling* include inorganic acids, various salt solutions, inorganic and organic bases, amines and amine complexes, and metal hydroxide solutions. In general, these treatments penetrate the fibre substrate through existing capillaries and pores, open already present voids between fibrillar elements, disrupt fibrillar associations, and finally enter the more easily accessible regions interlinking the crystallites forming the elementary fibrils. From there, they are able to penetrate at suitable treatment conditions; concentration and temperature, and to some extent tension during treatment, have to be considered from both ends into the lattice structure of elementary crystallites, which break open inter-molecular hydrogen-bonds and van der Waals

interactions between lattice layers, leading to a widening of lattice distances or even changes in the crystal lattice.(Krässig, 1993b)

3.1 Accessibility and swelling of cellulose

3.1.1 Cellulose water/moisture interactions

One of the most important features of cellulosic substrates is their propensity to absorb moisture from ambient air, expressed in terms of either moisture regain or moisture content. Water absorption causes swelling of the substrate, which alters the dimensions of the fibre, and this, in turn, will cause both changes in physical properties such as the size, shape, stiffness, and permeability of yarns and fabrics,(Morton & Hearle, 1993) as well as sorption/desorption characteristics (Široká et al., 2008), and in mechanical properties such as tensile modulus and breaking stress,(Kongdee et al., 2004) and, therefore, interaction between cellulose and water plays an important part in the chemistry, physics and technology of cellulose isolation and processing.

Cellulose accessibility largely depends on the available inner surface, supramolecular order, fibrillar architecture, and also fibre pore structure. In most cases, there is interaction with water which consequently destroys weak hydrogen-bonds, but cannot penetrate into the region of high order, in contrast to, for example, aqueous solutions of sodium hydroxide, and therefore cellulose is not dissolvable in water. In Fig. 8, an overview is given about the depth of fibre reorganization/dissolution and also indicates the fields of its application; sorbed water on such a polymer can cause structural changes predominantly in the amorphous or intermediate phases. However, there is also a significant role associated with pores, capillaries, and the network of voids, which do not have uniform size and shape.
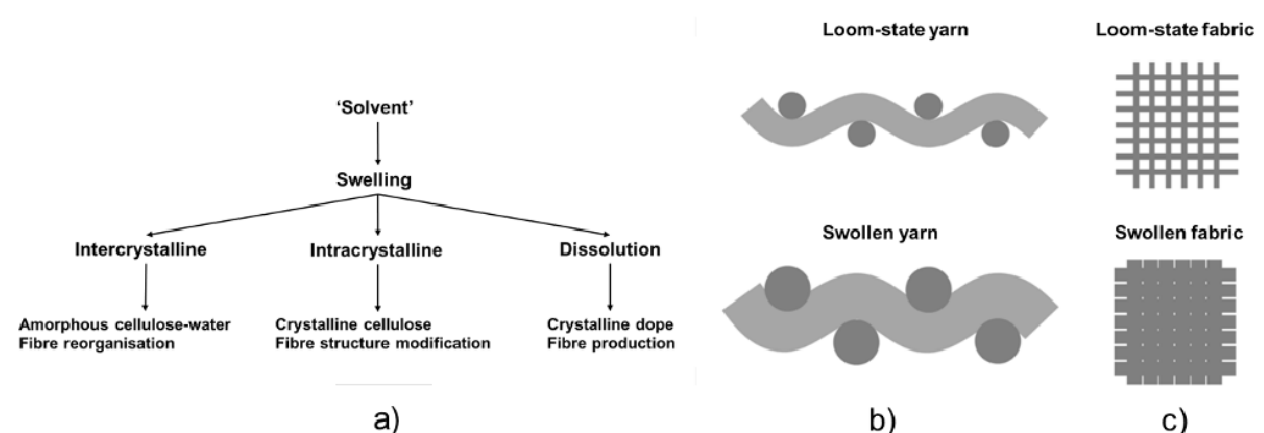

Fig. 8. Different stages of cellulose fibre reorganisation at different level: a) solvent, b) yarn, and c) fabric level.

From the chemistry perspective, cellulose-water interactions are basically a competition of hydrogen-bond formation between hydroxyl groups in the polymer and hydrogen-bond formation between one hydroxyl group of a cellulose chain and a water molecule or a water cluster.(Klemm et al., 1998) Differential scanning calorimetry (DSC) may be used as valuable technique to explore the interaction of either water or moisture with various natural and synthetic polymers with hydrophilic groups, and thermal properties of polymers and water.

Tatsuko and Hyoe Hatakeyama's classified different fractions of water in cellulose structures.(Hatakeyama & Hatakeyama, 1998) The first-order phase transition of water fractions closely associated with the polymer matrix is usually impossible to observe; such fractions are termed *non-freezing water* and it can directly interact with hydroxyl groups of cellulose. Another fraction of water, *freezing bound water*, is less closely associated and in contrast, it exhibits melting/crystallisation; it is able to interact with either hydroxyl groups of cellulose or water already absorbed to cellulose. The sum of the non-freezing and freezing bound water fraction is *the bound water content*. Water, whose melting/crystallisation temperature and enthalpy are not significantly different from those of normal (bulk) water, is designated as *freezing water*. *Bound water* in the water-insoluble hydrophilic polymers, such as cellulose, lignin, *etc.*, breaks hydrogen-bonding between the hydroxyl groups of the polymers, and its content depends on the chemical and supramolecular structure of each polymer. Schematic illustration of all kinds of water within the fibre structure is proposed in Fig. 9, where from it is obvious that the freezing (W_f) and non-freezing (W_{nf}) water provides a dry touch and dry perception respectively. However, with further water absorption within fibre structure, the bulk (W_b) and capillary water (W_c) provides a wet touch and hence, it imparts wet perception respectively.
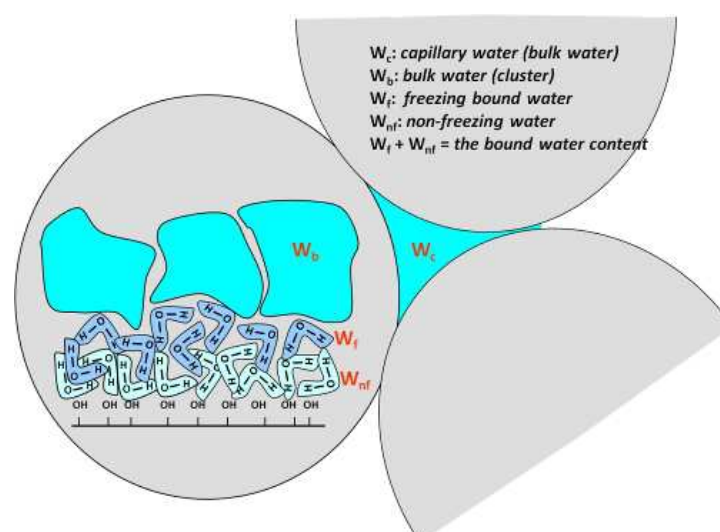

Fig. 9. Water in cellulosic fibre.

Transport of liquid or moisture within the porous solid such as textile fibre or fabric occurs by external forces or capillary forces only. If a liquid is spontaneously transported and it is driven inside porous solid, it is known as wicking. The capillary force increases as the capillaries; gaps between the individual fibres, become thinner – the finer the fibres, the smaller the gaps are, and the better the transport. Wicking is a result of spontaneous wetting in a capillary system due to fact that the capillary forces are caused by wetting. Wetting of fibres or fabric usually involves three phases which may be characterized the best as the displacement from a surface of a fibre-air interface with a fibre-liquid interface. It needs to be noted that the wicking and wetting are not two different processes, but wetting is a prerequisite for wicking.(Kissa, 1996; Rosen, 2004)

Surface wettability (wetting characteristics) of any fabric containing a single fibre type is identical to the wettability of its constituent single fibres.(Hsieh, 1995) Therefore, the fibre

surface and the liquid properties are determining factors of fibre wetting properties. The geometric configurations and the pore structure of the porous medium (*e.g.* woven fabric) determine its liquid transport properties and hence, capillary water differs in various types of fabric construction (plain-, twill- or sateen-woven fabrics). Fabric geometry and fabric construction influence properties of macro-pores (pore size, pore size distribution, pore connectivity, total pore volume).(Hsieh et al., 1992) Pores in woven fabrics can be intra-fibre, inter-fibre and inter-yarn;(Hsieh, 1995) intra-fibre pores are smallest and are discontinuous, not being merged with neighboring fibres. Structure and dimensions of inter-fibre and inter-yarn pores are influenced by yarn structure and yarn density in woven fabrics and thus, the observed differences are mainly determined by fabric construction.

When cellulose fibres are dried there is a subsequent reduction in the extent of swelling when the fibres are re-wet; the loss of swelling resulting from a drying and re-wetting cycle is so-called "*hornification*" or "*zip up of voids*".(Crawshaw & Cameron, 2000) Basically, some voids "*zip up*" after drying of swollen substrate by the formation of additional hydrogen-bonds between cellulose molecules, and this may lead to re-crystallization or to spot-wise bridging, which produces non-crystalline, brittle, inaccessible domains on a larger scale. According to this model, during wetting, cellulose chains are hydrated with water molecules, re-arrangement of cellulose chains takes place due to opening of closed pores and joining up of small pores. When drying, the water molecules are partially removed and hydrogen-bonds between cellulose molecules are generated. This interaction induces re-arrangement of fibre structure, loss of fibre pores and collapse of large pores, which is not recovered by re-wetting. Furthermore, amorphous cellulose may become re-crystalline on drying. This change results in lowered pore volume and surface area that is especially found in non-crosslinked type fibres. The limited re-expansions can also be attributed to covalent interactions, such as the formation of lactone bridges between hydroxyl and carboxylic groups in the polymer chains (Diniz et al., 2004). There is also some evidence of drying-induced crystallization in cellulosics, to which is also attributed the phenomenon of hornification (Brancato, 2008). Accessibility and reactivity of cellulosic fibres are reduced due to the already mentioned *hornification* phenomena. In accordance with Crawshaw et al. (2000) findings on drying, the void fraction falls and the void size rises, suggesting that a large number of voids "*zip up*", essentially, some voids merge and creates larger ones. These authors proposed a schematic illustration of water-swollen and dried Tencel fibres. Another widely accepted explanation is so-called fibrillar 'fusion', the formation of hydrogen bonds between surface hydroxyls, which causes the reduction of interfibrillar interstices and hence, the accessible and reactive internal surface is decreased.(Krässig, 1993b) This fusion is enhanced the lower the crystalline order and the higher the degree of swelling prior to drying of cellulose substrate from the water wet state.(Krässig, 1993b) The same reference states that the effect of hornification can be avoided by appropriate swelling treatment (*e.g.* ammonia pre-treatment) or by drying after solvent exchange to more hydrophilic liquids.

An additional effect can be expected due to differences in cross-section type of fibres used. These differences will influence pick-up, sorption properties, and fibre swelling in respect to structural differences and also macroscopic properties like stiffness and handle. Usually, fibres of different cross-section are used in specific applications, *e.g.* hygiene and personal care or technical applications and thus, systematic scientific comparisons on fabric level are rare.

3.1.3 Cellulose-aqueous alkali hydroxide interactions

The process of caustic treatment was devised in 1844 by John Mercer and he was later granted a patent(Mercer, 1851) for work he had done on vegetable fabrics and fibrous material (cotton, flax) and other textures with treatment of caustic soda, potassium hydroxide, dilute sulfuric acid or zinc chloride. The process did not become popular, however, until H. A. Lowe improved it into its modern form in 1890; by holding the cotton during treatment to prevent it from shrinking, Lowe found that the fibre gained a lustrous appearance and good dyeability.(Beaudet, 1999) Afterwards, treatments with aqueous sodium hydroxide solutions found numerous applications as the primary step in many industrial practices leading to acetyl, ether or ester derivatives of cellulose.

One of the most important steps in cellulosic fabric processing is the treatment in aqueous solutions of alkali hydroxides, particularly aqueous sodium hydroxide solution. In general, mercerization and alkalization, respectively of cellulose is a conventional swelling treatment of cellulosics substrates with aqueous alkali solutions, usually carried out in concentrations between 6.8 to 7.6 mol dm^{-3} NaOH, and is a prerequisite to the preparation of many cellulose derivatives, the spinning of viscose ramie and lyocell, or the manufacturing of cellulose-based sponges.(Porro et al., 2007) In its interaction with cellulose, aqueous sodium hydroxide above a certain concentration is able to penetrate the cellulose crystalline lattice to yield a series of more or less well-defined crystalline complexes holding a number of sodium ions and water molecules within their crystalline lattice. From analysis of these complexes by X-ray diffraction it has been found that cellulose and alkali solutions interact strongly with the consequence of swelling of cellulose fibres. This interaction at low alkali concentration with cellulosic fibres causes an increase in their cross-sectional area with simultaneous shrinkage in length; the extent of the dimensional changes caused by the swelling depends on the alkali treatment concentration and temperature.(Krässig, 1993a) This effect is most probably influenced by the degree of swelling observed previously for cotton(Warwicker, 1969), which herein at its maximum (between 3.00 and 3.75 mol dm^{-3} for continuously treated lyocell fabrics) decreases with increasing temperature of the treatment liquor.(Široký et al., 2010) Treatment with aqueous sodium hydroxide solution improves the fabric's mechanical and chemical properties such as dimensional stability, fibrillation tendency, tensile strength, dyeability, reactivity, lustre and smoothness.(Široký et al., 2009) Therefore, the strong swelling tendency of lyocell in alkali solutions substantially influences substrate properties such as the pore structure, crystallinity, fibrillation tendency, and surface characteristics in fibres, and yarn crimp and stiffness in fabrics.(Široký et al., 2010) In addition, during wet processing, lyocell fabrics are sensitive to the generation of permanent crease marks and alkali pre-treatments are recommended to counteract this (Široký et al., 2009).

Recently, Goswami et al.(Goswami et al., 2009) observed that sodium hydroxide treatment causes the density, orientation and crystallinity of lyocell fibres to decrease with increasing sodium hydroxide concentration, and that the greatest change in fibre properties occurs between 3.0 and 5.0 mol dm^{-3} NaOH. This was attributed to the onset of formation of sodium (Na)-cellulose II at 3.0 mol dm^{-3} NaOH; a fully formed Na-cellulose II structure was observed above 6.8 mol dm^{-3} NaOH. In addition, alkalization without tension can increase the moisture regain at a given relative humidity to 1.5 times its previous value;

mercerization under tension does not cause such a large increase,(Morton & Hearle, 1993) and generally causes an increase in fibrillar (crystalline) orientation.(Krässig, 1993a) Moreover, cellulose is susceptible to limited degrees of dissolution in alkali solutions, leading to weight loss in substrates. For instance, lyocell fibre mass reduces by 2-10% with increasing NaOH concentration up to 10 mol dm^{-3}.(Jaturapiree, 2007; Zhang et al., 2005)

The ability of cellulose to adsorb alkali hydroxide ions was originally considered to be a chemical process. In 1907, Vieweg observed two ranges of caustic soda concentrations at which the uptake of sodium hydroxide reached a plateau by applying so-called "change-in-titer" method;(Krässig, 1993a) the principle of this method was to measure the drop in alkali concentration of a given caustic soda solution by a known weight of immersed cellulose, and, at the time, had been use for a decade as a convincing observation for the occurrence of a defined chemical reaction following stoichiometric rules. Nevertheless, Vieweg's findings (and those of other research groups) were subjected to criticism by Leighton (1916) who introduced the centrifugation method; he mainly criticized the assumption made by Vieweg that no water is taken up by solid phase and he showed that "his method" allowed the separation of the uptake of water and the uptake of sodium hydroxide. Moreover, Leighton's method revealed that there is initially a preferential water uptake, which has a maximum at medium concentrations, whereas the uptake of sodium hydroxide steadily increases over the whole concentration range, except at the lowest concentrations. The balance of the two separate uptakes explains the plateau in Vieweg's curve of apparent sodium hydroxide uptake.

From these observations, it was concluded that the uptake of alkali hydroxides by cellulose is an adsorption phenomena based on the Donnan equilibrium theory,(Donnan, 1924; Neale, 1929) rather than a chemical process. It is assumed that cellulose, behaving as a very weak monobasic acid, forms a sodium salt to an extent increasing with the concentration of the alkali. Excess alkali diffuses into the mechanically separable cellulose phase. It results in an unequal distribution of ions what causes an osmosis or movement of water which distends the cellulose until the osmotic pressure is balanced by the forces arising from the cohesion of the gel and therefore, the cellulose swells. In addition, Neale's theoretical osmotic curves showed that as the temperature falls the maximum osmotic pressure rises, and the maximum occurred at a lower concentration of alkali. One of the difficulties with the absorption theory was based on the fact that uptake by native cellulose substrates is not smooth and reversible as might be expected for an adsorption process.(Krässig, 1993a) Another issue with the earlier investigations and results interpretation is that the effect of the morphology, fine structure, and accessibility of the cellulosic fibre substrate was, in most cases, ignored and it was assumed that the fibres were equally accessible throughout.

A comprehensive study of parameters, such as *sodium hydroxide concentration* and *temperature*, which influence the formation of various sodium-celluloses was conducted by Sobue et al. (1939) using an X-ray technique. They proposed a phase diagram of ramie cellulose and its various Na-cellulose crystalline complexes. They also revealed a new highly swollen and poorly crystalline allomorph, namely *Na-cellulose Q*, occurring at NaOH concentrations between 7% to 10% (1.75 to 2.50 mol dm^{-3} NaOH) and temperatures between –10 and 1°C. More recently, it was found that if an adequate pre-treatment of cellulose was applied, within the *Q phase*, total dissolution of cellulose can occur;(Kamide et al., 1984) solutions of 5% (w/v) cellulose could be obtained at a sodium hydroxide concentration of

9% (2.25 mol dm^{-3} NaOH) and temperature of 4°C and below. It is generally accepted that the immersion of ramie or cotton fibres into 12-16% (w/v) NaOH (3.0 to 4.0 mol dm^{-3} NaOH) yields *Na-cellulose I*, whereas the use of more concentrated alkali, typically 20-30% (w/v) NaOH (5.0 to 7.5 mol dm^{-3} NaOH), gives another allomorph: *Na-cellulose II*. The conversion of *Na-cellulose I* into *Na-cellulose III* is obtained by vacuum drying *Na-cellulose I*, whereas washing *Na-cellulose I* and *Na-cellulose II* until neutrality, yields the sodium-free *Na-cellulose IV*, which in its turn will give *cellulose II* upon drying. As Porro *et al.*(2007) stated, the analysis of the X-ray data alone may not be sufficient to give a clear picture of the interaction of the Na^{+} ions with the cellulose molecules. Therefore, Porro suggested a thorough analysis of ^{13}C solid-state NMR data of the various Na-cellulose complexes due to the low spectral resolution of X-ray which did not lead to a clear assignment of the resonances belonging to the various complexes. These authors proposed a phase diagram, based on the occurrence of *Na-cellulose I* and *Na-cellulose II* together with the *Q region* where cellulose is essentially soluble. It defines six regions, two of them being border zones where two phases are present at the same time.

4. Sodium hydroxide treatment of lyocell woven fabrics in continuous process

The key area in this part will be to examine the effect of aqueous sodium hydroxide treatment (alkalisation) of cellulosic natural-based polymer, in particular lyocell fabric, which are of cellulose II crystalline structure. The alkali treatment or NaOH uptake of cellulose is a long-lasting issue, regarding cotton and other cellulose materials. Sufficient information of alkali pad-batch process (no tension applied) to cellulose substrates is available with its effect onto cellulose fabrics. For example, the maximum NaOH uptake/swelling is between 2.0 – 2.5 mol dm^{-3} for fabric, high shrinkage force is present during treatment causing strong dimensional changes (shrinkage) to treated material, effect on crystallinity and dye sorption was reported. While numerous publications concerning NaOH treatment of cotton have been published, a gap in alkalisation knowledge of lyocell fabrics exists. Limited information is available on the continuous treatment process which constitutes important part of commercial operations. Therefore, a pilot-scale pre-treatment with NaOH was performed with a washer, a special semi-scale apparatus simulating a real alkali process to undertake a comprehensive study of various process parameters on lyocell woven fabric and its physico-chemical and sorption properties. Herein, the influence of NaOH treatment concentration, treatment temperature, tension applied to fabric and their effects to treated substrates will be discussed. Also, an influence of fabric structure/geometry (plain-, twill-, sateen-woven fabrics) on NaOH release (wash-off) from woven lyocell fabrics will be considered.

Before considering the relationship between the structure of cellulose substrates and their physical and chemical properties it is appropriate briefly summarise alkalisation process in textiles. Swelling is a special feature of porous substrate causing its expansion at different levels, *e.g.* fibre, yarn, or fabric. Particularly, this expansion results in close contact of fibres and yarns which in turn, reduces yarns mobility and increases swelling restriction. Therefore, the deformity or irregularity in the fibre cross-sectional area of, for example, lyocell fabric rises with increasing NaOH concentration (0-6 mol dm^{-3}) as observed recently(Goswami et al., 2009) and porosity decreases. Swelling reduction induces restricted

effect of chemicals to be swollen and hence, the accessibility of fabric decreases significantly. This effect can be seen in wash-off or alkali release from alkali treated lyocell fabrics which is discussed and shown in recent publication(Široký et al., 2011a). On the level of fabric, the fabric construction has a crucial effect as the swelling and wet pick-up differs for various fabric constructions (*e.g.* plain-, twill- or sateen-woven lyocell fabrics).
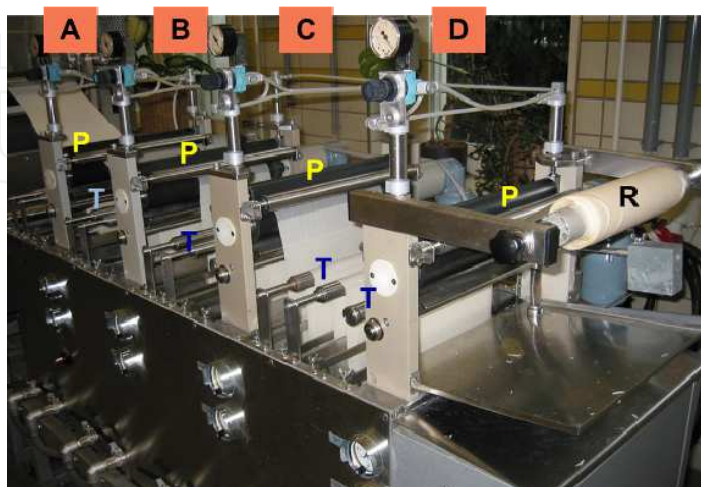

Fig. 10. Picture of apparatus used in continuous alkali pre-treatment process.

The continuing process of alkali pre-treatment was done with a washer simulating real alkali process which is given in Fig. 10. It was divided into four stages (A, B, C, D), each with two sub-compartments (1 and 2) that could be heated independently; the four stages were alkali treatment (A2), stabilisation treatment (B2), washing (C1 and C2), neutralisation (D1), and final washing (D2). The fabric was passed through the apparatus over a series of rollers including tension compensators (T) and pressurised squeeze rollers (P). The fabric after passing through the last compartment (D) was wound on a take-up roller (R). In treatment stage, the NaOH concentration, applied tension and temperature varied. Due to changes in the concentration in the treatment stage (caused by process), the "effective" concentration of alkali was established at 0.0, 2.53, 3.33, 4.48, 4.65 and 7.15 mol dm^{-3} for treatment bath and 0.0, 0.73, 1.08, 1.18, 1.48 and 2.15 mol dm^{-3} for stabilization bath. Residence time was adjusted at 75±2 s and 71±3 s in treatment bath and stabilization bath respectively. Tension in treatment compartments was applied either at 49 N m^{-1} or 147 N m^{-1}, tension in stabilisation compartment was applied at 147 N m^{-1}, and tension in washing and neutralization compartments was applied at 49 N m^{-1}. During the alkali treatment stage the temperature of the solution was set at 25 °C or 40 °C, and in the stabilization stage the temperature was 60°C. The speed of passage of fabric through the system was set at 2 m min^{-1}. Entire process and its all adjustments during the process are described in detail in our previous work.(Široký et al., 2009)

4.1 Influence of physical properties

Alkali treatment has a substantial influence on dimensional and mechanical properties as well as on morphological, molecular and supramolecular properties of cellulose II fibres (*e.g.* lyocell type) causing changes in their structure and performance. These physical changes were observed and examined by dimensional change, flexural rigidity (in dry and wet

state), mass per area, water retention and pick-up, abrasion resistance, tensile strength, elongation at break, and crease recovery following continuous treatment of the lyocell plain woven fabrics with aqueous sodium hydroxide solution under varying condition parameters.

The influence of process parameters in alkali treatment of lyocell fabrics by a continuous process on dimensional and mechanical properties was examined with focus on: alkali concentration, treatment temperature, and tension applied on fabric.(Široký et al., 2009) The alkali concentration and treatment temperature exerted significant influence on these fabric properties, but no significant influence of tension was observed in the results. It was proposed herein, that at the maxima of fibre swelling in alkali influencing fabric macroscopic structure and properties at certain NaOH concentrations and temperatures (observed peaks) the greatest NaOH effect occurs. Peaks of fabric shrinkage were observed in samples treated with 3.33 mol dm^{-3} NaOH at 25°C, and with 4.48 mol dm^{-3} NaOH at 40°C. The shrinkage peaks corresponded to peaks in flexural rigidity, and minima in water retention, crease recovery, and breaking force. The shrinkage in fabrics and corresponding changes in their properties are attributed to fibre swelling in alkali influencing fabric macroscopic structure and properties. In the range of concentrations examined in this particular work(Široký et al., 2009), the best combination of properties was observed in fabrics treated with 2.53 mol dm^{-3} NaOH. These fabrics exhibited low wet flexural rigidity, high water retention, high crease recovery, high abrasion resistance, and high breaking strength as compared to the untreated fabric as well as among alkali treated fabrics. Also, it was found that the NaOH concentrations in treatment baths decreased during the course of fabric passage through liquors while, the NaOH concentration in the stabilisation baths increased into extents that increased with rise in liquor alkali concentrations. The NaOH depletion was attributed to sorption of alkali by substrates, and the rise in the stabilisation bath was attributed to the transport of NaOH from the treatment to the stabilisation bath by the fabric.

4.2 Attenuated total reflectance fourier-transform infrared spectroscopy to characterize crystallinity changes

In the structure of cellulose, a linear 1,4-β-glucan polymer, there are three hydroxyl groups able to interact through intra- and inter-molecular hydrogen bonding, which form highly ordered structures. Alkali treatment of all allomorphs of cellulose has a substantial influence on morphological, molecular and supramolecular levels, causing changes in crystallinity as a result of the degree of swelling, the rate of fibre swelling, changes in the voids and pore networks, and further, on supramolecular level, the diffusion of alkali solution into the less ordered amorphous and quasi-crystalline phases of the cellulose II polymer. Fourier-Transform Infrared spectroscopy (FT-IR) is currently one of the best available techniques in the textile science to obtain structural information (Široká et al., 2011), which has been universal accepted for many years as a powerful tool for analytical and chemical characterisation in wide range of scientific disciplines and widely used in polymer characterisation, providing information about chemical nature, isomerisation, conformational order, state of order, and orientation. Using FT-IR, a clear relationship between interaction of hydroxyl groups and crystallinity in cellulose has been established, and numerous papers have been published in relation to infrared spectroscopy analysis of

native cotton and mercerised cotton as well as regenerated fibres (Hurtubise & Krassig, 1960; Nelson & O'Connor, 1964; Široký et al., 2010) in order to establish or develop the ratio indices of absorption bands, crystallinity indices, the so-called '*total crystallinity index*' (TCI) and '*lateral order index*' (LOI). TCI represents the overall degree of order in cellulose given by the ratio of absorption at 1372 cm^{-1} (C–H deformation in cellulose II) and 2892 cm^{-1} (C–H stretch in cellulose II). LOI reflects the ordered regions perpendicular to the chain direction, which is greatly influenced by chemical processing of cellulose. This index is calculated as the ratio of two signals, at 1418 cm^{-1} (CH$_2$ scissoring at C(6) in cellulose II) and at 894 cm^{-1} (C–O–C valence vibration of β-glycosidic linkage). First band decreases and second one increases as crystallinity decreases. Attenuated Total Reflectance Fourier-Transform Infrared (ATR-FTIR) spectroscopy analysis is appropriate methods for gathering spectroscopic data, IR absorbance bands are particularly sensitive to the vibrations of polar groups such as OH groups as well as quite reasonable to the non-polar skeletal bonds such as C–C and C–O, and C-H. Therefore, it was used to observe the qualitative crystallinity changes in lyocell fabrics following continuous treatment with sodium hydroxide.
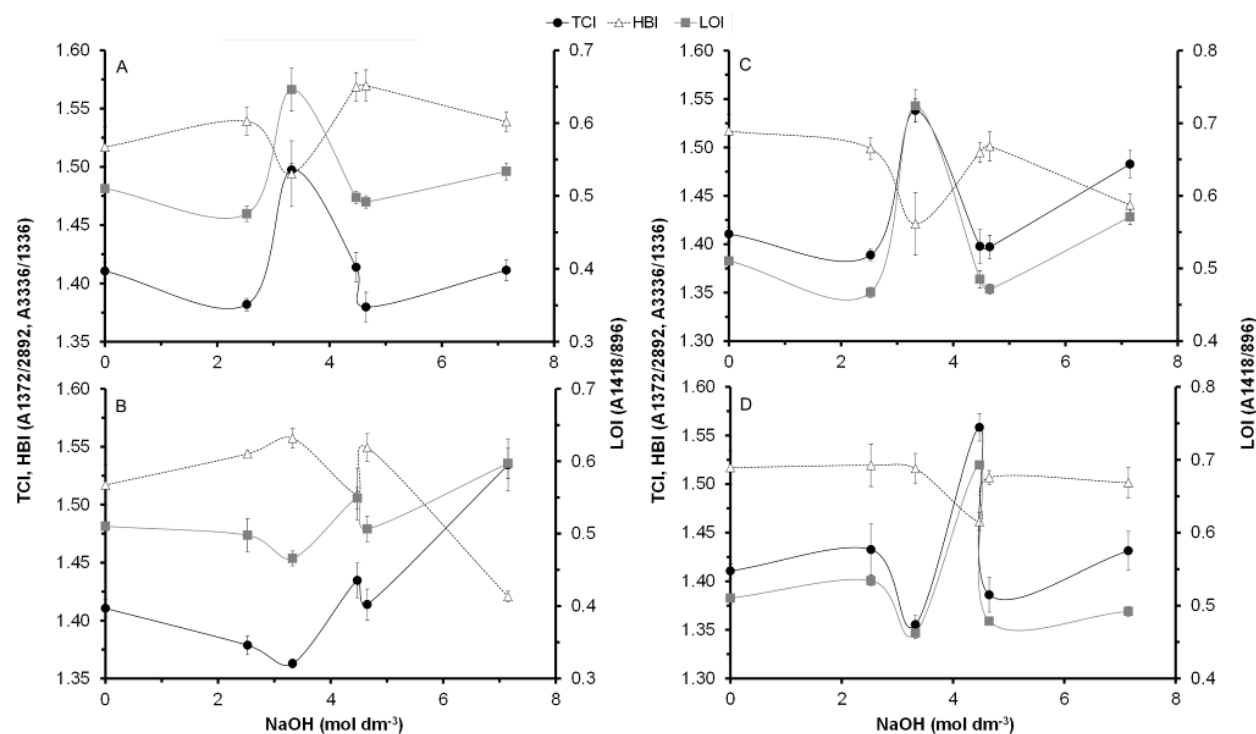

Fig. 11. Total crystallinity index (TCI; ◆), lateral order index (LOI; ●) and hydrogen bonding intensity (HBI; ○) of plain woven lyocell fabrics with increasing sodium hydroxide concentration in treatment stage, under varying (49 or 147 N m^{-1}) and temperature (25 or 40 °C) in treatment stage of continuous alkali treatment: A) 49/25; B) 49/40; C) 147/25; D) 147/40.

The results and comparisons of crystallinity indices (Fig. 11), TCI and LOI, and hydrogen-bond intensity (HBI) against NaOH treatment concentration shown parallel behavior over the whole range of concentrations and process conditions, although the absolute values differ. There were observed maxima for TCI and LOI, and minima for HBI for all examined lyocell fabrics at effective concentrations of 3.33 and 4.48 mol dm^{-3} NaOH, when treated at

25°C and 40°C, respectively. Under these treatment conditions, it was proposed therein that maximum molecular reorganisation occurs in the amorphous and quasi-crystalline phases of the cellulose II polymer, which are corresponding to the changes evidenced from evaluation of physico-chemical properties (Široký et al., 2009). Moreover, it was demonstrated that even subtle changes in ATR-FTIR spectra can substantially affect crystallinity indices.

4.3 Sorption properties

It is well known that the regenerated cellulosic fibres absorb significant quantities of water by the expansion of void spaces within the semi-crystalline morphology, forming a water-cellulose two-phase structure. Dyestuffs used for cellulosic fibres are highly water soluble, with molecular structures which are designed to interact at the internal interface between cellulose and water. The uptake of dyes is often used to monitor changes in fibre properties brought about by variations in processing, hence, dyes can be considered as coloured probe molecules that provide information on the detailed internal pore structure of fibres (Ibbett et al., 2006). The adsorption study of *hydrolyzed reactive dye*, namely C.I. Reactive Red 120 (RR120), on lyocell fabric was performed (Široký et al., 2011b) to gather information of the alkali treatment effect on the thermodynamics of the dye sorption and on changes in the fabric/fibre structure. Hydrolyzed reactive dye behaves essentially like a direct dye, which provides particular advantages of assurance that covalent bonding between the dye and fibre did not interfere with sorption, the substantivity (physical adsorption) is high and therefore, relatively short dyeing times can be employed as well as being used as molecular sensors to characterize cellulose substrate properties such as pore structure.(Inglesby & Zeronian, 2002; Luo et al., 2003)

Thorough study of dye adsorption revealed that sorption observed herein may occur *via* a combination of Langmuir, typical of limited side-specific adsorption, and Freundlich, indicating unlimited adsorption at non-specific sites, isotherms, although, sorption theory teaches that the interaction between dye molecules and cellulosic fibres is typically of Freundlich isotherm and based on hydrogen bonding and van der Waals interactions. On other site, carboxylate function groups, which are formed through oxidation of cellulosic fibres following mercerisation, are capable to provide anionic side-specific sides for adsorption. Interesting relation was obtained when the observations for equilibrium dye sorption (q_e) from aqueous solution onto a lyocell was compared with the *reacting structural fraction* (RSF) concept developed and established by Fink *et al.* (1986). The q_e of hydrolyzed RR120 by lyocell fabrics treated with varying concentrations of NaOH showed very similar shape of the plots with a maximum at *ca.* 3.50 mol dm^{-3} NaOH for lyocell, assigned to transition of cellulose II to its Na-cellulose II form following break of inter-molecular hydrogen bonds. Subsequent decrease within the respective transition ranges occurred to *ca.* 4.50 mol dm^{-3} NaOH for cellulose II. A second maximum occurred at *ca.* 4.75 mol dm^{-3} for cellulose II which is caused by an additional increase in the RSF of the polymer, relative to disruption of the intra-molecular hydrogen bonds in the Na-cellulose II form. Increasing treatment concentration of NaOH causes strong lateral fibre swelling and subsequently increases accessible internal volume within the structure of the fibre. Therefore, the observed differences in sorption may be explained by the accessible pore volume (APV) of lyocell fibres to probes as a function of NaOH concentration previously studied by Özturk *et*

al. (2009) using inversion size exclusion chromatography (ISEC). It was demonstrated that for pore diameters of 19 Å and below that APV increased with increasing NaOH concentration to a maximum around 2.5 mol dm^{-3} NaOH, which was ca. 10% higher than for untreated lyocell. Applying molecular dynamics, the geometry and electronic properties of hydrolyzed RR120 were explored, and it was found that the dimensions of employed dye are about 30 Å (length) × 14 Å (wide) × 3.5 Å (depth) in one of the minimum energy states, providing a molecular diameter of 14 Å (end-on). It is less than 19 Å and therefore, it is likely that the maximum APV at around 2.5 mol dm^{-3} NaOH observed by (Özturk et al., 2009) influences the accompanying maxima in the theoretical monolayer capacity (q_0) and adsorption energy (ΔG^0) also known as a standard free energy of dyeing or standard affinity of the dye for the substrate, which was indeed observed from the experimental results.

The measurement of *iodine sorption* has been frequently applied in order to study an accessibility of cellulosic fibers.(Nelson et al., 1970; Schwertassek K., 1956; Široká et al., 2008; Strnad et al., 2001) This method has also been employed as a measure of fiber crystallinity.(Elesini U. S. & Cuden A. P., 2002; Hessler & Power, 1954; Zemljic et al., 2008) The computation of substrate crystallinity from iodine sorption value is based on the principle that iodine sorption in substrates is limited only to amorphous regions. However, earlier studies have shown that iodine penetrates into crystalline regions when the adsorption exceeds 11-12%, and the potassium iodide, in which the iodine is dissolved, acts as a swelling agent for cellulose.(Doppert H. L., 1967) These factors will influence results of iodine sorption. Hence, the iodine sorption may be better regarded as a general measure of overall accessibility in substrates. From the iodine sorption experiments performed on alkali treated lyocell fabrics, it was observed that the results do not follow the crystallinity results obtained by ATR-FTIR method. It seems that not only crystallinity of alkali treated lyocell fabrics swelling which is generally considered to increase accessibility of substrates, but also the construction of substrate can significantly influence the accessibility to iodine.

4.4 Woven lyocell structure effect on sodium hydroxide release (wash-off)

While in previous sections the discussion was oriented to the extended study of lyocell plain woven fabrics with effect of alkali concentration, treatment temperature and applied tension based on the previous work (Široký et al., 2010, 2011b; Široký et al., 2009), in this chapter, the influence of fabric structure (plain-, twill-, or sateen-woven fabrics) on NaOH release from lyocell after pad-batch pre-treatment (Široký et al., 2011a) will be explored by conductivity measurements in the system of deionized water-NaOH impregnated assemblies-the wash-off bath. Weaving of the fabric is distinguished according to the manner the yarns or threads, longitudal-warp and lateral-weft, are interlaced to form fabric or cloth. Three basic weaves are used the most, plain-, twill- or sateen-weaving. Differences in fabric weaving or construction provide also differences in terms of accessibility, substrate surface and compactness, fabric diffusion, swelling, and fabric bulk density and porosity.

Different fabric construction of the same fibre and yarn, herein weaving, plays a crucial role in liquid-fabric interactions. For example, wet pick-up (*WPU*) differs, which in turn effects the swelling, bulk density, or porosity of such a porous substrate as it shown in Fig. 12. Due to mathematical complexicity, only the changes on the macro-level were further investigated by measuring the conductivity in the wash bath and applying Crank's approximation, the Crank's equation for the flow through a membrane(Crank, 1975):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\exp\left(\frac{-\pi^2 D t}{l^2}\right) \tag{1}$$

where, M_t is conductivity at a given time (mS cm^{-1}), M_∞ is conductivity at wash-off equilibrium or the corresponding conductivity during infinite time (mS cm^{-1}), D is the diffusion coefficient (m^2 s), l is half of the sheet (layer) thickness, because diffusion takes place from both its sides (m), and t is time (s). Herein, the factor ($-\pi^2 D/l^2$) was used as "alkali transport coefficient" K and was determined from the slope of $\ln(1 - M_t/M_\infty) = f(t)$.
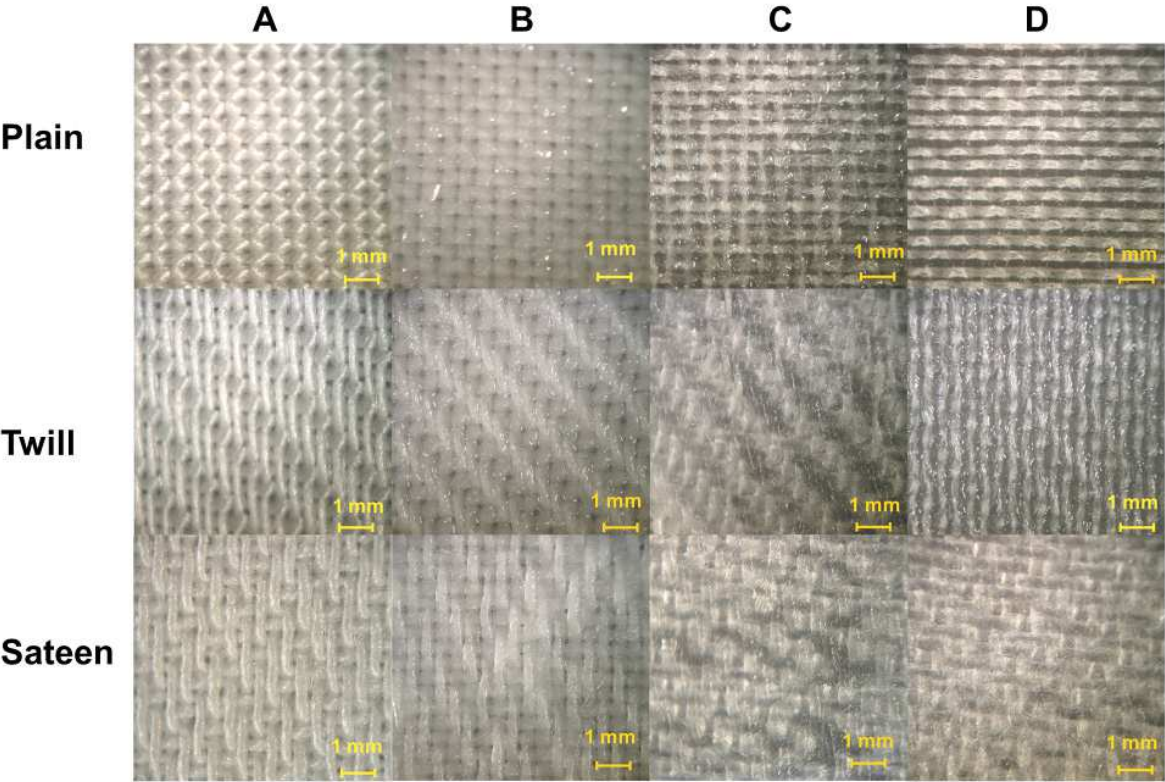
Fig. 12. Changes in wet pick-up and porosity of loom-state fabric (A-untreated) and swollen fabric after dropping NaOH solution of different concentration: B-0.7, C-3.0, or D-5.0 mol dm^{-3} on fabric of different construction (plain-, twill-, or sateen-woven fabric). An optical microscope (Krüss, Germany) combined with a digital camera (Canon Power Shot S40) was used for taking microphotographs. A sample of 1 x 1 cm size was placed on a glass slide and NaOH solution was dropped on the substrate. After 10 s, the picture was taken.

The kinetics of the system is a complex system with many parameters/components involved. Briefly, cellulose accessibility is dependent on the available inner surface, supramolecular order (range of degrees of order), fibrillar architecture, and pore structure. Interactions of cellulose with water which consequently destroys weak hydrogen-bonds, but cannot penetrate into regions of high order, in contrast to aqueous solutions of sodium hydroxide. Additionally, a significant role associated with pores, capillaries, and the network of voids, which do not have uniform size and shape need to be considered, and also NaOH treatment causes changes in pore structure (shape and size).(Bredereck & Hermanutz, 2005) Liquid absorption leads to swelling of the substrate (see Široký et al.

(2011a)), which alters the dimensions of the fibre, and this, in turn, causes changes in both physical properties (size, shape, stiffness, and permeability of yarns and fabrics, sorption/desorption characteristics)(Morton & Hearle, 1993; Široká et al., 2008) and mechanical properties (tensile modulus, breaking stress).(Kongdee et al., 2004) Moreover, the "skin-core" effect of lyocell fibres exists, wherein a fibre structure consists of different regions, which may lead to a diffusional boundary layer and hence, cause significant changes in concentration gradient within the substrate.
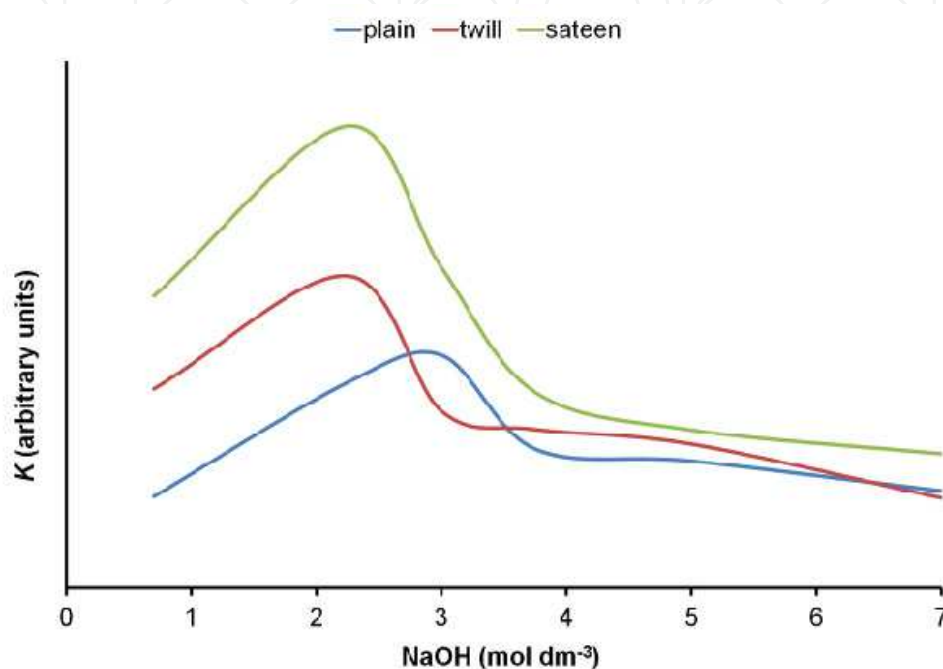
Fig. 13. Trend lines based on calculated liquid transport coefficients (*K*) at different NaOH treatment concentrations.

An alkali transport coefficient (*K*) was established to quantify alkali release, which represents the liquid-side mass transfer of alkali release after a pad-batch process into the wash-bath.(Široký et al., 2011a) Three regions of NaOH-release behavior were observed (Fig. 13) and two competitive phenomena related to swelling, an increase of the substrate surface, and the substrate compactness, have been recognized. Firstly (up to 2.25 mol dm^{-3}), the influence of fabric-alkali interactions and non-uniform access of NaOH determines alkali release, and also the absolute K value is mainly determined by the bulk densities (plain 0.4998, twill 0.4622 and sateen 0.4096 g cm^{-3}) and porosities (plain 0.671, twill 0.696 and sateen 0.731) and thus, it increases continuously as the material is still not fully swollen. The maximum swelling of cellulose fibers occurs between 2.25-3.00 mol dm^{-3} NaOH; here, maximum K is observed as well as dependency on fabric construction is still determining factor. Above 3.75 mol dm^{-3} NaOH, the treated substrates are highly swollen sheets and the K does not show dependency on fabric constructions, thus, the fabric construction is not relevant at this range anymore for the alkali-diffusion and the approximation of plain sheet diffusion corresponds to the real situation. As shown in this study, alkalization and release during wash-off are governed by fabric structure and alkali concentration. This finding is of particular relevance for an optimized processing of fabrics from regenerated cellulose fibers.

5. Conclusion

The unique feature of cellulosic substrates to absorb moisture from the air or absorption of water or other solution, for example sodium hydroxide, causes swelling of this substrate. Then expansion of the fibre, yarn, or fabric occurs due to the swelling in liquid media. By continuous growth of fibre, yarn, or fabric, the accessibility becomes restricted as the porosity or the inter- and intra-yarn pores and/or inter-spaces diminish. Hence, NaOH treatment influences physical properties such as stiffness, shrinkage, water retention value and wet pick-up, mechanical properties such as tension, break force, elongation, crease recovery angle and mass loss.

Also, it was shown and discussed herein that alkalization and release during wash-off are governed by fabric structure and alkali concentration. This finding is of particular relevance for an optimized processing of fabrics from regenerated cellulose fibres. While in technical processing, materials consisting from the same type of fibre and with similar mass per area are considered to behave identical during alkalization the present results show the need for individual process adaptation.

It is obvious that the cellulose is very complex material and there is still limited knowledge available in this field rather containing more questions and uncertainties. A representative example is alkali treatment of this substrate with ongoing research more than 160 years and always some gaps within this area are recognised. In recent years, it can be seen that the field of cellulose, cellulose derivatives, or polysaccharides is expanding largely due its recognised wide potential and also its environmental benefit. Therefore, the long-term task for present and future research in cellulose is the development of novel processes which yield no or minimal ecologically harmful by-products. If these efforts are successful, cellulose will maintain and strengthen its position as a renewable and environmentally beneficial, industrially important raw material competing with synthetically produced polymers.

6. Acknowledgment

7. References

Abu-Rous, M. (2006). *Characterisation of the wet-state pore structure of lyocell and other man-made cellulosic fibres by fluorescence and electron microscopy.* PhD Thesis, University of Innsbruck, Dornbirn.

Beaudet, T. (1999). In: *What is Mercerized cotton?*, Available from: http://fiberarts.org/design/articles/mercerized.html

Biganska, O. (2002). *Etude physico-chemique des solutions de cellulose dans la N-methylmorpholine-Noxyde.* PhD Thesis, Centre de Mise en Forme des Materiaux (CEMEF), Sophia Antipolis, France.

Brancato, A. A. (2008). In: *Effect of progressive recycling on cellulose fiber surface properties.*, Retrieved 23.11.2009, Available from: http://etd.gatech.edu/theses/available/etd-07292008-213453/

Bredereck, K., & Hermanutz, F., (2005). Man-made cellulosics. *Review of Progress in Coloration and Other topics,* Vol. 35, No. 1, pp. 59-75,

Crank, J. (1975). Diffusion in a plane sheet, In: *The mathematics of diffusion*, pp. 44-68, Clarendon Press, ISBN: 0-19-853411-6, Oxford

Crawshaw, J., & Cameron, R. E., (2000). A small angle X-ray scattering study of pore structure in Tencel cellulose fibres and the effects of physical treatments. *Polymer,* Vol. 41, No. 12, pp. 4691-4698,

Crawshaw, J., Vickers, M. E., Briggs, N. P., Heenan, R. K., & Cameron, R. E., (2000). The hydration of TENCEL cellulose fibres studied using contrast variation in small angle neutron scattering. *Polymer,* Vol. 41, No. 5, pp. 1873-1881,

Diniz, J. M. B. F., Gil, M. H., & Castro, J. A. A. M., (2004). Hornification - its origin and interpretation in wood pulps. *Wood Science and Technology,* Vol. 37, No. 6, pp. 489-494, ISSN: 0043-7719

Donnan, F. G., (1924). The theory of membrane equilibria. *Chemical Reviews,* Vol. 1, No. 1, pp. 73-90, ISSN: 0009-2665

Doppert H. L., (1967). Adsorption of iodine from aqueous solutions by samples of tire yarn from regenerated cellulose. *Journal of Polymer Science. Part A-2: Polymer Physics*, Vol. 5, No. 2, pp. 263-270, ISSN: 0449-2978

Elesini U. S., & Cuden A. P., (2002). Study of the green cotton fibres. *Acta Chimica Slovenica,* Vol. 49, No. 4, pp. 815-833,

Fink, H. P., Dautzenberg, H., Kunze, J., & Philipp, B., (1986). The composition of alkali celluloce - a new concept. *Polymer,* Vol. 27, No. 6, pp. 944-948, ISSN: 0032-3861

Gindl, W., Martinschitz, K., Boesecke, P., & Keckes, J., (2006). Orientation of cellulose crystallites in regenerated cellulose fibres under tensile and bending loads. *Cellulose,* Vol. 13, No. 6, pp. 621-627, ISSN: 0969-0239

Goswami, P., Blackburn, R. S., El-Dessouky, H. M., Taylor, J., & White, P., (2009). Effect of sodium hydroxide pre-treatment on the optical and structural properties of lyocell. *European Polymer Journal,* Vol. 45, No. 2, pp. 455-465, ISSN: 0014-3057

Harvey, A. (2007). *Physicochemical mechanisms involved in the binding of antimicrobial agents to textile fibres.* PhD Thesis, University of Leeds, Leeds, UK.

Hatakeyama, H., & Hatakeyama, T., (1998). Interaction between water and hydrophilic polymers. *Thermochimica Acta,* Vol. 308, No. 1-2, pp. 3-22, ISSN: 0040-6031

Hessler, L. E., & Power, R. E., (1954). The Use of Iodine Adsorption as a Measure of Cellulose Fiber Crystallinity. *Textile Research Journal,* Vol. 24, No. 9, pp. 822-827, ISSN: 0040-5175

Hollemeyer, K., Altmeyer, W., Heinzle, E., & Pitra, C., (2008). Species identification of Oetzi's clothing with matrix-assisted laser desorption/ionization time-of-flight mass spectrometry based on peptide pattern similarities of hair digests. *Rapid Communications in Mass Spectrometry,* Vol. 22, No. 18, pp. 2751-2767, ISSN: 1097-0231

Hsieh, Y. L., (1995). Liquid Transport in Fabric Structures. *Textile Research Journal,* Vol. 65, No. 5, pp. 299-307, ISSN: 0040-5175

Hsieh, Y. L., Yu, B. L., & Hartzell, M. M., (1992). Liquid Wetting, Transport, and Retention Properties of Fibrous Assemblies .2. Water Wetting and Retention of 100-Percent and Blended Woven Fabrics. *Textile Research Journal,* Vol. 62, No. 12, pp. 697-704, ISSN: 0040-5175

Hurtubise, F. G., & Krassig, H., (1960). Classification of Fine Structural Characteristics in Cellulose by Infrared Spectroscopy - Use of Potassium Bromide Pellet Technique. *Analytical Chemistry,* Vol. 32, No. 2, pp. 177-181, ISSN: 0003-2700

Ibbett, R. N., Kaenthong, S., Phillips, D. A. S., & Wilding, M. A., (2006). Characterisation of the porosity of regenerated cellulosic fibres using classical dye adsorption techniques. *Lenzinger Berichte,* Vol. 85, No., pp. 77-86,

Inglesby, M. K., & Zeronian, S. H., (2002). Direct dyes as molecular sensors to characterize cellulose substrates. *Cellulose,* Vol. 9, No. 1, pp. 19-29, ISSN: 0969-0239

Jaturapiree, A. (2007). *Porosity and transport properties in the system cellulose fibre/aqueous medium-determination and modification of porosity* PhD Thesis, University of Innsbruck, Dornbirn, Austria.

Kamide, K., Okajima, K., Matsui, T., & Kowsaka, K., (1984). Study on the Solubility of Cellulose in Aqueous Alkali Solution by Deuteration Ir and C-13 Nmr. *Polymer Journal,* Vol. 16, No. 12, pp. 857-866, ISSN: 0032-3896

Kissa, E., (1996). Wetting and wicking. *Textile Research Journal,* Vol. 66, No. 10, pp. 660-668, ISSN: 0040-5175

Klemm, D., Heublein, B., Fink, H. P., & Bohn, A., (2005). Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie-International Edition,* Vol. 44, No. 22, pp. 3358-3393, ISSN: 1433-7851

Klemm, D., Philipp, B., Heinze, T., Heinze, U., & Wagenknecht, W. (1998). Fundamentals and analytical methods, In: *Comprehensive Cellulose Chemistry*, Wiley - VCH, Weinheim, Germany

Kong, K., Davies, R. J., McDonald, M. A., Young, R. J., Wilding, M. A., Ibbett, R. N., & Eichhorn, S. J., (2007). Influence of domain orientation on the mechanical properties of regenerated cellulose fibers. *Biomacromolecules,* Vol. 8, No. 2, pp. 624-630, ISSN: 1525-7797

Kongdee, A., Bechtold, T., Burtscher, E., & Scheinecker, M., (2004). The influence of wet/dry treatment on pore structure-the correlation of pore parameters, water retention and moisture regain values. *Carbohydrate Polymers,* Vol. 57, No. 1, pp. 39-44,

Krässig, H. A. (1993a). *Cellulose: Structure, Accessibility and Reactivity*, Gordon and Breach Science, ISBN: 2881247989, Yverdon, Switzerland

Krässig, H. A. (1993b). Effect of structure and morphology on accessibility and reactivity, In: *Cellulose: Structure, Accessibility and Reactivity*, pp. 215-277, Gordon and Breach Science, ISBN: 2881247989, Yverdon, Switzerland

Kutschera, W., & Rom, W., (2000). Ötzi, the prehistoric Iceman. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* Vol. 164-165, No. 0, pp. 12-22, ISSN: 0168-583X

Leighton, A., (1916). The adsorption of caustic soda by cellulose. *Journal of Physical Chemistry,* Vol. 20, No. 1, pp. 32-50, ISSN: 0022-3654

Luo, M., Zhang, X. L., & Chen, S. L., (2003). Enhancing the wash fastness of dyeings by a sol-gel process. Part 1: Direct dyes on cotton. *Coloration Technology,* Vol. 119, No. 5, pp. 297-300, ISSN: 1472-3581

Mercer, J. (1851). Improvement in chemical processes for fulling vegetable and other textures, England, Patent No. 8,303, US Patent.

Morton, W. E., & Hearle, J. W. S. (1993). An Introduction to fibre structure, In: *Physical Properties of Textile Fibres*, pp. 1-73, The Textile Institute, ISBN: 1-870812-41-7, Midsomer Norton, Bath, UK

Neale, S. M., (1929). The swelling of cellulose, and its affinity relations with aqueous solutions. Part I - Experiments on the behaviour of cotton cellulose and regenerated cellulose in sodium hydroxide solution, and their theoretical interpretation. *Journal of the Textile Institute Transactions,* Vol. 20, No. 12, pp. T373-T400,

Nelson, M. L., & O'Connor, R. T., (1964). Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Type. Part II. A New Infrared Ratio for Estimation of Crystallinity in Celluloses I and II. *Journal of Applied Polymer Science,* Vol. 8, No. 3, pp. 1325-1341,

Nelson, M. L., Rousselle, M.-A., Cangemi, S. J., & Trouard, P., (1970). The Iodine Sorption Test. Factors Affecting Reproducibility and a Semimicro Adaptation. *Textile Reseach Journal,* Vol. 40, No. 10, pp. 872-880,

Okano, T., & Sarko, A., (1984). Mercerization of Cellulose .1. X-Ray-Diffraction Evidence for Intermediate Structures. *Journal of Applied Polymer Science,* Vol. 29, No. 12, pp. 4175-4182, ISSN: 0021-8995

Özturk, H. B., Potthast, A., Rosenau, T., Abu-Rous, M., MacNaughtan, B., Schuster, K. C., . . . Bechtold, T., (2009). Changes in the intra- and inter-fibrillar structure of lyocell (TENCEL[R]) fibers caused by NaOH treatment. *Cellulose,* Vol. 16, No. 1, pp. 37-52, ISSN: 0969-0239

Porro, F., Bedue, O., Chanzy, H., & Heux, L., (2007). Solid-state C-13 NMR study of Na-cellulose complexes. *Biomacromolecules,* Vol. 8, No. 8, pp. 2586-2593, ISSN: 1525-7797

Rosen, M. J. (2004). Wetting and its modification by surfactants, In: *Surfactants and interfacial phenomena*, M. J. Rosen (Ed.), Wiley-Interscience, Hoboken, New Jersey

Schuster, K. C., Aldred, P., Villa, M., Baron, M., Loidl, R., Biganska, O., . . . Jericha, E., (2003). Characterising the emerging lyocell fibres structures by ultra small angle neutron scattering. *Lenzinger Berichte,* Vol. 82, No., pp. 107-117,

Schwertassek K., (1956). Praktische Methoden der Strukturforschung an Faserstoffen. *Textilpraxis,* Vol. 11, No., pp. 762-767,

Široká, B., Noisternig, M., Griesser, U. J., & Bechtold, a. T., (2008). Characterization of cellulosic fibers and fabrics by sorption/desorption. *Carbohydrate Research,* Vol. 343, No. 12, pp. 2194-2199,

Široká, B., Široký, J., & Bechtold, T., (2011). Application of ATR-FT-IR Single-Fiber Analysis for the Identification of a Foreign Polymer in Textile Matrix. *International Journal of Polymer Analysis and Characterization,* Vol. 16, No. 4, pp. 259 — 268,

Široký, J., Blackburn, R. S., & Bechtold, T., (2011a). Influence of fabric structure on NaOH release from woven lyocell type material. *Textile Research Journal,* Vol. 81, No. 16, pp. 1627-1637,

Široký, J., Blackburn, R. S., Bechtold, T., Taylor, J., & White, P., (2010). Attenuated total reflectance Fourier-transform Infrared spectroscopy analysis of crystallinity changes in lyocell following continuous treatment with sodium hydroxide. *Cellulose,* Vol. 17, No. 1, pp. 103-115, ISSN: 0969-0239

Široký, J., Blackburn, R. S., Bechtold, T., Taylor, J., & White, P., (2011b). Alkali treatment of cellulose II fibres and effect on dye sorption. *Carbohydrate Polymers,* Vol. 84, No. 1, pp. 299-307, ISSN: 0144-8617

Široký, J., Manian, A. P., Široká, B., Abu-Rous, M., Schlangen, J., Blackburn, R. S., & Bechtold, T., (2009). Alkali Treatments of Lyocell in Continuous Processes. I. Effects of Temperature and Alkali Concentration on the Treatments of Plain Woven Fabrics. *Journal of Applied Polymer Science,* Vol. 113, No. 6, pp. 3646-3655, ISSN: 0021-8995

Sobue, H., Kiessig, H., & Hess, K., (1939). The cellulose-sodium hydroxide-water system subject to the temperature. *Zeitschrift Fur Physikalische Chemie-Abteilung B-Chemie Der Elementarprozesse Aufbau Der Materie,* Vol. 43, No. 5, pp. 309-328, ISSN: 0372-9664

Strnad, S., Kreze, T., Stana-Kleinschek, K., & Ribitsch, V., (2001). Correlation between structure and adsorption characteristics of oriented polymers. *Materials Research Innovations,* Vol. 4, No. 2-3, pp. 197-203, ISSN: 1432-8917

Warwicker, J., (1969). Swelling of Cotton in Alkalis and Acids. *Journal of Applied Polymer Science,* Vol. 13, No. 1, pp. 41-54,

Woodings, C. R., (1995). The development of advanced cellulosic fibres. *International Journal of Biological Macromolecules,* Vol. 17, No. 6, pp. 305-309, ISSN: 0141-8130

Zemljic, L. F., Persin, Z., Stenius, P., & Kleinschek, K. S., (2008). Carboxyl groups in pre-treated regenerated cellulose fibres. *Cellulose,* Vol. 15, No. 5, pp. 681-690, ISSN: 0969-0239

Zhang, W. (2004). *Characterisation of cellulosic fibres: The structure of cellulose fiber and changes of fibre properties in textile processing.* PhD Thesis, University of Innsbruck, Innsbruck, Austria.

Zhang, W. S., Okutbayashi, S., & Bechtold, T., (2005). Fibrillation tendency of cellulosic fibers - Part 4. Effects of alkali pretreatment of various cellulosic fibers. *Carbohydrate Polymers,* Vol. 61, No. 4, pp. 427-433, ISSN: 0144-8617

Woven Fabrics

Edited by Prof. Han-Yong Jeon

ISBN 978-953-51-0607-4

Hard cover, 296 pages

Publisher InTech

Published online 16, May, 2012

Published in print edition May, 2012

"Woven Fabrics" is a unique book which covers topics from traditional to advanced fabrics widely used in IT, NT, BT, ET, ST industry fields. In general, woven fabrics are known as the traditional textile fabrics for apparel manufacturing and are used widely in various fabric compositions as intermediate goods that affect human activities. The relative importance of woven fabrics as traditional textile materials is extremely large and currently application fields of woven fabrics as technical textiles are rapidly expanded by utilizing its geometric features and advantages. For example, the book covers analytical approaches to fabric design, micro and nano technology needed to make woven fabrics, as well as the concept for industrial application.

INTECH

open science | open minds