A New Method to Visualize and Characterize the Pore Structure of TENCEL® (Lyocell) and Other Man-Made Cellulosic Fibres Using a Fluorescent Dye Molecular Probe

Mohammad Abu-Rous,[1]* Ksenija Varga,[1] Thomas Bechtold,[1] Kurt Christian Schuster[2]

[1]*Christian-Doppler Laboratory for Textile and Fibre Chemistry in Cellulosics, Institute of Textile Chemistry and Textile Physics of the Leopold-Franzens University Innsbruck, A-6850 Dornbirn, Austria*
[2]*Textile Innovation, Lenzing AG, A-4860 Lenzing, Austria*

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ABSTRACT: The internal porous structures of the man-made cellulosic fibers Lyocell (TENCEL®), Modal, and Viscose fibers were visualized by applying fluorescence microscopy on fiber cross sections. The fiber pore structure was probed by the optical brightener Uvitex BHT, and the dye penetration depth was measured. The main differences in the pore structures of these three fiber types could be visualized. Only TENCEL shows a significant difference between dried and never-dried fibers. A fiber structure model of TENCEL was obtained, which discriminates three different porous zones with respect to dye diffusion kinetics. The results are discussed in relationship with the fiber physical and chemical properties. The dye penetration depth and kinetics in TENCEL fibers was found to be sensitive to the production and treatment conditions, in particular to changes in the pore system by drying, and following alkali swelling processes. The performance of surface-specific enzymatic peeling could also be observed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2083–2091, 2007

Key words: structure; fluorescence; dyes/pigments; diffusion; cellulosic fibers

INTRODUCTION

A key to a better comprehension of the phenomena which occur on cellulosic fibers at the swollen state during the aqueous textile processes and treatments would be the understanding of the cellulose/pore network. The structure of fibers can and must be described at various ranges of size and levels of organization.[1] Cellulose molecules vary in the length of chains (the average degree of polymerization, respectively) and its distribution. The supramolecular structure is described in terms of crystalline and noncrystalline regions by the degree of crystallinity, orientation, and dimensions of these regions.[2,3] The higher morphological structure includes fibrillar elements and pores.[4–6] Finally, the shape and homogeneity of fiber cross section is a marked feature.

In the man-made cellulosic fibers, the resulting pore structure depends on the spinning and precipitation conditions of each fiber type.

The main process to produce man-made cellulosic fibers is the Viscose process, based on transforming the cellulose into cellulose xanthate which is soluble in alkali solutions, and precipitating the spun fibers into acid. The combination of cellulose xanthate coagulation and the cellulose regeneration leads to the known skin/core structure of the Viscose fibers. Already in earlier works descending from the 50s of the last century,[7,8] the relationship between the spinning and the precipitation conditions in Viscose technology and the resulting fiber morphology were discussed. The understanding thereof built the basis of the further improvements in this technology.

Modal is a further development in the Viscose technology, modifying the regeneration bath[9,10] and obtaining fibers of high wet modulus, which have an all-skin structure (compared with the Viscose fibers with the two characteristic structure zones). The fibers have a much higher tensile strength without decreasing the elongation. They also perform a higher dye uptake and a higher stability toward alkali swelling than classical Viscose fibers. Although Modal fibers have been commercially available since the 60s, not many detailed investigations in the fiber

Correspondence to: K. C. Schuster (c.schuster@lenzing.com).
*Present address: Textile Innovation, Lenzing AG, A-4860 Lenzing, Austria.
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pore network were published on this fiber type, as far as known.

The internal porous network structure of TENCEL® (generic name: Lyocell) fibers has been a subject of debate. The round fiber with the smooth surface differs radically from the other known cellulosics. The shape difference includes also differences in the precipitation process, crystallization form and grade, the orientation, and hence the surface morphology and the pore structure of the resulting fibers.[11–14]

Based on the general model for the precipitation of polymers at spinning[15] and on microscopic observation on the precipitation of blocks of NMMO (*N*-methyl-morpholine-oxide)-dissolved cellulose, a recent model was made by Biganksa on the morphology resulting from different precipitation conditions. Following this model, fibers result from a fast crystallization, which would provide for a system with compact fiber core, a porous middle zone and a semipermeable fiber skin (Fig. 1).[16]

Although this model was achieved following experiments on the crystallization out of dope blocks in size of millimeters and not in the dynamic spinning process leading to fibers of some 10 μm diameter, some parallel characteristics can also be seen in the structure of TENCEL fibers.

Known methods, such as water retention value (WRV) measurements give quantitative information about the pore structure.[17] Inverse size exclusion chromatography (ISEC) gives also the pore size distribution.[18] The results from dye kinetic studies based on measuring the direct dye uptake from the solution did not show any direct correlation with the WRV and ISEC results.[6,19] Both approaches deliver average values of the pore size and accessibility, but until now no much systematic work was done to visualize the dye kinetics inside the internal fibril structure of TENCEL.

A study by Kasahara et al.[20] delivered a correlation between the WRV and the ISEC results and suggested that the differences between the two methods are to be attributed to properties of the water absorbed on the fibers surface, which amount is more significant for the WRV than for the ISEC method. The correlation was also given for Lyocell fibers dyed with monofunctional reactive dyes, but a deviation from the correlation equation was observed on fibers dyed with bifunctional dyes, which was attributed to specific dye/crosslinking effects.

A more detailed investigation by Gruber[19] showed that applying direct dyes divided the cellulosic fibers into three groups, namely, cotton fibers, solvent spun fibers (Lyocell and Cupro), and Viscose fibers (Viscose and Modal). It showed that the dyeing depends on the chemical constitution and the structure and size of the dye molecules and probably on the

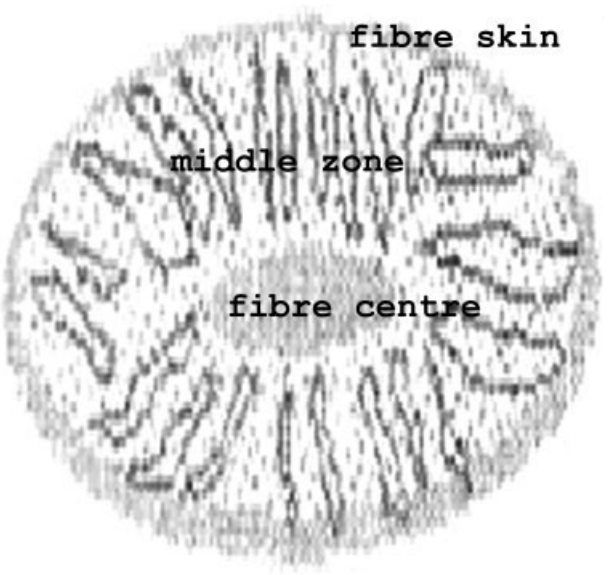

Figure 1 A structure model of TENCEL fibers following the crystallization model of cellulose solids from NMMO by Biganska[16] based on the membrane formation theory.[15] The model proposes a semipermeable, very thin skin, a porous middle zone, and a rather compact fiber center.

absorption mechanism of the dye uptake by cellulosic fibers. The study showed also that for a better understanding of the difference in dye uptake a more detailed knowledge is required about the dimensions and the distribution of the accessible fiber pores and their role in the interaction with the dye.

Dye absorption has been used for studying the porous structure of cellulosic fabrics. Recent work by Ibbett and Kaenthong characterized various manmade cellulosic fibers according to there quantitative accessibility for textile dyes.[21]

One missing detail in earlier studies was the localization of the absorbed dyestuff within the fiber pore network, and more generally the distribution of pores in the cross section of the fiber. A transmission electron microscopy (TEM) study visualized the localization and size distribution of water-filled pores in cellulosic fibers. Different zones of porosity could be shown within the fiber cross section.[22,23]

The nanometer-sized, very evenly distributed pores in TENCEL appear to be connected to the special comfort-in-wear properties of TENCEL textiles.[24]

To localize the zones and to visualize the pore distribution within the fiber with respect to the dye penetration, dyeing with specific substances and fluorescence microscopy on fiber cross sections dyed with Uvitex BHT was found to be a new simple method to investigate the pore distribution within the fiber by visualization.[25]

The fluorescent brightener agent Uvitex-BHT (CIBA-Ceigy, Grenzach, Germany) is a recommended whitening agent for cellulosic fibers.[26] It con-

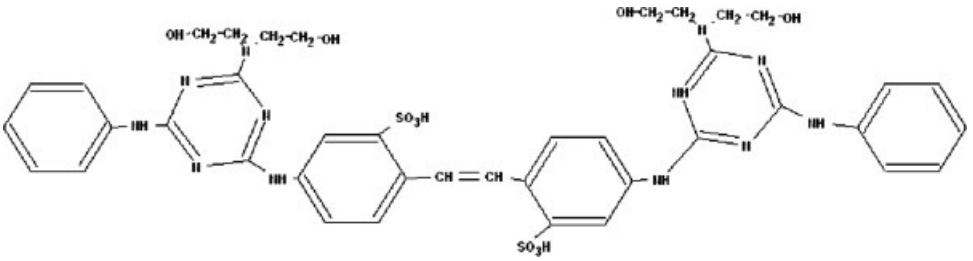

Figure 2 Chemical structure of Calcofluor.

tains a fluorescent dye based on diaminostilbenedisulphonic acid (DAS), which is characterized by a planar molecule and a conjugated ring system.[27] It has a high substantivity and is usually carried on the fibers by applying the exhausting process.[28] The structure is similar to the well-known Calcofluor M2R (MW 960; Fig. 2). It was noticed that it has a limited diffusion into the fiber insides. It is known from earlier works on substantive dyes[29] that the diffusion depends obviously on the properties of the porous zones and on the aggregation form of the dye. In the commercial product Uvitex BHT, the fluorescent dye seems to be held in a highly disperse form leading to a higher solubility than the dye calcofluor.

MATERIALS

Lyocell is the generic name for cellulose fibers spun from organic solvents, commercially in NMMO. Lenzing (Lenzing, Austria) AG produces Lyocell fibers under the brand name TENCEL. As recently several other solvents are approaching technical use, we use the brand name TENCEL for the fibers used in this work.

In this work, 1.3 dtex fibers were investigated.

For the experiments on the caustic-treated fabrics, 100% 1.3 dtex TENCEL, 50/1 Nm ring yarns, plain weave were investigated.

All fiber and fabric samples were kindly supplied by Lenzing AG. Table I gives an overview of the investigated samples.

Oversaturated aqueous preparation (120%) of Uvitex-BHT™ was purchased from CIBA-Ceigy (Germany).

TENCEL®, Lenzing Modal®, and Lenzing Viscose® fibers were kindly supplied by Lenzing AG, Austria.

Embedding resin Technovit™ was delivered by Kulzer, Vienna, Austria. It contains the basic solution based on 2-hydroxyethylmethacrylate, Hardener I, and Hardener II.

Fiber cross sections were prepared using a Reichert microtome (model: 1140/Autocut).

The fluorescence imaging was performed using an Olympus BX microscope equipped with a mercury burner lamp, monochromatic filters, and a digital camera system (Analysis; Olympus, Hamburg, Germany).

For the enzymatic treatment, Econase HC 400 (AB Enzymes, Rajamäki, Finland) and Celluclast (Novozymes AIS, Kalundborg, Denmark) were used in a 1 : 2 mixture. One volume part of the mixture was diluted with 2 parts H_2O and 27 parts acetate buffer, pH 4.02 (50 mM sodium acetate, pH set with acetic acid).

TEM: For the sample preparation, Isopren, Aceton, and azobis-isobutyronitrile (AIBN) were purchased from Fluka. The cross-section preparation and TEM were performed at FELMI, Technical University of Graz.

EXPERIMENTAL

One gram of a shaken technical oversaturated 120% solution of Uvitex BHT from CIBA, used as supplied (contains fluorescent dye in a highly dispersed form), was dissolved in 1 L water. The solution filtered on a microfilter (0.45 μm HV) to remove visible particles. This solution (1 mL) was diluted with water to 50-fold and the UV spectrum was measured. The absorption maxima are at 207 (absorption 0.441), 238 (absorption 0.361), and 349 nm (absorption 0.311).

In a closed flask on a shaking platform (250 r/min), 0.2 g sample was dyed in 40 mL of this solution for different times (10 min, 4 h, and 24 h if no other dyeing time mentioned). The samples were washed twice 10 min in water in the same device, and dried at room temperature.

TABLE I
Specification of the Investigated Fibre and Woven Fabric Samples

Sample	Fibre type	From	Sample	Stage
1	TENCEL	Fibres	1A	Never-dried
			1B	Dried – lab, 60°C, 6 h
			1C	Dried – plant, 120°C, 10 min
			1D	Enzyme-treated, 60 min
			1E	Enzyme-treated, 120 min
2	Viscose	Fibres	2A	Never-dried
			2B	Dried – lab, 60°C, 6 h
3	Modal	Fibres	3A	Never-dried
			3B	Dried – lab, 60°C, 6 h
4	TENCEL	Woven fabric	4A	Untreated
			4B	NaOH-treated

The fiber bundles resp. yarns were inserted through a hole in the lower part of a gelatin capsule and the hole was closed using a commercial glue.

One gram of Hardener I was dissolved in 100 mL of base solution (5 min). This solution is stable for 4 weeks at 4°C. To 15 mL of this solution, 1 mL Hardener II was added. The resulting solution was poured immediately into the capsules while the sample is kept in a vertical position. The capsules were closed and the polymerization started within few minutes. The hardening process is terminated in ~ 2 h at room temperature.

Fiber cross sections with the thickness of 8 μm were prepared using a Reichert microtome (model: 1140/Autocut). The sample cross sections were cut at room temperature into a glycerine drop, taken out carefully, positioned flatly into a glycerine drop on a microscope slide, and covered with a quartz plate.

The fluorescence on fibers and fiber cross sections was observed using an Olympus BX microscope equipped with a mercury burner lamp, monochromatic filters, and a digital camera system (Analysis). The dye penetration depth was observed.

The imaging was performed on the cross section at 380–425 nm excitation, and 450 nm emission wavelength.

The dye penetration depth was measured at each fiber in the sample at 2000× magnification and an average was calculated. The standard deviation was around 0.2–0.3 μm within a sample.

The visible width of the dyed ring was measured manually (Fig. 3) and determined from the average of at least 15 different representative fibers of each sample. The maximum penetration depth, i.e., when the dye reached the fiber center, was 7 μm.

The penetration depth measurements were taken using Analysis imaging program. The resolution on the screen is obviously higher than on any printed image. The depth measurements were therefore taken directly on the screen. The measurement begins on the sharply seen fiber surface, and ends in the point where ''black'' is considered. The measurement was repeated by the same operator on several fibers. The deviation within the blurry uncertainties is about 0.5 μm. The standard deviation was around 0.2–0.3 μm within a sample.

The dye intensity was compared subjectively after imaging the samples at 200× magnification at the same exposure time within a series of samples.

Alkali treatment on woven fabric was performed at 14 °Bé (105 g/L) NaOH concentration. The fabric samples were dipped in the alkali solution, pressed at 1 bar, and washed after 2-min retention time (foulard).

Based on the TEM preparation technique of Hagege et al.,[30] the sample preparation for TEM by fixation of the swollen state by polymerizing isoprene inside the swollen pores after a slow solution exchange from water to acetone/isoprene was performed as published in an earlier work with OsO_4 staining of the polyisoprene.[23]

In the images, polyisoprene-filled pores appear dark (electron-dense), cellulose appear bright.

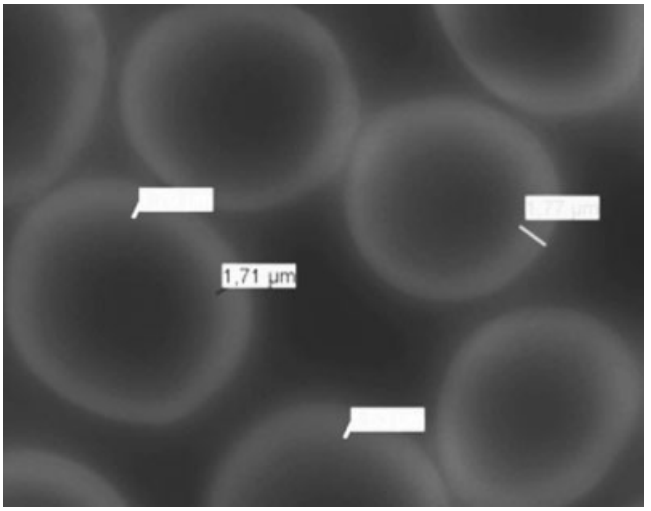

Figure 3 Measurement of dye penetration depth into TENCEL fibers.

RESULTS AND DISCUSSION

The method was applied to following issues:

A comparison between cellulosic fiber types

A comparison of the intrusion of Uvitex BHT into TENCEL, Viscose, and Modal fibers was made (Fig. 4). While on TENCEL fibers the diffusion depth increased with the time, the penetration depth on Viscose and Modal did not exceed the external zones. On Viscose fibers, the dye intensity increased in the shell zone without reaching the core. On Modal the intensity on the surface did not increase after reaching a certain limit. Having nonaccessible core zones, Viscose and Modal both have a relatively narrow dye diffusion zone. The method was found to be more sensitive on TENCEL, where the diffusion could be observed in a larger zone through the cross section. In this fiber type, the depth and the velocity of the dye penetration depend obviously on the fiber properties resulting from the treatment history.

The internal pore structure of TENCEL fibers

It was further possible to characterize the surface and the pore structure of TENCEL. The fluorescence microscopy observation (Fig. 5) delivers a dye distri-

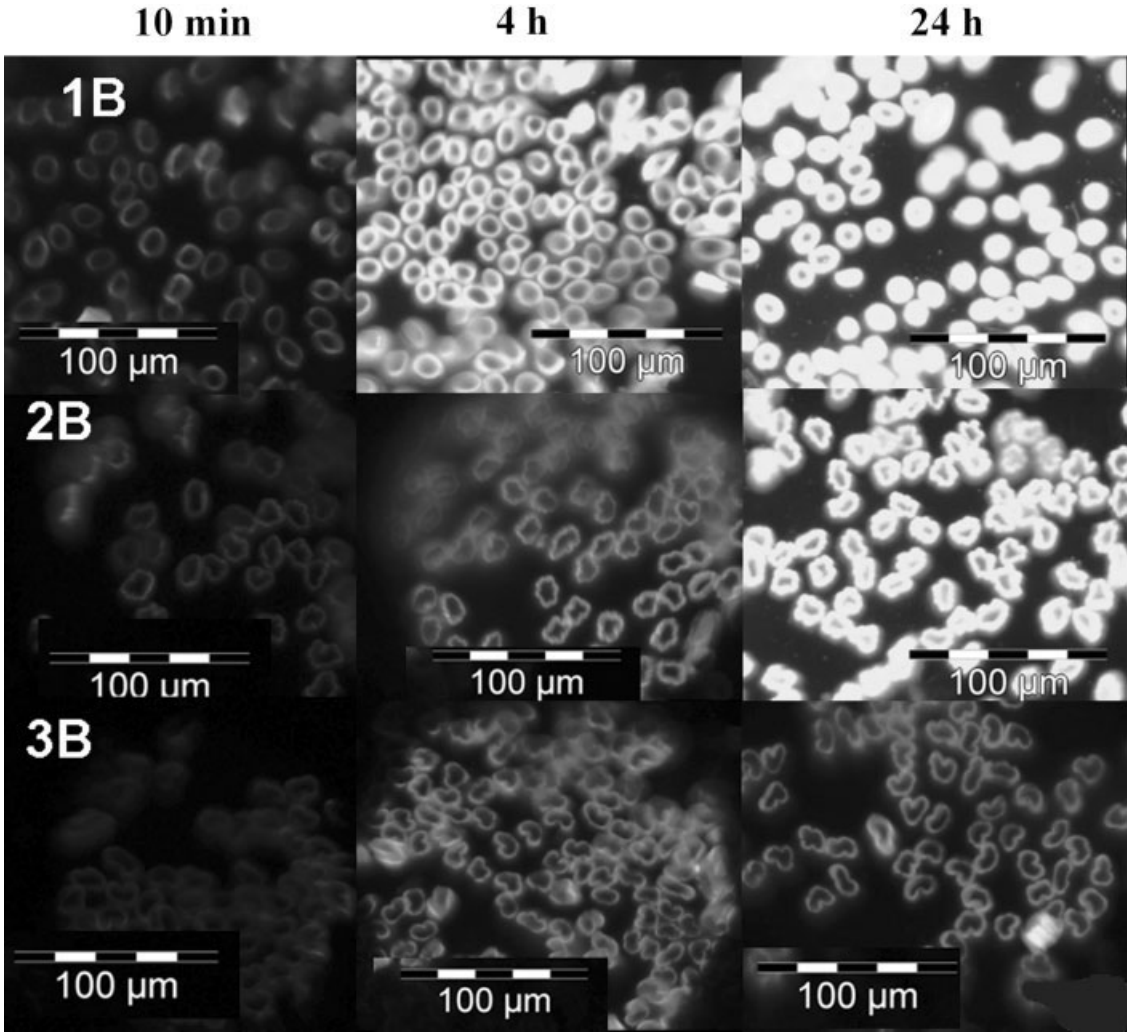

Figure 4 Diffusion of Uvitex BHT into TENCEL (sample 1B, top), Viscose (sample 2B, middle), and Modal (sample 3B, bottom), imaged with the same exposure time after 10 min, 4, and 24 h of dyeing.

bution profile which fits partly with the model mentioned earlier (Fig. 1). The membrane skin on the fiber surface can be illuminated with the fluorescent dye. The dye diffusion through the fiber inside appears to be faster than through the fiber skin, which seems to serve as a semipermeable membrane (Fig. 5, left).

Comparison to TEM

In the TEM micrograph (Fig. 6), it is obvious that beneath the skin zone (~ 0.3–0.5 µm) a less compact zone is situated, followed by the compact center. The fibril aggregations become gradually denser after the first 2–3 µm leaving the fiber surface. These

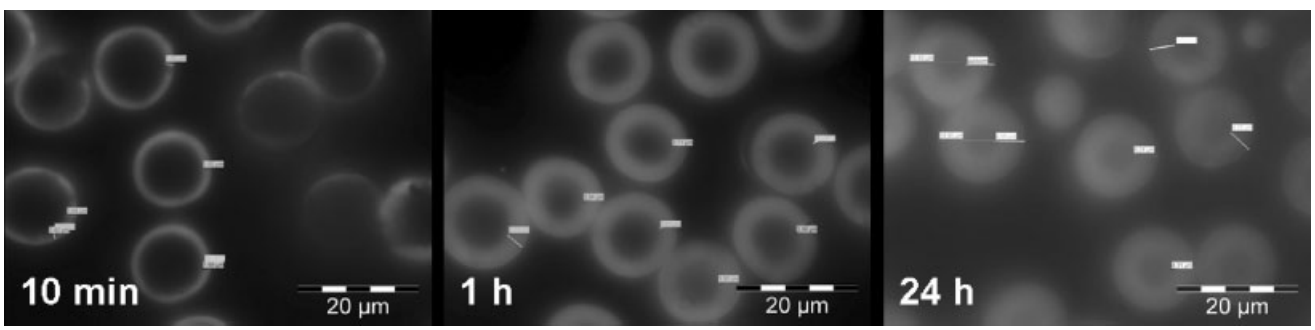

Figure 5 Calcofluor intrusion into a TENCEL (sample 1B) cross section after 10 min (left), 4 h (middle), and 24 h (right).

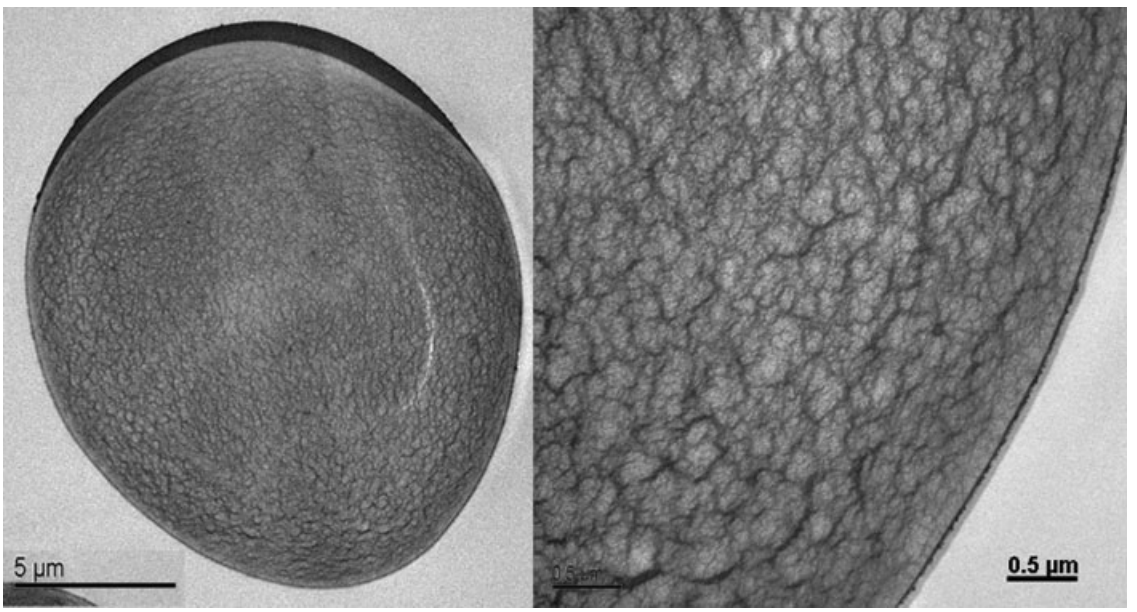

Figure 6 TEM micrographs of a cross section of a TENCEL fiber (sample 1B).

3 µm are mostly the zone, where the dye diffusion takes place. The rather gradual change in porosity observed by TEM is reflected in the diffusion zones as seen by Uvitex intrusion. The exact penetration depth depends on the pore properties of the fiber, which varies following the different treatments. An alkali treatment loosens the dense fiber center and makes deeper dye diffusion possible.

For the skin (0.2–0.3 µm as shown in TEM), the fluorescence microscopy method is limited by the limits of the light microscopy (2× wave length as minimal size can be seen). The fluorescence microscopy can determine the accessibility of this skin, but not its dimensions.

Structural changes during the production steps and textile treatment on cellulosic fibers—Examples

Effect of the first drying on Viscose, Modal, and TENCEL (Fig. 7)

On TENCEL fibers, two drying conditions were investigated. The fibers were dried in the laboratory at 60°C for 8 h resp. at 120°C within a few minutes in the production plant. Viscose and Modal fibers were only dried in the laboratory for 6 h at 60°C.

On dried TENCEL, the fiber core remains inaccessible for the dye, indicating a more compact pore structure in the fiber center. The fiber center was partly reached only in the case of never-dried fibers. This effect was observed only on TENCEL.

On Viscose and Modal fibers the effect of the first drying was marginal. On Viscose the drying reduced the dye intensity in the accessible zones. The dye penetration depth remains unchanged.

No changes by the first drying were observed on Modal.

Figure 8 shows the dye penetration depths into TENCEL fibers before and after the first drying. While in the never-dried stage the fiber center is completely intruded by the dye, the pore system seems to collapse after the drying, leading to less accessibility. Even after the longest applied diffusion time (48 h),

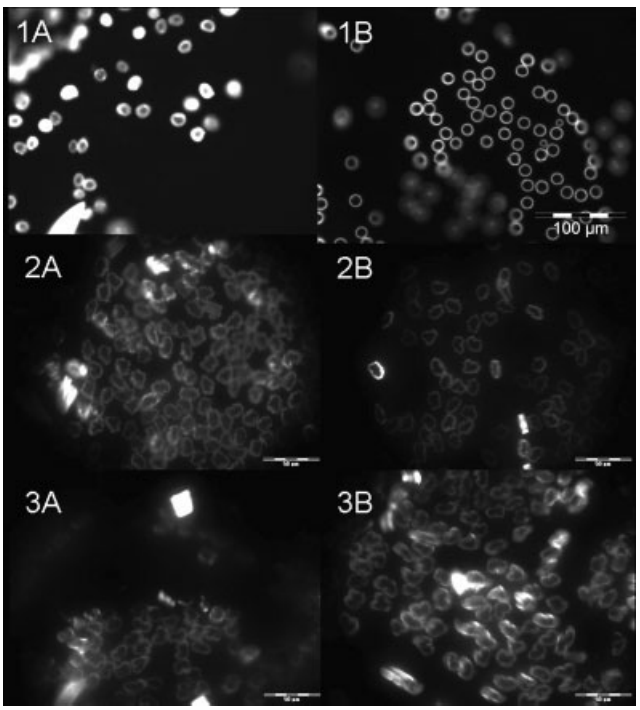

Figure 7 Dye penetration into never-dried (left) and dried (right) fibers of TENCEL (top), Viscose (middle), and Modal (bottom) fibers.

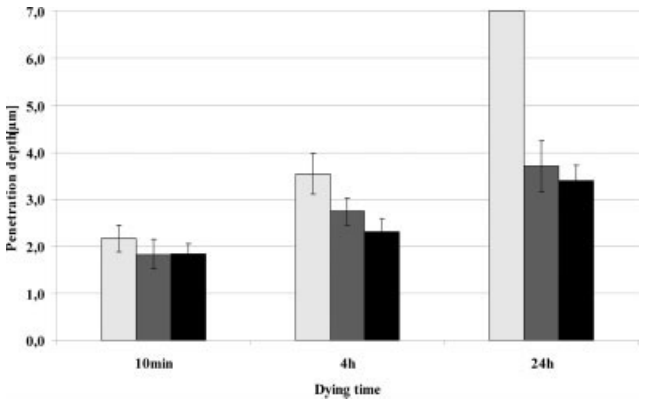

Figure 8 Dye penetration into standard TENCEL fibers in the never-dried stage (□, sample 1A), and after drying at 60°C (■, sample 1B) and 120°C (■, sample 1C).

the fiber center was not reached by the dye. A slight difference in the accessibility change following the drying at 60 or 120°C was observed. A high drying temperature seems to lead to more pore collapse.

Effect of caustic lying

Standard and lyed (14 °Bé, 105 g/L NaOH) TENCEL fabrics were dyed with Uvitex BHT for 10 min, 4, and 24 h. The penetration of dye into the fibers was measured (Fig. 9). Although initially similar (10 min values), the intrusion was finally deeper into the lyed than into the normal fibers (4 and 24 h values). In both cases the fiber center could not be reached by the dye. The fluorescence intensity was in all cases higher on the lyed than on the untreated fibers. This means that the lying enhances the accessibility in the fiber internal zones (dye penetration after 4 and 24 h) and also changes the pore structure in the accessed zones towards a high amount of dye uptake (intensity).

Effect of an enzymatic treatment

TENCEL fibers were treated according to the enzymatic peeling procedures of Sjöberg et al.,[31] originally developed to characterize pulp.

A time series of enzyme treatment in a diluted 1 : 2 mixture of Econase HC 400 (a Xylanase/β-Glucanase preparation, and Celluclast 15 L (a cellulase preparation)) was performed at a liquor ratio of 1 : 10 at room temperature, with gentle shaking, leading to very low mechanical forces on the fibers. The enzymatic reaction was stopped after 60 and 120 min by washing in cold water and heating to 100°C to obtain the fibers for morphological analysis. The weight loss on the fiber was 0.34% after 60 min and 0.77% after 120 min of treatment.

Figure 10 shows the dye penetration depth after 1 and 24 h dyeing on the untreated sample (1B) and on the samples treated for 60 min (1D) and for 120 min (1E). It is obvious that the enzymatic peeling makes the surface or skin of the fibers easier to penetrate, allowing more dye accessibility. No important difference in the penetration depth was observed after 120 min. The peeling already reached its maximum at 60 min. In the fiber middle zones no importance difference was observed. The effect of the enzymes was limited to the surface and could not reach the compact fiber center.

A more detailed kinetic study of TENCEL porosity

The effect of the first drying and the alkali treatment was investigated with a higher local resolution.

Plotting the dye penetration depth against time for each fiber, measuring the dye penetration depth at several times (Fig. 11), two main phases of the experiment with a quasi linear character were observed.

A common observation could be made on three samples, showing that the diffusion slows down after the first 2 µm into the fiber depth. The samples differ only in the time needed to reach this depth. While the first drying of the never-dried fibers leads to a reduction of accessibility in both diffusion zones, the alkali treatment enhances the accessibility of the outer zones almost to the level of the never-dried. The alkali-treated showed even a higher diffusion in the very initial time phase (30–60 min). This

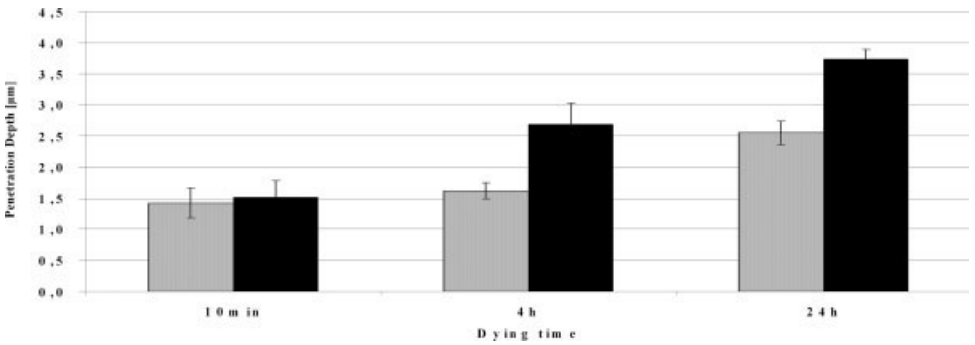

Figure 9 Intrusion depth of Uvitex-BHT into normal (□) and alkali-treated (■) TENCEL fibers in fabric samples 4A and 4B.

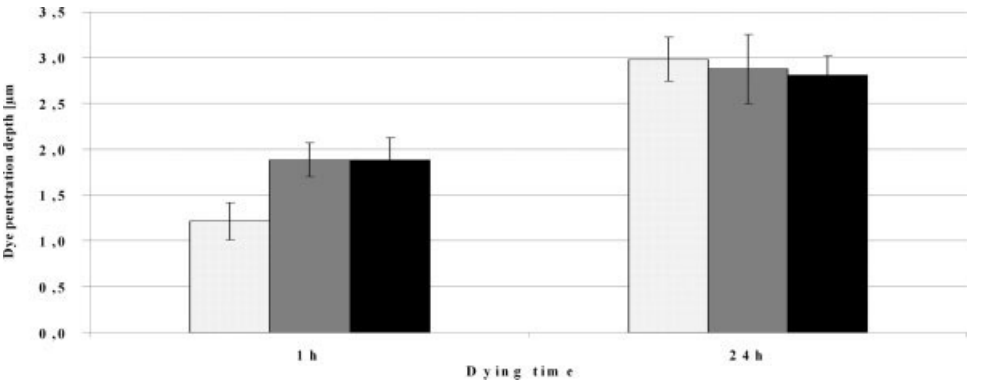

Figure 10 Dye penetration depth into the untreated TENCEL sample 1B (□) and the enzymatic treated samples 1D and 1E after 60 (▩) resp. 120 (■) min of enzymatic treatment.

means that the outer fiber skin, being the first obstacle to dye diffusion, might have been removed or opened up by the alkali. The effect of the alkali treatment is less remarkable (in this case) toward the fiber center.

The slope of each curve might serve a specific working constant to characterize the accessibility of various fiber types and to distinguish zones of different accessibility within the fiber cross section. A calculation of diffusion constants from this method seems in principle possible, given a sufficient data matrix is available, and a local quantification coupled with dye uptake quantification was made.

CONCLUSIONS AND OUTLOOK

Uvitex BHT was found to be an appropriate molecular probe to investigate the local porous system and the accessibility along cross sections of TENCEL fibers by visualization. Fibers were prepared by impregnation with dye solution for defined times, drying, and cross-sectioning of the resin-embedded fibers. The depth of intrusion of the dye corresponding to the impregnation time was measured from fluorescence micrographs.

The dye penetration depth and kinetics are sensitive to the production and treatment conditions of TENCEL fibers, in particular to changes in the pore system following aqueous and alkali swelling processes, but also to the differences in the pore structure which correspond to the different spinning parameters. The performance of surface-specific enzymatic peeling could also be observed.

In Viscose and Modal fibers, only the shell of the fiber was reached by Uvitex BHT. This is a main difference to TENCEL, which has a more homogenous fiber structure. No further accessibility studies were made on Viscose and Modal, but the main differences between these three fiber types could also be visualized.

Only TENCEL showed a significant difference between dried and never-dried fibers (Viscose and Modal did not).

Beside the accessibility, which was assessed by these experiments, a combination with localized measurements of the dye intensity within the fiber

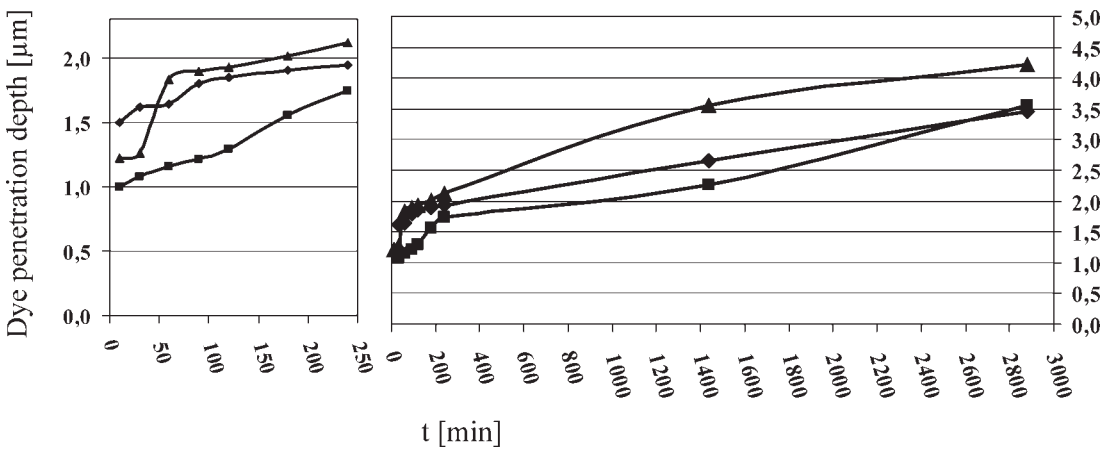

Figure 11 Time run plot of dye penetration on never-dried (▲), dried (◆), and alkali-treated (■) standard TENCEL fibers.

cross section would deliver an important complementary analysis on the pore system

For a deeper understanding thereof, more detailed investigations are to be done to create a larger data matrix. Results regarding apparent diffusion coefficients will be the subject of a further publication. A local quantification of the dye within the fiber cross section would be possible by applying space-resolved analytical methods.

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