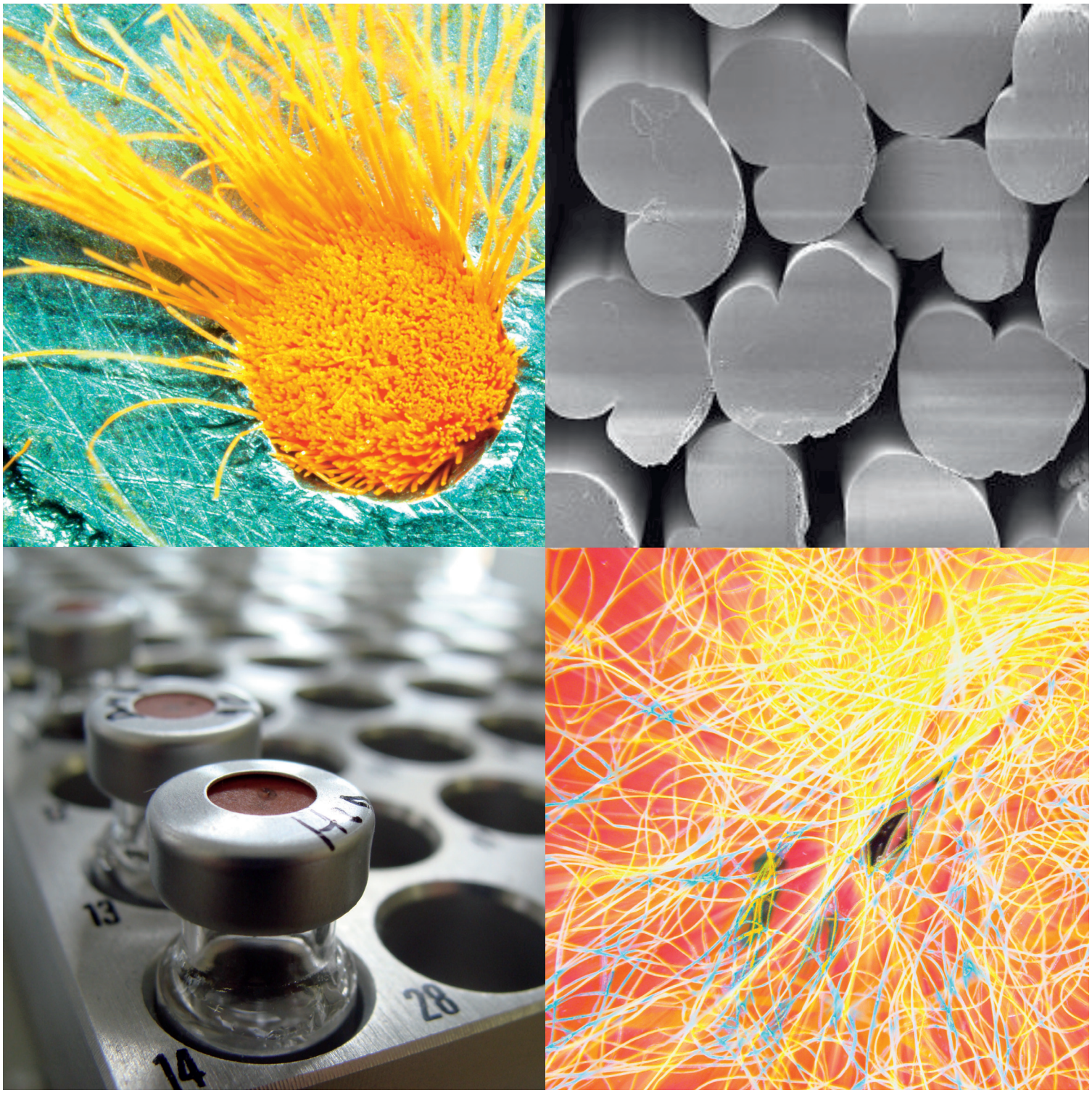

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Scientific reports on wood, pulp and regenerated cellulose

„Am Baum der Erkenntnis hängen keine Äpfel, sondern harte Nüsse."

Dr. Herbert A. Frenzel

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SUSTAINABLE CELLULOSICS

PROTECTION AND COMFORT

APPLICATIONS BESIDES TEXTILES

CELLULOSE AND CELLULOSE DERIVATIVES

A Vision of the World of Cellulosic Fibers in 2020

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In this article we will examine the development of the fiber market over the last 50 years and look 10 years ahead into the future to determine whether cellulose fibers boast growth potential.

Figure 1 shows the development of the fiber market in the first decades after 1960 and the strong dominance of synthetic fibers. This success story of synthetics from a market share from close to 0% in 1960 up to almost 70% in 2010 was due to the excellent ratio of its physical properties and wearing features to costs. Man-made cellulosic (MMC) fibers including cotton lost ground during that period. Experts believe that cotton production will be limited to 28 million tons in 2020 due to the reduction of arable land and limitations in water availability in the light of the fact that cotton is grown in warm climates. The irrigation with freshwater is frequently a prerequisite.

The fiber market has expanded by 3% annually on average over the last five decades. In the beginning the development followed a simple correlation with population growth which has significantly changed during the last 10 years.

The consumption of fibers has been driven by the industrialized countries and on a consumer level is highest in the USA, reaching more than 40 kg/capita, compared to around 10.7 kg per capita on average in the world in 2010 (Figure 2). Due to increasing demand in the developing countries, a global average amounting to 13.2 kg per capita in 2020 is predicted, leading to a global consumption of 102.4 mn tons (2010: 73.8 mn tons). This will comprise an average growth of 3.3% for all fibers, in which case the 2.2% per capita increase is more significant than the corresponding population growth of 1.1%.

These predictions of growth reflect significant regional differences in fiber consumption per capita, strong expected GDP growth in emerging markets and China which mean these markets will come close to reaching the current European level of fiber consumption totaling 25 kg per capita by 2020.

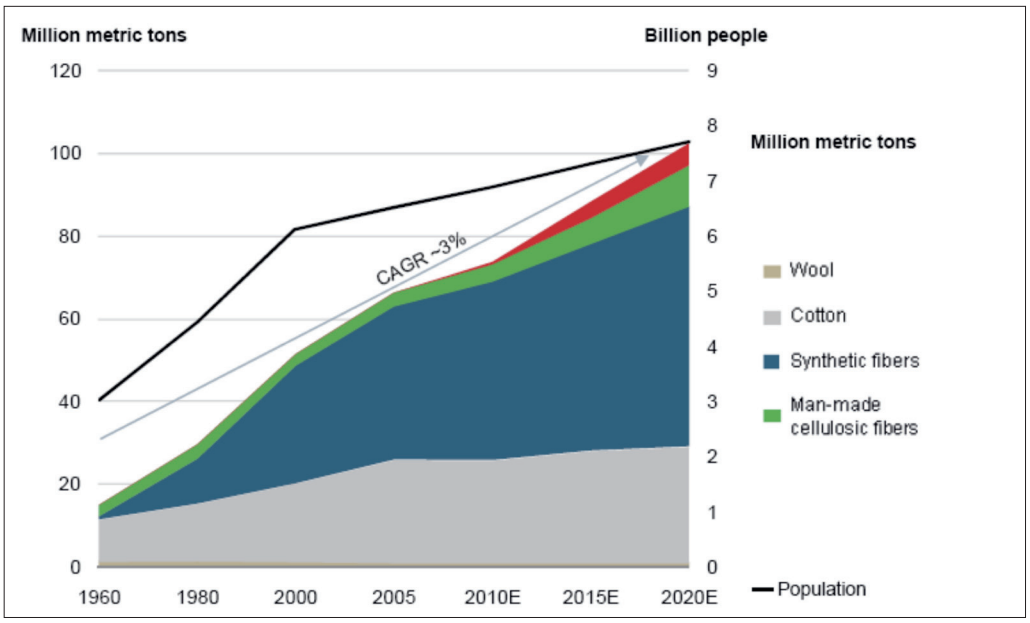

Figure 1. *Fiber market growth by type of fiber (1960-2020E) [1].*

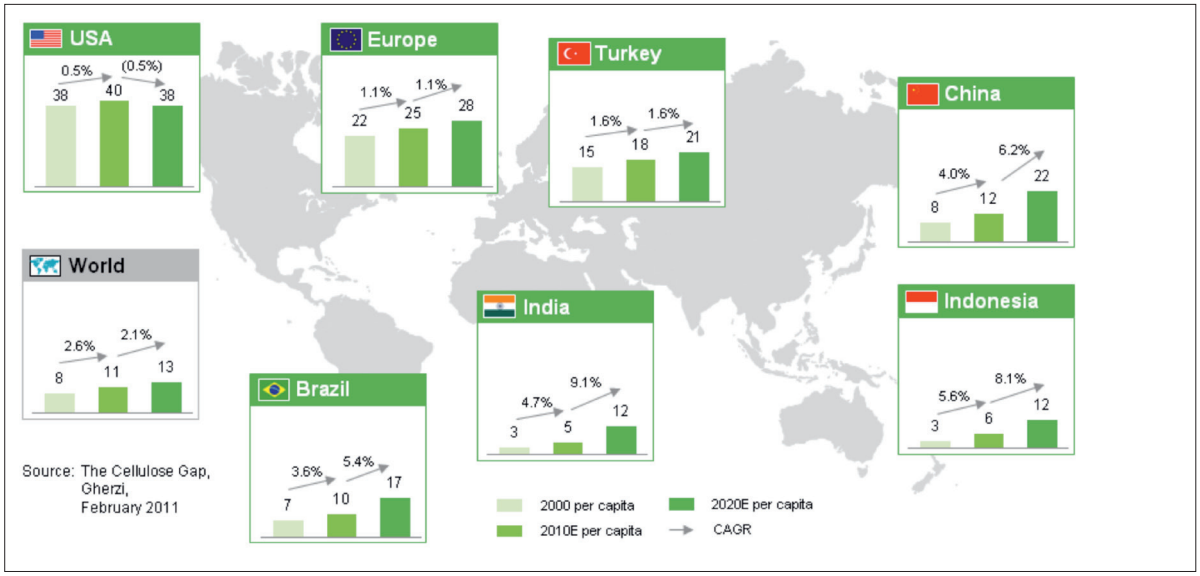

Figure 2. *Geographical fiber consumption per capita 2000-2020E (kg) [1].*

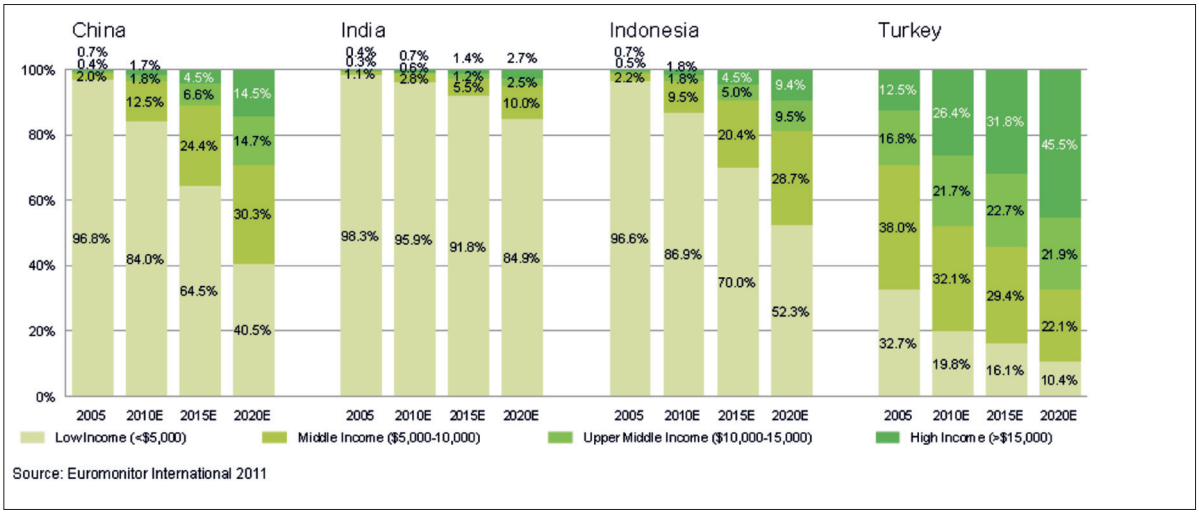

Figure 3. *Income distribution 2005-2020E [2].*

The increase in demand is in line with the megatrend of rising prosperity (Figure 3):

- Rising income in key Asian markets has led to a shift in income distribution.
- In China, the portion of middle to high income people is expected to increase from 16.0% to 35.5% from 2010E-2015E

We expect that population and prosperity will drive fiber consumption and accordingly it will grow by approx. 30 million metric tons globally (Figure 4).
The major factor is increasing prosperity as continuous growth of fiber consumption per capita has continuously moved up over the last decades and is expected to continue growing. This will be fuelled by the emerging markets (Figure 5) as average fiber consumption per capita is directly related to income levels.
Future fiber demand (Figure 6) can only be met by man-made fibers in the light of the stagnant or shrinking production of natural fibers. Cotton production growth is negatively influenced by limited input factors (arable land, water). MMC (man made cellulosic) fibers comprise the best substitute for cotton since synthetics cannot offer certain properties (e.g. absorbency). However, cotton fabrics that do not require cotton properties (e.g. technical textiles) must be replaced by synthetics to fill the entire gap. Consequently MMC fibers will experience the biggest growth at 9.1% until 2020, followed by synthetics posting 3% growth and cotton with 1.3%.

In 2020 it is estimated that synthetics will have a market share of 56.5%, cotton 27.3% and MMC fibers 9.8% with an upside potential of 5.2% due to the cellulose gap.

Similar properties of MMC fibers make them the best substitute for cotton as clothing textiles due to their superior moisture management (Figure 7).
Compared to cotton, MMC fibers and synthetics can be modified in thickness and are suitable for superfine fibers (Table 1).

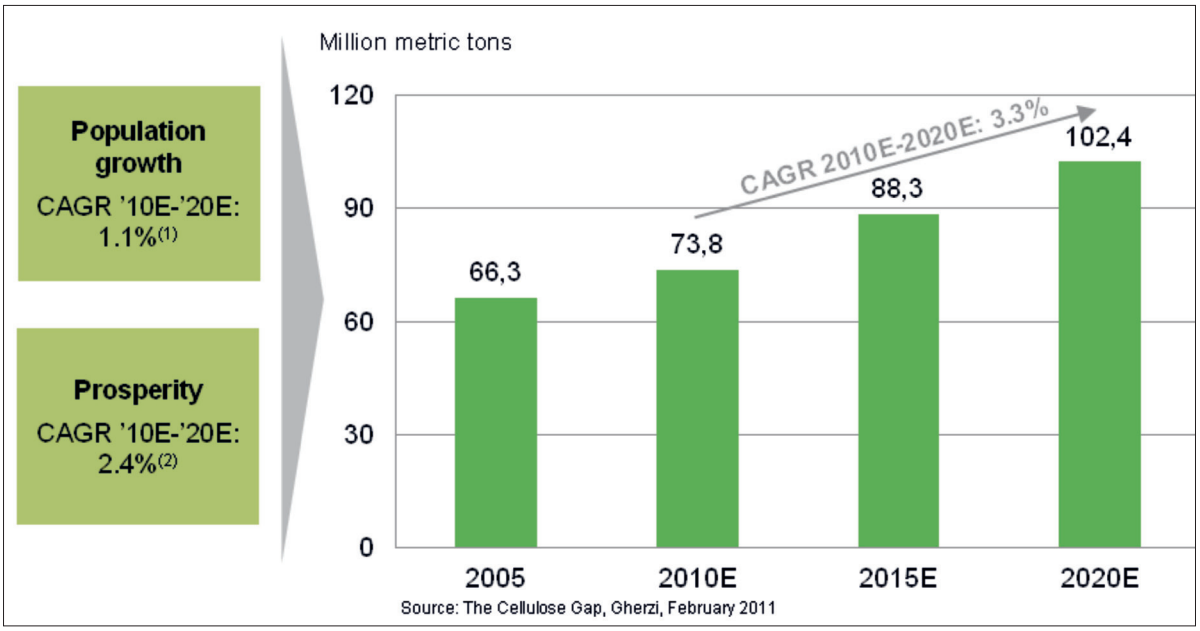

Figure 4. *Total fiber consumption 2005-2020E [1].*

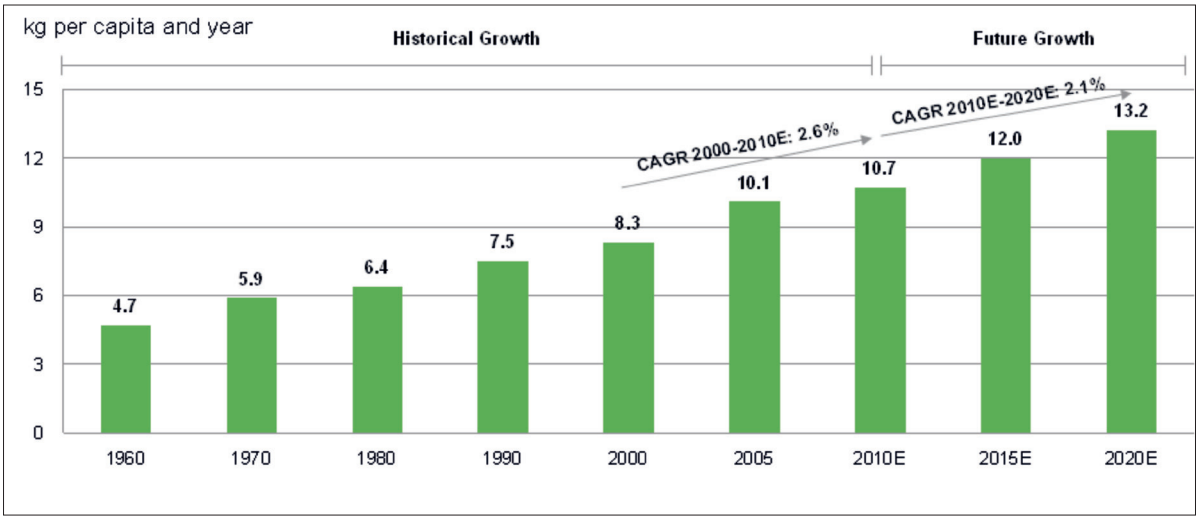

Figure 5. *Fiber consumption per capita 1960-2020E [1].*

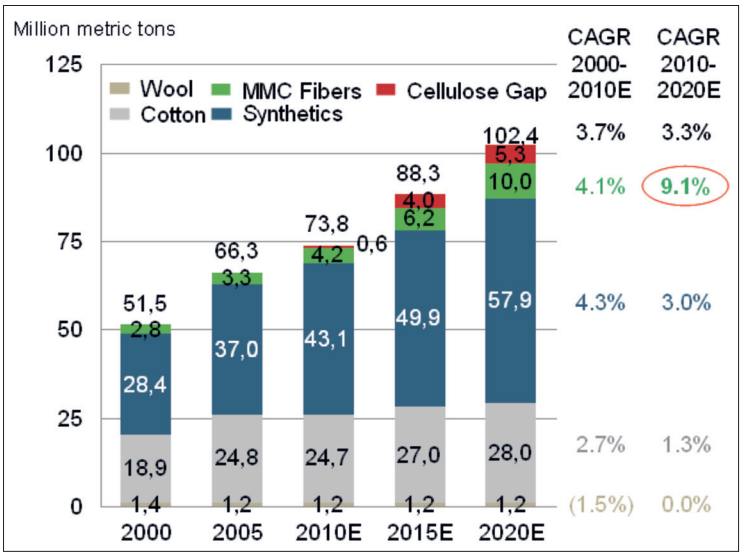

Figure 6. *Fiber production 2000-2020E [1].*

Accordingly, MMC fibers are the preferred blending partner for cotton due to their similar physical characteristics (Table 2).

In addition Lenzings MMC fibers have a green footprint and follow botanic principles. Wood is the source and fuel for MMC fiber production. It is sustainable, a renewable resource and MMC fibers are fully biodegradeable. The natural polymer cellulose is produced by a natural chemical process called photosynthesis where carbon dioxide with water under the energy input of sunlight is converted into cellulose and oxygen which is the basis of all life. This could suggest that MMC fibers are a contribution to reducing CO2 in the atmosphere due to the fact that the trees assimilate carbon dioxide.
In 2006 and 2007 Lenzing commissioned the Copernicus Institute of Utrecht University, Netherlands, to conduct a first-time comparative life cycle analysis for Lenzing Viscose® (Austria, Asia), Lenzing Modal® and TENCEL® (Austria) in direct comparison to cotton (USA and China), polyester fibers (Western Europe) and polypropylene fibers (Western Europe). The result showed a very low impact of Lenzings MMC fibers as well as the synthetic fibers compared to cotton. The major impact of cotton on the environment is the freshwater ecotoxicity and terrestrial ecotoxicity caused by the use of fertilizers and pesticides (Figure 9).

But also in the dyeing and finishing processes, Lenzings MMC fibers can contribute to a reduced environmental influence. Specifically TENCEL® which is of superior quality and based on an environmental friendly technology, boasts a higher moisture uptake than cotton, but was initially hampered by difficulties in dyeing and finishing. In the meantime, it has been increasingly accepted by the textile industry. Figure 10 demonstrates the reduction of COD (carbon oxygen demand) due to higher dye uptake (according to the Kisco test) of TENCEL® in comparison to cotton. This has a positive effect, given that the load waste water treatment is significantly reduced and saves water and energy.

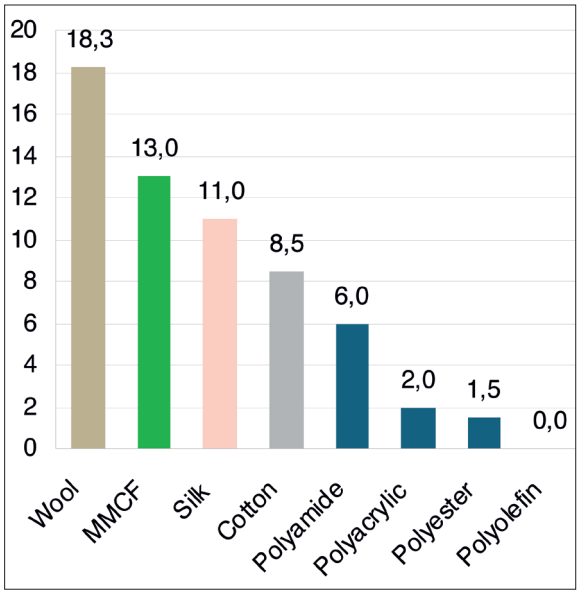

Figure 7. *Moisture regain of textile fibers [5].*

Table 1. *Fiber thickness [1].*

Fiber	Thickness of Fiber
Cotton	1.3 - 4.5 dtex
Wool	1.8 - 4.5 dtex
Angora	0.9 - 4.3 dtex
Viscose	**1.2 - 8.0 dtex**
MicroModal	**0.8 - 1.0 dtex**
Lyocell	**0.9 - 20.0 dtex**

Also Lenzing's MMC fibers such as Modal can be effectively used in highly efficient new spinning processes like the air jet spinning technology, where productivity is three times (open end) to more than 20 times higher than existing spinning technologies.
A consumer survey done carried out by Cotton Inc showed that comfort, durability and performance features are becoming increasingly relevant for the consumer as purchasing criteria. Cotton and man-made cellulosic fibers are both based on the same polymer, namely cellulose, which provides for moisture uptake as an essential factor in comfort. This creates opportunities for fibers such as the man-made cellulosics that provide the factor of inherent comfort.

Table 2. *Fiber characteristics [1].*

	Cotton	Viscose	TENCEL®
Tenacity (cN/tex)	24 - 28	24 - 26	40 - 42
Elongation (%)	7 - 9	18 - 20	15 - 17
Loop Tenacity (cN/tex)	20 - 26	7	20
Fibrillation	2	1	4 - 6
Water Absorbance (%)	50	90	70
Moisture Content (%)	8	13	11.5
Crystallinity (%)	75 - 90	25	60
Swelling in Water (%)	35	88	67

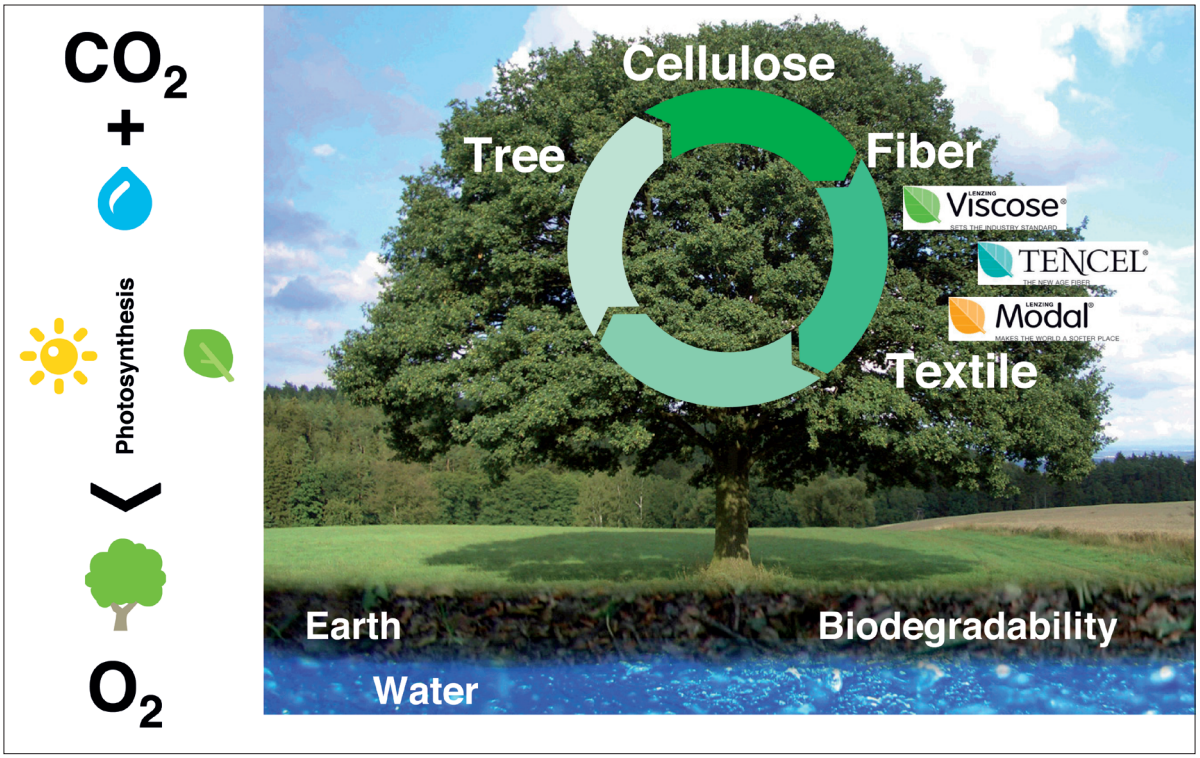

Figure 8. *Botanic principles – photosynthesis.*

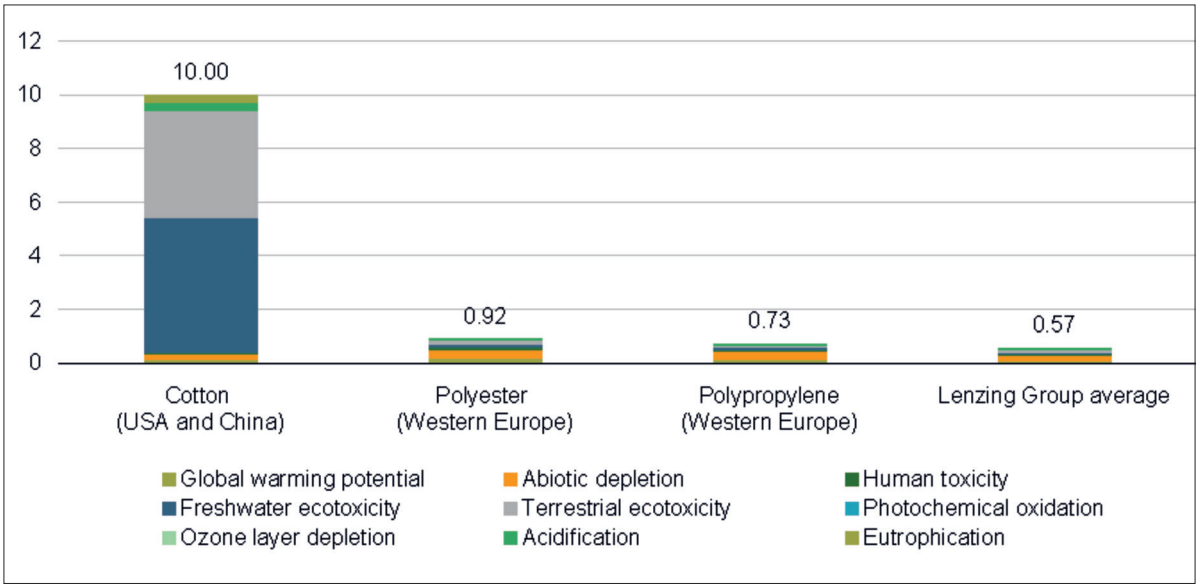

Figure 9. *Sustainability profile analysis shows Lenzing's low environmental impact [3].*

In order to predict the future of fibers as they have rather long life cycles, a long-term trend concept has to be applied. Nikolai Kondratieff, a Russian economist, as described the development of the economies in different long terms (40 to 60 years) as so-called "Kondratiev waves" or cycles of boom followed by depression. These waves were driven by core innovations (Figure 11). These waves started from 1780 with the industrial revolution. The steam engine was the basis for mass production as the core innovation. The second phase facilitated by the railroad supported the distribution of goods and logistics. The third wave put mass consumption on the basis of chemical and electronic advances in place. Automobiles and petrochemicals have been responsible for the mass traffic in the fourth cycle and in the fifth period globalization and world economy were driven by information technology. Leo A. Nefiodow, an information technology scientist, has postulated a sixth Kondratieff wave predicting the quality of life and health. In this phase a conscious well-being oriented phase emphasizing the feel good factor will be important.

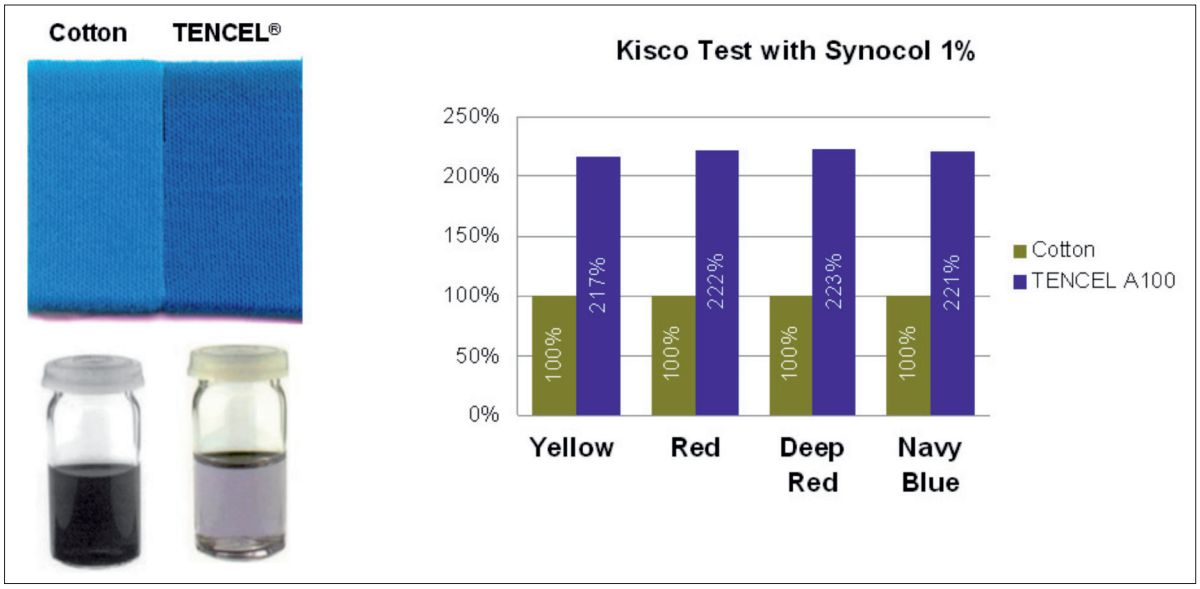

Figure 10. *TENCEL®: Reduced resources and environmental impact possible in dyeing.*

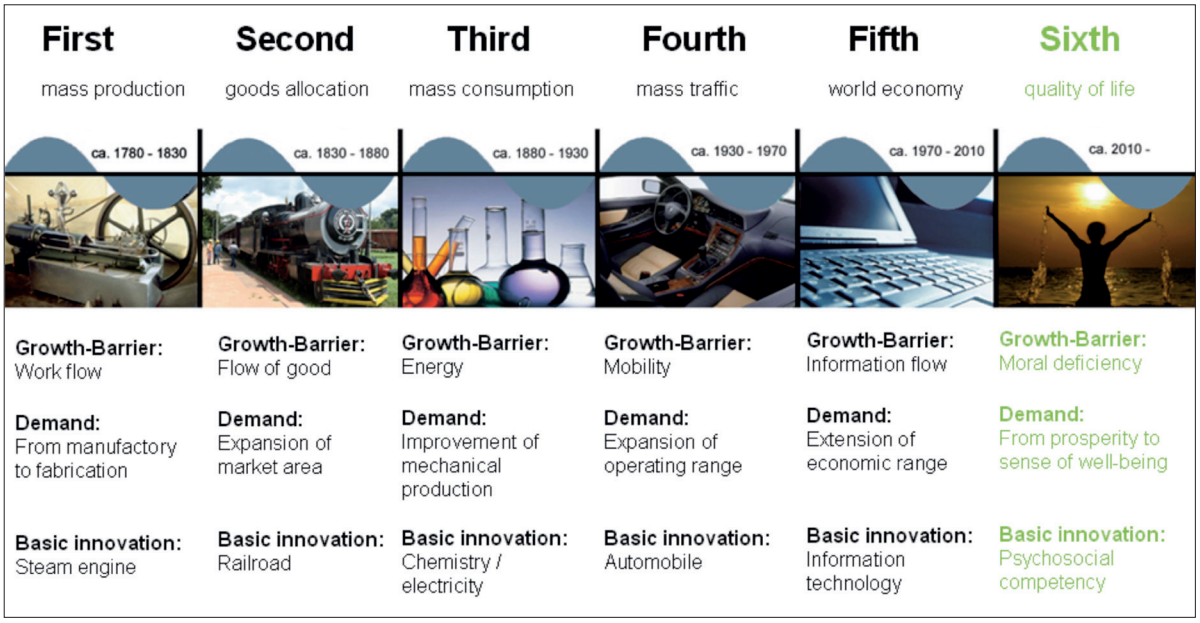

Figure 11. *Kondratieff long waves by Nefiodow. [4]*

Do man-made cellulosic fibers fit into that trend? TENCEL® has been the breakthrough technology in man-made fibers over the last 20 years, receiving several awards for its environmental-friendly process. It can demonstrate best why cellulosic fibers will contribute to this 6th wave. Scientific investigation showed that the superior moisture management of TENCEL® is essential as it keeps the body dry and generates a kind of natural air conditioning. It is even possible to cool the body and keeps you warm at the same time. As a consequence TENCEL® regulates the temperature in bed creating relaxing sleeping conditions, and has opened a new segment for cellulosic fibers (Figure 12).

In addition, another feature of TENCEL® fibers and fabrics is that microorganisms such as bacteria cannot grow as the fiber absorbs and moves away moisture which in combination with the very smooth surface of the fiber makes it ideal for sensitive skin. This has been confirmed from several global institutes. Also in bedding the low moisture leads to an atmosphere where molds and dust mites can hardly exist. Functional elements can be added by sunblockers in order to protect the skin. For this reason, TENCEL® SUN has been introduced into the market in order to make light fabrics with UV protection possible. Recently Lenzing has launched a fiber called TENCEL® C which is covered with Chitosan, the 2nd biggest polymer in nature which has demonstrated

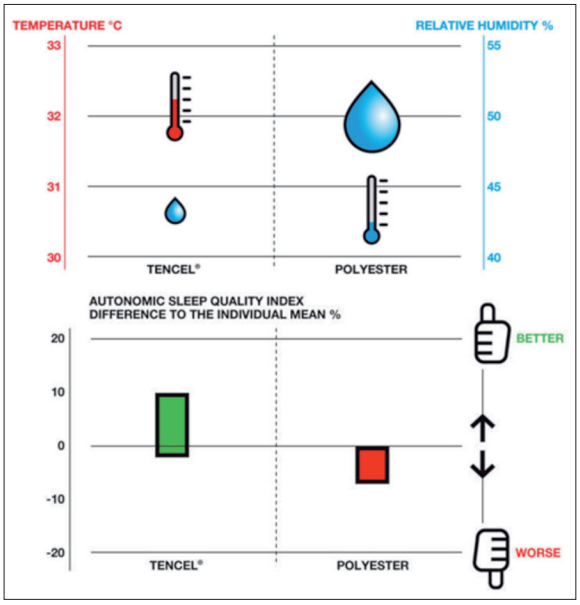

Figure 12. *Temperatur regulation in bed – comparison TENCEL® and polyester.*

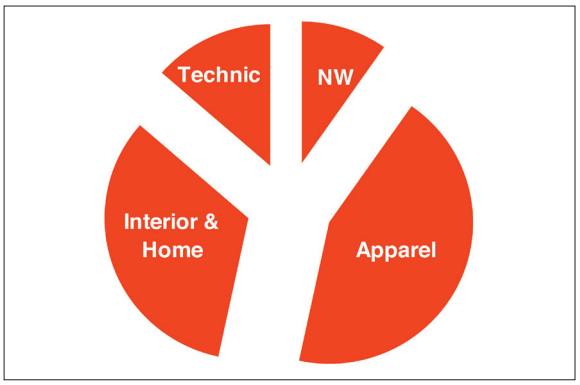

Figure 13. *Market potential for MMC fibers in 2020.*

healing effects. It has been demonstrated that the aging of skin is retarded by TENCEL® C which could consequently lead to skin cosmetics.

In protective clothing Lenzing FR® is the ultimate solution for extreme situations in fire fighting, military or industry e.g. the oil, metal and electricity industries. Protection and body performance are secured at the same time.

These examples show that new high tech fibers based on the natural resource of cellulose with an environmental-friendly production process have emerged with a new set of properties. In turn, this will open doors for new applications for man-made cellulosics (Figure 13).

All these developments mean that man-made cellulosic fibers will have a bright future, not only because of the expected cellulose gap created by the limited cultivation of cotton but also due to new cellulose fiber categories such as Lenzing Modal® and TENCEL® which have overcome the previous disadvantages of strength. Moisture uptake and controlled release are inherent, as well as softness, skin compatibility and finally production processes which are in line with the megatrend of sustainable and environmentally-friendly production.

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Greening of the Denim Supply Chain

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Abstract

Substituting TENCEL® into fabric to replace conventional cotton can significantly reduce the environmental footprint of a product. However this positive effect can be totally negated through the effects of textile wet processes such as dyeing and finishing of fabrics & garments. Denim is a case in point, where TENCEL® has made significant in-roads into this product category. However the market is looking for a more holistic approach and demanding that issues of water, chemical and energy use are addressed at every stage. This paper looks at new approaches to responsible dyeing and finishing of TENCEL® denim fabrics and garments which results in minimum use of resources but still achieving a commercially viable product.

Some years ago a feature on a BBC TV introduced the subject of "Sustainability in Fashion" and began the feature by interviewing a "so-called" textile specialist to discuss the eco index that she had been personally developing. The camera shot switched to a young woman clutching a pair of baby blue denim jeans in both hands. She proceeded to rub them gently against her right cheek, explaining that they were "made of 100% cotton", which in itself meant that "they were totally natural". She continued to extol their virtues such as that "they felt extremely soft and comfortable" and finished by saying that in terms of her self generated eco index cotton denim jeans were classified as a "9 out of 10" (10 being the best score).

This feature highlighted the general ignorance and ever present ingenuous view that exists around this ubiquitous product area. Of all the categories in modern apparel, denim jeans and the denim industry that produces them, has probably been guilty of some of the worst environmental excesses ever; from the use of conventional cotton fiber through to disposing untreated effluent directly into waterways from the commercial laundries that wet processed 95% of all denim jeans manufactured. Thankfully today within the industry things are improving, with new thinking and new techniques being applied throughout the supply chain and genuine textile technologists and textile chemists with real expertise applying science to the metrics that are being used to measure the environmental improvement along the denim supply chain. This paper attempts to document some of those improvements.

Denim matters in the context of sustainability because it is such a large part of the textile industry. This industry category could accurately be described as having a global reach, with denim fabrics and garments still being manufactured on five continents.

Some time ago a quote from Cotton Incorporated [1] estimated that approximately 10% of the annual cotton crop is used in denim products. If we try and study the industry numbers more closely, the latest "Global Market Review of the Denim and Jeanswear Industries"[2] conservatively estimates that by the beginning of 2012 the global jeans market will be worth US$54,235 million at retail. This represents 1,910 million units at an average unit price worldwide of US$28.40. If you accept that an adult garment will take 1.5 linear metres of fabric per garment, this converts to almost 2.9 billion linear metres or 4.35 square metres of fabric. At an average fabric weight of 424 gsm this equates to the use of 1.84 million tonnes of fiber; add in 12% spinning mill losses from bale to clean cotton then you arrive at a figure which is not so far away from 10% of the ICAC 2010 estimate for cotton production of 24.74 million tonnes.

Since the 1950s, jeans have been a constant part of all western wardrobes, worn by an ever increasing age range of consumers. The original jeans generation, who are now aged 60-years plus, have refused to grow old gracefully, and continue to wear their badge of denim youthfulness. Today, as the brands fight to convince the young that denim is still cool, (even if their parents are wearing it), the marketing of jeans has incorporated concepts such as product authenticity, music connotations, celebrity endorsements and product placement in films. The new frontiers for the jeans market are the middle classes of India and China, who aspire to dress like westerners and are rapidly adopting the symbols of a wealthy society such as the wearing of jeans.

So what is Lenzing's interest in this apparel category? Well it could be argued that this product area alone is responsible for existence of TENCEL® today. During the early days of the fiber being commercially available, the fabric production was difficult because it was blighted by the tendency of the fiber to fibrillate and swell significantly during wet processing. This resulted in fabrics exhibiting damage marks, creases and a hairy pilled surface and potentially severely limiting the adoption of the fiber into the fashion industry. Therefore the path of least resistance proved to be the garment processing route. This route became central to the successful commercializing of TENCEL®. The main reason being that the garment processing machines, that existed at the time, and the chemicals and conditions used for processing cotton goods in those machines could also be adapted to effectively control fibrillation and swelling of TENCEL® .So no invention of product or process was required to successfully commercialize TENCEL® garments, just adaptation.

Japanese manufacturers were the first to work out how to successfully use TENCEL® fabrics through the garment route. The first commercial iteration of a TENCEL® was a lightweight denim garment made from an indigo warp-dyed 230gsm 2x1 woven twill, garment washed in a front loading washing machine. This since has become an iconic product within textile apparel fabrics.

Garment washing and garment dyeing of garments made from woven TENCEL® fabrics and blends of, became the "bread and butter" of the business, and the resulting profits of that route paid for the necessary research into viable fabric processing routes. Following almost 10 years of commercial development sufficient progress was made in fabric dyeing and finishing technology for the industry eventually to take lyocell more seriously as an alternative cellulose.

For most of the time since commercialization of TENCEL®, the fiber has been used in products due to the final aesthetic that could be achieved on the fabric. Subsequently performance aspects became better understood and relevant products developed. However the main USP (unique selling proposition) of the fiber, i.e. the sustainability story, remained a very difficult sell as the market was not ready for such a concept. It is only in the last few years that it has become the focus and in some cases the main focal point of certain brands and retailers.

In terms of sustainability, the greatest direct contribution that TENCEL® has made to the denim jean category is its environmental profile versus conventional cotton. Although it is believed that the first pairs of jeans manufactured by Levi Strauss were actually made from hemp sailboat canvas during the California Gold Rush (the word canvas is taken from the Latin cannabis)[3], currently and for the last few decades in the denim industry, cotton has been the dominant fiber used in jeans. This, to an extent, will always be true; however today there is a much greater willingness to include other fibers in fabric blends in jeans, and outside of stretch fibers such as elastane or textured polyester, TENCEL® is achieving good penetration into this market.

TENCEL® fiber is present in the market in denim products from minority blend fabrics with cotton through to 100% TENCEL® fabrics. For the majority of the denim market jeans are far and away the most important end use. The jean is defined here as a man's, woman's or child's trouser, most probably, but not exclusively, with five pockets (the five-pocket Western jean). It is estimated that the jeans participation share within the total denim industry lies between 75% and 80%, by both volume and value [2].

Thanks to the "Life cycle assessment of man-made cellulose fibers"[4] made by Utrecht University in 2008 and published in 2010, we are able to compare key data for lyocell versus cotton. The Life Cycle Impact Assessment measures various types of emissions and the raw material requirements and converts them into environmental impact categories, such as the contribution to global warming or acidification. The study included two types of environmental indicators, resources and environmental impacts. Resources include things such as non-renewable energy use (NREU), renewable energy use (REU), cumulative

energy demand (CED), water use, land use etc. Environmental impacts include things such as global warming potential (GWP) and pollution categories such as abiotic depletion, ozone layer depletion, human toxicity, fresh water aquatic ecotoxicity, terrestrial ecotoxicity, photochemical oxidant formation, acidification and eutrophication.

Considering three key areas of the LCA (Figure 1) – water, land and pollution - the comparison between TENCEL® and conventional cotton can be seen.

Looking at water, 5730 m³/t is the average usage for US & Chinese cotton. This is required for irrigation and processing, fertilizer use and herbicides/insecticides use. There is no artificial irrigation for trees and pulp and TENCEL® fiber production requires water only for processing and cooling, so the comparative water consumption figure for TENCEL® is 266 m³/t. This represents over 20 times less water than cotton. US & Chinese cotton represent "best practice" in terms of global cotton: in fact certain cotton data reports up to an average of 29,000 m³/t of water consumed for cotton in Sudan – over 100 times more than TENCEL®.

Considering land, this refers to the land use for biomass production, i.e. agricultural and forest land use. Cotton average for US & China is 0.82 ha/t with cotton world average at 1.06 ha/t. TENCEL® is 0.21 ha/t, thus cotton requires about 4-5 times more land per tonne of fiber than eucalyptus-based TENCEL®. Furthermore and probably more importantly the trees used for wood pulping are grown on what is known as "marginal land" which is unsuitable for food crops whereas cotton has to be grown on agricultural land.
For the toxicity impacts of cotton (i.e. human toxicity, freshwater aquatic ecotoxicity, terrestrial ecotoxicity and eutrophication), Only the impacts from US cotton are considered. Chinese cotton uses different pesticides and fertilizers, many of which cannot be assessed, thus causing an underestimation. Using US cotton as a proxy for the toxicity impacts probably still underestimates the toxicity impacts of Chinese cotton, because US cotton farming has to comply with stricter legal requirements on fertilizer and pesticide use than many other conventional cottons. Cotton has the highest fresh water ecotoxicity and terrestrial ecotoxicity mainly due to pesticides use. The fresh water ecotoxicity and terrestrial ecotoxicity of cotton account for 70% and 20% of the total impacts of cotton, respectively. Furthermore, the use of fertilizer is the main cause of the eutrophication impact.

So all in all if Lenzing production was substituted with cotton this would cause additional emission of 300,000 tons of carbon dioxide, require an additional 340,000 hectares of arable land and consume an additional 2.2bn cubic meters of water per annum. Therefore in terms of impact on the environment in the denim category, the simple addition of TENCEL® to a conventional authentic cotton jean can improve the environmental profile significantly. Trials have shown that adding up to 45% blend of TENCEL® to a cotton jean will not noticeably change the appearance or handle of the product. It could therefore be argued that by simply replacing cotton with TENCEL® the embedded environmental burden could be reduced.

Indigo dyeing and it's environmental effects

The next step along the denim supply chain that has the potential to cause serious environmental issues

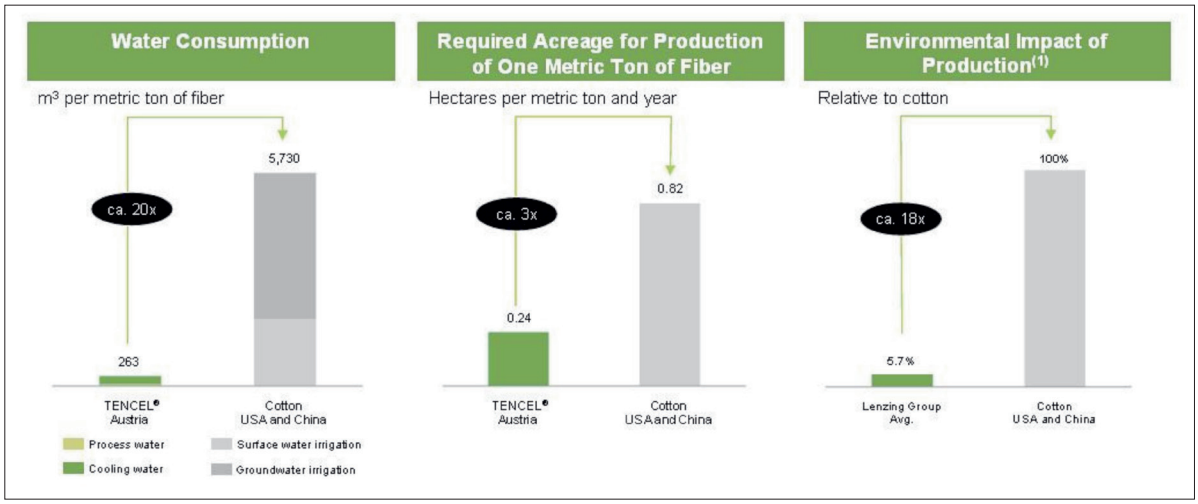

Figure 1. *Comparison between Cotton and Lenzing Man-made cellulose fibers.*

from both chemical and waste effluent is indigo dyeing. The roots of indigo go back into the Stone Age when our ancestors used indigo in cave art. The oldest evidence for use as a textile dye dates back 6,000 years to the Indus Valley and it is suggested that this is why we call it indigo, a Greek word meaning "coming from India".[5]

Even after more than 150 years of organic chemistry it is still the most efficient blue dye or pigment. In fact there is no other substance that creates such intensive blue color. In 1883 Adolf von Baeyer, a German professor and Nobel chemistry prize winner, discovered the chemical structure of indigo. Synthetic indigo production on an industrial scale was subsequently developed at Badische Anilin & Soda Fabric (BASF). Within only a few years synthetic indigo almost completely replaced the natural indigo imported from overseas.

In the last few years there has been a clamor to return to natural dyes, as many businesses and individuals naively presume it to be more sustainable. However there are numerous challenges with natural dyes, not only chemical but practical.

Merely on a practical basis, cultivating plants to produce natural dyes is unsustainable. Instead of being derived from oil/coal like synthetic dyes, natural dyes are derived from some part of a vegetative plant. A high percentage of a growing plant is water and the proportion of coloring matter to vegetable matter is low. If we only consider the needs for the dyeing of cotton the figures extrapolated from the British textile chemist, Glover [6] would suggest the following scenario. Glover calculated 1g of synthetic dye is equivalent to 440g of fresh dye plant. Therefore using the following assumptions that:

- the world's current cotton production is approx 25 million tons
- using an average depth of shade of 2%

then the total usage of synthetic dye would be around 500,000 tons, the weight of dye plant needed to replace synthetic dyes would be 220 million tons, resulting in creating some 213 million tons of plant waste.

What would be the effect on land utilization of cultivating this tonnage of dye plant?

A small quantity of indigo is still produced naturally and Indian government statistics[6] show that one ton of indigo dye is derived from 77 hectares of land. Assuming that all natural color giving plants furnish the same color yields as the indigo plant, (indigo is regarded as being one of the more efficient plants in terms of color potential), then the 7 million tons of pure vegetable color needed to dye the world's cotton would require some 539 million hectares. Based on World Bank statistics there are 13,000,000,000 hectares of total global land area [7] with arable land equating to 10.7% of this total i.e. 1,391,000,000 hectares[7].

So based on the above figures the plantation area for naturally derived dyes for cellulosic based textiles would be equivalent to 38% of the world's agricultural land today. This is a startling percentage and would require an area 16.8 times larger than is currently needed to grow the world's annual cotton crop. Considering only cotton use for denim, (approx 10% of the crop), requirements for 'naturally' indigo dyeing denim alone would still be significant.

Further detrimental effects that need to be considered are the issues of dealing with disposal of huge amounts of waste vegetable matter and the water pollution from the fermentation processes to extract the color.

In summary, based on the above calculations, the evidence substantiates the author's view that in terms of environmental impact and maintaining the natural order, it is impossible to consider using natural indigo dyes as a viable alternative for the denim industry. This view is corroborated by Schrott and Saling[8] using the BASF Eco-efficiency analysis tool who conclude in a comparative study that indigo derived from plants performed worse in terms of both ecological and economic criteria, since the cultivation and isolation of indigo on a large scale results in a considerable environmental impact and high costs.

Natural indigo consumption globally is still below 1% of the total indigo use and synthetic indigo is currently the only viable commercial route.

Synthetic indigo is obtained by using N-phenylglycine and N-phenylglycine-o-carboxylic acid. It is not soluble in water, so to dye a cellulosic yarn indigo needs to be made into a water soluble form therefore indigo is known as a vat dye. Indigo dyeing is unique and because of the complex chemical reactions that take place and as such it could be seen as an art underpinned by chemical engineering knowledge.

The solubility of indigo in water solutions is only possible in alkaline and reducing mediums, whereas alkaline salts of leuco indigo are water-soluble. The solution takes a yellow color when the blue-colored indigo

is reduced to the leuco compound. This yellow-colored compound dyes the cellulose, and this reduced product is oxidized on the yarn by the oxygen from air to blue-colored indigo.

The main reducing agent used in indigo dyeing for typical vat dyes is sodium hydrosulphite ("hydros" or sodium dithionite). An excess of hydrosulphite must be present in the dyeing bath because sodium dithionite is sensitive to atmospheric oxygen. Sodium dithionite is oxidized by consuming NaOH when atmospheric oxygen is present in the alkaline medium. Indigo that has been reduced and has taken the leuco form during vatting takes the form of oxidized indigo during the oxidation process. Depending on the pH, the reduced form of indigo may occur in different forms. So the target for indigo dyeing going forwards is to avoid all the current use of excess dyestuff and excess reducing agents in the process, which cause pollution and consume excessive resources. More recent efforts using synthetic indigo have focused on process optimization and reducing excess chemicals but ultimately high tech solutions will have to be sought.

The first real market advance in this area was in the introduction of pre-reduced indigo in the late 1990s because of environmental reasons. DyStar (formerly BASF) could claim to be the technology leader in this area, and it was during BASF times that they discovered that holding the prepared aqueous solution of leuco-indigo in an inert (nitrogen) atmosphere they could achieve excellent indigo dyeings on cellulosics, with the benefit of very low sodium sulphate levels, low BOD and COD emissions to effluent, and almost eliminating the use of any other reducing agents or auxiliary chemicals.

Today Dystar claim that their "Indigo Vat 40% Solution" to be the best available technology, in terms of total production cost, quality and ecological impact. An eco-efficiency analysis of alternative indigo sources and application processes claimed advantages of pre-reduced indigo over natural and synthetic parent pigment forms of indigo and showed the combination of pre-reduced indigo prepared by catalytic hydrogenation and its use in electrochemical dyeing as the most eco-efficient process.

The latest laboratory research developments [9], which are close to industrial realization, show the potential of the electrochemical dyeing process, which is in principle the cleanest and most economic indigo dyeing process, and offers the perspective of an automation of the dyeing process.

Bacterial-driven reduction of indigo is currently confined commercially to a minor role for niche products. In terms of future developments, it is foreseen that the bacterial system will remain a small-scale process compared with the large-scale chemical and electrochemical systems for delivering pre-reduced indigo. However, the bacterial system does offer a sustainable process that uses renewable and cheap carbohydrate resources.

Wet processing in the supply chain

The last significant area of concern in the supply chain is that of garment wet processing. Historically, garment processing was on the periphery of the industry carried out mainly by general laundries whose business was also washing products such as bedlinen (hospitals and hotels) and rental workwear. Today the fashion garment processing industry is completely separate from the general laundries, and is at the centre of the denim industry in terms of product development and technological advancements.
Most casual garments today will have been through some laundry process, from a simple softening or soft wash to easy-care resin finish to a complex jeans process. Originally, all jeans on the market were stiff and uncomfortable when first purchased, due to how denim fabrics were finished. Consumers would have to wash their newly bought garments several times at home to break down the starch or size that was on the fabric before they were comfortable to wear.

The first step in the jeans processing evolution was to produce laundered garments to sell in store. These slightly faded "pre-washed" jeans became the fashion despite the extra cost. The next part of the evolution was to produce garments that looked like they had been previously worn. In these pioneering days of jeans washing, the techniques developed were quite crude, and to achieve a worn look involved the use of abrasive stones to accelerate the ageing process. "Stone washing" was born - pumice stones were tumbled around with damp jeans at a ratio of about 2:1, which resulted in abrasion to belt lops, hems, pockets etc. Further evolutionary steps added to this crude physical degradation technique by the introduction of chemicals. Bleaching agents, particularly chlorine bleaches, were found to accelerate the fading of the indigo and so the "indigo washed down" was born.

This technology was being developed and used during the late 1980s and in the subsequent 20 years or so there has been a significant change in the industry. It has transformed from a segmented part of the textile industry, with institutional laundries using "Black Art"

techniques to become an integral part of textile industry, with dedicated commission and vertical companies, leading in product and process development and is now at the forefront of meeting the seemingly insatiable demands from the market for new product ideas. During the 1990s there was a quiet revolution, when different enzymes were introduced into the industry. For the denim washing industry these included:

Amylase for removing starch-based sizes, catalase for removing hydrogen peroxide after bleaching, cellulase for modify the surface of cellulosic fabrics to achieve a desired hand or surface effect and laccase for decolorizing indigo during denim processing.

The commercial success of this biotech in the replacement of pumice stones in stonewashed denims was seen as being the future at the time. A cupful of enzymes were able to replace hundred times the weight of stones, resulting in less wear and tear on the machinery, less dust as well as improved and consistent output. However the idea that "stone washing" had been put back where it belonged in the Stone Age proved to be premature.

The general garment processing industry is organized into washing, dyeing and finishing (see Figure 2). Garment washing involves hand improvement, color removal, de-hairing and imparting distress. Garment Dyeing is color addition and garment finishing is about imparting performance.

Techniques applied under these descriptions are as follows:

Garment Washing
- Hand Improvement - soften, stoning, enzyming
- Color Removal – bleaching, ozone
- De-Hairing - enzyming
- Impart Distress - sandblasting, brushing, laser

Garment Dyeing
- Color Addition - reactives, directs, sulphurs, pigments

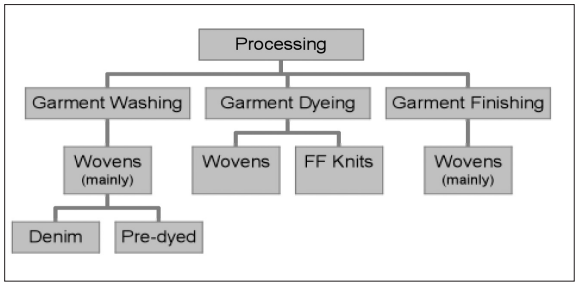

Figure 2. *Scheme of general garment processing.*

Garment Finishing
- Impart Performance - wrinkle free, repellency

New denim finishing technologies

In fact, "new" techniques introduced over the last 20 years have actually only gone on to supplement the older more crude techniques rather than replace them. This resistance to newer techniques was driven by designers who believed that enzymes could not convincingly replace the aesthetics achieved with stones. It is only the recent and growing concerns over environmental and social issues that have started to drive real change in finishing techniques employed in the denim industry.

Two technologies in particular are making the headlines – the use of laser and ozone.

Previously dry technologies included hand brushing, hand scraping and sandblasting and wet techniques included the use of pumice stone washing, perlite washing, bleach spray and enzyme washing. The use of lasers now has the ability to replace current abrasive techniques all of which have different combinations of issues related to ecology or worker safety. Additionally the laser can be attached to a CAD/CAM system which allows for 100% reproducibility from garment to garment, something that previously was impossible.

Ozone-induced fading of denim was known about for many years but in a negative way. Garments stored over a period of time would start to fade especially when exposed to sunlight. Ozone breaks the double bond in the indigo molecule, and the oxidation by-products of indigo formed are isatin, anthranillic acid and complexes of the two products. These two decomposition products together give a faded yellowish color. Poorly fixed dye tended to be more susceptible to ozone. So finally the use of ozone technology has been put to a more positive use by being an environmentally credible replacement for the bleach-down process.

Depending on the desired effect, several bleaching processes have been developed to accelerate the fading down of denim jeans, including such chemicals as sodium hypochlorite, potassium permanganate, glucose, and laccase. Issues surrounding such bleaching products include huge water use, chemical load of effluent, product reproducibility, processing costs and worker health and safety.

Ozone offers an ecological and practical bleaching alternative. Air from the atmosphere is transformed into

a blend of active oxygen & ozone called plasma in a totally self contained machine. The plasma is transformed back into purified air before being returned to the atmosphere. Due to its effective oxidizing potential, denim jeans processing can benefit from significant savings; From a case study of actual production in the US, the company claims that using G2 can result in 67% savings in energy and water, 55% savings in time and 85% saving in chemicals and can thus provide a saving of $0.44 per garment washed besides contributing to environmental protection and reducing health hazards for the workers [10].

Combining laser techniques with ozone technology now has the potential to create a step change in the industry in terms of reducing the environmental footprint of producing denim jeans.

Finally the industry is waking up to the above technologies, because on many levels there are savings to be made in water, energy, effluent treatment and worker safety which positively affects the bottom line.

Additionally brands and retailers are also driving change as they adopt more and more sustainable practices as part of their CSR policy. An example of this has been the banning of sandblasting by the majority of western brands. Finally the industry has had to recognize the growing number of cases of ssilicosis as a result of workers being exposed to inhalation of crystalline silica, as used in abrasive blasting [11].

Finally tools are now being developed which help individual companies to assess potential environmental improvements and consequently be confident that any investments along those lines will result in financial savings. The Environmental Impact Measuring tool (E.I.M.) is the first software specifically designed for the garment processing industry. It has been created to provide the laundries and garment finishers with a tool that helps them to build more sustainable processes.

Washing managers in many companies today are eager to reduce pollution and they are keen to make their processes sustainable. However garment finishing processes are complex and the number of combinations of laundry processes to produce a particular look is infinite. Such a scenario can be daunting, even for a professional technician or manager, so the creation of this simple and efficient tool is a positive development for the whole industry.

This software from Jeanologia [12] aims to show the environmental impacts of the following individual categories (Figure 3):

- Water consumption
- Energy consumption
- Chemical product used
- Worker health

Inputting information from existing processes provides the user the opportunity to identify the major causes of environmental hazards of his washing process

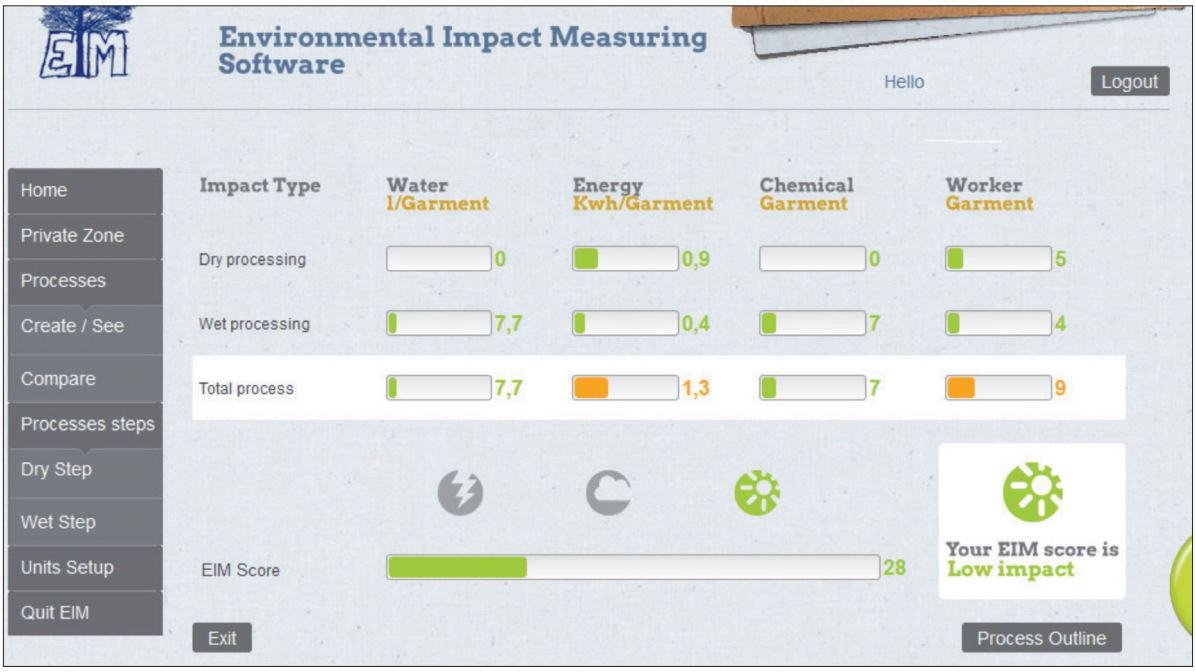

Figure 3. *Screenshot of the Jeanologia software [12].*

and thus help him arrive at a decision on which processes need to be changed.

Environmental awareness and fashion consciousness are not necessarily mutually exclusive. Finally parts of the textile and fashion industry that have been ignoring their environmental and social responsibilities for a long time are starting to change. It could be argued that this change is being driven by the promise of financial savings, but at least those savings are directly linked to improvements in water saving, energy savings, pollution reduction and worker safety.

Lenzing are happy to be associated with the denim industry and are working with many partners in the supply change to initiate change for good. Plans are in place to develop this work further coming together with key industry figures. It is hoped that such a project can influence the widest audience yet in the need for the industry to adopt a holistic environmental stance.

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Major changes of the human skin microbiota associated with wearing of Polyester-based sports textiles next to the skin

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Abstract

Human skin harbours up to one million bacteria per cm^2 containing more than five hundreds of different species. Under certain conditions (e.g. enhanced sweat production) and in association with textiles these high levels of bacteria can cause problems like odour generation, discoloration and loss of performance of the textiles. Since some textiles, especially sports- and underwear, are in physical contact with the skin, it can be speculated that they might directly influence the composition of the skin microbiota. For this purpose we performed wearing-trials using sports textiles made of 100% polyester. The composition of the skin microbiota before and after the wearing trials was analyzed by using a culture-independent method based on DNA sequence analysis of the bacterial metagenome of the skin. We found that polyester-based textiles directly influenced the composition of the skin microbiota. The most surprising result was a drastic change in the relationship between Gram-positive and Gram-negative bacteria, before (94% Gram-positives versus 4% Gram-negatives) and after (63% Gram-postives versus 37% Gram-negatives) the wearing trials. Preliminary experiments indicate that this effect seems to be material-dependent, since such drastic changes in the microbiota were not found in wearing trials using TENCEL®-based textiles.

Keywords: *sports textiles, skin bacteria, polyester, TENCEL®*

Introduction

Recent investigations using culture-independent methods have revealed the skin to harbour one of the largest human-associated bacterial communities [1-3]. Although there seems to be a core set of specific bacterial taxa commonly found on human skin, a high intra- and interindividual variability in community composition was found. Some factors driving this variability have been investigated in more detail. Not surprising, there is a great diversity of bacteria within and between distinct areas of the skin [4,5]. These areas show a broad range of differences in pH, temperature, moisture, sebum and lipid content and skin structures. Therefore the high variability of the skin microbiota reflects the physiological conditions of the different areas [6]. In addition, the skin microbiota will also be influenced by more external factors. For example, the community composition of the microbiota of hands is significantly affected by washing procedures [7]. Another factor with a high potential to significantly influence the skin microbiome might be textiles.

Textiles are in permanent contact with skin bacteria, either by sweat containing bacteria or by direct contact with skin. They have a strong effect on sweat production and consequently have much influence on bacterial growth, since enhanced retaining of sweat by textiles will lead to a persistent increase of the metabolic and growth activity of bacteria. As a result, the increased bacterial activity can cause problems like odour generation, discoloration, and loss of performance of the textile. Recent investigations have demonstrated selective growth of specific skin bacteria on different textile materials. Selective enrichment of potential odour producing and haemolytic bacteria on synthetic materials compared to organic materials was found [8,9]. This seems be due the different physicochemical properties of textile materials, which consequently in-

fluence attachment and retaining of specific bacteria present on skin or in sweat [10].

Therefore, one might also presume that textiles, especially sports textiles and underwear, may directly influence the physiological skin microbiota, because they are in physical contact with skin. For this purpose, we have investigated whether Polyester-based (PES) sports textiles can induce a change in the bacterial diversity of the human skin. Polyester fibres are extensively used in sports textile industry, because they provide specific advantages for sports textiles like a good moisture transport and fast drying. Nevertheless, synthetic textiles can produce odour and are perceived by many as having a less-natural feel compared to fabrics woven from natural fibres. Therefore, there is some trend to replace synthetic materials also for sports textiles.

For our investigations we have performed wearing trials and have analyzed the skin microbiata before and after the trials by culture-independent methods using PCR amplification and DNA sequencing to overcome the serious limitation of culture-based techniques. In addition, we have performed preliminary experiments using TENCEL®-based textiles to investigate material-dependent differences.

Materials and Methods

WEARING TRIALS

Polyester (100%) and TENCEL® (100%) based arm warmers, similar to that used in bike sports, were worn for 8h per day for a 6-day time period. The material was prewashed by 3 cycles before the wearing tests.

SAMPLE COLLECTION

Swabs from superficial skin were obtained from the volar left forearm of three healthy subjects, with no history of dermatological disorders or other chronic medical disorders and with no current skin infections. None of the subjects had received any antibiotics for at least one month. Subjects were instructed not to wash with anything for an 8-h interval prior to sampling. Samples were taken from 2 x 2 cm of skin, from the central area of the volar left (flexor) forearm, midway between wrist and elbow, by swabbing the skin for 1 min with a sterile cotton swab that had been soaked in sterile 0.15 M NaCl with 0.1% Tween 20. To minimise sample cross-contamination a fresh pair of sterile gloves was used for each individual sampling process. Reagent controls consisted of sterile cotton swabs moistened with a solution of sterile 0.15 M NaCl and 0.1% Tween 20 and placed directly in 1.5 mL microcentrifuge tubes.

DNA EXTRACTION FROM SKIN SWABS

DNA was extracted using the DNeasy Blood and Tissue Kit (Qiagen, Hilden, Germany). Since Gram-positive bacteria are more resistant to lysis than Gram-negative bacteria, the manufacturer's protocol for genomic DNA isolation from Gram-positive bacteria was followed with modifications. The cotton tip of each swab was broken off directly into a 1.5 mL tube to which 180 μL of lysis buffer had been added. The tubes were capped and shaken by hand horizontally for 30 seconds. The remaining steps were performed as suggested by the manufacturer.

16S RDNA AMPLIFICATION, CLONING PROCEDURE AND SEQUENCING

PCR amplification was performed with primers specific for conserved bacterial 16S rDNA sequences. PCR primers F 8: 5´- AGAGTTTGATYMTGGCTCAG - 3´ and R 1401: 5´- CGGTGTGTACAAGACCC - 3´ amplified a bacterial 16S rRNA encoding gene fragment from nucleotide positions 8 to 1401 (Escherichia coli numbering, GenBank J01859). These primers span over 8 (V1-V8) of the 9 hypervariable regions of the bacterial 16S rRNA and were chosen due to the fact that most sequences in databases are available for regions V1-V8. PCR amplification was performed using the following conditions (final concentrations): 1x GoTaq reaction buffer (Promega Madison, WI, USA), 0.2 mM dNTPs, 50 pmol of each primer and 2.5 U GoTaq Polymerase (Promega, Madison, WI, USA) and 10 ng of DNA in a total volume of 50 μL. 30 cycles of PCR amplification were performed. Each of them entailed denaturation at 95°C for 60 s, annealing at 48°C for 60 s and primer extension at 72°C for 60 s. PCR products were analyzed on 1.2% agarose gels, stained with ethidium bromide. The PCR fragments were gel eluted using Wizard® SV Gel and PCR Clean-Up System (Promega, Madison, WI, USA). 10 ng of DNA was ligated with the pGEM-T vector (Promega, Madison, WI, USA) and transformed into E. coli DH5α competent cells. The complete insert was cycle sequenced using M13 primers for amplification and T7 and SP6 primers for sequencing on an ABI PRISM 3100 Genetic Analyser.

DATABASE AND PHYLOGENETIC ANALYSIS

Analysis of closest relatives was done by comparison of the entire amplified rDNA sequence (without primer sequences) with sequences available in the Ribosomal Database Project (RDP) II (RDP Release 10.23) and GenBank databases, by using the standard nucleotide-nucleotide BLAST program (BLASTN-megablast). A 98% sequence identity cut-off was used for defining bacterial species.

Results and Discussion

COMPARISON OF THE SKIN MICROBIOTA BEFORE AND AFTER WEARING TRIALS WITH PES-BASED TEXTILES

Table 1 gives an overview of the bacterial species and sub-species present on the skin before and after the wearing trials of all persons investigated. For each person 96 bacterial clones were analyzed. All together 72 different bacterial species were identified on the analysed area (2 x 2 cm) of the forearm, supporting the high diversity of the skin microbiota as described previously [3,4]. 32 different species were identified on the skin before the wearing trial. Propionibacterium acnes was found to be

Table 1. *Bacterial species present on skin before and after the wearing trials with PES textiles. Gr^+ = Gram-positive bacteria, Gr^- = Gram-negative bacteria.*

		Skin before	Skin after	Skin1	PES1	Skin2	PES2	Skin3	PES3
Gr+	Actinomyces oris	4						4	
Gr+	Aeromicrobium erythreum		1						1
Gr+	Arcanobacterium haemolyticum	1						1	
Gr+	Bacillus amyloliquefaciens/subtilis		12		7		5		
Gr+	Brachybacterium arcticum	2						2	
Gr+	Brevibacterium casei		1				1		
Gr+	Brevibacterium linens	2						2	
Gr+	Brevibacterium pityocampae	2						2	
Gr+	Corynebacterium appendicis	2						2	
Gr+	Corynebacterium aurimucosum		1				1		
Gr+	Corynebacterium casei	1						1	
Gr+	Corynebacterium coyleae/mucifaciens/ureicelerivorans	12	1		1	1		11	
Gr+	Corynebacterium diphtheriae	3						3	
Gr+	Corynebacterium kroppenstedtii	2						2	
Gr+	Corynebacterium mucifaciens	2	1					2	1
Gr+	Corynebacterium striatum		1				1		
Gr+	Corynebacterium tuberculostearicum	3	4	1		1	2	1	2
Gr+	Corynebacterium variabile	2						2	
Gr+	Deinococcus aquatilis		4		4				
Gr+	Dietzia cinnamea/maris	2		2					
Gr+	Geobacillus pallidus	2	4	2	2		2		
Gr+	Kocuria palustris	2						2	
Gr+	Kocuria rhizophila	1						1	
Gr+	Lactobacillus brevis		1				1		
Gr+	Lactobacillus sakei	1						1	
Gr+	Leuconostoc carnosum		1				1		
Gr+	Micrococcus luteus	1						1	
Gr+	Nesterenkonia flava		6				4		2
Gr+	Propionibacterium acnes	82	33	37	4	43	6	2	23
Gr+	Propionibacterium freudenreichii	1						1	
Gr+	Propionibacterium propionicum	1				1			
Gr+	Rothia dentocariosa/mucilaginosa	2		1				1	
Gr+	Solirubrobacter soli	1						1	
Gr+	Sphaerobacter thermophilus		2						2
Gr+	Staph. capitis/caprae/epidermidis/aureus/haemolyticus	2	10	2	1		5		4
Gr+	Staphylococcus hominis/pasteuri		2				2		
Gr+	Streptococcus agalactiae	1						1	
Gr+	Streptococcus pneumoniae/mitis/pseudopneumoniae		1		1				
Gr+	Streptococcus sanguinis		3		1		2		
Gr+	TM7 phylum sp.		2				1		1
Gr+	Tsukamurella inchonensis	1		1					
Gr-	Acidovorax avenae		1				1		
Gr-	Acidovorax delafieldii		1						1
Gr-	Acidovorax temperans		2		1		1		
Gr-	Acinetobacter johnsonii	1						1	
Gr-	Acinetobacter parvus	1						1	
Gr-	Acinetobacter radioresistens		1		1				
Gr-	Acinetobacter septicus		1		1				
Gr-	Aggregatibacter segnis		5				4		1
Gr-	Alkanindiges hongkongensis		1		1				
Gr-	Bosea massiliensis/thiooxidans	1		1					
Gr-	Brevundimonas intermedia		1		1				
Gr-	Brevundimonas subvibrioides		5		5				
Gr-	Caulobacter vibrioides		1				1		
Gr-	Coprococcus catus		1		1				
Gr-	Escherichia coli	2	1			2			1
Gr-	Haematobacter massiliensis		1						1
Gr-	Haemophilus parainfluenza/meridiana		3				3		
Gr-	Halomonas nitritophilus		1						1
Gr-	Hymenobacter rigui		1		1				
Gr-	Klebsiella oxytoca		3		1		1		1
Gr-	Mesorhizobium mediterraneum		1						1
Gr-	Methylobacterium adhaesivum		1		1				
Gr-	Methylobacterium jeotgali		6		6				
Gr-	Methylotenera mobilis/Microbacterium lacticum		6		6				
Gr-	Paracoccus versutus		1						1
Gr-	Prevotella loescheii		1		1				
Gr-	Rhizobium tropici		2				1		1
Gr-	Rhodanobacter terrae		4				2		2
Gr-	Veillonella dispar/parvula	1		1					

the most prominent species on the skin of person 1 and 2 and Corynebacterium sp. was predominant in person 3. The diversity of bacterial species before the wearing trial was low, which is typical for a relative dry and unprotected skin area. However, the species diversity was increased after the wearing trial, with 46 species detected. This suggests that textiles indeed directly influence the diversity of the skin microbiota. Interestingly, the number of Propionibacterium acnes of person 1 and 2 was drastically decreased, and a significant increase in Bacillus subtilis could be observed after the wearing trial. In person 3, the predominant Corynebacterium sp. disappeared and there was an increase in Propionibacterium sp.

The significant enhancement in diversity is also indicated by the number of bacteria phyla found before and after the wearing trials (Figure 1). Before the wearing trials the skin of all persons showed a relatively simple phyla composition, which was found to be much more complex after the wearing trials.

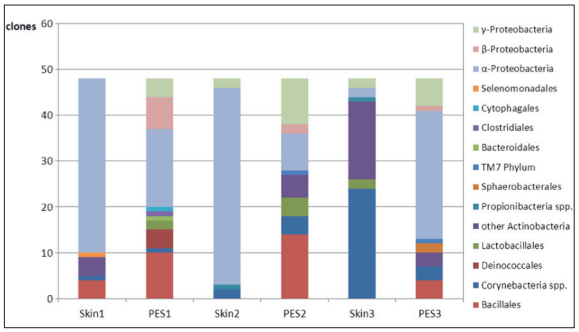

Figure 1. *Relative abundance of the most prevalent bacterial phyla present on the skin of the persons investigated (1-3), before (Skin 1-3) and after (PES 1-3) the wearing trials.*

A closer look to the major changes induced by the wearing trials revealed that there was a drastic change in the relationship between Gram-positive and Gram-negative bacteria after the trials (Figure 2 A and B). Before the wearing trials almost all bacteria present were Gram-positives (95.8%) and the Gram-negatives were highly underrepresented (4.17%). However, this relationship was significantly changed after the wearing trials, with a strong increase of Gram-negatives (36.81%) and a decrease of Gram-positive species (63.1%).

We did not find remarkable permanent changes in skin parameters, like skin pH or skin moisture during the wearing trial (data not shown), which could account for the changes found. Therefore, we suggest that the hydrophobic PES might induce some temporary changes in the microenvironment of the skin, which favours enhanced growth of Gram-negative bacteria. It is a well known fact that Gram-negative bacteria are more sensitive to harsh environmental conditions. Thus, the „protective" microenvironment generated by the PES textile might favour growth of this group of bacteria. Whether this effect has positive or negative consequences needs to be proven by further studies. However, it is noteworthy that growth of Bacillus subtilis, which is known to be an odour producing bacterium [11], was enhanced after the wearing trial. In addition, also some potential pathogens, like Klebsiella pneumoniae and Haemophilus influenza were detected on the skin after the wearing trials.

PRELIMINARY RESULTS FROM WEARING TRIALS USING TENCEL®-BASED TEXTILES

To investigate, whether the influence on the skin microbiota found with PES-based textiles is material-dependent or a more general mechanism, we performed the same wearing trials as described above with TENCEL®-based textiles. As evident from the results presented in Figure 3, no drastic change in the relationship between Gram-positive and Gram-negative bacteria was found using this material. These results strongly support the idea that different materials have diverse effects on the skin microbiota. In contrast to PES, TENCEL® is a more hydrophilic material, which probably prevents a significant chance of the microclimate of the skin, which might occur with the PES material.

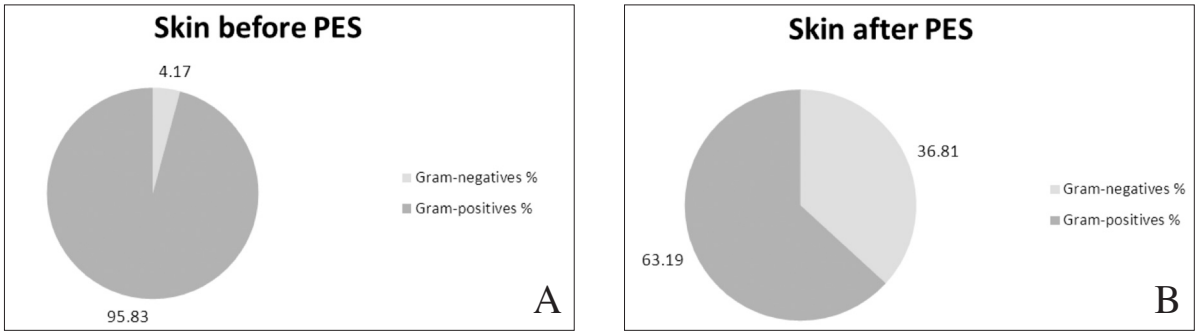

Figure 2. *Changes in the relationship between Gram-positive and Gram-negative bacteria after the wearing trials with PES textiles. A) before the wearing trials, B) after the wearing trials.*

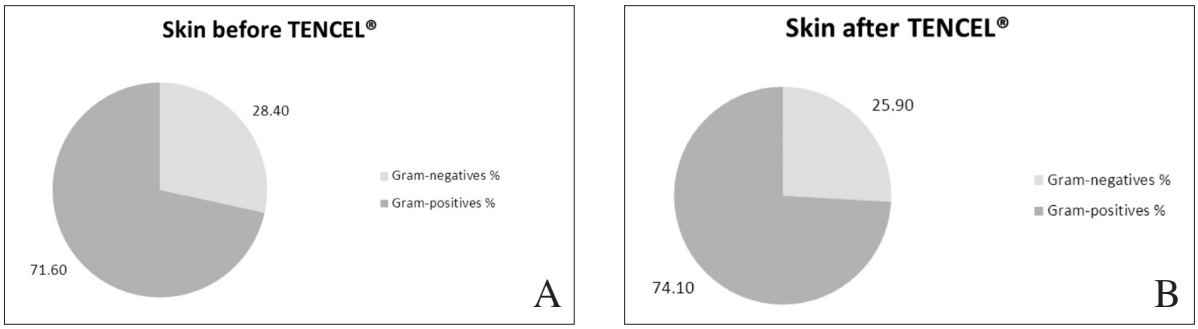

Figure 3. *Changes in the relationship between Gram-positive and Gram-negative bacteria after the wearing trials with TENCEL® textiles. A) before the wearing trials, B) after the wearing trials.*

Conclusions

Our investigations clearly demonstrated that the diversity of the skin microbiota can be directly influenced by textiles, especially by those worn next to the skin. A drastic change of the relationship between Gram-positive and Gram-negative bacteria was found after wearing trials with PES-based textiles. We conclude that PES favours growth of the more sensitive Gram-negatives, which is probably due to temporary changes in the microenvironment induced by this material. This effect seems to be strongly material-dependent, since no relevant change in the Gram-positive/Gram negative composition was found in skin after wearing trials with TENCEL® -based textiles.

Acknowledgements

The authors would like to thank the Österreichische Forschungsförderungsgesellschaft (FFG) for financial support.

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A new viscose fibre with intrinsic natural flame retardancy

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Abstract

Nowadays, cellulosic and, especially, viscose fibres find more and more functional applications.
While they were originally designed as a substitute for cotton, it was soon found out that through modification of production parameters, fibres with special properties - like flame retardancy - could be made.
„Verdi“ is a 100% anionic viscose fibre which is self-extinguishing without any additional chemical additives, for example halogen, phosphorus or bor, thus it is perfectly suited for a consumer market which prioritizes protection, comfort, freedom of potentially hazardous substances and sustainability.

Keywords: *Viscose, flame retardancy, Kelheim Fibres*

Introduction

Most people already know some fibres and their chemical additives which can be used for flame-retardant protective clothing and it is obvious that such protective clothing is necessary for certain workwear (e.g. for firemen).

But while the importance of flame-retardant clothing is evident in the professional sector, the private sector is rather neglected. Many people like to think „that will not happen to me“, or they abstain from possible protective clothing for fear of hazardous chemical agents in the clothing they wear on their skin. In recent years, lots of fires which caused heavy injuries to people, children, elderly people and adults were started because their clothing caught fire.

The goal of flame-resistant clothing is to save and protect the lives of the consumer by preventing loose clothing from catching fire. The primary concern is the fact that people are not always as careful as they should be around open flames, such as candles and fireplaces.

In the end, consumers need to decide if concerns about chemical use outweigh their concerns about fire safety.
With „Verdi“, Kelheim Fibres provides a 100% cellulosic based flame-retardant viscose fibre without any additional chemical agents, which is free of halogen, phosphorus and bor - consumers don‘t need to make a compromise any more. They get flame-retardance as a real benefit wi thout any tradeoffs.

Materials and Methods

Initially, the investigation was based on a comparison of two different nonwoven fabrics containing 100% Viscose with 1.7dtex, and 100% Verdi, with 1.9dtex, in weights of 100g/m² and 210g/m² each.
The samples ware created at STFI in the development of the project „Cellulosic fibres with a new functionalitiy for protective clothing against cold“ („Cellulosefasern mit neuer Funktionalität für Kälteschutzkleidung“) in collaboration with the Hohenstein Institute. Additional research in testing the flammability of blends of Verdi and other cellulosic fibres is still in progress.

LOI

The LOI (Limiting oxygen index) can be used to specify the flammability of a textile. It is measured by applying an oxygen/nitrogen-mix to the burning sample; if the sample burns for longer than 180s or the burning reaches a predefined mark, the oxygen level is gradually reduced. The LOI describes the minimum concentration of oxygen in an oxygen/nitrogen-mix which supports combustion. Thus, high LOI values mean good flame-retardancy; LOI values are determined by a standardized test, such as ISO 4589.

BURNING BEHAVIOUR TESTS ACCORDING TO DIN EN 14878

The nonwoven samples were tested according to DIN EN 14878, "Textiles-Burning behaviour of children's nightwear – Classification schemes". The specifications of this test standard can also be used for children's clothing in general, like nonsnug-fitting garments which might get in contact with open fire.

WEARER COMFORT

The thermophysiological wearer comfort, which was developed as a testing method by the Hohenstein Institute, allows measuring the comfort of textile garments. It is measured with a skin simulation model based on correlation between test devices and real persons, in the climate chamber. It allows predicting whether the garment will feel warm to a customer, if it will feel wet when the customer is sweating or if it will feel cold to the touch.
For the first round of trials, the following tests were carried out:

- Thermal Insulation ($R_{ct} \cdot 10^3$ m² K/W)
  Test Equipment: The Hohenstein Skin Model
  Test Methods: see DIN EN 31 092 (02/94)/
  ISO 11 092 (10/93)

- Water Vapour absorbency potential (F_i g/m²)
  Test Equipment: The Hohenstein Skin Model
  Test Methods: see DIN EN 31 092 (02/94)/
  ISO 11 092 (10/93)

Results and Discussions

LOI

Verdi showed a higher LOI than Viscose, Cotton and then polyester; it showed a similar performance to wool (Figure 1).
As Verdi is aimed for the private consumer market, no comparisons to FR fibres (e.g. Trevira CS) were made.

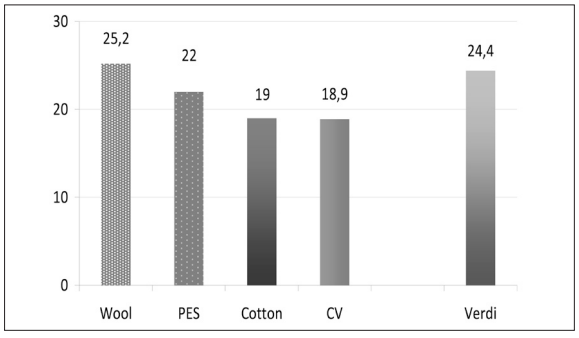

Figure 1. *Comparison of LOI (limiting oxygen index) of various fibres.*

BURNING BEHAVIOUR TESTS ACCORDING TO DIN EN 14878

Referring to DIN EN 14878, samples were examined lengthwise and laterally and marker threads were attached to the samples in order to be able to determine the speed of flame spreading. (1st marker thread: 22cm; 3rd marker thread: 52cm).
Then the samples were put into an ignition chamber. Afterwards, the samples were tested for side-effects (like holes, melted spots).

Verdi is self-extinguishing, i.e. the flames stop spreading. After extinction, the fibre continues to smoulder. The balance between burning and carbonisation is shifted more towards carbonisation, generating less energy.

Compared to a standard viscose fibre, the speed of flame spreading with Verdi was over 95% slower.

The following chart shows the speed of flame spreading in mm/s (lower is better) (Figure 2).

WEARER COMFORT

In order to test the wearer comfort for the consumer, we carried out some tests with the Hohenstein Skin Model.

THERMAL INSULATION ($R_{ct} \cdot 10^3 M^2$ K/W)

With identical weight, Verdi showed a slightly better thermal insulation compared to a standard viscose fibre (Figure 3).

WATER VAPOUR ABSORBENCY POTENTIAL (FI G/M²)

The measurement of water vapour absorbency potential defines the capability of the fabric to absorb moisture from the skin.
Verdi showed an increase in water vapour absorbency potential of over 32% compared to a standard viscose fibre (Figure 4).

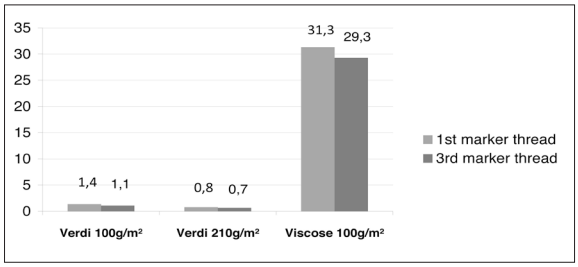

Figure 2. *Burning behaviour tests according to DIN EN 14878.*

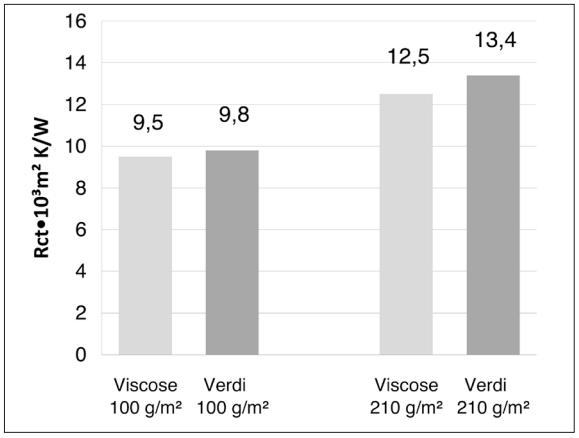

Figure 3. *Thermal Insulation (R_{ct}·10³ m² K/W).*

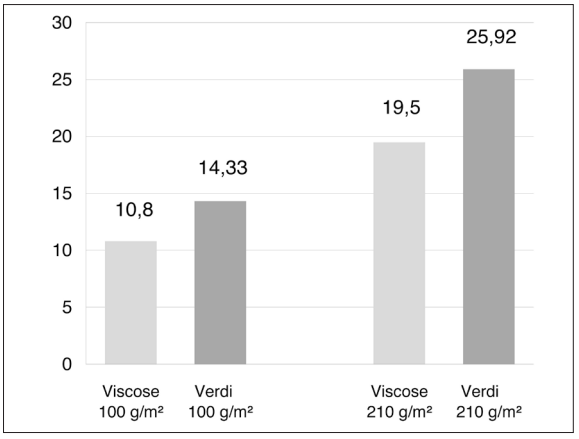

Figure 4. *Water Vapour absorbency potential (Fi g/m²).*

Conclusions

Verdi will help to save lives - by providing time through self-extinction.

The intrinsic flame-retardant effect of Verdi is achieved by an additive which is applied during fibre production and it is not necessary to use chemical agents in a finishing process afterwards. Thus, the effect is permanent and cannot be washed out. The additive in Verdi is certified for use in foods; It is halogen-, phosphorus- and bor-free.
With Verdi, there is no danger to the health by potentially dangerous chemical agents - garments can be worn directly on the skin. In first trials, Verdi showed similar good processability compared with a standard textile viscose fibre with a similar fibre titre.
All in all, Verdi is the no-compromise fibre for a private consumer market - it adds real benefits without any downsides while bringing protection and the comfort of a 100% cellulosic fibre.

Thus, Verdi is the best natural solution to prevent severe injuries caused by burning clothes while being environmentally friendly.

Acknowledgements

The author would like to thank all colleagues who helped in the creation of this project in general and this paper in particular.

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Flame Protection with Comfort from Lenzing Fibers

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Introduction

TENCEL® lyocell has been available in the market for seventeen years. In it's early stages of introduction the market accepted lyocell for its ability to generate new and exciting aesthetics, particularly because of its softness and peach-like touch.
More recently lyocell has found applications in market segments that are driven more by performance than fashion. These applications utilise more conventional dyeing and finishing technology such as full open width processing often coupled with resin finishing to control the fiber fibrillation in subsequent washing.
Recent studies in Lenzing have demonstrated that lyocell fibers have a unique semi-micro fibrillar fiber structure which gives rise to extremely valuable moisture handling and comfort properties. The paper will briefly explain some of these studies.
The main body of the paper will report on studies made investigating the application of conventional Flame Retardant (FR) topical treatments, showing advantages in terms of comfort, softness and performance that can be realised in 100% lyocell fabrics together with blends of lyocell with cotton.

Why use TENCEL®?

FOR THE ENVIRONMENT

TENCEL® lyocell is produced from 100% natural raw materials – woodpulp. This pulp is obtained from sustainable forest management, where the trees are farmed on a ten year growing cycle.
The production process is a state of the art closed loop solvent spinning process, whereby wood pulp, water and solvent are the only inputs and fiber, water and solvent are the only outputs. The solvent, N-Methylmorpholine-N-Oxide is non-toxic and is 99.9% recycled.
Figure 1 below shows the fiber production process in schematic form.

FOR COMFORT

A Microporous structure

TENCEL® fibers are man-made cellulosic fibers produced by the lyocell process, a direct dissolution spinning process through regeneration from a solvent (N–Methylmorpholine–N–Oxide) [1] [2]
In high magnification transmission electron micrographs (Figure 2) it can be seen clearly that the pore structure of lyocell is a submicro-fibrillar structure.

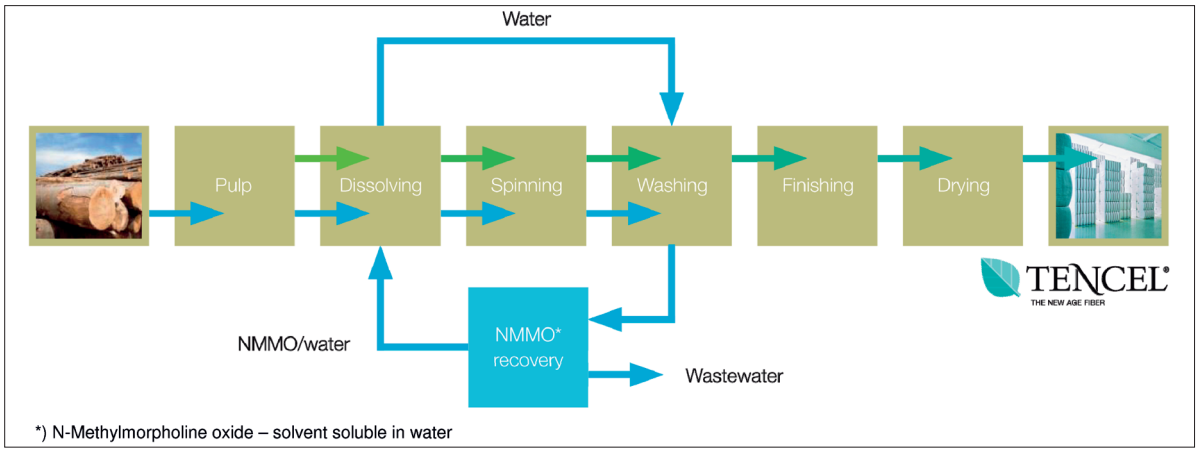

Figure 1. *TENCEL® lyocell fiber production process.*

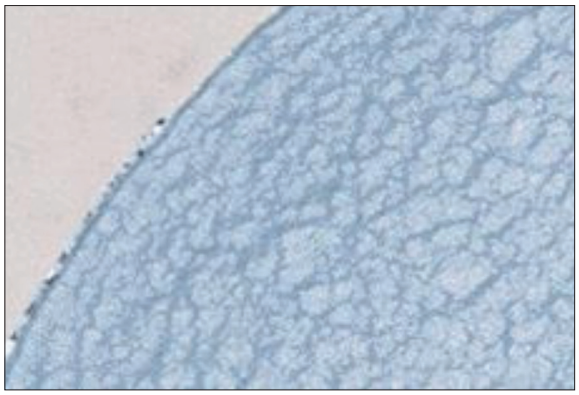

Figure 2. *Transmission Electron Micrograph Image of TENCEL® lyocell fiber.*

This is unique amongst all man–made cellulosic fibers. Lyocell consists of countless, very hydrophilic, crystalline fibrils, which are arranged in a very regular manner. The fibrils themselves do not absorb water; water absorption only takes place in the capillaries between the fibrils. A single lyocell fiber, therefore, will behave like an ideally wetting micro multifilament, something which does not exist in the synthetic fibers world. This is the reason for the excellent water management and the very good comfort in wear of textiles containing TENCEL® [3]

Water Absorbency

The inherent physiological properties depend on the amount of water which is absorbed and how it is distributed within the swollen fiber structure. TENCEL® lyocell has a very high absorption capability and a very smooth surface. As a result, all these physiological functions are much more pronounced for TENCEL® than for other cellulosic fibers.

Transmission electron microscopy can be used to show the location of water in a fiber. For imaging, water-containing pores are filled and stained with a contrasting substance. The water-containing pores show up black, but the cellulose without stain shows up white. Figure 3 shows the cross-sections of four water swollen cellulosic fibers [4].

Cotton absorbs much less water than lyocell, modal or viscose. The crystalline skin of modal contains less water than the core. The water distribution of lyocell is very uniform over the whole fiber cross section. Modal and viscose have a rather coarse pore system with a wide range of pore size distribution from nanometer to micrometer size dimensions. The voids in lyocell are very small and quite uniform, in the nanometer range.

Fiber Surface Smoothness

Textiles come into contact with the skin in various ways. The surface condition and moisture greatly influence the skin's sensory perception. Coarse and wet

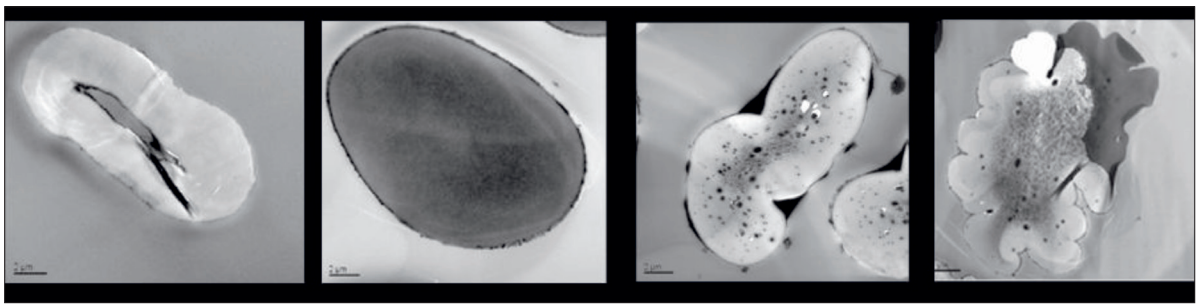

Figure 3. *Position of Absorbed Water in cellulosic fibers. Transmission electron micrographs. Water appears black (electron dense).* Cotton – Lyocell – Modal – Viscose

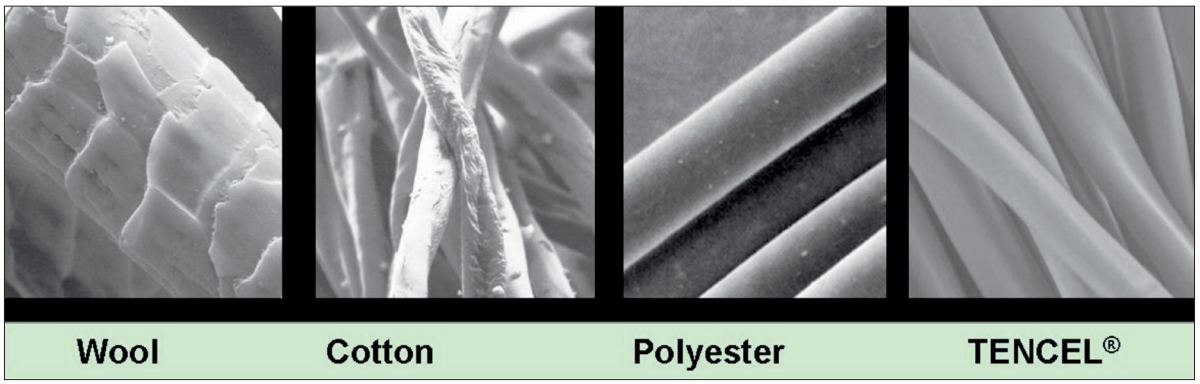

Figure 4. *Electron Micrographs comparing fiber surface features.*

textiles can irritate the skin due to higher friction resistance. TENCEL® lyocell is smoother than other natural fibers. It has a high absorbency that removes moisture from the fiber surface, thus keeping the textile next to the skin much drier and creating less friction. Figure 4 shows the fiber surface.

The inherent physiological properties depend on the amount of water which is absorbed and how it is distributed within the swollen fiber structure. TENCEL® has a very high absorption capability, a unique submicrofibril structure and a very smooth surface. As a result, all these physiological functions are much more pronounced for TENCEL® than for other cellulosic fibers [3].

Topical Flame Retardant Treatments

Fabrics can be treated to make them flame retardant by applying an appropriate chemical to the fabric. The first FR treated fabrics used inorganic salts such as aluminium hydroxide, antimony trioxide and borates to make cotton fabrics flame retardant. These were effective but were not durable to washing. The sparingly soluble inorganic salt is gradually removed by successive washes until there is insufficient left to make the fabric flame retardant. Inorganic salts are used to flame retard fabrics where washing is not normally required such as theatre curtains and back coating of upholstery fabrics.
Organic phosphorous containing compounds that are reacted onto the cotton either by grafting or network formation are more durable and are widely used. Two of the leading brand names are Proban (Rhodia) and Pyrovatex (Huntsman). These finishes are durable to extended washing but they can be removed by harsh chemical treatments. The level of finish reduces with successive wash cycles and it is common practice to use an excess of finish so that sufficient is still present at the end of the life of the fabric. The finish application has an adverse stiffening effect on the fabric. FR cotton fabrics of this type are in use for protection from flame.
FR treated cotton fabrics are of noticeably stiffer hand than non FR cotton fabrics and their surface tends to be rougher. These factors make the garments made from FR treated cotton fabric less comfortable to wear than garments made from untreated cotton and they may be unpleasant to the touch. Treatment with an FR finish reduces the physical properties of the fabric particularly tear strength, and can significantly affect the fabric hand and softness. This can have a marked effect on the service life of garments made from the fabrics. To overcome this weakening of the fabric, it is common to produce heavier weight fabrics so that the measured tear strength meets the specification for fabrics used for protective clothing and in order to give an acceptable in use performance and service life. Heavier weight fabrics are in general stiffer and thus even less comfortable to wear.
We have already seen in the market a number of chino style trousering applications developed from lyocell alone or more often in blend with cotton that have proved successful as they produce fabrics that are softer, more comfortable, retain strength better on easy care finishing and retain color exceptionally well through multiple washing.
Since the main disadvantages of FR treatments on cotton primarily relate to stiffness of hand and uncomfortable over constructed heavy fabrics an opportunity would seem to exist for lyocell to improve these comfort and wearing properties.

APPLICATION OF FR FINISHES TO LYOCELL AND LYOCELL / COTTON BLENDS

Although simple organic salts can impart excellent flame retardant properties to cellulose, durability to laundering is a prerequisite requirement for apparel applications. The most successful durable flame retardants for cellulose are based on phosphorous and nitrogen containing chemical systems that either react with the fiber or form crosslinked structures on the fiber surface. These are either based on N-methylol dimethylphosponopropionamide or tetrakis(hydroxymethyl)phosphonium chloride or THPC. The former will form crosslinks with the fiber and is commonly available in the market from a number of suppliers of which the most well known is Pyrovatex CP from Huntsman. The latter forms a polymeric structure on the fibers and is a process licensed by Rhodia, well known as Proban.
Whether the system forms crosslinks with the fiber is a key property when considering its performance on lyocell, because crosslinking is needed to prevent fiber fibrillation in laundry.

Pyrovatex CP type
The normal approach is to react the N-methylol dimethylphosponopropionamide in combination with trimethylol melamine and phosphoric acid as catalyst in a pad-dry-cure process. The required add-on is normally 20-30%depending on the weight of the fabric. Washing is needed after curing to remove the acid. These high levels of acid can also result in fiber degradation during the process, so often fabrics need to be over engineered to allow acceptable to be retained after the process.

Table 1. *Effect of Pyrovatex treatment on lyocell and cotton.*

	Fill Tensile strength before treatment (daN)	Fill tensile strength after treatment (daN)	% change	EN532 before washing Afterburn / Afterglow secs	EN532 after 25 x 140ºF washes
100% lyocell	75	63	16	0/0	0/0
100% cotton	59	39	32	0/0	0/0
50/50 lyocell / cotton	69	49	28	0/0	0/0

$(CH_3O)_2P{=}OCH_2CH_2C{=}OCNHCH_2OH$ ➡ OH-Cell
$(CH_3O)_2P{=}OCH_2CH_2C{=}ONHCH_2O$-Cell

A comparison was carried out of the effect of this process on cotton, lyocell and an intimate 50/50 lyocell / cotton blend.

Fabrics:
Warp 80/2 Ne, Fill 1/16 Ne, 97e/in, 51p/in, semi-hopsack structure, 5oz/sq yard
Application recipe:

400g/l Pyrovatex CP – LF
60g/l Knittex MLF new (melamine)
23g/l Phosphoric Acid (80%) (catalyst)
30g/l Turpex ACN new (softener)
30g/l Ultratex FSA new (softener)
5ml/l Invadine (wetter)
80% wet pick up
Pad, dry at 120ºC, cure 5 mins at 150 ºC
Wash off and neutralize.

The test results can be seen in Table 1.

These results are typical. Strength loss of like for like treatments on like for like fabric structures show a significant lower strength loss for lyocell fabrics than on cotton. This is a trend also seen in resin finishing.
It is also important to note that the lyocell fabric remains significantly softer after the treatment than 100% cotton, and that the appearance after washing remains excellent. The crosslinking function of the Pyrovatex finish prevents fibrillation of the lyocell fibers in washing.

Comfort Properties of lyocell / cotton fabrics treated with Pyrovatex CP and comparison with 100% cotton
The comfort properties were assessed using ISO 11092[5] "Textiles- Physiological Effects – Measurement of Thermal and Water Vapour Resistance under Steady state Conditions (Sweating guarded hotplate test)"

This test works as follows:
For the determination of the water vapour resistance, Ret, an electrically heated porous plate is covered by a water-vapour permeable but liquid water impermeable membrane. Water fed to the heated plate evaporates and passes through the membrane as vapour, so that no liquid water contacts the test specimen. With the test specimen placed on the membrane, the heat flux required to maintain a constant temperature at the plate is a measure of the rate of water evaporation and from this the water vapour resistance of the samples is measured.
Basically, the water vapour is driven through the fabric by means of a pressure gradient, resulting from different relative humidities.
The result can be seen in Figure 5.

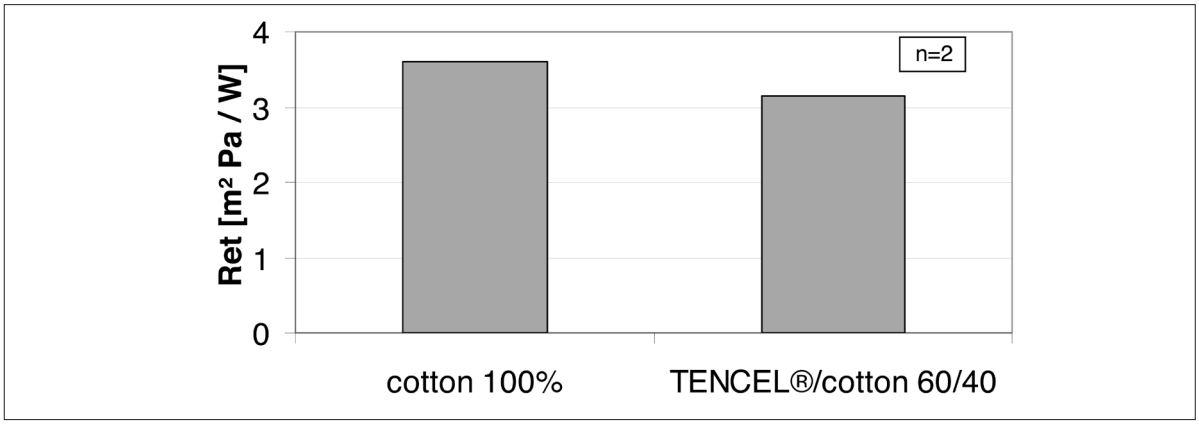

Figure 5. *Water vapour resistance (Ret).*

The results are relatively similar in this measure. This is to be expected as the value is largely dependent on the fabric construction and thickness. Fibre chemistry generally does not affect this property too much.

However, from these test results we can measure the Fi value (Figure 6).

The Fi value is determined by weighing the fabric before and after the test which takes 1.5 hours. The value in g/sq m is the amount of water vapour taken up by the fabric in 1.5 hours.
The difference between the cotton and the lyocell / cotton blend (9.8 v 13.2) represent a difference of 26% we would expect from this, that wearing comfort to be significantly better as the buffering capacity for water vapour is significantly enhanced.

Another interesting measure is that of water activity. The result is shown in Figure 7

Water activity describes the equilibrium amount of water available for hydration of materials at a given temperature and moisture. It is defined as the ratio of the water vapor pressure over a sample to that over pure water at the same temperature. In other words, it is a measure for the free, available water in a material. In general, "free water" represents the basis for the

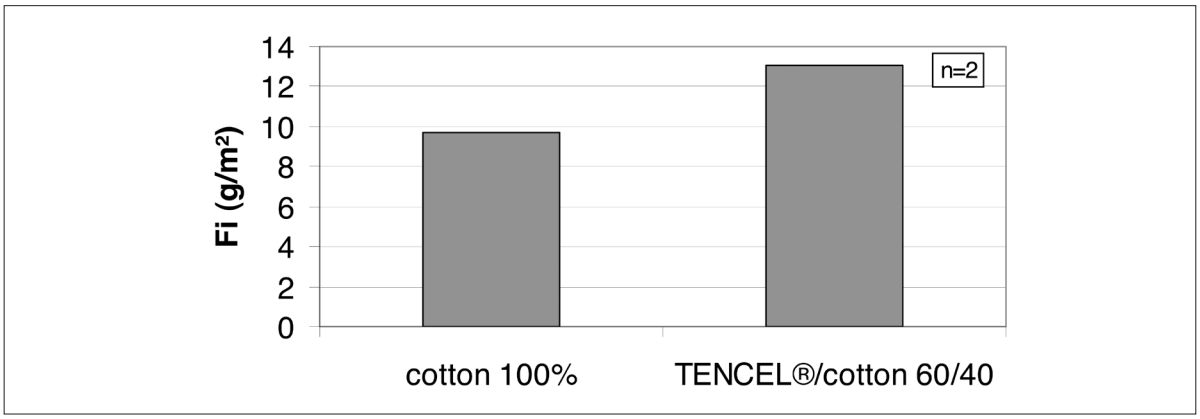

Figure 6. *Water vapour absorption (Fi).*

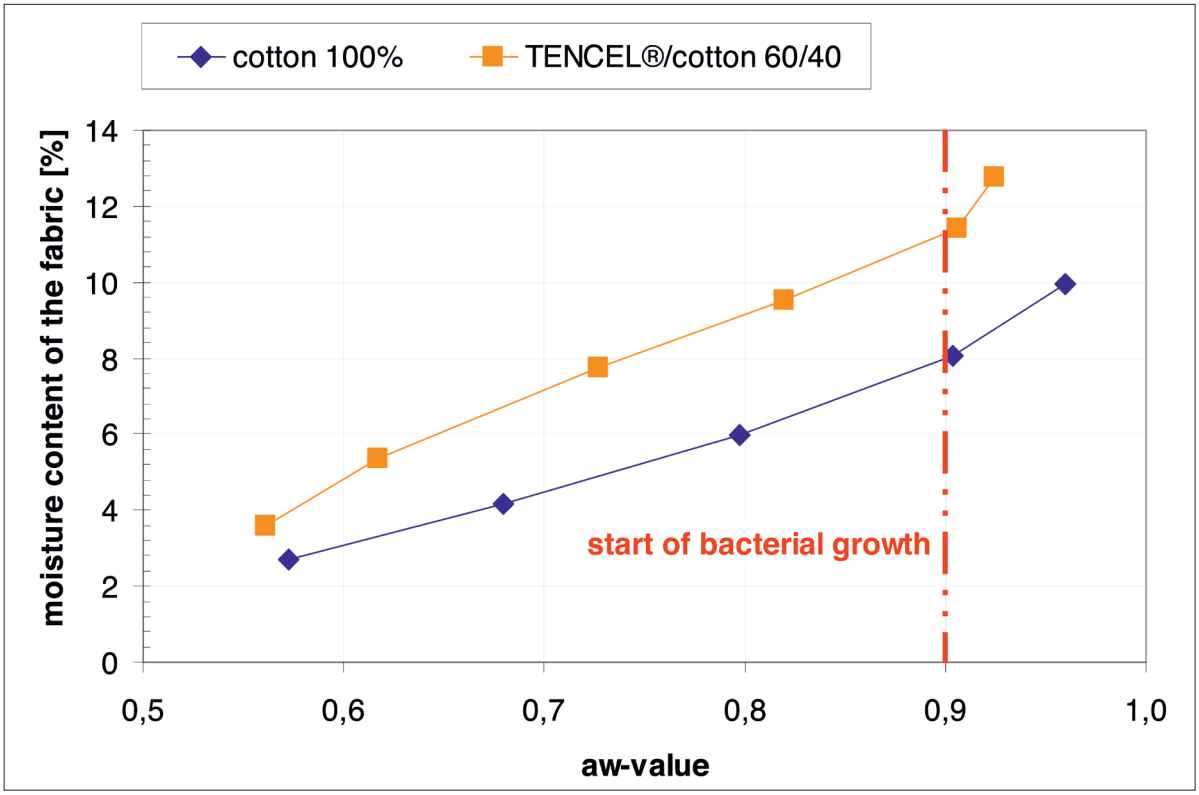

Figure 7. *Water Activity.*

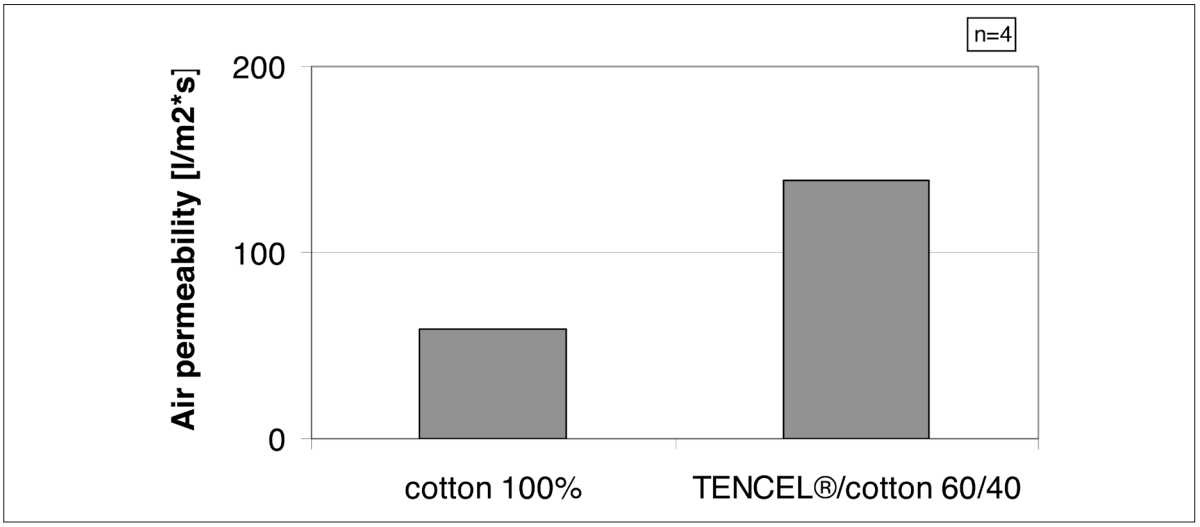

Figure 8. *Air permeability.*

growth of microorganisms. a_w can range from 0 to 1. At $a_w > 0.9$, bacteria start to grow. A low amount of "free water" (low water activity) results in a retarded growth of microorganisms. So for hydrophilic fibers, the amout of free water is lower than for synthetics as they do not absorb water.
The lowest line is for the cotton. The result shows that it can absorb about 8% moisture before the water activity value reached 0.9 and bacteria can grow.

The other sample is the lyocell blend. It is superior to the cotton, reaching up to almost 12% moisture before the critical 0.9 value is reached.

The final measure that is very relevant to comfort is that of air permeability and the result is shown in Figure 8. The results show that the lyocell / cotton blend is much more breathable than the cotton fabric. The constructions are identical – the difference deriving from the lean, regular yarns in the lyocell blend.
The FR performance and durability is identical – the lyocell / cotton blend simply outscores the cotton for comfort related properties.

Proban type
The key ingredient in this finish is THPC which is made from the reaction of phosphine, formaldehyde and hydrochloric acid. The THPC will react with urea to form a precondensate with heat. This precondensate is padded onto the fabric and the fabric dried to ~15% moisture content. The fabric is then exposed to ammonia vapours in a special reaction chamber followed by oxidation in hydrogen peroxide which converts the phosphorous atoms to their highest oxidation state that results in cellulosic goods with very durable flame retardancy. One of the drawbacks of this technology is the stiffness of the treated fabrics although carefully chosen softeners and mechanical finishing provide commercially acceptable fabrics.
The polymer that forms is primarily located on the surface of the fiber and it does not effectively crosslink the fiber. Treatment of lyocell fiber with the Proban type of finish produces a softer fabric than the equivalent cotton fabric as expected. However, the fact that no crosslinks are formed means that the fabric will fibrillate during laundry giving the fabric a distressed appearance even though the flame retardant properties are effectively maintained.

In order to achieve acceptable washability with respect to fabric surface appearance it is necessary to carry out a secondary finishing process after the Proban application to impart protection against fibrillation which is an unwanted process addition.

A second alternative was to investigate the use of TENCEL® A100. This fiber is crosslinked during the fiber manufacture. A trial was carried out to treat a knitted TENCEL® A100 fabric in Proban and then to subject the fabric through repeated washing – in this instance 150 cycles at 140ºF. The appearance was maintained and no fibrillation was visible even after this extended washing trial. FR protection was maintained and phosphorus level tests demonstrated that the Phosporus level had only fallen from 2.8% to 2.6% even after 150 wash cycles. Whilst this shows extremely good potential, a number of issues still remain to be overcome. TENCEL® A100 is not fully stable to vat dye application, so current knowledge would restrict the applications to where reactive fastness is sufficient.

An interesting note is that reactive dyes are not normally used on cotton with Proban owing to the severe

Table 2. *Effect of Proban finishing on reactive dye light fastness.*

DYE	COTTON		TENCEL® A100		DIFFERENCE
	BEFORE	AFTER	BEFORE	AFTER	
LEVAFIX					
Br YELLOW CA	4-5	4	5-6	4-5	+
RED CA	4-5	3	4-5	3-4	+
BLUE CA	5	3-4	5	4	+
OLIVE CA	5	2-3	5	5	+++++

reduction in light fastness. TENCEL® A100 shows better light fastness than cotton and although light fastness falls on treatment with Proban the resultant figures are still significantly better than on cotton.

Table 2 shows some typical light fastness results.

Conclusions

TENCEL® lyocell can be subjected to commercial flame retardant finishes of the Pyrovatex and Proban type. With Pyrovatex, less strength losses are seen than on cotton and with both types of finish, the fabric hand is significantly softer.
The cross linking behavior of the Pyrovatex chemistry is sufficient to prevent fibrillation on repeated laundering.
With Proban, the fabric hand is significantly better on lyocell than cotton. The polymer generated during the Proban finishing does not effectively crosslink the fiber and so the fabric appearance will deteriorate on washing as a result of fiber fibrillation. To prevent this a secondary finish is necessary. If this is undesirable, then TENCEL® A100 gives an opportunity to apply Proban and achieve excellent long term wash durability.

OPPORTUNITIES FOR TENCEL AND TENCEL / COTTON BLENDS
Improved softness in FR fabrics
Improved comfort resulting from lyocell's unique properties of moisture management and wearability.
Less strength loss gives opportunity to use lighter-weight fabrics
Excellent retention of hand, softness and appearance through multiple wash treatments.
Excellent environmental and sustainability credentials

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TENCEL® - Improved performance for workwear

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Abstract

The workwear market is meanwhile quite complex and elusive. Products cannot be clearly defined and supply chains vary a lot due to different channels to the market. The question "what represents good workwear" cannot be answered sufficient without taking into consideration the interests of the various stakeholders.
The end user would rather go for wearing comfort and design, but he is seldom the decision maker. The everlasting price topic can also not be the only driver, but will always rank high for those who take the investment, although actually the final life cycle costs of a garment are much more important as they consider the durability. This is especially important for industrial laundries, who on the other hand create new challenges for the garments by adapting their processes in order to save resources like water and energy. And finally sustainability with all its aspects is spotlighted more and more.
To meet all these requirements best possible, textiles for workwear have to be constructed in a clever way using best performing materials.
This paper will report on findings of a prototyping project, which compared new constructions using Lenzing's lyocell fiber TENCEL® with conventional workwear fabrics. Target of these new constructions is to offer improved performance and comfort without increasing the costs.

Workwear market

WHAT IS WORKWEAR?

Workwear - garments which prevent the wearer from any dirt or soil during work

Corporate wear - garments which create a corporate identity between wearer and employing company

Protective wear - garments which prevent the wearer **(PPE)** from any harm caused by work (require certification by notified body)

TARGET GROUPS

industry - metal (e.g. engineering, automotive, electronics), chemical (e.g. oil, plastics, pharmaceutical)

health care sector hospitals, care taking centres, wellness/Spa

hospitality hotels, restaurants, food industry

authorities police, military, fire brigade, domestic affairs

service sectors banking, post, transportation (railway, airlines)

MARKET DATA

Today the world work wear market is worth around 4 billion US$ [1].
If we add also the corporate wear business, we talk about almost 10 billion US$[1]!
Any forecasts for the near future are difficult these days. On the one hand population grows and so does the number of workers. Also the standard of living increases continuously in the third world countries and more companies are ready to provide work wear to their employees.

But on the other hand many companies and especially state owned authorities are forced to reduce their budgets due to the credit crunch.

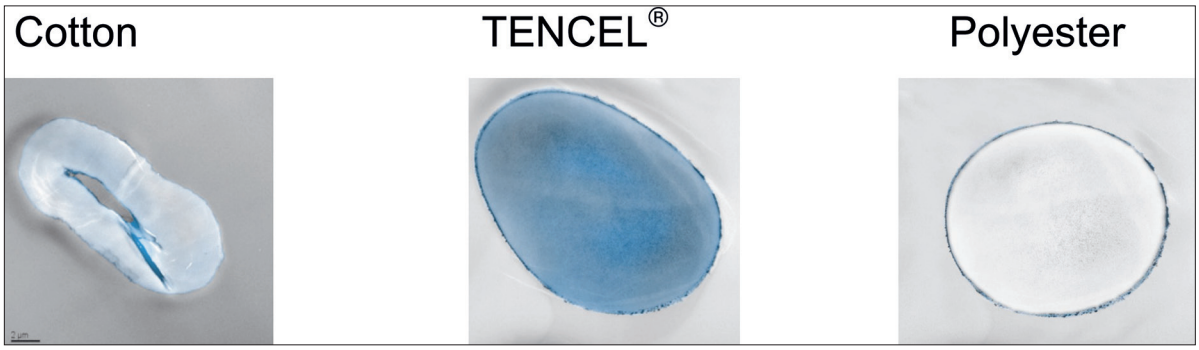

Figure 1. *Visualisation of water absorption by transmission electron micrographs (using blue coloured water).*

CHANNELS TO THE MARKET

- from textile rental companies / industrial laundries - charge per week for use and laundry
- from wholesalers - provide garments ex-stock to smaller industrial and service companies
- from suppliers by tendering (direct selling, contract has to be published, e.g. EU) - suppliers respond to invitations to quote
- direct from suppliers via catalogue – specialist mail order companies offer ex-stock to end use buyers
- by direct contract negotiation – several suppliers compete

Benefits of TENCEL®

HIGH STRENGTH

Due to the different production process (almost completely closed solvent cycle – physical process > see also "Sustainability") which leads to a special arrangement of cellulose molecules, TENCEL® has with 37cN/tex the highest strength of all commercial cellulosic fibers.
Even in wet stage it is with 30cN/tex on one level with high quality cotton.

SUPERIOR ABSORPTION CAPACITY

Compared to Cotton and PES – the mainly used fibers for workwear - TENCEL® has a significant higher absorption capacity. PES is hydrophic and the single fiber cannot absorb any moisture. Absorption within a textile structure happens only between the fibers and the absorption capacity is very low. Cotton can absorb about 40% of its own weight and does not reach the capacity of TENCEL®, which absorbs about 70% of its own weight.
This high capacity is based on the uniform distribution of the moisture over the whole fiber cross section. Figure 1 shows the cross-sections of the water swollen fibers [2].

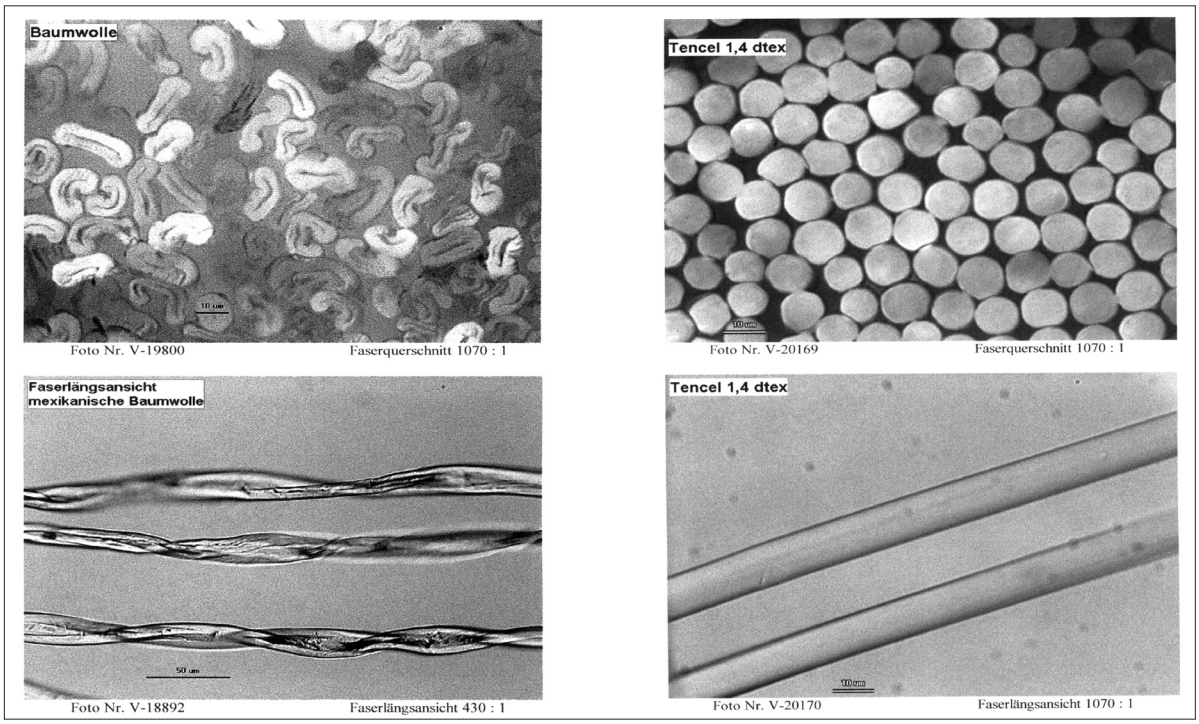

Figure 2. *Cross sections and longitudinal views of Cotton (left) and TENCEL® (right) (visualized by electron microscopy).*

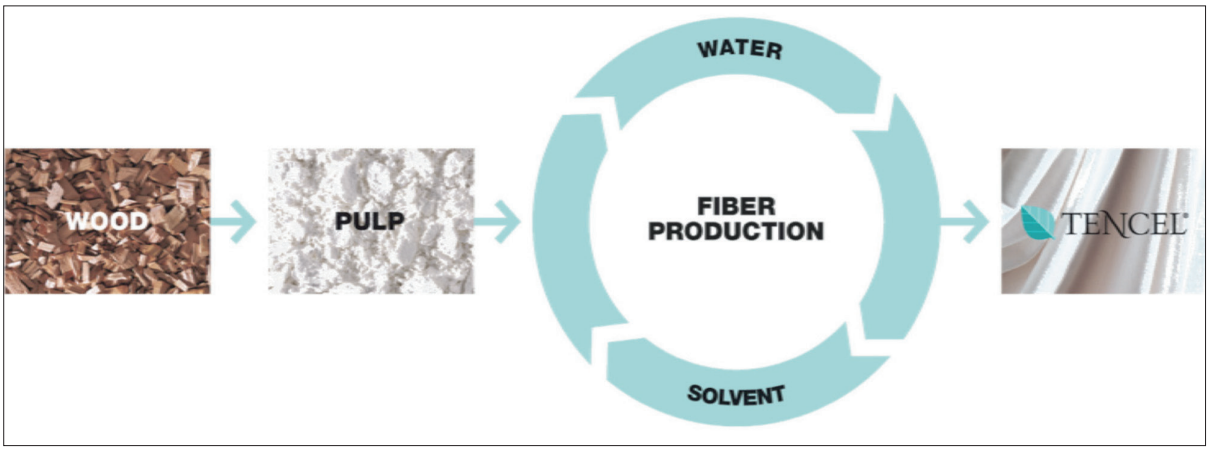

Figure 3. *TENCEL® production process.*

SMOOTH SURFACE / ROUND CROSS SECTION

The high absorption capacity and the smooth surface make TENCEL® especially suitable for sensitive skin. While irregular or coarse surfaces of natural fibers such as cotton or wool can cause irritations due to the mechanical action, TENCEL® offers tactile comfort.

SUSTAINABILITY

TENCEL® is made of eucalyptus pulp and the lyocell production process is characterized by a closed solvent cycle. The solvent is non-toxic and recycled by 99.9%.

Wood from sustainable forest plantation goes here hand in hand with a sustainable production process using persistent recovery technologies.

Prototyping

INITIAL SITUATION

When we look at the overall workwear market, there is one dominating fabric which is used in big volumes for several applications. It's a 65/35% Polyester / Cotton twill with around 250g/m². This fabric shall be replaced by a new construction using TENCEL®.

APPROACH

Based on the inherent characteristics, less TENCEL® than Cotton is needed in an identical fabric construction to achieve the same wearing comfort. The thereof resulting higher PES share helps to increase the durability of the fabric and the final life cycle costs of a workwear garment decrease.

TEXTILE CONSTRUCTIONS

Warp: Nm 28/1 ring – 32 ends/cm loom-state
Weft: Nm 17/1 ring – 18 picks/cm loom-state
Weave: twill 2/1
Blend 1: 65% PES 1.5dtex/38mm semi-dull
35% Cotton combed
Blend 2: 65% PES 1.5dtex/38mm semi-dull
35% TENCEL® 1.3dtex / 38mm bright
Blend 3: 80% PES 1.5dtex/38mm semi-dull
20% TENCEL® 1.3dtex / 38mm bright

DYEING & FINISHING

Workwear requires special colour fastnesses for a long life time, so the dyeing & finishing processes and the dyestuffs have to be selected very carefully. In order to follow the market, fabrics were dyed dark blue.

Process:
Singing, desizing, heat-setting, mercerizing
PES disperse dye thermosol
Cellulose vat dye
Resin finish
Sanfor

COMFORT PROPERTIES

To determine the comfort properties, we used the sweating guarded hot plate test which follows ISO 11092 ("Textiles- Physiological Effects – Measure-

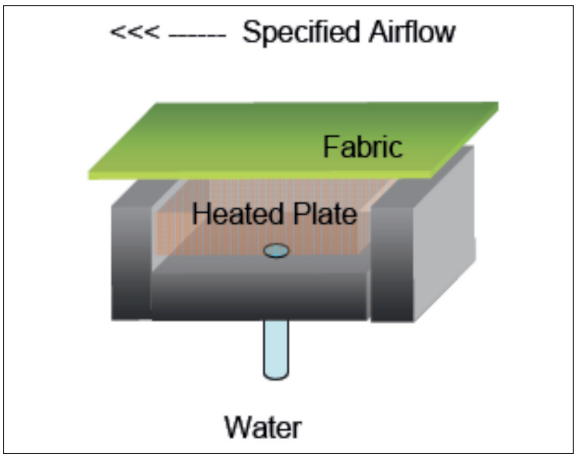

Figure 4. *Principle of the sweating guarded hot plate test.*

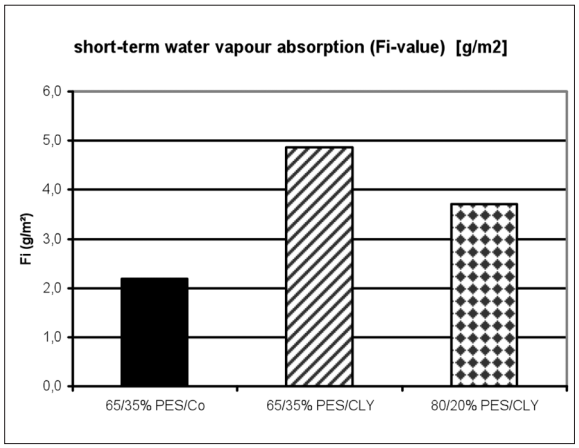

Figure 5. *Results of the short-term water vapor absorption (Fi-value).*

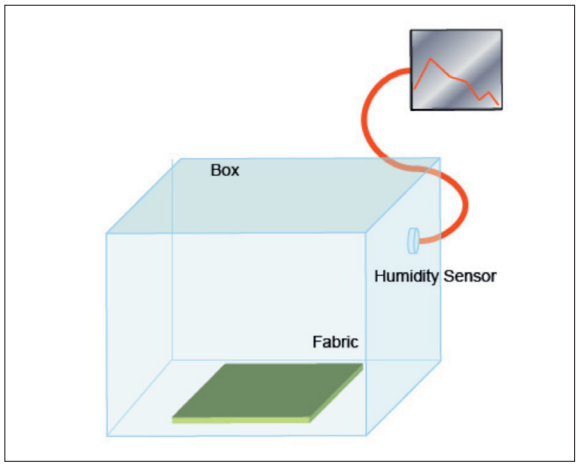

Figure 6. *Principle of the water activity test.*

ment of Thermal and Water Vapour Resistance under Steady state Conditions").
This test device simulates the heat and the moisture transfer of a human body. It consists of a micro-porous heated plate, which is able to emit water vapor (test conditions: 35°C, 40% rel. humidity). The apparatus is placed in a climatic chamber with a constant airflow moving over the fabric specimen.

The actual result derived from this test is the water vapor resistance Ret. But this value reflects much more the textile construction and the thickness of a fabric than the material itself. As the prototyping concentrates on exactly similar constructions, there are no significant differences in Ret-values.
However, this test allows the determination of the Fi-value – the short-term water vapor absorption. This test takes 90min and gives as a result the difference of the fabric weight before and after the test. The result can be seen in Figure 5.
The 65/35% PES/TENCEL® blend (red column) showed about 55% more vapor absorption than the 65/35% PES/Co blend (blue column) - (2.19 versus 4.86). This result

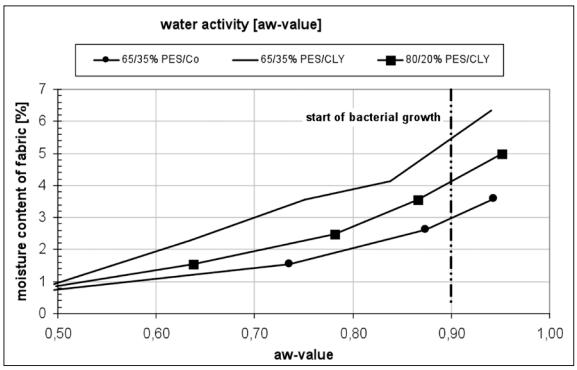

Figure 7. *Results of the water activity (aw-value).*

confirmed the original approach and allowed a reduction of the TENCEL® share from 35% to 20%.
And even the 80/20% PES/TENCEL® blend (purple column) showed about 40% more vapor absorption than the benchmark fabric (2.19 versus 3.71).
To back up this finding, another test was used - the water activity (aw-value).
Water activity is defined as "free" or "available water" in a system and is important to determine microbial growth rates. If the fiber is able to absorb more water, less free water is remaining in the fabric, which results in a slower growth of micro organism.

Water activity can range from 0 to 1 and most of bacteria start to grow at aw > 0.9.
Figure 7 shows that the 65/35% PES/Co blend (blue line) reaches the critical aw-value of 0.9 already with 3% moisture content, while the identical blend using TENCEL® (red line) allows a moisture content of about 5.4% before bacteria start to grow. Here again also the blend with the reduced TENCEL® share (purple line) is still superior to the cotton blend.

The test results showed that a fabric made of 80/20% PES/TENCEL® can easily compete with the benchmark blend 65/35% PES/Co regarding wearing comfort.
Based on this blend a second project phase was initiated, which should identify the best construction for best utility performance. This assessment concentrated mainly on the influence of the yarn technology.

UTILITY PERFORMANCE

The yarn technology has a significant influence on the later performance of fabrics.

Due to the positioning of the fibers and the way they are bound within the yarn structure, yarns have different strength and different hairiness. When comparing ring, siro, airjet and open end yarns, the ring yarns are more hairy than the others. Figure 8 shows the longitudinal view of the 4 different yarns [3].

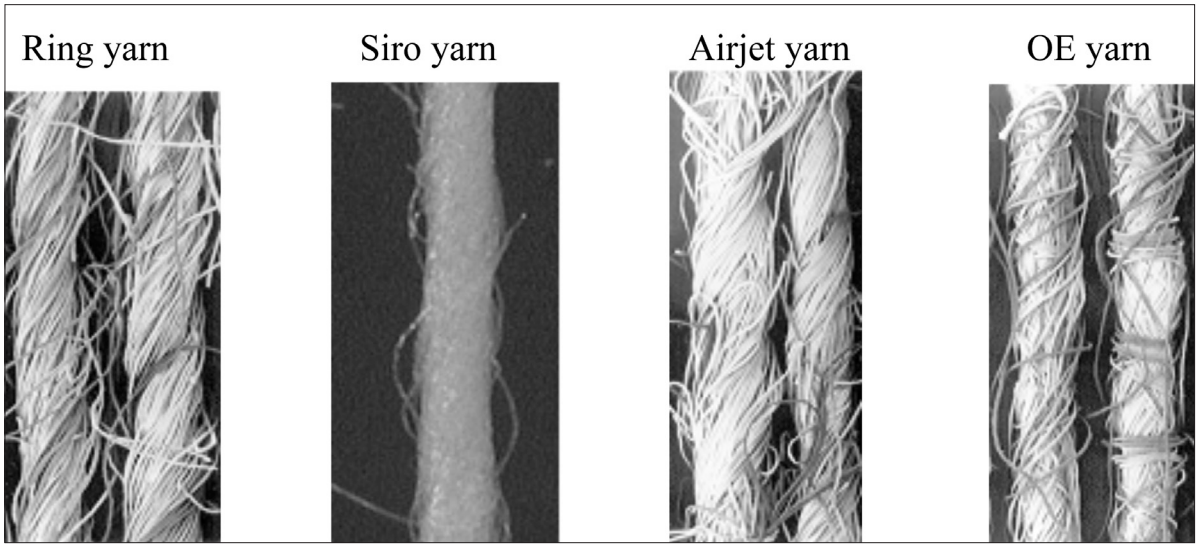

Figure 8. *Micrographs of different yarns.*

To determine the performance of workwear fabrics, the tensile strength was assessed acc. DIN EN ISO 13934-1 "Determination of maximum force and elongation at maximum force using the strip method".
Figure 9 shows the results of all fabrics for warp and weft.

The second parameter which was evaluated, is the tear strength acc. DIN EN ISO 13937-2
"Determination of tear force of trouser-shaped test specimens (Single tear method)".
Figure 10 shows the results of all fabrics for warp and weft.

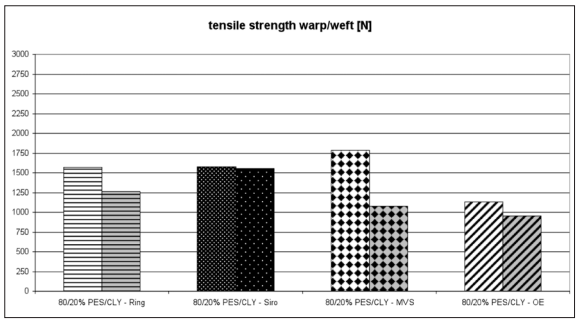

Figure 9. *Tensile strength acc. DIN EN ISO 13934-1.*

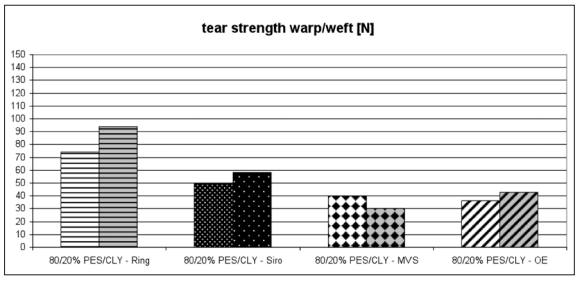

Figure 10. *Tear properties acc. DIN EN ISO 13937-2.*

In this test every threat is torn separately and the measured strength depends a lot on the ability of this single threat to move within the textile structure.
If it can move before it finally tears, the measured strength is higher.

Some might have noticed that the tear strength decreases over the time.
This fact is related to the constant wash-off of softeners with every laundry cycle.
Softeners are normally used in the final finish of fabrics to enable exactly this movement of threats within fabrics when being tailored.
For more constant tear strength it might be helpful to use small amounts of softener in each wash cycles. But this solution requires careful handling, as too much softener often has a negative influence on pilling. In this case the pills rather move on the slightly greasy fabric surface and break later than on a very dry fabric surface.

Pilling is mainly caused by the migration of fibers from the yarn to the fabric surface.
It depends very much on the hairiness of a yarn and the strength of the fibers.
Cellulosic fibers create rather small pills which fall off quickly, but synthetic fibers have higher inherent strength, so the pills cling persistent to the fabric.
So it is not surprising that 80/20% PES/TENCEL® blends show unpleasant PES pilling.
But the right selection of yarn technology can solve this issue.

Figure 11 shows the assessment of the pilling behaviour acc. DIN EN ISO 12945-2 ("Determination of fabric propensity to surface fuzzing and to pilling -- Modified Martindale method"). The fabrics were as-

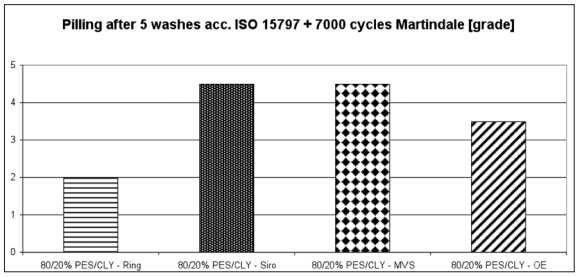

Figure 11. *Pilling behaviour acc. DIN EN ISO 12945-2.*

sessed after 5 industrial laundry cycles acc. ISO 15797 at 75°C and 7.000 Martindale cycles.
Pilling reflects directly how the fibers are bound in the yarn structure.
In this respect the conventional ring spun version has a clear disadvantage compared to the other technologies.

A further property which is important for workwear is the abrasion resistance.
It was assessed acc. DIN EN ISO 12947-2 ("Determination of the abrasion resistance of fabrics by the Martindale method -- Determination of specimen breakdown").

Abrasion resistance is linked again to the way how fibers are bound within the yarn structure, but also has a direct correlation to the pilling performance.
When both parameters are considered, the fabric made of MVS yarns has a clear advantage.

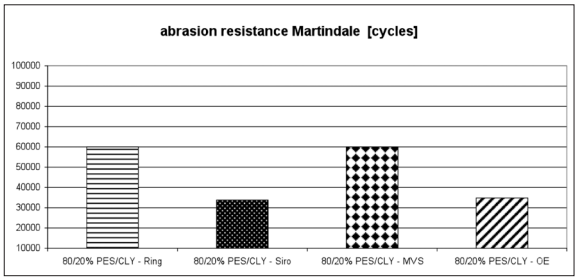

Figure 12. *Abrasion resistance acc. DIN EN ISO 12947-2.*

Conclusions

PES/TENCEL® blends offer improved performance in terms of wearing comfort and durability due to the excellent moisture management of TENCEL®.
Compared to conventional PES/Co, the improved moisture management of TENCEL® allows increasing the PES share in PES/TENCEL® blends for higher durability without loosing any wearing comfort.
The use of TENCEL® and a proper selection of yarn technology support the longevity of workwear garments and increase so their profitability.

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Functional Viscose Fibre for Cold Protective Clothing

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Presented with the title "Cellulosic fibre with a new functionality" at the 50th Dornbirn Man-Made Fibers Congress, 14 – 16th September 2011, Austria

Abstract

Spunlaced and needlefelt nonwovens were made from high-absorbency speciality viscose fibres. Tensile properties of the produced materials were equal or better as those of a reference nonwoven made from standard viscose fibre. Up to 40% higher nonwoven absorbencies were achieved using the viscose specialities.

The increased water absorbent properties of the new specialty viscose fibres also positively effect the thermophysiological properties of fabrics made out of these fibres. The vaporous and liquid sweat uptake is increased by at the same time only minor reduced thermal insulation which makes them suitable for cold protective clothing under higher physical strain i.e. a higher metabolic rate. An elongated drying time due to the higher amount of water in the fibre results in a long lasting cooling effect for higher ambient temperatures or thermal injuries of the skin. Additional inherent reduced flameability with an LOI of 24 mainly derives from the additives included in some of these new fibres being also responsible for the high water absorbency.

Keywords: *viscose fibres, nonwoven, absorbency, cold protective clothing, clothing physiology, thermal insulation, water vapour absorbency, liquid sweat uptake, LOI; Kelheim Fibres; Hohenstein Institut für Textilinnovation*

Introduction

The viscose fibre process was introduced already over one hundred years ago[1,2,3], but still forms the basis of many new fibre developments. Due to its high versatility this process is excellently suited to produce modified viscose fibres, with their properties fine tuned to a broad range of different finished products, ranging from textile over hygiene up technical end-uses. As a producer of viscose specialities Kelheim Fibres has recently introduced a range of new speciality fibres aimed for the use in different applications [4]. Benefits of these fibres e.g. for a fine-tuning of paper applications were reported earlier [5]. Viscose fibres as 100% cellulosic fibres are particularly hydrophilic and absorbent and are therefore known for their good moisture management. The newly developed specialized fibres with even further improved absorbency, be it through the nature of the fibre itself, or through the specific properties of nonwovens formed from them, are therefore especially suited for high-performance clothing applications. It was the objective of this study to understand better the specific benefits that can be obtained in these applications using highly absorbent fibres and nonwovens.

As a predestinated application of these new specialized fibres especially cold protective clothing for workers in cold environment (i.e. cold storage houses) can be considered. Thermal insulation is the main function of this kind of PPE. If workers exceed the metabolic rate for which this clothing system was designed for they rapidly begin to sweat which results in a wet insulation layer. The unique water (liquid sweat) and humidity (vaporous sweat) sorption properties can be of great advantage in clothing physiology of these garments. This effect is needed because the thermal insulation R_{ct} of these

Table 1. *Viscose fibre parameters.*

Fibre type	Titer [dtex]	fibre length [mm]	Elongation [%]	Tenacity [%]	W.I. [%]
Bellini	1,7	40	17,0	18,0	185
Bramante	3,3	40	20,0	15,0	234
Verdi	1,9	40	19,0	22,0	156
Dante	3,3	40	22,0	16,0	314
Danufil	1,7	40	21,0	23,0	80

garments declines dramatically when the insulating nonwoven gets humid or wet by hard exercises or numerous ambient climate changes of the wearer.
Furthermore some of these new fibres have a self-extinguishing behaviour which provides an additional value in the matter of occupational safety.

Materials and Methods

MATERIALS

Regular Danufil® viscose fibres as well as four types of specialized viscose fibres were used in this study.
All viscose fibres in this report were produced by Kelheim Fibres and used in the indicated cut length, with the exception of paper testing, which was done with 6mm short-cut fibres.
Fibre parameters are given in Table 1.

VISCOSE FIBRE MODIFICATIONS

Different types of modified fibres were used in this work (Figure 1).

The *Bellini* fibre is a very thin, flat and flexible fibre with a high surface area. This gives the fibre unique properties, for example in paper applications where fibre-fibre bonding is important.
The *Bramante* fibre shows a closed structure in the dry state, but when wetted the fibre opens to give a hollow structure, where water is enclosed within the fibre. This enclosed water is not released under pressure, thus giving the fibre a water imbibition three times as high as a regular viscose fibre. This effect is reversible an unlimited number of times when drying and wetting the fibre again.
The *Verdi* fibre carries an anionic modification which gives the fibre a range of different properties, among them higher swelling, higher water imbibition, and a unique surface touch in the wet state.
The *Dante* fibre combines the properties of the Bramante and the Verdi fibre. In the wet state it is a hollow fibre with an additional anionic modification. In combination this gives the fibre a water imbibition four times high than a regular viscose fibre.

METHODS

For the determination of the mechanical properties paper sheets and nonwoven materials were made from 100% of viscose fibre as given in Table 1.

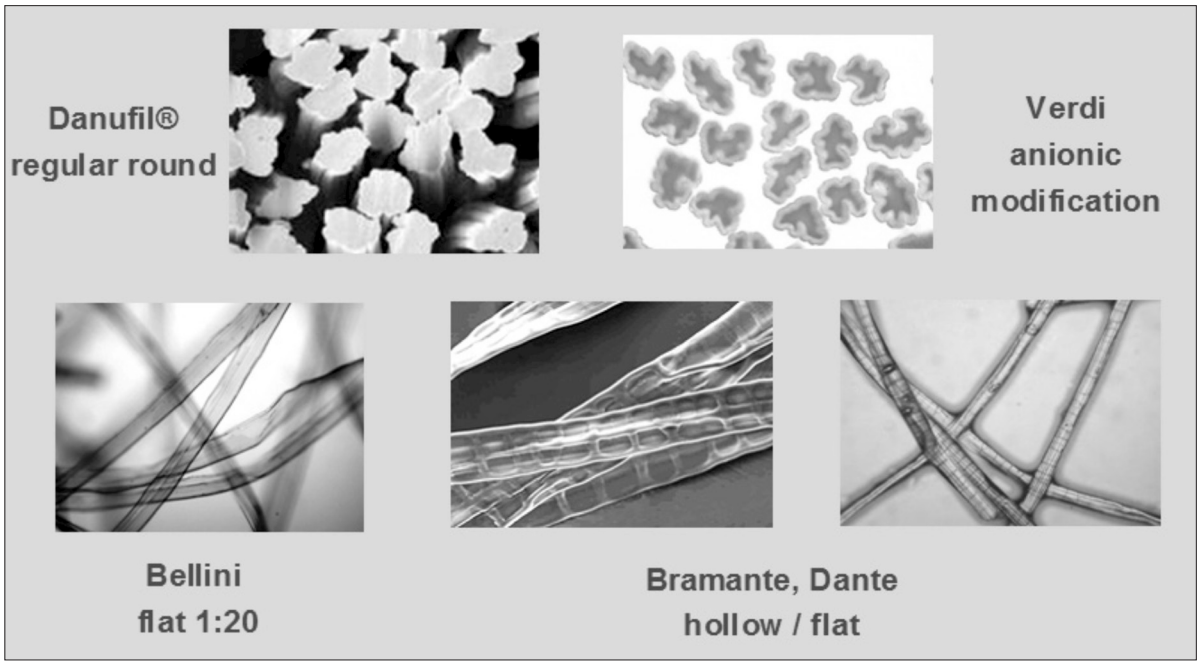

Figure 1. *Viscose fibre modifications.*

For paper testing Rapid-Köthen sheets in 80g/m² were produced according to DIN EN ISO 5269-2; tensile strength was tested according to DIN EN ISO 1924-2. Nonwovens were produced as 80g/m² spunlaced and 210g/m² needlefelt using identical machine settings for all fibre types. Tensile strength of the nonwoven materials was tested according to DIN EN ISO 29073-3. In order not to account for differences in the fibre orientation, strength in MD and CD was summed for evaluation. Water imbibition of fibres was measured according to DIN 53814 and the absorption of nonwovens was measured according to DIN 53923 at the Hohenstein Institute.

All thermophysiological parameters of the spunlace and needlefelt nonwovens were investigated on the Hohenstein Skin Model (sweating guarded hotplate) according to ISO 11092 (R_{ct}, F_i) and validated Hohenstein in house methods (F, G_2, R_{ct*}) [6,7]. The LOI values were determined according to ASTM D 2863-76.

Results and Discussion

IMPROVED MECHANICAL PROPERTIES IN PAPER AND NONWOVENS

It was expected, that compared to standard fibres, modified viscose fibres would show a different behaviour in conversion as well as different strength in nonwovens made of them. In order to understand this better, paper and nonwovens were made from the set of fibres, using always the same fibre length and the same machine parameters.

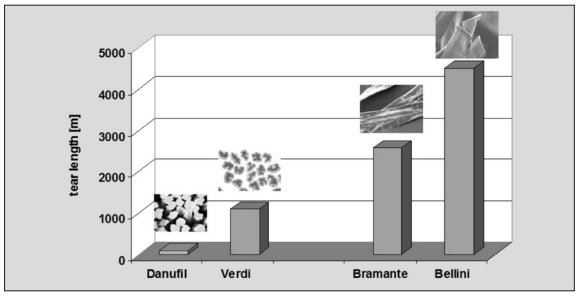

Figure 2. *Strength of paper sheets from 100%Viscose.*

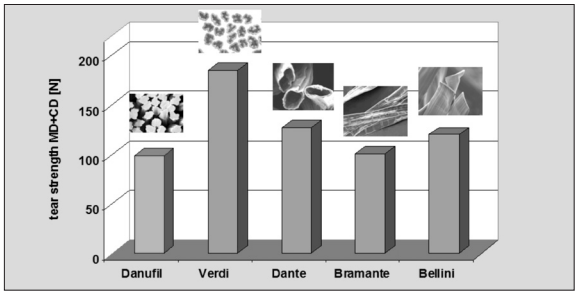

Figure 3. *Strength of spunlaced nonwovens from 100% Viscose.*

a) Paper

It is known, that without the use of further additives it is not possible to form paper from 100% of regular viscose fibre due to the lack of intra-fibre bonding. Consequently tear length of a paper from 100% Danufil® is zero. The anionic modification of the Verdi fibre increases the intra-fibre bonding to give sheets with a tear length of over 1000 metres, which already allows handling the sheet without having it falling apart. The high surface area of Bramante and especially Bellini increase the bonding to a higher degree. The Bellini fibres give a sheet with a tear length of 4500 metres, which is already in the range of refined hardwood pulp (Figure 2).

b) Spunlaced

Spunlaced nonwovens were made from all fibres investigated and it showed that at identical settings, all fibres gave very similar tensile strength in the nonwoven, with the exception of Verdi (Figure 3). The tensile strength of the Verdi spunlaced was nearly twice as high as the strength of the Danufil® reference spunlaced. This is attributed to the surface effect of the anionic Verdi fibres which promotes intra-fibre bonding in a wet process.

c) Needlefelt

The modified viscose fibres in this work showed good bonding properties in wet processes. As an example of a dry nonwoven process, needlefelt nonwovens were produced. The tensile strength of all samples was found to be in a similar range, with exception of the Bellini nonwoven, which displayed a 25% higher strength than the reference (Figure 4). This is attributed to the higher flexibility of the Bellini fibre which allows for a better entangling of the fibre.

IMPROVED ABSORBENT PROPERTIES

All modified viscose fibres in this study show higher water imbibitions than regular viscose fibres (W.I., see Table 1). The spunlaced and needlefelt nonwovens that were produced were tested for absorbency, in order to confirm that the higher single-fibre absorbency would also translate into a higher absorbency of the nonwoven structure.

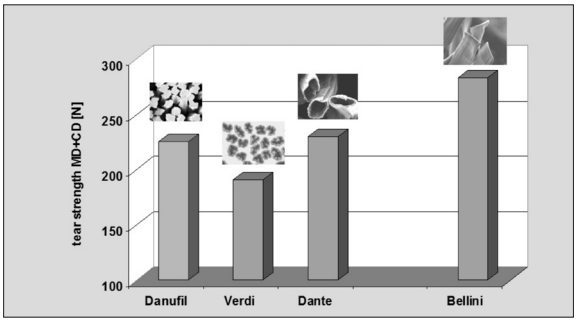

Figure 4. *Strength of needlefelt nonwovens from 100% Viscose.*

a) Spunlaced
The absorbeny of spunlaced nonwovens made from Verdi and Bellini was at the same level as the sample from standard Danufil® fibres. These two fibres only show a moderately increased single fibre absorbency compared to regular viscose, and in the flat spunlaced structure there is no additional benefit from the nonwoven structure. Bramante and Dante fibres, with very high single fibre absorbency, gave both markedly improved nonwoven absorbencies, which was in the case of the Dante fibre 40% higher compared to the sample made from regular viscose fibre (Figure 5).

b) Needlefelt
In the more three-dimensional structure of a needlefelt nonwoven the structure of the absorbent body is becoming increasingly more important for the overall absorbency of the nonwoven structure. Consequently the Verdi needlefelt did only give an absorbency comparable to the nonwoven from regular Danufil® fibres, whereas the nonwovens from the fibres with a higher specific surface gave markedly higher absorbencies, which in the case of the Bellini fibre was 40% higher than when using regular viscose fibres (Figure 6).

IMPROVED MOISTURE MANAGEMENT PROPERTIES IN NONWOVENS

As all modified viscose fibres in this study showed a higher water imbition and absorption than regular viscose, the next step was to investigate their vaporous and liquid moisture management in terms of clothing physiology.

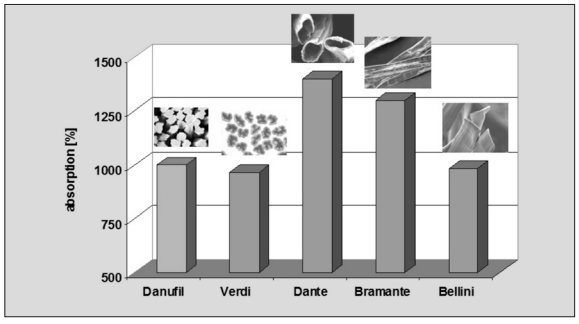

Figure 5. *Absorbency of spunlaced nonwovens from 100%Viscose.*

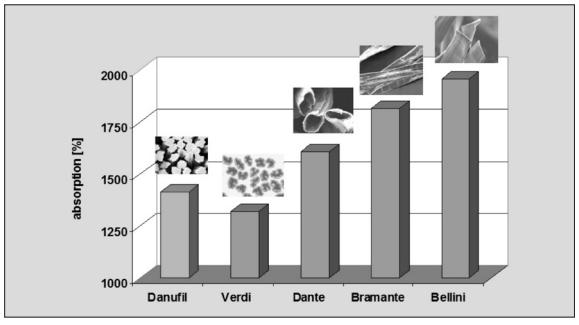

Figure 6. *Absorbency of needlefelt nonwovens from 100% Viscose.*

a) short time water vapour absorbency (F_i)
The short time water vapour absorbency was measured on the Hohenstein skin model under stationary / normal wear conditions by performing the water vapour resistance R_{et} method and weighing the samples before and after the measurement.
Dante and Verdi fibres can absorb much more water vapour than the standard viscose fibre (Figure 7). A difference in absorption between spunlace and needlefelt can also be observed. The hollow structure of the Dante fibre results not in a higher absorbency. Therefore the modified viscose matrix is the main factor in improved water vapour absorption and can be further improved by the "open" structure of the needlefelt.

b) buffering capacity of liquid sweat: sweat transport (F)
After the stationary conditions the instationary conditions with heavier i.e. liquid sweating were performed on the Hohenstein skin model determining the liquid sweat transport capabilities of the spunlace nonwovens. This gives a clear picture of how much liquid sweat can be transported trough the fabric away from the skin.
Bellini fibre has the highest sweat transport capabilities due to increased inter filament capillary effects deriving from the flat structure and the hollow Date fibre has the lowest values. The hollow structure holds back most of the liquid trapped in the internal fiber capillaries. Verdi and standard Viscose have comparable good values (Figure 8). It is interesting to see that the lighter spunlace nonwovens show all higher values which is mainly based on the lower thickness of the material.

c) buffering capacity of liquid sweat: sweat uptake (G_2)
Still in the instationary condition with heavy liquid sweating the G_2 value indicates the amount of sweat which is taken up by the fabric and not transported away from the skin. The lower the numbers the better the comfort of the spunlace nonwovens.

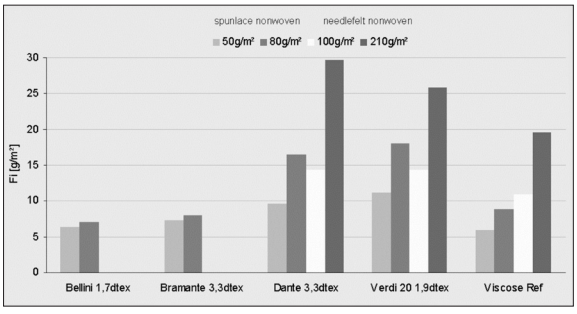

Figure 7. *Short time water vapour absorbency (F_i) of spunlace and needlefelt nonwovens.*

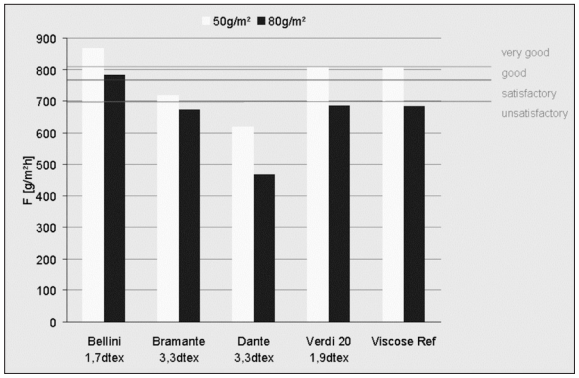

Figure 8. *Buffering capacity of liquid sweat / liquid sweat transport (F) of spunlace nonwovens.*

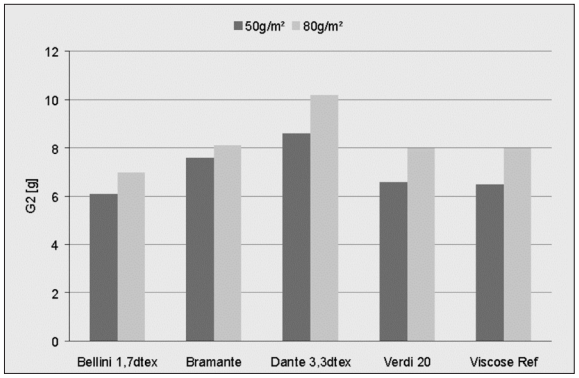

Figure 9. *Buffering capacity of liquid sweat sweat uptake (G_2) of spunlace nonwovens.*

Dante due to the hollow structure which holds back a lot of liquid sweat has the highest values. Verdi and standard Viscose show comparable good results (Figure 9).

Taking into account all the performed thermophysiological characterisation methods for textile moisture management, the Verdi fibre shows the broadest improvement compared to the standard viscose fibre.

IMPROVED THERMAL MANAGEMENT

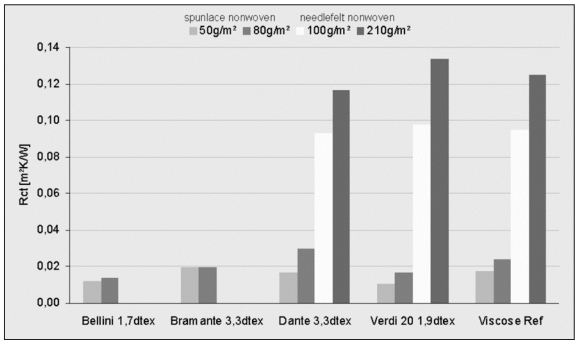

Figure 10. *Thermal resistance or thermal insulation (R_{ct}) of spunlace and needlefelt nonwovens.*

PROPERTIES IN NONWOVENS

For cold protective clothing thermal insulation is the main function. As soon as the insulation layer gets wet the thermal insulation will be vastly reduced. The new specialty fibres have shown that they can absorb more moisture compared to standard viscose fibres. How this behaviour affects the thermal insulation properties of these nonwovens was investigated by the following thermophysiological methods

thermal insulation / thermal resistance (R_{ct})

Thermal resistance was again measured on the Hohenstein skin model under stationary / normal wear conditions. Under these conditions there is a time-constant heat flux from the wearer's body to the ambience and the measured spunlace and needlefelt nonwovens are in the dry state.

Dante and Verdi show nearly the same good thermal insulation as the standard viscose fibre by at the same time having higher uptake capabilities of vaporous and liquid sweat (Figure 10). This shows that the vaporous and liquid sweat is stored in the fibre matrix itself and not on the fibre surface or in between the single filaments.

thermal insulation / thermal resistance of the moist fabric (R_{ct*})

Aside from cold protective clothing, another interesting property of fibres with enhanced water uptake is a longer drying time and a thus related cooling effect. This could be of importance in treatment of sunburn or other thermal injuries of the skin. Also physical activity under hot climate conditions where additional cooling is needed to prevent the person from heat stroke is a possible application area.

The thermal resistance / insulation and drying time of the moist fabric R_{ct*} was measured on the Hohenstein skin model to determine the cooling effect of the needlefelt nonwovens. In the R_{ct*} value and drying time Verdi and standard Viscose are quite comparable but the

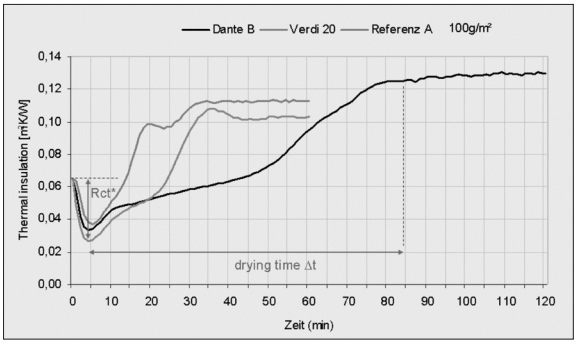

Figure 11. *Thermal resistance of the moist fabric (R_{ct*}) of different viscose needlefelt nonwovens.*

drying curve shows a quite different behaviour. In the Verdi curve the drying process inside the fiber matrix can be observed with a small plateau at 20 minutes which indicated the diffusion of the water to the surface of the fibre (Figure 11). The Dante fibre gives a completely different picture. While the R_{ct*} value is comparable the drying time much longer. The curve shows the drying of the hollow space between 10 and 50 minutes and afterwards the drying of the fibre mantle. This makes the Dante fibre most applicable for long-lasting cooling effects in wet state.

ADDITIONAL SELF EXTINGUISHING BEHAVIOUR OF VERDI FIBRES

Another interesting additional effect of the ne fibres is the inherent self extinguishing behaviour which makes it suitable for applications where conventional flame retardency is not legally required.

The LOI - the so called Limiting Oxygen Index - of the Verdi fibre was determined and compared with the literature LOI data of other commercially available fibre polymers. The LOI of the Verdi fibre is much higher that other cellulosic polymers like native CO and standard Viscose (Figure 12). It even comes close to wool which is often used in reduced flameability applications. This effect mainly derives from the additives included in these ne fibres being also responsible for the high water absorbency.

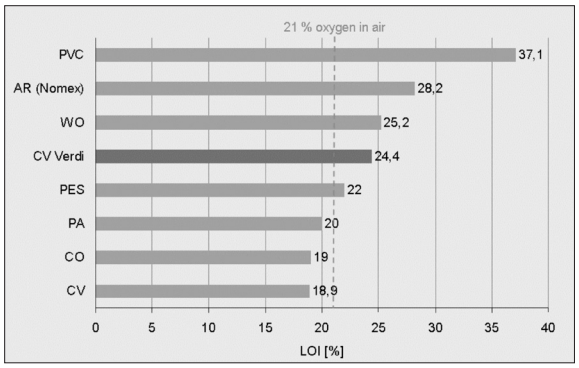

Figure 12. *Flamability properties (LOI Index) of Verdi Viscose compared to other fiber types.*

Conclusions

On different nonwoven constructions made from highly absorbent speciality viscose fibres it was shown that an equal or better tensile strength of the nonwoven can be achieved as when using regular viscose fibre. Additionally it was confirmed, that these speciality fibres do not only display high single-fibre absorbency, but that also highly absorbent nonwoven structures can be made out of them.

A high buffering capacity or uptake of vaporous and liquid sweat by at the same time high thermal insulation a clear advantage of the Verdi fibre compared to standard viscose was proven by sweating guarded hotplate measurements. Due to the altered water uptake and release behaviour of the Verdi fibre a stronger and longer cooling effect can be observed during so called Rct* measurements compared to unmodified fibres. Furthermore an additional inherent self extinguishing behaviour could be observed.

Acknowledgements

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New Antimicrobial Cellulose Fibres for Work Wear for the Food Processing Industry

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Abstract

Antimicrobial functionalized textiles should protect the humans against microbial impurities. In food processing industry unhygienic work clothes can be responsible for the transfer of infections to food. In this project three antimicrobial functionalized cellulosic fibres were developed which can used without problems for yarn production in the ring spinning. The new antimicrobial cellulose fibres were produced according to the ALCERU®-process by doping with zinc, zinc oxide or silver nitrate as antimicrobial substances. The investigation of woven and knitted fabrics with the new yarns shows that the quality is high enough for the usage of work wear in the food processing industry. The thermophysiological and skin sensorial comfort of the fabrics is good. So the new fibers are a good alternative for work wear and the results show that the amount of cellulosic regenerative fibres can be up to 70% by woven fabrics and 60% by knitted fibres with a high product quality and product performance for work wear. The developed fibres and fabrics can be used for leasing fabrics.

Keywords: *antimicrobial cellulosic fibres, work wear, Hohenstein quality standard 701ff, wear comfort, industrial laundry*

Introduction

Antimicrobial functionalized textiles should protect the humans against microbial impurities. In the food processing industry unhygienic work clothes can be responsible for the transfer of infections to food. Therefore in the food processing industry the work wear should protect the food for negative influences and should avoid that the food bring risks to the people. So antimicrobial work wear are used in food processing industry and are often made by antimicrobial synthetic fibres e.g PES. The wearer of work clothes expect the protective function of the work clothes and also a high mechanical durability, a long life span as well as a good wash ability and easy care properties. Beyond that good physiological function of the clothes is important, which protects against heat or cooling stress, the work wear should have good wear comfort to support the productivity of the wearer.
In the paper the results of the research project (IGF 16305BG) are presented. The aim of the project was the development of new antimicrobial cellulosic synthetic fibres by renewable fibre material for work clothes in food processing industry. The new antimicrobial cellulose fibres were produced according to the ALCERU®-process by doping with zinc and in an ion exchange fibre with zinc oxide or silver nitrate as antimicrobial substances. The second step was the investigation of the spin process of the new fibre material and the production of waved and knitted fabrics. Finally the quality of the fabrics was determined by investigation of important textile physical parameters, and the thermophysiological parameters under consideration of the industrial washing process and the leasing properties of the clothing.

Materials and Methods

At the TITK the new antimicrobial fibres based on regenerated cellulosic fibres were developed and produced according to the ALCERU®-process (see Figure 1).

In this study three types of fibres were produced:
1. Zinc oxide (ZnO) (V1)
2. Ion exchange fiber with ZnO (V2)
3. Ion exchange fiber with AgNO3 and TiO2 (V3)

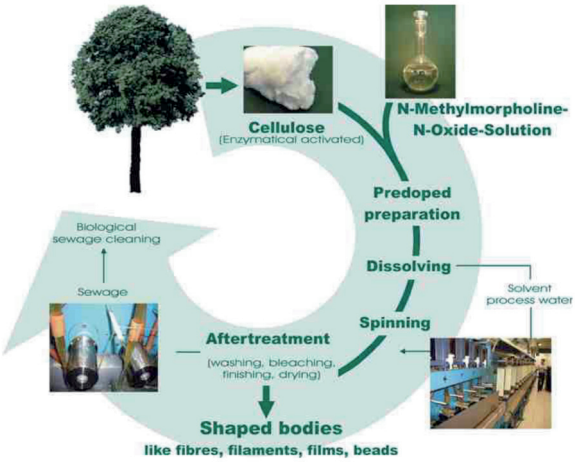

Figure 1. *scheme of ALCERU®-process.*

The Ion exchanger was a super absorber based on Sodium poly acrylate (SAP) with particle size < 10μm.

The next step was the yarn Production and the production of woven and knitted fabrics at the STFI. The yarn production can be influenced on the quality of the new fibres.
At least the quality of woven and knitted fabrics was investigated at the HIT. The reprocessing quality of the woven and knitted fabrics was investigated after a certain number of industrial wash cycles according the DIN EN ISO 15979 [1]. The antimicrobial activity was investigated after the test method DIN EN ISO 20743 with test micro organisms Staphylococcus aureus ATCC 6538 and Klebsiella pneumonia ATCC 4352 [2]. The quality of the fabrics was tested according the Hohenstein Quality Standard 701ff [3]. The Hohenstein Quality Stand 702 [4] for work wear was used for the woven fabrics and the Hohenstein Quality Standard 704 [5] for Shirts and Polos were used for knitted fabrics. The proofed parameters are the tensile properties, the bursting strength, the abrasion resistance, the pilling propensity, the dimensional change, the crease recovery and the hypochlorite bleaching fastness and the torsion of seams. The comfort of the woven and knitted fabrics was investigated by different clothing physiological characteristics by measurement with the Hohenstein Skin Model [6]. The thermoregulatory model of human skin - Skin Model for short - is a test device which simulates the dry as well as the sweating human skin. With the Skin Model the specific thermophysiological quantities of textiles as layers, relevant to wear comfort, are determined.

The following thermophysiological parameters are proofed: thermal resistance, water vapour resistance, water vapour permeability index, short-time water vapour absorbency, moisture regulation index, buffering index, liquid moisture transport and water retention). In addition the following sensorial parameters are proofed: the sorption index, the wet cling index, the surface index, the number of contact point fabric/skin and the stiffness.
As the result of fundamental research out of the specific thermophysiological quantities of textiles their thermophysiological wear comfort to be expected can be expressed by a comfort vote WC_T.

Woven fabric:
$$WC_T=a_3*R_{et}+b_3*F_d+c_3*K_f+d_3*F_i+e_3*\Delta G+ß_3$$

Knitted fabric:
$$WC_T=a_4*i_{mt}+b_4*F_i+c_4*F_d+d_4*K_f+ß_4$$

WC_T - thermophysiological comfort
R_{et} - Water vapour resistance [m² Pa W -1]
F_d - moisture regulation index
K_f - buffering index
F_i - short time water vapour absorbency [g]
ΔG - water retention [%]
$a_n, b_n, c_n, d_n, e_n, ß_n$ - Factors

As the result of fundamental research out of the specific skin sensorial quantities of textiles their skin sensorial wear comfort to be expected can be expressed by a comfort vote WC_s.

Woven fabric:
$$WC_s=a_1*i_{mt}+b_1*i_K+c_1*i_B+d_1*i_o+e_1*n_K+f_1*s+ß_1$$

Knitted fabric:
$$WC_s=a_2*i_{mt}+b_2*i_K+c_2*i_B+d_2*|j-i_o+e_1*n_K+f_2*|16-sl+ß_2$$

$TK^{(H)}$ - skin sensorial comfort
i_{mt} - Water vapour permeability index
i_K - wet cling index
i_B - sorption index
i_O - surface index
n_k - number of contact points
s - stiffness
$a_n, b_n, c_n, d_n, e_n, f_n, \beta_n$ - Factors

The resulting wear comfort of textiles worn next to the skin and perceived subjectively is determined by the textiles thermophysiological as well as by their sensorial properties. Fundamental tests have shown that the latter are nearly as important as the thermophysiological properties. Practically this means that a textile - even with good thermophysiological proper-

Figure 2. *Colours of the fibre specimen with Silver.*

ties - can be perceived as uncomfortable, if the sensorial quantities are not correct. In order to judge the total wear comfort to be expected with the samples tested, the comfort votes WC_T and WC_S according to the results of a fundamental research project, have been combined into one vote WC:

$$WC = 0.66\ WC_T + 0.34\ WC_S$$

The precision of the WC-vote can be assumed to 0.3 (standard-deviation). Differences between fabrics in the WC-vote of 0.5 or more are registered subjectively by the wearer.

Results and Discussion

PRODUCTION OF THE THREE FIBER SPECIMENS

Fibre specimen 1 was produced with content of zinc oxide of 20% related to cellulosic content for a sufficient antimicrobial of the fibres. Before starting the production of fiber specimen 2 the ion exchanger was milled to a size less than 10 μm with a fluidised bed opposed jet mill (Hosokawa Alpine AFG 100). The cellulose was doped with 10 % SAP and doped with different concentration with a zinc sulfate solution with concentrations between 0.05-0.1 mol/L. After the zinc sulfate bath the fibers were washed three times in water and dried at 70°C. Fiber type 3 was produced with the ion exchanger and silver nitrate. Fibres with silver darken if they stay on the light and to avoid the darkening the ion exchange fiber were first doped with silver nitrate, second with potassium bromide and sodium jodide. Also the potassium doped fibers show a darkening. The doping with sodium jodide shows a light yellow colour (see Figure 2).

Table 1 shows the data of the characterization of the three fibre specimens.

The characteristic parameters of the three fibre specimens show that the doping of the Lyocell-fibres with

Table 1. *Characteristic parameters of the three fibre specimens.*

Parameters	Zn-doped fiber V1	Zn-doped Ionic exchange fiber V2	Ag- doped Ionic exchange fiber V3
Cutting length [mm]	38	38	38
Fineness [dtex]	2,6	7,0	2,7
Tenacity [cN]	7,0	12,7	6,8
Elongation at break, dry [%]	12,2	9,3	14,4
Elongation at break, dry [cN/tex]	27,2	18,1	26,0
Knot tenacity [cN/tex]	5,8	4,8	9,0
Zn/Ag content [g/kg]	125	15,5	58,0
Zn/Ag release in water after [mg/L]			
1h	3,7	0,4	5
2h	3,5	0,3	21
4h	7,5	0,3	20
6h	5,7	0,4	25

Zinc oxide or Silver nitrate is possible. The produced fibre specimens show typical fibre parameters and this is the requirement for the next step of the fabric production. The fineness of the second fibre specimen V2 is not sufficient. This problem was solved in the fibre specimen V3 where the ion exchanger was milled smaller than 10 μm.

PRODUCTION OF YARNS

For the yarn production in the ring spinning a three component mixtures of polyester (GRISUTEN®), un-doped cellulosic regenerate fibers (Lenzing TENCEL® A100) and the new antimicrobial doped cellulosic regenerate fibres was defined. Table 2 shows the used fibres mixtures for the production of the woven and knitted fabrics.

Because cotton or regenerate cellulosic fibres are favoured from the wearer of work wear the amount of cotton or regenerate cellulosic fibres was be chosen as main component.

The next Figures show the microscopic pictures of the yarn cross section of the yarn with Zinc-doped ion ex-

Table 2. *Fiber mixtures for the yarn production.*

Method of production	Mixtures of fibres	Yarn fineness
Knitting	30/60/10 PES/CLY/$CLY_{antibacteriell\ doped}$	14 tex (Nm 140/2)
Weaving	40/60/10 PES/CLY/$CLY_{antibacteriell\ doped}$	29 tex (Nm 34/1)

changer (fiber specimen V2). The difference of the yarn fineness of the three components of the yarn mixture can be clearly detected. Some of the new developed fibers are on the yarn surface and this can cause problems during the usage of the fibres. The outer fibres can be damaged by the abrasion during usage of the fabric. If the outer fibres possess the antimicrobial function the antimicrobial activity can be decrease because of the abrasion.

The aim was to develop white yarn because the colour white is often use for work wear and is also a sign for cleanness. The fabrics with fibres specimen V3 show as well the light yellow colour (see Figure 5). The fabrics with fibre specimen V1 and V2 show white colour with a different whiteness. This effect is caused by different used bleaching process.

The incorporation of Zn and Ag components should give an antimicrobial activity to the fabrics. The antimicrobial activity was tested in original state and after 50 and 100 wash cycles because the fabric should have the antimicrobial activity over the whole life time. The antimicrobial activity was judged by the reduction of the test micro organisms Staphylococcus aureus ATCC 6538 and Klebsiella pneumonia ATCC 4352 and the used classification is shown in Table 3.

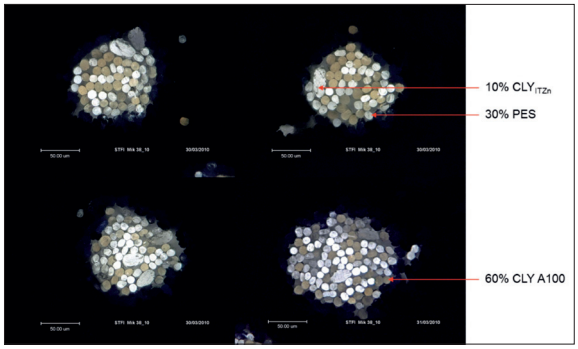

Figure 3. *Yarn cross section 14 tex (Nm 79/1), knitted fabric with fiber specimen V2.*

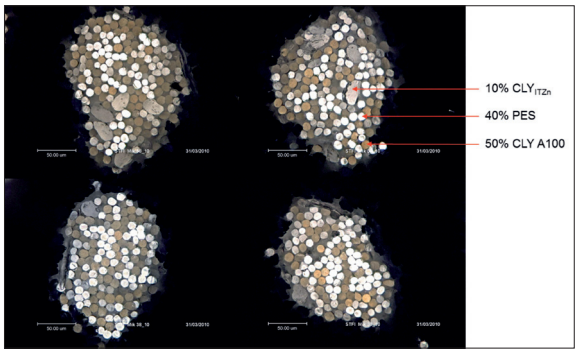

Figure 4. *Yarn cross section 29 tex (Nm 34), woven fabric with fiber specimen V2.*

The diagram in Figure 6 shows the result of the antimicrobial test. Also after 50 and 100 industrial washing cycles the fabrics show strong microbial activity.

Tables 4 and 5 show the results of the conformity test on the compliance with the Hohenstein Standard 702 and 704. Values with a star marked do not fulfil the requirements. For fabric V2 the ion exchanger was not milled sufficient and this is the reason why the fabric V2 does not fulfil all requirements. The woven fabric V2 and V3 show a high pilling propensity; in contrast the comparable knitted fabric show good pilling propensity. The different behaviour has to be investigated in further projects because the reason of the differences is not explainable. The specimens of the woven and knitted specimen V3 show the best results. In contrast to the specimen V2 the ion exchanger was milled to a smaller size and the yarn production was

Table 3. *Classification of the microbial activity.*

Antimicrobial activity	Reduction of organisms [log KBE]
No	< 0.5
Light	0.5 to 1
Significant	1 to <3
Strong	3

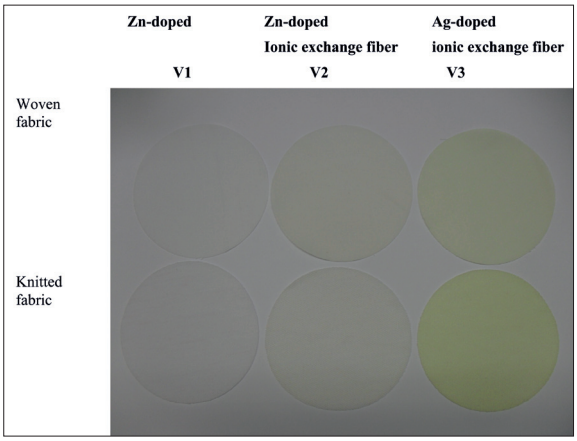

Figure 5. *Colour of the woven and knitted fabrics.*

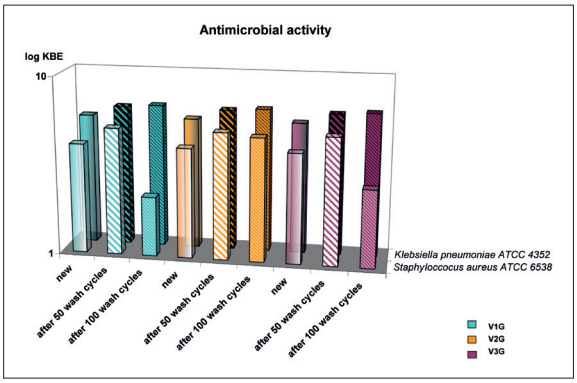

Figure 6. *Antimicrobial activities of the woven fabric specimens in original state and after 50 and 100 washing cycles.*

Table 4. *Results of the conformity test on the compliance with the Hohenstein Quality Standard 702.*

	V1G	V2G	V3G
Tensile properties maximum force dry [N]	warp 973 weft 513	warp 1137 weft 545	warp 1513 weft 549
Abrasion resistance	still undestroyed after 30.000 tours	destroyed after 27.500 tours	still undestroyed after 30.000 tours
Pilling propensity (after 5 processing cycles (DIN ISO EN 15797))	4-5	1*-2*	1*-2*
Dimensional change (after 5 processing cycles (DIN ISO EN 15797)	longitudinal +0.5 0.0 -1.5 transverse -4.5* -4.0* -4.5*	longitudinal -4.5* -5.0* -4.5* transverse -2.5 -2.5 -2.0	longitudinal -2.0 -2.0 -2.0 transverse -1.0 -1.5 -1.1
Crease recovery	4	3.3	4
Hypochlorite bleaching fastness	5	5	5

Table 5. *Results of the conformity test on the compliance with the Hohenstein Quality Standard 704.*

	V1M	V2M	V3M
Bursting strength [kPa]	537*	478*	618
Pilling propensity at 7000 rotations (after 5 reprocessing cycles DIN EN ISO15797)	4	3	3
Dimensional change (after 5 reprocessing cycles DIN EN ISO 15797)	longitudinal -7.0* -7.0* -7.5* transverse -2.5 -4.5 -2.5	longitudinal -2.5 -4.5 -2.5 transverse -5.5* -6.5* -6.0*	longitudinal -7.0* -7.0* -5.0 transverse -6.0* -4.0 -6.0*
Crease recovery	3.2	3	3
Hypochlorite bleaching fastness	5	5	5
Torsion of seams	0.76	2.7	3.2

carry out in an industrial process. So the results show that the three new antimicrobial fibres specimens can be used in mixtures with PES and original regenerative cellulosic fibres for work wear in woven and also in knitted fabrics. The qualities of the yarns in the investigated mixtures are good.

The tables 6 and 7 show the thermophysiological results of all proofed woven and knitted fabrics. Out of experience for the evaluation of the thermophysiological comfort properties of woven fabrics for work wear or protective clothing the following criteria can be applied. The lower the fabric's water vapour resistance R_{et}, the better its "breathability". However, water vapour resistance as well as thermal insulation strongly depend on the fabric's thickness. This means that a higher thermally insulating and, thus, thicker fabric inevitably possesses a higher absolute water vapour resistance than a thinner fabric. Therefore, to judge the physiological quality of a fabric a quantity must be chosen in which the influence of the fabric's thickness is eliminated. This demand is met by the water vapour permeability index i_{mt}. It is defined via the ratio of thermal to water vapour resistance and, thus, expresses the fabric's relative moisture transport properties. The physiological quality of a fabric has to be judged the better, the higher this i_{mt}-value turns out to be. Woven fabrics for work wear or protective clothing should possess an i_{mt}-value of at least 0.15. In a wear situation with increased sweating, in order to keep the "microclimate" next to the body as dry as possible, a fabric must possess a good buffering capacity of water vapour, effected partly by a high and fast water vapour transport, and partly by a fast water vapour absorption. The combined effect of these properties is shown by the moisture regulation index F_d. It should be as high as possible. Particularly fabrics for work wear and protective clothing should possess an F_d-value of at least 0.40. In wear situations combined with heavy sweating, for the resulting wear comfort of a textile particularly a high sweat transport F is important. To be judged as "good", with work wear or protective clothing the F-value at 25°C, 50 % r.h. must be larger than 765 g/m²h. Together with the sweat transport the sweat uptake G_2 determines the fabric's buffering capacity of liquid sweat, expressed by the buffering index K_f. The higher the K_f-value, the better is the buffering capacity. The minimum K_f-value to be demanded from fabrics for work wear or protective clothing is 0.78. However, from a physiological point of view it is the better, the more sweat is transported through the fabric and the less moisture remains in the textile next to the skin. In order that in rest periods after physical activity, combined with heavy sweating, no unpleasant and under certain conditions health-damaging post-exercise-chill is caused, fabrics for work wear or protective clothing should have a low water retention ΔG.

According to Table 6 a thermal insulation R_{ct} is found, typical for woven fabrics of the type of work wear. The six fabric specimens show a water vapour resistance R_{et} below 5 m²Pa/W combined with good relative moisture transport properties, the latter expressed by the i_{mt}-value above 0.15. Thus, the fabric's "breathability" has to be judged as good. As it is typical for fabrics with a high cotton content, the sample's water vapour absorbency F_i is high. Together with the

Table 6. *Thermophysiological data of the fabrics.*

	Thermal resistance R_{ct} [m² K W⁻¹]	Water vapour resistance R_{et} [m² Pa W⁻¹]	Water vapour permeability index i_m	Short-time water vapour absorbency F_i [g/m²]	Moisture regulation index F_d
Woven fabric					
V1G	0.0079	2.68	0.18	4.25	0.52
V2G	0.0137	3.26	0.25	3.62	0.51
V3G	0.0141	3.24	0.26	2.50	0.47
Knitted fabric					
V1M	0.0205	3.79	0.32	7.75	0.60
V2M	0.0254	3.97	0.38	7.50	0.67
V3M	0.0211	3.84	0.35	7.13	0.66

Table 7. *Thermophysiological data of the fabrics.*

	Buffering index K_f	Liquid moisture transport F_1 [g/m²hmbar]	Liquid moisture transport F at 25°C/50% r.F. [g/m²]	Water uptake G_2 [g]	Water retention G [%]
Woven fabric					
V1G	0.95	23.03	930	5.24	49.82
V2G	0.88	20.96	847	5.42	50.31
V3G	0.89	21.49	868	4.92	44.79
Knitted fabric					
V1M	0.98	17.36	701	7.85	63.85
V2M	0.99	16.75	677	8.32	66.43
V3M	0.99	17.29	698	8.02	63.10

moisture regulation index F_d larger than 0.40 (see Table 7) this indicates a good buffering capacity of water vapour of the fabric tested. The woven fabrics show an F-value significantly above 810 g/m²h and the fabric‘s liquid sweat transport is very good. In contrast the knitted fabric V1M and V2M show an F-value above 695 g/m²h and the fabric‘s liquid sweat transport is sufficient. Only knitted fabric V2M shows an insufficient F-value with 677 g/m²h. The fabric‘s buffering capacity of liquid sweat of the woven fabric V1G has to be rated as very good and of the two other woven fabrics V2G and V3G only as good. All knitted fabrics show a very good buffering capacity of liquid sweat. The values of the water retention ΔG shown in Table 7 are higher for the knitted fabrics as for the woven fabrics. The drying time of the three knitted fabrics was also determined and with 42 min the drying time of the knitted fabric is long. The drying time Δt should be below the critical value of 37 min indicates. The kitted fabrics V2M and V3M show a drying time of 36 min and they are below the critical value. In practical use the two knitted fabrics will not cause a post-exercise-chill.

The Table 8 show the results of the skin sensorial investigations.

Out of experience for the evaluation of the sensorial comfort properties of woven fabrics for or protective clothing the following criteria can be applied. For a good sensorial comfort, the wet cling index i_K of a fabric worn in contact with the skin must be smaller than 15. Otherwise an unpleasant clinging of the fabric to skin wetted by sweat is to be expected. The surface index i_o of a woven fabric for work wear or protective clothing must lie between 3 and 15 in order not to be felt as too smooth on the one hand or too rough/scratchy on the other. With regard to good sensorial comfort the number of contact points between fabric and skin n_K should be less than 1500, and the woven fabric‘s stiffness s should lie below 60. Out of experience the sorption index i_B should not be higher than 270, because a fabric‘s sensorial comfort is not only determined by its physical surface structure, but also by its ability to keep the wearer‘s skin dry. Dry skin, namely, is less sensitive to mechanical irritations, causing a subjectively unpleasant sensation, than moist skin. This is the reason why in the predictive formula for the sensorial comfort vote WC_S also the moisture permeability index i_{mt} is included. Table 8 shows that the fabric‘s wet cling index i_K as well as its stiffness s lie well within the sensorial neutral regions. The sorption index i_B of all fabric specimens confirms the Skin Model test results of good liquid sweat transport. The surface index i_O of fabric specimen V1G is lying below 3.0 and that indicates that the fabric will be perceived as some what too smooth on the skin. Also with the number of contact points n_K significantly above 1500 it tends to be felt as clammy on the skin when the wearer is sweating more heavily. All other five fabric specimens show a surface index in the neutral region and also the number of contact points is under 1500 for each fabric specimens.

Table 8. *Skin sensorial data of the fabrics.*

	Sorptions-index i_B	Wet cling index i_K	Surfaceindex i_O	Number of contact points fabric/skin n_K	Stiffness S
Woven fabric					
V1G	0.3	7.7	2.7	1535	24.6
V2G	1.3	7.5	4.2	1440	31.7
V3G	3.3	6.8	3.7	1482	25.5
Knitted fabric					
V1M	0.1	5.1	3.3	1152	9.5
V2M	0	6.5	3.0	1013	9.3

Table 9 and the Figures 7, 8 and 9 show the results of the calculation of the skin sensorial comfort vote, the thermophysiological comfort vote and the comfort vote of the six tested specimens.

Summarizing the physiological properties of the fabric tested, as discussed above, according to Table 9 for the six fabric specimens a thermophysiological comfort vote WC_T between 1.7 and 2.5 (in all cases “good”) results. For the sensorial comfort the WC_S-vote differs from 1.4 to 2.0 (between “good” and “very good“).

Table 9. *Skin sensorial comfort vote, thermophysiological comfort vote and comfort of the tested fabrics.*

	Skin sensorial vote WC_s	Thermophysiological vote WC_t	Comfort vote WC
Woven fabric			
V1G	1.7	1.7	1.7
V2G	1.6	2.5	2.2
V3G	1.4	2.3	2.0
Knitted fabric			
V1M	2	2.5	2.3
V2M	1.6	1.9	1.8
V3M	1.9	2.2	2.1

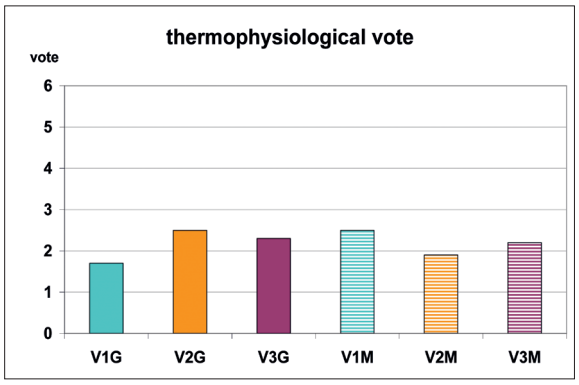

Figure 7. *Comparison of the thermophysiological vote of the woven and knitted fabrics.*

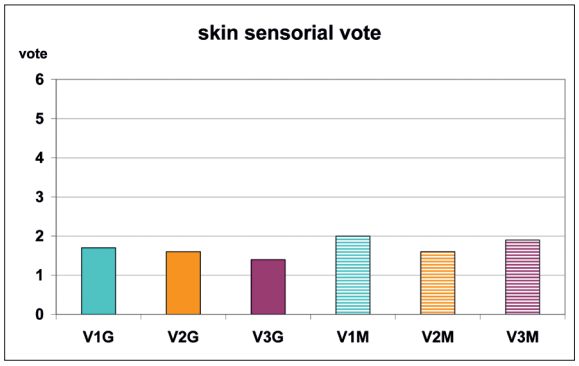

Figure 8. *Comparison of the skin sensorial vote of the woven and knitted fabrics.*

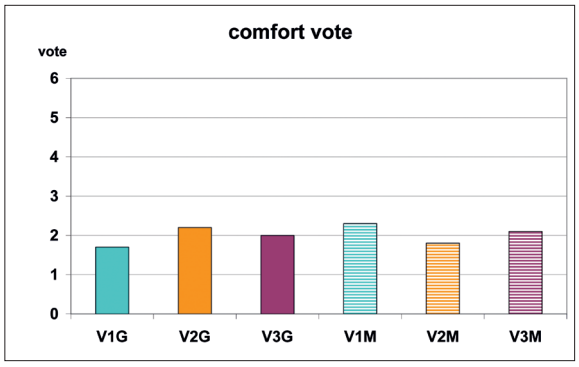

Figure 9. *Comparison of the comfort vote of the woven and knitted fabrics.*

The total wear comfort, including the fabric's thermophysiological and skin sensorial properties, based on the WC-vote between 1.7 ad 2.3 of the six specimens verbally has to be rated as good. Differences between fabrics in the WC-vote of 0.5 or more are registered subjectively by the wearer. So the results show very small differences and the quality is very similar between the six fabric specimens. The results show that the comfort vote depends on the construction of the fabrics and that it is necessary to proof the woven and knitted fabric because the quality can be differ. The different doping of the fibres doesn't lead to significant differences between the comfort vote of the 3 fibre specimens.

Conclusions

The aim of the project was the development of a work wear for the food processing industry consisting of antimicrobial regenerated cellulosic fibres which are suitable for leasing. For the antimicrobial function the cellulosic fibres were successfully doped with different antimicrobial substances. The doping with zinc components leads to white fibres. The integration of an ion exchanger and Silver components leads to fibres with a light a yellow color. The size of the ion-exchanger has a large influence of the fiber properties and the results show that the ion exchanger has to be milled to a size smaller than 10 μm. The yarn production in mixtures of PES and untreated cellulosic fibres is possible and leads to yarn with good properties. In this project the mixture rate was 60CV/30PES/10CVdoped for knitted fabrics and 50CV/40PES/10CVdoped for woven fabrics. The three antimicrobial fibres can be used with other fibers in mixtures and for yarn without any problems in the yarn production. At least the qualities of knitted and woven fabrics are determined and it is possible to weave and knit fabrics with a good quality. Also the thermophysiological comfort and the sensorial comfort can be judged as good. So it is possible to produce a good quality of woven and knitted fabric which can be used for work wear in the food processing industry. Also the high amount of 70% cellulosic fibres (60% untreated and 10% treated cellulosic fibres) in knitted fabrics and the amount of 60% (50% untreated and 10 treated cellulosic fibres) lead to a work wear with a high leasing performance.

Acknowledgements

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Spun–Dyed High–Visibility Man–Made Cellulosics

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Abstract

Fluorescent cellulose fibers for use in reflective safety clothing have been developed and the patent has been filed. The developed man–made fluorescent cellulosics can simultaneously be flame resistant. Unlike existing fluorescent fibers, which are typically made from synthetics such as polyester, the cellulose textiles are comfortable to wear, less prone to the development of odors and less susceptible to the development of electrostatic charges, which can be dangerous, leading to explosions in certain environments. The yellow fluorescent man–made fibers satisfy the light–fastness requirements of international standards and whose colorations are not significantly bleached by exposure to radiation of xenon–lamps. They also fulfill the standard requirements for light density factor, color–space and rub fastness (both, dry and wet). The positive results can be achieved by correct incorporation of various color and fluorescent pigments into spinning dope during the fiber processing.

Keywords: *high–visibility fibers, Lenzing FR®, protective textiles.*

Introduction

In the last decade and especially now–a–days the developments in the segment of the fibers and textiles pay huge attention to the safety and protective fibers, fabrics and clothing. The flame–resistant protective materials have to be stable at high–temperatures, and on the other hand enable comfort in wear to prevent the heat stress of the workers. To fulfill all their requirements, a combination of hygroscopic, natural and synthetic fibers gives a proper solution. The synthetic fibers give performance and natural, hygroscopic fibers enable moisture sorption and wear comfort. Recent developments in protective clothing deal with high–visibility clothing [1].

There are many standards which define the properties of the high–visibility protective clothing. The standards are specific for each country or continent. In general, there are two main application segments of high–visibility clothing: the clothing for professional use and for non–professional use (sportswear, for example) [2,3]. The most important standards for high–visibility clothing are European standards EN ISO 471m EN ISO 1150, Canadian standard CAN/CSA Z96–02, USA standards ANSI/ISEA 207–2006 and BS EN 417:2003 [4–7].

Figure 1 shows different areas of use of high–vis clothing. Besides green, pink, red, violet or fluorescent blue colors, orange and yellow colors are mostly applied due to the higher “visibility” to the human eyes, especially in dark work places.

In modern high–visibility clothing, the most used fiber type is spun–dyed polyester. The pigments do not get changed during the melt spinning procedure and are stable after Xenotest exposure. Very common is the use of optical brighteners to improve the fluorescent appearance. In the case of synthetic fibers, bath dyed cotton or viscose fibers are blended with synthetic fibers. But only reactive dyeing of cellulose with yellow fluorescent dyes is possible, there are no existing orange fluorescent dyestuffs.

Concerning the use of certain color for protective wear, fluorescent yellow and green are used for railway workers and fire-fighters. Fluorescent orange is more used for construction workers and for fire fighters as well. For emergency personnel, fluorescent red is recommended.

The main goal of this work was to develop high–visibility fibers with flame–resistant properties for protective clothing which fulfill international standards. In this publication, the focus is placed on **yellow high–visibility Lenzing FR®** fibers.

Materials and Methods

MATERIALS

For the fiber spinning, the fluorescent pigments were supplied from company Swada. Lunar Yellow 27, RTS Serie, particle size 3–4 μm pigments were used. The applied color pigment for the yellow fibers was a blend of various components Unisperse Yellow and Aquarineyellow. The color pigment is necessary for achieving high light–fastness. Fluorescent pigment is necessary to achieve high luminance. As FR–agent, additive based on phosphor/sulfur is used. The exact composition of the components in the fibers was not given due to the secrecy reasons.

METHODS

Fiber development

The fiber spinning was performed on small scale viscose plant in Lenzing AG R&D department. The fibers in various finesses were developed for different application areas. Thinner fibers are for example, more suitable for T–shirts and lighter clothing (high–visibility clothing for non–professional use), and thicker fibers are more suitable for the blends with synthetic fibers and wool, because the blending partners are polyester (>2 dtex), modacrylic (>2 dtex) or wool (broader range of fiber fineness) fibers.

Color coordinates and luminance factor

These measurements were performed at the Austrian Institute for Ecology, Technology and Innovation in Vienna according to standard EN ISO 471. The exposition time was determined according to standard EN ISO 105–B02. Exposure should continue until the blue scale control standard number 4 has changed to step 4 of the grey scale. The tester Minolta CM–508c was used with artificial daylight. The luminance factor was determined by using a 45° measurement geometry.

Testing of fastness properties

The fastness properties were measured according to: ISO 105–B02 (standard for light fastness); ISO 105–A02 (standard for laundering, 60°C); ISO 105–A02 (standard for rub fastness, dry and wet); ISO E04 (sweat fastness, acid and alkali) and high–temperature polyester over–dying (130°C for 45 min).

Visualisation of high–visibility fibers

For the SEM micrographs, the samples were Au–coated for 60 s. A Hitachi S–400 SEM was used with an accelerating voltage of the electron beam of 5 kV.

Results and Discussion

The quality of the developed fibers is primarily measured by the color properties after Xenotest exposure. Special sensitive property is the luminance factor. A high luminance factor can be achieved by using a high content of the fluorescent pigments. For yellow color, the luminance factor after Xenotest exposure has to be min. 0.76. It is dimensionless unit and it represent the amount of reflected light form the materials. The results show that the proper combination of the pigments, the standard EN 417 and also EN 1150 can be fulfilled. The luminance factor of yellow high–visibility Lenzing FR® is 0.98 before exposure and 0.81 after Xenotest exposure. XY–color coordinates match with standard.

Figure 1. *High–visibility clothing for professional and non–professional use.*

Table 1. *Color properties before and after Xenon exposure.*

Lenzing FR® high–visibility yellow fibers	Luminance factor		Color coordinates			
	before	after	before exposure		after exposure	
1.7 dtex	0.98	0.81	X 0.400	Y 0.528	X 0.398	Y 0.488

Additionally to the color properties after Xenotest exposure, the fastness properties of the fibers in their usage are of the big importance. The results in the Table 2 show that the yellow high–vis Lenzing FR® fibers correlate with the requirements in the standards.

The SEM micrographs in two magnifications (Figure 2) show very homogenous distribution of the pigments on the whole fiber length.

Table 2. *Fastness properties of Lenzing FR® high–visibility yellow fibers.*

Fastness properties		
Light ISO 105-B02	4–5	
Domestic laundering 60 °C ISO 105-C06	Color change 5	Color staining CV sample 5 Wool sample 4–5
Rub / dry ISO 105-A02	4	
Rub / wet	2	
Sweat Acid ISO-E04	Color change 5	Staining Viscose fabric 5 Wool fabric 4–5
Sweat Alkali	Color change 5	Staining Viscose fabric 5 Wool fabric 4–5

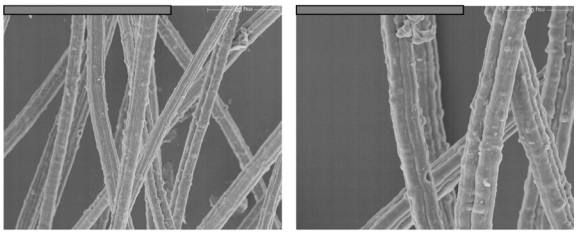

Figure 2. *SEM micrographs of yellow high–visibility Lenzing FR®.*

Conclusions

This publication highlights the properties of fibers newly developed by the Innovation Department of Lenzing AG: high–visibility Lenzing FR® fibers. Here, in this publication, the focus was placed on high–visibility yellow Lenzing FR® fibers.
With a suitable combination of color and fluorescent pigments high–quality fibers can be produced. These high–visibility fibers fulfill the strict requirements defined in international standards with respect to color coordinates and luminance factor after Xenotest exposure, rub (dry and wet) and wash fastness. Besides the high–visibility requirements, the fibers enable good moisture sorption and provide comfortable wear during the usage of protective clothing. Besides the development of the yellow fluorescent fibers, Lenzing also works on the development of orange high–visibility fibers for protective wear.

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Lenzing Modal® Loft in towels: Functional ECO-solution for the institutional towel market

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Abstract

Utility values significant for institutional towels were investigated in terry fabrics of identical constructions, consisting of different fiber materials. The performance of Lenzing Modal® Loft and cotton in blends with polyester were compared.
After repeated washing cycles, Lenzing Modal® Loft towels showed better textile performance than cotton-based towels.
Towels made from Lenzing Modal® Loft /Polyester compared to cotton/polyester had a significant advantage with regard to energy-saving.
Lenzing Modal® Loft blends showed better water absorbency without compromising the drying performance of the items. This can be attributed to the better transportation (spreading) of liquid water in Modal/polyester fabric.

Keywords: *Lenzing Modal® Loft, towel, industrial laundry, drying time, drying energy*

Introduction

Industrial laundry is a business growing not only in turnover worldwide. Institutional market is evolving worldwide. Consumer numbers and buying potential are increasing in Western industrial countries as well as in Asia, due to booming tourism and globalized business.

Growth also results into ecological concerns, e.g. a laundry generates the largest single waste water source that is sent to the waste water plant. Alone US laundries use 600 million m^3 per year, whereas the worldwide laundry consumption is estimated to be the 10-fold [1]. In term of energy, the optimization of consumption during drying processes represents not only an economical challenge, but also an ecological one.

A comparative life cycle analysis based on the ISO 14040 series demonstrated the necessity of replacing cotton, which was found to have the heaviest ecologi cal foot print among the compared fibers (cotton, polyester, Lenzing man-made cellulosics) [2].

The quality requirements are rising. Hotel chains differentiate by using distinguishing branded items. This also implies higher textile quality requirements at professional textile leasing.

Higher hygiene requirements in sectors like hospitals, food and pharmaceutical industry have resulted in increased material and energy turnover in the laundry processes. This causes time extensive and cost intensive laundering processes, due to regulations by law.

In other sectors with still national standards, such as hotels, the situation gets even more complicated, by

having no uniform laundry process and no defined quality criteria.

On the textile side, quality requirements with regard to performance and longevity are becoming higher. Longevity itself expresses both, the economical aspects in terms of investment costs as well as ecological aspects in terms of depletion of resources and disposal. Appearance, fabric touch are important factors in evaluating longevity.

Within industrial laundry, terry towels compose a critical group in terms of energy consumption: In towels water uptake is on one hand performance attribute, but leads on the other hand to higher energy consumption in the drying process. Additionally, and different to other items, the terry fabrics must be completely dried during the process, as no further drying step (i.e. ironing) is foreseen.

Due to the ecological need to replace cotton and the economical aspects in terms of basic cost, longevity and also energy saving, polyester has become a welcome blending partner. Cotton can not be completely replaced by synthetics due to the hydrophobic properties of the latter. Man-made cellulosics are an interesting replacement, as long as they are able to fulfill the performance requirements of institutional towels. Opposite to viscose (rayon), the modal fiber was developed to cope with wet treatments. Lenzing Modal® Loft is a further development within the modal fiber to fit to the quality requirements of the toweling. The 2.5 dtex fiber is coarser than the typical textile fiber (1.3 dtex). A higher volume of terry fabric can be reached without losing softness.

Having higher water absorbency than cotton, modal towels would be able to absorb more water than standard (100% cotton) towels are able to. This advantage in use might be a disadvantage in the drying process, because more energy is expected to be needed to remove the water again. On the other hand, hydrophobic synthetic fibers (i.e. polyester) would be in advantage in terms of easier water removal during spinning as well as fabric longevity. This would lead to less water uptake, bad hygiene and less comfort. A combination of materials seems to be necessary. Cotton/polyester blends are already applied in this sector for economical reasons.

The task of this study is to investigate the suitability of energy-saving towels based on Lenzing Modal® Loft for industrial laundry, as well to assess the advantage of the same in comparison to common cotton/polyester blends.

Material and Methods (experimental)

Towels made from cotton, cotton/polyester, modal/cotton and modal/polyester, with identical fabric construction, were manufactured by Framsohn Frottier (Austria). Typical approx. 480 g/m² institutional toweling construction with 50/50% cotton/polyester base and two-ply pile has been selected.

Pile Variations:

50/50% Lenzing Modal® Loft /Cotton
50/50% Lenzing Modal® Loft /PES
50/50% Cotton/PES
100% Cotton

UTILITY VALUES

Comparison of surface appearance and hand after repeated laundry washing cycles according to ISO 15797:2002 (75°C, 20 min.)

The washing performance, evaluated by fabric hand was compared after 10, 20, 30 and 50 wash cycles.

Loop removal strength

Loop removal strength was tested according to the Austrian Textile Norm ÖTN 069.

Fabric drape

The fabric drape was tested following WSP 90.4.
A conditioned (23°C, 50% rH, 24 h) round sample (30 cm) sample is placed horizontally between two smaller glass plates (18 cm). A light source is centered below the assembly. After 30 seconds the light source is turned on and the shadow which is thrown on a defined paper surface is lined. The lined shadow is cut away and the drape coefficient [DC] is calculated by the weight percentage of the cut "shadow" to the total paper weight. The smaller the shadow, the higher the fabrics drape.

MEASUREMENT OF WATER ACTIVITY

The water activity was tested according to ISO 21807:2004
The water activity value (a_w) is a measure of the free (available) water in the material. It is defined by the ratio of the partial vapor pressure over the surface (p) to the vapor pressure over pure water surface (p_o)
$a_w = p / p_o$

MEASUREMENT OF ENERGY CONSUMPTION (DRYING RATE)

10 towels (approx. 2.5 kg) were weighed and wetted for 5 minutes in water. After spinning at 1200 rpm in a MIELE W824 washing machine the weight was

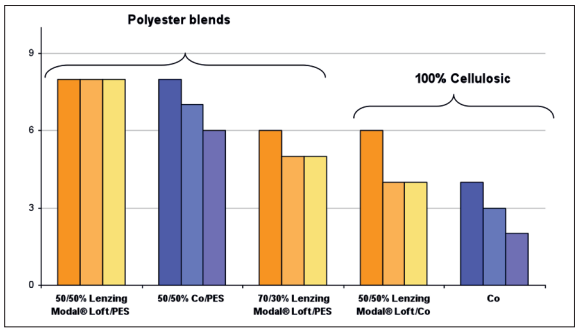

Figure 1. *Subjective Evaluation of fabric hand of towels based after 10, 20 and 30 washes.*

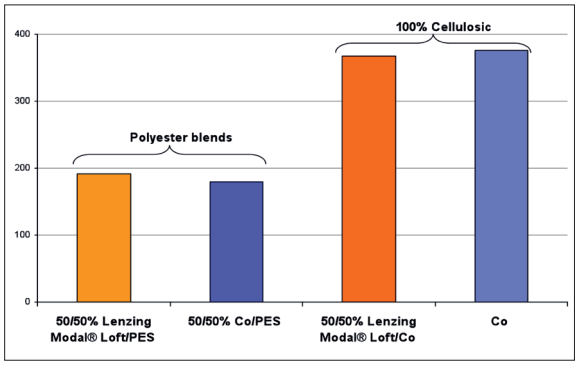

Figure 2. *Loop Removal Strength measured following Austrian Textile Standard OTN 069 [N/mm].*

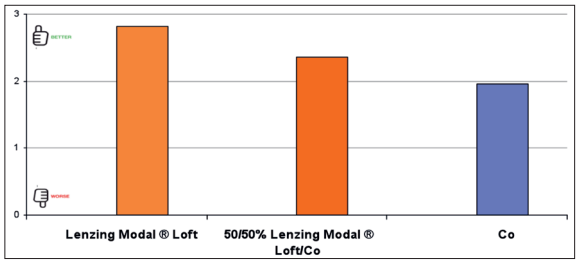

Figure 3. *Drape of cotton, Lenzing Modal® LOFT and its blend [D= 1/DC.100].*

controlled again. The towels were dried in a MIELE T440C condense tumbler, equipped with an electricity meter.

Results and discussion

UTILITY VALUES

Comparison of surface appearance and hand, after repeated laundry washing cycles

Already after the first washing cycle, the advantage of Lenzing Modal® Loft / PES blend in pile was remarkable. After 30 washes, the difference is significant and show the ability the comparison showed a clear advantage of Lenzing Modal® Loft against cotton in the same blend.
The hand evaluations expressed in softness grades (0 for worst; 10 for best) (Figure 1).
Lenzing Modal® Loft fiber can maintain its smoothness after repeated washing and drying cycles.

Loop removal strength

Loop removal strength is a crucial quality criterion for terry fabrics used in institutional use.
The results of the loop removal strength are presented in Figure 2. Although the modal fiber is known to be smooth, the loop removal strength of terry fabrics made from Lenzing Modal® Loft is comparable with the corresponding fabrics using cotton.

Fabric drape

The fabric drape determines the rigidness of the fabric and its ability to adapt itself to the human body. Drape expresses the fabric softness and hand and it is an important factor for toweling, affecting the dynamic functionality, respectively, it is a decisive performance criteria.
Due to the smoothness of the modal fiber, the drape directly correlates with the share of Lenzing Modal® Loft in the fabric (Figure 3).

WATER ACTIVITY (A_W-VALUE)

Water activity is often defined as “free” or “available water” in a system and is important to determine microbial growth rates (It is widely used in food science as a simple measure of the dryness of food). Less free water available in the fabric, results in a slower growth of microorganism. This effect of natural hygiene is an important attribute in institutional use. Higher cellulosic ratio leads to lower water activity. The water activity results (Figure 4) show higher bonding of humidity (hence lower water activity) in Lenzing Modal® Loft fibers compared to cotton.

Bacterial growth on Lenzing Modal® Loft requires higher overall humidity level on the fiber.
This means a reduced growth of bacteria and fungi without applying biocides. The natural hygiene aspect might be of advantage for the health care sector.

ENERGY CONSUMPTION AT TUMBLER DRYING

Decisive for the drying rate and hence the energy consumption during the drying process is the initial amount of water after spinning and the mechanism of water transport within the fabric.
Water transport within the fabric is crucial for the evaporation surface, which determines the drying speed.
Lenzing Modal® Loft absorbs more water than cotton does (Figure 5). This fact, which is an advantage in toweling, might be a disadvantage at drying.
Although Lenzing Modal® Loft is able to absorb more water, respectively, keeps more water after spinning, the Lenzing Modal® Loft/polyester blend showed even less energy consumption per kg than the cotton/polyester blend (Figure 6).

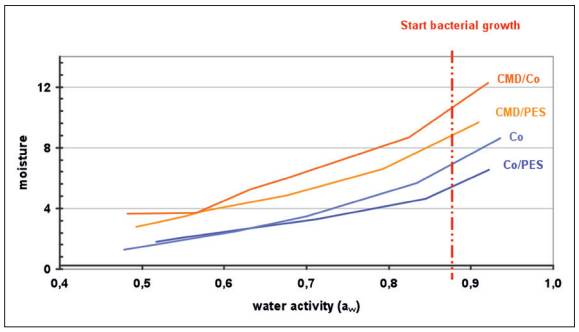

Figure 4. *Available water (water activity).*

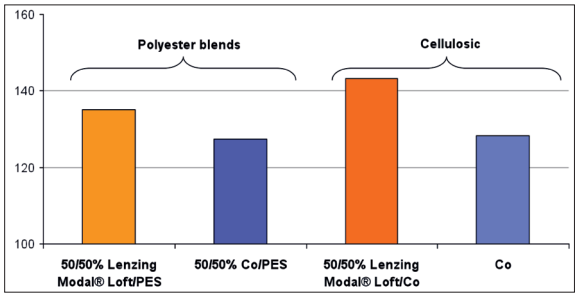

Figure 5. *Residual moisture content after spinning (rel. to dry weight, %).*

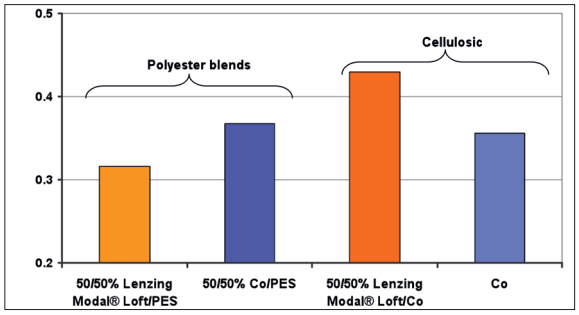

Figure 6. *Energy consumption of the towels at tumbler drying (kWh/kg wet).*

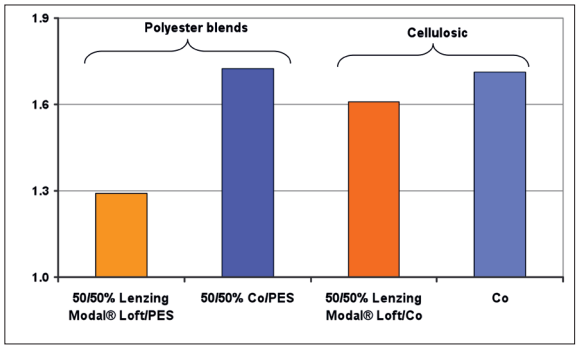

Figure 7. *Comparison of energy consumption during drying per liter of evaporated water (kWh/L)*

The energy consumption per evaporated water amount shows the efficiency of Lenzing Modal® Loft, in the blend with polyester. Lenzing Modal® Loft blend clearly outperforms the comparable cotton product, despite the higher initial moisture (Figure 7).

Conclusions

The ecological aspect of Lenzing Modal® Loft fiber is not limited to the sustainable fiber source and the ecologically friendly fiber spinning process.
Starting with comparable utility values to the cotton/polyester blends, a package of advantages for institutional application is offered: The optimized terry towel fabric construction using 50:50 Lenzing Modal® Loft /polyester in the pile offers energy saving in the drying process. The difference in the required drying energy between tested and commonly used institutional towels will even be higher in scaled-up industrial washing and drying systems, leading to significantly lower costs.
Lenzing Modal® Loft containing fabrics showed lower amounts of free water, which retarded bacterial growth and hence reduced smell development. This natural hygiene aspect makes the fiber of high interest not only of the hospitality sector, but also health care.
Lenzing Modal® Loft towels maintain their pleasant fabric hand after repeated wash and dry cycles, this extending their longevity and time in use. The point where a hospitality towel is to be replaced can be retarded by the new fiber. This saving of materials is of both, ecological and economical significance.
So, Lenzing Modal® Loft is both, the economical answer and ecological solution for institutional towels.

Acknowledgements

Karsu Tekstil, 38560 Kayseri, Turkey, and Borckenstein Qualitätsgarne, 8292 Neudau, Austria, for providing the yarns Framsohn Frottier, 3860 Heidenreichstein, Austria, for manufacture of terry towels Karin Kämpf, Herta Pixner and Agnes Uwaleke, Lenzing AG for monitoring and performing the textile and performance testing.

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TENCEL® Carbon Precursor

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Abstract

Cellulosic fibers are well established as precursor materials for carbon fiber manufacture, with a history dating from the earliest days of the carbon fiber industry. TENCEL®, the state of the art cellulosic fiber, provides exceptional purity and the performance characteristics demanded of carbon fiber precursors in the 21st Century.
This paper deals with the property profile of TENCEL® and how it could influence the resulting carbon fiber performance. Laboratory scale carbonisation trials were carried out with selected TENCEL® types under various conditions. The evaluation of different processed carbon fibers derived from TENCEL® was focused on areas like fiber strength, purity, surface and thermal properties. The picture of these results shows the potential for TENCEL® as a precursor for existing carbon fiber uses which include structural, thermal and other applications.

Keywords: *Lyocell, cellulose, precursor, carbonisation, carbon fiber*

Introduction

There are some existing publications dealing with lyocell as a precursor for carbon fibers. Some papers concentrate on thermal degradation and carbon yield,[1,2] whilst others deal with the use of different impregnation treatments[3] and furthermore others focus on tensile strength development.[4,5] An interesting study was done with different thermal pre-treatment or oxidation steps for viscose rayon, which showed clearly the influ-

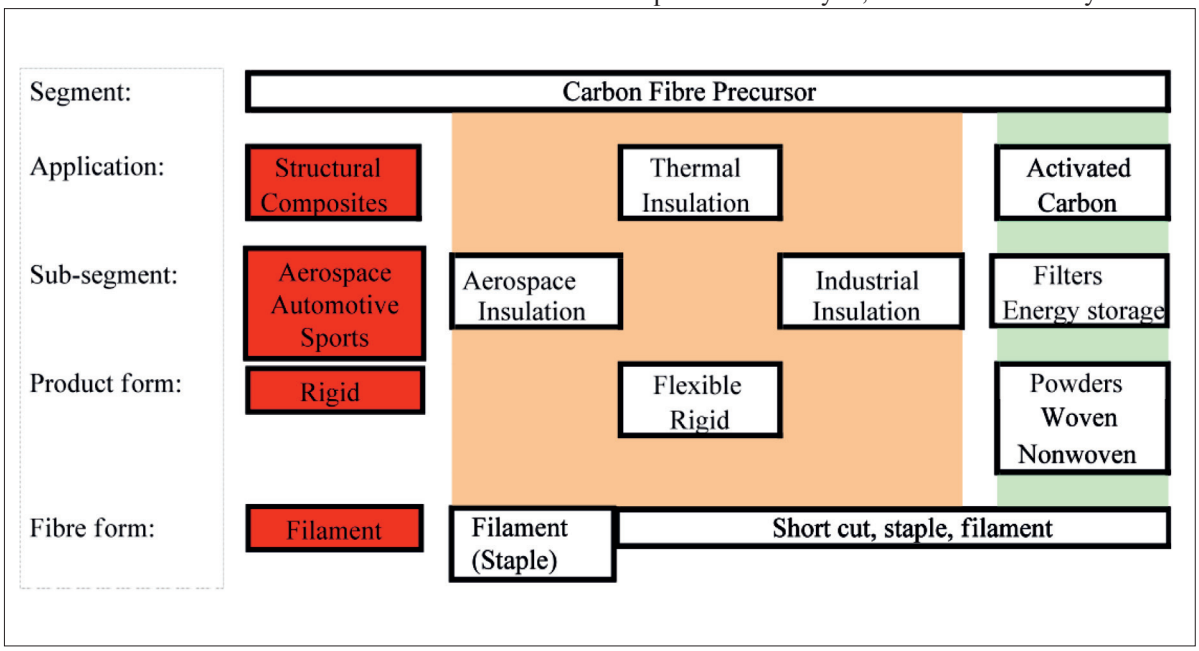

Figure 1. *Overview on carbon fiber application segments.*

ence of thermal pre-treatment on carbon yield, but not on strength.[6] For thermal properties of lyocell derived carbon fibers no publications were found to date although some exist for viscose rayon based carbon fibers. [7] None of the existing studies ever combined all of those properties to give an overall picture. In this paper we would like to present a comparative study of lyocell and viscose rayon fibres in their carbonisation behaviour, selecting different oxidation and carbonisation conditions to also highlight the yield development of the different fiber types and titers. Tensile strength development with different pre-treatment steps for lyocell will also be covered. Additionally, thermal properties of the lyocell derived carbon fibers were tested and compared to carbon fibers derived from other precursors. In addition to thermal pre-treatment a chemical pre-treatment step was chosen to show development of yield and strength properties. Finally, the different activation behaviour of lyocell and rayon was studied. From an analysis of the results conclusions were drawn as to the suitability of TENCEL®, as a carbon precursor in differing application areas. Figure 1 shows possible applications with carbon fibers. This work should give an indication of those segments where TENCEL® could be used as a precursor.

Experimental

MATERIALS

For all trials tow samples were used. Each tow piece had a length of 20 cm and an approximate weight of 20 grams. The fiber types used for the trials were lyocell fiber TENCEL® 1.7 and 3.3 dtex, viscose rayon type A 1.7 and 3.3 dtex and viscose rayon type B 3.3 dtex. The viscose rayon samples are from different commercial sources and are used as carbonisation precursors.

THERMAL AND CHEMICAL PRE-TREATMENT

In some historical studies the influence of thermal oxidative treatment of viscose rayon fibers was described[8] . According to these, the fiber samples were heated up to 210, 225, 240, 250 and 260°C under synthetic air with dwell times of 30 min at temperatures of 110°C, 150°C 200°C and at the chosen maximum temperature of oxidative treatment.

For chemical pre-treatment the flame retardant diammoniumhydrogen phosphate (DAHP) was chosen as it was promoted as the most efficient reagent for yield enhancement[9] . Therefore the fibers were impregnated with a 3% DAHP solution at ambient temperature for 30 minutes. Excess solution was removed by centrifugation, so that the fiber was loaded with approximately 2 wt% of DAHP after drying over night at 70°C in vacuum.

After the pre-treatment the fiber samples were carbonised.

CARBONISATION

The carbonisation process was carried out under inert atmosphere in a chamber furnace. Argon was chosen as the inert gas with a gas flow of 5x the volume of the oven chamber per hour. The temperature ramp rate up to 600°C was 0,6°C/min with dwell times of 30 minutes at 200, 300, 400, 600 and 950°C, then the ramp rate was increased to 5°C/min up to 2000°C with a dwell time at 2000°C for 30 min. The cooling rate was 5°C/min.

ACTIVATION

Activation trials were carried out in a horizontal tube furnace.

For activation DAHP treated TENCEL® and viscose rayon samples were heated up to 850°C, 920°C and 1000°C under inert atmosphere and then, held at this temperature for 120 minutes under carbon dioxide atmosphere. Gas flow was 5 x the tube volume per hour.

PHYSICAL PROPERTIES

White fiber analysis

Moisture content of the samples was determined to ensure correct calculation of the carbon yield. A TG-Analysis in Argon atmosphere with a ramp rate of 10°C/min was carried out to visualize the differences in thermal degradation of the different samples. Physical properties like tensile strength and elongation were determined; crystallinity of the samples was determined by NMR and purity by ICP.

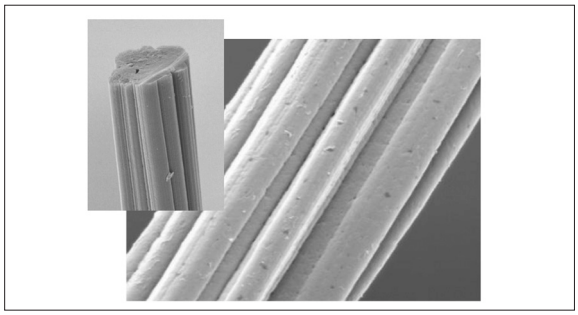

Figure 2. *SEM picture of a viscose rayon fiber.*

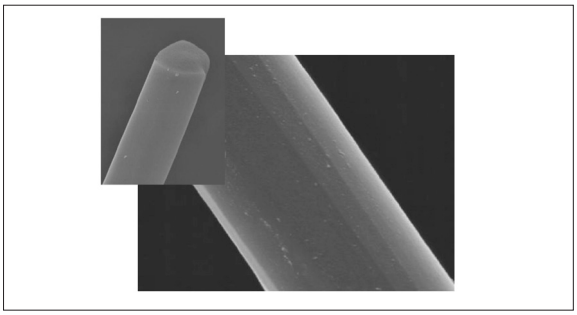

Figure 3. *SEM picture of a TENCEL® fiber.*

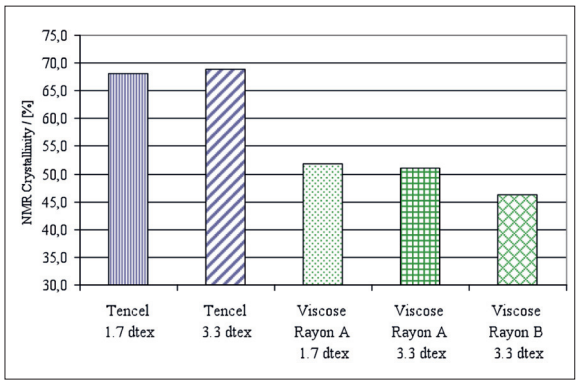

Figure 4. *Precursor crystallinity of TENCEL® and viscose rayon derived fibers.*

Table 1. *ICP-analysis of TENCEL® and viscose rayon samples.*

Element	Tencel ® [ppm]	Viscose Rayon A [ppm]	Viscose Rayon B [ppm]
Al	< 10	< 10	< 10
Ca	< 20	< 300	< 50
Fe	< 10	< 10	< 10
K	< 20	< 30	< 500
Mg	< 10	< 100	< 10
Na	< 300	< 500	< 2000
P	< 5	< 5	< 5
Pb	< 1	< 5	< 1
S	< 100	< 500	< 600
Zn	< 5	< 10	< 30

Carbon fiber analysis

From the resulting carbon fibers yield was measured by a gravimetric method, CHN-analysis was carried out, single fiber tensile strength of the 3.3 dtex fibers was determined with a modified Zwick tensile test. For this method a single fiber is cleaved bonded to a cardboard frame, which is then clamped into the Zwick, after that the sides of the cardboard frame are cut and the tensile resistance is measured.

Furthermore the thermal insulation properties at very high temperatures were tested. This was carried out by the institute Thermicar, Laboratoire Interetablissements Treffle (France) according to the method described in literature[10] .

From the activated carbon fibers SEM pictures were taken to visualize the pores and a BET analysis was done to obtain values for the activated surface.

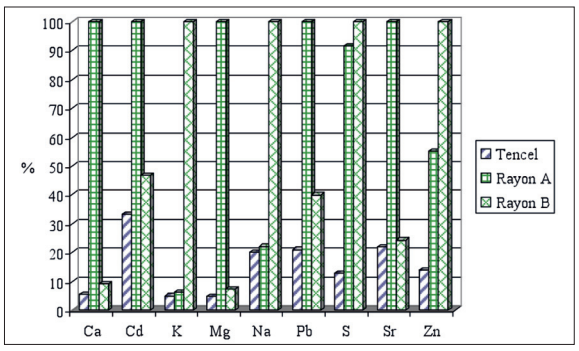

Figure 5. *Relative comparison of trace element loading of carbonisation emissions from TENCEL®, viscose rayon A and viscose rayon B.*

Results and discussion

PRECURSOR ANALYSIS

Figures 2 and 3 show clearly the difference between viscose rayon fiber and the lyocell fiber TENCEL®. The latter has a smooth surface and a round cross section. TENCEL® also has a significantly higher crystallinity compared with the viscose rayon types which is shown in Figure 4. Viscose B has an even lower crystallinity than viscose A. Also purity is different for the samples. The ICP values show significantly lower numbers across a range of trace elements for TENCEL® compared to viscose rayon.

Tensile strength of the TENCEL® fibers was around 65 percent higher than viscose rayon A and 30 percent higher than viscose rayon B. Elongation was 10 and 14% for the TENCEL® fibers, 17% for viscose A and 12% for viscose B.

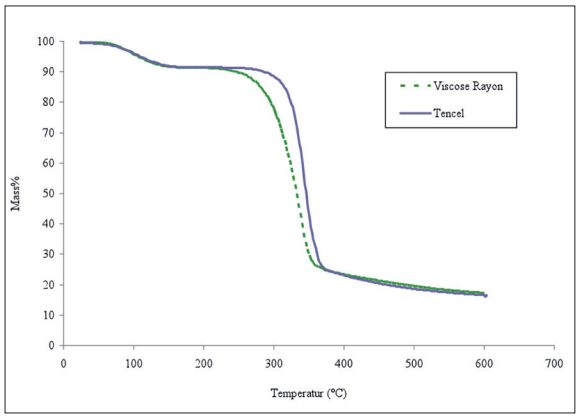

Figure 6. *TGA-curve for TENCEL® and viscose rayon B.*

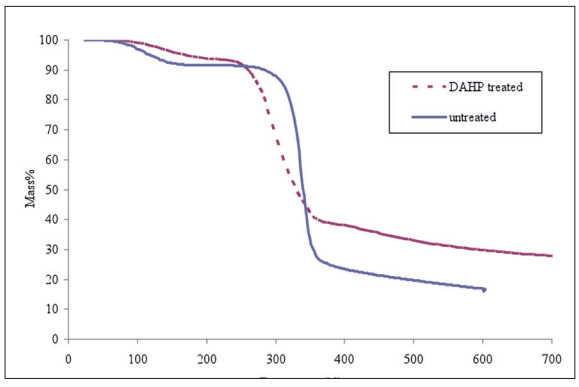

Figure 7. *TGA-curve for 2% DAHP treated and untreated TENCEL®.*

Table 2. *Mass yield after carbonisation for different fiber types and different pre-treatment processes, as thermal pre-treatment (TP) and chemical pre-treatment (CP).*

Carbonisation yield [wt%]	C2000	TP210 C2000	TP225 C2000	TP240 C2000	TP250 C2000	TP260 C2000	CP C2000
Tencel 1.7	21,0	21,7	23,4	24,9	25,3	23,8	31,1
Viscose Rayon A 1.7	21,6	22,9	23,5	24,8	24,6	23,6	31,1
Tencel 3.3	21,9	22,3	22,4	25,0	25,8	25,6	31,5
Viscose Rayon A 3.3	23,6	24,0	24,3	24,8	24,5	23,5	31,0
Viscose Rayon B 3.3	20,8	22,4	17,7	20,5	23,0	14,7	30,9

CARBON FIBER ANALYSIS

CHN-analysis gave a carbon content of 99-100% for all carbonised fibers except for the chemically pre-treated fibers. Those had a carbon content of around 97%.
Interestingly although trace element impurity differences between TENCEL® and rayon in the white fiber state the differences are quite significant, while similar numbers were found for the resulting carbonised fibers. One possible hypothesis for this finding are significantly higher emission levels resulting from viscose rayon compared to TENCEL®. Figure 5 shows the relative comparison of some of the trace elements in the carbonisation emissions setting the highest number to 100% and the others in relation to it.

In Figure 6 the TGA curves of TENCEL® and viscose rayon B are shown. Degradation of TENCEL® starts at higher temperature which could result from higher crystallinity, smoother surface, more regular shape and higher DP. The resulting yield at 600°C shows a similar behaviour for both fiber types.
The thermal degradation of the chemically pre-treated TENCEL® shows a faster degradation start at lower temperatures, but a significantly higher yield at 600°C.

The carbonisation mass yield for all fiber types and different pre-treatment and carbonisation programs is shown in Table 2. It is interesting to note that all differing pre-treatments led to optimum pre-treatment temperatures to

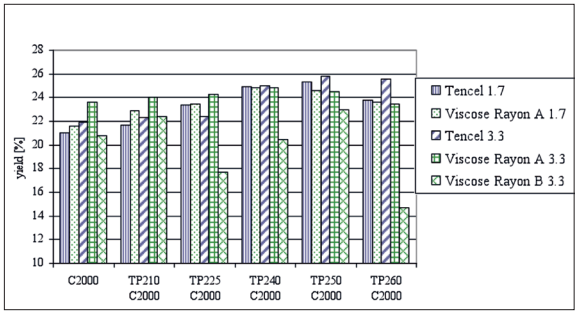

Figure 8. *Carbonisation mass yield after thermal pre-treatment (TP) at different temperatures.*

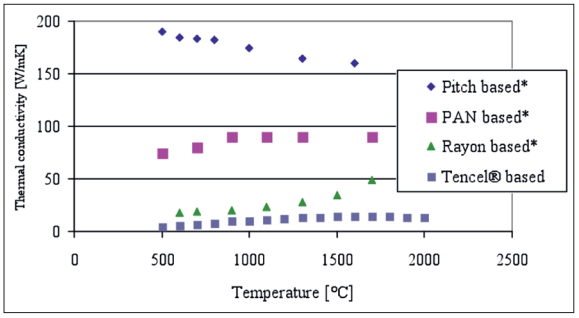

Figure 10. *Thermal conductivity of carbon fibers derived from different precursors.*
** Comparative values from reference 1.*

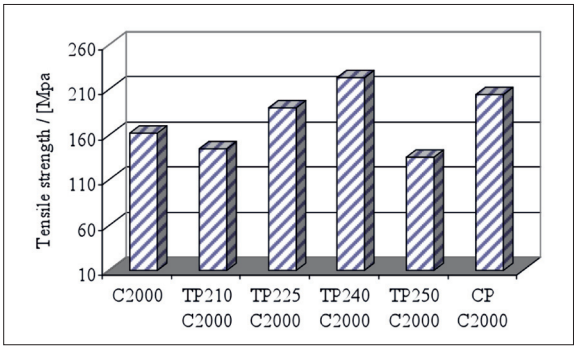

Figure 9. *Tensile strength of carbon fibers derived from TENCEL® 3.3 dtex, pre-treated thermally at different temperatures (TP) and chemically pre-treated with DAHP (CP).*

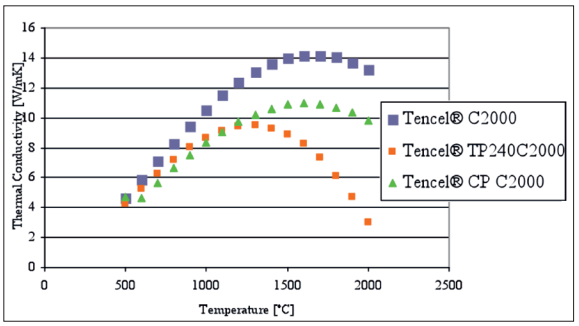

Figure 11. *Thermal conductivity of differently processed carbon fibers derived from TENCEL® precursor, TP-thermal pre-treated, CP-chemically pre-treated, C-carbonised.*

Table 3. *Mass yield and surface characteristics of activated TENCEL® and viscose rayon fibers at different activation conditions.*

Sample	Activation Temperature	Yield	BET	Total Pore Volume	Micro pore Volume
	[°C]	[wt%]	[m²/g]	[cm³/g]	[cm³/g]
Tencel 1.7	850	28,6	681	0,277	0,267
Tencel 1.7	920	24,3	1079	0,439	0,418
Tencel 1.7	1000	18,3	1883	0,800	0,755
Viscose Rayon 1.7	850	27,1	716	0,297	0,278
Viscose Rayon 1.7	920	23,6	1182	0,491	0,454
Viscose Rayon 1.7	1000	15,7	1557	0,627	0,584

maximise yield. Viscose rayon A type shows for both titers an increase in yield up to a pre-treatment temperature of 240°C and then a decrease. The B type viscose does not show such a clear peak but has the highest yield at an oxidation temperature of 250°C although is far below the A type viscose. Both TENCEL® types show the yield peak also at an oxidation temperature of 250°C having significantly higher yields compared to either viscose rayon types. The highest mass yield of 25.8 wt% was attained for TENCEL® 3.3 dtex (see also Figure 8). The chemically pre-treated fibers show similar results for all fiber types but significantly higher mass yields than the oxidised fibers of up to 31.5 wt%. The carbon content is howeer lower at 97 wt% compared to 99-100 wt% for the pre-oxidised and carbonised fibers.

In terms of strength a slightly different picture appears. Both pre-treatment steps show an increase in tensile strength. Similar to mass yield a peak at a certain pre-treatment temperature was measured. In the case of TENCEL® 3.3 dtex this was measured at an oxidation temperature of 240°C. (Figure 9) Contrary to mass yield the oxidative pre-treatment resulted in higher tensile strength than the chemically pre-treated fibers. Overall, the tensile strength levels are very low compared to those achieved with PAN precursors. But it must be mentioned that these values are without fiber stretching during the carbonisation process. Optimisation of tensile strength is to be carried out in future studies. A combination of chemical and thermal pre-treatment of the precursors could also be a next step for enhancement of both, mass yield as well as tensile strength.

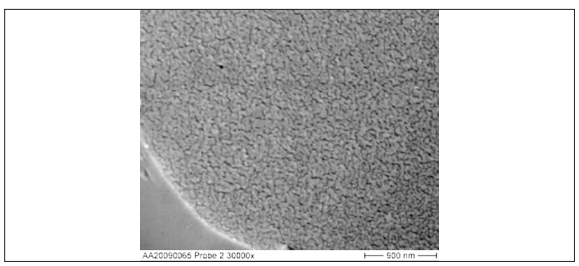

Figure 12. *SEM picture of activated TENCEL®.*

Single fiber measurements of thermal conductivity shown in Figure 10 gave very good results for TENCEL® based carbon fibers with respect to thermal insulation properties. Additionally at very high temperatures thermal conductivity was stable and did not increase. Compared to values for PAN, pitch and viscose rayon derived carbon fibers TENCEL® based carbon fibers give excellent results. Looking more deeply at the different processed TENCEL® based carbon fibers (Figure 11) one can see that the differences are very small. But it seems that the oxidative pre-treated fibers possess the best insulation properties for high temperature insulation applications.

ACTIVATED FIBER ANALYSIS

Table 3 shows the results for the activation trials for TENCEL® 1.7dtex as well as viscose rayon 1.7dtex based carbon fibres. TENCEL® again gives higher mass yield values and selection of the best conditions develops a much higher surface area than viscose rayon. The pores after activation under the chosen activation conditions are mainly micro pores. Figure 12 shows a SEM micrograph of the activated TENCEL® surface.

Conclusions

Under optimised process conditions, TENCEL® delivers higher carbonisation mass yields in comparison to viscose rayon fibers currently offered in the market. This could be related to the higher crystallinity, the smoother fiber surface, the higher DP or the lower impurity level of TENCEL®. The high purity of TENCEL® fibers can also result in a cleaner process with lower impurity load in the carbonisation emissions and high purity products. The thermal properties of TENCEL® derived carbon fibers are excellent with respect to high temperature insulation. An oxidative thermal pre-treatment gives improvements at high temperatures. Strength values of non-stretched carbon fibers derived from TENCEL® are not in the range for structural applications. Additional development trials would have to be done in this field. It can be said that thermal oxidative as well as chemical pre-treatments enhance tensile strength of the resulting carbon fibers to some extent. For applications in activated carbons TENCEL® has optimal characteristics as a precursor. It can build up high porosity at reasonable yields depending on the activation process conditions. From this study it can be concluded that TENCEL® qualifies as a carbonisation precursor outperforming viscose rayon in significant applications like high temperature insulation and activated carbon fibers.

Acknowledgements

Many thanks to Robert Putz, Christian Fürst and their team of the Kompetenzzentrum Holz GmbH for carrying out the oxidation and carbonisation trials, many thanks also to Lenzing's lab team for the good cooperation in this research work.
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Viscont HT – the future of high performance viscose filaments and their textile applications

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Abstract

The viscose process is more than 100 years old. Nonetheless the potential of cellulose based fibers for technical and textile applications is still not fully utilized. This publication is going to present recent developments towards high tenacity filaments for textile applications with a breaking force above 40cN/tex. In addition the basic features of this new product family by Glanzstoff Industries will be presented. Special focus will be paid to the production parameters and features of the permanent flame retardant multi-filament Viscont® FR.

Introduction

The demand for man-made-fibers is steadily growing. Looking at the yearly production volume of synthetic filaments between 1992 and 2009 a compound annual growth rate (CAGR) of 7.4% was seen [1]. Cotton had in the same period a CAGR of only 1.2% with a significant decrease from 2007 onwards. Viscose as the "oldest" man-made-fiber has seen a steady increasing demand for staple fibers, especially in the first decade of the new millennium. The share of viscose staple fibers of the total fiber production was 4.5% in 2009. It is expected that the demand for cellulose based fibers with their unique properties will increase, since cotton production cannot keep up with the average fiber-CAGR of approximately 4.5% until 2030. The resulting gap is known as the "cotton gap".

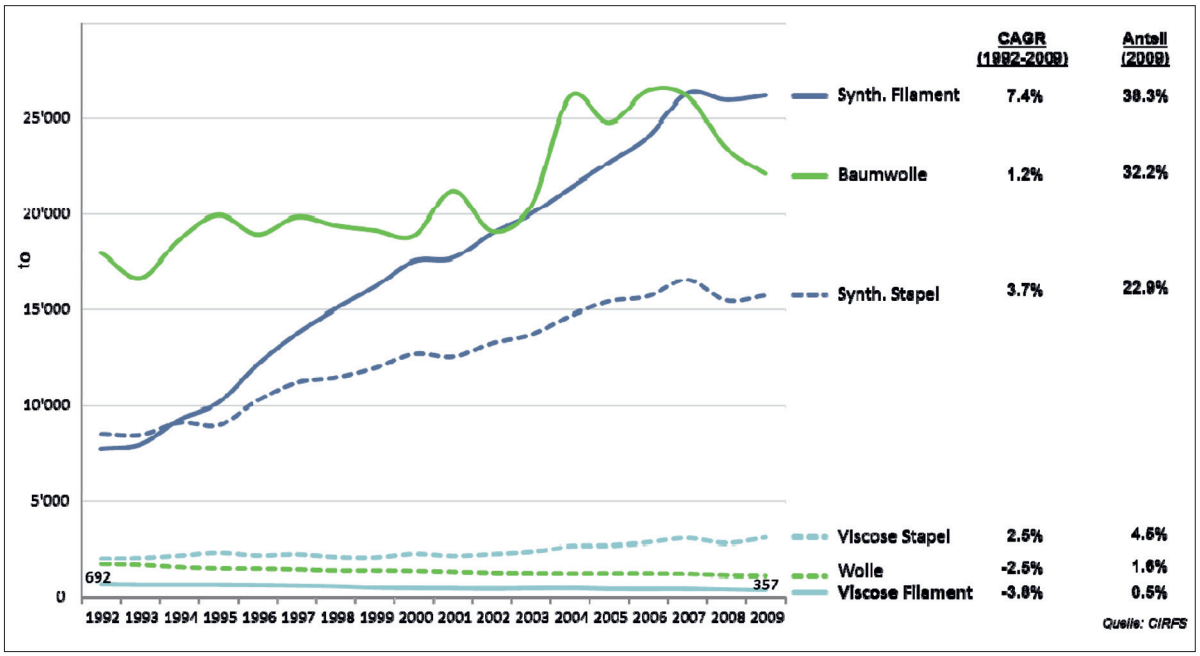

Figure 1. *Market overview fibers.*

Table 1. *Currently available yarns counts Viscont® HT together with some physical parameters.*

Material	Tenacity cond. [cN/tex]	Tenacity wet [cN/tex]	Elongation cond. [%]	Elongation wet [%]
110f60	36-40	20-24	6-10	15-22
167f92	36-40	20-24	6-10	15-22
200f110	36-42	22-26	6-10	15-22
290f160	36-42	22-28	6-10	15-22
500f270	36-44	24-28	6-10	15-22
840f480	36-44	24-28	6-10	15-22

In contrary to viscose stable fibers, the viscose filament production and market share has significantly decreased over the last 20 years. This might be due to changing customer habits on the one hand or a lack of innovations on the other. While the increasing awareness of limited resources has sped up the development of multi-functional man-made-fibers produced from regenerative sources in general especially staple fibers, hardly any improvement has been reported for textile viscose multi-filaments [2]. One major exception is the introduction of high speed continuous spinning technologies. Therefore the overview by Ninow and Heidenreich regarding properties of viscose filaments, although published in 1990 is still valid to our time [3]. One of their predictions was that viscose filaments are not able to compete with the tenacity and dimensional stability of synthetic fibers.

In this paper it will be demonstrated, that it is possible to produce multi-filament yarns for textile purposes with a higher dry tenacity than comparable polyester-yarns while keeping the full range of properties viscose is well known for. In addition a further development, a permanent flame retardant multi-filament yarn with the trade name Viscont® FR_2 will be discussed in more detail.

History of Viscont®

Viscont® is the brand name for viscose multi-filaments produced by Glanzstoff-Bohemia s.r.o., a member of Glanzstoff Industries, especially designed for highend textile applications.

In former times viscose or rayon was also known under the synonym "Glanzstoff" referring to the silk like brightness of the first man-made-fiber produced in bulk. Therefore the first viscose producers in Germany and Austria had Glanzstoff in their company name when they were founded at the turn of the last century. Nowadays Glanzstoff-Bohemia s.r.o. is the last remaining of these pioneers with this reminiscence in its company name.

The development of Viscont® was started at Glanzstoff Austria in 2006 on pilot scale and further developed in Glanzstoff-Bohemia s.r.o. from beginning of 2009 onwards. Despite decades of experience in the production of rayon for reinforcement applications on the one hand, and know-how of spinning standard- and micro-

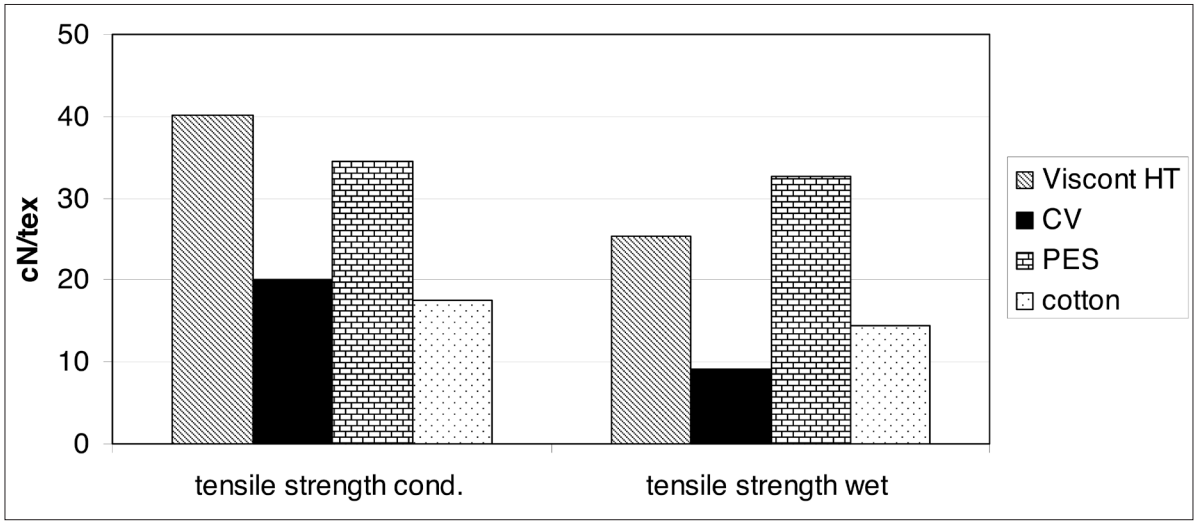

Figure 2. *Breaking force conditioned and wet of Viscont(R) HT and other yarns.*

filaments with "Continue –technique" on the other it was still a long way to *Viscont® – comfort in protection*.

Viscont® - General features

The features of Viscont® are as follows:

- high-tenacity rayon multi-filament
- "viscose like" wearing comfort
- gentle to the skin
- breathable
- available from yarn count 67 to 2440
- biodegradable
- good to excellent dying properties

High-tenacity rayon multifilament Viscont® HT

The first commercially available product produced with the new spinning process is Viscont® HT. HT is the acronym for high tenacity and refers to one of the outstanding properties of this new multi-filament fiber. Table 1 gives an overview of the currently available yarn counts together with some technical parameters. Viscont® HT has been OEKO-Tex labeled.

Breaking force conditioned and wet

In comparison to "standard" viscose filaments the tenacity conditioned of Viscont® HT is almost twice as high. While the guaranteed minimum tenacity cond. is 36 cN/tex, the average tenacity cond. is 40 to 42 cN/tex thereby surpassing even polyester yarns (see Figure 2).

Next to the breaking force in conditioned state, the wet tenacity is of special interest. In Figure 2 the values for various materials are compared. In general this has been a shortcoming of viscose based fibers, but even for the finest yarn count - Viscont® HT 110 dtex f60 - the wet tenacity found is more than 20cN/tex. The breaking force of a standard viscose filament for example is below 10cN/tex and even a comparable cotton yarn is 25% lower. The wet tenacity of higher yarn counts such as Viscont® HT 200 dtex f110 is on average above 25cN/tex. This value is still lower than comparable polyester filaments of more than 30cN/tex, but by far higher than any viscose filament commercially available for textile applications.

Despite the high tenacity the water retention according to DIN 53814:1974 is still "viscose like" high. For example the water-retention for Viscont® HT 167 dtex f92 is 38.7, while a standard viscose filament with comparable yarn count of 167 dtex f76 has 54.9. The slightly decreased ability to retain water has no negative impact on the wearing comfort. In contrary this feature has been general appreciated by textile developers (see Figure 3).

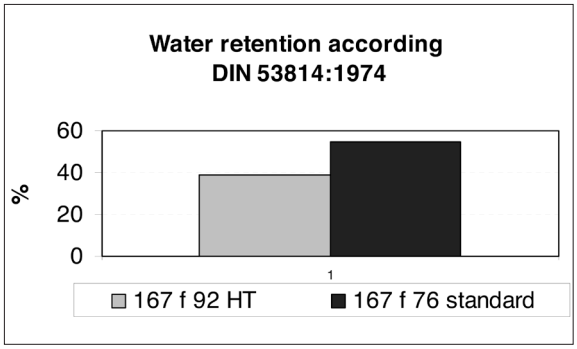

Figure 3. *Water-retention Viscont® HT versus standard viscose filament.*

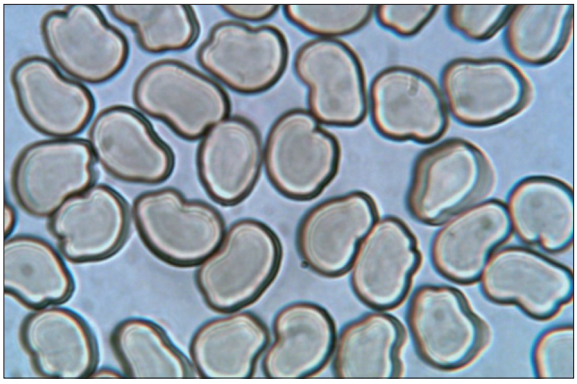

Figure 4. *Cross section of Viscont® HT produced by Glanzstoff Bohemia s.r.o.*

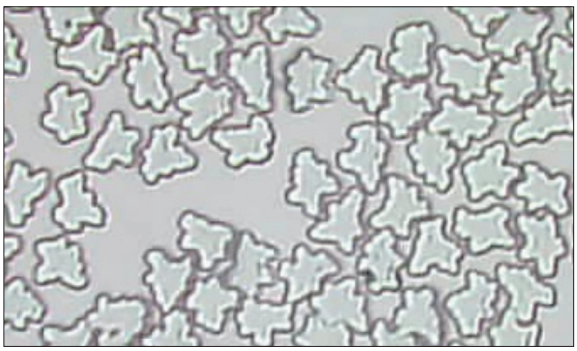

Figure 5. *Cross section of standard textile viscose produced by Glanzstoff Austria.*

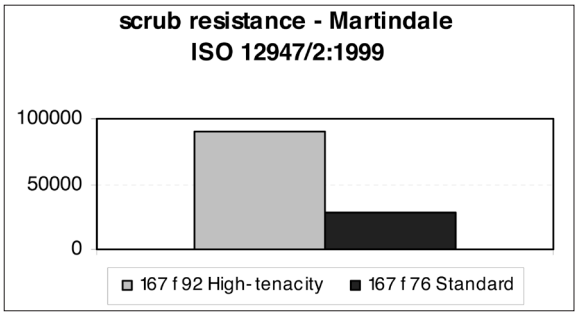

Figure 6. *Comparison of abrasion according to Martindale between Viscont® HT and standard viscose filament.*

Cross section

The cross section of Viscont® HT compared with standard viscose reveals another consequence of the new spinning technology. While the standard textile viscose has the well-known serrated surface (Figure 5), Viscont® HT has a very smooth and regular surface (Figure 4). The appearance is silk like and is comparable and almost similar with to viscose produced by the Cuproxam-process.

Abrasion

Another value adding property for high end textile applications is the abrasion behavior of Viscont® HT. In comparison with a standard textile rayon yarn, such as 167 dtex f76 produced in Glanzstoff Austria the abrasion measured according to Martindale ISO 12947/2:1999 is 4 times higher. This quadruplication seems to be a consequence of the augmented crystalline regions obtained by the Viscont® spinning process.

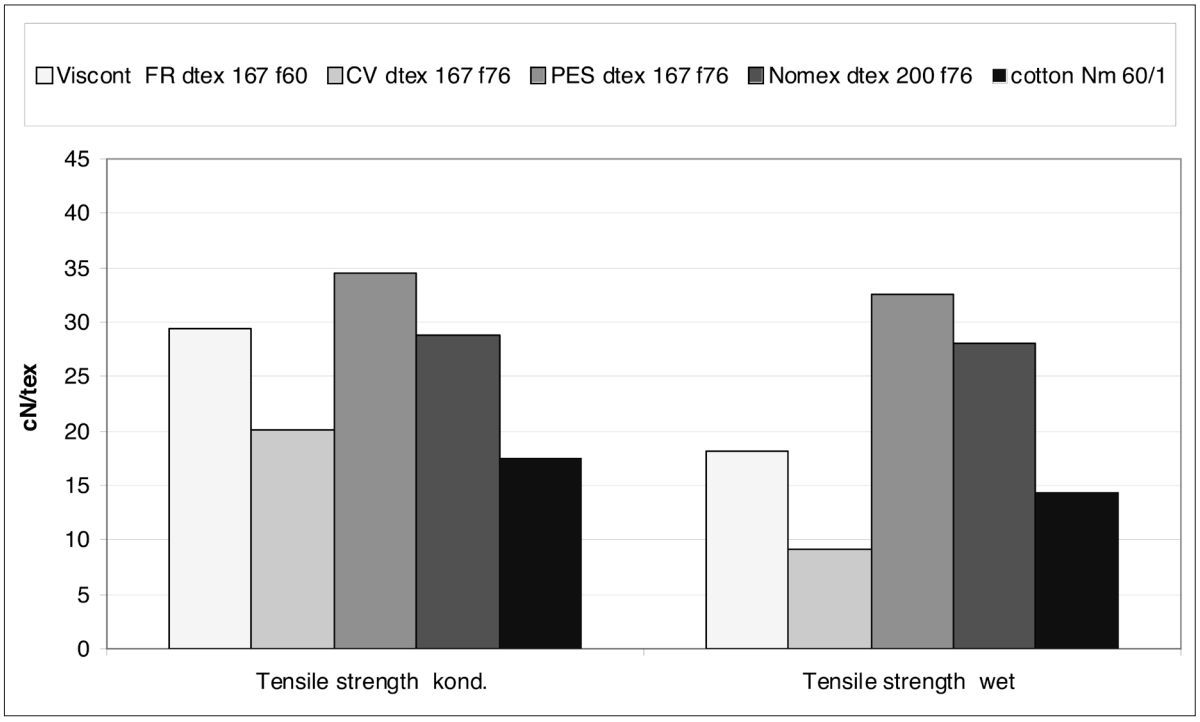

Figure 7. *Comparison of tenacity between Viscont® FR and other flame retardant yarns.*

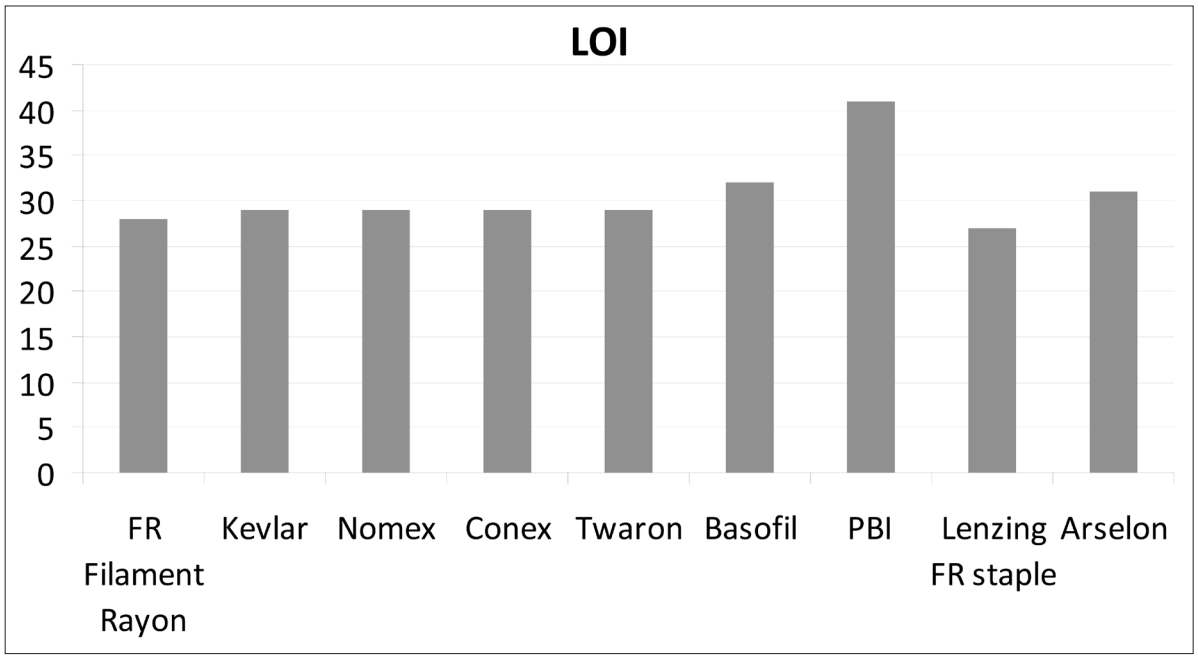

Figure 8. *Comparison of synthetic fibers used in the PPE market today versus Viscont® FR.*

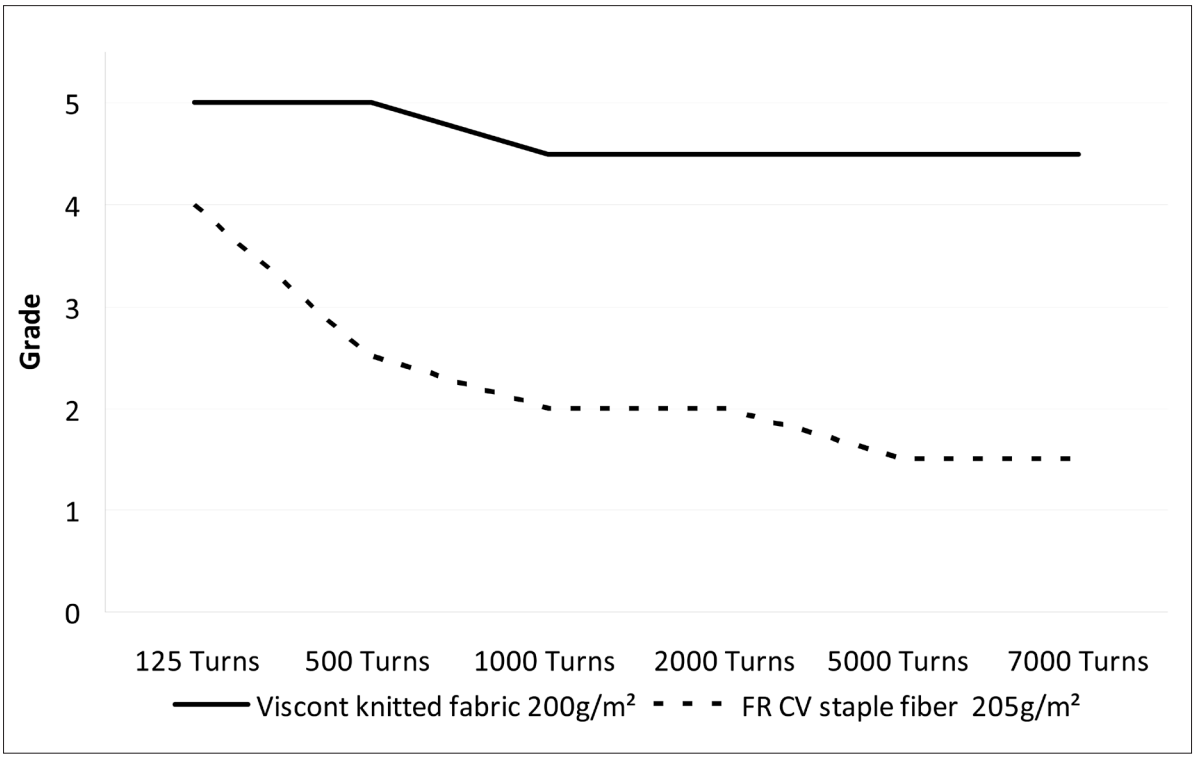

Figure 9. *Pilling determined for knitted fabric with 100% Viscont® FR and a knitted fabric made of 1:1 mixture Viscont® FR and viscose FR staple fiber.*

Permanent flame retardant rayon multifilament Viscont® FR

The need for flame retardant fabrics has been steadily increasing over the last years. Especially permanent flame retardant yarns are of high interest. There are a number of well-established synthetic fiber products available, but so far a permanent flame retardant multi-filament based on cellulose using non halogen, organic flame retardant substances was not commercially available.

The Production Process

The production of permanent flame retardant rayon staple fibers is well-known and has been described in literature before [4]. While some challenges in production of staple fibers and filaments are similar, the main difference results from the "endless" nature of filament. Every deviation in the production parameters such as viscosity of the spinning viscose, zinc content in the spinning bath, washing water and tem-

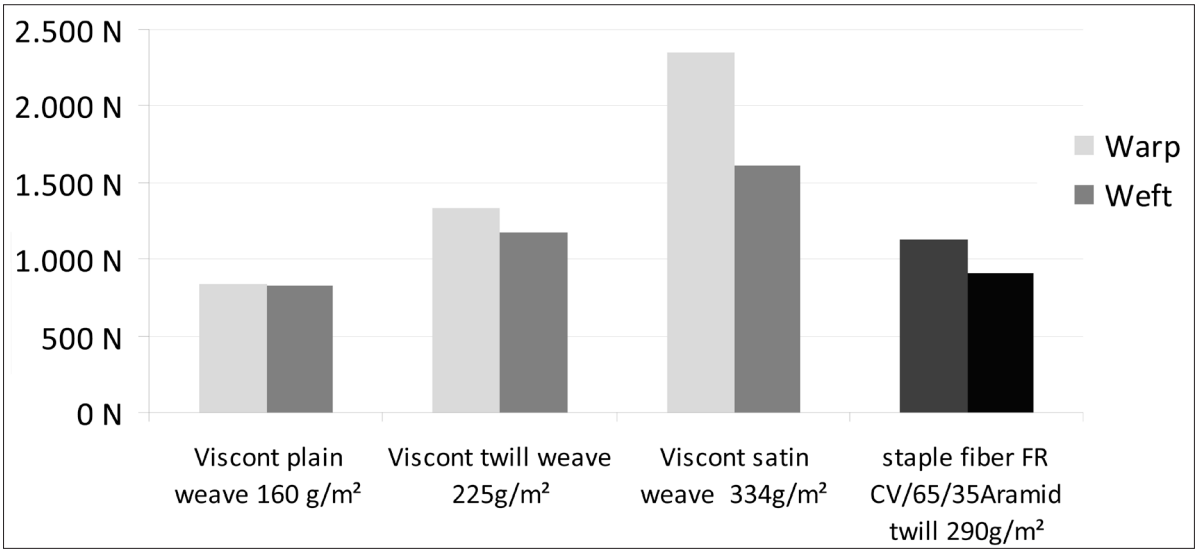

Figure 10. *Comparison between different fabrics made of of Viscont® FR filament and a currently used construction in fire fighter jackets.*

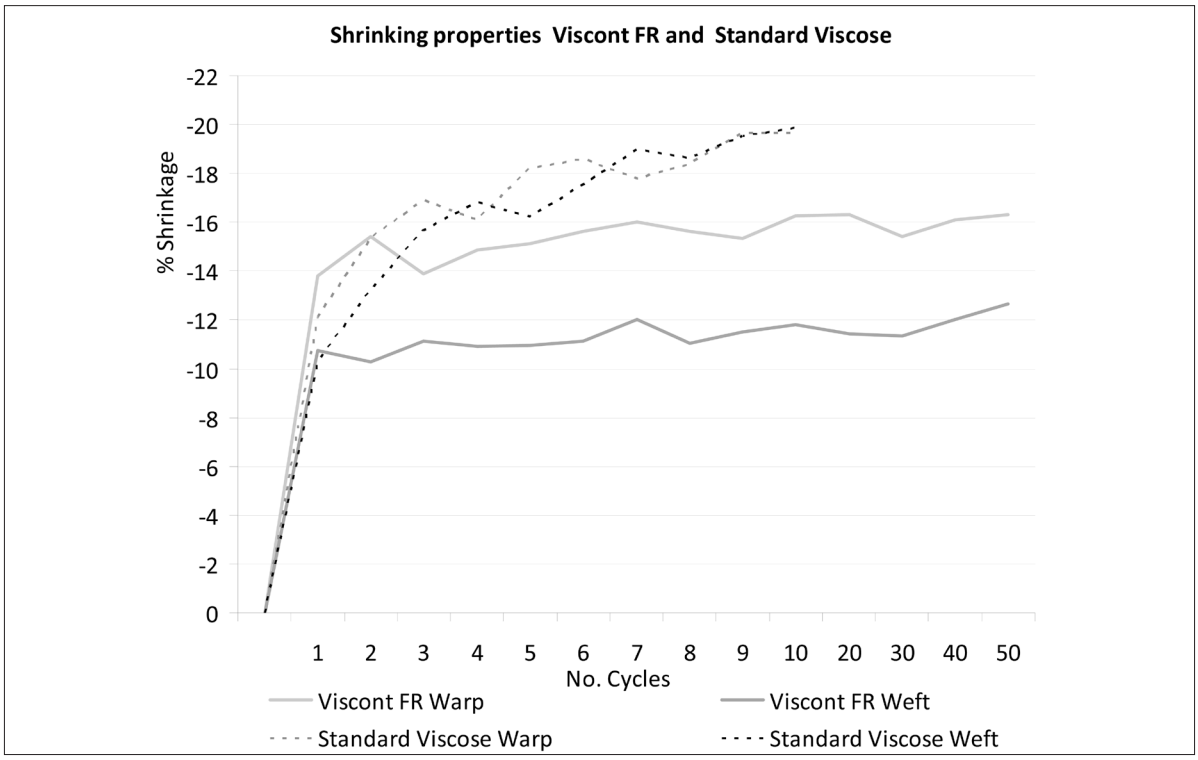

Figure 11. *Comparison of the hot water shrinkage between standard textile viscose and Viscont® FR over 50 washing cycles.*

perature and finally drying have an influence on the appearance of the filament and can cause off-grade quality.

Therefore one key to produce Viscont® FR on large scale is a very precise regulation of the spinning parameters to ensure minimum color differences on the one hand and a very low number of breakages on the other. To obtain the permanent flame retardant properties it is necessary to homogeneously incorporate up to 22 w/w% of the phosphor based compound in the viscose matrix. This high amount of the particles "disrupt" the highly ordered cellulose matrix thereby decreasing the tenacity by approximately 20% to 30% compared to a non-flame retardant filament.
Another key is a newly developed color dosing device enabling the precise addition of flame retardant dispersion into the viscose stream before spinning. The medium size of the particles in the dispersion has to be below 1 µm. Crucial for the homogeneous distribution are the facilitated dispergators, otherwise the spinning process can be and is disturbed by reagglomeration.

The spinning process of Viscont® FR is a continuous one. After the acidic coagulation bath the yarn is stretched in a second bath, before it is washed, dried and wound up. The yarn is regularly checked with the methyl orange to make sure that the yarn is free of any acidic contamination. In addition a strict separation between the operators of the acidic "wet" and neutral "dry" side is executed. It takes less than 3 minutes from the spinneret to the final, untwisted yarn. Depending on the yarn count the spinning speed of Viscont® FR varies but is in general slower than for Viscont® HT.

Tenacity

The tenacity conditioned of the untwisted yarn is in a range of 26 to 34 cN/tex. While this is lower than the tenacity of Viscont® HT, it is still higher than most purchasable ordinary textile viscose filaments. The wet tenacity is roughly 50% of the conditioned one and lies between 13 and 20 cN/tex. Standard viscose has in general a wet tenacity below 10 cN/tex. In comparison to cotton, the wet tenacity of Viscont® FR is still more than 20% higher. This offers new possibilities to knitters and weavers to produce lighter fabrics, since the mechanical strength of the yarn is higher.

The tenacity of flame retardant polyester yarn is superior to Viscont® FR. But since Viscont® FR is not a thermoplastic it does not melt under thermal stress like polyester does. Thinking of applications like liners this is a big advantage over fabrics made of polyester. In addition rayon has a much better moisture uptake and wearing comfort than polyester.

Numerous PPE-applications use Nomex® by DuPont®. Therefore it has become a benchmark within the market. In comparison with Nomex® filament 200 dtex f76 the breaking force conditioned of Viscont® FR 167 dtex f92 is on the same level. A summary of the results is given in Figure 7.

Fluffs

A critical parameter for textile applications of filaments is the number of fluffs/breakages per kg yarn. This was one of the biggest challenges in the development of Viscont® FR since a lot of parameters can cause breakages of capillaries. In general it was necessary to find a balance between spinning speed, particle size of the flame retardant, stretching, spinning bath temperature and capillary titer. According to our research capillary titers below 1.8 dtex are not suited to achieve acceptable fluff values for yarn counts below 400 dtex. In general the production/spinning of fine titers like 110 dtex f46, which is the finest yarn count commercially offered yet, is more difficult than the spinning of heavier yarn counts such as 500 or 2440. Currently we are developing yarn count 67 and 84 on pilot scale and push the limits for permanent flame retardant viscose filaments even further.

Limited Oxygen Index (LOI)

Another important feature for flame retardant yarns and fabrics is the Limit of Oxygen Index (LOI). This value - despite being an industry standard - however is slightly misleading, since not the yarn itself but only fabrics made out of the yarn (knitted or weaved) are tested. In addition, the more open the fabric is and the finer the yarn count is, the easier it burns. The consequence is that knitted fabrics in general have a lower LOI value than weaved ones. Therefore additional test methods were developed for comparison, such as vertical flame tests.

The LOI of Viscont® FR is above 26 and on average 28 for all yarn counts. This compares favorably with other synthetic FR fibers – filament and staple fiber - that are used in the PPE market today (see Figure 8)

Utilization

Viscont® FR filament rayon fabric has been woven or knitted for a variety of applications, meets diverse specifications and passes the requirements of e.g. EN ISO 11612. Fabric weights have ranged from 160g/m^2 and up with full FR compliance when tested for example by ASTM D 6413, vertical flame test method. Beside the flame retardant properties a number of textile parameters are of importance such as pilling and strength.

Pilling

To further validate the pilling of Viscont® FR filament two fabrics were tested. Fabric 1 was knitted with 100% Viscont® FR filament 200 dtex f76 S90 and had a fabric weight of 200g/m^2. Fabric 2 had a fabric weight of 205g/m^2 and was knitted, too. Instead of 100% filament only 50% of Viscont FR 200 dtex f 76 S 180 and 50 % FR Viscose-stapel-fiber 20 tex/1 was applied.

Despite a comparable weight and construction, the pilling behavior according to ISO 12945-2 (modified Martindale method) is different as expected different. While fabric 2 shows significant pilling with a load of 155g after 500 turns fabric 1 is almost unaffected. It is well known that a filament can resist the mechanical abrasion better than staple fiber yarns, however the very low pilling after 7000 turns found for fabric 1 was unexpected.

Strength

Since many years end users of personnel protection equipment are asking for lighter fabrics. This goal can be achieved primarily with finer yarn counts or “smarter” constructions. Both solutions have their limitations.

Viscont® FR filament and Viscont® HT filament give textile developers a new opportunity to reduce weight, thanks to their high tenacity properties. To demonstrate the potential a few fabrics with Viscont® FR filament were compared with an existing fabric made of a staple fiber blend used in fire fighter jackets.

The reference material has a fabric weight of 290g/m^2 and strength (warp/weft) of 1124/908 N. Fabric 2 is 30% lighter and weighs only 225g/m^2. However the strength is 19% higher in warp and 29% higher in weft. Fabric 1 weighs only 160 g/m^2. This adds up to 80% weight reduction compared with the reference fabric. Stupendously the strength is only 8% lower in weft and 25% in warp while being in full compliance with the flame retardant properties.

Fabric 3 is the heaviest of the sample fabrics at 334 g/m^2. The strength however is by far higher than the by

15% increased weight. The values found for the warp were 2345N corresponding with a 110% increase in strength. 1611N were measured for the weft which adds up to a 77% higher strength.

Despite the uniquely high strength, the viscose typical wearing behavior is not affected or reduced.

Hot-Water Shrinkage

One characteristic trait of viscose in general is the hot-water shrinkage. Once again Viscont® FR filament behaves differently than ordinary textile viscose filaments. While textile viscose keeps on shrinking with every wash cycle, Viscont® FR stabilizes after the first washing. This is an effect which seems connected with the high crystallinity of the cellulose-matrix. The initial shrinkage is comparable with standard viscose and Viscont and lies in the range of 10% to 16%. After 50 wash cycles the residual strength of the fabric is still more than 55% while the additional shrinkage is below 3%.

Therefore we advise to use Viscont® FR as pre-shrunk yarn primarily for weaving applications.

Conclusions

Viscont® - Comfort in protection is a new viscose based product-line by Glanzstoff Industries. The first commercially available products are Viscont® HT with its conditioned tenacity above 40 cN/tex and the permanent flame retardant Viscont® FR filament. Viscont® FR filament, like Viscont® HT, has been blended within fabrics in an end and end construction and with different weft yarns in order to meet the end user requirements. They can be supplied flat, twisted and textured. Twisting or texturing will not reduce the flame retardant properties of the yarn. Viscont® can be plied or covered with other fibers or yarn at a yarn or fabric level. Yarn sizes of Viscont® range from 110dtex through 2440dtex. According to our knowledge 110 dtex yarn is the finest denier Filament FR yarn available world-wide.

The fabric - examples given should demonstrate the new opportunities Viscont® high tenacity viscose filaments offer the textile community. In principle Viscont® can help to realize lighter and more mechanically resistant fabrics with an equal or even increased wearing comfort. Dying properties are excellent and since cellulose is a renewable resource it perfectly meets the demands of the 21st century for sustainable alternatives to synthetic fibers.

Acknowledgements

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Steering of Dispersibility of Spunlaced Nonwovens with Fibre Properties and Spunlacing Parameters

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Abstract

The dispersibilty of spunlaced nonwovens based on pure viscose fibres was investigated. The main target was to discover fibre and nonwoven parameters which support the dispersion of a spunlaced nonwoven. A variety of different viscose fibres was developed and tested to investigate the influence of fibre parameters like geometry (titre, length, shape of diameter), surface properties and tensile strength. At first the processability of the different fibres was explored at a broad range of hydroentanglement intensity. It became obvious that in particular the tensile strength of the nonwovens depended very much on the type of fibre.
The dispersibilty of the nonwovens was probed with a "Flush Tube Tester". The fibre and nonwoven parameters were further optimised to facilitate a good compromise of nonwoven strength and dispersibility. Main fibre and nonwoven parameters which support dispersibility could be identified.
Furthermore the flushability of spunlaced nonwowens was tested in the so called "Netherlands Sewer Pump Test". A good correlation between results of the tube test and of the sewer pump test was observed.

Keywords: *viscose fibres, spunlaced nonwovens, break-up of nonwoven, dispersibility of fibres, flushability*

Introduction

An important market for spunlaced nonwovens is the use as wet wipes for personal hygiene applications. In the same way as for toilet paper, customers consider a disposal of used wet wipes into the sewer system as convenient. Thus a huge amount of wet wipes is flushed into toilets. It is important that flushed nonwovens do not block the wastewater system [1] [2]. They should break up, disperse and disintegrate into single fibres and finally biodegrade completely. Today typical wet wipes consist of pure cellulosic fibres or of mixtures with polyester fibres. A general advantage of cellulosic fibres like viscose compared to polyester is their complete biodegradability.

SCOPE AND AIM OF THE INVESTIGATION

The dispersibility of spunlaced nonwovens based on 100% viscose fibres was investigated. Web bonding of the fibres was carried out solely via hydroentanglement. The main target was to discover fibre and nonwoven parameters which support the dispersion of spunlaced nonwovens. Spunlacing process parameters were investigated and fibre and nonwoven properties were optimized to improve dispersibility.

FACTORS AND MECHANISMS FOR BREAK-UP AND DISPERSION

In principle the fibre-fibre interaction and the water-fibre interaction depend very much on the structure and properties of the single fibre.

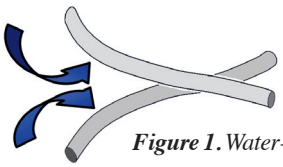


Figure 1. *Water-fibre and fibre-fibre interaction.*

Similarly the structure and properties of the nonwoven have a considerable impact on the fibre-fibre and water-fibre interactions.

The following interactions and mechanisms for the break-up of nonwovens and disintegration to single fibres in water were assumed as possible influencing factors: fibre-fibre friction, fibre-water friction in flowing or moving water, momentum transfer from water to fibres (collisions between water and fibres), hydrogen bonding between cellulosic surfaces of fibres, level of entanglement of fibres and break of single fibres. These theoretically possible interactions and mechanisms may depend in one way or another on single fibre properties like fibre diameter (titre), shape of cross section, length, tensile strength, bending stiffness and surface structure as well as a surface gel effect.

Materials and Methods

VISCOSE FIBRES

Based on the theoretical assumptions about break-up of nonwovens and dispersion of fibres, viscose fibres with varying parameters were selected: Titre from 0.9 to 4.2 dtex, different shape of cross section (e.g. round, flat, trilobal), length from 12 to 40 mm, tensile strength from 9 to 21 cN/tex, corrugated or smooth surface and a surface gel effect.

SPUNLACING PROCESS PARAMETERS

The nonwoven webs were manufactured from the different types of viscose fibres via carding. Basis weight was adjusted to 50 g/m². The laydown of the nonwoven web was carried out with an aerodynamical process which delivered in most cases more or less an isotropic laydown (MD/CD-ratio ≈ 1).

The bonding of nonwovens was carried out solely via hydroentanglement with 3 waterjet beams. Hence to achieve a hydroentanglement from both sides of the nonwoven two passages were necessary. In a typical 1st passage pressures of 0.5/1.5/1.5 MPa were applied. For the 2nd passage the pressures were varied from 0/1.0/1.0 MPa up to 0/14/14 MPa.

FLUSH TUBE TEST

The dispersibility of the nonwovens was probed with a tube tester (Figure 2). The tube was partially filled with water and turned several times by 180° (max. 50 turns). The level of break-up of the nonwovens and dispersion of fibres was observed

Figure 2. *Tube Tester.*

To judge the dispersibility six criteria were defined (Figure 3):

(0) solid nonwoven
(1) break-up at edges
(2) 1 hole in the nonwoven
(3) formation of 2 or 3 pieces
(4) more than 3 pieces
(5) complete dispersion of fibres in water

NETHERLANDS PUMP TEST

Per run 60 nonwoven specimen were fed in into an operating sewer pump.

All subsequent test pieces were loaded with 10 second intervals.

During the run the level of rising power consumption was observed.

In this test the electric power consumption of the pump reflects the flushability of nonwovens. Blocking of the pump by nonwovens leads to increased power consumption.

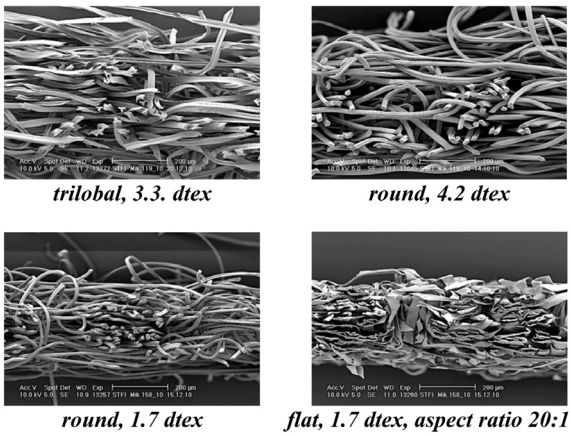
Results and Discussion

THICKNESS AND AIR PERMEABILTY OF SPUNLACED NONWOVENS

The structure of the nonwovens depended very much on the type of viscose fibre used (Figure 4).

(0) (1) (2) (3) (4) (5)

Figure 3. *Flush tube test, dispersibility criteria.*



trilobal, 3.3. dtex ***round, 4.2 dtex***

round, 1.7 dtex ***flat, 1.7 dtex, aspect ratio 20:1***

Figure 4. *SEM, stucture of spunlaced nonwovens.*

Fibres with large diameter (e.g. 4.2 dtex) delivered much bulkier nonwovens than finer fibres (e.g. 1.7 dtex). The shape of the fibre cross section also had a considerable influence on the thickness of the nonwovens (figures 4 and 5). The nonwoven thickness increased with trilobal fibers and was significantly reduced with very flat fibres (aspect ratio of cross section 20:1) compared to round fibres.

The air permeability of the nonwovens increased with rising fibre diameter due to the growing nonwoven bulkiness (Figure 5). However another important role plays the shape of the fibre cross section. The nonwovens with the largest bulkiness due to trilobal fibres did not have the highest air permeability, since the high total fibre surface increased the friction between flowing air and the fibres. Hence in terms of air permeability the effect of increased bulkiness due to trilobal fibres is counterbalanced by the effect of increased total fibre surface of trilobal fibres.

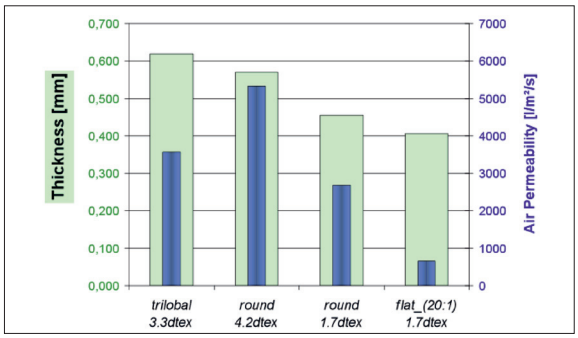


Figure 5. *Thickness (broad, pale colums) and air permeability of spunlaced nonwovens with different fibres.*

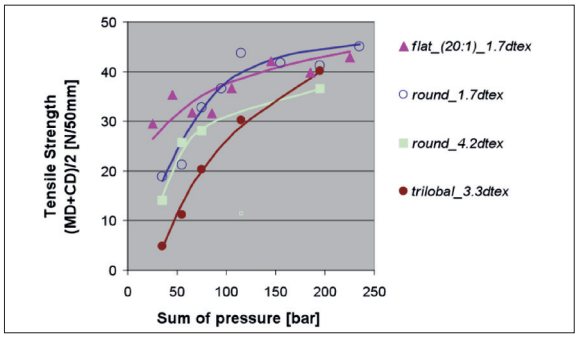


Figure 6. *Tensile strength of spunlaced nonwovens.*

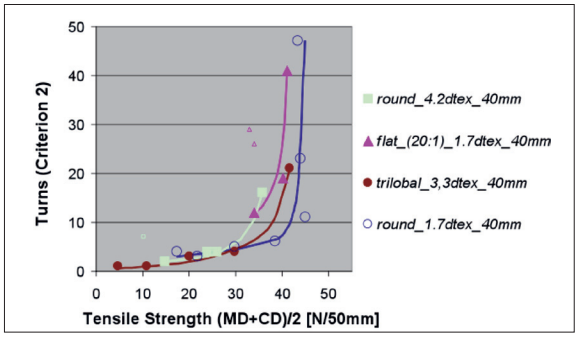


Figure 7. *Required turns for break-up (hole formation) of nonwoven with 40 mm fibre length in flush tube test.*

Nonwovens with very flat fibres (aspect ratio 20:1) delivered the lowest air permeability of all tested samples due to the low nonwoven bulkiness and in addition to the preferred orientation of the flat fibre surface in the plane of the nonwoven. The low bulkiness of these nonwoven is in line with an observed paper like touch.

TENSILE STRENGTH OF SPUNLACED NONWOVENS

The tensile strength depended very much on the pressure of hydroentanglement and of the shape of fibre cross section (Figure 6).

Fibres with flat cross section (aspect ratio 20:1) combined with a smooth surface as well as fibres with a surface gel effect delivered high tensile strength of nonwovens already at a low level of hydroentanglement pressure. At the same low pressure trilobal fibres showed the lowest tensile strength. Short cut fibres with a length of ≤ 20 mm required higher pressure than staple fibres (40 mm).

DISPERSIBILITY OF SPUNLACED NONWOVENS

Initial tendency of nonwovens to break up was similar for all types of tested staple fibres with 40 mm length (examples shown in Figure 7).

Weak fibres with incorporated particles and fibres with a surface gel effect did not improve the break-up of nonwovens and dispersion of fibres.

In general nonwovens with low tensile strength of the web are easier to break up. A further crucial factor is the fibre length. Nonwovens with standard staple fibre length (40 mm) formed ropes even after initial break-up into several pieces. A disintegration into single fibres was prevented.

Short fibres (≤ 20mm) were required to allow complete dispersion. The probability to achieve complete dispersion rised with decreasing fibre length. However to achieve a certain web strength in the tested range

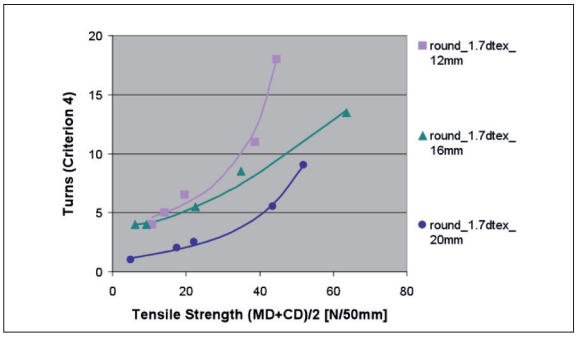


Figure 8. *Required turns for break-up (formation of > 3 pieces) of nonwoven with fibres of 12, 16 and 20 mm length.*

of short fibres (12 – 20 mm) the required pressure of hydroentanglement increased with decreasing fibre length. The essential higher pressure for web bonding made it more difficult to break up the web (Figure 8). Hence fibre length and hydroentanglement pressure had to be balanced to achieve sufficient web strength, easy break-up of web and complete dispersion of fibres. Therefore fibres should be as long as possible to allow low hydroentanglement pressure and fibres should be as short as necessary to avoid roping. However, figure 9 with data of nonwovens with 20 mm fibre length shows that other parameters than fibre length also played a role for the nonwoven break-up.

Nonwovens produced with round fibres and with a new type of fibre (patent in preparation) were easier to break-up than nonwovens produced with flat fibres and with a fibre having a surface gel effect.

SEWER PUMP TEST

A good correlation between results of the tube test and of the sewer pump test was observed. Nonwovens with short fibres showed less increase of power consumption than webs with staple fibres of standard length. Hence nonwovens with staple fibres of 40 mm length and high web strength failed in the sewer pump test (Figure 10). Webs with short fibres (12 – 20 mm) had the potential to pass the test, even at high web strength.

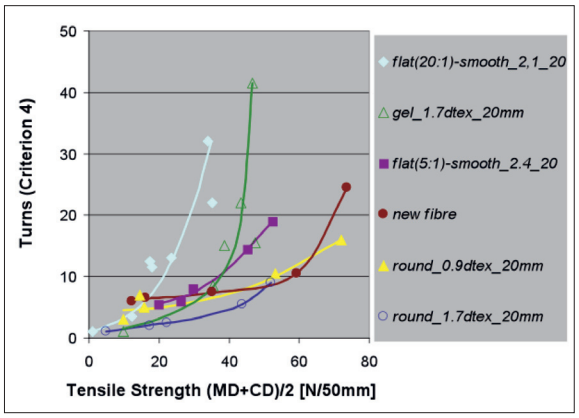


Figure 9. *Required turns for break-up (formation of > 3 pieces) of nonwoven with different types of fibres.*

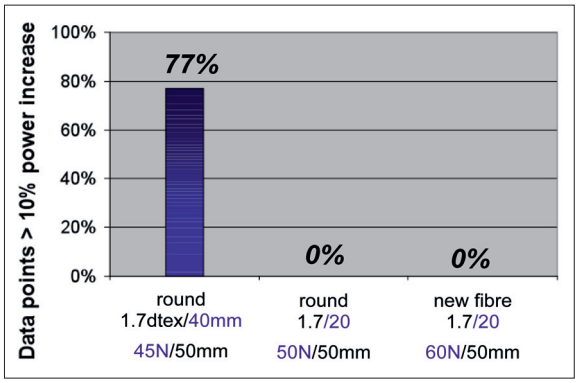


Figure 10. *Sewer pump test results of nonwovens with different fibre length [mm] and web strength [N/50mm].*

Conclusions

The structure and properties of nonwovens could be controlled by the use of different type of viscose fibres. In particular, the structure and air permeability of nonwovens depended very much on the diameter and shape of cross section of the fibres. For the break-up of nonwoven and the dispersion into single fibres in moving water the most crucial factors were the tensile strength of the nonwovens and the length of the fibres. Nonwovens with typical staple fibres could not be fully disintegrated into single fibres due to roping. In the range of shorter fibres the fibre length and hydroentanglement pressure had to be balanced to achieve sufficient web strength, easy break-up of web and complete dispersion of fibres. Results of tube tests gave a good indication about the potential of nonwovens to pass the Netherlands Sewer Pump Test. Nonwovens which broke up easy and dispersed completely in the tube test were also easily transported through the sewer pump with little increase of power consumption.

Acknowledgements

We would like to thank the German Federal Ministry of Economics and Technology (BMWi) for funding the investigations.

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Effects of pre-treatment and dissolution conditions for improved solution and processing properties of cellulose in ionic liquids

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Abstract

Different ionic liquids are suited for dissolution and processing of cellulose. Depending on the chemical constitution of the used ionic liquid the applied pre-treatment and dissolution conditions are of special importance for an optimal processing. The paper discusses investigations about the influence of pre-treatment steps such as preswelling, basicity adjustment or an addition of stabilizers on the dissolution and shaping of cellulose using imidazolium based ionic liquids, also from the perspective of a solvent recycling. Ionic liquids with chloride, acetate and diethylphosphate anions are considered, and the effects of the pre-treatment steps are discussed by means of rheological properties of the cellulose solutions as well as textile-physical properties and molecular mass distributions of the prepared fibres.

Keywords: *cellulose degradation, dissolution conditions, ionic liquid, pre-treatment, solution state.*

Introduction

Ionic liquids, which are classified as salts with melting points below 100°C [1], attracted in the last decade to widely used solvents in cellulose chemistry. After the first report from Graenacher [2] in the year 1934 about the dissolution of cellulose in benzylpyridinium and allylpyridinium chloride it was a long time period of calm concerning the ionic liquids in cellulose chemistry. Up to the year 2002, where Swatlosky [3] et al. describe the dissolution of cellulose in imidazolium based ionic liquids. Today, considering the growing ionic liquid family, especially ionic liquids with ammonium, pyridinium and imidazolium cations are known to dissolve cellulose.[4] The anions may include for example chloride, formate, acetate, diethyl phosphate and methyl phosphate. Pinkert et al.[5] give here a good overview. Particularly the homogeneous chemical modification of cellulose to various cellulose ethers or esters [6-8] and the shaping of cellulose to fibres [9, 10] and films [11] is of a special interest. In general, the imidazolium based ionic liquids, in particular the butyl-methyl-imidazolium chloride was classified as a non-derivatizing solvent.[12-14] Further analytical investigation has shown that side reactions with the cellulose carbonyl groups, e.g. reducing end groups [11] and degradation processes of the solvent while the dissolution process are possible.[15]In addition, for example the homogeneous etherification and esterification in imidazolium acetates with the corresponding chlorides and anhydrides yields mixed or pure cellulose acetate samples, which is based on the in situ formed acetic acid esters or mixed anhydrides. So it can be pointed out that in this case the acetates may not solely act as pure solvents.[16, 17]

Due to their good dissolution power ionic liquids gain a remarkable interest for dissolution and subsequent shaping cellulose into fibres.[9, 10, 18, 19] Compared

to cellulose solutions in NMMO monohydrate cellulose/ionic liquid solutions have a better thermal stability and it appears that they have no potential for thermal runaway reactions. The processing conditions and handling of the dopes are quite similar to the Lyocell process using NMMO. Especially the NMMO process has emerged to be an efficient tool in order to design functional textile fibres and fabrics for special applications.[20-22] This option is available with ionic liquids, too. Furthermore, thermal irregularities start later than in comparable NMMO solutions when functional additives are admixed in cellulose solutions, which was shown on silver-nanoparticles and activated charcoal containing solutions.[23] Finally, higher cellulose concentrations are possible for example while using the imidazolium acetates and higher fibre tensile strengths might be realize e.g. when butylmethyl imidazolium chloride is used instead of NMMO.[9] Therefore, ionic liquids are predestined to open up new ways in the manufacturing of functionalised textiles.

In both cases, the homogeneous chemical modification and the manufacturing of cellulose fibres and membranes, in general, the obtained products and the processing conditions are depending on the used process liquid and different polymer properties. Beside pulp characteristics especially pre-treatment conditions, such as cellulose pre-swelling, the basicity adjustment or the addition of stabilizers, may impact the solution state of the polymer, the change of the molecular weight as well as molecular weight distribution of the cellulose and the resulting fibre properties, respectively.

In this context we would like to report the influence of the different pre-treatment conditions for fibres shaping using typical Lyocell pulp and imidazolium based ionic liquids. Textile-physical fibres parameters as well as the molecular mass distribution of the cellulose are additionally discussed to the rheological properties of the solutions.

Experimental

MATERIALS

The investigations were carried out using dissolving eucalyptus pulp (S-517). The determined analytical data of the pulp are listed in the discussion of the results.

Ionic liquids – 1-n-butyl-3-methylimidazolium chloride (BMIMCl), 1-ethyl-3-methylimidazolium acetate (EMIMAc) and 1- ethyl-3-methylimidazolium diethylphosphate (EMIMDEP), manufactured by BASF and Iolitec respectively, were partly used in analytical grade and partly in technical grade (purity ≥ 95%). All the solvents were used without any further pre-treatment.

All other chemicals used were obtained in analytical grade (respectively HPLC-grade for SEC measurements) and used without any further pre-treatment.

PREPARATION OF CELLULOSE SOLUTIONS

The preparation of cellulose solutions was carried out using a special vertical kneader system, linked with a RHEOCORD 9000 (HAAKE). Temperature, torque moment and revolutions per minute (rpm) vs. reaction time were determined on-line.

Before being applied in the dissolution process the cellulose was disintegrated by means of an Ultra-Turrax shearing tool using water as dispersing medium. Excess water was separated from the cellulose pulp and the pulp was afterwards transferred in an aqueous solution of the ionic liquid. The ratio between water and ionic liquid in this suspension was selected by 1:1 for adjustment of a definite basicity and a dosage of stabilizers. The obtained persistent pulp suspension was poured into the kneading chamber.

The excess water was removed at temperatures between 90 and 120°C, at reduced pressure down to 5 mbar and shearing rates between 5 and 50 rpm. The starting dissolution process becomes visible in a strong increasing of the torque moment. The resulting viscous gel was homogenised within a so-called “after-dissolution” time of one hour at 120°C, a constant torque rate of about 10 rpm and constantly reduced pressure.

SPINNING TRIALS

Spinning trials were carried out by dry-wet spinning experiments for preparation of staple fibres of about 1.7 dtex fineness using a laboratory spinning equipment, which is described in former publication.[9]

Spinning nozzles, containing 30 capillaries with holes diameters of 100 μm were used for all spinning experiments. The spinning temperatures were selected in each case according to the rheological properties of the used cellulose solution.

Methods

CELLULOSE CHARACTERISATION

The used pulp and regenerated cellulose samples from the dissolution and spinning tests were characterised by capillary viscosity for the determination of the average degree of polymerisation (DP_{Cuoxam}) and by size exclusion chromatography (SEC) for the investigation of the molecular mass distribution.

The DP_{Cuoxam} was determined by the cuoxam method using an internal institute standard. For this purpose the intrinsic viscosity in cuoxam $[\eta]_{Cuoxam}$ (ml/g) was detected by means of an automatic capillary viscometer measurement (SCHOTT AVS 360). The DP_{Cuoxam} was calculated according to the equation (1).

$$DP_{Cuoxam}=2 \cdot [\eta]_{Cuoxam} \quad (1)$$

SEC-MEASUREMENTS

Sample preparation: 2 g of a cellulose sample were swollen in water. The water was pressed up and exchanged three times, 15 min at 80°C in an ultrasonic bath against dimethylacetamide (DMAc, 50 ml). Then the samples were equilibrated at 4°C for about 16 h. 0.02 - 0.045 g (dry content) of the sample was weighted in a 20 ml volumetric flask and 2 ml of a solution of 8 wt-% LiCl in dimethylacetamide were added. The cellulose was allowed to dissolute over 7 days and then the flask was filled up to 20 ml with DMAc. The obtained clear solution was filtered through a 0.45 μm PTFE filter and injected on the chromatographic system.

The SEC analysis was performed with a triple detection size exclusion chromatography system (SEC, Viscotek, USA) consisting of an online two channel degasser, a high pressure pump, an auto sampler (all parts integrated in the GPCmax, Viscotek, USA), a 0.5 mm stainless steel in-line filter with a PTFE membrane, three serial connected PLGel mixed A (20μm) columns and pre-column from Agilent technologies, USA, a temperature controlled triple detector array (TDAmax 305, Viscotek, USA) with a differential refractometer at = 660 nm (RID 3580), a right angle (90°) light scattering detector (RALS) and a low angle (7°) light scattering detector (LALS) with a semiconductor laser diode at λ= 670 nm and a four capillary, differential Wheatstone bridge viscometer. The SEC conditions were as follows: a polystyrene standard (MW = 99209 g/mol, Mw/Mn = 1.01, $[\eta]$ = 0.477 dl/g, Polycal Standards™ for Triple Calibration, Viscotek) in DMAc with 0.8 wt-% LiCl at a flow rate of 0.7 ml/min and 80°C was used to normalize light scattering detector and a dn/dc of 0.148[1] was used for the Mw calculation. Data acquisition and processing were carried out by use of OmniSEC 4.1 software (Viscotek Corporation).

[1] personal report from Malvern Instruments GmbH

ANALYTICAL CHARACTERISATION OF CELLULOSE SOLUTIONS

An optical characterisation of cellulose solutions was carried out by means of polarisation microscopy (ZEISS Axiolab). The rheological measurements were realised as described below. The determination of the solids contents of the solutions was performed by means of weighing precipitated films, after exhaustive solvent extraction and drying.

RHEOLOGICAL CHARACTERISATION

The rheological characterisation of cellulose solutions was performed using a rheometer HAAKE MARS with cone / plate measuring system (4° angle geometry) and electrically heated cone & plate unit with active cone heater.

Zero shear viscosities were calculated from creep attempts in the rotation mode at shear stress of 90 Pa.

The determined cellulose solutions showed significant viscoelastic behaviour. A characterisation of the viscoelastic properties was realised in the oscillation mode. Oscillation tests were carried out as frequency sweeps (0.046 – 14.7 Hz, deformation: 0.07) at different temperatures. The WLF-transformation was used for calculation of master curves and relaxation spectra. This method permits an interpolation of the frequency / angular rate range over several decades and is an evaluated method for the determination of viscoelastic properties of polymer solutions. Details of the rheological dope characterisation had been described in former publications. [24-27]

FIBRE CHARACTERISATION

The textile-physical fibre parameters were determined according to the following methods:

- fineness according to DIN EN ISO 1973,
- tensile strength and elongation according to DIN EN ISO 5079 and
- loop tenacity according to DIN 53843, part 2.

Results and Discussion

Solution states of cellulose in ionic liquids as well as the cellulose fibres properties obtained by dry-wet shaping of these solutions are affected by different parameters. Some effects of the used ionic liquids and pulps are already reconsidered in former publications [9, 28]. Here we would like to discuss different effects of pre-treatment conditions at solution preparation, such as pulp preparation, pulp suspension basicity and the influence of stabilizers.

DISSOLUTION AND SHAPING OF CELLULOSE USING THE IONIC LIQUID BMIMCL

Imidazolium based ionic liquids with chloride anions are some of the most intensively investigated solvents for cellulose. The majority of the published works describe the dissolution of cellulose in such solvents

using well dried cellulose and ionic liquids [3, 5] A degradation of the cellulose material was often established in these cases.[10] But a significant cellulose degradation, particularly with imidazolium based ionic liquids with chloride anions, can be avoid using certain processing parameters.[9, 30]

One useful opportunity for the cellulose solutions preparation in ionic liquids at technical relevant concentrations is the following procedure: a disintegration of the pulp sheets in an strong stirred aqueous dispersion, followed by suspending the wet pulp in an aqueous solution of the used ionic liquid and subsequently the dissolution step by removing the excess water, hereinafter referred to as "wet dissolution process". This approach was used to investigate the influence of the basicity of the starting suspension and of propyl gallate (PG) as stabilizer in solution state and on fibre properties when BMIMCl was used as dissolution medium. The preparation of cellulose solutions using a "dry dissolution process" was also tested for comparison.

Table 1 contains some analytical data of the prepared cellulose solutions using eucalyptus pulp S-517 (DP_{Cuoxam}: 517). The solids contents of the solutions are listed in column 1 ($c_{cellulose}$). The adjustment of a definite basicity had been realized by addition of aqueous sodium hydroxide to the pulp suspension in aqueous BMIMCl (water : BMIMCl = 1:1, w/w). This basicity adjustment was carried out by measuring of the pH-value (10.5, 9.5 and 8.0), knowing full well, that the definition of pH is restricted to diluted aqueous solutions, only. As stabilizer PG was used at an amount of 0.5 wt-%, referring to cellulose. A characterisation of the obtained cellulose dopes was performed directly after the solution preparation and after an additional step maintaining the temperature during 20 hours at 80°C, respectively. Such a tempering step precedes the used laboratory spinning process, i.e. the tempered samples are closer to the spinning samples. The last three right columns contain the DP_{Cuoxam} of reprecipitated cellulose directly after the solution preparation (DP_S), of the tempered samples or of the fibres (DP_F) and the percentage of DP-degradation of DP_F compared to the DP of the starting pulp (517).

As it can clearly be seen, a definite adjustment of the basicity is necessary to avoid a significant DP-degradation of the cellulose using the solvent BMIMCl.

In spite of PG-addition, the zero shear viscosities of fresh prepared solutions decrease from 21880 Pas at pH 10.5, to 19140 Pas at pH 9.5 and to 12860 Pas at pH 8.0, and the DP_{Cuoxam} of obtained fibres declines from 477 to 425. This corresponds to a DP-degradation of 7.7 to 17.8%. Added PG stabilises pulp solutions, particularly at lower pH, but nevertheless a small impact was detectable on the rheological parameters of tempered samples and on the obtained fibres characteristics, which should be discussed in the following chapter.

A definite adjustment of the pH value is impossible in the case of dry dissolution process without water removing. This led to cellulose dopes with significant reduced viscosity levels and a DP-degradation of 37.5% as listed in table 1. PG addition didn't give any

Table 1. *Analytical data of cellulose solutions in BMIMCl.*

$c_{cellulose}$ [wt-%]	Used conditions Dry or wet / pH / PG-Addition	η_0 (85°C) [Pas] After dissolution[4]	η_0 (85°C) [Pas] 20 h 80°C[5]	DP_S	DP_F	DP-Degradation [%]
12.1	Wet / 10.5 / 0.5% PG	21880	23180	484	477*	7.7
12.1	Wet / 10.5 / without PG	21610	17990	484	481*	7.0
12.2	Wet / 9.5 / 0.5% PG	19140	18550	470	461*	10.8
12.4	Wet / 8.0 / 0.5% PG	12860	11230	428	425*	17.8
12.2	Wet / 8.0 / without PG	3052	1057	351	337*	34.8
12.0	Dry / - / without PG [1]	1489	1171	335	323*	37.5
12.1	Dry / - / 0.5% PG [2]	817	693	298	283*	45.3
11.9	Dry / - / 0.5% PG [3]	8351	5820	464	454**	12.2

[1] Dissolution temperature 100°C, 3.5 h dissolution time

[2] Dissolution 3.5 h at 100°C + 2 h at 110°C + 1 h at 120°C

[3] Dissolution temperature 100°C, 3.5 h dissolution time, many undissolved pulp particles

[4] Solution characterisation after solution preparation, η_0 (85°C): zero shear viscosity at 85°C

[5] Solution characterisation after additional tempering step 20 h at 80°C

DP_S: DP_{Cuoxam} of precipitated cellulose after solution preparation

DP_F: DP_{Cuoxam} of the fibre* or of precipitated cellulose after additional tempering step 20 h at 80°C**

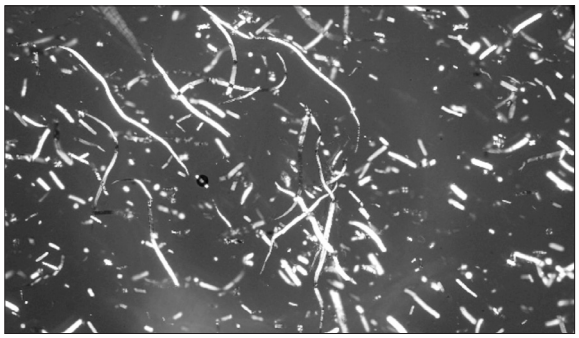

Figure 1. *Micro picture (bright field image, polarised light, 10x-objective) of a dry dissolved sample (11.9 wt-% S-517 in BMIMCl) with addition of 0.5% PG, 3.5h dissolution time at 100°C.*

stabilising effect in this case, which is in accordance with the results from Bentivoglio et al.[10] Compared to dry dissolution process without PG-addition the dissolution temperature and time have to be increased to achieve the same homogeneous dissolution state when PG was already added to the pulp suspension. As a result, the DP of the cellulose was decreased at 45.3%. Using comparable dissolution conditions with and without addition of PG (3.5 hours dissolution time at 100°C) the DP-degradation was lower (12.2%)

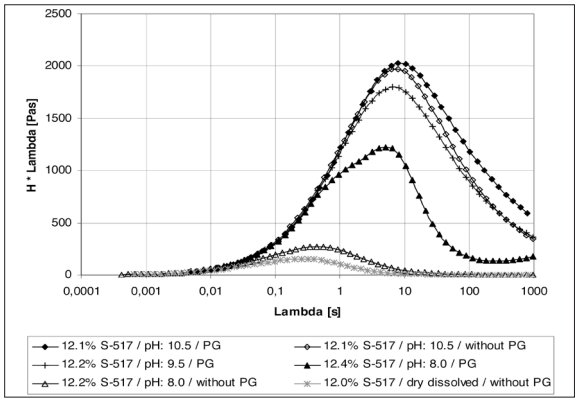

Figure 2. *Weighted relaxation time spectra of cellulose solutions in BMIMCl.*

in the case of the PG-stabilised sample, but the solution state was very incomplete und the micro picture of these sample shows many undissolved fibre residues (Figure 1).

Rheology and SEC were used to clarify the changes in

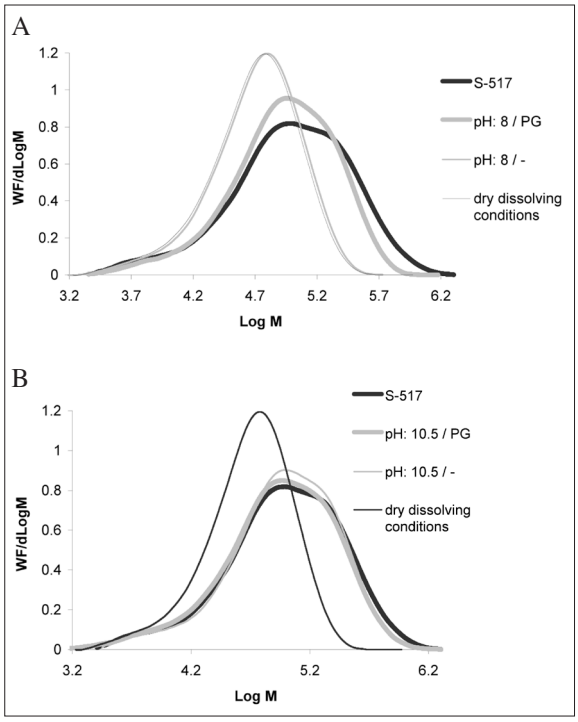

Figure 3. *Molecular mass distributions from SEC-measurements of pulp S-517 and prepared fibres using the solvent BMIMCl.*

the molecular mass distribution of the celluloses at different dissolution conditions. For the rheological characterisation of the prepared solutions tests at oscillation mode were used for the calculation of weighted relaxation time spectra at a reference temperature of 95°C (Figure 2).

These spectra of polymer solutions at comparable polymer content in the same solvent should be comparable with the molecular mass distributions of such polymer chains which are involved in the solution state. Figure 2 shows, that only small differences exist between the solutions at adjusted pH value of 10.5 (with and without PG) and of 9.5 (with PG), whereas the curve at pH 10.5 (with PG) may be indicative of increased longer-chain amounts. Significant differences are visible using pH 8 (with PG). The curve indicates a significant polymer degradation, which is strengthened using both pH 8 (without PG) and dry dissolving conditions. The significant decreasing peak heights are influenced by the strong changes in the rheologi-

Table 2. *Results from SEC-measurements of pulp S-517 and prepared fibres using the solvent BMIMCl.*

	S-517	pH 10,5 / PG	pH 10,5 / -	pH 8 / PG	pH 8 / -	Dry dissolving conditions
M_n (Daltons)	46,498	41,136	50,188	47,101	33,124	31,294
M_w (Daltons)	165,732	145,175	150,911	125,769	69,035	65,656
Mw / Mn	3.5	3.5	3.0	2. 7	2.1	2.1

cal properties of the solutions, especially the low viscosity levels.

SEC measurements which were used for the direct characterisation of the molecular mass distribution of the cellulose fibres, which are prepared from the discussed cellulose solutions, confirm these rheological evaluations. Figure 3 (A and B) contains the molecular mass distribution curves of the cellulose fibres and the starting pulp S-517, respectively. In Table 2 the M_w and M_n values are given. The results using dry dissolving conditions in Figure 3 and Table 2 are the results from the dissolution without PG.

The celluloses from the solutions at pH 10.5 with and without PG (B) show a similar but slightly decreasing of the longer-chain content compared to the starting raw material. Fibres, prepared from solutions at pH 8.0 containing added PG (A), indicate a noticeable shifting to some shorter chain length amounts. The fibres cellulose resulting from the shaping of solutions at pH 8.0 and without PG as well as using dry dissolution conditions (without PG) have molecular mass distributions which are significantly shifted to smaller molecular masses.

Remarkable effects indicate also a comparison of the textile-physical properties of the prepared fibres (Figure 4).

The dry-wet shaping of the cellulose/BMIMCl dopes into fibres at a fineness of 1.7 dtex was carried out at comparable spinning conditions and with an adaption of the spinning temperature regarding to the determined rheological properties of the spinning dopes. In general cellulose fibres with good properties were obtained. Tensile strengths in the conditioned state were between 49.5 and 59.5 cN/tex. In the wet state they lay between 45.2 and 54.5 cN/tex. The loop tenacities showed values between 13.1 and 21.5 cN/tex and the elongations were determined between 10 and 12%. The tensile strengths showed distinctive differences depending on the PG-addition. The fibres made from the solutions at pH 8 without PG and using dry dissolution conditions had comparatively good tensile strengths despite the low DP and corresponding molecular mass distribution, but decreased loop tenacities. The elongation values didn't show any dependence on the dissolution conditions.

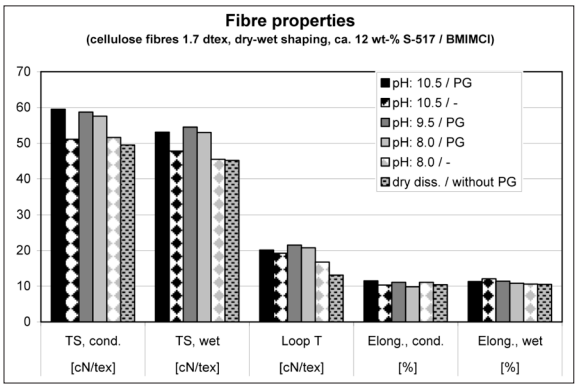

Figure 4. *Textile-physical properties of cellulose fibres from BMIMCl.*

TS, cond.: Tensile strength, conditioned state
TS, wet: Tensile strength, wet
Loop T: Loop tenacity, conditioned state
Elong., cond.: Elongation, conditioned state
Elong., wet: Elongation, wet

EMIMAC AS CELLULOSE PROCESSING MEDIUM

Because of the chemical composition of EMIMAc the adjustment of basicity of the starting pulp suspension

Table 3. *Analytical data of cellulose solutions in EMIMAc (pulp S-517).*

$c_{cellulose}$ [wt-%]	Used conditions pH / PG-Addition	η_0 (85°C) [Pas] After dissolution[1]	η_0 (85°C) [Pas] 20 h 80°C[2]	DP_S	DP_F	DP-Degradation [%]
21.3	pH: 8.0 / 0.5% PG	65920	44750	468	464*	10.3
21.2	pH: 8.0 / -	39410	17050	443	440*	14.9
21.4	rec. EMIMAc[3] pH: 8.0 / 0.5% PG	84130	67360	464	466*	9.9
21.2	rec. EMIMAc[3] pH: 8.0 / -	3207	2600	268	271**	47.6

[1] Solution characterisation after solution preparation, η_0 (85°C): zero shear viscosity at 85°C

[2] Solution characterisation after additional tempering step 20 h at 80°C

[3] Use of recycled EMIMAc from previous cellulose processing

DP_S: DP_{Cuoxam} of precipitated cellulose after solution preparation

DP_F: DP_{Cuoxam} of the fibres (*) or of precipitated cellulose after additional tempering step 20 h at 80°C (**)

in aqueous solvent was carried out only at pH: 8. An adjustment to higher pH values could lead to a significant decomposition of the EMIMAc itself during the cellulose processing. The addition of the stabilizer PG remarkably influences the solution states and in particular the cellulose dissolution using a recycled solvent (Table 3). Due to the high cellulose concentrations only the typical wet dissolution process was investigated.

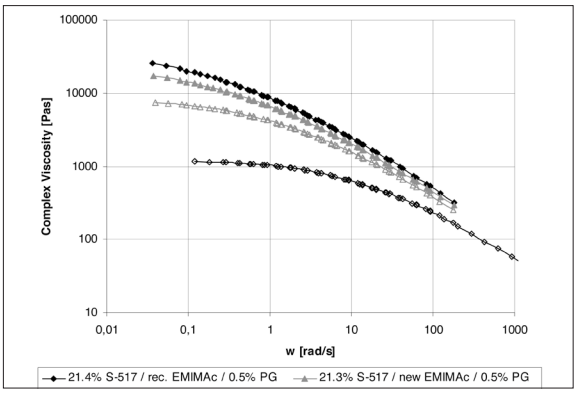

Figure 5. *Viscosity curves resulting from master curves (reference temperature: 95°C) of cellulose solutions (pulp S-517) in EMIMAc using new and recycled (rec.) solvent with and without PG-addition (0.5 wt-%, in relation to cellulose).*

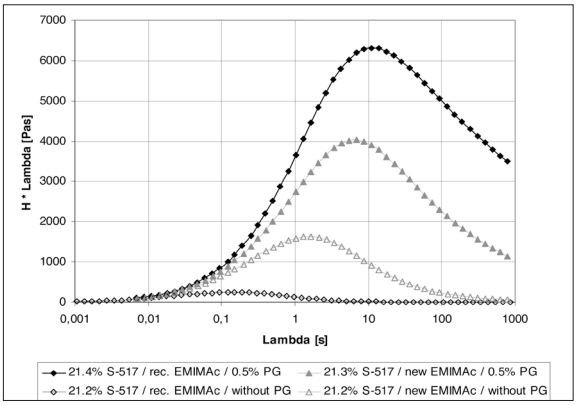

Figure 6. *Weighted relaxation time spectra, calculated from master curves (reference temperature: 95°C) of cellulose solutions (pulp S-517) in EMIMAc using new and recycled (rec.) solvent with and without PG-addition (0.5 wt-%, in relation to cellulose).*

The rheological characterisation of cellulose solutions in EMIMAc reveals significant differences of the solutions states compared to such in BMIMCl. The zero shear viscosities as well as the viscosity curves of the master curves from the oscillation tests decrease distinctively during the tempering step. The fact, that no significant further DP-degradation during the tempering step is visible, suggests polymer chain moving processes in the cellulose solution.

The addition of PG influences significantly the solution states of the cellulose solutions obtained. An addition of 0.5% PG, related to cellulose, decreases the DP-degradation of prepared fibres from 14.9% (without PG) to 10.3%. Additionally a significant influence on the rheological properties of the solutions has been observed.

The stabilizing effect of PG becomes more evident using already processed EMIMAc without additional cleaning. The preparation of cellulose solutions using such solvent without addition of PG resulted in a dramatic cellulose degradation of 48%, whereas the DP-degradation with addition of 0.5% PG was comparable to the sample using new solvent and PG-addition.

The rheological characterisation of the cellulose solutions suggests beside the decreasing DP also an influence of the PG-addition on the solution states. The viscosity curves of the cellulose solutions with PG-addition show a higher level compared with the cellulose solution using new EMIMAc without PG (Figure 5). A significant lower viscosity level was detected from the cellulose solution using recycled EMIMAc without PG. However, this was caused on a significant DP-degradation.

The weighted relaxation time spectra of the samples

Table 4. *Analytical data of cellulose solutions in EMIMDEP (pulp S-517).*

$c_{cellulose}$ [wt-%]	Used conditions pH / PG-Addition	η_0 (85°C) [Pas] After dissolution[1]	η_0 (85°C) [Pas] 20 h 80°C[2]	DP_S	DP_F	DP-Degradation [%]
12.1	pH: 10.5/ 0.5% PG	19810	19060	465	459	11.2
12.1	pH: 10.5/ -	14480	11430	473	473	8.5
12.4	pH: 8.0 / 0.5% PG	15240	13710	449	477	7.7
12.5	pH: 8.0 / -	12020	11210	468	454	12.2

[1] Solution characterisation after solution preparation, η_0 (85°C): zero shear viscosity at 85°C

[2] Solution characterisation after additional tempering step 20 h at 80°C

DP_S: DP_{Cuoxam} of precipitated cellulose after solution preparation

DP_F: DP_{Cuoxam} of the fibre

(Figure 6) point out a comparable gradation and suggest direct interactions of the PG with the cellulose solutions because of the significant higher curves peaks compared to the sample using new EMIMAc without PG.
Those samples, which showed strong polymer degradation in EMIMAc, were inappropriate for a comparable dry-wet shaping to fibres. The other samples showed no significant influence on the fibre properties of the producible cellulose fibres.

CELLULOSE PROCESSING WITH EMIMDEP

A considerably lower level of interferences by pH adjustment and PG-addition are observed using EMIMDEP as dissolution medium for cellulose. Some analytical data of such cellulose solutions are listed in Table 4.
The zero shear viscosities of the cellulose solutions showed marginally higher values both using higher pH values and at comparable pH values using PG-addition. A significant dependence of polymer degradation and the textile-physical properties of producible cellulose fibres on these dissolution conditions wasn't detectable.
The use of recycled solvents was also tested in the case of EMIMDEP. In contrast to EMIMAc no increased degradation of cellulose was observed using recycled EMIMDEP without PG-addition. This also applies for the use of recycled BMIMCl. The cellulose degradation is comparable using new and recycled BMIMCl at basicity adjustment (pH: 10.5) and without addition of the stabilizer PG.

Conclusions

Different ionic liquids are suited for dissolution and processing of cellulose. Depending on the used ionic liquid adapted pre-treatment and dissolution conditions had to be found for an optimal processing.
In the case of the usage of imidazolium based ionic liquids with chloride anions a definite adjustment of the basicity is essential to avoid a strong degradation of the cellulose. This might be attributed to the marginal elimination of the strong acid HCl (hydrochloric acid), which causes chain scission of the cellulose. In addition, the investigations showed a possible effect on the attainable tensile strength improvement of the prepared fibres using BMIMCl, when PG was added as a stabilisation agent.
A significant influence of PG on the solution states was determined on cellulose solutions in EMIMAc. On the one hand PG-addition affects the rheological properties of the cellulose solutions in EMIMAc, on the other hand PG can avoid strong degradation of the cellulose in particular by means of using recycled EMIMAc.
Comparably low effects of the tested pre-treatment and dissolution conditions were determined using EMIMDEP as cellulose processing medium.
The use of recycled ionic liquids, that means ionic liquids, which were already used several times for cellulose processing without any cleaning process, revealed significant differences depending on the used ionic liquid. The use of recycled EMIMAc caused a strong cellulose degradation which could avoid by addition of the PG as stabilizer, whereas in case of EMIMDEP and BMIMCl no changes in cellulose degradation could be detected using recycled solvents. Instead, the adjustment of pH value is essential in the case of BMIMCl.
To conclude, it was found that pre-treatment and dissolving conditions as well as aqueous pre-treatment and starting conditions, adjustment of the basicity or an addition of stabilising agents are decisive using ionic liquids for cellulose processing. In any case it is necessary to determine optimal conditions depending on the used ionic liquid, especially subject to the ionic liquid anion.

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Study about the efficiency of esterification of cellulose under homogeneous condition: dependence on the chain length and solvent

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Abstract

The homogeneous acylation of the cellulose dissolved in dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF×3H_2O) or *N,N*-dimethylacetamide (DMAc)/LiCl was studied. The dissolved cellulose was allowed to react with carboxylic acid anhydride and carboxylic acid activated *in situ* with *N,N'*-carbonyldiimidazole (CDI) under mild reaction condition and using 3 mol acylation agent per mol anhydroglucose unit. The products possess values of the degree of substitution (DS) between 0.45 and 2.27. The cellulose esters were characterized by means of NMR- and IR spectroscopy, as well as by GPC and solubility.

Keywords: *Esterification, Cellulose, In situ activation, DMSO/TBAF, Carboxylic acid/ CDI*

Introduction

Cellulose is the most abundant natural polymer on earth and a very important renewable resource. Cellulose derivatives have found applications in various fields such as pharmaceutics, cosmetics, food and packing [1-3]. Esterification and etherification are efficient methods to modify the properties of the polysaccharide. Cellulose esters are produced industrially under heterogeneous conditions, at least at the beginning of the conversion. However, homogeneous derivatization offers the enormous advantage of good accessibility of the hydroxyl groups. Thus, a better control of the degree of substitution (DS) and a uniform distribution of the functional groups along the polymer chain may occur. The most applied solvent in lab-scale cellulose esterification is *N,N*-dimethylacetamide (DMAc) combined with LiCl [4]. Recently, a mixture of dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF×3H_2O) was found to dissolve cellulose, and has been investigated for homogeneous derivatization of the biopolymer [5]. Chemical modification of wood pulp, microcrystalline cellulose, sisal based cellulose and cotton linters including acylation, carboxymethylation and benzylation has been successfully carried out [5-11].

The acylation of cellulose in DMAc/LiCl using acyl chlorides and acid anhydrides with short alkyl chain is conducive to a high degree of substitution [12-13]. The conversion of cellulose with carboxylic acids by *in-situ* activation under homogeneous condition is an efficient method of cellulose esterification. The activation of the carboxylic acid with *p*-toluenesulfonyl chloride [14-17], and 1,3-dicyclohexylcarbodiimide (DCC) in combination with 4-pyrrolidinopyridine (PP) is a typical example of this synthesis path [18-19], although the reagents or the side products formed during the esterification (e.g., *p*-toluenesulfonic acid) lead to degradation of polymer chains, and reagent toxicity must be taken into account. In contrast, the *in situ* activation of carboxylic acid with *N,N'*-carbonyldiimidazole (CDI) is a mild and efficient process [20].

Homogeneous esterification of cellulose with (4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride) and *N*-alkyl-2-halopyridinium salts as activating agents in DMSO/TBAF×3H_2O was also carried out [21]. Recently, cellulose acylation by activation of carboxylic acid with 1*H*-benzotriazole was reported; the acyl-1*H*-benzotriazole acts as acylation agent that could be synthesized according to Katrizky et al. [22-23]. The reaction using acyl-1*H*-benzotriazole as acylation agent proceeds completely under homogeneous and mild conditions in DMSO/TBAF×3H_2O [24].

Although many esterification methods have been successfully carried out in the solvent DMSO/TBAF×3H_2O, their efficiency has not been compared. Thus, the focus of this work was the study of the reactivity of cellulose dissolved in the DMSO/TBAF×3H_2O by applying different esterification agents. For this purpose, we compared the acylation using carboxylic acid anhydride, carboxylic acid activated with CDI and with the new agent acyl-1*H*-benzotriazole. Carboxylic acids with different molecular structures, i.e., different saturated and unsaturated/aromatic carboxylic acids were used. Activation of carboxylic acid with toluene-4-sulfonyl chloride and carboxylic acid chlorides was not included because DMSO reacts with the acid chloride in a kind of Pummerer rearrangement or according to the Swern oxidation forming various by-products [25]. Esterification of cellulose was also carried out in DMAc/LiCl to compare the acylation efficiency of the cellulose solvent. The cellulose esters were characterized by means of NMR- and IR spectroscopy, as well as by GPC and their solubility.

Experimental

MATERIALS

The cellulose Avicel® PH-101 (degree of polymerization, DP_n = 260 measured by GPC intetrahydrofuran after percarbanilation) was used as starting polymer. The cellulose, DMSO, TBAFx3H_2O, DMAc, LiCl, acid anhydrides, carboxylic acids, and CDI were supplied by Fluka and used as received.

MEASUREMENTS

^{1}H NMR spectra were measured with a Bruker AVANCE 400 spectrometer in $CDCl_3$ (50 mg/mL) at 60°C. The number of scans was 16. ^{13}C NMR spectra were acquired with a Bruker AVANCE 250 spectrometer, in $CDCl_3$ (80 mg/ml) at room temperature. The scan number was 1024.

The FTIR spectra were recorded on a BioRad FTS 25 spectrometer (ATR-technique) at room temperature. All spectra were recorded with 64 scans in the range of 4000 to 400 cm^{-1} and a resolution of 4 cm^{-1}.

For gel permeation chromatography (GPC), an Agilent1200 series instrument was used including degasser, isocratic pump and RI-detector. THF was applied as eluent (35°C, 1 mL/min). The separation was carried out using PSS SDV lin M (Polymer Standards Service, Mainz) columns packed with styrene divinylbenzene copolymer network. Polystyrene standards were applied for calibration.

SYNTHESIS

Dissolution of cellulose in dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF×3H_2O, solution S1)

Cellulose (1.0 g, 6.2 mmol, dried for 6 h at 110°C under vacuum and KOH) suspended in 60 ml DMSO and 6.6 g TBAF×3H_2O were stirred at room temperature for 30 min, yielding a clear cellulose solution.

Dissolution of cellulose in N,N-dimethylacetamide (DMAc)/LiCl (solution S2)

Cellulose (1.0 g, 6.2 mmol, dried for 6 h at 110°C under vacuum and KOH) and 40 mL DMAc were stirred for 2 h at 130°C. LiCl (3.0 g, dried at 150°C for 6 h under vacuum and KOH) was added and the slurry was allowed to cool to room temperature under stirring. After 24 h a clear cellulose solution was obtained.

Acylation of cellulose with carboxylic acid anhydride in DMSO/TBAF×3H_2O

For a typical conversion, acetic anhydride (1.75 mL, 3 mol/mol AGU) was added dropwise to the cellulose solution (**S1**) and allowed to react for 3 h at 60°C under stirring. The product was isolated by precipitation in 200 mL ethanol, washed three times with 100 mL ethanol, and finally dried under vacuum and KOH at 60°C, product **1**.

Yield: 1.03 g (79%)

DS = 1.18 determined by ^{1}H NMR spectroscopy after peracetylation.

FTIR (ATR): 3441 ν (OH), 2966, 2939, 2877 ν (CH), 1731 ν (C=O), 1460, 1254 ν (CH, CH_2), 1160, 1013 ν(COC) cm^{-1}.

The sample is soluble in DMSO, DMF, DMAc, pyridine, and NMP.

Esterification of cellulose with carboxylic acid activated with CDI in DMSO/TBAF×3H_2O

For a typical conversion, CDI (3.0 g, 3 mol/mol AGU) was dissolved in DMSO (20 mL), propionic acid (1.38 mL, 3 mol/mol AGU) was added and stirred for 1 h at room temperature, (until no gas formation was detected). This solution was added dropwise to the cellulose solution (**S1**) and allowed to react for 3 h at 60°C under stirring. The reaction mixture was precipitated in 200 mL ethanol, filtrated and washed three times with 100 mL ethanol. After drying under reduced pressure in the presence of KOH at 60°C, cellulose propionate (**11**) was obtained.

Yield: 1.65 g (94%)

DS = 2.20 Determined by ^{1}H NMR spectroscopy after peracetylation.

FTIR (ATR): 3435 ν (OH), 2915 ν (CH), 1725 ν (C=O), 1453, 1270 ν (CH, CH_2), 1112, 1024 ν (COC) cm^{-1}.

The sample is soluble in DMSO, DMF, DMAc, pyridine, NMP, and chloroform.

Acetylation of cellulose with carboxylic acid activated with CDI in DMAc/LiCl

CDI (3.0 g, 3 mol/mol AGU) was dissolved in DMAc (20 mL) under stirring at room temperature. Butyric acid (1.70 mL, 3 mol/mol AGU) was added dropwise and stirred for 1 h at room temperature, (until no gas formation was detected). The solution was added dropwise to the cellulose solution (**S1**) and allowed to react for 6 h at 100°C under stirring. The polymer was isolated by precipitation with 200 mL ethanol. The solid was filtered off, washed three times with ethanol and dried in vacuum over KOH at 60°C, product **22**.

Yield: 1.27 g (83%)

DS = 1.32 determined by ^{1}H NMR spectroscopy after perpropionylation.

FTIR (ATR): 3465 ν (OH), 2925 ν (CH), 1745 ν (C=O), 1437, 1374 ν (CH, CH_2), 1237, 1040 ν (COC) cm^{-1}.

The sample is soluble in DMSO, DMF, DMAc, pyridine, and NMP.

Peracylation of cellulose ester, typical example

To determine the DS of cellulose ester by means of ^{1}H NMR spectroscopy, peracylation of the remaining hydroxyl groups was carried out. Cellulose acetate (0.30 g, samples **1**, **10**, and **20**) was suspended in pyridine (7 mL) and propionic anhydride (7 mL) and 4-dimethylamino-pyridine (4-DMAP, 0.2 g) as catalyst was added. After 24 h at 80°C under stirring, the mixture was cooled to room temperature and precipitated in 200 mL ethanol. The product was isolated and washed three times with 100 mL ethanol and finally dried over KOH in vacuum at 60°C.

FTIR (ATR): no ν (OH), 1739 ν (CO_{ester}) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 5.2 – 3.4 (H_{AGU}), 2.5 – 2.2 (CH_2-propionate), 2.2 – 1.9 (CH_3-acetate), 1.3 – 1.0 (CH_3-propionate) ppm.

All other cellulose esters were synthesized comparably with acetic anhydride.

DS value of the cellulose esters were calculated from the ^{1}H NMR spectra according to the following equations:

For samples **1**, **10**, and **20**:

$$DS_{acetate} = \frac{7I_{acetyl}}{3I_{AGU}}, \quad (1)$$

where I_{acetyl} peak integral of methyl protons of acetyl at 2.2-1.9 ppm and I_{AGU} peak integral of protons of anhydroglucose unit at 5.2-3.5 ppm.

For samples **6** and **15**:

$$DS_{benzoate} = \frac{7I_{benzoyl}}{5I_{AGU}}, \quad (2)$$

where $I_{benzoyl}$ peak integral of benzoyl protons at 8.1-6.9 ppm and I_{AGU} peak integral of protons of anhydroglucose unit at 5.2-3.5 ppm.

All other samples:

$$DS_{ester} = \frac{7I_{methyl}}{3I_{AGU}} \quad (3)$$

where I_{methyl} peak integral of methyl protons at 1.0-0.9 ppm and I_{AGU} peak integral of protons of anhydroglucose unit at 5.2-3.5 ppm.

Percarbanilation of cellulose

About 0.3 g of cellulose was suspended in 20 ml DMSO and stirred for 4 h at room temperature. 5.0 ml phenyl isocyanate was carefully added and the reaction mixture was stirred for 18 h at 80°C. The solution was cooled to room temperature. Dry methanol was added to eliminate the excess of phenyl isocyanate. The product was precipitated into 200 ml ethanol, filtered off, washed three times with 100 ml ethanol and finally dried in vacuum over KOH at 60°C.

FTIR (ATR): 3410 (NH), no (OH), 1710 (CO_{ester}), 1413 (CH, CH_2), 1219 (COC) cm^{-1}.

Results and discussion

DMSO/TBAF×3H_2O dissolves cellulose without pre-treatment within a few minutes and has been successfully applied for homogeneous acylation. The first studies of esterification of cellulose in DMSO/TBAF×3H_2O were carried out using carbo-

Table 1. *Results of esterification of cellulose in dimethyl sulfoxide/tetrabutylammonium fluoride trihydrate at 60°C for 3 h applying a molar ratio of 3 mol acylation agent/ mol anhydroglucose unit.*

Reaction conditions	Products										
Acylation agent	No.	DS_{ester} [a]			DP_n [c]	Solubility [d,e]					
		Total	6	2,3		DMSO	DMF	DMAc	Pyridine	NMP	$CHCl_3$
Ethanoic anhydride	**1**	1.18	0.53	0.61	142	+	+	+	+	+	-
Propanoic anhydride	**2**	1.02	0.40	0.62	247	+	+	+	+	+	-
Butanoic anhydride	**3**	1.00	0.39	0.61	154	+	+	+	+	+	-
Pentanoic anyhdride	**4**	1.06	0.41	0.65	220	+	+	+	+	+	-
Hexanoic anhydride	**5**	1.12	0.46	0.66	157	+	+	+	+	+	-
Benzoic anhydride	**6**	0.45	n.d. [b]	n.d.	106	+	+	+	o	+	-
Tetradecanoic anhydride	**7**	1.59	0.60	0.99	74	-	-	-	-	-	-
Hexadecanoic anhydride	**8**	1.60	0.64	0.96	n.d.	-	-	-	-	-	-
Octadecanoic anhydride	**9**	1.94	n.d.	n.d.	60	-	-	-	-	-	-
Ethanoic acid imidazolide	**10**	2.25	0.95	1.30	156	+	+	+	+	+	+
Propanoic acid imidazolide	**11**	2.20	0.93	1.27	233	+	+	+	+	+	+
Butanoic acid imidazolide	**12**	2.09	0.92	1.17	84	+	+	+	+	+	-
Pentanoic acid imidazolide	**13**	2.25	0.97	1.28	95	-	+	+	+	-	+
Hexanoic acid imidazolide	**14**	2.27	0.96	1.31	120	-	+	o	+	-	+
Benzoic acid imidazolide	**15**	1.26	n.d.	n.d.	111	+	-	-	o	-	-
Decanoic acid imidazolide	**16**	2.18	0.96	1.22	n.d.	-	-	-	-	-	o
Tetradecanoic acid imidazolide	**17**	2.00	0.80	1.20	49	-	-	-	-	-	-
Hexadecanoic acid imidazolide	**18**	2.23	0.98	1.25	n.d.	-	-	-	-	-	
Octadecanoic acid imidazolide	**19**	1.45	0.62	0.83	69	-	-	-	-	-	

a) Degree of substitution (DS) calculated from ^{1}H-NMR spectra
b) Not determined
c) DMSO = dimethyl sulfoxide, NMP = *N*-methylpyrrolidone, DMF = *N*,*N*-dimethylformide, DMAc = *N*,*N*-dimethylacetamide
d) Soluble (+), insoluble (-), swollen (o)

xylic acid vinyl esters as acylation agents. At a ratio of 2.3 equivalent acylation agent per anhydroglucose unit (AGU), DS values of 1.04 for cellulose acetate, 0.86 for cellulose butyrate, and 0.95 for cellulose benzoate were attained, with a reaction time of 70 h at 40°C. Cellulose laurate reached a higher DS of 1.47 [5]. This result shows that the obtained DS values are dependent from the chain length of the carboxylic acid.

Esterification in the solvent DMSO/TBAF×3H_2O

Starting from the above mentioned results, a solution containing 9.1% (w/w) TBAF×3H_2O in DMSO with 1.4% (w/w) cellulose was allowed to react with different acylation agents; carboxylic acid anhydride and carboxylic acid activated with CDI. To study the efficiency and the selectivity between the acylation agents, a molar ratio of 3 mol reagent per mol AGU was used and the conversion was carried out at 60°C

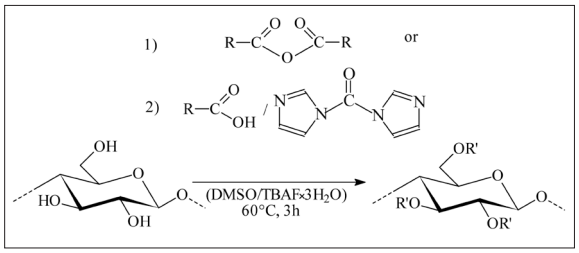

Figure 1. *Reaction scheme for the cellulose acylation in DMSO/TBAF×3H$_2$O applying carboxylic anhydride or carboxylic acid activated with N,N'-carbonyldiimidazole.*

for 3 h (Figure 1). Reaction conditions for and results of the cellulose esterification are summarized in Table 1. The FTIR spectra of the samples show the decrease of hydroxyl group absorption at about 3300 cm^{-1} and a signal at about 1725 cm^{-1} (C=O$_{ester}$) indicating the presence of the ester.

Peracylation of the cellulose esters provides products soluble in $CDCl_3$ that could be characterized by means of ^{1}H NMR spectroscopy. Figure 2 shows representative ^{1}H NMR spectra (range from 5.5 – 0.5 ppm) of peracylated cellulose valerate (sample **4** with DS 1.06 and sample **13** with DS 2.25). The peaks were assigned according to the results published in references [5] and [26].

The ^{1}H NMR spectrum for peracetylated cellulose valerate shows the signal for the protons of the AGU at δ = 5.2 -3.5 ppm. The CH_2 groups of position 8 (see Fig. 2) of the valerate chain at position 6 appeared at δ = 2.4 ppm, and for position 2,3 are found at δ = 2.3 ppm. The signal at δ = 2.1 ppm is assigned to acetate methyl groups for position 6, and the signal at δ = 2.0 – 1.9 ppm belongs to acetate methyl groups at positions 2 and 3. The signals of the CH_2 moiety of the alkyl chain are located between δ = 1.7 and 1.2 ppm and the methyl groups of valerate substituent are shifted to δ = 0.9 ppm. By comparing both spectra, it can be observed that sample 13 possesses an almost complete derivatization with valerate moieties at position 6 due the lack of the signal at δ = 2.1 ppm.

The cellulose dissolved in DMSO/TBAF×3H$_2$O was treated with carboxylic acid anhydrides (acetic, propionic, butyric, valeric, caproic, benzoic, myristic, palmitic and stearic, respectively). With increasing akyl chain length from C_2 to C_6, DS value between 1.00 and 1.18 was reached, i.e. the DS is almost equal. Under the same reaction condition Ass et al. obtained cellulose acetate with a DS of 0.90 [8], which is comparable to the results of the present studies (DS of cellulose acetate **1**, 1.18). For higher fatty acid esters of cellulose, the DS values increase remarkably to about 1.6 (cellulose myristate, C_{14}, **7** and cellulose palmitate, C_{16}, **8**) and to 1.94 for cellulose stearate (C_{18}, **9**). Ciacco et al. explained these findings as being due the long hydrocarbon chain which disturbs the intermolecular hydrogen bonds in solution, leading to dissociation of the chains, and therefore increasing the accessibility of the polymer backbone [6]. Similar results were obtained by esterification of cellulose with acyl-1*H*-benzotriazole reagent [24]. Applying three equivalents of acyl-1*H*-benzotriazole for 3 h at 60°C, it was found that by increasing the alkyl chain from C_1 to C_{13}, DS values between 0.79 and 1.07 were achieved. For long chain carboxylic acids like stearic, a much higher DS of 1.86 was found.

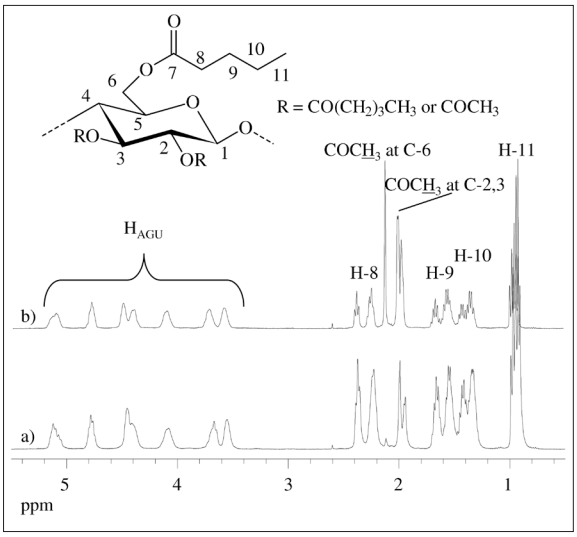

Figure 2. *^{1}H NMR spectra (range between 5.5 and 0.5 ppm) of peracetylated cellulose valerate sample a) **4**, degree of substitution (DS) 1.06, b) **13**, DS 2.25.*

The ^{1}H NMR analysis shows the preferred substitution of the primary OH groups (2.4 ppm) followed by secondary OH groups (2.3 ppm). The different reactivity between the hydroxyl groups can be explained by the lower hindrance of the primary OH at position 6.

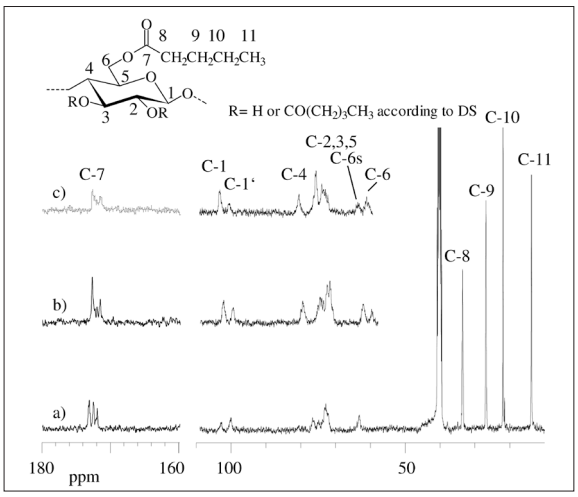

Figure 3. *^{13}C NMR spectra (range between 180 - 160 ppm, and 110 - 10 ppm) of cellulose valerate sample a) **13** with degree of substitution (DS) = 2.25, b) **23** with DS = 1.40, and c) **4** with DS' = 1.06.*

Table 2. *Results of esterification of cellulose in N,N-dimethylacetamide/LiCl at 100°C for 3 h applying a molar ratio of 3 mol carboxylic acid imidazolide/ mol anhydroglucose unit.*

Reaction conditions		Products									
Acylation agent	No.	DS_{ester} [a]			DP_n [b]	Solubility [c]					
		Total	6	2,3		DMSO	DMF	DMAc	Pyridine	NMP	$CHCl_3$
Ethanoic acid imidazolide	**20**	1.65	0.72	0.93	150	+	+	+	+	+	-
Propanoic acid imidazolide	**21**	1.38	0.70	0.68	224	+	+	+	+	+	-
Butanoic acid imidazolide	**22**	1.32	0.68	0.64	135	+	+	+	+	+	-
Pentanoic acid imidazolide	**23**	1.40	0.72	0.68	183	+	+	+	+	+	-
Hexanoic acid imidazolide	**24**	1.41	0.72	0.69	n.d. [d]	+	+	+	+	+	-
Decanoic acid imidazolide	**25**	1.22	0.63	0.59	n.d.	-	o	+	+	-	+
Tetradecanoic acid imidazolide	**26**	1.29	0.66	0.63	90	o	-	-	o	-	o
Hexadecanoic acid imidazolide	**27**	1.37	0.69	0.68	n.d.	-	-	-	-	-	-
Octadecanoic acid imidazolide	**28**	1.31	0.70	0.61	100	-	-	-	-	-	+

a) Degree of substitution (DS) calculated from ^{1}H-NMR spectra.
b) Degree of polymerization calculated from GPC data.
c) DMSO = dimethyl sulfoxide, NMP = *N*-methylpyrrolidone, DMF = *N,N*-dimethylformide, DMAc = *N,N*-dimethylacetamide, soluble (+), insoluble (-), swollen (o).
d) Not determined

A preferred reaction at the primary hydroxyl groups at position 6 appears, which is usually found as a result of homogeneous acylation of cellulose [1,2].

In a further series of experiments, cellulose dissolved in DMSO/TBAF×3H_2O was esterified using carboxylic acid activated *in situ* with *N,N*'-carbonyldiimidazole (CDI). The imidazolides of the carboxylic acids were obtained by conversion of the carboxylic acid with CDI in DMSO at room temperature (up to C_5 alkyl chain) or 80°C (for C_9 to C_{17} alkyl chain) for 1 h until no CO_2 formation could be detected. Subsequently, the carboxylic acid imidazolide in DMSO was added to the cellulose solution and the reaction proceeded for 3 h at 60°C. Cellulose acetate with a DS of 2.25 (sample **10**) was obtained that corresponds to remarkable reaction efficiency of 76%, indicating that the carboxylic acid imidazolide is a more effective esterification reagent for cellulose in DMSO/ TBAF×3H_2O compared to acid anhydrides. By increasing the reagent alkyl chain from C_1 to C_{17} only slight variation of DS values was observed. Cellulose esters with a DS range from 2.00 (sample **17**) to 2.27 (sample **14**) were obtained. Thus, this acylation path is very effective. An exception was found for cellulose stearate (sample **19**) with a lower DS value of 1.45 (by repeating the experiment a DS of 1.37 was obtained) and for cellulose benzoate (sample **15**) with a DS of 1.26.

Analysis of the regioselectivity of reaction of cellulose with the carboxylic acid imidazolides revealed that the reaction occurs faster at the primary hydroxyl groups (Table 1). In the case of cellulose palmitate (sample **18**), a complete functionalization of position 6 was found at a total DS of 2.23.

It is possible to obtain information about the distribution of the ester moieties between position 2 and 3 by means of ^{13}C-NMR. Figure 3 shows NMR spectra of cellulose valerate (samples **4**, **13**, and **23**). For sample **13** (DS 2.25, Figure 3c), the signals at δ = 68 to 78 ppm and at δ = 12 to 36 ppm result from the AGU-carbon atoms C-2, C-3, C-4 and C-5 and carbon resonances of the valerate ester chains, respectively. Three carbonyl resonances are found at 172 – 173 ppm. A peak for esterified position 6 appears at δ = 62 ppm ($C\text{-}6_s$). The absence of a signal at δ = 60 ppm indicates complete derivatization of position 6, within the detection limits of ^{13}C NMR spectroscopy, and confirms the findings of ^{1}H NMR spectroscopic studies (DS at position 6 was found to be 0.97). Two C-1 peaks are evident at δ = 102 (C-2 with OH) and 99 ppm, which

is due to the influence of the valeroyl substitution at the adjacent C-2. The C-4 signal appears at δ = 80 ppm and is influenced by derivatization at C-3 position, in this case the signal is shifted to about δ = 75 ppm. The C-4 signal at δ = 80 ppm is very weak, indicating an almost complete esterification of OH groups at C-3, which is a remarkable result. Usually the distribution of the introduced group of cellulose using homogeneous reaction conditions is O-6 > O-2 > O-3 (higher reactivity of the OH group at C-2 due to greater acidity, compared to C-3) [27], however here we find an nearly complete derivatization at O-3, whereas at position O-2 possesses about 1/3 partial substitution (total DS 2.25, DS_6 0.97, DS_3 about 1.0, then DS_2 about 0.30). Similar unexpected distribution was obtained by esterification of bacterial cellulose in the ionic liquid 1-*N*-butyl-3-methylimidazolium chloride [28].

GPC analysis of the peracetylated esters was applied to investigate hydrolytic degradation of the polymer chain during the reaction (Table 1). All derivatives were prepared with microcrystalline cellulose as starting polymer, having a degree of polymerisation (DP_n) of 260. The depolymerization of the polymer during the acylation procedure is moderate. DP_n values between 49 and 247 were found. Interesting is that, independent of the esterification agent, the DP_n values decrease with increasing the alkyl chain length. This effect could be explained by retardation of large branched molecules, showing artificial lower molar mass. The longer alkyl chain may penetrate into the column packing, and anchor the molecule [29].

ESTERIFICATION IN THE SOLVENT DMAC/LICL

The cellulose solvent DMAc/LiCl, first described by McCormick [4], is the most frequently used and widely exploited one for esterification of the biopolymer. Acylation in DMAc/LiCl with carboxylic acid imidazolides was carried out to compare efficiency with the newer solvent, DMSO/TBAF×$3H_2O$. Cellulose acetate with a DS value of 0.45 was obtained using 3 mol acetic anhydride /mol AGU or 3 mol acetic acid imidazolide/mol AGU at 60°C for 3 h. These results indicate that esterification in DMAc/LiCl needs harsher derivatization conditions, like higher reaction temperature such as 110°C (DS 1.9 [30]), or a longer reaction time such as 18 h (DS 1.9 [31]) to reach higher DS. In order to obtain cellulose esters with higher DS values, cellulose dissolved in DMAc/LiCl was allowed to react with three equivalents carboxylic acid activated with CDI (acetic, propionic, butyric, valeric, caproic, caprinic, myristic, palmitic and stearic, respectively) at 100°C for 3 h. The imidazolides of the carboxylic acid were prepared as described before. The results are summarized in Table 2.

As expected the cellulose ester shows the ester carbonyl absorption at 1725 cm^{-1} in the FTIR spectrum. A DS of 1.65 was found for cellulose acetate (sample **20**), while cellulose propionate possesses a lower DS of 1.38. By increasing the alkyl chain from C_2 to C_{17} little deviation of the DS was observed: values between 1.22 (sample **25**) and 1.41 (sample **24**) was obtained. A preferred acylation at the primary hydroxyl groups (DS_6 between 0.63 and 0.72) compared to the secondary hydroxyl groups ($DS_{2,3}$ between 0.59 and 0.93) occurs. The DP_n values of the cellulose esters synthesized in DMAc/LiCl are found between 135 and 224, showing comparable polymer degradation as for acylation in DMSO/TBAF×$3H_2O$.

SOLUBILITY

The solubility of the cellulose esters was tested in aprotic polar solvents such as DMSO, *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), pyridine, *N*-methylpyrrolidone (NMP), chloroform, and hexan (Table 1 and 2). The solubility of cellulose esters depends on their DS and the chain length of the carboxylic acid. Cellulose acetate, propionate, butyrate, valerate, and caproate with DS up to 1.65 are soluble in all solvents tested, with exception of $CHCl_3$. Cellulose palmitate and stearate with DS between 1.30 and 2.23 are insoluble in the tested solvents. The cellulose esters synthesized in this work are not soluble in nonpolar solvents such as hexane.

Conclusions

The influence of chain length and type of acylation agent on cellulose esterification in DMSO/TBAF×$3H_2O$ was studied. Applying 3 mol carboxylic acid anhydrides per mol AGU, products with DS values between 0.45 and 1.94 were obtained. Slight variation on the DS value was found for cellulose esters with alkyl chains from C_1 to C_5, while longer chain leads to higher values. Similar behaviour was found using carboxylic acid vinyl ester and acyl-1*H*-benzotriazole as acylation agents. The highest efficiency (70 to 76%) was reached with carboxylic acid imidazolides. Cellulose ester with alkyl chain between C_1 and C_{15} reached a range of DS from 2.09 to 2.27, after that the DS decreased to 1.45 for cellulose stearate. A preferred substitution of the primary OH groups followed by secondary OH groups was observed. The distribution of the ester groups of the products synthesized with carboxylic acid imidazolides is O-6 > O-3 > O-2. Esterification of cellulose in DMAc/LiCl with carbo-

xylic acid imidazolides requires harsher derivatization conditions (e.g. 100°C for 6 h). Cellulose esters with DS between 1.22 and 1.65 were obtained. Little influence of acyl chain length was observed.

Acknowledgements

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Recent Developments in Structure Design of 3-*O*-Ethers of Cellulose

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Abstract

Recent developments in the synthesis of 3-O-functionalized cellulose ethers are reviewed. It is demonstrated that advanced synthesis methods, in particular the application of silicon-based protecting groups, are important to get the regioselectively functionalized cellulose ethers of high structural uniformity. The 3-*O*-alkyl celluloses described possess a variety of properties like solubility in different organic solvents and in water, as well as tendency of aggregation in the dissolved state and presence of a lower critical solution temperature. Moreover, novel derivatives could be prepared thereof in subsequent reactions like oxidation and copper-catalyzed 1,3-dipolar cycloaddition reaction of azide- and alkyne compounds.

Keywords: *biopolymer, cellulose, hydrogen bonding, NMR, thermal properties*

Introduction

The repeating anhydroglucose unit (AGU) of cellulose bears 3 hydroxyl groups of different reactivity: one primary hydroxyl group at position 6 and two secondary ones at position 2 and 3 (Figure 1). A typical conversion of cellulose, e.g., the conversion with alkyl halides in the presence of aqueous alkali yields a product, where the ether moieties are randomly located at every hydroxyl group. Therefore, up to seven differently functionalized repeating units can be detected in cellulose derivatives. The number of different repeating units is further increased in case of hydroxyalkylations, because side chains may grow.

It is well known that the properties of cellulose derivatives are not only determined by the type of substituent and its degree of substitution. An important factor is also the functionalization pattern within the repeating unit and along the polymer chain.

Understanding the properties in relation to the functionalization pattern in details requires:

- synthesis of cellulose derivatives with well-defined structure
- detailed structure analysis
- evaluation of properties.

This information is very useful in particular for understanding the action of cellulose ethers in aqueous mixtures. Thus, exact knowledge of such structure-property-relationships is an important prerequisite to improve the performance of cellulose-based products. Numerous work has been done regarding the synthesis and characterization of 2,3-di-*O*-functionalized cellulose ethers and compounds derived thereof.[1-4] Cellulose derivatives functionalized at position 3 only are of particularly interest as the OH group of the lowest reactivity is functionalized with extraordinary high selectivity.

The structure of cellulose is strongly connected with a network of hydrogen bonds. Regioselective functionalization can be used to block hydrogen bonds in a selective way without disturbing the structure of cellulose remarkably. An example is the methylation of position 3. Thus, the hydrogen bond from position 3 to the ring oxygen of the adjacent AGU, which is

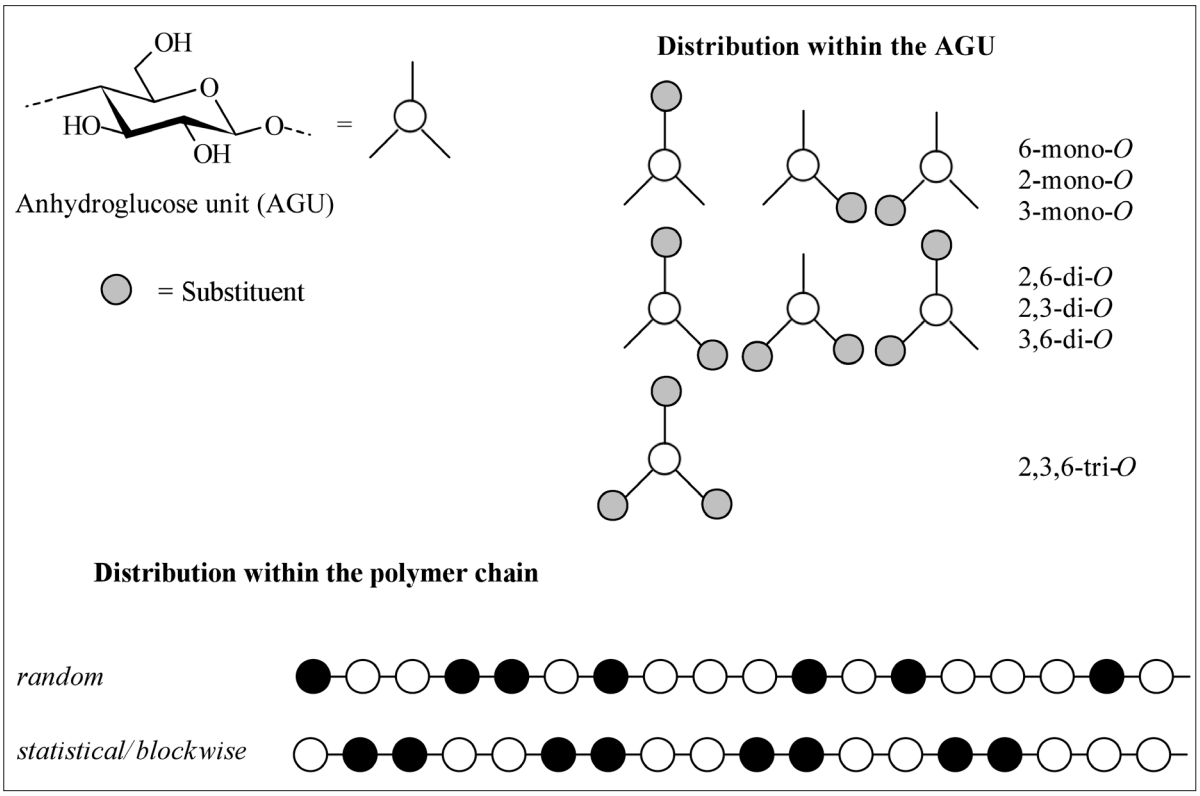

Figure 1. *Functionalization pattern of cellulose derivatives at the structural level of both anhydroglucose unit and polymer chain.*

known to influence the molecular stiffness of the polymer, can be selectively switched off.[5]

This paper reviews the synthesis pathways of 3-*O*-functionalized cellulose ethers adequately considering own research results. Information on structure analysis and structure-property-relationships will be given. Moreover, further modifications of 3-*O*-functionalized cellulose ethers will be described as well.

Precursors for 3-*O*-alkyl celluloses

The functionalization of position 3 of the AGU without affection of the other OH groups requires the temporary protection of position 2 and 6. In this case, typical demands for protecting groups are:

- high selectivity of introduction
- stability during subsequent functionalization
- easy selective deprotection with low affection of the polymer (degradation).

Silicon-based protecting groups meet these requirements very well. Appropriate reagents are the corresponding chlorosilanes. Trialkylchlorosilanes, e.g. trimethylchlorosilane, are known to react readily with cellulose.[6-9] However, they do not react with desired hydroxyl groups and may give fully functionalized silyl alkyl ethers. In order to turn them into selective reagents, it is necessary to replace at least one *n*-alkyl group by a bulky branched alkyl moiety, e.g., by tert.-butyl- and tert.-hexyl residues. Tert.-hexyldimethylchlorosilane (TDMSCl) and tert.-butyldimethylchlorosilane (TBDMSCl) are valuable reagents for the selective protection of OH groups in cellulose. The use of TDMSCl was described in most of the studies. The advantage of TDMSCl is that its regioselectivity can be controlled by the reaction conditions (Figure 2), i.e., two differently protected cellulose derivatives can be prepared using this reagent applying a heterogeneous and a homogeneous path, that is a peculiarity of polymer analogous reactions with cellulose.

The conversion of cellulose activated with liquid ammonia and *N*-methylpyrrolidone with TDMSCl leads to a 6-mono-*O*-TDMS cellulose.[10,11] The selectivity towards position 6 is superior compared with the for-

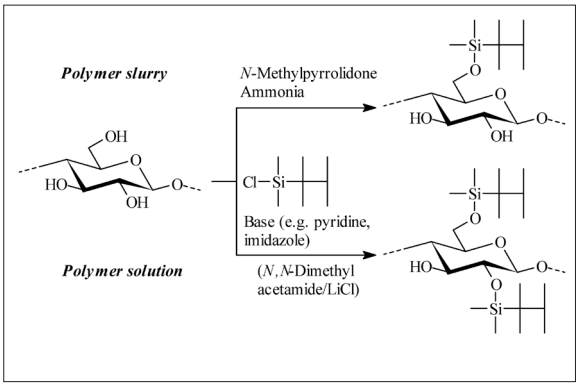

Figure 2. *Selectivity of thexyldimethylsilylation of cellulose in dependence on the reaction medium.*

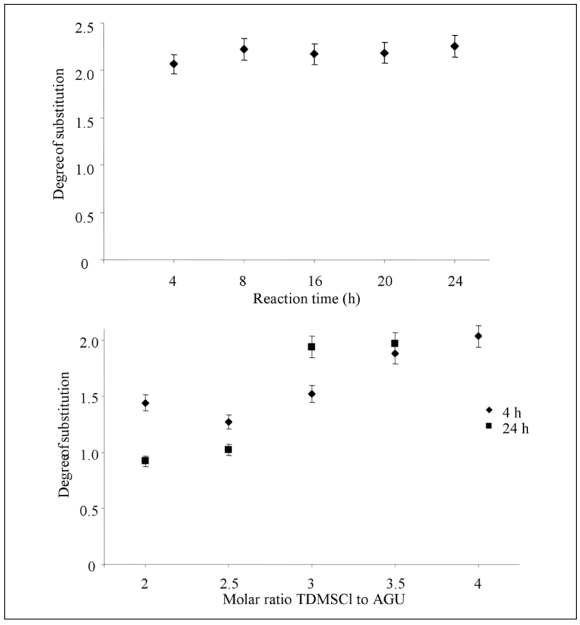

Figure 3. *Degree of substitution (DS) obtained by the conversion of cellulose dissolved in N,N-dimethyl acetamide/LiCl with thexyldimethylchlorosilane (TDMSCl) in the presence of imidazole. Dependency of the DS from the reaction time (top, molar ratio anhydroglucose unit, AGU:TDMSCl:imidazole 1:4:4.7) and from the molar ratio AGU:TDMSCl at 4 and 24 h reaction time (bottom, adapted from [14]).*

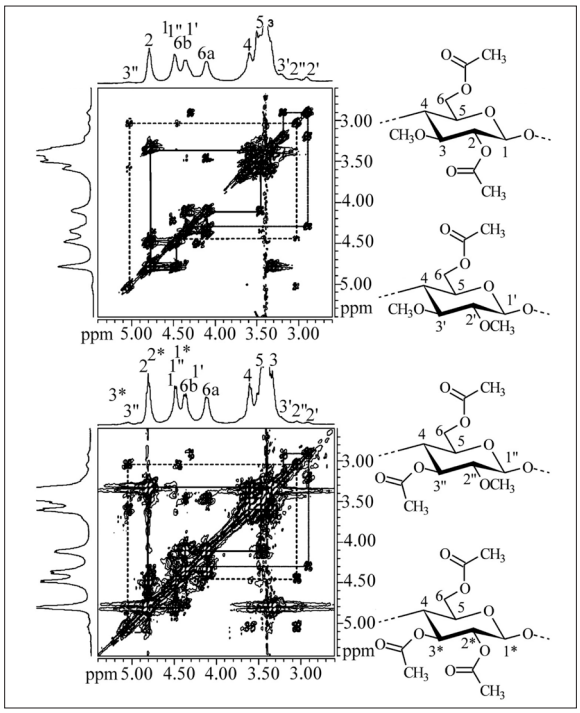

Figure 4. *^{1}H/^{1}H-COSY-NMR spectra of tert.-butyldimethylsilyl (TBDMS) celluloses synthesized at room temperature (top, degree of substitution of TBDMS groups, DS_{TBDMS} 1.98) and 100°C (bottom, DS_{TBDMS} 2.11) after methylation, desilylation, and acetylation. (adapted from [16]).*

mation of 6-O-triphenylmethyl ethers of cellulose.[12] On the contrary, treatment of cellulose dissolved in *N,N*-dimethyl acetamide (DMA)/LiCl with TDMSCl and pyridine as base affords TDMS cellulose, which is silylated not only at position 6 but also at position 2.[11]

A fully 2,6-di-*O*-silylated TDMS cellulose (degree of substitution, DS 2) was accessible by conversion of the dissolved cellulose with TDMSCl (molar ratio AGU:TDMSCl 1:4) in the presence of the efficient base imidazole for 24 h at 100°C.[13]
Microcrystalline cellulose is used as staring material in many studies due to their easy handling. However, the degree of polymerization is low and, hence, the products prepared from this starting material are hard to compare with commercially available derivatives. Fenn et al. investigated the 2,6-di-*O*-silylation of cotton linters with degree of polymerization 1433 in DMA/LiCl solution.[14] In order to ensure the formation of optically clear cellulose solutions, the cotton linters was mercerized prior to the dissolution process. It was found that the maximum DS was reached already after 4 h reaction time (Figure 3, top). The molar ratio of AGU:TDMSCl may be reduced from 1:4 to 1:3 provided the reaction is conducted for 24 h (Figure 3, bottom). NMR investigations of the polymer after methylation of position 3, desilylation and acetylation revealed the structural uniformity of the 2,6-di-*O*-TDMS cellulose.

Although the formation of TBDMS cellulose with DS 0.7 was described by Pawlowski et al. in 1987[15], this derivative did not receive much attention in regioselective cellulose chemistry during the past years. Klemm et al. reported the synthesis of TBDMS cellulose with DS 0.97.[8] In both cases, selective silylation of position 6 was described. Heinze et al. investigated the TBDM silylation of cellulose up to DS 2.[16] In contrast to the TDMS cellulose, those synthesis requires a temperature of 100°C, a reaction already at room temperature yields 2,6-di-*O*-TBDMS cellulose with DS 2. Detailed NMR investigations after methylation, desilylation, and acetylation revealed the structural uniformity of this polymer (Figure 4). Moreover, a conversion at a temperature of 100°C was found to be inappropriate because side reactions occur, i.e., a change in selectivity; 6-mono-*O*-TBDMS-, 3,6-di-*O*-TBDMS- and 2,3,6-tri-*O*-TBDMS moieties were detected.

3-*O*-Ethers of cellulose

The preparation of 3-mono-*O*-functionalized cellulose ethers follows the general scheme of 2,6-di-*O*-protection, 3-*O*-alkylation, and 2,6-di-*O*-deprotection.

Table 1. *3-O-Alkyl celluloses known up to now and their solubility.*

Table 1. 3-*O*-Alkyl celluloses known up to now and their solubility.

Alkyl	Starting material DP[a]	Solubility[b]					DP[c]	Reference
		Ethanol	DMSO	DMA	H_2O (<20°C)	H_2O (20°C)		
Methyl	MCC, 280	-	-	-	-	-	n. g.	[13]
Ethyl	MCC, 300	-	+	+	+	+	n. g.	[17]
Hydroxyethyl	CL, 1433	-	+	+	+	+	170	[18]
Methoxyethyl	SSP, 560	-	+	+	+	+	72	[19]
Methoxyethyl	MCC, 419	-	+	+	+	+	46	[19]
3'-Hydroxypropyl	MCC, 222	-	+	+	+	+	n. g.	[20]
Allyl	MCC, 280	-	+	+	-	-	n. g.	[13]
Propyl	n.g.	+	+	+	+	-	n. g.	[21]
Propargyl	MCC, 280	-	+	-	-	-	n. g.	[22]
Butyl	SSP, 590	+	+	+	-	-	n.g.	[23]
n-Pentyl	MCC, 280	+	+	+	-	-	16478	[24]
iso-Pentyl	MCC, 280	+	+	+	-	-	1309	[24]
Dodecyl	MCC, 280	-	-	-	-	-	200	[24]
Oligo(Ethylenglycol)	n.g.	-	-	-	-	-	n. g.	[25]

Alkylating agents are usually alkyl iodides, while alkyl bromides, -chlorides, and sulfonic acid esters are scarcely applied. Due to its high reactivity, sodium hydride is used as base under anhydrous conditions. Sodium hydroxide, which is much easier to handle, can not be used. Anhydrous conditions are hardly to achieve with this reagent and traces of water induce partial desilylation and, hence, loss of structural uniformity. Finally, the silyl ethers are cleaved off by treatment with tetrabutylammonium fluoride trihydrate. The 3-*O*-alkyl celluloses known up to now and the typical solubility are summarized in Table 1.

[a] Starting material: Microcrystalline cellulose (MCC), cotton linters (CL), sprice sulfite pulp (SPP), degree of polymerization (DP), not given (n. g.)

[b] Dimethyl sulfoxide (DMSO), *N,N*-dimethyl acetamide (DMA), soluble (+), insoluble (-)

[c] Degree of polymerization, not given (n. g.)

Their structures were confirmed by means of NMR spectroscopy (see Figure 5 for some examples). The synthesis of 3-mono-*O*-propargyl cellulose bears some challenges.[22] Although the proton of the triple bond is remarkably acidic, there is no hint of chain elongation by formation of C-C-bonds, i.e., pure 3-mono-*O*-propargyl cellulose was obtained. However, hydrogen bonds are present that hinder a detailed structure characterization by means of two-dimensional NMR techniques.

Table 1 shows that not only short chain ethers were prepared. Interestingly, Kadla et al. were able to synthesize 3-*O*-ethers bearing long-chain methoxypoly(ethylene glycol) ethers with 3-16 ethylene glycol moieties by conversion of 2,6-di-*O*-TDMS cellulose with methoxypoly(ethylene glycol) tosylates in the presence of imidazole.[26] Applying methoxypoly(ethylene glycol) iodide as alkylating agent in the presence of sodium hydride yielded products having a DS as high as 0.8.[25]

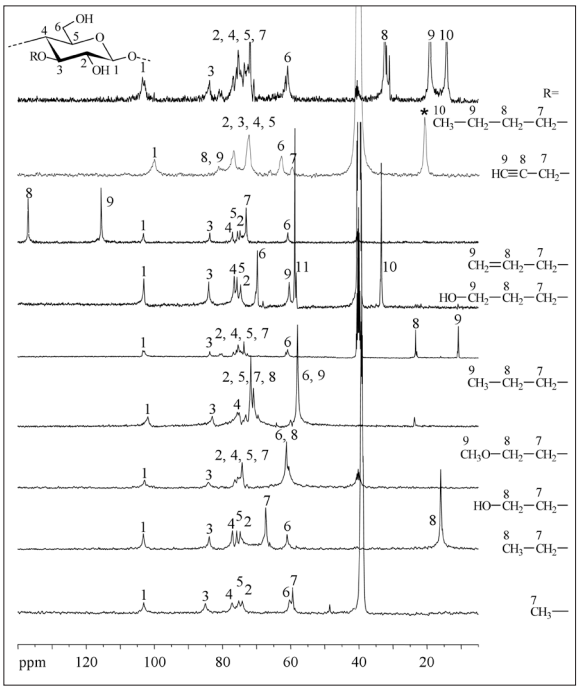

Figure 5. *^{13}C-NMR-spectra of selected 3-O-functionalized cellulose ethers (see Table 1). *This is the CH_3 group of acetate because the peracetylated sample was measured due to solubility reasons.*

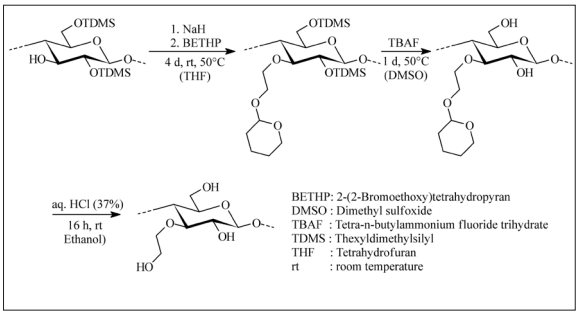

Figure 6. *Preparation of 3-mono-O-hydroxyethyl cellulose from 2,6-di-O-thexyldimethylsilyl cellulose via orthogonal protecting groups. (Adapted from [18]).*

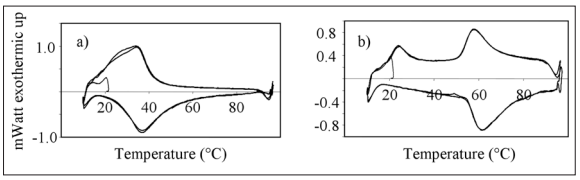

Figure 7. *Micro-DSC results for aqueous solutions (4%, w/w) of ethyl cellulose with random functionalization pattern (a) and 3-mono-O-ethyl cellulose (b).*

APPLICATION OF ORTHOGONAL PROTECTING GROUPS

The use of protecting group strategies enables the preparation of cellulose ethers, which are not accessible by conventional synthesis procedures. Hydroxyalkyl

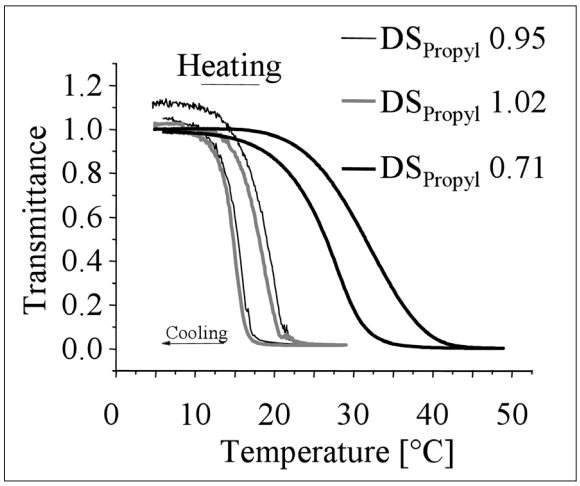

Figure 8. *Temperature dependent transmittance of aqueous 3-O-propyl cellulose solutions with varying degree of substitution of propyl groups (DS_{Propyl}).[21] With kind permission from Springer Science+Business Media: Polym. Bull. 2010, DOI 10.1007/s00289-010-0345-3, Copyright Springer-Verlag 2010.*

celluloses are prepared in technical scale by conversion of cellulose with alkylene oxides. As mentioned above, oxyalkylene side-chains are formed. In case of hydroxyethyl cellulose, neither ethylene oxide nor 2-bromoethanol will yield a uniform product. This could be avoided by using orthogonal protecting group approach (Figure 6).[18]

Thus, 2-bromoethanol was allowed to react with 3,4-dihydro-2*H*-pyran in the presence of *p*-toluene-

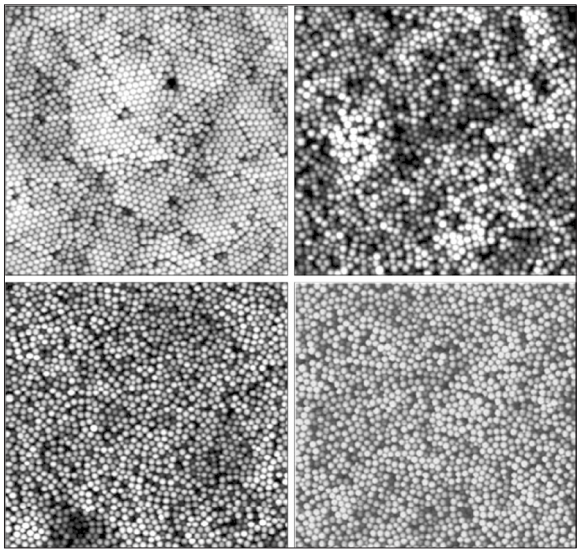

Figure 9. *Topographic AFM images of polystyrene latex particles (PSL, upper left), PSL coated with statistically functionalized ethyl cellulose (upper right), 3-mono-O-ethyl cellulose (lower left), and carboxymethyl cellulose (lower right, according to [33]). Image size is 10 µm× 10 µm (Reprinted from [32], Copyright (2008), with permission from Elsevier.)*

sulfonic acid as catalyst to yield 2-(2-bromethoxy)tetrahydropyran as the alkylating agent.[27] The order of deprotection of the alkylated 2,6-di-*O*-TDMS cellulose was found to be very crucial, i.e., the TDMS groups have to be removed first before acid treatment cleaves off the tetrahydropyran moieties.[18] Obviously, the comparably non-polar TDMS groups prevent the proton-induced hydrolysis.

The ether moiety regioselectively introduced at position 3 can be used as protecting group itself. Despite the stability of the alkyl ethers, the removal of allyl groups is comparably easy, e.g., by isomerization to the 1-propenyl ether followed by acidic cleavage[28] or by a palladium-catalyzed reaction.[29] This makes the allyl ether to a valuable protection group. Methylation of 3-mono-*O*-allyl cellulose and subsequent deallylation affords the corresponding 2,6-di-*O*-methyl cellulose[29], which is not accessible by other polymer analogous reactions.

This derivative was found to be insoluble in organic media and in water. Moreover, a high crystallinity was detected, which might prevent the polymer from being dissolved.

Properties of 3-*O*-alkyl celluloses

SOLUBILITY AND THERMAL BEHAVIOUR

The solubility of 3-*O*-alkyl celluloses strongly depends on the type of ether substituent. 3-mono-*O*-methyl cellulose was found to be insoluble in common organic solvents and water.[13] However, swelling in aprotic dipolar solvents was observed. Addition of LiCl afforded polymer solutions, which was explained with the breakage of hydrogen bonds. FTIR spectroscopy in combination with a line fitting method exhibited that instead of intramolecular hydrogen bonds between the hydroxyl group of position 3 and the ring oxygen of the adjacent AGU, another intramolecular hydrogen bond between the hydroxyl groups at position 2 and 6 may exist in 3-mono-*O*-methyl cellulose. The strong interchain bonds indicated by the absorption at 3340 cm^{-1} were also formed, causing crystallization with relatively high degree of crystallinity.[5]

Extension of the alkyl chain by one CH_2 moiety changes the solubility remarkably. 3-mono-*O*-Ethyl cellulose is soluble in aprotic-dipolar organic media without addition of LiCl. Moreover, this compound is soluble in water.[17] The impact of functionalization pattern on thermal behaviour was demonstrated by comparing the properties of 3-*O*-ethyl cellulose and randomly functionalized ethyl cellulose with similar

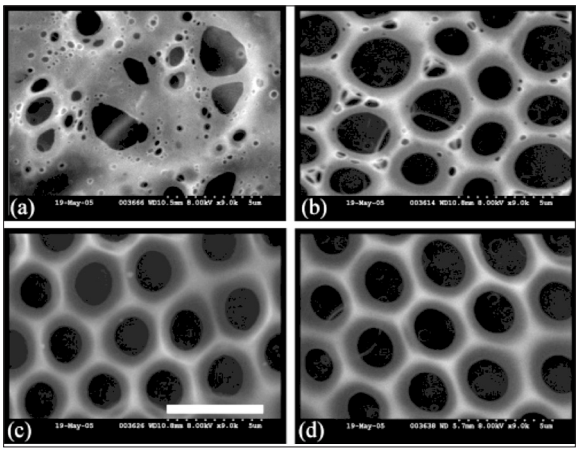

Figure 10. *SEM images of honeycomb films made from (a) 2,6-thexyldimethylsilyl (TDMS) cellulose, (b) 3-O-(methoxy poly(ethylene glycol),EG)$_3$-2,6-TDMS cellulose, (c) 3-EG$_7$-2,6-TDMS cellulose, and (d) 3-EG$_{16}$-2,6-TDMS cellulose. Scale bar 5 mm.[26] (Reprinted with permission from [26]. Copyright 2007 American Chemical Society).*

DS. While the randomly functionalized ethyl cellulose became insoluble at approximately 30°C, the cloud point temperature of the regioselectively functionalized product is at 60°C. This could be assessed by eye and was measured using the techniques of ^{1}H-NMR spectroscopy, oscillatory rheology, and micro-differential scanning calorimetry (Figure 7).[30] Several processes are thought to occur during association and gelation of these ethyl cellulose derivatives. These were separated with respect to temperature, to varying degrees, on cooling and have been modelled using DSC data. Contrasting with previous work[31], the rheological measurements do not show ‘‘two distinct waves of structure formation’’ at the present concentrations and the DSC measurements show, on cooling, an extremely wide separation in temperature of the processes for the 3-mono-*O*-ethyl cellulose.

3-mono-*O*-Propyl cellulose dissolves also in *N*,*N*-dimethyl formamide (DMF) and dimethyl sulfoxide

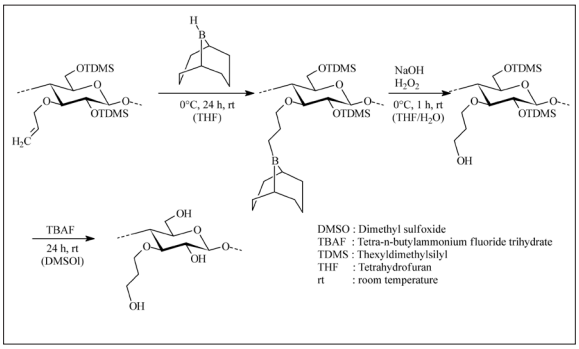

Figure 11. *Preparation of 3-mono-O-(3'-hydroxypropyl) cellulose by hydroboration/ oxidation of 3-mono-O-allyl cellulose.*

(DMSO). Solubility tests in water at room temperature revealed an insoluble polymer.[21] However, an almost clear solution was formed upon storage in a refrigerator. Temperature dependent turbidity measurements indicated cloud point temperatures between 15.2°C (DS 1.02) and 23.5°C (DS 0.71), that depend on the DS (Figure 8).

Randomly functionalized ethyl cellulose as well as 3-mono-*O*-ethyl cellulose did adsorb on polystyrene particles, which indicated a favorable interaction between ethyl cellulose and polystyrene latex particles, however, in a different manner depending on the structure of ethyl cellulose (Figure 9).[32] The conventionally synthesized ethyl cellulose with statistical functionalization pattern formed much stronger networks with polystyrene latex particles than 3-mono-*O*-ethyl cellulose did. The lower phase separation temperature and the slightly higher molecular weight of the conventional ethyl cellulose gave it higher preference for interacting with polystyrene latex particles to form network.

3-mono-*O*-Hydroxyethyl-[18], 3-mono-*O*-methoxyethyl-[19], and, 3-mono-*O*-(3'-hydroxypropyl) cellulose[20] were found to be water soluble as well. However, neither gelation nor flocculation of the aqueous solution at elevated temperatures could be observed.

Starting with 3-mono-*O*-allyl cellulose, the higher 3-*O*-alkyl celluloses loose their water solubility. However, the pentyl-, isopentyl-, and dodecyl ethers become soluble in less polar solvents like methanol and ethanol and even tetrahydrofuran (THF) in case of the dodecyl ether.[24] Light scattering measurements revealed a distinct aggregation behavior that depends on the type of substituent. The highest aggregation number of 182 was found for the 3-*O*-pentyl ether, while the 3-*O*-dodecyl ether does not show aggregation. Once the OH group at position 3 is blocked, the remaining OH groups will randomly form hydrogen bonds among different chains, until a particle with a surface of mainly alkyl chains is obtained. The monomolecular solubility of the 3-*O*-dodecyl ether demonstrates that such aggregation can be prevented if the side chain is long enough.

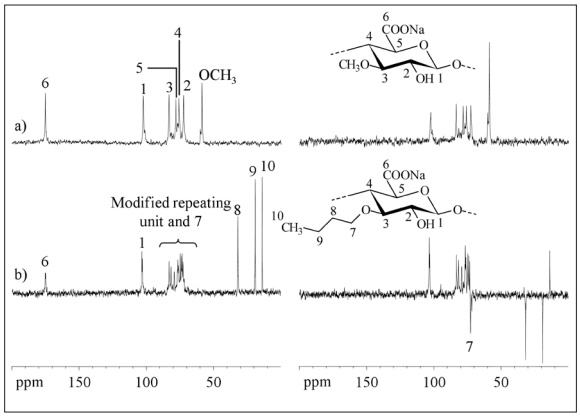

Figure 12. *^{13}C NMR- and DEPT135 NMR spectra of 3-mono-O-methyl-6-carboxy cellulose (a) and 3-O-butyl-6-carboxy cellulose (b) (Reprinted from [36], Copyright (2009), with permission from Elsevier).*

STRUCTURE FORMATION

Kadla et al. investigated the structure formation of films prepared from 2,6-di-*O*-TDMS cellulose and methoxypoly(ethylene glycol) ethers at position 3.[26] The films were cast from chloroform or toluene solution onto glass slides, dried in running air at a relative humidity of 70-80% and evaluated by microscopic techniques. It could be demonstrated that 2,3-di-*O*-TDMS cellulose did not form regular structures. The introduction of methoxypoly(ethylene glycol) ethers at position 3 led to the formation of regular honeycomb structures. While a short chain substituent (3 ethylene glycol moieties) led to irregular honeycombs, films of compounds with 7 and 16 ethylene glycol moieties were of very regular shape (Figure 10).

Subsequent reactions

OXIDATION

Oxidation of regioselectively functionalized cellulose ethers afforded novel derivatives. One possibility follows the hydroboration/oxidation scheme of alkenes yielding primary alcohols as demonstrated with a 2,6-di-*O*-TDMS-3-mono-O-allyl cellulose (Figure 11).[20] The TDMS-groups render the polymer THF soluble. The compound was allowed to react with 9-borabicyclo[3.3.1]nonane to yield the borane derivative and then the oxidative cleavage with a NaOH/H_2O_2 mixture yields the primary alcohol.

Subsequent treatment with TBAF afforded the 3-mo-

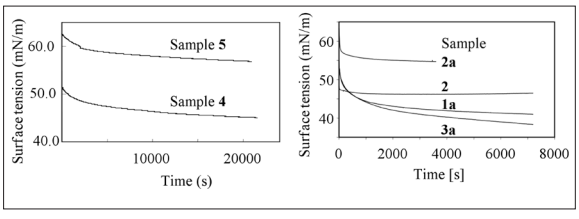

Figure 13. *Plot of surface tension of aqueous solutions (left, 1%, v/v) 3-mono-O-methoxyethyl cellulose* **4** *and 3-mono-O-methoxyethyl-6-carboxy cellulose* **5***[35] and (right, 0.5%, v/v) of 3-mono-O-methyl-6-carboxy cellulose (***1a***), 3-mono-O-ethyl cellulose (***2***), 3-mono-O-ethyl-6-carboxy cellulose (***2a***), and 3-O-butyl-6-carboxy cellulose (***3a***) versus measuring time (Reprinted from [36], Copyright (2009), with permission from Elsevier).*

no-*O*-(3'-hydroxypropyl) cellulose. This polymer is soluble in aprotic dipolar media (DMF, DMSO) and in water. In contrast to commercially available hydroxypropyl cellulose, a product functionalized at position 3 containing primary hydroxyl groups only was designed. The structure was clearly evidenced by spectroscopic techniques. Two-dimensional NMR spectroscopic measurements of the peracetylated sample indicate the presence of substructures, although to a low extent.

The oxidation of the primary OH group at position 6 of 3-*O*-alkyl cellulose yields 6-carboxy-3-*O*-alkyl cellulose. The 2,2,6,6-tetramethylpiperidine-1-oxyl radical-mediated oxidation is the best way to achieve this goal because it proceeds in aqueous medium under mild reaction conditions without the need of hazardous substances.[34] Yin et al. reported the oxidation of 3-mono-*O*-(2-methoxyethyl) cellulose in aqueous solution.[35] ^{13}C-NMR spectroscopic investigations revealed complete oxidation of position 6 of the repeating unit. The typical polyelectrolyte behaviour of the final product could be evidenced by capillary viscometry as well as by polyelectrolyte complex formation with cationic compounds. Interestingly, it became obvious that the introduction of carboxylate groups did not increase the surface activity of the polymer. The influence of the alkyl chain length located at position 3 on the polyelectrolyte behaviour of the oxidized products was studied.[36]

It could be demonstrated that in addition to water soluble 3-mono-*O*-ethyl cellulose also water insoluble cellulose ethers (3-mono-*O*-methyl- and 3-*O*-butyl cellulose) could be completely oxidized in aqueous medium. In that case, the heterogeneous mixture turned into a homogeneous one with increasing conversion. ^{13}C-NMR spectroscopic investigations revealed the absence of CH_2OH groups and, hence, a complete oxidation of position 6 (Figure 12). A certain depolymerization of approximately 30-50% related to the initial molar mass must be taken into account, which does not depend on the reaction scheme, i.e. starting homogeneously or heterogeneously. However, 3-mono-*O*-methoxyethyl cellulose seemed to form aggregates in aqueous solution because a significant increase of the molar mass after oxidation was found.[35] Obviously, the hydrophobic alkyl chains (methyl, ethyl, butyl) at position 3 of the derivatives discussed in[36] do not support the polymer aggregation.

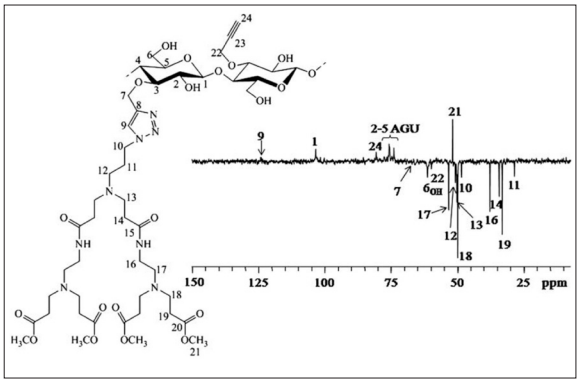

Figure 14. *DEPT135 NMR spectrum of second generation of 3-O-(4-methyl-1-N-propyl-polyamidoamine-[1,2,3-triazole]) cellulose of second generation, recorded in dimethyl sulfoxide-d_6 at 60°C.[22] (Reprinted from [22], Copyright (2009), with permission from Elsevier).*

Surface tension measurements of the aqueous solutions were used to evaluate the surface active properties of the oxidized derivatives (Figure 13). It became obvious that the longer alkyl chain the lower σ value was determined (3-mono-*O*-methyl-6-carboxy cellulose σ = 42.1 mN/m, 3-*O*-butyl-6-carboxy cellulose σ = 40.5 mN/m). Obviously, the butyl chain acts as hydrophobic part of the amphiphile formed after the oxidation, which is insufficiently achieved by the comparably small methyl ether. A comparison of the surface activity before and after oxidation of 3-mono-*O*-ethyl cellulose indicated that the introduction of carboxy moieties does not decrease the surface tension of the aqueous solution. While a σ value of 46.2 mN/m was determined for 3-mono-*O*-ethyl cellulose, 3-mono-*O*-ethyl-6-carboxy cellulose exhibits a σ value of 54.7 mN/m. The phenomena are comparable with results obtained with 3-mono-*O*-methoxyethyl cellulose (Figure 13).[35]

CLICK-REACTION OF 3-*O*-PROPARGYL CELLULOSE

The copper-catalyzed 1,3-dipolar cycloaddition reaction of alkynes and azides (Huisgen reaction, click-reaction)[37] is a valuable synthetic tool, which can also be applied in cellulose chemistry. The versatility of the click-reaction was demonstrated with 6-deoxy-6-azido cellulose dissolved in aprotic-dipolar media that was allowed to react with various alkynes yielding unconventional cellulose derivatives.[38]

Click-reactions with 6-azido-6-deoxy cellulose could also be carried out in ionic liquids as reaction medium. 1-Ethyl-3-methylimidazolium acetate dissolves 6-azido-6-deoxy cellulose with a DS of 0.75 very well as observed by optical microscopy and represents a suitable reaction medium for the homogenous conversion of the cellulose derivative with propargyl-polyamidoamine (PAMAM) dendrons via copper-catalyzed Huisgen reaction that was carried out for the first time.[39]

Not only 6-deoxy-6-azido cellulose could be applied as reactant in click-reactions. Cellulose *p*-toluenesulfonic acid esters could be converted with propargyl amine to 6-deoxy-6-aminopropargyl cellulose, which can react

with azides. Dendronized structures could be introduced by conversion with azido-functionalized dendrons.[40]
To attach dendrons at position 3 of the AGU, 3-mono-*O*-propargyl cellulose was allowed to react with azido-functionalized dendrons.[22] This derivative is readily soluble in DMSO and could undergo click-reaction with azido-propyl-PAMAM dendrons in the presence of $CuSO_4$ pentahydrate and sodium ascorbate as catalyst. In case of the 1st generation of the dendrons, 25% of the triple bonds were converted. The reactivity of the 2nd generation dendrons is less but even 13% of the triple bonds reacted with the azide. ^{13}C-NMR spectroscopy clearly proofed the proposed structure (Figure 14).
The polyamidoamine-dendronized cellulose derivatives obtained by conversion of 6-deoxy-6-azido cellulose with propargyl-PAMAM contain a high amount of accessible amino groups and are capable of forming monolayers on the surface of various substrates. Enzymes like glucose oxidase can be subsequently bound to the amino groups via glutaraldehyde as linker.[41]

The quality of enzyme coupling on the solid supports was determined by specific enzyme activity, reproducibility, coupling efficiency, and storage stability.
6-Deoxy-6-azido cellulose was rendered water-soluble by the introduction of anionic carboxymethyl groups. The solubility is not changed by the click-reaction with propargyl-PAMAM dendrons.[42] Viscometric techniques and analytical ultracentrifugation were employed to characterize the macromolecular properties of these derivatives. An important finding is that dendronization leads to an increase in sedimentation coefficient (with increasing dendritic generation), however, a decrease in intrinsic viscosity. It could be shown from sedimentation conformation zoning that the carboxymethyl deoxy-azido cellulose and the carboxymethyl 6-deoxy-(1-*N*-[1,2,3-triazolo]-4-polyamidoamine) cellulose derivatives possess a semi-flexible coil conformation. The values of persistence length obtained from combined analysis for these samples also indicate a semi-flexible coil conformation in solution. Thus, dendronization of carboxymethylated deoxy-azido cellulose has no or only a rather small influence on the chain stiffness and the conformation in solution.

Conclusions

The preparation of cellulose derivatives possessing well-defined structures is still a very challenging task. Derivatives resulting from the synthesis strategies, namely the regioselective functionalization via selectively protected cellulose derivatives and subsequent conversions, are valuable materials for the establishment of structure-property-relationships. The research discussed in this review article clearly indicates the importance of regiochemistry on cellulose. It was demonstrated that the functionalization of the lowest reactive site in the repeating unit of cellulose could be accomplished by using different protecting group techniques. Moreover, some regioselectively functionalized cellulose ethers served as starting materials for derivatives that are not easily accessible by conventional chemical methods.

Acknowledgements

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Carbohydrate degradation reactions during alkaline steeping of dissolving pulp - Influence of air exclusion

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Abstract

The production of cellulose fibres by the viscose process has been known for more than a century, but still some aspects are not sufficiently understood. The carbohydrates in the pulp are exposed to varying conditions during the manufacturing process. In the first step the strong alkaline treatment leads to undesirable loss reactions. The behaviour of cellulose in alkaline environment was subject of several studies and a number of kinetic models describing cellulose degradation were suggested. In a number of investigations the experiments were performed under the exclusion of oxygen to prevent undesirable oxidation reactions. However, this approach differs from industrial process conditions where the presence of air could introduce some oxygen. To estimate the effect of oxygen on cellulose degradation, final bleached beech Mg-based acid sulfite pulp was treated with sodium hydroxide at 50°C in the presence and absence of argon for time periods up to 63 hours. The results suggest that oxygen-initiated homolytic degradation pathways, similarly to those occurring during the aging process, are responsible for the additional γ-cellulose formation in the presence of oxygen at long steeping time. In the case of short steeping treatments, as occuring during industrial processes, the influence of air-oxygen on the yield loss and COD formation is, however, negligible.

Keywords: *Dissolving pulp, viscose pulp, steeping, alkaline degradation, air exclusion*

Introduction

The viscose process is still the dominating process for the manufacture of man-made cellulose fibres. The broad field of applications and the possibility of property adjustment contribute to the dominance of the viscose fibres. Although the process has been applied for more than a century, further improvements regarding yield increase and the application of by-products seem to be possible. During the manufacturing process the carbohydrates in the pulp are exposed to strongly alkaline conditions during viscose preparation and strongly acidic conditions during the regeneration process. The steeping of pulp with a 5 M sodium hydroxide aqueous solution affects the conversion of cellulose I to cellulose II [1]. The change in structure is necessary to ensure a good accessibility for the xanthation reaction. Parallel to the change of the crystal structure hemicelluloses and short-chain cellulose are dissolved. The well mixed slurry of alkali and pulp is dewatered to obtain alkali cellulose prior to the aging process where the degree of polymerisation is adjusted to the required level in the final product [2]. While DP reduction during aging is performed under controllable conditions until a target value is reached, the degradation reactions during steeping cause undesirable yield losses. In the case of aging, the chain cleavage of alkali cellulose was shown to follow a radical chain mechanism with atmosphere oxygen involved [3]. As already mentioned, alkali cellulose

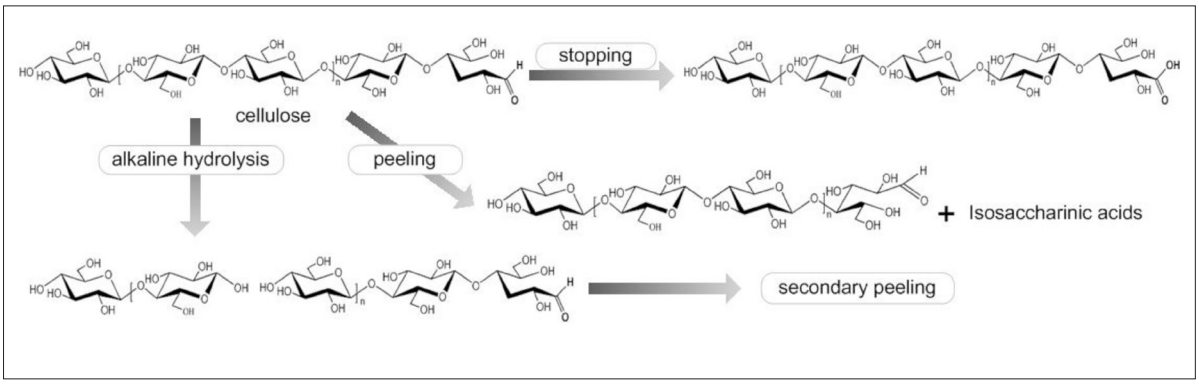

Figure 1. *Cellulose reactions during alkaline steeping.*

with a cellulose content of about 35 wt% and an alkali content of about 15 wt%, respectively is obtained by pressing the steeped pulp suspension. The press cake is subsequently shredded to provide adequate surface areas to ensure uniform reactions [4]. Transition metal ions are optionally used as catalysts to accelerate cellulose degradation during aging [5].

The beta-elimination or *peeling-off* reaction is the dominating chemical reaction occurring during alkaline steeping. This reaction is associated with yield loss initiated by endwise degradation of sugar units from the reducing end group [6]. As the main degradation products of the eliminated anhydroglucose unit, isosaccharinic acids are formed via benzilic acid rearrangement. The peeling reaction proceeds until it is stopped chemically by a different rearrangement reaction or physically by reaching the crystalline regions of the fibre [7]. The stopping reaction leads to the formation of alkali stable metasaccharinic acid at the reducing end of the molecule by which further successive molecule degradation is prevented. The temperature dependent ratio of both reaction rates is crucial for the scale of undesired cellulose yield loss [8].

Alkaline hydrolysis causes the shortening of the cellulose chain which usually takes place at higher temperatures [9]. Figure 1 provides an overview of possible cellulose degradation reactions occurring under steeping conditions.

Several studies were performed concerning the cellulose behaviour in alkaline environment and at moderate temperature, especially regarding radioactive waste repository conditions [10, 11]. Thereby certain models describing the reaction kinetics were proposed.

The objective of the study was to evaluate the effect of air-oxygen on the carbohydrate degradation of a pulp during alkaline steeping.

Experimental

PULP TREATMENT

A TCF bleached beech Mg-based acid sulfite pulp was used for the experiments. The dry sheets were disintegrated to pieces as small as possible to enable a thorough lye penetration. Aqueous solution of sodium hydroxide (18 ± 0.02%) was used as a steeping medium at a pulp to liquor ratio of 1:60. The treatments were carried out in a round-bottom flask equipped with a magnetic stirrer and a thermometer. The lye was preheated to 50°C and added to the pulp under vigorous stirring to ensure a homogenous distribution of the fibres in the solution. The temperature of the medium was kept constant during the entire treatment time.

For the experiments with air exclusion, the sodium hydroxide solution was flushed with argon before heating. Subsequently, the whole apparatus was evacuated and flushed with argon several times. After the initial steeping time, the suspension remained in the reactor, gently stirred for up to 63 hours.

FRACTION SEPARATION

After expired time the suspension was filtered and the After the targeted time was reached, the suspension was filtered and the solid residue was neutralized with 20% acetic acid, washed until neutral and allowed to dry under ambient conditions. The yield of the insoluble cellulose fraction was determined gravimetrically. Intrinsic viscosity measurements of the insoluble cellulose fraction were performed after dissolution in Cupriethylenediamine according to the SCAN-CM 15:99 method. The amount of carboxylic groups in the insoluble fraction was determined by the methylene blue adsorption method [12, 13].

The dissolved β-cellulose fraction was precipitated by the addition of an equal volume of dilute sulphuric acid (H_2SO_4:H_2O 1:3) to the lye under vigorous stirring. For quantitative analysis the precipitate was filtered through a 0.45 µm cellulose filter. To obtain lar-

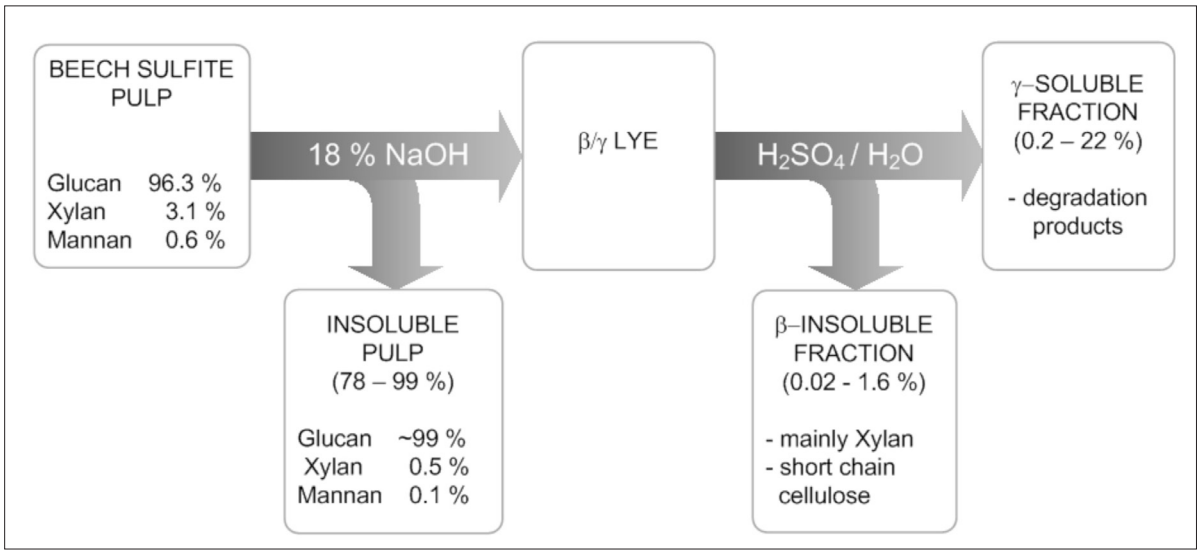

Figure 2. *Treatment of the pulp and the residuals.*

ger quantities for the analytical characterisation, the suspension was centrifuged and the precipitate washed with water several times. The residue was freeze dried. The strong acidic filtrate contained the remaining soluble degradation products denoted as γ-cellulose fraction.

The amount of the dissolved organic compounds in both liquid fractions was determined as total organic carbon (TOC) according to EN 1484, while the chemical oxygen demand (COD) was determined according to DIN 38 409.

An overview of the obtained fractions and their composition is given in Figure 2.

Results and discussion

The experiments of the pulp yield loss reactions during steeping were carried out under inert gas conditions to avoid any oxidation. However, the exclusion of oxygen is not common in industrial steeping operations. Thus, the objective of the study was to comparatively evaluate the effect of air-oxygen on the yield loss reactions.

The beech sulphite dissolving pulp used for the steeping experiments contained 3.1% xylan and 0.6% mannan. After the preliminary steeping time the xylan and mannan content decreased to 0.6% and 0.1%, respectively and remained at this level throughout the whole treatment time. This change in the carbohydrate composition provides an evidence for an immediate dissolution of the hemicellulose and a consistent subsequent degradation of the substrate. Further it lead to the assumption that mostly cellulose remained in the insoluble fraction and was subject to degradation.

The effect of the presence of atmospheric oxygen on cellulose yield is shown in Figure 3. Short steeping as occurring under industrial conditions does not show any influence of air oxygen on the yield loss. However, with progressive steeping duration, the yield loss enhances in the presence of oxygen. A remarkable yield difference was detected after 20 hours of steeping which evidences the enhanced yield loss due to the presence of oxygen. As a consequence of permanent stirring, the long exposure of the surface to the air causes additional gas diffusion into the solution and thus an elevated concentration inside the liquid. This is prevented by using argon to ensure an inert atmosphere. Thereby the peeling reaction is almost exclusively responsible for the chain shortening as revealed by the presence of peeling products (*e.g.* isosaccharinic acid etc.) in the γ-cellulose fraction.

Figure 3 compares the weight and intrinsic viscosity losses as a function of time for the steeping reaction in the presence of air-oxygen. The intrinsic viscosity loss amounts up to 20% whereas the maximum weight decrease remains lower than 15% based on the particular initial value. While weight loss is attributed to

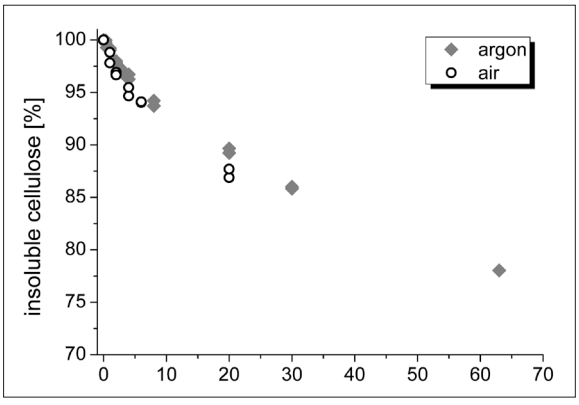

Figure 3. *Decrease of the cellulose yield loss in presence and absence of the inert gas.*

peeling-off reactions, cellulose depolymerisation is mainly caused by alkaline hydrolysis (in the absence of oxygen) and homolytic degradation reactions initiated by the presence of oxygen.

In Figure 5 of the regenerated pulp in presence of air-oxygen (T = 50°C; L:S = 60:1).

Figure 4 illustrates the course of intrinsic viscosity and the carboxylic group content of the regenerated pulp as a function of steeping time in the presence of air-oxygen. The increase in acidic group concentration can be assigned to metasaccharinic acid formation due to the stopping reaction. As a result, the remaining cellulose becomes stable to the successive peeling reaction; however, random chain scission by alkaline hydrolysis followed by secondary peeling reactions as well as undefined homolytic degradation pathways parallel to primary peeling leads to progressive viscosity (Figure 5) and weight losses (Figure 3).

The formation of soluble degradation products was monitored by the determination of total organic carbon and the chemical oxygen demand of the solutions. Therefore both parameters were analysed in the original lye and in the aqueous solution after the precipitation of beta-cellulose by acidification and the subsequent removal of the remaining solid residue. The difference in both measurements was defined as β-cellulose fraction which is mainly composed of xylan and small amounts of short chain cellulose.
The obtained results are displayed in Figure 6. It shows the independence of the content of the β-cellulose fraction on air-oxygen. A slight decrease can be identified due to a progressive degradation of the short chain cellulose of the β-cellulose fraction, but it proceeds similarly in both cases.
The total amount of the soluble γ-cellulose fraction increases slightly faster in the presence of air-oxygen than in the absence of air-oxygen. This behaviour proceeds parallel to the yield loss development.

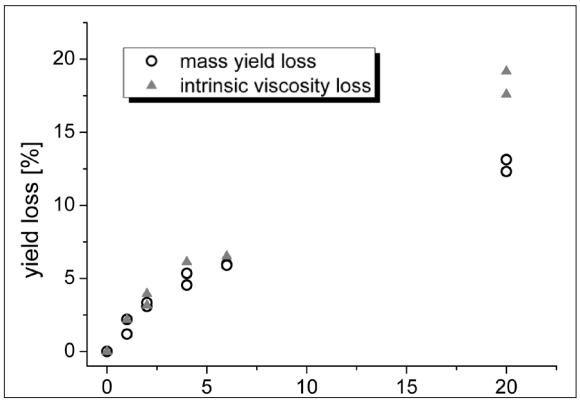

Figure 4. *Comparison of the gravimetrically determined cellulose yield loss and the corresponding intrinsic viscosity loss of the regenerated pulp in presence of air-oxygen (T = 50 °C; L:S = 60:1).*

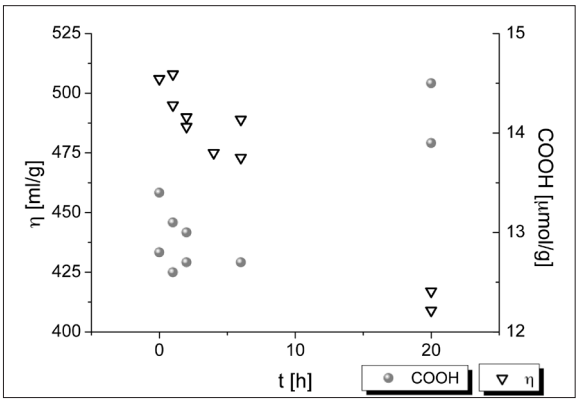

Figure 5. *Intrinsic viscosity and carboxyl group content of the regenerated pulp as a function of the treatment time in presence of air-oxygen. (T = 50°C; L:S = 60:1).*

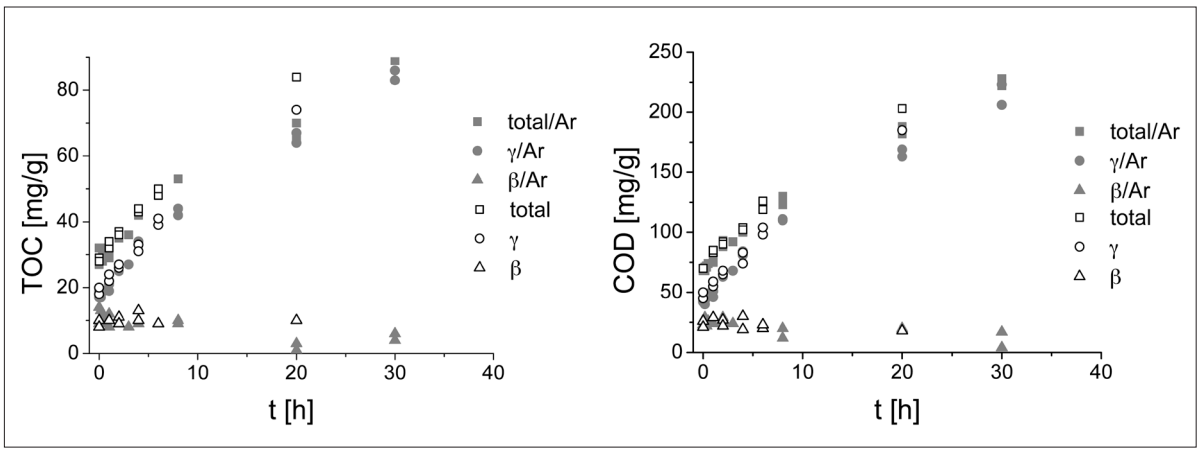

Figure 6. *TOC and COD contents of the residual lye at 50°C; β– and γ - fractions obtained after precipitation with H_2SO_4:H_2O (1:3).*

Conclusions

The results obtained in this study show that the presence of air-oxygen during alkaline steeping of beech Mg-based acid sulphite dissolving pulp enhances its yield loss, particularly at longer treatment times. The time dependency of the yield loss increment suggests that oxygen-initiated homolytic degradation pathways, similarly to aging, are responsible for the additional γ-cellulose formation in the presence of oxygen. Kinetic investigations, however, revealed that the progressive increase in both yield loss and chain scission at longer reaction times – as occurring also in the absence of oxygen - may be mainly attributed to random hydrolysis followed by secondary peeling as monitored by COD and TOC measurements. In the case of short steeping treatments, as occuring during industrial processes, the influence of air-oxygen on the yield loss and COD formation is, however, negligible.

Acknowledgments

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